DATA ANALYSIS ISSUES TRACKING SYSTEM

As the Chesapeake Bay Program Mainstem Monitoring Program reached its fifth anniversary, EPA initiated a systematic review of the program design and implementation. In the process of this review, numerous questions were raised which required investigation. To insure that all of these issues received appropriate attention and to provide thorough documentation of this process for future users of this important database, a tracking system was designed which is known as the Data Analysis Issues Tracking System (DAITS).

DAITS is a central collection point for the registry of all issues which are raised by those involved in the management, operation and review of the Chesapeake Bay Program (CBP) monitoring programs. The DAITS will encompass issues relating to any programs contributing data to the CBP data base.

Issues focused on the current water quality monitoring program as well as historical data sets are included. Quality Assurance (QA) data set issues are included in this system as well. The magnitude of the issue is not a concern. Issues need not be fully developed before they are introduced into the system. Issues can be informally introduced to the system with a brief note although contributors are strongly urged to follow the elements of the format provided below to assist in accomplishing the appropriate follow-through.

DAITS issues may be addressed at meetings of the Analytical Methods and Quality Assurance Workgroup, the Data Analysis Workgroup and, as appropriate, the Monitoring Subcommittee. Action items are the key element of this tracking system.

DAITS Issues List

DAITS 001: Criteria for censoring nutrient concentration data (June 26, 1990)
DAITS 002: Kjeldahl Nitrogen adjustment for OEP/CRL data from 1984-1985 (May 14, 1990)
DAITS 003: Field replicate methods at mainstem laboratories (May 14, 1990)
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DAITS 012: Criteria for selecting data in the CBP historical water quality data base. (September 4, 1990)
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DAITS 015: Adjusting Chesapeake Biological Laboratory (CBL) Orthophosphate (PO4F) data for salinity effect (December 10, 1990)
DAITS 016: Adjusting Maryland Dept. of Health and Mental Hygiene (MDHMH) Total Phosphorus (TP) and Total Dissolved Phosphorus (TDP) data (December 10, 1990)
DAITS 017: Percent recovery calculation method (December 19, 1990)
DAITS 018: Manual injection carbon data (January 29, 1991)
DAITS 019: Methods matrix of field and laboratory methods at mainstem laboratories (May 5, 1991)
DAITS 020: Heuristic adjustment for ODU Kjeldahl Total Nitrogen data (July 11, 1991)
DAITS 021: Examination of Chesapeake Bay Program Carbon Monitoring Data (December 1991)
DAITS 023: PC/PN Filter and Rinsing Study (November 21, 1991)
DAITS 024: Method detection limit (MDL) methods documentation May 20, 1992
DAITS 025: Pycnocline identification and location of mid-water nutrient samples (June 26, 1992)
DAITS 027: Fluorometric Chlorophyll Data Structure(October 6, 1992)
DAITS 029: Discrepancy in Maryland data, between WQ and Biomonitoring discrete measurements of chlorophyll (affected parameters are CHLA and PHEA). (December 17, 1997)
DAITS 031: Submission of Tributary Water Quality Data Consistent
With Mainstem Data (November 4, 1994)
DAITS 032: Virginia Tributary SI and NO23 data: (February 1, 1996)
DAITS 033: Below Detection Limit (March 14, 1996)
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DAITS 037: Chlorophyll Method Comparison and Revision (March 29, 1999)
DAITS 038: Light Attenuation Parameter Names and KD Calculation (April 30, 2003)
DAITS 39: Variability in station depth (July 21, 2005)
DAITS 040: Pycnocline Calculation: Different methods for WQ sample collections and for Designated Use boundary delineation. (June 2006)
DAITS 041: Analytical Method Changes in Total Nitrogen Measurements for the Virginia Tributaries (November 2006)
DAITS 042: Analytical Method Changes in Total Phosphorus Measurements for the Virginia Tributaries (September 2006)
DAITS 043: Comparability of parameter estimates from whole water and filtered samples for MD Department of Health and Mental Hygiene data (June 2006, revised April 2009)
DAITS 044: Secchi Hits Bottom and still visible 16-April 16, 2008
DAITS 045: Investigation of TSS Step Trend at Virginia mainstem stations (June 2008)
DAITS 045v2: Investigation of TSS Step Trend at Virginia mainstem stations (June 2008)
DAITS 046: Comparison of chlorophyll and pheophytin analyzed at DHMH and CBL (May 2009)
DAITS 048: Comparison of total suspended solids samples analyzed using Whatman and Environmental Express filter pads (January 2010)
DAITS 049: Comparison of alkaline phenol and salicylate NH4 analysis methods at the Maryland Department of Health and Mental Hygiene (September 2010)

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (DM,DS) 001

CATEGORY CODE: DM,DS

TITLE: Criteria for censoring nutrient concentration data

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: June 26, 1990

STATEMENT OF ISSUE:

Censoring of nutrient concentrations sampled by the Chesapeake mainstem water quality monitoring programs seems to have been begun by submitting laboratories or agencies at certain times during the monitoring program. For example, we are aware of censoring by Maryland Department of the Environment (MDE) of whole water nutrient concentrations received from Chesapeake Biological Laboratory due to suspected contamination of high total suspended solids. We have also identified values identified as suspect by Old Dominion University that appear as missing in recent submissions but exist in the data base in submissions made as early as October 1987.

PROPOSED SOLUTION:

Submission of specific censoring criteria and date of onset of censoring of whole water nutrient concentrations and other parameters that are done by laboratories or state agencies that submit water quality monitoring data to the Chesapeake Bay Program.

DISCUSSION:

The presence of "suspect" data identified by ODU in two forms (data present; data as missing ".") in the data base recently came to our attention in the course of updating analyses of phosphorus data. The extent of these discrepancies in the data base is not presently known.

The practice of MDE with respect to nutrient particulate species came to the attention of CBP in March 1990 in the course of some QA questions. In response to an inquiry by John Posey, Harry Wang of MDE sent a copy of an internal MDE memo dated February 2, 1989 from Bruce Michael to Chesapeake Bay and Special Projects Data Analyses Workers. This memo stated the following:

"The procedures for using the 'TS' Analyses Problem Code when the Total Suspended Solids value is exceedingly high (usually above the upper critical boundary of 250 or when other whole water parameters are adversely affected) shall be as follows:

1. The TSS value should be left as reported and the APC should be left blank.

2. All whole water values (ie.[sic] TKNW, TP, TOC and TON) that are
affected by the high TSS shall be deleted and labelled with an APC of 'TS'.

This will allow the analyzer the opportunity to make a judgement on the validity of the TSS value and other values based on the TSS value that is exceedingly high, yet has not been deleted [sic]. The whole water samples that are not valid values and have been deleted will not influence analysis of other data being analyzed".

What the CBP needs are the criteria that define "adversely affected whole water parameters" and when this practice, and any other of censoring, began. Our examination of data files (June 1984 through October 1989) received from MDE revealed the following when we searched for 'TS' codes associated with Kjeldahl whole water nitrogen (TKNW), particulate carbon (PC), total phosphorus (ACTP), particulate phosphorus (PP), or particulate nitrogen (PN):

1. The earliest date of a 'TS' code was October 5, 1987.

2. Flags occurred on PC, PN, and PP concentrations; none were found on ACTP or TKNW concentrations. Not all whole water determinations of an affected sample were necessarily deleted.

3. All of the 'TS' flagged samples occurred with TSS values less than 250 mg/l; the range of TSS in the flagged samples was from 46.6 to 102.3 mg/l.

4. Censoring occurred on samples taken at these stations and dates. The number in parentheses indicates the number of affected water samples:

	CB3.3C	CB3.3W	CB4.2W	CB4.3W	CB4.4	CB5.1	CB5.2	CB5.3	LE2.3
Oct0587									(1)
Mar1788	(2)		(2)	(1)					
Dec0588						(1)	(1)		
Mar0689					(2)			(1)	
Mar2189	(3)								
Oct2489		(1)							

This table shows that only data associated with a subset of MDE stations have been censored, i.e. those at and south of the Bay Bridge and that March and October samples predominate in the censored set.

5. All censored samples were bottom or below pycnocline samples; some were replicated samples.

6. There are instances of high below pycnocline or bottom TSS [Avalues in MDE data prior to October 1987 at stations below the Bay Bridge that are associated with relatively high total phosphorus or particulate phosphorus concentrations. Thus, the CBP needs to determine the specific criteria which have been applied in any data censoring activities and their onset in order to insure that data which exist within the CBP data base are of known quality.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

Reference to laboratory procedures or data screening procedures.

PRIORITY RANKING: 1 (High).

SUBMITTER/RESPONSIBLE PARTY:

NAME: Dr. Susan Brunenmeister, (301)-267-0061 ext. 206

ORGANIZATION: Computer Sciences Corporation
Chesapeake Bay Program
410 Severn Avenue, Suite 113
Annapolis, MD 21403

ACTIONS TO DATE:

6/22/90 Submitted to EPA Project Officer J. Macknis

Issue referred to Data Management and Acquisition workgroup and will be discussed among members via a conference call on 9/12/90, 9-11 a.m. (202) 245-4230

9/12/90 Discussed briefly in conference call. It was agreed that censoring criteria should be submitted by all labs/program managers and reviewed. Peter Bergstrom mentioned that the issue was raised in the AMQAW meeting (7/12/90) and Rick Hoffman agreed to collate responses.

1/15/91 Rick Hoffman called Peter Bergstrom and said he was preparing to send out the issue to each lab and program agency.

2/11/91 Steve Sokoloski called Susan Brunenmeister to clarify the reference to ODU data concerning the presence or absence of 'suspect' data in the CBP files. He recalled that intially (as of Cruise #2, when Steve association with the program began) ODU was requested to submit all data to the CBP and at that time the values identified by ODU as suspect were set to missing at the CBP. Later (Steve couldn't recall when) ODU set suspect values to zero before submitting the data to the CBP. Susan said she would respond with more specifics of her findings.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA,AM) 002

CATEGORY CODE: QA, AM

TITLE: Kjeldahl Nitrogen adjustment for OEP/CRL data from 1984-1985

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: May 14, 1990

STATEMENT OF ISSUE: The Maryland main bay Kjeldahl nitrogen analyses during June 1984-May 1985 were done by OEP/CRL personnel with the helix digestion method. However, the helix digestion method did not digest phytoplankton as effectively as the block digestion method, producing low TKNW results from samples with elevated phytoplankton levels. Helix results for TKNF were also lower than block results. Charlie App requested an adjustment for the OEP/CRL TKN helix data to use in the 3D model, to increase the accuracy of the model's predictions for nitrogen.

PROPOSED SOLUTION: Adjustment equations derived from a side-by-side comparison data set with a block digester collected at CRL in 1984 was used to reduce the bias in the TKN helix data from OEP/CRL. The equations correct the low bias in TKN helix data, for both TKNW and TKNF.

DISCUSSION: See the final report for details:

Bergstrom, P. 1992. Adjusting helix Kjeldahl nitrogen results: Maryland Chesapeake Bay Mainstem Water Quality Monitoring program, 1984-1985." Chesapeake Bay Program, CBP/TRS 44/92, Annpolis, MD.

PRIORITY RANKING: 5 (to the modelers)

SUBMITTER/RESPONSIBLE PARTY:

Name: Dr. Peter Bergstrom

Organization: Computer Sciences Corp.
EPA Chesapeake Bay Liaison Office
410 Severn Ave. Suite 110
Annapolis, MD 21403
(301) 267-0061, (800) 523-2281

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

The initial (NOT final) equations used for TKN helix data (Maryland mainstem, Cruise 1-18) were:

TKNW = (TKNW - 0.07306 + 0.0377*ln(CHLA))/0.5716

TKNF = (TKNF - 0.04287)/0.5907

These were used to adjust BAYSTATS files on a trial basis on April 3, 1991. However, reviewers of the draft document requested a regression method that accounted for below detection limit data, so the equations were re-calculated. This was done using tobit regression, and the new (FINAL) equations are:

TKNW = (TKNW - 0.03033 + 0.0332*ln(CHLA))/0.6172

TKNF = (TKNF + 0.1166)/0.8445

These were used to re-adjust the BAYSTATS files on 8/2/91; TN data adjusted by these new equations were used in the trend analyses done by CSC for "Trends in Nitrogen in the Chesapeake Bay (1984-1990)," CBP/TRS 68/92, March 1992, and for the Water Quality Characterization Report, Part II (not yet completed as of 4/9/92). The second set of equations were approved for permanent adjustment of TN data in the CBP data base by the Analytical Methods and Quality Assurance Workgroup (AMQAW) on 11/21/91 and by the Monitoring Subcommittee (MSC) on 1/22/92.

This adjustment to the BAYSTATS data has not yet been made as of 4/9/92. In the adjusted data, the method code is set to 'A' and the original below detection limit flags in the data were not changed, even though the data were adjusted upward.

The original helix TKNW and TKNF data, and TN calculated from them, are still available in the CBP directories.

UPDATE As of 7/24/92: TKNF and TKNW data from this method (CRL, 6/84-5/15/85) were adjusted in our BAYSTATS directories by CSC staff on 8/24/91. Calculations checked by John and Peter on 4/21/92, TKNF calculations for 1985 were corrected. TKNW_M and TKNF_M were both changed to 'A' to show data had been adjusted, and the original values in TKNW_D and TKNF_D were retained, even though the adjusted values were all above the original detection limit (0.2).

RECOMMENDED ACTIONS:

ACTION NUMBER: 002.01

1.Designated Respondent: (Data user)

Modeling coordinator (or Carl Cerco)
EPA Region III, 3WM10
841 Chestnut St.
Philadelphia, PA 19107

2. Action: Study the proposed adjustment equations, and respond as to whether they meet the need for improving model calibration.

3. Resources Needed:

4. Due Date: August 6, 1990

5. Action Item Resolution Summary:

ACTION NUMBER: 002.02

1. Designated Respondent: (Data originating organization, and head of Data Analysis Workgroup)

Robert Magnien
MDE
2500 Broening Highway
Baltimore, MD 21224

2. Action:

Review the proposed adjustments for OEP/CRL TKN data, and either approve them for the suggested use (model calibration), or propose alternatives. Identify other uses that would be appropriate for these adjustment equations. DAWG members should review the report, in addition to review by MDE personnel.

3. Resources Needed:

4. Due Date: August 6, 1990

5. Action Item Resolution Summary:

Received comments from Magnien 10/18/90, no mention of DAWG consideration.

ACTION NUMBER: 002.03

1. Designated Respondent:

Bettina Fletcher
Chair, Analytical Methods and Quality Assurance Workgroup
EPA CRL
839 Bestgate Rd.
Annapolis, MD 21401

2. Action:

Review the proposed adjustments for OEP/CRL TKN data, and comment on any issues relevant to analytical methods or quality assurance.

3. Resources Needed:

4. Due Date: August 6, 1990

5. Action Item Resolution Summary:

Discussed at AMQAW meeting, 10/23/90. Decision is pending seeing revised report. Final AMQAW approval on 11/21/91.

SYS$CBPMONITOR:[DAITS]DAITS002.WP

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA/AM/FM) 003

CATEGORY CODE: (QA, AM, FM)

ISSUE TITLE: Field replicate methods at mainstem laboratories

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: May 14, 1990

STATEMENT OF ISSUE:

Results from field replicate nutrient analyses are used to assess sources and magnitudes of variability in monitoring data from main bay monitoring laboratories (CBL, ODU, and VIMS). The CBP data base needs to contain detailed information on how those replicates were collected and analyzed, now and in the past, to make analyses of field replicate data possible.

PROPOSED SOLUTION:

Field and laboratory personnel at each agency and laboratory should document the methods they use to collect, handle, and analyze field replicates.

DISCUSSION:

Many of the analyses currently under way for the Chesapeake Bay Program, including trend analyses, QA analyses, and power analyses, require estimates of the precision (variability) in the monitoring data. The three mainstem laboratories now send us results from field replicates, but the exact methods used to collect, handle, and analyze the replicates have not been fully documented. When these methods have changed over time, all the changes need to be documented as well. The methods should be documented by the person(s) directly involved if possible. For example, if field crews changed, a member of the old crew should document the old methods, and a member of the new crew should document the new methods.

Specific items that need to be documented to facilitate analysis of replicate data are:

1. Where each field replicate data are submitted; usually field replicates are submitted to CBLO in the monitoring data sets, but not always.

2. Whether field replicate values represent means or individual observations. Since means tend to have less variability, this is very important. For example, MDE and CBL personnel may have done laboratory replicates on samples that were field replicates, and reported means of the lab replicates as field replicate concentrations in the monitoring data base, but we are not sure when or how often this occurred.

3. How field replicates are collected. Some are two samples collected in rapid succession, some are field split samples, and some were two bottles filled alternately from the same hose. This determines what sources of variability are measured.

4. Whether any changes in field or laboratory methods are known to have affected variability of field replicates. If any changes in methods were undertaken to reduce replicate variability, they need to be documented fully, including the first cruise affected by each change. For example, CBL personnel changed from two-piece to one-piece digestion caps for TDP and TDN on October 6, 1986, which appeared to reduce the variability of TDP field replicates analyzed after that date.

SENSE OF THE RESOURCES REQUIRED TO RESPOND: This could be a major project for all parameters; it could be prioritized by parameter, starting with phosphorus parameters for trend analysis (TP, TDP, PHOSP, and PO4F). Some field methods would apply to groups of parameters.

PRIORITY RANKING: 5, for trend and power analyses
3, for QA analyses

SUBMITTER/RESPONSIBLE PARTY:

Name: Sally Bowen (301) 974-3238

Organization: Maryland Dept. of the Environment
416 Chinquapin Round Rd.
Annapolis, MD 21401

CSC contact - Dr. Peter Bergstrom

ACTIONS TO DATE:

This issue was discussed at the AMQAW meeting on 7/12/90, and Sally Bowen agreed to send out the request and collect the responses.

Sally Bowen sent out the attached request for information on 8/30/90. It was accompanied by a blank table to be filled out by each respondent. Her request was scanned and added to this file on 9/4/90. Her request is considerably broader than the original request, including split sample data and other quality assurance data. Steve Sokolowski called on 9/4/90 to say that he would ask her to send out a new memo limiting the request to field replicate data only.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:
Reference appropriate documents as required. To be completed after all actions have been addressed:

RECOMMENDED ACTIONS:

ACTION NUMBER: (QA/AM/FM) 003.01

1.Designated Respondents:

Bruce Michael (old field methods)
MDE
2550 Broening Highway
Baltimore, MD 21224

Carl Zimmermann/Carolyn Keefe (lab)
CBL
Box 38
Solomons, MD 20688-0038

Sally Bowen (new field methods)
MDE
416 Chinquapin Round Rd.
Annapolis, MD 21401

2. Action: Document all methods used for creating, analyzing, and reporting field replicates, and any changes in those methods over time. Include how field replicates are collected and any other details that could affect the sources of variability measured by field replicates. Lab personnel should comment on changes in analysis methods that could have changed the variability of field replicates.

3. Resources Needed:

4. Due Date: September 28, 1990

5. Action Item Resolution Summary:

ACTION NUMBER: (QA/AM/FM) 003.02

1.Designated Respondent: Steve Sokolowski
ODU AMRL
Norfolk, VA 23529-0456

Rick Hoffman
VSWCB
2111 N. Hamilton St.
Richmond, VA 23230

2. Action: Document all methods used for creating, analyzing, and reporting field replicates, and any changes in those methods over time. Include how field replicates are collected, and any other details that could affect the sources of variability measured by field replicates.

3. Resources Needed:

4. Due Date: September 28, 1990

5. Action Item Resolution Summary:

ACTION NUMBER: (QA/AM/FM) 003.03

1. Designated Respondent:

Betty Salley
VIMS
Gloucester Point, VA 23062

Rick Hoffman
VSWCB
2111 N. Hamilton St.
Richmond, VA 23230

2. Action: Document all methods used for creating, analyzing, and reporting field replicates, and any changes in those methods over time. Include how field replicates are collected, and any other details that could affect the sources of variability measured by field replicates.

3. Resources Needed:

4. Due Date: September 28, 1990

5. Action Item Resolution Summary:

SYS$CBPMONITOR:[DAITS]DAITS003.WP

August 30, 1990

MEMORANDUM

To: CBP Lab Data/Field Data Coordinators

FROM: Sally Bowen, MDE

SUBJ: Bay Program Replicates

As you may recall from the July QAQC Workshop we were all asked to document both the existence of replicate results in our data bases and the methods used to generate replicate data. This documentation will be officially incorporated into the Bay Program's new Issue Tracking System as Item Number 003. A copy or the actual "Statement of Issue" is enclosed. To help me compile your responses, I have taken the issue statement a step further and developed some guidelines which hopefully you will be able to use when formulating your response. These guidelines include a set of definitions, a set of potential computer identification codes, and a possible format. Since these guidelines are based on my limited experience with our field program, I expect there may be problems adapting them to other programs. If you cannot easily use the given guidelines, call me, maybe between us we can improve their usefulness and then pass the "revised" version on to everyone else.

I want to apologize for sending this out so late. Since a complete response to this issue could potentially be quite time consuming, I would like to suggest a four level response process. Level One would require providing information on the current types of replicates which you routinely generate in your program, whether this information is sent to CBP, and the starting date for each type of replicate. The target date for Level One replies would be September 28, 1990. Level Two would ask that you document when and how your routine replicates have changed since 1984. The target date for replies to this Level would be October 17, 1990. Level Three would require listing the types of non-routine replicate information which you have available. This could include special studies to resolve analytical questions or special studies to verify the impact of method changes. Basically anything you've done to check precision and/or accuracy of your data is a candidate for this level. You should also include dates of method modifications which had the potential to affect your data even if you did not do a lab study. If trend plots show a subtle change for your numbers but not for other areas of the Bay, we may be able to link the change to a method modification. Level Four would require submitting data to CBP for items in Level Three that impact a current area of concern.

If everyone can respond by October 17th to levels one and two, then I should be able to have the information available for the next QAQC meeting on October 23rd. This would give us a basis for further discussion of the impact that the various types of replicates have on trend analysis and what our recommendations will be regarding those impacts. At the October meeting we can set a deadline for your response to the Level Three information.

Thanks for your cooperation in this matter. Remember if my suggested guidelines are inappropriate for your situation, please call. You can reach me at (301)974-3238.

SB/gat

Enclosures

cc: Bruce Michael, MDE
Carl Zimmermann/Carol Keefe, CRL
Steve Sokolowski, ODU
Rick Hoffman, VSWCB
Betty Salley, VIMS
Alvin Bober, MDHMH
Peter Bergstrom, CBP
Joe Macknis, CBP
Bettina Fletcher, EPA
Tim Payne, MDHMH

I. Definitions: Please keep these in mind when responding to the issues statement.

Result: The numeric value generated by an analytical test.

Replicate: Defines results which had multiple values generated for each test run. If an entire sample (all parameters) are run in replicate than one would expect 2 or more complete sets of results to appear in the data set for a particular station, date and depth. If a specific parameter is run in replicate than one would expect only a single result (the mean of the replicate values for that specific parameter) to appear for that parameter in the data set. A single parameter can be run in replicate with each replicate value reported individually but this would be unusual.

Sample:-Defines the set of bottles, tubes, filters, etc. normally submitted to a lab in order to run the full suite of parameters which are used to define water quality at a specific station for a particular date and depth. If multiple samples are submitted for the same station, date and depth then each sample

set is called an ALIQUOT. The results generated for each individual aliquot represent "replicate" results. The aliquots generated can all be delivered to the same lab or they can be delivered to multiple labs. REPLICATE SAMPLES implies sample splitting occurred before the laboratory began analysis of the submitted sample containers. If an analyst runs a test multiple times from a single aliquot then the results are also "replicate" results but they are PARAMETER REPLICATES not replicate samples. By definition parameter replicates are subsets from a single source container. Replicate Samples, on the other hand, can be collected simultaneously, sequentially, or as subsamples from single source container.

Replicate Sample Types: Since the collection technique used to generate the aliquots submitted for Replicate Samples defines the type of variability observed it is important to know the collection technique used. The codes and descriptions below apply to replicate samples. Remember; replicate parameters are all subsplits. If you need a different code, add it.

S: Subsplit Aliquots: A single large container is filled (filling method is irrelevant) with sufficient water. While stirring constantly all replicate sample aliquots are filled from this large composite container. All subsamples are obtained from a single source container.

C: CoCollected Aliquots: All sample bottles are filled either sequentially or simultaneously. All collections occur at approximately the same time and from approximately the same location. This type applies to multiple bottles when each is filled separately from an overboard pump or sampler. It also applies if two boats sample at the same time within sight of each other.

L: Same Location, Samples: Describes samples from the same location but collected at different times of the day (time difference greater than 1 hour).

II. Possible Computer Code System

Once we compile a list of replicate records and their collection types how do we make this information easily available to a data user. Storing the information in an accessory description file provides an analyst with info about the data set but not with an easy way to use that information. Finding a way to store that information inside the record for the replicate sample would allow an analyst to easily manipulate the records based on their type of replicate variability.

A mechanism to indicate parameter "replicates" already exists. By using the same single digit field that is used for

the < or > designation we could develop other codes that apply only to a specific parameter within a specific record. For example, if a high value for ammonia is checked and double checked to confirm that it really is twice as high as expected than the analyst would average the 2 or 3 values obtained, report the average, and put an M in the qualifier box for ammonia. We used to use this box to indicate that a particular value had been adjusted (A) for some reason. For instance, we sometimes adjusted D.O. when meters drifted or this designation could be used on the TKN values that CBL wanted to adjust. If we questioned the accuracy of a piece of data we put an E next to the value to indicate the result was estimated. This told people that a value was probably good but if it looks odd, then they should throw it out. The qualifier box gives you the option to flag a piece of data that is different. If it plots as an outlier an analyst can look up the code and elect to run their analysis without that value.

A mechanism to identify the collection technique for whole records might be harder to find. MDE data files currently have a single digit field that is used to identify replicate records. The value 1 automatically is stored if only 1 aliquot was analyzed. If additional aliquots are analyzed then the field becomes 2 or 3, or 4 etc. depending on the number of aliquots run. By substituting the replicate sample codes of S, C or L for the default value (1), we could indicate that that record is part of a replicate sample set which was collected by x technique. The other aliquots in the set would remain aliquot 2, 3, etc.

My computer codes are strictly something to think about. If something like this would be easy to add to your computer system, maybe we want to work out some details. If we're talking total system rewrite, it isn't worth the effort. The computer codes are just an idea to provide a discussion point for October.

[end of 8/30/90 memo from Sally Bowen]

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA/DM) 004

CATEGORY CODE: QA, DM

ISSUE TITLE: MONITORING DATA RE-SUBMISSION TO ASSESS TRANSFER ERRORS

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: MAY 14, 1990

STATEMENT OF ISSUE: The Chesapeake Bay Program has several procedures to assure accuracy of monitoring data. However, incorrect data points are still found in mainstem monitoring data that have been "signed off" by the data originator. Data analysts need an estimate of the rate and magnitudes of data transfer errors in the monitoring data sets, especially when data transfer procedures have changed over time.

PROPOSED SOLUTION: Virginia Institute of Marine Science (VIMS) personnel re-entered nutrient and physical data from bench sheets for all stations from two monitoring cruises, Cruise 40 (June 10, 1986) and Cruise 58 (May 6, 1987). To complete the analysis, similar re-submissions of two cruises of monitoring data are needed from Old Dominion University (ODU) and Chesapeake Biological Laboratory (CBL).

DISCUSSION: Before a data set is analyzed, it must be checked for accuracy if the analysis is to be reliable. The Chesapeake Bay Program has several ways to achieve data accuracy, including Quality Assurance procedures and data submission, double-key entry of data, range checks, and formal sign-off of data sets as correct by the data originator. However, data analysis by CSC during the last 1.5 years has uncovered incorrect data points in the monitoring data from all mainstem laboratories. Obviously it is impossible to eliminate all incorrect data points, but for many analyses, it is very useful to have an estimate of the rate and magnitudes of the data transfer errors in the data set. This was accomplished for VIMS monitoring data with the re-submission described above. The re-submitted data sets were compared to the previously submitted data for those cruises, assuming that any differences were due to data transfer errors in the original submission. The rate of differences was less than 1%, and only 2 of the differences found were large (more

than 10% of the new value). The two cruises were chosen by two methods: examining the monitoring data for periods that had some high nutrient concentrations, and choosing periods when VIMS was using different data transfer procedures than they are using currently. CBL and ODU should re-submit data for the same two cruises if possible for consistency. If their data transfer procedures have not changed since Cruise 58, they could re-submit data from Cruise 40 and a cruise about a year earlier, in the Cruise 20-25 range.

SENSE OF THE RESOURCES REQUIRED TO RESPOND: VIMS personnel would know how long this took them. My impression was it took two people about two to three weeks.

PRIORITY RANKING: 3, for analyses that require estimates of variability

SUBMITTER/RESPONSIBLE PARTY:
Name: Todd Blanc/Peter Bergstrom

Organization: Computer Sciences Corp.
EPA Chesapeake bay Program
410 Severn Ave. Suite 110
Annapolis, MD 21403

ACTIONS TO DATE:

Re-submission and analysis of differences in VIMS monitoring data, described above, sent to VIMS on 4/2/90.
Issue referred to Data Management and Acquisition Workgroup and will be discussed among members via a conference call on 9/12/90, 9-11 a.m. (202) 245-4230.
During call, decided it had low priority, did not want to act on it now.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:
Reference appropriate documents as required. To be completed after all actions have been addressed:

RECOMMENDED ACTIONS:

ACTION NUMBER: 004.01

1. Designated Respondents:

Steve Sokolowski
ODU AMRL
Norfolk, VA 23529-0456

Rick Hoffman
VSWCB
2111 N. Hamilton St.
Richmond, VA 23230

2. Action: Re-enter two cruises of monitoring data from bench sheets, for all stations and parameters, using current data entry and data transfer procedures. Submit re-entered data as SAS data sets to CBLO for comparison to data in the CBP data base. Consult with CBLO staff concerning selection of cruises, following guidelines given above.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

ACTION NUMBER: 004.02

1. Designated Respondents:

Carl Zimmermann
CBL
Box 38
Solomons, MD 20688-0038

Bruce Michael
MDE
2500 Broening Highway
Baltimore, MD 21224

2. Action: Re-enter two cruises of monitoring data from bench sheets, for all stations and parameters, using current data entry and data transfer procedures. Submit re-entered data as SAS data sets to CBLO for comparison to data in the CBP data base. Consult with CBLO staff concerning selection of cruises, following guidelines given above.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA/DS) 005

CATEGORY CODE: (QA, DS)

ISSUE TITLE: Control chart submission with laboratory QA data

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: May 14, 1990

STATEMENT OF ISSUE: The three mainstem laboratories submit Quality Assurance data to the Chesapeake Bay Program, but it is difficult to interpret and use in raw form. The QA data would be much more useful, both to the laboratories and to CBP personnel, if displayed graphically in control chart format.

PROPOSED SOLUTION: All three laboratories should produce control charts of their laboratory precision and percent recovery data, and submit these with their QA data submissions. CSC will produce control charts form the submitted data, and check them against the submitted charts to check data transfer accuracy. The charts will then be used by the CBP QA Officer to review the submitted QA data. VIMS sent control charts with their latest QA data submission, using a SAS/GRAPH program sent to them by CSC.

DISCUSSION: The three mainstem nutrient analysis laboratories (CBL, ODU, and VIMS) have sent within-laboratory Quality Assurance (QA) data to the Chesapeake Bay Program since May 1985 (for CBL) or October 1986 (for ODU and VIMS). Some of them produce control charts for their own use, but some do not. CSC began producing control charts of the submitted QA data in 1989, and they uncovered several problems with the QA data sets from some laboratories. Control charts show important trends over time, especially changes in variability, that are not shown by tables of critical limits. One of the problems discovered was data transfer errors in VIMS QA data, so we are requesting each lab to submit control charts with their QA submission. By checking these against control charts made by CSC, any data transfer errors can be detected. These plots will be very useful to the laboratory, as well as to CBP personnel.

SENSE OF THE RESOURCES REQUIRED TO RESPOND: Once the SAS/GRAPH or other program is in place, this would require making two plots per parameter (one for precision, one for accuracy) for about 14 parameters, 28 plots total, for each submission. How long this takes will depend on the plotter or printer used.

PRIORITY RANKING: As a QA issue, 3

SUBMITTER/RESPONSIBLE PARTY:

Name: Dr. Peter Bergstrom

Organization: Computer Sciences Corp.
EPA Chesapeake Bay Program
410 Severn Ave. Suite 110
Annapolis, MD 21403

ACTIONS TO DATE:

VIMS has submitted control charts of QA data (see above).

Issue referred to Data Management and Acquisition Workgroup and will be discussed among members via a conference call on 9/12/90, 9-11 a.m. (202) 245-4230. Tentatively decided this has lower priority, will encourage but not require submission. Will encourage labs to make charts for their own use, will revisit issue in 6-8 months.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:
Reference appropriate documents as required. To be completed after all actions have been addressed:

RECOMMENDED ACTIONS:(Copy next section for as many actions as needed)

ACTION NUMBER: 005.01

1. Designated Respondent:

Carl Zimmermann
CBL
Box 38
Solomons, MD 20688-0038

Bruce Michael
MDE
2500 Broening Highway
Baltimore, MD 21224

2. Action: Start sending control charts for all nutrient parameters to CSC with future QA data submissions. These should show at least the submitted data, and preferably data from the previous quarter or year for comparison. The SAS/GRAPH programs used by CSC for making control charts can be used, or another control chart program. Charts should be made from the SAS data sets submitted to CSC, to be useful in checking for data transfer errors. Laboratory personnel should compare them to their own QA results, then send copies to CSC with the submitted QA data. Since MDE creates the SAS data sets from CBL data, MDE should make the control charts, and send copies to CBL before QA data submission, and to CSC with each QA data submission.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

ACTION NUMBER: 005.02

1. Designated Respondent:

Steve Sokolowski
ODU AMRL
Norfolk, VA 23529-0456

Rick Hoffman
VSWCB
2111 N. Hamilton St.
Richmond, VA 23230

2. Action: Start sending control charts for all nutrient parameters to CSC with future QA data submissions. These should show at least the submitted data, and preferably data from the previous quarter or year for comparison. The SAS/GRAPH programs used by CSC for making control charts can be used, or another control chart program. Charts should be made from the SAS data sets submitted to CSC, to be useful in checking for data transfer errors. Laboratory personnel should compare them to their own QA results, then send copies to CSC with the submitted QA data.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

ACTION NUMBER: 005.03

1. Designated Respondent:

Betty Salley/Kevin Curling
VIMS
Gloucester Point, VA 23062

Rick Hoffman
VSWCB
2111 N. Hamilton St.
Richmond, VA 23230

2. Action: Continue sending control charts with future QA data submissions. The only modification needed is to use standard deviation for the precision charts rather than range, since the submitted data use standard deviations.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 006

CATEGORY CODE: (QA, DS)

ISSUE TITLE: Setting of range check limits

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: May 25, 1990

STATEMENT OF ISSUE: Water quality data submitters select the upper and lower range checking limits using different criteria from each other and through time. The limits are used by a computer program to check the water quality data when it is submitted to the CBP. Any values outside the limits are sent to the submitter for verification. Values flagged are not necessarily errors but should be investigated for validity. If different sensitivities have been used to screen the data it is possible that bias has been introduced.

PROPOSED SOLUTION: A standardized method of determining the range limits should be used. The extent of biasing must be determined. If biasing has occurred it should be corrected if possible.

DISCUSSION: Currently water quality data submitters give the CBP a table with upper critical, upper warning, lower warning, and lower critical limits for each parameter they submit. The tables are reviewed for updating as needed. Only values outside the critical limits are flagged for inspection. A dataset check list is sent with all flagged values to the data submitter. The data submitter checks the flagged values, notes any corrections, and returns the check list to the CBP. The CBP then makes any corrections noted to the database. Currently VIMS uses the lower method detection limit (MDL) - 0.001 as the lower critical limit, and the mean plus five times the standard deviation for the upper critical limit. The method ODU and MDE uses is not currently known. When checking VIMS and MDE data sets it is normal for about ten to twenty values to be flagged. ODU seldom has any values flagged which may be due to inordinately broad ranges.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

PRIORITY RANKING:

SUBMITTER/RESPONSIBLE PARTY:

Name: Todd Blanc

Organization: Computer Sciences Corp.
EPA Chesapeake Bay Program
410 Severn Ave. Suite 110
Annapolis, MD 21403

ACTIONS TO DATE:

Issue referred to Data Management and Acquisition Workgroup and will be discussed among members via a conference call on 9/12/90, 9-11 a.m. (202) 245-4230

Issue was discussed during referenced conference call (9/12/90). It was proposed that CSC develop seasonal limits by either segment or individual station. This effort, particularly if limits are established for every station, will be time consuming, to the resources required to perform the work will be an issue. It was felt that each lab should submit their range check values for review by CSC. CSC would then develop a comprehensive set of limits for each season, contributor, station (or segment). It was pointed out that the existing data processing programs already have hooks in place to perform more elaborate limits checking when more elaborate and comprehensive limits are defined.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

On 9/12/90 it was recommended that all data contributors submit their current list of range check values. CSC would then evaluate those values and formulate range check values that reflect seasonal, station versus station, or segment versus segment variations in the data which would make more than one set of range check values a more accurate method of performing range checks.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 007

CATEGORY CODE: FM

ISSUE TITLE: Secchi disk variability

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: August 1, 1990

STATEMENT OF ISSUE: While verifying Maryland and Virginia water quality parameters, it was discovered that secchi disk readings were taken at what appeared to be extremely low light conditions.

PROPOSED SOLUTION: Establish a time window for taking and recording Secchi disk measurements.

DISCUSSION: In the process of reviewing the water quality monitoring data base, it appeared that on various sample dates secchi disk readings had been taken in such low light conditions that the validity of those data was in doubt. It was determined that more documentation was needed and that sampling procedures needed to be refined.

Letters were sent to Maryland and Virginia agencies requesting documentation on secchi disk determination and sources of secchi disk variation. The issue was discussed at the 7/12/90 AMQAW meeting.

Respondents confirmed that the reported times for secchi measurements are correct and indicated procedures used to take secchi readings during these low light conditions. AMQAW members felt that secchi measurements are low technology measurements subject to numerous sources of variation which may cause more significant changes than those related to dawn and dusk low light conditions. These sources of variation are documented below:

a. The depth of disappearance of the disk varies inversely with the average amount of attenuating material between the surface and the disk.
b. The depth of disappearance of the disk varies inversely with the optical state of the sea surface.
c. The depth of disappearance of the disk varies inversely with the relative amount of reflected luminance of sky in the sea surface compared to the luminance transmitted upward from below the surface.
d. The depth of disappearance of the disk varies inversely with the reflectance of the water body.
e. The depth of disappearance of the disk varies directly with its reflectance.
f. The depth of disappearance of the disk varies directly with its diameter.
g. The depth of disappearance of the disk varies directly with sun

altitude.

h. The depth of disappearance of the disk varies inversely with the immediate height of the observer above the sea surface.

i. The depth of disappearance of the disk is larger if the water path of sight between disk and observer is more shadowed; it is larger if the water path beyond the disk is less shadowed.

SUBMITTER/RESPONSIBLE PARTY: Todd Blanc, CSC

PRIORITY RANKING: 3

OVERALL RESOLUTION/RECOMMENDED ACTIONS:

Continue current practice and use codes EST (Eastern Standard Time) or EDT (Eastern Daylight Time) to indicate more accurately the time the sample was taken.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 008

CATEGORY CODE: DM, DS

ISSUE TITLE: Data transfer procedures for QA and monitoring data

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: August 28, 1990

STATEMENT OF ISSUE: During analysis of these data, it became apparent that CBLO was lacking some necessary documentation on how data was sampled, coded, handled in the laboratory, and transferred to the Bay program. Documenting all of these phases in the collection and transfer process will save time in the future and make our data base much more useful and reliable.

PROPOSED SOLUTION: Each mainstem laboratory should provide a detailed list of the steps used in data transfer for Chesapeake Bay Program monitoring data.

DISCUSSION: Analysis results are uncertain when we cannot completely document the data base. While data set documentation is submitted with each data file, they are often incomplete in the areas of missing data and laboratory procedures. In addition, project documentation should be updated each grant year.

SENSE OF THE RESOURCES REQUIRED TO RESPOND

PRIORITY RANKING: 3
SUBMITTER/RESPONSIBLE PARTY:
Name: Nancy Kaumeyer
Organization: CBL
Box 38
Solomons, MD 20688

ACTIONS TO DATE:

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

Nancy sent draft to Peter on 3/4/91. CSC converted this to WordPerfect format on 5/20/91, and sent to AMQAW members for final review. Nancy sent Peter a revised draft on 5/31/91, which he distributed to AMQAW members

on 6/12/91 (see memo below). Since no further comments were received, the issue was closed for mainstem labs. See the file DAITS008.TAB in this directory for the mainstem matrix. Then adding tributary information was requested; this was completed on 12/4/92.

RECOMMENDED ACTIONS

ACTION NUMBER: 008.01
1. Designated Respondent: AMQAW members
2. Action: Review attached draft, correct or add information as necessary.
3. Resources Needed:
4. Due Date: June 30, 1991

DATE:6/12/91

SUBJECT:Revised draft of DAITS #8, Data Transfer Sequence
FROM: Peter Bergstrom
TO: Nancy Kaumeyer, Bruce Michael, Kevin Curling, Steve Sokolowski, Don McCall, Dave Clements
COPIES: Claudia Walters, Joe Macknis, Bob Stone

Attached is a revised version of what Nancy sent me on May 31. I have added the steps done by CSC after we get the data, and made a few additions to clarify the lab steps in data transfer. These additions were based on the 1990 on-site visits in which I participated, and I used underlining to highlight them. Please check these over to make sure they are still correct.

Please check over all the information for your laboratory or program, and send me any corrections by July 1, 1991. If I don't hear from you by that date, I will assume you have no changes to suggest. The final version will be distributed to all AMQAW members before the next meeting, and also to Bob Stone's Data Management Workgroup.

DATE: 12/4/92
SUBJECT:Revised DCRA information for DAITS #8, Data Transfer Sequence
FROM: Peter Bergstrom
TO: Al Robertson, Cliff Jarmon, DCRA
COPIES: Hamid Karimi, Claudia Walters, Joe Macknis

Thank you for sending the DCRA information for DAITS #8. Attached is a revised version of the tributary table for DAITS #8, including this information. Please check this over to make sure the DCRA information is correct. The STORET transfer was listed later in the sequence for DCRA than for DCLS because based on your memo, STORET submission by DCRA it is done after CBPO generates SAS data sets.

Please send me any corrections by December 18, 1992. If I don't hear from you by that date, I will assume you have no additional changes. The final version will be distributed to all AMQAW members before the next meeting, and also to the Data Management and Acquisitions Workgroup.

Chesapeake Bay Program TRIBUTARY Monitoring Data Management Procedures

Peter Bergstrom December 4, 1992 (CSC)

MDHMH/MDE (revised by Asoka 7/15/92)	DCLS/VWCB (revised by Norma 3/19/92)	DCRA/CRL (revised by Al R. & Cliff J. 12/3/92)
	Samples received in laboratory + Analyses run	
Peak heights read manually. Std. curve used in calculations. TDP, TP, TOC, DOC calculations use regression analysis. TSS weighed manually.	Peak heights and spectrophotometric absorbances read manually for NH4, PO4F, SI, low range TP (& TDP); computer generates conc. for TKN, (hi range) TP (& TDP), NO23, NO2. NO3 calculated manually. Std. curve used in calculations. TOC & TSS done by Bob Potts lab.	Peak heights read manually for all inorganic nutrients from strip chart Std. curve used in calculations, using computer, except calculator used for TP, TKNW, TDP, TOC and DOC. TSS manually weighed.
Raw results transferred to data sheets by hand.	Raw results transferred to summary sheet by hand,	Raw results transferred to summary sheet by hand.
QA/QC checks by MDHMH staff.	QA/QC checked by DCLS staff	QA/QC checked by another analyst, results outside QA/QC limits are reanalyzed if within regulation holding times. Summary sheets verified for accuracy back to the data books. Acceptable data are submitted to DCRA for data entry.
Copies of lab sheets sent to MDE Chesapeake Bay Special Project Office	Data sheets sent to VWCB Div. Info. Services (DIS) for entry	
		Data entered on PC in DBASE, single key entry, by DCRA staff. Keypunch verification from hard copy by different staff member.
	Data entered on IBM mainframe, single key entry, by DIS staff	
Data entered by key entry service, double key by different people		Final editing of DBASE files by DCRA data manager.
	Data verified: range checks, dummy STORET storage run to check for errors, tabulation of # samples per station, criteria violations (parts > whole, etc.).	
Software developed by MDE staff verifies and checks data for codes, descriptive information, ranges; calculates derived variables. Range checks and plots generated to facilitate identification of problems.		
MDE staff familiar with verification and edit software make necessary corrections. Corrections documented in accompanying computer file.		
All data then reviewed by MDE Principal Investigator.		
	Report printed and reviewed by CBO staff.	All data then reviewed by DCRA Principal Investigator.
No other QA/QC checks at MDE--QA/QC data not sent from MDHMH to MDE	No other QA/QC checks at VWCB--QA/QC data not sent from DCLS to VWCB	No other QA/QC checks at DCRA--QA/QC data not sent from DCRA/CRL to DCRA
Data acceptable OR Data not acceptable; if data not acceptable, MDE staff go back to MDHMH staff for more information	Data acceptable OR Data not acceptable; if data not acceptable, CBO staff go back to DCLS staff for more information	Data acceptable OR Data not acceptable; if data not acceptable, DCRA staff go back to DCRA/CRL staff for more information.

Chesapeake Bay Program TRIBUTARY Monitoring Data Management Procedures, DAITS #8 Page 2

MDHMH/MDE (revised by Asoka 7/15/92)	DCLS/VWCB (revised by Norma 3/19/92)	DCRA/CRL (revised by Al R. & Cliff J. 12/3/92)
Data file name(s) sent to CSC/CBPO in cover letter to EPA/CBPO Monitoring Coordinator.	When data approved by CBO, DIS transfers SAS files to CBPO via DECNET.	Data sent to CSC/CBPO on in ASCII files on floppy disk with cover letter to EPA/CBPO Monitoring Coordinator.
CSC/CBPO receives transmittal letter from MDE, copies data to CBP directory, runs MONITOR program. MONITOR program does range checks, converts data to CBP format if needed, and standardizes variable and station names.	CSC/CBPO receives data and transmittal letter from VWCB, runs MONITOR program. MONITOR program does range checks, converts data to CBP format if needed, and standardizes variable and station names.	CSC/CBPO receives data and transmittal of DSDOC file from DCRA, loads data from floppy disk, runs MONITOR program. MONITOR program does range checks, converts data to CBP format if needed, and standardizes variable and station names.
		DCRA data manager uses SAS data sets generated at CBPO to produce STORET files. STORET data verified: range checks, dummy STORET storage run to check for errors, tabulation of # samples per station, criteria violations (parts > whole, etc.). Report printed and reviewed by DCRA data manager, files submitted to NCC_STORET.
		CSC/CBPO prepares Data Set Checklist and printout to return to DCRA for checking with letter from EPA/CBPO Monitoring Coordinator.
CSC/CBPO prepares Data Set Checklist and printout to return to MDE for checking with letter from EPA/CBPO Monitoring Coordinator.	CSC/CBPO prepares Data Set Checklist and printout to return to VWCB for checking with letter from EPA/CBPO Monitoring Coordinator.	DCRA reviews checklist and printout, signs off on data and/or notes corrections to be made.
MDE reviews checklist and printout, signs off on data and/or makes corrections, and sends them to EPA/CBPO Monitoring Coordinator.	VWCB reviews checklist and printout, signs off on data and/or makes corrections, and sends them to EPA/CBPO.	CSC/CBPO makes any updates to the data set and returns checklist to DCRA. If no additional corrections, CSC/CBPO runs BAYSTATS program to calculate additional variables (PHOSP, TN, etc.) and makes the data available to users upon release by DCRA.
CSC/CBPO makes any updates to the data set and returns checklist to MDE. If no additional corrections, CSC/CBPO runs BAYSTATS program to calculate additional variables (PHOSP, TN, etc.) and makes the data available to users upon release by MDE.	CSC/CBPO makes any updates to the data set and returns checklist to VWCB. If no additional corrections, CSC/CBPO runs BAYSTATS program to calculate additional variables (PHOSP, TN, etc.) and makes the data available to users upon release by VWCB.	DAITS008_trib.TAB

Chesapeake Bay Program *Mainstem* Monitoring Data Transfer Sequence, DAITS #8

Nancy Kaumeyer May 31, 1991 (Lab)
Peter Bergstrom July 14, 1992 (CSC), REVISED

(Edits to lab sections underlined, based on 1990 on-site visits)

Samples received in laboratory + Analyses run

CBL	ODU	VIMS
	(ASCII file transfer added 7/14/92)	
Peak heights read manually for NO23, PO4F, TDN, TDP, PHOSP Std. curve used in calculations Peak heights computer read for NO2, NH4, SI; TSS manually weighed PC/PN calculated by instrument software Data hand calculated for NO23, PO4F, TDN, PHOSP; All other parameters calculated by instrument software Calculated results hand written in lab notebooks, carbon copy made, original sent to MDE	Peak heights and spectrophotometric absorbances read manually for all inorganic nutrients Std. curve used in calculations DOC integrated peaks computer generated TSS weighed manually PC/PN calculated by instrument software Raw results transferred to summary sheet by hand	Peak heights read manually for all inorganic nutrients (from 1/92, PO4F & TDP only) Std. curve used in calculations TSS manually weighed PC/PN and DOC calculated by instrument software; from 1/92, same for other params. except PO4F & TDP Raw results transferred to data sheet by hand (from 1/92, for PO4F, TDP, DOC only)
Data entered into Lotus 1-2-3 file, single key entry	Data entered on PC, single key entry, calculated by computer	Data entered (from 1/92 for PO4F, TDP, DOC only, with ASCII file transfer for other params); calculated by computer in NUTMAIN: Pascal processing program All keyed data entered twice by same person
Data verified, errors corrected within Lotus file	Data verified by supervisor	Data computer verified by comparing both NUTMAIN files. If any errors are found, the entries are changed
Each file is sorted by sample number QA/QC checks are made: salinity and parts > totals Data not acceptable Data acceptable Reanalysis	Control charts generated Data not acceptable Data acceptable Reanalysis	QA/QC checks are made Data not acceptable Data acceptable Reanalysis
Data verified and error codes added Print files prepared and renamed to .DAT files DAT files, hard copy, and original lab sheet sent to MDE Chesapeake Bay Special Project Office	Supervisor transfers data from PC printout to summary report by hand All data reductions completed by this point	Data verified Print NUTMAIN cruise summary Check for missing data, outliers, and part < totals Reprint cruise summary NUTMAIN creates ASCII.SIR file and loads into Hydronal nutrient data base Corrections and error codes added Cruise QC and data report made Verify Hydronal data report against NUTMAIN cruise summary Cruise QC report checked Parameter QC report made for control limits of each parameter Data verified
Data uploaded onto VAX 8600. Software developed by MDE staff verifies and checks data for codes, descriptive information, ranges; calculates derived variables. Range checks and plots generated to facilitate identification of problems.	Computer tech enters data from summary report into SAS, double key (different people) Double key entry screened by computer program	Hydronal data base transfers data report into SAS
MDE staff familiar with verification and edit software make necessary corrections. Corrections documented in accompanying computer file.	All data then reviewed by MDE Principal Investigator.	ODU Lab manager screening review; point by point verification with checks for outliers and other items of ecological significance

CBL	ODU	VIMS
Data file name(s) sent to CSC/CBPO in cover letter to EPA/CBPO Monitoring Coordinator.	Data sent to CSC/CBPO on tape with cover letter to EPA/CBPO Monitoring Coordinator.	Data sent to CSC/CBPO on tape with cover letter to EPA/CBPO Monitoring Coordinator.
CSC/CBPO receives transmittal letter from MDE, copies data to CBP directory, runs MONITOR program. MONITOR program does range checks, converts data to CBP format if needed, and standardizes variable and station names.	CSC/CBPO receives data and transmittal letter from ODU, loads data from tape, runs MONITOR program. MONITOR program does range checks, converts data to CBP format if needed, and standardizes variable and station names.	CSC/CBPO receives data and transmittal letter from VIMS, loads data from tape, runs MONITOR program. MONITOR program does range checks, converts data to CBP format if needed, and standardizes variable and station names.
CSC/CBPO prepares Data Set Checklist and printout to return to MDE for checking with letter from EPA/CBPO Monitoring Coordinator.	CSC/CBPO prepares Data Set Checklist and printout to return to ODU for checking with letter from EPA/CBPO Monitoring Coordinator (copy of cover letter to VSWCB).	CSC/CBPO prepares Data Set Checklist and printout to return to VIMS for checking with letter from EPA/CBPO Monitoring Coordinator (copy of cover letter to VSWCB) .
MDE reviews checklist and printout, signs off on data and/or makes corrections, and sends them to EPA/CBPO Monitoring Coordinator.	ODU reviews checklist and printout, signs off on data and/or makes corrections, and sends them to VSWCB.	VIMS reviews checklist and printout, signs off on data and/or makes corrections, and sends them to VSWCB.
	VSWCB reviews ODU signoff and sends to EPA/CBPO Monitoring Coordinator with VSWCB signoff of data.	VSWCB reviews VIMS signoff and sends to EPA/CBPO Monitoring Coordinator with VSWCB signoff of data.
CSC/CBPO makes any updates to the data set and returns checklist to MDE. If no additional corrections, CSC/CBPO runs BAYSTATS program to calculate additional variables (TP, TN, etc.) and makes the data available to users upon release by MDE.	CSC/CBPO makes any updates to the data set and returns checklist to ODU and VSWCB. If no additional corrections, CSC/CBPO runs BAYSTATS program to calculate additional variables (TP, TN, etc.) and makes the data available to users upon release by VSWCB.	CSC/CBPO makes any updates to the data set and returns checklist to VIMS and VSWCB. If no additional corrections, CSC/CBPO runs BAYSTATS program to calculate additional variables (TP, TN, etc.) and makes the data available to users upon release by VSWCB.
		DAITS008.TAB

Proc means with data transfer
Date: July 8, 1997

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 009

CATEGORY CODE: DM, DS

ISSUE TITLE: USING THE SAS PROC MEANS AS PART OF THE DATA SUBMITTAL

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: AUGUST 28, 1990

STATEMENT OF ISSUE: The opportunity exists for data to be lost or incorrectly modified during data submissions. A method is needed to help ensure data received is the same as what was or should have been sent.

PROPOSED SOLUTION: Each submitter should perform a PROC MEANS on the data and include the listing in the documentation file for the data submittal. Upon receipt of the data set, the CBLO will perform a PROC MEANS and check the listing generated against the listing in the documentation file.

DISCUSSION: Currently a table of frequencies for each parameter is a required part of the documentation for each data submittal to the CBLO. It would be more effective to add a SAS PROC MEANS listing. A PROC MEANS gives several important statistics about each numeric parameter in a data set. Frequency, mean, standard deviation, minimum, and maximum are several of the statistical parameters one can request from the PROC MEANS procedure. Frequency would be exactly the same as currently submitted. One could look at minimum and maximum values to spot probable outliers. The mean and standard deviations will tell something of the distribution of the data.

SENSE OF THE RESOURCES REQUIRED TO RESPOND: Both frequency and means are SAS procedures, and the means procedure would be added to the frequency procedure. This would increase computer run time slightly.

PRIORITY RANKING: 3

SUBMITTER/RESPONSIBLE PARTY:
Name: Todd Blanc
Organization: CBLO/CSC

ACTIONS TO DATE:

Issue referred to Data Management and Acquisition Workgroup (DMAW) and will be discussed among members via a conference call on 9/12/90, 9-11 a.m. (202) 245-4230.

Issue was discussed on 9/12/90 during the DMAW conference call. It was recommended that data submitters perform both a PROC FREQ and PROC

MEANS on their data sets and include the results in the data set documentation file. The CBLO could also perform a PROC MEANS and compare the results. DCRA and SRBC do not submit their data as SAS data sets, so this issue is not pertinent to them.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: 009.01
1. Designated Respondent: Steve Sokolowski

ODU AMRL
Norfolk, VA 23529-0456

2. Action: Please inform Todd when this will start, or call him if you have any questions.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

ACTION NUMBER: 009.02
1. Designated Respondent: Kevin Curling

VIMS
Gloucester Pt. VA

2. Action: Please inform Todd when this will start, or call him if you have any questions.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

ACTION NUMBER: 009.03
1. Designated Respondent: Harry Wang

MDE
2500 Broening Highway
Baltimore, MD 21224

2. Action: Please inform Todd when this will start, or call him if you have any questions.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA/AM/HI) 010

CATEGORY CODE: QA, AM, HI

ISSUE TITLE: INVENTORY OF CBP METHOD COMPARISON DATA SETS

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 9/4/90

STATEMENT OF ISSUE:

Field and laboratory methods for nutrient analyses at Chesapeake Bay Program (CBP) laboratories have changed over time, since the CBP does not require particular methods. Data analysts often need to know if the old and new methods gave comparable results. This inventory was made to collect information on all the "side-by-side" or method comparison data sets collected by CBP laboratories. The Analytical methods and Quality Assurance Workgroup (AMQAW) asked for this inventory at their meeting on 7/12/90.

PROPOSED SOLUTION:

This inventory, when completed, will be made available to any data users concerned with effects of method changes on CBP monitoring data.

DISCUSSION:

The attached matrix includes all the method comparison data sets currently available on the CBLO VAX computer. These guidelines were used:

1. Include any method comparison data sets you have, even if sample sizes are small. Sample sizes of 50 pairs are good and 100 pairs are better, but in some cases a small data set is all that exists.

2. Split sample data sets involving two different laboratories would not normally be useful, unless they were collected for method comparison purposes. Most split sample data do not have large enough sample sizes over a short enough time period; the VIMS/ODU data on DOC are an exception. MDE split sample data comparing CBL and MDHMH methods in the Patuxent should also be included. Comparing methods over long time periods (more than a year) is less reliable because details of one or both methods may change during that time. Data sets comparing field methods (e.g., filter type) or sample preservation methods should also be included.

3. Please indicate whether the data set is in hard copy or digital form, and whether you will be sending it to CBLO to put on the VAX. We would like to have all the data sets here, at least in hard copy. If it is in hard copy only, you can omit the descriptive statistics if the data set is large, but please include the sample sizes for each parameter.

4. The "N > MDL" sample size should exclude any pairs with any of the constituents less than MDL. For example, this would exclude a pair of TN data if TKNW, NO23, TDN, or PON were below MDL.

5. The descriptive statistics (mean, minimum, and maximum) should include below detection limit data. Their purpose is to show the total range of the data. Make sure the "old" and "new" methods are entered correctly.

6. Exclude any field replicate data (REP_NUM=2) from the sample sizes and statistics, since they are not independent data points. These should be left in the data sets, of course, with the REP_NUM variable. Some analysts may want to analyze these data separately.

7. The inventory excluded any POC & TOC comparisons. This was done because PC direct, the new method, detects both inorganic and organic carbon. The old method, POC = TOC - DOC, includes only organic carbon.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

Should take a few hours per laboratory, depending on number of data sets and how they are stored.

PRIORITY RANKING: 4 (medium high)

SUBMITTER/RESPONSIBLE PARTY:

Name: Peter Bergstrom
Senior Statistician
Organization: CSC/CBLO
410 Severn Ave. Suite 110
Annapolis, MD 21403 (800) 523-2281

ACTIONS TO DATE:

1. The Kjeldahl data set from CRL was keypunched, checked, and stored on the CBLO VAX in a SAS data set by CSC/CBLO staff.

2. The following method comparison analyses have been done on CBP data:

D'Elia, C., R. Magnien, C. Zimmermann, P. Vaas, N. Kaumeyer, C. Keefe, D. Shaw, and K. Wood. 1987. Nitrogen and phosphorus determinations in estuarine waters: A comparison of methods used in Chesapeake Bay Monitoring. Report to EPA Chesapeake Bay Program, Annapolis, MD.

Brunenmeister, S. 1989. Trends in Total Phosphorus and Total Nitrogen in Chesapeake Bay, October 1984 to September 1988: A preliminary analysis. (Includes method comparisons for TN and TP at CBL, ODU, and VIMS; ODU data were incomplete due to changed variable names).

Bergstrom, P. 1991. Adjusting Kjeldahl Helix Nitrogen results: Mary land Chesapeake Bay Mainstem Water Quality Monitoring Program, 1984-1985. EPA Chesapeake Bay Program CBP/TRS 44/91, Annapolis, MD. (Compares Kjeldahl helix to Kjeldahl block results at EPA Central Regional Laboratory.)

3. 3/1/91: Betty Salley sent a comparison data set from VIMS from 1985-86, comparing TDN direct (persulfate) to TDN = TKNF (manual digestion) + NO23. This was scanned and added to the CBPO data base on 4/30/91.

4. 4/30/91: Updated issue sent out to AMQAW members: please review table for any corrections or additions, for final approval at meeting on 5/14/91.

5. Approved at meeting of AMQAW on 5/14/91.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: QA/AM/HI 010.01

1. Designated Respondent:

AMQAW/CSSP members (mailed to 25 people, 12/13/90, see below)

2. Action: Please add information on any method comparison data sets you have to the attached matrix and return it to Peter Bergstrom by 2/1/91. Indicate when data sets can be sent to CBLO if possible, and include citations as above for any method comparison reports done. Please check any entries currently in the matrix from your laboratory if they appear to be incorrect.

3. Resources Needed: If data are digitized, requires running PROC MEANS or equivalent program. If data are in hard copy, requires counting sample sizes.

4. Due Date: 2/1/91

5. Action Item Resolution Summary:

Betty Salley (VIMS) sent additional data on 3/1/91 (see above). She also provided information on the DOC comparison data on 2/19/91. Steve Sokolowski called to say that ODU had no additional comparison data.

DATE: December 13, 1990

FROM: Peter Bergstrom

TO: Analytical Methods and Quality Assurance Workgroup (AMQAW) members and Coordinated Split Sample Program (CSSP) participants

SUBJECT: Method comparison data sets inventory

At their meeting on July 12, 1990, AMQAW members requested an inventory of method comparison data sets involving Chesapeake Bay Program laboratories. I have written up this inventory, including all the method comparison data sets we have on the CBLO VAX computer. Please add the same information for any other method comparison data sets you have, and return it to me by February 1, 1991. You could also check any listings for data from your laboratory if they look incorrect. I will type up the responses and distribute them before the next AMQAW meeting.

The next AMQAW meeting is planned for the day before the next Monitoring Subcommittee meeting, if this does not conflict with the cruise schedule or other meeting. The February MSC meeting was just changed from Wed. Feb. 27 to Wed. Feb. 20 to avoid conflicting with the EPA National Estuary Program symposium in Florida. This would put the next AMQAW meeting on Tues. February 19, 10:00 at CBLO, if that us not a cruise week. Please contact me and Bruce Neilson if you can't make it that day; otherwise I will assume that date is acceptable.

If you have received a request for information for one of the other DAITS issues being considered by AMQAW, please send your responses in soon. At the 10/23/90 AMQAW meeting we discussed these additional pending DAITS issues that concern AMQAW:

#1/Data censoring/TSS issue (Rick Hoffman, omitted from minutes)
#2/Kjeldahl helix (myself, being revised)
#3/Field replicate methods (Sally Bowen)
#8/Data Handling (Carl Zimmermann)
#11/Lowering trib detection limits (myself, sent to CRL/DCRA & DCLS)
#12/Selecting historical data (Marcia Olson).

I hope there will be some progress to report on all of these issues at the February AMQAW meeting.

Finally, the CSSP Annual Report for 1989 is at the printer, and should have been back last week. You will all get copies soon. I will start working on the next round of Interim Reports soon, probably starting with the Virginia component.

CHESAPEAKE BAY PROGRAM: METHOD COMPARISON DATA SETS Page 1

DATA ANALYSIS ISSUES TRACKING SYSTEM (DAITS) ISSUE 10, REVISED 4/30/91

LABORATORY	PARAMETER(S) OLD	PARAMETER(S) NEW	N (pairs)	N > MDL (pairs)	MEAN OLD/NEW	MIN OLD/NEW	MAX OLD/NEW	DATES START	DATES END	NOTES
VIMS & ODU	DOC OI ampule (ODU)	DOC Shimadzu (VIMS)	453	453	3.7/4.2	2.3/2.4	9.8/9.3	1/8 /90	6/26 /90	ODU did DOC samples for VIMS before start date
CRL Central Regional Laboratory	TKNW Helix	TKNW Block	167	130	0.34/0.60	0.2/0.29	0.79/0.95	7/12 /84	10/22 /84	Aft. 10/84, Block used for Potomac, Helix for Mainstem
	TKNF Helix	TKNF Block	165	97	0.31/0.45	0.2/0.22	0.70/0.88	"	"	
CBL Chesapeake Biological Laboratory	TN = TKNW + NO23 (Block)	TN = TDN + PN	648	647	0.72/0.72	0.24/0.38	2.3/2.4	6/11 /86	9/24 /86	Analyzed in D'Elia et al. 1987 report
	TDN = TKNF + NO23 (Block)	TDN	649	648	0.56/0.53	0.18/0.27	1.5/1.6	"	"	
	PN = TKNW - TKNF	PN	651	651	0.16/0.19	-0.45/0.03	1.5/1.7	"	"	
	TP	TP = TDP + PHOSP	668	638	0.054/0.043	0.019/0.011	0.22/0.19	"	"	
	PHOSP = TP - TDP	PHOSP	668	638	0.033/0.022	-0.044/0.0023	0.20/0.17	"	"	
ODU Old Dominion University	TN = TKNW + NO23 (Block)	TN = TDN + PN	64	47	0.49/0.43	0.32/0.15	0.81/1.4	10/5 /87	12/14 /87	12/87 data set had "TKNU" and "TPU" variable names, now changed to TKNW &TP
	TDN = TKNF + NO23 (Block)	TDN	75	50	0.35/0.27	0.19/0.094	0.58/0.56	"	"	
	PN = TKNW - TKNF	PN	67	65	0.13/0.16	-0.06/0.05	0.45/1.3	"	"	
	TP	TP = TDP + PHOSP	77	57	0.041/0.040	0.017/0.10	0.10/0.10	"	"	
	PHOSP = TP - TDP	PHOSP	77	57	0.014/0.013	-0.001/0.007	0.056/0.064	"	"	

(see notes at end)

LABORATORY	PARAMETER(S) OLD	PARAMETER(S) NEW	N (pairs)	N > MDL (pairs)	MEAN OLD/NEW	MIN OLD/NEW	MAX OLD/NEW	DATES START	DATES END	NOTES
VIMS	TN = TKNW + NO23 (Macro manual digestion)	TN = TDN + PN	196	167	0.50/0.57	0.33/0.13	1.0/1.4	10/5 /87	12/18 /87	
	TDN = TKNF + NO23 (Macro manual digestion)	TDN	140	140	0.47/0.49	0.25/0.26	1.2/1.4	9/30 /85	1/14 /86	1985 data
	TDN = TKNF + NO23 (Macro manual digestion)	TDN	199	168	0.40/0.47	0.22/0.10	1.3/1.0	10/5 /87	12/18 /87	1987 data
	PN = TKNW - TKNF	PN	198	197	0.11/0.10	-0.79/0.01	0.43/0.90	"	"	
	TP	TP = TDP + PHOSP	96	87	0.026/0.026	0.013/0.014	0.075/0.082	11/16 /87	12/18 /87	PHOSP started
	PHOSP = TP - TDP	PHOSP	96	87	0.012/0.012	0.00/0.005	0.064/0.067	"	"	11/87, not 10/87

NOTES: 1. "N > MDL" includes only pairs of data with ALL constituents > MDL.

2. Mean, Minimum, and Maximum INCLUDE below detection limit data.

3. All N, mean, min, max values EXCLUDE any REP_NUM=2 values (CBL & ODU field replicates), since they are not independent.

4. POC & TOC comparisons were excluded because PC direct (new method) picks up inorganic and organic carbon, not just POC.

5. All data sets are on the CBLO VAX computer unless otherwise noted.

CHESAPEAKE BAY PROGRAM METHOD COMPARISON STUDIES
NUTRIENTS, CHLOROPHYLL, AND CARBON

Bergstrom, P. 1992. Adjusting helix Kjeldahl nitrogen results: Maryland Chesapeake Bay Mainstem Water Quality Monitoring Program, 1984-1985. CBP/TRS 44/92, Chesapeake Bay Program, Annapolis, MD.

Chesapeake Bay Program (CBP). 1992b. Trends in Nitrogen in the Chesapeake Bay (1984-1990). CBP/TRS 68/92, Chesapeake Bay Program, Annapolis, MD. [includes ODU Kjeldahl step trend adjustment]

D'Elia, C., et al. 1986. Methodological comparisons for nitrogen and chlorophyll determinations in estuarine water samples. University of Maryland, Center for Estuarine and Environmental Studies, Publication UMCEES-CBL-86-55.

D'Elia, C., et al. 1987. Nitrogen and phosphorus determinations in estuarine waters: a comparison of methods used in Chesapeake Bay Monitoring. CBP/TRS 7/87, Chesapeake Bay Program, Annapolis, MD.

Magnien, R. 1986. A comparison of estuarine water chemistry analysis on the filtrate from two types of filters. Maryland Office of Environmental Programs, Baltimore, MD.

Salley, B., et al. 1992. A comparison of two methods of measuring dissolved organic carbon. Special Scientific Report #128, Virginia Institute of Marine Science (VIMS), Gloucester Point, VA.

Zimmermann, C. 1991. Estuarine nutrient analyses: A comparison of sample handling techniques and analyses of carbon, nitrogen, phosphorus, and chlorophyll a. Report submitted to EPA through Technology Applications, Inc. by Chesapeake Biological Laboratory, Solomons, MD.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (AM) 011

CATEGORY CODE: AM, DA

ISSUE TITLE: Lowering method detection limits at tributary laboratories

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: September 4, 1990

STATEMENT OF ISSUE:

Method detection limits (MDLs) for nutrients measured at laboratories participating in the Chesapeake Bay Tributary Monitoring Program tend to be higher and more variable than MDLs at laboratories in the Chesapeake Bay Mainstem Monitoring Program. Low MDLs are needed in the mainstem because concentrations tend to be lower there, but the lower reaches of some tributaries also have low nutrient concentrations. There are several benefits to the Chesapeake Bay Program if tributary MDLs were lowered. The benefits of lower MDLs in the tributary monitoring program will increase over time as nutrient reductions are achieved, and water quality goals based on living resource habitat requirements are implemented.

PROPOSED SOLUTION:

Achieve lower MDLs at current tributary monitoring laboratories. Having tributary monitoring done by laboratories with lower MDLs is an alternative solution used by MDE.

DISCUSSION:

The tributary laboratories cannot be expected to have MDLs as low as those in the mainstem because the tributary laboratories analyze a high volume of samples with a wide range of concentrations and matrices. The mainstem laboratories (VIMS, ODU, and CBL) are all research institutions which tend to sample a narrower range of concentrations and matrices, use different analytical methods, and analyze fewer samples per day. However, the benefits of lower MDLs would be realized if the tributary MDLs could be lowered to the lowest level achieved by a tributary laboratory. It is also important to establish that laboratories are achieving their stated MDLs in Chesapeake Bay Program monitoring samples.

There are four benefits to the Chesapeake Bay Program of lower and more consistent MDLs at tributary laboratories:

1) Better tracking of nutrient reductions and trends:

As nutrient levels go down in tributaries, high MDLs will limit the ability of the monitoring program to track further reductions. Managers of nutrient reduction programs need to know if the programs are achieving the desired results. The main parameters currently affected are Total Phosphorus (TP) and Total Nitrogen (TN).

2) Greater ability to determine whether water quality meets habitat requirements

of living resources:

Habitat requirements for Submerged Aquatic Vegetation (SAV) have now been identified for Dissolved Inorganic Nitrogen (DIN), Dissolved Inorganic Phosphorus (DIP), Chlorophyll a (CHLA), Total Suspended Solids (TSS), and light attenuation (Kd). The MDLs for DIN and DIP at some of the laboratories participating in the Chesapeake Bay Tributary Monitoring Program are close to the habitat requirements for SAV. The SAV Technical Synthesis has concluded that existing mid-channel tributary monitoring programs can be used to determine whether seasonally averaged water quality has met SAV habitat requirements in nearby SAV habitats. Thus, the laboratories doing tributary monitoring need to have MDLs lower than the SAV habitat requirements. The MDL should be half or less of the habitat requirement to achieve good resolution at or near the habitat requirement, allowing for field and laboratory precision. The parameters affected are ammonium (NH4) and nitrite + nitrate (NO23), since DIN = NH4 + NO23, and orthophosphate filtered (PO4F), which is the same as DIP.

3) Higher comparability of results in split sample programs:

The Coordinated Split Sample Program would benefit from lower MDLs because samples with below detection limit results at one or more laboratories may not be comparable. Since sampling is only done quarterly, this may eliminate a substantial portion of a year's data. Consistency of MDLs is also useful, because if results are below the MDL, they are more comparable if the MDLs are the same at different laboratories.

4) More information from monitoring results:

Some nutrient parameters are almost always below detection at some stations or in some seasons. For example, Nitrite (NO2) is usually below detection at Virginia fall line stations. Monitoring of these parameters would provide more information for the same expenditure of effort if detection limits were lower.

The relevant detection limits for tributary laboratories are listed below. Some represent the lowest standard used; MDHMH limits are 2% of full scale, and DCLS limits are 3 times the standard deviation of 7 low-level replicates.

Current Lowest Method Detection Limits (MDLs) at Tributary Laboratories

	MDL (mg/l)						
Laboratory	NH4	NO23	DIN	NO2	TN	DIP (PO4F)	TP
DCLS	0.04	0.04	0.08	0.01	0.14	0.01	0.01
MDHMH	0.008	0.02	0.028	0.002	0.12	0.004	0.01
CRL/DCRA	0.04	0.04	0.08	0.01	0.24	0.007	0.01
PADER	0.02	0.04	0.06	0.004	0.24	0.005	0.02
USGS (low)	0.002	0.01	0.012	0.001	0.21	0.001	0.001
OWML	0.01	0.01	0.02	0.01	0.11	0.01	0.01
MINIMUM	**0.002**	**0.01**	**0.012**	**0.001**	**0.11**	**0.001**	**0.001**
Next higher	0.008	0.02	0.02	0.002	0.12	0.004	0.01
MAXIMUM	0.04	0.04	0.08	0.01	0.24	0.01	0.01

(DCLS = Division of Consolidated Laboratory Services, MDHMH = Maryland Dept. of Health and Mental Hygiene, CRL/DCRA = Central Regional Laboratory/Dept. of Consumer and Regulatory Affairs, PADER = Pennsylvania Dept. of Environmental Resources, USGS = US Geological Survey, OWML = Occoquan Watershed Monitoring Laboratory.)

If all the tributary laboratories could achieve the minimum MDL (usually the one at USGS), or at least the next higher one, the four benefits would be realized. For example, the lowest SAV habitat requirements for nutrients are for Widgeongrass (Ruppia maritima), which needs habitats with < 0.14 mg/l of DIN, and < 0.01 mg/l of DIP. Two tributary laboratories, DCLS and CRL/DCRA, have detection limits for DIN and DIP that are greater than half of this requirement. These are underlined in the table above. The two lowest MDLs for DIN and DIP are well below the requirements. Since both DCLS and CRL/DCRA monitor areas of actual or potential SAV growth, their limits need to be lower to assess the effects of water quality on SAV growth.

The Maryland Department of the Environment (MDE) has dealt with this issue by transferring the monitoring of Patuxent River stations from MDHMH to Chesapeake Biological Laboratory (CBL). Apparently the main reason was to document nutrient reductions more accurately. This solution does not appear to be practical for all the tributary monitoring programs.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

AMQAW recommended sending this issue to the two laboratories with the highest limits, and asking them to determine the feasibility of this request. In some cases it might require different analytical methods or equipment, which might be expensive.

PRIORITY RANKING: Medium

SUBMITTER/RESPONSIBLE PARTY:

Name: Peter Bergstrom

Organization: CSC/CBLO
410 Severn Ave. Suite 110
Annapolis, MD 21403
(800) 523-2281

ACTIONS TO DATE:

Discussed issue at AMQAW meeting on 10/23/90, prepared this description of the issue, sent to DCLS and CRL/DCRA on 11/20/90.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: AM **011.01**

1. Designated Respondent: Hamid Karimi/Al Robertson, DCRA
Norma Roadcap, DCLS

2. Action: Review issue and respond with comments on feasibility and cost of the proposed changes, and indicate how much limits could be lowered. Recommend any alternative actions as appropriate.

3. Resources Needed:

4. Due Date: 12/17/90

5. Action Item Resolution Summary:

REPLY from Roadcap received 12/18/90, added to this file via scanner. Reply from Al Robertson received 10/28/91, added to file via scanner, along with reply to Al from Peter Bergstrom dated 10/31/91 requesting more

information. Waiting for reply from Robertson with new MDLs.

ACTION NUMBER: AM **011.02** (not sent yet)

1. Designated Respondent: Chair, AMQAW

2. Action: Review laboratory responses on feasibility after they are received and recommend actions as appropriate.

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

November 20, 1990

Hamid Karimi
DCRA
2100 Martin Luther King Ave. SE, Rm. 203
Washington, DC 20020

Dear Hamid:

Method detection limits for nutrients are discussed in the Submerged Aquatic Vegetation (SAV) Technical Synthesis, which will be released in the near future. This report points out that in some cases, detection limits for tributary laboratories are at or near the habitat requirements for some species of SAV. This makes it difficult to determine from monitoring data whether a particular tributary has water quality that meets the habitat requirements. The analyses done at CRL by DCRA personnel have some of the highest detection limits in the Chesapeake Bay Program for important species of nitrogen and phosphorus.

In the attached issue statement, we are asking you to evaluate the feasibility and cost of lowering the CRL/DCRA detection limits for these parameters. The habitat requirements for SAV growth include Orthophosphate and Dissolved Inorganic Nitrogen (Ammonium + Nitrite/Nitrate). If you could lower your detection limits for these parameters to less than half of the SAV habitat requirements, the usefulness of the monitoring data you collect would be increased. Once we have received your response, the issue will be discussed by the Analytical Methods and Quality Assurance Workgroup. If you have any questions about the attached issue description, call me or Peter Bergstrom at (800) 523-2281.

Yours sincerely,

Joseph Macknis
Monitoring Coordinator

cc: A. Robertson, P. Bergstrom

SYS$CBPMONITOR:[DAITS]DAITS011.WP

November 20, 1990

Norma Roadcap
DCLS
1 N. 14th St. Room 337
Richmond, VA 23219

Dear Norma:

Method detection limits for nutrients are discussed in the Submerged Aquatic Vegetation (SAV) Technical Synthesis, which will be released in the near future. This report points out that in some cases, detection limits for tributary laboratories are at or near the habitat requirements for some species of SAV. This makes it difficult to determine from monitoring data whether a particular tributary has water quality that meets the habitat requirements. The analyses done at DCLS have some of the highest detection limits in the Chesapeake Bay Program for important species of nitrogen and phosphorus.

In the attached issue statement, we are asking you to evaluate the feasibility and cost of lowering the DCLS detection limits for these parameters. The habitat requirements for SAV growth include Orthophosphate and Dissolved Inorganic Nitrogen (Ammonium + Nitrite/Nitrate). If you could lower your detection limits for these parameters to less than half of the SAV habitat requirements, the usefulness of the monitoring data you collect would be increased. Once we have received your response, the issue will be discussed by the Analytical Methods and Quality Assurance Workgroup. If you have any questions about the attached issue description, call me or Peter Bergstrom at (800) 523-2281.

Yours sincerely,

Joseph Macknis
Monitoring Coordinator

cc: R. Hoffman, C. Cook, P. Bergstrom

SYS$CBPMONITOR:[DAITS]DAITS011.WP

COMMONWEALTH OF VIRGINIA
DEPARTMENT OF GENERAL SERVICES

DIVISION OF
CONSOLIDATED LABORATORY SERVICES
1 NORTH 14TH ST.
RlCHMoND vlRGINlA 232l9-3691

December 14, 1990

Environmental Protection Agency
Chesapeake Bay Program
410 Severn Avenue
Annapolis City Marina
Suite 109-110
Annapolis, MD 21403

Dear Mr. Macknis:

After reviewing your letter dated November 26, 1990, regarding the need for lower detection limits for Ammonia, Ortho-phosphorus, nitrate and nitrite, I met with Loretta Kirk (Section Chief) and Ed LeFebvre (Director, Bureau of Chemistry). We discussed what would be entailed in order to comply with your request. Due to current budget constraints, buying any new Technicon instrumentation would not be feasible. Having scanned the existing inventory of spare Technicon components, I feel that we could build one new system, possibly two, if time permits. Sherry Lacy and I have agreed to undergo this project when our water samples begin to decline in number. As of this time, we have not had a decline in numbers. The amount of extra work these changes entail would be significant. We have reviewed several methods in our library. Also, several methods have been requested of other agencies currently using this low detection limit.

In the meantime, if you should know of any funding that may be available, please let us know. Any private or public funds would be greatly appreciated. At this time, we are very interested in having data that will be functional in statistical analysis of the Chesapeake Bay. This issue will be a valid concern of the lab during 1991.

Thank you for your cooperation in this important quality assurance program. If you have any further questions regarding this matter, you may contact me at (804) 786-4853.

Sincerely,

Norma N. Roadcap
Chemist Supervisor, Feed/Nutrients Lab Bureau of Chemistry

GOVERNMENT OF THE DISTRICT OF COLUMBIA
DEPARTMENT OF CONSUMER AND REGULATORY AFFAIRS
ENVIRONMENTAL REGULATION ADMINISTRATION
2100 MARTIN LUTHER KING. JR. AVENUE S.E WASHINGTON, D.C. 20020

October 28, 1991

Mr. Peter Bergstrom
US EPA, Region 111 CBLO
410 Severn Avenue
Annapolis, MD 21404

Dear Peter:

Please forgive our delay in responding to DAITS issue #011- Lowering method detection limits at tributary laboratories. We support all efforts to increase the usefulness of our data to benefit the various programs within the Chesapeake Bay community.

With that goal in mind, we have pursued your recommendation of lowering our detection limits for Dissolved Inorganic Nitrogen -DIN (NH4 and N02 + N03) and Dissolved Inorganic Phosphorous - DIP. Our present instrumentation, Technicon AAll and with minimal "troubling of the waters" (not too much system overhauling) has allowed us to lower P04F. (See table below) The method detection limits for NH4 and N02+N03 are the best that our AAll can reliably provide.

MDLs(mg/l):	N02+N03	NH4	PO4
current	0.04	0.04	.007->.005
proposed*	<0.035	<0.035	<.005

*based upon SAV requirements of Widgeongrass for nutrients. Needs habitat of < 0.14 mg/l of DIN (N02+N03 and NH4) and <0.01 of DIP (P04). Stated goal is less than half of the SAV requirements for DIN and DIP.

DCRA has in its possession a Traacs 800, which was recently delivered to CRL for our use. The two channel system will be able to analyze NH4 and P04F. From what I can determine from the literature, we can effectively lower the mdl for NH4 down to your recommended level.

Our remaining task would be to lower the mdl for N02+N03 and that can be achieved as well. We would have to purchase additional hardware to be able to analyze this chemistry. If we can be of further assistance, please don't hesitate to contact me.

Sincerely,

Al Robertson, Environmental Specialist
Environmental Regulation Administration
Water Resources Management Division

cc: Claudia Walters, QCO, Chesapeake Bay Program
Jim Collier, Acting Program Manager, Water Resources Management Division
Peggy Zawodny, QCO, EPA CRL
Nicoline Schulterbrandt, Environmental Specialist, WRMD:Lab Branch
Wanda Boyd, Environmental Specialist, WRMD: Lab Branch

November 4, 1991

Al Robertson, Environmental Specialist
DC DCRA
839 Bestgate Rd.
Annapolis, MD 21401

Dear Al:

Thank you for your letter of 10/28/91 concerning method detection limits (MDLs) for the DCRA/CRL laboratory for Potomac River monitoring. You addressed the three parameters discussed in the Data Analysis Issues Tracking System (DAITS) Issue # 11, sent on 11/20/90. However, based on a phone conversation I had with you a few weeks ago, I was expecting a list of revised MDLs for all parameters. You said you did not know when or how the current DCRA/CRL MDLs were calculated, and that they were being re-calculated using the CBP method, 3 times the standard deviation of 7 replicates of a low-level sample. Has this been done, and were the three MDls given in your letter (for NO23, NH4, and PO4F) calculated by this method? Please send us a list of your revised MDLs for all parameters as soon as it is available, with an example of how the MDLs were calculated.

Concerning the proposed DCRA/CRL MDLs for NO23 and NH4 (0.035 mg/l for both), I am not sure why they are higher than limits for other laboratories using the same equipment. The MDLs for NO23 at CBP mainstem laboratories have never been above 0.02 (VIMS), 0.01 (ODU), or 0.0009 (CBL). The original MDL for NH4 for OEP/CRL was 0.02, which was raised to 0.04 in February 1985, just before CBL took over Maryland mainstem monitoring. At the current mainstem laboratories, the MDL for NH4 has never been above 0.02 (VIMS), 0.01 (ODU), or 0.003 (CBL). Is there a reason why your equipment can't achieve MDLs of 0.02 or 0.01 mg/l for these two parameters? They should be possible with the TRAACS 800, if not with your current equipment. When do you anticipate having the TRAACS operational? Are you planning to add NO23 to its capabilities?

Please call me if you have any questions concerning this issue.

Sincerely,

Peter Bergstrom
Senior Statistician, CSC/CBPO

cc: C. Walters
J. Collier
P. Zawodny
N. Schulterbrabdt
W. Boyd

REPLY RECEIVED FROM AL ROBERSTON 11/4/92:

Proposes lowering their MDLs in "6-8 months" using TRAACS 800 if funding is available, as follows:

	MDL (mg/l)						
Laboratory	NH4	NO23	DIN	NO2	TN	DIP (PO4F)	TP
OLD LIMITS:							
CRL/DCRA	0.04	0.04	0.08	0.01	0.24	0.005	0.01
NEW LIMITS:							
CRL/DCRA	0.01	0.02	0.03	0.001	0.22	0.0012	0.01

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 012

CATEGORY CODE: HI/DM/QA

ISSUE TITLE: Criteria for selecting data in the CBP historical water quality data base.

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: September 4, 1990

STATEMENT OF ISSUE:

This issue was raised in the Monitoring Subcommittee meeting held in Richmond, August 22, 1990, with respect to the selection of data included in the trend analysis of dissolved oxygen in the Bay.

The CBP historical water quality data base is an assemblage of data from many sources and collected for different purposes. Most of the data sets were acquired in the late 1970's and early 80's for use in evaluating the water quality of Chesapeake Bay and the documentation for these data is often incomplete in such areas as sampling design and protocol, analytical methods, internal quality assurance, treatment of "below-detect's" - all of which affect the quality and representativeness of the data base. In addition, errors - some random, some systematic - were introduced in the data transfer and conversion process.

In most instances, it is not possible to validate individual values, and "expert" judgement is required to decide whether to include or exclude individual data points, particular stations, or entire data sets. Since
this data base has been and will be serving as a main source of data for analyzing trends and the effects of management actions on the water quality of Chesapeake Bay, guidelines for excluding and including data should be formulated and generally agreed upon.

PROPOSED SOLUTION:

9/11/90:

The CBLO will host a workshop to develop such guidelines. The participants will include representatives from the state and

federal agencies in the Monitoring Program as well as invited "experts", such as laboratory analysts and /or principal investigators from the EPA Annapolis Field Office (AFO) and Central Regional Lab (CRL), USGS, MD/DNR, Johns Hopkins Chesapeake Bay Institute (CBI) and other academic groups that were major contributors to the historical data base. CBLO, with input from appropriate workgroups of the Monitoring Subcommittee (DAWG, AMQAW, Data Management and Data Acquisition), will develop specific issues for discussion, resolution, and documentation through the Data Analysis Issues Tracking System (DAITS).

DISCUSSION:

"Suspect" and problematic data occur in the historical data base in a variety of forms:

1) Obvious errors, e.g., salinities of 100, that are easily identified and more or less easily resolved. However, in the absence of absolute knowledge of the true value, should the value be set to missing, or if a reasonable correction can be deduced from additional evidence, should a corrected value be inserted?

2) Values that appear too high or too low based on "typical" values with no other corroboration.

3) Values that appear too high or too low based on related parameters, e.g., dissolved fraction larger than total, replicates very different, high particulate fraction associated with locally high TSS values, an artifact, POSSIBLY, of disturbing bottom sediments during sample collection (see also DAITS issue 001).

4) Detection limit indicators not included in many data sets; below-detects treated differently in each data set: some set to missing, some set to 0.0, some set to the detection limit, but no detection-limit flag identifies the value. In some cases, laboratory detection limits can be determined in general from reports or lab records, but can not be confirmed for the specific values in question. In other cases, the zeros and "missings" can not be separated from true zero or missing data without original data records.

5) Data derived by different methods under the same variable name, e.g., same analytical method, but different filter pore size; metered versus titrated measurements; similar methods with "slight" modifications; direct measurement versus values derived by summing or subtracting the parts, some methods assigned without complete (or any) supporting documentation.

6) Biases introduced by study designs of the source data:

a) unrepresentative values at affected stations in environmental impact studies or special characterization studies (for example: power plant, sewage treatment, industrial effluent studies; studies of anoxia in the deep trench). Impact stations are not identified as such in the data base. Criteria for station selection are unknown for many source data sets.

b) incomplete sampling profiles: e.g., surface only or fixed depths, not to bottom; sample depth not relative to water column stratification;

7) QAQC data virtually nonexistent for historical data, i.e., precision and accuracy unknown, but presumed to be different for each data source.

8) Unknown number of random transcription errors, systematic errors of data format conversion, systematic errors due to incompatible measurement units, etc.

In addition to the problems of identifying and resolving questionable data, there is the problem of documenting each action and the underlying rationale.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

External participants may need to sort through archives at respective institutions to produce additional documentation for historical data sets.
Compensation for non-CBP workshop participants may be problematic.

PRIORITY RANKING: 2 (second to highest)

SUBMITTER/RESPONSIBLE PARTY:

Name: Marcia Olson (301) 266-6873, ext 215 (CSC)
Bettina Fletcher (CBLO)

Organization: Chesapeake Bay Program Liaison Office
410 Severn Avenue, Suite 112
Annapolis, MD 21403

ACTIONS TO DATE:

9/11/90 Draft Statement of Issue submitted for internal review.

9/12/90	Draft Statement of Issue submitted to initial oversight group: Tina Fetcher (CBLO), Rob Magnien (MDE), Steve Sokolowski(ODU) and Lacy Williams (CSC).
9/18/90	Conference call. Participants were Joe Macknis, Marcia Olson,Tina Fletcher, Steve Sokolowski and Bruce Michael.
10/24/90	Summary of action to date to Monitoring Subcommittee. Bob Stone of Data Acquisition Workgroup added to this oversight group.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: HI/QA 012.01

1.Designated Respondents: Tina Fletcher, CBLO
Steve Sokolowski, ODU
Rob Magnien, MDE

2. Action: Review this document and recommend changes and workshop participants. Phone comments to Marcia Olson, telephone # above.

3. Resources needed:

4. Due Date: 9/18

5. Action Item Resolution Summary:

Respondents participated in a conference call on 9/18/90. Bruce Michael represented MDE and in future will be the designated respondent from MDE on this issue. The group agreed that data sets had to be brought "on line" for analysis only after screening and some formal inclusion process, and to the greatest extent possible, data originators should be included in the screening process.

ACTION NUMBER: HI/QA 012.02

1. Designated Respondent: Marcia Olson, CSC/CBLO

2. Action:

a) Prepare a list of the water quality data sets at CBLO, a brief description of their contents and importance. Suggest a priority

for each.

b) Prepare a straw document of questions needing resolution that will standardize the validation/documentation process for each data set. Base the format on the CBP Data Set Documentation Form.

c) Prepare current status report for two sample data sets with high priority.

d) Send copies of these items to above respondents. Set up another meeting (conference call) for the first week of October.

e) Be sure that DAWG includes data quality review as first part of trend analysis protocol.

3. Resources needed: a), b), and c) are already prepared; need only to be expanded for this purpose.

4. Due Date: 9/21

5. Action Item Resolution Summary:

Data screening software
Date: July 8, 1997

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 013

CATEGORY CODE: DM

ISSUE TITLE: Data Screen

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: September 12, 1990

STATEMENT OF ISSUE:

Resolution of data quality issues related to data submission required 900 hours of staff time in the period between March 1989 and March 1990. An equivalent amount of time was spent by the data submitters in responding to EPA questions concerning the accuracy of the data. Implementation of the proposed activities will provide 1800 hours in cost avoidance for each subsequent year.

PROPOSED SOLUTION:

Develop a SAS software program for the data submitters to "screen" the data prior to submittal. This data screen would uncover routine problems that generate considerable demands on staff time of both the reporting agency and the Chesapeake Bay Program to resolve. Often these 'errors' are routine and often obvious problems from data entry or data recording.

DISCUSSION:

Address background, justification for recommended actions and benefit of action or implications of inaction as is appropriate. Provide example where possible.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

It would take approximately 60 hours to write the SAS program and 40 hours to assist in on site implementation. Estimated Total cost 100 hours.

PRIORITY RANKING: 4

SUBMITTER/RESPONSIBLE PARTY:

Name: Todd Blanc

Organization: CSC
410 Severn Ave
Annapolis MD, 21403

ACTIONS TO DATE:

Issue referred to Data Management and Acquisition Workgroup and will be discussed among members via a conference call on 9/12/90, 9-11 a.m. (202) 245-4230.

9/12/90 - Rob Magnien, MDE, and Rick Hoffman, SWCB, sent a memo to the group to use in the conference call discussion. Their response was "ODU, VIMS, MDE, and other water quality data submitters can provide a summary of their existing error checking software to see if this is sufficient and if exchange of existing software is feasible and/or desirable." CSC will examine these and respond with any suggestions if appropriate.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER:

1. Designated Respondent:
   (Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 014

CATEGORY CODE: DM

ISSUE TITLE: REPORTING OF VARIABLE "WINDSPD"

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: September 28, 1990

SUBMITTER/RESPONSIBLE PARTY:

Name: Todd Blanc

Organization: CSC
410 Severn Ave
Annapolis, MD 21403

PRIORITY RANKING:

STATEMENT OF ISSUE: The three bay mainstem labs each report the variable WINDSPD differently. VIMS reports the variable WAVHGT which is the same as the Beaufort Scale of Wind Forces and can be converted to WINDSPD. The Maryland Department of the Environment (MDE) reports the minimum and maximum wind speeds which the CBP averages and converts to the CBP variable WINDSPD. Old Dominion University reports the value in the CBP format as WINDSPD and needs no conversion. The Beaufort scale is universally known and is more precise than the variable WINDSPD.

PROPOSED SOLUTION:

Several options exist that could result in more uniformity and improvement in the reporting of the variable WINDSPD:

1) No change.

2) Require all data submitters to report WINDSPD based on the Beaufort scale.

3) Require VIMS and MDE to report WINDSPD in the same format as ODU.

4) Convert (at CBP) the VIMS variable WAVHGT to WINDSPD, either for future submissions only, or retroactively, which would require reprocessing all prior VIMS data sets.

The author recommends option number 2.

DISCUSSION:

OVERALL SOLUTION/RECOMMENDED ACTIONS:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA, AM) 015

CATEGORY CODE: QA, AM

ISSUE TITLE: Adjusting Chesapeake Biological Laboratory (CBL) Orthophosphate (PO4F) data for salinity effect

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 12/10/90

STATEMENT OF ISSUE:

There is a systematic refractive index absorbance error for saline orthophosphate (PO4F) determinations measured on an AutoAnalyzer using standards diluted in distilled water.

PROPOSED SOLUTION:

A correction factor was determined by analyzing samples for PO4F twice: once without the color reagent, and again with the color reagent. The first determination gave the blank correction, since without the color reagent any orthophosphate detected must be due to the salinity of the sample. This blank amount, which depends on salinity, should be subtracted from any PO4F values from CBL before May 1990.

DISCUSSION:

The curved ends of the flowcells of AutoAnalyzers cause differences in apparent absorbance measured at the phototube which are related to differences in the refractive indices of the solutions in the cells. This problem is found in determinations where the proportion of sample is large relative to the amount of reagents in the sample stream. The only analyte for which we have found a detectable difference in refractive index among freshwater samples, saline samples, standards made in deionized water and standards made in seawater is orthophosphate (PO4F). The apparent concentration of orthophosphate as a result of the systematic error from refractive index for a range of salinities up to 36 parts per thousand (ppt) on our Technicon AutoAnalyzer is a linear relationship with an R^2 of 0.929. Higher salinity causes higher apparent concentrations. For example, the refractive index-caused apparent orthophosphate concentrations for some of the salinities encountered in the Maryland Mainstem Monitoring Program are:

Salinity	Apparent Orthophosphate Concentration (due to salinity)
l ppt	.0001 mg P/l
5	.0004
10	.0009
20	.0017

For the lower salinities, the apparent orthophosphate concentration due to refractive index would certainly be considered negligible, especially when compared to the relatively large concentrations of orthophosphate. However, at the higher salinities the systematic error due to refractive index is larger. Whether the refractive index error is a significant component of the orthophosphate concentration depends on the concentration of orthophosphate in the sample. At some times of the year, the amount of apparent orthophosphate due to the refractive index is large relative to the total concentration of orthophosphate.

The equation for correcting PO4F based on CBL data is:

PO4F CORRECTED = APPARENT PO4F - (0.000087 X SALINITY)

This regression equation originally calculated using LOTUS 1-2-3 was verified using SAS software. The regression was forced through zero to obtain the most accurate correction factor (Loder & Glibert, 1977; Froelich & Pilson, 1978).

Before submission to MDE, all data analyzed by CBL for orthophosphate samples taken after May 1, 1990, have been corrected for refractive index error.

By February 1, 1991, MDE will have completed correcting the historical orthophosphate data from March, 1985, to April 30, 1990, that had been analyzed and submitted by CBL.

The current status of the need for this correction at each CBP laboratory is as follows:

CBL: Distilled standards, correction needed & applied (MDL is 0.0006, maximum salinity is 20 ppt)

VIMS: Saline matrix standards, correction not needed

ODU: Saline matrix standards, correction not needed (see attached letter)

MDHMH: Distilled standards, but at their usual maximum salinity (10 ppt) correction is less than 1/4 of their detection limit (0.004 mg/l), so Al Bober said they don't need it (see attached letter).

DCLS: Distilled standards, but at their usual maximum salinity (5 ppt) the correction is only 4% of their detection limit (0.01 mg/l), so Norma Roadcap said (by phone on 2/28/91) that they don't need it.

CRL/DCRA: Working on response (2/28/91). MDL is 0.007 mg/l.

HRSD: Uses saline standards, so should not need this correction. However, Drew Francis ran some 1990 PO4F samples from the Elizabeth River with and without the color reagent, and got measurable concentrations without the color reagent. Drew will talk to Carolyn, Carl, and Steve about this (based on phone call 2/28/91). Their current MDL is 0.01 mg/l, maximum salinity is about 22 ppt.
Any CBP laboratories that analyze saline samples should respond to the following items:

1. Are your PO4F standards diluted in fresh or saline matrix?

2. If a fresh matrix is used, is the salinity correction described here used on your PO4F data?

3. If the salinity correction is not used, is it needed for the PO4F concentrations and detection limit at your laboratory?

4. If standards are diluted in a saline matrix, does the salinity of the standards always approximate the salinity of all samples closely enough that any apparent P04F concentration salinity error is non-detectable, as defined by your method detection limit? (This question from Steve Sokolowski.)

Please send these answers to Peter Bergstrom at CBLO to add to this summary.

REFERENCES

FFroelich, P. N., and M. E. Q. Pilson. 1978. Systematic absorbance errors with Technicon AutoAnalyzer II colorimeters. Water Research 12:599-603.

Loder, T. C., and P. M. Glibert. 1977. Blank and salinity corrections for automated nutrient analysis of estuarine and seawaters. University of New Hampshire Sea Grant No. UNH-5G-JR-101 and Woods Hole Oceanographic Institute No. 3891. 29 pp.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

PRIORITY RANKING:

3 medium

SUBMITTER/RESPONSIBLE PARTY:

Name: Carolyn Keefe
Senior Faculty Research Assistant

Organization: Chesapeake Biological Laboratory
PO Box 38
Solomons, MD 20688

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS: (not yet complete 4/9/92)

AMQAW gave final approval to make the correction on 5/14/91. MDE provided adjusted PO4F data for January 1986-April 1990 with a letter from Magnien to Macknis dated 3/27/91 (see below, will be scanned & added). Following the instructions in that letter, the equation above was also used to adjust March-December 1985 PO4F data. These changes were made to BAYSTATS files on April, 1994. Due to missing salinity data, this produced missing PO4F data for some layers for March-December 1985. The March-December 1985 PO4F data were replaced in BAYSTATS files with corrected data from MDE on April, 1994. All MD trib data were resubmitted in the 1998-1999 timeframe.

RECOMMENDED ACTIONS:

ACTION NUMBER: QA/AM 015.01

1. Designated Respondent: AMQAW members

2. Action:

Review summary of issue and approve it or suggest changes. Other laboratory personnel should check whether the correction is needed for their PO4F data and send responses to Peter Bergstrom. AMQAW chair will report to Monitoring Subcommittee on AMQAW action.

3. Resources Needed:

4. Due Date: February 19, 1991.

5. Action Item Resolution Summary:

At 2/19/91 AMQAW meeting, there were no comments or changes to this issue. Final approval was given at the 5/14/91 meeting.

SYS$CBPMONITOR:[DAITS]DAITS015.WP

December 10, 1990

Carolyn Keefe
Chesapeake Biological Laboratory
PO Box 38
Solomons, MD 20688

Dear Carolyn:

As you know, I was informed in a letter from Rob Magnien on 10/12/90 that CBL monitoring data for Orthophosphate (PO4F) need a correction for blank values. At the October AMQAW meeting, you said you would write up the adjustment for the Data Analysis Issues Tracking System (DAITS). I have copies of your correspondence explaining the problem and the solution, but I think it would be best if you summarized the issue. The outline for this DAITS issue is on the enclosed IBM floppy in ASCII format. Please add to this file and return the diskette to me with an ASCII or WordPerfect file. CSC will then convert this to a VAX Wordperfect file to store in the DAITS directory.

The priority for documenting this adjustment is high. We receive data requests for CBL monitoring data frequently. Please indicate in your account of the issue exactly when the adjustment should start and end. The summary should be complete enough to allow a data user to apply the adjustment. MDE said they will send us corrected data, but some data users may prefer to correct the data they already have.

Sincerely,

Joseph Macknis
Monitoring Coordinator

cc: B. Michael, P. Bergstrom

LABORATORIES ADMINISTRATION
DEPARTMENT OF HEALTH AND MENTAL HYGIENE
201 WEST PRESTON STREET A P.O. BOX 2355 A BALTIMORE, MARYLAND 21203 A 301-383-2880

Mr. Peter Bergstrom
US EPA, Region III
CBLO
410 Severn Avenue
Annapolis, MD 21404

Dear Peter:

We are looking forward to the February 19, 1991 meeting of AMQAW in Annapolis.

In response to your inquiry about our P04F salinity adjustment, we will answer each question in the same sequence as you asked them.

1. At DHMH P04F standards are diluted in deionized water.

2. We do not use the salinity correction described by the CBL Laboratory on our P04F data.

3. The detection limit for P04F in our laboratory is 0.004 mg P/L and most of our samples are fresh water with a salinity between 5-10 ppt (according to Bruce Michael). Since our detection limit is more than twice the interference at 2O ppt reported by CBL, the salinity correction described by them is not needed for our P04F concentrations.

Peter, should we make an effort to lower our P04F detection limit? We wish to be in step with the rest of the testing community. We are not impacted by a fourth decimal place in our work.

Sincerely,

Alvin Bober
Chief
Environmental Chemistry Division

OLD DOMINION UNIVERSITY

Applied Marine Research Laboratory
College of Sciences
Norfolk, Virginia 23529-0456
804-683-4195

January 14, 1991

Dr. Peter Bergstrom
Computer Science Corp.
c/o EPA-Chesapeake Bay Program
410 Severn Ave.
Annapolis, MD 21403

Dear Peter:

I received Joe Macknis' mailing of the summary/status of DAITS issues which are pending before AMQAW.

With regard to DAITS issue #15 (adjusting phosphate-P data), we have always prepared calibration standards for orthophosphate-P and dissolved phosphate-P by standard additions. Therefore, corrections for salinity and other non-analyte background interferences have always been incorporated into the analytical procedures.

With reference to the January 7, 1991 draft of this issue, I recommend adding another question (page 2) for response from other CBP laboratories: 4. If standards are diluted in saline matrix, does the salinity of the standards always approximate the salinity of all samples closely enough that any apparent P04F concentration salinity error is non-detectable, as defined by your method detection limit? This could become pertinent as salinity increases, particularly when the analyses are performed using a higher instrument sensitivity for very low analytical ranges such as when working with lower concentrations in the less-estuarine areas of the Bay.

Please contact me if you have any questions.

Sincerely,

Steven W. Sokolowski
Marine Scientist Sr.

cc: Dr. R.W. Alden III
Ms. S.C. Doughten
Ms. Carolyn Keefe

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA, AM) 016

CATEGORY CODE: QA, AM

ISSUE TITLE: Adjusting Maryland Dept. of Health and Mental Hygiene (MDHMH) Total Phosphorus (TP) and Total Dissolved Phosphorus (TDP) data

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 12/10/90

STATEMENT OF ISSUE:

Based on split sample data from 1987-1990, MDHMH data for Total Phosphorus (TP) and Total Dissolved Phosphorus (TDP) were higher than comparable results from CBL, ODU, or VIMS. The MDHMH results for TP and TDP were usually about 0.03 - 0.05 mg/l higher than the results from the other laboratories.

PROPOSED SOLUTION:

Investigate and document the cause(s) of higher MDHMH data for TP and TDP, and dates of applicability. Revise and analyze relevant data to determine if a correction factor can be used to correct the problem. Adjust MDHMH data, if possible, to increase accuracy.

DISCUSSION:

Phosphorus is a critical chemical parameter used in evaluating the success of management strategies designed to reduce nutrient loads to the Chesapeake Bay and its tributaries in order to improve water quality. It is therefore crucial that the phosphorus values reported be as accurate as possible.

Data collected by the Maryland Department of the Environment (MDE) for the Coordinated Split Sample Program (CSSP) has indicated that TP and TDP values analyzed at MDHMH laboratories from 1987 through 1989 show a consistently high bias when compared to other laboratories--CBL, ODU, and VIMS for these parameters. In the process of determining why MDHMH lab values were consistently high, it was discovered that MDHMH lab was not using the calibration data or blank data obtained during analysis from the Technicon II instruments in calculating the slope and Y-intercept for determining the results for TP and TDP from 1984 through 1989. During this time period, all data were assumed to have a slope of 2 and a y-intercept of 0.

Investigations by MDE showed that for 1984 to 1989, the correct slope was 1.8888 and the correct y-intercept was 0.0419. These have been used to correct 1984-1989 TP (or TDP) data from MDHMH as follows:

TP = (TP*1.8888/2) - 0.0419; (same for TDP)

These equations will be used by MDE to correct 1984-1989 TP and TDP values in MDHMH data for re-submission to the CBP data base. Note that they will produce some adjusted values below the Method detection Limit (MDL), which is 0.01 for both TP and TDP. These must be adjusted up to the detection limit using the equation above as follows:

IF . < TP (or TDP) < 0.01 THEN TP (or TDP) = 0.01;

The first part of this formula must be used or SAS will set all missing values to 0.01, since missing values are treated as less than numerical values in SAS.

Starting in 1990, a more exact correction was possible, using a slightly different slope and intercept for different samples. Thus, 1990 and 1991 TP and TDP data from MDHMH were corrected by MDE and re-submitted to the EPA Chesapeake Bay Program data base on 9/27/91. These data were added to the CBP data base; verification of them is pending a submission of PROC MEANS output by MDE.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

0.2 FTE, MDE, and 0.1 FTE, MDHMH

PRIORITY RANKING: 5 (high)

SUBMITTER/RESPONSIBLE PARTY:

Name: Bruce Michael, QA Officer

Organization: Maryland Department of the Environment
2500 Broening Highway
Baltimore, MD 21224

ACTIONS TO DATE:

This summary sent to Peter Bergstrom, CSC/CBPO, on 2/19/91, without correction factors. Bruce gave Peter correction factors by phone on 2/22/91. Corrected 1990-91 data were received from MDE on 9/30/91. This summary revised by Peter to include the need for below detection limit adjustments on 6/26/92.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: QA/AM 016.01

1. Designated Respondent: AMQAW

2. Action: Review issue and approve or suggest changes.

3. Due date: Discuss at meeting on 11/21/91, decide on due date.

This issue was discussed at the AMQAW meeting, adjustment was approved. Completion of issue is pending, waiting for Bruce to finish writing it up and adjusting 1989 and earlier data.

December 10, 1990

Bruce Michael
Maryland Department of the Environment
2500 Broening Highway
Baltimore, MD 21224

Dear Bruce:

You mentioned in your talk on phosphorus trends at the CRC conference that the MDHMH tributary monitoring data for TP and TDP had been adjusted. Peter Bergstrom discussed this with you, and you said you would write up the adjustment for the Data Analysis Issues Tracking System (DAITS). The form that we use for this is enclosed, with the start of the write-up for this issue. If you can use WordPerfect on our VAX, you can edit the file directly (in Version 4.2) using the filename indicated. If you prefer to write this up on another system, you can use the outline on the enclosed IBM floppy in ASCII format. When you return the disk, CSC staff will then convert this to a VAX Wordperfect file to store in the DAITS directory.

The priority for this adjustment is high. We receive data requests for MDHMH monitoring data frequently, and have some pending now. Peter needs the adjustment for the next Coordinated Split Sample Program reports, which he is working on now. Please indicate in your account of the issue exactly when the adjustment should start and end, and when the MDHMH data we receive will include this adjustment.

Sincerely,

Joseph Macknis
Monitoring Coordinator

cc: T. Payne, P. Bergstrom

SYS$CBPMONITOR:[DAITS]DAITS016.WP

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (AM, QA) 017

CATEGORY CODE: AM, QA

ISSUE TITLE: Percent recovery calculation method

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 12/19/90

STATEMENT OF ISSUE:

Two different methods have been used by CBP laboratories to calculate percent recovery from spike sample data. In the interests of comparability, the same formula should be used for all percent recovery data used by the CBP. The two formulas are:

1. Spike recovery (EPA formula):

% recovery = (Sample + spike conc.) - (original conc.) / (spike) x 100

2. Sample + spike recovery (Alternate formula):

% recovery = (Sample + spike conc.) / (original conc. + spike) x 100

PROPOSED SOLUTION:

An evaluation of the two calculation methods was done to determine which formula is preferable for the defined uses of percent recovery data in the Chesapeake Bay Program. Two approaches were taken, one based on theoretical factors, the other based on data analysis (empirical). The main criterion used for the empirical approach was independence from concentration effects, which is desirable in an estimate of percent recovery. This was evaluated previously for CBL data, and now has been done for ODU and VIMS data.

DISCUSSION:

The calculation method used is different at the three mainstem laboratories, although the EPA method is used for all data stored in the CBPCC data base. Formulas used in current data submissions are:

VIMS: submitted using spike recovery (EPA formula), stored in that form.

CBL: data submitted using sample + spike recovery (alternate formula), changed to spike recovery by CSC (through 1988 data) or by MDE (starting in 1989). Spike dilution is 1:1 (VIMS & ODU use super-concentrated spikes and do not correct for dilution), so both spike and original concentrations must be divided by 2 to use the formulas above.

ODU: data submitted using sample + spike recovery, which are changed to spike recovery by CSC (through Cruise 125 data currently).

Previous data analysis (see below, letter from Bergstrom to Zimmermann, 1/26/90) on CBL data showed that sample + spike recovery (the alternate method) was usually less affected by concentration than spike recovery (EPA method). The same analysis was applied to VIMS and ODU data, with the following results:

(add new analysis results here)

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

AMQAW members need to study the issue and be prepared to make a recommendation at the next AMQAW meeting.

PRIORITY RANKING:

SUBMITTER/RESPONSIBLE PARTY:

Name: Carl Zimmermann

Organization: Chesapeake Biological Laboratory
University of Maryland
PO Box 38
Solomons, MD 20688 (301) 326-4281

ACTIONS TO DATE:

See correspondence below. The status as of the latest letter (1/26/90) was that the alternate formula was less affected by concentration based on CBL data, but analyses of ODU and VIMS data had not been done. Sections on the uses of percent recovery data and theoretical considerations need to be added to this document. The letter from Drew Francis was scanned and added to the file on 5/16/91, and the file was sent to Carl Zimmermann on a diskette on 5/16/91.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS: (Copy next section for as many actions as needed)

ACTION NUMBER: 017.01

1. Designated Respondent:

AMQAW members

2. Action: Review these recommendations, discuss and arrive at a decision at next meeting.

3. Resources Needed:

4. Due Date:by (next meeting)

5. Action Item Resolution Summary:

RELEVANT CORRESPONDENCE (in order):

CSC/CBLO April 12, 1989

Pauline A. Vaas
Maryland Dept. of the Environment
2500 Broening Highway
Baltimore, MD 21224

Dear Pauline,

I will be analyzing the routine QA data submitted by MDE. We already had June 1984-May 1985 data from you, and we recently received your April 1985-December 1988 data, as CBLQAQC.SSD. Please send documentation with all future data set submissions. I have several questions about the data, concerning items highlighted on the printout from PROC MEANS:

1. Please explain what CONC, EXPECTED, and ACTUAL represent for spikes (p. 1). I assume that % recovery = (ACTUAL/EXPECTED)*100, CONC is the sample concentration before spiking, EXPECTED is the sum of CONC and the amount of spike, and ACTUAL is the measured value for the mixture of sample and spike. However, the mean for CONC exceeds both of the other means, possibly due to a keypunch error for TOC (see below).

2. Please define APDP and APUP (p. 2).

3. Why does MONTH sometimes go up to 11 only (p. 2 & 4)?

4. Did you check the data for out-of-bounds values? The 86.0 for DOC (p. 2) and 109.9 for TOC (p. 4) seem high, and both are higher than EXPECTED or ACTUAL. For TOC, EXPECTED and ACTUAL look like year and month data (p. 4).

5. Why were there no spikes done for PC and PN (p. 3)?

6. Is PO4 (p. 3) PO4F or PO4W?

7. Why are there no QA data for TKNF, TKNW, and TSS (included in 84-85)?

Thanks for looking into this,

Sincerely,

Peter W. Bergstrom, CSC, for

Richard Batiuk
Monitoring Coordinator

encl.
cc: R. Batiuk

THE UNIVERSITY OF MARYLAND SYSTEM
CENTER FOR ENVIRONMENTAL AND ESTUARINE STUDIES

11. May 1989

Mr. Bruce Michael
Chesapeake Bay and Special Projects
Dept. of the Environment
2500 Broening Highway
Baltimore, MD 21224

Dear Bruce:

This letter is in response to the questions raised by CSC concerning the routine QA nutrient data analyzed by our laboratory and submitted to you as part of the Chesapeake Bay Mainstem Water Quality Monitoring Program.

1. Laboratory Spikes: A total of four spikes are analyzed at random per cruise- one each for the first and third day and two for the second day. A spike consists of adding a known volume of standard to a known volume of sample (effectively diluting both by 1/2). We routinely add 1 ml of a known to 1 ml of the sample. This sample is then analyzed and calculated as if it were a normal sample. A comparison is then made of this actual value and the expected value, calculated as the mean of the original concentration and the concentration of the spike.
Here is an example:

a) Sample #45 Original concentration = 0.98 mg Si/l

b) Expected 1/2 Sample #45 + 1/2 1.124 mg Si/l [this is the standard]
1/2 0.98 mg Si/l + 1/2 1.124 mg Si/l
0.49 mg Si/l + 0.562 mg Si/l
= 1.05 mg Si/l

"EXPECTED" IS DETERMINED BY CALCULATION ONLY

c) Actual:
1/2 sample #45 + 1/2 1.124 mg Si/l * F-factor = Concentration
85.9 chart units * 0.0124 = 1.06 mg Si/l "ACTUAL"
IS THE VALUE DETERMINED BY THE INSTRUMENT

2. APDP= Acid persulfate dissolved phosphorus [=TDP]
APUP= Acid persulfate whole water phosphorus [=TP]

The "acid persulfate" is the type of method used- Menzel, D.W. and N. Corwin. 1965. The measurement of total phosphorus in seawater based on the liberation of organically bound fractions by persulfate oxidation.

Limnol. Oceanogr. 10:280-282. [on phone said this was a "temporary method," summer 1987]

3. The QA samples for TOC, APDP and APUP were performed for the December 1986 Mainstem Cruise but were inadvertently not entered into the data file. We will correct these omissions and send the entire affected files to you along with our quarterly QA update (within the next 10 days).

4. I have checked our data files and could not find the two questionable values (p.2; 86 for DOC and 109.9 for TOC, p.4). What they look like to me are the actual percent recoveries. I would agree with Mr. Bergstrom that for TOC, EXPECTED and ACTUAL look like year and month data. Could these discrepancies have occurred in the transfer process?

5. There are no spikes performed for PC or PN. The method used to determine these analytes is a high temperature combustion technique where particulate N and C are vaporized to nitrogen and carbon dioxide gases. We see no way to add a known concentration of particulate N and C to a water sample. We have analyzed standard reference marine sediment with excellent results and also participated in a calibration exercise with Woods Hole and Horn Point a year and 1/2 ago. The results of this exercise were also excellent. To keep our QA commitment, we continue to analyze twice as many duplicates as required.

6. PO4 is filtered.

7. We will be happy to work with you concerning the TKNF, TKNW, and TSS QA files. TSS will be the easiest for us to deal with at this time- but just like PC/PN, we have no way to spike them. We will double the amount of duplicates normally performed and will be a part of the 1989 QA data set. Please be assured that all this data is in our laboratory notebooks.

I hope this answers the questions raised by Mr. Bergstrom and if you need any additional information, please contact me at your convenience.

Sincerely,

Carl F. Zimmermann

cc: Nutrient Analytical Services file

COMPUTER SCIENCES CORPORATION
410 SEVERN AVENUE SUITE 1lO ANNAPOLIS, MARYLAND 21403

May 31, 1989

Carl Zimmermann
Chesapeake Biological Laboratory
Box 38
Solomons, MD 20688

Dear Carl,

As I told you on the phone, I recently received your letter of May 11 to Bruce Michael concerning the QA data. I have been reviewing methods used to calculate percent recovery, and I found that you have not been using the EPA method for this. The enclosed printout shows the method I used to calculate the EPA values from your results; often these differ significantly from the values from your method. The EPA results are usually more variable than your results, and differ from yours by a mean of up to 12% (for NH4). I also enclose a printout of the values with the largest discrepancies; please check these over to see if there were any typographical errors in your data submission, and mark these and return them to me if you find any.

It would also be helpful if you could use more standard variable names in your data submission. We are currently revising the Data Management Plan for Water Quality Data, but the QA variable names will not be changed from those in the last version. (The Plan calls for using separate variable names for each parameter, although your system of single variables with a PARAM character variable can be converted to that format.) Assuming you will keep your present format, the correct QA variable names are:

PARAM_SK = measured concentration of sample + spike
= ACTUAL in your current data sets,

PARAM_C known value of spike
= EXPECTED - (CONC/2) in your current data sets,

CONC = background concentration of sample
= CONC/2 in your current data sets.

The enclosed page from EPA 1984, Chapter 5, gives the formula for percent recovery; in terms of the variables above, this is

% recovery = ((PARAM SK - CONC) / PARAM C) * 100 (EPA 1984)

based on the recovery of the spike only. You have been using an alternative method based on the recovery of the sum of the background and spike, or

% recovery = (PARAM SK / (PARAM C + CONC)) * 100 (alternative)

which has also been used by ODU. VIMS has been using the EPA method.

In the interests of comparability, I am asking all laboratories to use the same method to calculate percent recovery, the EPA 1984 method. Since can calculate this for your past data, no resubmission i9 required. Pleas indicate clearly in documentation accompanying future QA data se submissions that the method has changed; if you could change you parameter names to the ones above at the same time, that would help make the method change clearer.

Thank you for your detailed answers to my questions in my letter of April 12. They were very helpful. I will let you know if I need the TKNF, TKNW and TSS QA data from before 1989. A quarterly reporting schedule for Q data would be satisfactory.

Sincerely,

Peter W. Bergstrom
Senior Member Technical Staff

encl.
cc: B. Michael, P. Vaas, R. Batiuk, B. Fletcher

THE UNIVERSITY OF MARYLAND SYSTEM

CENTER FOR ENVIRONMENTAL AND ESTUARINE STUDIES

23. January 1990

Dr. Peter Bergstrom
Computer Sciences Corp.
410 Severn Ave., Suite 113
Annapolis, MD 21403

Dear Peter:

It was a pleasure meeting you last week and I thought it best that I respond to some of the points raised in our discussions as quickly as possible.

Calculation of spike and ammonium percent recoveries:

1. We will provide Maryland Dept. of the Environment with the concentration of our spike additions. I will contact Bruce Michael to ascertain exactly where in the file these data should go and when it should be implemented.

2. I am including a figure of the past two years' ammonium spike data. The percent recoveries calculated by the formula:

(PARAM_SK/(PARAM_C + CONC))*100

are more concerned with the recovery of spike and sample mixture than recovering only the spike. They also show a more uniform randomness than the data you prepared for us on 17 Jan. 1990 (copy enclosed).

I agree with Steve Sokolowski that the formula for percent recovery that ODU and CBL use is a better estimate than EPA's Chapter 5. While EPA provides guidance, they are not the end all and be all of nutrient analyses. If they were, we would still be doing Kjeldahl analysis. My point is that if the data can be presented in a clearer, more representative fashion, then that is the way they ought to be presented.

I have also reviewed the ammonium spike data sent to me late last Spring (May 31, 1989). The differences between the two methods of calculation which you found are in large part due to the way PARAM P was calculated (EXPECTED/ACTUAL). Had they been calculated ACTUAL/EXPECTED, as we routinely do and as you noted in your letter, the data, I believe, would have been much more comparable (example enclosed). Also, some of the back calculated spike concentrations were not calculated correctly, leading to a faulty ACTUAL and, therefore, a faulty EXPECTED/ACTUAL.

The fact that most of these percent recoveries are greater than 100% is due to a salt error introduced when the sample is diluted with a fresh water spike. We are immediately instituting a change whereby the ammonium spike will be prepared from a seawater or similar matrix standard.

2. Higher nitrate standard deviations during the spring seasons: Highest concentrations of nitrate in our portion of the Bay occur during maximum runoff- usually early Spring. These concentrations are typically 0.5 mg N/l or greater.

Since the standard deviations of these duplicate analyses are concentration dependent, it would be expected that the standard deviations for the higher concentrations would be greater than for the lower. The following data sets illustrate this:

HIGH CONCENTRATIONS	LOW CONCENTRATIONS
76.	.073
73.	.076
74.	.074
78.	.078
MEAN: 75.25	.07525
STD. DEV.: 2.22	.00222
CV: .0295	.0295

Perhaps a concentration [in]dependent statistic (coefficient of variation) would be more appropriate when the concentrations of the parameter span three orders of magnitude within a cruise data set.

3. Phosphorus Data: I do not have adequate data to assist you in solving this apparent problem in phosphorus between VIMS and CBL. Our laboratory will be pleased to help in any way we can.

The field/laboratory variation which we discussed is real and a fact of life. Small changes in the water quality of the Bay are easily masked because of it.

I am also enclosing the results of the December, 1989 Split Sample Program.

If there are any questions or I can be of further assistance, please contact me at your convenience.

Sincerely,

Carl F. Zimmermann

cc: Bettina Fletcher
Bruce Michael

January 26, 1990

Carl Zimmermann
Chesapeake Biological Laboratory
Box 38
Solomons, MD 20688-0038

Dear Carl:

I also enjoyed meeting you last week. Thank you for the prompt response to my letter of 1/17/90, and for the December CB5.3 split sample data. The enclosed printout is a modified and expanded analysis of percent recovery, based on the one I sent you on 5/31/89 and the discussions at the AMQAW meeting on 1/17/90.

You are correct that there was a mistake in the SAS job I sent you on 5/31/89. I inadvertently calculated EXPECTED/ACTUAL instead of the correct ACTUAL/EXPECTED. I was not trying to create yet another method to calculate % recovery. I re-ran this job, and it is part of the enclosed printout. The plots of the two sets of % recovery values show that the EPA method, "spike recovery," gave consistently more variable results than the method you and Steve Sokolowski have been using, "sample+spike recovery." This is borne out by the standard deviations on the PROC CORR listings.

I compared the dependence of the two % recovery methods on concentration, expressed as both EXPECTED and CONC. The results show:

- The EPA method ("spike recovery") had higher and/or more significant correlations with concentration for five parameters: NO2, NO23, PO4F, TDN, and TP.

- The CBL method ("sample+spike recovery") had higher and/or more significant correlations with concentration for two parameters: NH4 and SI.

- Two parameters showed no detectable difference in dependence of the % recovery method on concentration: PHOSP (neither method was correlated), and TDP (both methods had about the same correlation).

Based on your data, the "sample+spike" recovery appears to be preferable. I will check the ODU data (or ask Steve to do this), and check the VIMS data when they are re-submitted. Then I'll send a memo to the workgroup with a recommendation, unless you or someone else would like to draft such a memo.

Concerning the NO23_S data that show peaks in the spring, you are correct that the standard deviation (SD) goes up with concentration in your NO23 data, which apparently produces the peaks. However, the coefficient of variation (CV) goes <u>down</u> significantly with increasing concentration, so if you substitute it for SD, there are fall peaks instead of spring peaks (see the enclosed time plots). I recommend estimating precision with SD for NO23, and indicating in documentation files when the SD depends on

concentration. When I revise the VAX program that will generate control charts for data users, I will build in a check for the dependence of both precision and accuracy on concentration so that users will be aware of this problem.

Feel free to call or write me if you have any questions about these analyses.

Sincerely,

Peter W. Bergstrom
Senior Member Technical Staff

cc: B. Michael, B. Fletcher, S. Sokolowski

HAMPTON ROADS SANITATION DISTRICT

May 7, 1991

Peter Bergstrom
Computer Sciences Corporation
410 Severn Avenue
Suite 113
Annapolis, MD 21403

Dear Peter:

This is the response I promised you regarding DAITS issue #17 -'Percent Recovery Calculation' to be discussed at the AMQAW meeting May 14, 1991. Apparently there is some difference of opinion as to how one might calculate percent recovery in evaluating methodology and analytical performance. The primary concern, as I understand it, focuses on whether the recovery of any associated background response should be included in the final calculation. I think you'll agree that any quality control effort should be designed to facilitate the recognition of influences that may impact data integrity. The inclusion of any background response in this calculation, however, appears to potentially diminish the sensitivity and power of the assessment. The objective is to evaluate whether the analytical variables involved (e.g., methodology, technique, etc.) are acceptable in terms of recovery of a known entity. If the background is considered a part of what is known, and it is large in comparison to the spike quantity, the actual recovery of the spike can be masked. Further, many would contend that the background is not known in the same sense as the concentration of a spike (e.g.,Larry Lobring EPA,ORD-Cin.). It also seems relevant that several EPA publications and college texts at my disposal uniformly calculate spike recovery by subtracting the sample background concentration. It appears in order, therefore, to conclude that the calculation for sample spike recovery in this program should also exclude any background response and focus only on the recovery of the material added.

A somewhat definitive discuss;on of this topic may be found in the following EPA publication:

Choosing Cost-Effective QA/QC Programs for Chemical Analysis, Radian Corporation, Austin, Texas, 1985, EPA/600/4-85/056.

Considering this reference and others dealing with the subject, it appears that this monitoring effort would benefit not only from standardizing the method of calculating recovery but also from establishing a set of criteria for the spiking process itself. I realize that most labs may already be employing such a protocol. Nevertheless, if the issues are clearly defined and uniformly followed, it can only serve to improve the comparability of the data. I offer the following as documentation of what may already be occurring or as suggested guidelines to potentially enhance the value of spike recovery data in this program:

1. The spiking process should not result in sample dilution greater than 10 %.
2. The concentration of the spike should be >=2x the sample concentration.

3. The response of the analytical system to the sample/spike combination should approximate 50-75 % full scale.

I hope the foregoing will be useful in providing some direction for resolution of the spike recovery issue.

Sincerely.

Drew Francis
Quality Assurance Officer

May 17, 1991

Carl Zimmermann
CBL
PO Box 38
Solomons, MD 20688

Dear Carl:

Thanks for agreeing to take over the DAITS issue 17 on percent recovery calculation methods. The write-up I started is enclosed on paper and on diskette, which also includes all the correspondence I have on the subject. It's in an ASCII file, and you should be able to import it to WordStar or any other word processor. The following items should also be addressed to justify a change from the standard EPA protocol to the new method:

1. Management needs and uses for percent recovery data, both at the laboratory and CBP levels. Management needs include application of DQOs, and use by EPA and by data users.

2. A discussion of the theoretical pros and cons of each calculation method, related to the management needs.

3. Analysis of VIMS and ODU data for correlations. Let me know if you want me to send VIMS QA data on a SAS transport tape or other format.

The data analysis I did was shown in the printouts sent with my letter to you of 1/26/90. It included X-Y plots of percent recovery calculated by both methods vs. sample concentration. I used both the expected concentration (background + spike) and the background concentration as the X variable; there wasn't usually much difference between plots using the two measures of sample concentration. I also ran correlation coefficients between these variables. Give me a call if you have any questions about the analysis.

You were right about DAITS Issue 8, Data Transfer Methods--I was going act on it next. The entries appear complete except MDE needs to fill in the last section for CBL data. Please ask Bruce or Harry (or however is most knowledgeable) to fill this in and return it to me. Handwriting on the form is fine, since it won't be much to type in. Please thank Nancy for collecting and typing the responses.

Sincerely,

Peter Bergstrom

cc: S.Sokolowski, C. Walters

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (AM,QA) 018

CATEGORY CODE: AM, QA

ISSUE TITLE: Manual injection carbon data

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 1/29/91

STATEMENT OF ISSUE:

Carl Cerco (US Army Corps of Engineers) noticed a step change upward in carbon results at Maryland mainstem stations in early 1985 in plots he made for calibrating the 3D water quality model. He asked Peter Bergstrom (CSC/CBLO) to investigate and see if any adjustment was possible to increase the agreement of Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) data across the method change that occurred.

PROPOSED SOLUTION:

Peter contacted laboratory personnel at Central Regional Laboratory in Annapolis, where Maryland carbon analyses were done until May 15, 1985, and distributed this memo for comments:

DATE: January 15, 1991

SUBJECT:Step change in DOC results in early 1985 Maryland data

FROM: Peter Bergstrom

TO: Carl Cerco, US Army Corps of Engineers

COPIES: M. Olson, B. Michael, N. Fritsche, N. Kaumeyer, B. Salley, A. Robertson, J. Macknis, C. Walters

I investigated possible causes for the step change in Dissolved Organic Carbon (DOC) levels you noticed in Maryland data in early 1985 (graph attached). Norman Fritsche at CRL told me that DOC was done with a manual injection method with a Beckman instrument during that period. He said that one of the problems with this method is that the results depended on how hard the plunger was pushed, and that the results should only be considered accurate to within the detection limit, or ∀ 1.0 mg/l. The same problem applies to TOC, and thus to POC data. The current DOC analyses at CRL use an Ionics unit which aspirates samples from a carousel, and are not affected by this problem. He said CRL may have run comparison data when they changed DOC instruments.

Nancy Kaumeyer, who currently runs DOC analyses at CBL, agreed that this is a problem with manual injection. She said that DOC analyses at CBL were done with an OI ampule instrument from 1985 to February 1987, and by OI direct injection since then.

I do not see a way to adjust the 1984-85 DOC data from CRL to agree more closely with later data. The variability in the older data would be highly operator-dependent. I recommend telling any users of these data of their inherent variability. If any of the analysts receiving a copy of this memo have other comments or recommendations, please contact me.

DISCUSSION:

Betty Salley (VIMS) called Peter on 1/17/91 and said that VIMS had also used a Beckman carbon instrument, before the Bay Program began in 1984. They got rid of it due to servicing problems, not to injection problems. However, theirs had a spring-loaded injection mechanism, not a manual plunger. She also mentioned in a call on 1/22/91 that the OI ampule method may give different results from OI direct injection, which may have caused a change in Maryland carbon results in February 1987. Peter mentioned this to Carl Cerco on 1/23/91, but he did not mention any marked change in the Maryland carbon data associated with that method change.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

Time to review this document, and possibly to review old carbon methods.

PRIORITY RANKING:

2 (Medium high)

SUBMITTER/RESPONSIBLE PARTY:

Name: Peter Bergstrom

Organization: Computer Sciences Corp.
Chesapeake Bay Liaison Office
410 Severn Ave.
Annapolis, MD 21403 (800) 523-2281

ACTIONS TO DATE:

Writing and distributing the above memo, comments received from Betty Salley.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:
Update As of 7/24/92: Mainstem TOC and DOC data from OEP/CRL (6/84 through 5/15/85) were unreliable so records in the database had the reported values deleted and were coded with problem code = 'V'.
RECOMMENDED ACTIONS:

ACTION NUMBER: 018.01

1. Designated Respondent:

Analytical Methods and Quality Assurance Workgroup
Bruce Neilson and Claudia Walters, Co-Chairs

2. Action: Please review this memo and either approve it or recommend changes.

3. Resources Needed:

4. Due Date: February 19, 1991 (next meeting)

5. Action Item Resolution Summary:

AMQAW members approved the issue as written on 2/19/91 with no comments. They asked to include what method(s) were used by DCLS.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 019

CATEGORY CODE: QA, AM

ISSUE TITLE: Methods matrix of field and laboratory methods at mainstem laboratories

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM:
05/05/1991

STATEMENT OF ISSUE:

PROPOSED SOLUTION:

DISCUSSION:
Address background, justification for recommended actions and benefit of action or implications of inaction as is appropriate. Provide example where possible.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

PRIORITY RANKING:
Subjective estimation made by submitter and/or modified by PO or QAO.
Five point scale where 1 is the lowest priority and 5 is the highest. Supply comments as required.

SUBMITTER/RESPONSIBLE PARTY:

Name: Mary Ellen Ley, CBP QAO (for Claudia Walters, CBP QAO in 1991)

Organization: CBP

ACTIONS TO DATE: See Method Matrix Attached.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

Reference appropriate documents as required. To be completed after all actions have been addressed. See Method Matrix Attached.

CBP Mainstem Monitoring Program
Analytical Systems Matrix

FIELD SAMPLING PROCEDURES

VARIABLE	CBL	VIMS	ODU
Field Oper. Crew	MDE pre 1995 DNR post 1995	Lab and Field staff	Lab and field staff
Station Location	Loran-C	GPS, verified by Loran-C	GPS
Station Holding	Anchor if required by weather or currents to maintain station	Anchor. Will drift over station if wind and current prevent anchoring.	Anchor when sea conditions permit; vessel positioned to drift through designated station when anchoring is unsafe or not practical.
Bottom Depth	Fathometer, station depth	Bottom sensor	Fathometer, CTD depth sensor
Pump & Field Instrument Configuration	Co-mounted; Depth controlled by meter wheel on winch. Excessive scoping depth confirmed by Hydrolab	Co-mounted; Depth controlled by CTD reading	Co-mounted; Depth controlled by CTD reading
CTD Model	Hydrolab Surveyor II	Applied Microsystems	YSI model 6000 and Hydrolab Surveyor II
Sample Container	New plastic milk jugs (1-2/depth); reused throughout cruise	Acid washed 1 gal plastic jugs (4); reused throughout cruise	Teflon-lined Niskin bottles or DPE carboys reused throughout cruise (rinsed well with sample before filing)
Filtration Apparatus	Gelman magnetic plastic filter holders to Glass flasks, AC vacuum pumps with pressure control	Gelman 300 mL towers, magnetic seal. Filter directly into sample bottles. AC vacuum pumps with pressure control.	Gelman plastic filtration towers. Samples for nutrient analysis collected in glass flasks; filtrate for POC, PON, and chlorophyll is discarded to waste container. AC vacuum pumps with pressure control.

Filtration Apparatus: Between sample rinse	DI water rinse; Sample rinse of glass flasks	DDI water rinse of filter tower, filter supports and outside of nalgene transfer tubing.	Ultrapure water rinse of filtering apparatus and flasks; sample rinse glass flasks
Filtration Apparatus: Decontamination Procedure	Soap wash, tap rinse, acid wash, tap rinse, DI water rinse	Soap wash, tap rinse, acid wash, DDI rinse	Soap wash, tap water rinse, acid rinse, ultrapure water rinse
Shipboard Sample Volume Measurement	Plastic graduated cylinders	Plastic graduated cylinders	Plastic graduated cylinders

SAMPLE HANDLING & PRESERVATION

VARIABLE	CBL	VIMS	ODU
On-board Temperature Conditions	All liquids and filters are frozen on-board. Silica is refrigerated.	All liquids and filters are frozen on board. Exceptions, Si and DOC, stored on ice.	Samples frozen when possible but packed in ice then frozen as soon as possible when using small boats.
Preservation	Freezing except Reactive Silica which is refrigerated.	Freezing. Exceptions Si - refrigeration DOC: 5 drops 6N HCl per 40 mL (pH < 2), 4°C.	Si samples refrigerated; all other samples frozen.
Holding time	28 days	28 days	Chlorophyll: 30 days (after extraction). Silica: 28 days. Particulates: 28-60 days. Dissolved: 28 days.

LABORATORY PARAMETERS

Particulate Carbon/Particulate Nitrogen

Variable	CBL	VIMS	ODU
Filter Type & Size	Whatman GF/F 25mm	Whatman GF/F 13mm	Whatman GF/F 13mm. Three per sample, analyzed separately.
Filter Pre Treatment	Precombust at 550°C for 1.5 hours	Precombust at 550°C for 20 minutes	Precombust at 550°C for 15 minutes. Desiccate until use.
Filter Handling	Folded in half	Flat in Petri dish	Folded in quarters; stored in precombusted glass vials with teflon-lined caps.
Sample Cup Treatment	Combust @ 875° C for 1 hour	No treatment of cups - cup blank is run.	Rinse with mixture of chloroform, methanol & DI water; dry @ 50°C overnight; blanks analyzed.
Sample Volume	50 - 300 mL (pads visible color).	50 mL each filter, two filters used per burn.	20 - 50 mL
Sample Treatment	Dry overnight at 50°C	Dried at 50°C for at least 30 minutes.	Dry overnight at 50°C
Standards	Acetanilide	Atropine	Chloramine T
Standard Reference Material (SRM)	PC: NIST Estuarine Sediment (SRM 1646) & NRC of Canada Marine Sediment (St. Lawrence)	NRC of Canada Marine Sediment BCSS-1	Cross-reference of Carlo Erba primary standard acetanilide and chloramine T working standard. Also, NRC of Canada marine sediment (St. Lawrence) and/or NIST estuarine sediment (SRM 1646).
Interlaboratory	Yes: Glibert/WHOI ICES Report No.	Yes - CBPO CSSP	Yes - CBPO CSSP

Comparisons	174 & CBP CSSP.		
Instrument	Exeter Analytical CE-440 Elemental Analyzer	Carlo Erba NA 1500	Carlo Erba NA 1500
Analytes	C, H, N	C and N	C and N
Burn Temperature	975°C	Nominal 1050°C	1050°C (actual burn temperature is > 1700°C at time of combustion due to catalytic effect of tin cups.)

Particulate Phosphorus (PHOSP)

Variable	CBL	VIMS	ODU
Reagent Storage	Ascorbic Acid stored at 4°C for 2 weeks.	4°C, Amber LPE, 1 month. Ascorbic fresh daily.	Ascorbic acid stored at 4°C for 2 weeks.
Standard Reference Materials	NRC of Canada Marine Sediment (St. Lawrence)	Extraction: None Calibration: SPEX-Orthophosphate	SPEX-SRM for Ortho-Phosphate
Instrument	Technicon AAII	SKALAR SAN^{plus}	SKALAR SAN^{plus}
Flow Cell	50mm	SKALAR - 50mm with matrix correction	50mm turbo (high-sensitivity) with matrix correction
Filter Treatment	Dried at then weighed for TSS. Stored at room temp until ready to extract for PHOSP. Extract in 1N HCl for min. 24 hours before analysis.	Rinsed with DDI after sample filters sucked dry. Folded in half and frozen in polystyrene Petri dish until analysis. Dried at 104°C, weighed for TSS, then extracted PPHOS.	Dried at 103°C then weighed for TSS. Rinsed 3 times with ultrapure water after sample filtration is complete. Filters dried to complete TSS analysis then digested for particulate phosphate analysis. Extra filters are folded in half then frozen in plastic filter holders.

Total Suspended Solids (TSS)

VARIABLE	CBL	VIMS	ODU
Filter Type & Size	Whatman GF/F 47mm	Whatman GF/F 47mm	Whatman GF/F 47mm
Filter PreTreatment	Dry at 104°C	3 DDI rinses, dry at 104°C and weigh twice.	
Filter Handling	Folded in half; placed in aluminum foil pouch.	Stored in 60°C oven until time of use then laid flat in acid washed polystyrene Petri dishes for transport.	Folded in half then stored in plastic filter holders on ice until return to lab. Dried at 103°C in aluminum weighing pans. Cooled in desiccator.
Sample Volume	Variable 100 1000 mL	500 mL whenever possible.	Maximum volume that can be filtered in 10 minutes at 12 PSI vacuum pressure; usually 300-500 mL.
Sample Treatment	Well mixed aliquot filtered and rinsed 3x with DI. Folded in half and frozen in Al foil pouch until analysis.	Well mixed aliquot filtered to dryness, then rinsed with DDI. Folded in half and frozen in Petri dish until time of analysis.	Filter immediately after collection (see filter handling)
Reagent Storage	None	None	N/A
Standard Reference materials (SRMs)		SPEX Residue.	SPEX Residue
Calibration	Balance calibrated yearly	Masses and Instrument-Annual certification.	Analytical balance is self-calibrating; calibration check w/ 100 mg class S weight before each use; calibration check with 5 class S weights (1-1000 mg) monthly; weights recalibrated yearly.

Instrument	Mettler AE 100 with Lotus Measure weight processing package	Mettler AE100 with BalanceTalk.	Sartorius model RC210S
Method	APHA, 1985 Method #208D Dry at 103°C for a minimum 24 hours.	Dry at 104°C at least four hours, then desiccate. Weigh, re-dry at least 1 hour, then re-weigh. Weight difference ≤ 0.5 mg.	ALPHA, 1989 method #209C: Dry at 104°C for at least 1 hr. Weigh, re-dry and re-weigh. Weight difference ≤ 0.5 mg.

Nitrite (No2)

VARIABLE	CBL	VIMS	ODU
Sample Container	Four ml polystyrene AutoAnalyzer Cup	Nalgene HDPE and LPE, 250 and 125 mL	HDPE plastic, 250 or 500 ml
Glassware	Acid wash with 10% HCl, numerous deionized water rinses	Acid wash with 10% HCl, 3x DDI rinse.	Soap washed, rinsed with tap water then 4M HCl, then ultrapure water.
Method	Automated colorimetric	SKALAR Method No. 467 (EPA 354.1 Automated)	Manual diazotization
Standards	0.0028 - 0.042 MgN/l	Stock: 1000 mg/L N as NO_2. KNO_2, amber glass, preserved with chloroform. Working standards subdiluted daily, DDI or NaCl.	Sodium nitrite stored at 4°C, shelf life 30 days
Standard Reference Materials (SRMs)	None available	None. Indirect comparison with SPEX SRM NO_3.	None available
Sample Preservation	Frozen at -20°C	Freezing at < -18°C	Frozen at ≤ -20°C
Reagent Storage	4°C	Amber HDPE, 4°C, 1 month.	Sulfalnilamide at 4 °C, shelf life 2 mos.; N-(1-napthyl)-ethylenediamine dihyrochloride at 4 °C, shelf life 1 mos
Spiking	0.02 mg N/l	Working standard. Add concentration = 0.020 mg/L	0.01 mg/L NO_2-N
Instrument	TrAAcs-800 (Bran & Luebbe)	SKALAR SAN^{plus} - Manifold SA 467-003	Perkin elmer model 559A dual beam micrprocessor-controlled spectrophotometer
Flowcell	50mm	50mm (SA6275) with matrix correction.	Not applicable

Nitrate + Nitrite

VARIABLE	CBL	VIMS	ODU
Sample Container	Four ML Polystyrene AutoAnalyzer Cup	Nalgene HDPE and LPE, 250 and 125 mL	HDPE plastic, 250 or 500 ml
Glassware	Acid wash with 10% HCl, numerous deionized water rinses	Acid washed 10% HCl, 3x DDI rinse.	Soap washed, rinsed with tap water, then 4M HCl, then ultrapure water.
Method	Automated cadmium/copper reduction	SKALAR Method No. 461-353.2 Cd Reduction (EPA Method 353.2 Automated)	Automated cadmium/copper reduction followed by diazotiaztion
Standards	.0049 to 1.4 mg NO_3-N/l	Stock: 1000 mg/L N as NO_3. K NO_3, amber glass, chloroform preserved. Working standards subdiluted daily, DDI or NaCl.	Potassium nitrate stored at 4°C, shelf life 6 months.
Standard Reference Materials (SRMs)	SPEX	SPEX QCS - NUT 1, prepared in DDI and 50% Low Nutrient Seawater. Blanks carried with lot.	SPEX standard reference material (nutrients)
Sample Preservation	Frozen at -20°C	Freezing at < -18°C	Frozen at ≤ -20°C
Reagent Storage	4°C for up to 6 weeks	NH_4Cl Buffer-4°C 1month Color reagent, 4°C, 1 month.	Ammonium chloride at room temperature; color reagent (Sulfanilamide and N-(1-naphthyl)-ethylenediamine Dihydrochloride) at 4°C, shelf life 1 month.
Spiking	4.2 mg N/l	Working standard. Add concentration = 0.080 mg/L	0.04 mg/L NO_3-N
Instrument	Technicon AutoAnalyzer II	Skalar San Plus. Manifold SA 461	Skalar San Plus.

Flowcell	50mm	50 mm (SA6275) with matrix correction	50mm turbo (high sensitivity) w/ matrix correction

Ammonium (NH4)

VARIABLE	CBL	VIMS	ODU
Sample Container	Four ml polystyrene AutoAnalyzer Cup	Nalgene HDPE and LPE, 250 and 125mL	HDPE plastic, 250 or 500 ml
Glassware	Acid wash with 10% HCl, numerous deionized water rinses	Acid washed 10% HCl, DDI rinsed 3X.	Soap washed, rinsed with tap water then 4M HCL then ultrapure water.
Method	Automated Phenol/hypochlorite	EPA 350.1 Automated Berthelot (Phenol)	Automated phenate (phenol/hypochlorite)
Standards	0.021-0.168 mg NH_4NCl	Stock - 1000 mg/L N as NH_3 $(NH_4)_2SO_4$, glass. Working standards subdiluted daily, DDI or NaCl.	Ammonium sulfate stored at 4°C, shelf life 6 mos
Standard Reference Materials (SRMs)	SPEX	SPEX QCS - NUT 1 prepared in both DDI and 50%. Low Nutrient Seawater. Blanks carried with lot.	SPEX standard reference material (nutrients)
Sample Preservation	Frozen at -20°C	Freezing at <-18°C	Frozen at -20°C.
Reagent Storage	4°C	Complexing Reagent - Amber HDPE, 4°C, 1 month. Nitroprusside - Amber HDPE, 4°C, 1 month. Hypochlorite - prepared daily. Phenolate - prepared daily.	Buffer at 4°C; phenol prepared fresh daily, hypochlorite at room temperature, shelf life 7 days, sodium niroprusside at 4°C, shelf life 1 month.
Spiking	0.09 mg N/l	Working standard. Add concentration = 0.080 mg/L	0.04 mg/L NH_4-N
Instrument	Bran & Luebbe TrAAcs - 800	SKALAR San^{plus}Manifold SA 156-0056	Skalar Sanplus.
Flowcell	50mm	50mm (SA6275) with matrix	50 mm turbo (high sensitivity) w/

		correction.	matrix correction

Total Dissolved Nitrogen (TDN)

VARIABLE	CBL	VIMS	ODU
Sample Container	30 ml test tube; autoclaved with potassium persulfate before use. One piece plastic screw cap.	Nalgene HDPE and LPE, 250 and 125mL	HDPE plastic, 250 or 500 ml
Glassware	Rinsed with deionized water after use.	25 mL borosilicate, threaded caps. Acid washed 10% HCl, DDI rinsed x Conditioned with OR prior to first use.	Soap washed, rinsed with tap water then 4M HCl, then ultrapure water.
Method	Alkaline persulfate method - modified Valderrama, 1981	Alkaline Persulfate method; modified Valderrama, 1981	Alkaline persulfate digestion, analyzed as nitrate -N using automated cadmium reduction.
Standards	.35 - 1.4 mg N/l	Inorganic Stock - 1000mg/L N. KNO_3, chloroform. Organic Stock - 1000 mg/L N. Urea Working standards prepared daily in fresh DDI. Standards carried through digestion procedure.	Potassium nitrate stored at 4°C, shelf life 6 months.
Standard Reference Materials (SRMs)	SPEX	SPEX QCS - NUT 2 (Glycine) Diluted in both DDI and 50% Low Nutrient Sea Water Blanks Carried with lot.	SPEX standard reference material (nutrients)
Sample Preservation	Frozen at -20°C.	Frozen at <-18°C for 28 days.	Frozen at ≤ -20°C
Reagent Storage	Alkaline persulfate prepared fresh daily. Borate buffer - room temp.	Oxidizing Reagent - prepared daily Boarte Buffer - glass, room temp., 2 months. NH_4Cl Buffer - amber, 4°C, 1 month.	Ammonium chloride at room temperature; color reagent (Sulfanilamide and N-(1-naphthyl)-ethylenediamine

		Color Reagent - amber, 4°C, 1 month.	dihydrochloride) at 4°C, shelf life 1 month; boric acid buffer at 4°C, shelf life 2 months; 0.45 N HCl at room temperature.
Spiking	4.48 mg N/l	Working standard. Add concentration = 0.45 mg/L	0.2 mg/L NO_3-N
Instrument	Technicon AutoAnalyzer II	SKALAR SAN^{Plus} No_x Manifold SA 461 - Dilution Coil	Skalar San Plus
Flowcell	50 mm	50 mm (SA6275) with matrix correction.	50 mm turbo (high sensitivity) w/ matrix correction

Orthophosphate (PO4F)

VARIABLE	CBL	VIMS	ODU
Sample Container	Four ml polystyrene AutoAnalyzer Cup	Nalgene HDPE and LPE, 250 and 125mL	HDPE plastic, 250 or 500 ml
Glassware	Acid wash with 10% HCl, numerous deionized water rinses	Acid washed 10% HCl, DDI rinsed 3X.	Dedicated to phosphate analysis. Rinsed with tap water then dried, soaked in sodium dichromate overnight then rinsed with ultrapure water.
Method	Automated molybdate/ascorbic acid	SKALAR Method 503-365.1 EPA Method 365.1 - two reagent.	USEPA method 365.3
Standards	.00372-.372 mg PO_4 - P/l	Stock - 50mg/L P as PO_4. KH_2PO_4 glass. Working solutions subdiluted daily in DDI or NaCl.	Potassium phosphate. Method of standard addition. Prepared in composite of filtered sample water.
Standard Reference Materials (SRMs)	SPEX	SPEX QCS - NUT 1, diluted in both DDI and 50% Low Nutrient Sea Water. Blanks carried with lot.	SPEX standard reference material (nutrients).
Sample Preservation	Frozen at -20°C.	Freezing at <-18°C	Frozen at ≤ -20°C
Reagent Storage	Ascorbic acid for up to weeks H_2SO_4 - Room temp. Antimony Potassium tartrate -Room temp. Ammonium molybdate - Room temp, dark for up to 2 weeks.	5N Sulfuric - 25°C, glass, indef. Molybdate Solution - amber LPE, 4°C, 1 month. Tartrate Solution - amber LPE, 4°C, 1 month Ascorbic acid - fresh daily.	Ascorbic acid 4°C for up to 2 weeks; molybdate reagent at 4°C for up to 1 month in amber container; sulfuric acid at room temp in ground glass stoppered container.
Spiking	0.372 mg P/l	Working standard. Add concentration = 0.020 mg/L	0.04 mg/L PO_4-P
Instrument	Technicon Auto	SKALAR SAN$^{plus.}$	Perkin Elmer model

	Analyzer II	Manifold SA 503	Lambda 1 single beam spectrophotometer
Flowcell	50mm	50 mm (SA6275) with matrix correction.	Not applicable

Total Dissolved Phosphorus (TDP)

VARIABLE	CBL	VIMS	ODU
Sample Container		Nalgene HDPE and LPE, 250 and 125mL	HDPE plastic, 250 or 500 ml
Glassware	30 ml test tube; autoclaved with potassium persulfate before use. One piece plastic screw cap. Rinsed with distilled H_2O after use.	25 mL borosilicate, threaded caps. Acid washed 10% HCl, DDI rinsed x Conditioned with OR prior to first use.	Dedicated to phosphate analysis. Rinsed with tap water then dried, soaked insodium dichromate overnight then rinsed with ultrapure water.
Method	Alkaline persulfate method - modified Valderrama, 1981	Digestion: D'Elia 1977 Alkaline persulfate CFAA: SKALAR 503-365.1	USEPA method 365.3
Standards	.0186-.0558 mg PO_4 - P/l DI H_2O sample matrix glycerophosphate 0.060 mg P/l	Inorganic Stock - 50mg/L P, glass. Organic Stock - 95.73 mg/L P Glycerophosphate. Working Stds- subdiluted daily in DDI and 50% LNS.	Potassium phosphate. Method of standard addition. Prepared in composite of filtered sample water.
Standard Reference Materials (SRMs)	SPEX	SPEX QCS Nut 2, Prepared in both DDI and 50% Low Nutrient sea water. Blanks carried with lot.	SPEX
Spiking	0.0595 mg P/l KH_2PO_4	Working standard. Add=0.034 mg/L P.	0.10 mg/L PO_4-P
Instrumentation	Technicon AAII; 880 nm	SKALAR SAN$^{plus.}$ Manifold SA 503	Perkin Elmer Model Lambda 1 single beam spectrophotometer
Flowcell		50 mm (SA6275) with matrix correction.	N/A

Dissolved Organic Carbon (DOC)

VARIABLE	CBL	VIMS	ODU
Sample Bottle Material	Glass; reusable	Borosilicate vials, teflon lined caps.	Borosilicate glass with teflon-lined caps
Sample Bottle Cleaning	Tap rinse, 10% HCl soak, DI water rinse	10% HCl, DI water rinse, combusted at 450°C for 2 hours	Dedicated to carbon samples. Rinsed with tap water, then mixture of chloroform, methanol and ultrpore water, acetone then ultrapure water rinse. soak in dichromic acid overnight, rinse with ultrapure water.
Instrument	Oceanographic International Model 700 - direct analysis - used through 1995. Any future work would be analyzed using Shimadzu 5000	Shimadzu TOC-5000	Oceanogrphy International model 524C
Optics	Single beam NDIR	NDIR	Horiba Dual-beam NDIR
Standard Reference Materials	SPEX reference material	SPEX-DEM, in both DDI and 50% LNS. Blanks carried with lot.	
Analysis Pattern	10% QC and 2 standards as samples every 12-15 samples	10% duplication and spiking. Standard run as unknown every 10 samples.	10% duplicates, spikes, and calibration check standards
Spiking level	5 mg/L	3 mg/L	4 mg/L
Calibration Material	Sodium Carbonate for DIC; KHP (potassium hydrogen phthalate for DOC)	Potassium hydrogen phthalate	Potassium hydrogen phthalate

NOTE 1: Nancy Kaumeyer, CBL, performed ad hoc study which demonstrated that for DOC samples after one day of storage at 4°C she received the lowest results from

samples which had been acidified and were neutralized prior to analysis. The next higher recovery was achieved with samples which were not acidified. The highest recovery was achieved from the sample which had been acidified and was not neutralized prior to analysis.

NOTE 2: Aged plastic containers, on the order of 15 to 20 years, are reported to be preferred for extremely low level DOC work, otherwise glass is preferred.

Silicate (SI)

VARIABLE	CBL	VIMS	ODU
Sample Container	Four ml polystyrene AutoAnalyzer Cup	Nalgene HDPE and LPE, 125mL bottles.	HDPE plastic 125 or 250 ml
Glassware	Acid wash with 10% HCl, rinse with DI	Plasticware used throughout Acid washed 10% HCl, 3x DDI rinse	Plastic ware used except volumetric pipettes; soap washed, rinsed with tap water then ultrapure water
Method	Automated molybdate/ascorbic acid	Automated molybdate/ascorbic	Automated molybdate/ascorbic acid
Standards	0.281-2.1 mg Si/l	Stock = Sodium Fluosilicate Na_2SiF_6 280.68mg/L DDI Working Solution - subdiluted daily in DDI.	Banco SiO_2
Standard Reference Materials (SRMs)	None available	Ocean Scientific Mixed Nutrients SD3	None available
Sample Preservation	refrigerated at 4°C	Refrigeration at < 4°C for 28 days	Refrigeration at 4°C for 28 days
Reagent Storage	Molybdate 1 week Ascorbic acid - 20°C 6 months others 2 months	Molybdate - amber HDPE, 4°C, 1 month. Ascorbic - amber LPE, 4°C, 1 month. Oxalic - LPE, 4°C, 1 month.	ascorbic acid at 4°C for 2 weeks, molybdate at 4°C for 1 month, oxalic acid at room temp for 1 month
Spiking	1.07 mg Si/l	Working Standard. Add conc = 0.562 mg/L Si	0.234 mg Si/L
Instrument	Bran & Luebbe TrAAcs-800	Technicon AAII	SKALAR SAN PLUS
Flowcell	50 mm	75 mm	50 mm turbo (high sensitivity) with matrix correction

Biogenic Silica (BIOSI)

VARIABLE	CBL	VIMS	ODU
Sample Container	Filter stored in plastic centrifuge tube	50 mL pp conical bottom tube.	50 ml polypropylene conical bottom centrifuge tube
Glassware Decontamination	10% NaOH soak, then copious DI rinses	Soaked in 5% NaOH prior to first use. DDI rinse only, thereafter.	Plasticware except volumetric pipettes
Method	Automated molybdate/ascorbic acid	Extraction : 0.2N NaOH at 100°C for 20 mins. timed. Quenched with 1.0 N H_2SO_4 after cooling in ice for 4 mins. CFAA: High range automated molybdate/ascorbic.	particulates concentrated on polycarbonate filter, digested using NaOH at 100°C for 20 min., cooled then acidified using H_2SO_4. Analyzed using automated molybdate/ascorbic acid method
Standards	0.007 - 0.042 mg Si/tube	Stock - Sodium Fluosilicate 280.68 mg/L DDI. Working Solutions - neat aliquot of stock.	Baco SiO_2
Standard Reference Materials (SRMs)	None available	NONE	None available
Sample Preservation	None	frozen at -18°C	frozen at -20°C
Reagent Storage	Ammonium molybdate in dark, room temp., 1 month. Antimony Potassium Tartrate	Molybdate - amber, 4°C, 1 month Ascorbic - amber, 4°C, 1 month Oxalic - amber, 4°C, 1 month	NaOH and H2SO4 at room temp, ammonium at 4°C for 1 month, ascorbic acid at 4°C for 2 weeks, oxalic acid at rom temp for 1 month
Spiking		0.7 mg/50ml addition made at instrument. Not digested.	0.4674 mg Si/L
Instrument	Technicon AutoAnalyzer II	Technicon AAII	SKALAR SAN PLUS
Flowcell	50mm	75mm	50 mm turbo(high sensitivity) w/ matrix correction

Chlorophyll (CHLA)

Variable	CBL	VIMS	ODU
Filter Storage	Store in Al foil package; Folded in half	Half-Folded into 2x4" ziploc bags. Frozen at < -18°C until macerated.	Folded in half in Al foil at < -20°C
Filter Treatment	1ml $MgCO_3$ (10mg/l) added as preservative to pad while filtering	1 mL $MgCO_3$ added as preservative during filtration.	1 mL saturated $MgCO_3$ added to sample as preservative immediately after collection

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 020 (QA,AM)

CATEGORY CODE: QA, AM

ISSUE TITLE: Heuristic adjustment for ODU Kjeldahl Total Nitrogen data

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: July 11, 1991

STATEMENT OF ISSUE:
Total Nitrogen (TN) data from Old Dominion University (ODU) show a step trend downward when methods changed from Kjeldahl to persulfate nitrogen, in October 1987. Unless this step trend is removed, trend analyses for TN will show downward trends at ODU stations, which may be due solely to the method change.

PROPOSED SOLUTION:
Adjust ODU TN data from the Kjeldahl method (before October 1987) downward to agree with VIMS TN Kjeldahl data, using VIMS/ODU split sample data. Due to its heuristic nature, the adjustment would be used only for trend analyses that cannot account for the method change by other means, and would not be applied to data in CBP data base.
UPDATED SOLUTION: DAWG agreed on method 2/4/92, Peter wrote SAS code, received full MSC approval at 4/1/92 meeting, correction was completed on 5/8/92. As with helix corrections, the affected method code, TN_M, was changed to 'A' to show data had been adjusted.

DISCUSSION:
See attached.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:
Please read attached statement and supply any comments or suggestions as soon as possible (by July 31, 1991).

PRIORITY RANKING:

5 (highest), decision is needed very soon to permit completion of trend analysis reports for the 1991 Nutrient Reevaluation.

SUBMITTER/RESPONSIBLE PARTY:

Name: Peter Bergstrom
Senior Statistician

Organization:
CSC/CBPO
410 Severn Ave.
Annapolis, MD 21403 (800) 523-2281

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

Issue discussed at Data Analysis Workgroup (DAWG) meeting on 6/27/91, referred to AMQAW for review of proposed adjustment. Prepared attached report. Report revised slightly based on written comments from Steve Sokolowski (ODU) dated 8/13/91 and comments received from Steve by phone on 8/30/91.

Steve raised concerns over the reduction in variability caused by the adjustment, and felt that this could bias results of any analyses using the data. After discussing this with Ray Alden he said that adjusted ODU TN data could be used for the Water Quality Characterization report analyses as long as a caveat was included that the adjustment had changed the variability of the early data. At their meeting on 11/21/91, AMQAW members agreed that a step trend exists that needs an adjustment, but that any further debate over statistical methods should be done by the Data Analysis Workgroup (DAWG). Issue was sent to Rob Magnien and other DAWG members on 1/14/92, for discussion at their next meeting.

At DAWG meeting on 2/4/92, consensus was that an adjustment using dummy variable coefficients was preferable to the original adjustment using split sample data. This avoided the reduction in variability and relied only on ODU data. These were calculated by Peter using the same parametric regression models used for the CSC report, "Trends in Nitrogen in the Chesapeake Bay (1984-1990)," re-calculated with average concentration so the units would be mg/l. The coefficients adopted are:

Table 1. Regression coefficients for dummy variables used to estimate the magnitude of the step trend downward in ODU TN data in October 1987.

STATION	COEFFICIENT (mg/l)	P	Standard error
CB6.4	-0.1041	0.0001	0.0171
CB7.3	-0.1389	0.0001	0.0163
CB7.3E	-0.1250	0.0001	0.0200
CB7.4	-0.1251	0.033	0.0573
CB7.4N	-0.1757	0.0001	0.0254
CB8.1	-0.1161	0.028	0.0515
CB8.1E	-0.1599	0.0047	0.0543
LE5.5	-0.1660	0.0001	0.0372

The method used was explained in the letter below, dated 2/14/92 from Lee Zeni, ICPRB to Jim Collier, DCRA. No replies from the Modeling or Monitoring Subcommittees were received. The use of this adjustment on CBP data bases was approved by the Monitoring Subcommittee (MSC) on 4/1/92.

RECOMMENDED ACTIONS:

ACTION NUMBER: 020.01

1. Designated Respondent: AMQAW members

2. Action: Review attached report and comment as appropriate.

3. Resources Needed: Time to read report and respond.

4. Due Date: **JULY 31, 1991**

5. Action Item Resolution Summary:

Comments received from Steve Sokolowski, discussed at AMQAW meeting 11/21/91, referred to DAWG for further action (see above).

ACTION NUMBER: 020.02

1. Designated Respondent: DAWG members

2. Action: Review attached memo dated 1/13/92 and comment as appropriate on statistical methods for adjustment.

3. Resources Needed: Time to read report and respond.

4. Due Date: **February 15, 1992** (need decision before next trend analyses)

5. Action Item Resolution Summary:

August 23, 1991

Steven Sokolowski
ODU AMRL
Norfolk, VA 23529

Dear Steve:

Thank you for your comments of 13 August on my draft report of 12 July on removing the step trend in ODU Total Nitrogen (TN) data. I understand your reservations about the adjustment procedure that was used, but I still feel that the only options available for certain analyses are to use the adjusted ODU TN data, or omit ODU data from TN trend analyses.

You proposed two alternatives to the adjustment method I used. I would be interested to see details of how to implement them. However, there is no time to use a different adjustment method for the current analyses, which must be finished in the next few weeks. I am currently involved in three separate trend analyses using TN data, and the status of ODU data for each analysis is as follows:

1. Parametric analysis using autoregressive models: The step trend can be accounted for with a dummy variable, so there is no need for an adjustment.

2. Three-dimensional interpolator used to calculate total mass and average concentration of nitrogen by CBP segment: The calculations for this analysis, which are time-consuming, are now complete. They were done with adjusted ODU TN data, and there is not time to re-do them before the due date for the report. The only segment with a majority of ODU stations is CB8 (see Table 1). The results of this analysis for CB8 (see Fig. 1) do not show any extreme values produced by adjusting the data. The unadjusted data showed a significant down trend for CB8, while the adjusted data do not. I plan to include enclosed figure in my report, with a caveat in the text about the effects of adjustment on variability. The interpolator doesn't work properly with stations missing.

3. Nonparametric analysis (seasonal Kendall test) for the Water Quality Characterization Report: The adjustment does not appear to have the deleterious effects on the results of this test that you outlined in your letter. The results on unadjusted and adjusted ODU data (attached) show that all three ODU segments have significant down trends with unadjusted data, presumably caused by the step trend. With adjusted data only MAINPOL3 has a significant down trend (CB7.4 and CB7.4N), while there is a small up trend at JAMESPOL (LE5.5). The heterogeneity of seasonal trends that you mentioned only occurred in two months for MAINPOL2, and they also had different trends in unadjusted data. Please study these seasonal Kendall results and the time plots I sent you previously and let me know if you still feel that adjusted data should not be used for the Water Quality Characterization Report. If you and Dr. Alden still

oppose using adjusted data, I feel strongly that ODU TN data should be left out of that report if they are not adjusted for the step trend.

Please reply concerning the use of ODU TN data for the Water Quality Characterization Report by next Thursday (8/29), since MDE staff are anxious to get the results for mainstem stations. Call me if you have any questions about my comments.

Sincerely,

Peter Bergstrom
Senior Statistician

cc: R. Alden
B. Neilson
S. Brunenmeister
D. Trent
C. Walters
J. Macknis
C. Zimmermann
R. Magnien
L. Williams

November 27, 1991

Steve Sokolowski
ODU AMRL
Norfolk, VA 23529-0456

Dear Steve:

I recently finished the minutes from the AMQAW meeting last week, which will be sent out soon. I had two follow-up questions concerning ODU issues discussed at the meeting:

1. Could you send me a brief description of how you determined the PQLs used as your lower reporting limits? I had said at the AMQAW meeting I would write up something on this for DAITS #11, but later realized I didn't know what procedure you had used. Please send this by December 18 so I can revise DAITS #11 for AMQAW review in January. I believe you said the PQL was the lowest detectable standard; please define "detectable" in your description.

2. In your reply to DAITS #20 on the ODU TN step trend, please include a list of specific statistical methods and questions that you would like DAWG to address in their review of the issue. You could send this after you send the disclaimer for the trend reports, which I need by next week (Dec. 5). I need the methods description by December 18 to send it to Rob so he can send it to DAWG members. DAWG considered the issue once before and referred it to AMQAW on 6/27/91 to resolve the analytical methods issues; in sending it back to them we need to be specific about what they should consider. They will need references and method descriptions for the statistical methods that could be used instead of ordinary least squares (OLS) regression. I would like to include the modified OLS method that Bruce Neilson is using in the DOC comparison study, since it does not assume one method is "correct."

Sincerely,

Peter Bergstrom
Senior Statistician

cc: R. Alden, C. Walters, B. Neilson

December 12, 1991

Dr. Ray Alden
ODU AMRL
Norfolk, VA 23529-0456

Dear Ray:

Thanks for sending the disclaimer text for the CBP trend reports in your fax of December 10. As I told you yesterday, this text applies mainly to the seasonal Kendall test, which I did not use in my report. Rob Magnien and other MDE staff are assembling the Water Quality Characterization Trend Report, which is where this text should be used. I plan to delete the references to nonparametric trend tests in Appendix II, because I did not use them in the report and it is confusing to mention them. Since I only used the step trend adjustment for graphs of interpolator output and calculation of percent changes, I propose using the following disclaimer in my report in Appendix II, p. 5, in place of the sentence starting "This would tend to increase the serial. . .":

> Time-series plots (Figures II-3 and II-4) illustrate that the unadjusted ODU total nitrogen data exhibit natural seasonal variability (with the exception of the step trend). After adjustment of the pre-October 1987 TN Kjeldahl data using the heuristic procedure, time series plots illustrate either a lack of seasonality or seasonality of diminished amplitude in the adjusted data, followed by sudden normal seasonal cycling in the post-October 1987 (unadjusted) data. This reduced variability is apparent in the graph of interpolated TN data for segment CB8 (Figure 9i), but it did not affect the parametric trend analyses done by station, since they used a dummy variable for ODU stations instead of adjusted data (see Methods). Adjusted ODU data were used for the percent change values in Table 1 for the eight ODU stations (CB6.4, CB7.3, CB7.3E, CB7.4, CB7.4N, CB8.1, CB8.1E, and LE5.5), but the reduction in variability would have little effect on these values since annual means were used.

The following sentence in Appendix II, indicating that I tried unsuccessfully another regression procedure that preserved the variability, will be retained, followed by a new sentence:

> The Data Analysis Workgroup of the Chesapeake Bay Program Monitoring Subcommittee is investigating other statistical methods to account for the step trend that can avoid the reduction in variability, to use in future trend reports.

I hope that these disclaimers are acceptable, since the nitrogen trend report needs to be finalized soon. The two editorial changes you requested at the end of your letter will also be made in the next draft, which will be sent out in the next few weeks. Please call me if you have any questions concerning this issue.

Sincerely,

Peter Bergstrom
Senior Statistician

cc: S. Sokolowski
R. Hoffman
R. Magnien
J. Macknis
C. Walters
L. Williams

[N.B. These changes were made, with slight modifications, to the Appendix II text on 1/22/92 before distribution to Monitoring Subcommittee.]

DATE: 2/14/92

SUBJECT: Removing the step trend in Old Dominion University (ODU) Total Nitrogen (TN) data: recommended data adjustment method

FROM: Lee Zeni (ICPRB), Chair, Monitoring Subcommittee

TO: Jim Collier (DCRA), Chair, Modeling Subcommittee

COPIES: Modeling Subcommittee and Monitoring Subcommittee members

Trend analyses of Total Nitrogen (TN) in the Chesapeake Bay Mainstem, performed by Old Dominion University (ODU) and Computer Sciences Corporation (CSC) staff, showed a step trend downward in TN data at ODU stations in October 1987. All three mainstem laboratories (CBL, VIMS, and ODU) changed their TN methods in October 1987. The step trend was apparently caused by the method change at ODU, since nearby stations monitored by VIMS showed no similar TN trend. VIMS and ODU used different Kjeldahl digestion methods to measure TN before the method change, which may account for this difference. Since the method change, all three laboratories have used the same methods to measure TN, calculating it as the sum of Total Dissolved Nitrogen (TDN) and Particulate Nitrogen (PN).

The step trend in ODU TN data was large enough, about 0.1-0.2 mg/l compared to usual concentration range of 0.3-0.9 mg/l, to require that some adjustment be made for it before data analysis. Without any adjustment, the effect of the method change might swamp any "real" signal in the ODU TN monitoring data.

The Analytical Methods and Quality Assurance Workgroup (AMQAW) and Data Analysis Workgroup (DAWG) of the Monitoring Subcommittee discussed evidence concerning the step trend in ODU TN data, and agreed on a method for removing the step trend. The recommended method is:

1. Perform multiple regressions of depth-integrated TN concentration on time, with a dummy variable to estimate the average difference between old and new TN results, accounting for seasonality, autocorrelation, and trends in the data. The dummy variables used were 0 before the method change and 1 after it.

2. Use the dummy variable regression coefficients to lower the ODU TN data that used the old method (August 1984 - September 1987) to make them agree with TN data from the new method.

The coefficients for each ODU station, with their approximate significance or P (all < 0.05), and standard error are given in Table 1.

Table 1. Regression coefficients for dummy variables used to estimate the magnitude of the step trend downward in ODU TN data in October 1987.

STATION	COEFFICIENT (mg/l)	P	Standard error
CB6.4	-0.1041	0.0001	0.0171
CB7.3	-0.1389	0.0001	0.0163
CB7.3E	-0.1250	0.0001	0.0200
CB7.4	-0.1251	0.033	0.0573
CB7.4N	-0.1757	0.0001	0.0254
CB8.1	-0.1161	0.028	0.0515
CB8.1E	-0.1599	0.0047	0.0543
LE5.5	-0.1660	0.0001	0.0372

These dummy variable coefficients generally agree in magnitude with two sources of Quality Assurance (QA) data concerning the step trend: method comparison data collected by ODU, and split sample results between ODU and Virginia Institute of Marine Science (VIMS). These coefficients should be used to lower the ODU Kjeldahl TN results (August 1984 - September 1987) for two reasons:

1. The new methods, using TDN and PN, have been shown to have superior precision and accuracy to the Kjeldahl method. This was the main reason the Mainstem Monitoring Program stopped using Kjeldahl methods in October 1987.

2. The new TN methods show high inter-organization agreement in split sample results, while the old (Kjeldahl) methods did not.

In conclusion, two workgroups of the Monitoring Subcommittee (MSC) have reviewed the ODU TN step trend issue. They recommended that adjusted data should be used for all present and future analyses of 1984-1987 ODU TN data. CSC staff will use these coefficients to adjust the ODU TN data in the CBP data base.

If you have any questions concerning this issue, you may contact Ray Alden at ODU at (804) 683-4195, or Peter Bergstrom at CSC/CBPO at (800) 523-2281.

Examination of Chesapeake Bay Program Carbon Monitoring Data

By
Lowell H. Bahner
CSC
December 1991

Carbon in Chesapeake Bay is monitored as part of the coordinated mainstem monitoring program. Dissolved organic carbon (DOC) and total organic carbon (TOC) were monitored between June 1984 and xx 19xx, and particulate organic carbon (POC) was computed as POC=TOC-DOC. Since xx 19xx, DOC, TOC, and POC have been measured parameters (check this statement and supply dates). For the period of June 1984 through June 1991, the mean values for these carbon species are listed in Table 1.

Table 1. Mean carbon values in Chesapeake Bay for June 1984 through June 1991. All means have been computed using unmodified data from the BAYSTATS data base. Values at or below detection used the detection level value for calculations.

	DOC		POC		TOC	
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Whole Bay	2.72	0.85	0.90	0.82	3.63	1.26
Maryland Bay	2.61	0.60	1.03	0.90	3.64	1.16
VIMS Bay	3.15	0.87	0.85	0.66	4.00	1.11
ODU Bay	2.23	0.70	0.55	0.46	2.77	0.88

During this monitoring program, analytical methods used for measuring carbon in water samples have changed. Therefore, the impact of these changes on the reported values for DOC, POC, and TOC were examined. During this examination, several documents and issues related to carbon analysis were compiled (Appendices A, B, C, and D). Betty Salley, VIMS, has prepared a document which reviews dissolved organic carbon analyses for the Virginia monitoring program (Appendix A). The CBP had compiled a file of all analytical methods which were current to 1988 and the methods for carbon are included in Appendix B. Appendix C contains a memo concerning quality assurance problems identified by CSC, and Appendix D contains Issue #18 from the CBP Data Analysis Issues Tracking System (DAITS) concerning carbon analyses. Methods used for carbon analyses since 1984 were extracted from these documents and are summarized in Table 2.

Table 2. Summary of methods used for carbon analyses for the Chesapeake Bay mainstem monitoring program.

Organization	Parameter	Method	Laboratory	Period Start	Through
MDE #B,#D	DOC	EPA Method 415.1	CRL-MD	6/01/84	5/15/85
MDE #B	DOC	Menzel & Vaccaro	CBL	5/16/85	2/ /87
MDE #C	DOC	OI direct inject	CBL	2/ /87	
VIMS #A,#C	DOC	OI carbon analyzer	ODU C Lab	6/01/84	9/30/87
VIMS #A,#C	DOC	OI carbon analyzer	ODU Lab 2	10/01/87	6/30/90
VIMS #A	DOC	Shimadzu analyzer	VIMS	7/01/90	
ODU #A	DOC	OI carbon analyzer	ODU C Lab	6/01/84	9/30/87
ODU #A	DOC	OI carbon analyzer	ODU Lab 2	10/01/87	
MDE	POC	Calculated POC=TOC-DOC		6/01/84	5/15/85
VIMS	POC	Calculated POC=TOC-DOC		6/01/84	9/30/87
ODU	POC	Calculated POC=TOC-DOC		6/01/84	9/30/87
MDE #B	PC	PE elemental anal.	CBL	5/16/85	6/30/86
MDE	PC		CBL	7/01/86	
VIMS #B	PC	Erbe elemental anal.	ODU	10/01/87	
ODU #B	PC	Erbe elemental anal.	ODU	10/01/87	
MDE	TOC	EPA Method 415.1	CRL-MD	6/01/84	5/15/85
MDE	TOC		CBL	5/16/85	9/30/85
MDE	TOC	EPA Method 415.1	CBL	10/01/85	
VIMS	TOC	EPA Method 415.1	ODU	6/01/84	
ODU	TOC	EPA Method 415.1	ODU	6/01/84	

#A Reference Appendix A.
#B Reference Appendix B.
#C Reference Appendix C.
#D Reject data, Reference Appendix D (DAITS #18).

These method changes, while aimed at improving results, cause additional uncertainty when attempting to combine data from different laboratories for analysis. As discussed in DAITS #18 (Appendix D), the MDE data for 6/84-5/85 should not be used when precision is required, since the results are only good to +/- 1 mg/l due to sample injection variability. Salley has determined (Appendix A) that the Shimadzu method used by VIMS recovered 0.491 mg DOC/l than the ODU OI method, and that the ODU DOC values should have 0.491 added to them to make them comparable to the VIMS values, assuming DOC concentrations are less than 7 mg/l and salinity between 12 and 28 parts per thousand. Direct injection was also reported to record 0.5 mg DOC/l lower than the ODU OI method--therefore, direct injection values should have 1.0 mg DOC/l added to make them comparable to the VIMS DOC values.

Particulate carbon methods have shifted from computing POC by difference of TOC and DOC to direct measurement of particulate carbon (PC), which includes both organic and inorganic

(carbonate) fractions. Steve Sokolowski (ODU) has reported that the carbonate fraction may be significant and that it can introduce error when attempting to compute mass balance of organic carbon using PC values rather than POC (Appendix C).

INVESTIGATION OF CBP DATA BASE

The initial search for outliers in the carbon data base indicated that three values were extreme. Station CB4.1W has a POC value of 27.7 and a TOC value of 33.73 for the 8/3/88 cruise. Station CB6.2 has a reported DOC value of 28.42 for the 9/19/88 cruise. These three values were approximately twice the next higher values in the data base.

The next analysis focused on the variablity of replicates in the data base. Each pair of replicated DOC and TOC values were differenced and the standard deviation of those differences were computed for June 1984 through June 1991. For MDE, the standard deviation was 0.55 mg DOC/l and 0.64 mg TOC/l, while for ODU, the standard deviation was 0.29 mg DOC/l and 0.34 mg TOC/l. As expected, these deviations are smaller than the standard deviations of the means (Table 1) but they contribute heavily to the overall variability in the sample measurements, meaning that within-sample variability contributes a large part of the overall variability of the carbon monitoring program. For MDE, 92% of the variabiltiy is due to repeated samples of DOC, while TOC is 55%. For ODU, replication provides 41% for DOC and 38% for TOC, respectively.

DATE: 12/5/91

SUBJECT:Carbon analysis QA problems

FROM:Peter Bergstrom

TO:Lowell Bahner

COPIES:Marcia Olson, Susan Brunenmeister

Since you are analyzing carbon trends, I prepared a summary of QA problems you need to examine; ask me if you want more details:

1. PC (direct) will often exceed POC = TOC - DOC, because some inorganic carbon (mainly bicarbonate) adheres to the particulates. Steve Sokolowski feels this is most common in the lower Bay. For the same reason, PC (direct) + DOC will often exceed TOC; Steve recommends against any comparisons of TOC using the different methods, because they measure different forms of carbon. This could produce a step trend upwards at the method change in Oct. 87, and CBL measured PC from May 1985 to June 1986 while VIMS & ODU used TOC & DOC.

2. ODU carbon data were done by a different lab at ODU (Wolfenbarger, not sure of the spelling) before mid-1987. In the older data, percent recovery for DOC ranged from 10-180%; Steve started doing these himself because he felt the numbers were unreliable. You should check with him on the date of the change, and whether he feels earlier data are usable.

3. Maryland carbon data from CRL (June 84 - May 15, 1985) should not be used (see DAITS #18, attached), due to unreliable manual injection. This produced a step trend upwards that Carl Cerco noticed.

4. The three labs currently use three different DOC analyzers, which give different results. The new Shimadzu at VIMS gives results about 0.5 mg/l higher than the OI ampule instrument at ODU (see attached); before Cruise 122 (7/1/90) ODU analyzed DOC for all VA stations. The OI ampule gives results about 0.5 mg/l higher than the OI injection instrument at CBL, although I have not seen comparison data to document this yet. CBL used OI ampule from 5/16/85-2/87. Thus, the VIMS results are currently about 1.0 mg/l higher than CBL results. Betty Salley is finishing up the comparison report.

5. Particulate carbon (PC) results from the three labs do not agree. Grace Battisto (VIMS) and Kathy Wood (CBL) did separate comparison studies and concluded that CBL results, which are the highest, are probably the most accurate. Based on 1989 split sample data, VIMS results for PC average 0.25 mg/l lower than CBL, apparently because VIMS rinses the filters with distilled water, which causes cell lysis and loss of PC. CBL and ODU do not rinse the filters. Although the difference was not statistically significant, ODU results averaged 0.15 mg/l lower than CBL results, apparently due to positive pressure filtration by ODU, and vacuum by CBL and ODU. Similar differences continued in 1990 data. VIMS has agreed to stop rinsing, and ODU will switch to vacuum, in Jan. 1992.

6. If you get into tributary data, DCLS does not analyze DOC, and TOC & DOC data from MDHMH are unreliable for saline samples starting in May 1989.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 023

CATEGORY CODE: AM, QA

ISSUE TITLE: PC/PN Filter and Rinsing Study

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 11/21/91

STATEMENT OF ISSUE:

On a quarterly basis, the three mainstem laboratories of the Chesapeake Bay Monitoring Program (VIMS, ODU and CBL) analyzed split samples obtained at CB5.3, a station located near the Virginia/Maryland border. Comparison of the Particulate Carbon (PC) and Particulate Nitrogen (PN) data (1987-1989), in the Chesapeake Bay Coordinated Split Sample Program Annual Report (Bergstrom,1990), showed statistically significant differences between results reported by the participating laboratories. CBL had consistently higher results than the other two laboratories.

PROPOSED SOLUTION:

As of January 1992, VIMS will not rinse the filters to be analyzed for PC/PN. ODU will use vacuum filtration to process PC/PN samples. Both labs will collect data to allow method comparison.

DISCUSSION:

The differences in the results reported are due to the variations in the Standard Operating Procedures (SOP's) utilized by the laboratories involved. The use of different Instruments, Carlo Erba NA1500 or Control Equipment 240XA, and different filters, Whatman GF/F or Gelman AE (13mm or 25mm), have been shown not to significantly affect results reported (Zimmermann,1992). This leaves only two differences in the SOP's used:

1. Rinsing vs. non-rinsing of the filters after filtration .
2. Vacuum filtration vs. Positive pressure filtration.

It is common practice to rinse filters processed for Total Suspended Solids with deionized water to remove dissolved salts. VIMS rinsed their filters processed for PC/PN to maintain consistency between the particulate fractions analyzed. CBL did not rinse PC/PN filters due to the possibility of lysing algal cells on the filter.

A limited study (Battisto,1992) of samples collected at various stations in the Virginia portion of the Bay has shown rinsing of the filters after filtration vs. not rinsing

to be a cause of a consistent bias. The non-rinsed PC/PN results are higher by as much 34% and 36% respectively. Although retention of DOC on the non-rinsed filter has been found to increase the concentration of PC on the filter (A.R. Abdel-Moati,1990), calculations on the results of this study indicate that a volume of 1.2 $\pm$ 0.74 mL is needed to account for the larger PC concentration on the non-rinsed filter. Since a 13mm filter will retain no more than 0.2 mL of liquid, most of difference is due to loss of carbon upon rinsing.

Further study (Battisto,1992) illustrated the rinse water analyzed for DOC does contain a large concentration of carbon. As much as 1.2 mg/L DOC was found in 40 mL of rinse water collected from a sample that has 2.85 mg/L DOC in the filtrate and 1.13 mg/L PC analyzed from the rinsed filters. The possibility of lysing algal cell on the filter is a valid reason to discontinue the rinsing of PC/PN filters.

During a comparison of sample handling techniques (Zimmermann, 1991), positive pressure (syringe) filtration produced lower PC/PN concentrations than vacuum filtration. It is indicated (Zimmermann, 1992) that more than half of the variation is due to differences in technique utilized during positive pressure filtration. There is no way to regulate the pressure generated, thus it will vary from technician to technician. To produce more consistent results vacuum filtration should be utilized.

REFERENCES CITED:

Abdel-Moati, A.R. 1990. Adsorption of Dissolved Organic Carbon (DOC) of Glass Fibre Filters during Particulate Organic Carbon (POC) Determination. Water Res. Vol. 24, No. 6, pp 763-764.

Battisto, G.M. 1992. Effects of Rinsing Filters on Particulate Carbon and Particulate Nitrogen Concentrations. NAL, Va. Inst of Marine Science, College of William and Mary, Gloucester Point, Va. 23062 pp 1-2.

Bergstrom, P. 1990. Chesapeake Bay Coordinated Split Sample Program Annual Report, 1989. Computer Sciences Corp., Chesapeake Bay Program, Annapolis, MD 21403. pp 24.

Zimmermann, C.F. 1991. Estuarine Nutrient Analyses: A Comparison of Sample Handling Techniques and the Analysis of Carbon, Nitrogen, Phosphorus and Chlorophyll-a U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio 45268. pp 12.

Zimmermann, C.F. 1992, Carolyn W. Keefe, Kathryn V. Wood, Nancy L. Kaumeyer. Comparison of Instrumentation and Filters Used for the Analysis of Particulate Carbon and NitrogeBn in Estuarine Waters. University of Maryland System C.E.E.S., Chesapeake Biological Laboratory, Solomons, MD. pp 5-6.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

One year of sampling, by both VIMS and ODU, so that each will obtain 100 or more data pairs that encompass all four seasons and a range of concentrations and conditions.

PRIORITY RANKING: 5 (high priority) - Revision of Mainstem SOP's necessary to provide continuity between the laboratories.

SUBMITTER/RESPONSIBLE PARTY:

Names:	Grace Battisto	Kathy Wood
Organizations:	VIMS Gloucester Pt. Va, 23062	CBL Solomons, MD 20688

ACTIONS TO DATE:

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: AM/QA 023.01

1. Designated Respondent:
   Betty Salley, VA. Inst. of Marine Science, College of William and Mary

2. Action:

During four monitoring surveys VIMS will process water samples from nine stations with PC/PN filters both rinsed and not rinsed with deionized water. These cruises will be roughly three months apart. Five of the nine stations will be those along the deep natural channel where pycnocline samples are collected as well as surface and bottom samples. The other four stations are ones which have shown variations and concentration ranges that differ from the deeper stations. Inclusion of these stations plus normal seasonal variations are expected to give a reasonably large range of concentrations.

The data will be organized, correlations tested and graphical presentations prepared and submitted to the Analytical Methods and Quality Assurance Workgroup for its review and approval.

3. Resources Needed: $ 3,300

4. Due Date: Spring of 1993

5. Action Item Resolution Summary:

ACTION NUMBER: AM/QA 023.02

1. Designated Respondent:

Steve Sokolowski, AMRL, Old Dominion University

2. Action:

During four monitoring surveys ODU will process water samples from various stations by both vacuum filtration and positive pressure filtration. The cruises should be roughly 3 months apart to represent each of the seasons. There should be one hundred or more data pairs so that statistical assessments are robust.

The data will be organized, correlations tested and graphical presentations prepared and submitted to the Analytical Methods and Quality Assurance Workgroup for its review and approval.

3. Resources Needed:

4. Due Date: Spring of 1993

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 024

CATEGORY CODE: QA, AM

ISSUE TITLE: Method detection limit (MDL) methods documentation

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 5/20/92

STATEMENT OF ISSUE:

While the Chesapeake Bay Program (CBP) maintains a list of detection limits for the CBP water quality monitoring program conducted in the mainstem and tributaries of the Bay, the associated documentation detailing the methods of detection limit calculation for water quality parameters is not uniformly available. This information is a necessary part of the CBP monitoring data documentation. It is important to know whether the MDL is based on an estimate of analytical uncertainty, and how it was calculated.

PROPOSED SOLUTION:

Request each chemical analysis laboratory that presently processes CBP water quality monitoring samples to provide the Chesapeake Bay Program Office with a description of the procedures that are used and have been used to determine detection limits of each water quality parameter analyzed at their laboratory. The parameters of primary concern are those evaluated from grab samples: nitrogen, phosphorus, carbon, silica, total suspended solids, chlorophyll a, and BOD5.

DISCUSSION:

The attached table of lower detection limits provides the list of water quality parameters of primary concern and the periods for which detection limit determination procedures are requested. Upper detection limits are not shown on this table. Specification of the associated upper limits, dates of applicability and method of determination are also requested. The protocol for determining when to re-estimate detection limits of each variable or suite of variables should also be described.

Statistical analysis of censored water quality data has received much attention in the literature. A knowledge of the exact methods used to determine censoring thresholds is vital to statistical analysts in the evaluation of the significance of changing detection limits of a variable, of differences between related water quality variables, and of differences between reporting laboratories for a variety of analysis settings.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

Written descriptions of laboratory procedures for current detection limit determinations are probably available at all participating laboratories.

Detection limits determined earlier in the CBP monitoring program and for discontinued analytical procedures may require some time to collate by reference to laboratory logs, etc.

PRIORITY RANKING:

5 (high)

SUBMITTER/RESPONSIBLE PARTY:
Name: Susan Brunenmeister/Peter Bergstrom

Organization: CSC/CBPO

ACTIONS TO DATE: This request distributed at AMQAW 7/16/92.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER:

1.Designated Respondent: Analytical Methods and Quality Assurance Workgroup (AMQAW) members

2.Action: Written documentation needed from each lab. Please provide on IBM WordPerfect or ASCII diskette if possible.

3. Resources Needed: see above

4. Due Date: **August 31, 1992, to** collate & distribute before next AMQAW meeting

5. Action Item Resolution Summary:

Method Detection Limit (MDL) Calculation Methods

Laboratories in the Chesapeake Bay Program submit data that are censored at a lower detection limit, called the Method Detection Limit or MDL. These are listed in Table 5; units are in mg/l as the element except where noted. Concentrations that are less than this limit are raised to the MDL, and the associated detection limit flag (variable_D) is set to "<". For example, if the MDL for ammonium (NH4) was 0.003 mg/l, and the measured concentration was 0.002 mg/l, the reported value would be 0.003 mg/l, and the variable NH4_D would be set to "<".

The method of calculating the MDL at mainstem laboratories varied over time, and at different laboratories. The current method at most laboratories was agreed upon by Analytical Methods and Quality Assurance Workgroup (AMQAW) members in 1988. Using this method, MDLs represent 3 times the standard deviation of 7 low-level replicates. This method has been used at CBL since 1987, and at VIMS starting 5/1/88. MDLs at CBL prior to 1987 were based on 3 times the standard deviation of laboratory duplicates for each analyte. MDLs at VIMS before 5/88 were based on the lowest standard used. VIMS limits varied before 5/88 because their MDL was the predicted value for the lowest standard, based on the regression for that cruise. ODU calculates 3 times the standard deviation of 7 low-level replicates, but only uses this as their MDL if that concentration has a peak height that is at least 1-2% of full scale for that parameter. ODU uses the concentration equal to 1-2% of full scale as their MDL if the calculated MDL is less than that value, similar to an Instrument Detection Limit. The MDL method used at OEP/CRL (the Maryland lab before 5/15/85) is unknown, but was probably based on lowest standard used. Some laboratories determine MDLs annually, while others determine them only when there is a method change. See the Chesapeake Bay Program Data Management Plan (CBP 1992a) for definitions of different types of detection limits.

Field parameter MDLs from MDE and ODU are "calibrated accuracy" from the manufacturer of the instrument they use (Hydrolab), and MDE & ODU field data are not censored at these values. VIMS MDLs for field parameters are determined by the replicate method using the Winkler method for dissolved oxygen and a salinometer for salinity. MDLs for their CTD and DO meter measurements are not available. The SECCHI MDL is the minimum depth marking.

Calculated parameters in the CBP data base are flagged "<" if any of the components are below the MDL. See Table 4, "Measured and calculated parameters" to determine which parameters were measured directly at each laboratory during each time period. During overlap periods, when two methods can be used for calculated parameters, the MDLs shown are for the newer method, which is what CBP data retrieval software uses for overlap periods. For example, when TN can be calculated as TKNW+NO23 or TDN+PON, CBP software uses TN = TDN+PON.

Some parameters also have upper detection limits, but since most parameters can be diluted and re-analyzed when these are encountered, these rarely result in censored values in the data base. Parameters analyzed directly from filters (e.g., POC and PON) cannot be diluted, and SECCHI can have an upper detection limit when the disk is visible on the bottom.

When using the values in this list for trend analysis, data users should be aware that there were not necessarily any reported values that were censored at the values shown. An examination of the data used is necessary to determine the highest censored concentration during the period analyzed. For calculated parameters, such as Total Nitrogen, there is the added complication that only one component may be censored, and it may make up a small part of the total. For more information see "Trends in Nitrogen in the Chesapeake Bay (1984-1990)" (CBP 1992b).

If the day of the month is not given, it is the start of the month for starting dates, or the end of the month for ending dates.

The data associated with Table 5. Lower Detection Limits of Water Quality Parameters was corrupted during a file conversion. For data associated with this table, contact the Chesapeake Bay Program Water Quality Database Manager.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (QA/AM) 025

CATEGORY CODE: QA/AM

ISSUE TITLE: Pycnocline identification and location of mid-water nutrient samples

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 6/26/92

STATEMENT OF ISSUE:

The design of the mainstem water quality monitoring program requires that the mid-water nutrient samples be taken relative to the region of water known as the pycnocline. Since the pycnocline is often a region of mixing of water masses, the goal is to sample above and below this layer to characterize the separate upper and lower water masses.

The top and bottom of the pycnocline region is identified in the CBP database by two variables, PDEPTHU and PDEPTHL (pycnocline depth upper and lower). If there in not a pycnocline present during the monitoring of a station these variables should be set to missing. When there is a pycnocline, there has been some inconsistencies in the usage of these variables between the field crews of MDE, VIMS, and ODU.

- MDE averages the two sample depths in which the difference in conductivity exceeds the computed threshold value (CTV). For PDEPTHU these values are the first pair from the surface and for PDEPTHL the first pair from the bottom that exceed the CTV.

- VIMS and ODU set the value of PDEPTHU similar to MDE, except both VIMS and ODU assign the value of PDEPTHU to the shallower of the two sample depths that exceed the CTV (not the average). VIMS defines them differently, so that PDEPTHU and PDEPTHL in the database are the same. ODU sets the value of PDEPTHL similar to MDE, except the value is the deeper of the two sample depths.

- When sampling 'non pycnocline' stations these fields are often ignored (missing) even though the conductivity profile indicates that there is a pycnocline.

The placement of nutrient samples in the water column differs between the three mainstem sampling institutions. Since VIMS does not identify the lower pycnocline depth, but MDE and ODU identify it, the "Below Pycnocline" sample for VIMS is on average shallower than where MDE and ODU would have placed the sample. These differences may affect data analyses, particularly on those types of analysis which subset the data based on the variable LAYER.

PROPOSED SOLUTION: Each field crew document current methods, AMQAW members determine consensus method and all field crews adopt it. Consistency is needed.

DISCUSSION:

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

Basic protocol should be in Project Plan, may need details added.

PRIORITY RANKING: High

SUBMITTER/RESPONSIBLE PARTY:
Name: John Posey
Organization: CSC/CBPO

ACTIONS TO DATE: This summary prepared and distributed for discussion at AMQAW meeting on 7/16/92.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER: QA 025.001

1. Designated Respondents:

Sally Bowen, MDE Field Crew
Betty Salley, VIMS Field Crew
Suzanne Doughten, ODU Field Crew

2. Action:
Please document current methods in writing for discussion at next AMQAW meeting. Please provide text on IBM WordPerfect or ASCII diskette if possible.

3. Resources Needed:
See above.

4. Due Date: **August 31, 1992**

5. Action Item Resolution Summary:

SYS$CBPMONITOR:[DAITS]DAITS025.WP

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 027

CATEGORY CODE: QA/AM/DS

ISSUE TITLE: Fluorometric Chlorophyll Data Structure

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 10/06/92

STATEMENT OF ISSUE: In-situ fluorometric chlorophyll data are collected as part of the Water Quality Monitoring Program. Continuous ("horizontal") measurements of surface chlorophyll are made while the boat is underway between stations. On station, discrete ("vertical") measurements are made at 1-m intervals through the water column. Fluorometric chlorophyll data were not originally required in the Program, but MDE, VIMS, and ODU collect and submit fluorometric data, and the data are regarded as valuable additions to the data base. To date, no consistent submission format or management strategy for these data has been formally adopted at CBP.

PROPOSED SOLUTION: The CBPO data management staff is seeking consensus of the program managers and principal investigators on a consistent format for submission and storage of the data.

DISCUSSION: Submitted variables and variable names are inconsistent among data submitters:

MDE	ODU	VIMS
TRIB_COD	.	.
DATE	DATE	DATE
TIME	TIME	TIME
SER_NUM	CRUISE	CRUISE
.	EVENT	.
decoded	LATITUDE	LAT
decoded	LONGITUDE	LON
CHLA	CHLA	CHLORO
.	FLUOR	.
AMETHOD	.	in documentation
STAT_DEP	DEP_STAT	STAT_DEP
STAT_DES	DES_STAT	STAT_DES
DIS_MM	CUM_INT	.
DIS_INIT	.	.
FC_INIT	.	.
DISBETWE	.	.

There are a number of general questions which have arisen:

1) How should these data sets be structured and related to the main water quality data base, i.e,

a) What are the key relational variables--temporal and spatial?
b) What, if any, data are duplicated in the two data bases?
c) Should the data--particularly the vertical measurements--be integrated with the main data base?

2) How should calibration data be handled/documented?

3) What are the methods and procedures involved and are they documented? For example, what instruments, filter wavelengths, etc. is each data collector using. How is the instrument calibrated initially? How often and/or under what circumstances are calibration chlorophyll samples collected? What/when/where is a "correction" applied to the data? What are the data that are submitted - digital readouts? hand entries from a strip chart?

John Posey at the CBPO computer center encountered these and other questions in the course of working with the data, and he has prepared a document containing additional comments, questions, and suggestions for the data sets.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

The data generators and the CBPO data base manager need to meet together to reach mutual understanding of the processes and procedures involved, and to reach consensus on the submission and storage structures.

PRIORITY RANKING: 2 (processing of the data at CBPO cannot go forward without a data submission and data management plan.

SUBMITTER/RESPONSIBLE PARTY:
Name: John Lecourt, Data Base Manager, CBPO Computer Center

Organization: Computer Sciences Corporation, computer services contractor at the EPA Chesapeake Bay Program Office

ACTIONS TO DATE: Some preliminary data processing software has been developed during which many of these problems were encountered. The DAITS issue has been formalized and referred to the MSC Data Management and Acquisition Workgroup.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS: Tami Huber (WQDM) spoke to Jackie Johnson re: this issue, who said this was taken care of and can be found in the 2000 Living Resources Users Guide (via web). See the Submitter's Appendix.

RECOMMENDED ACTIONS: none now (2006)

ACTION NUMBER:027.01

1. Designated Respondent:
   Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

Form Revision No.: 1

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 029

CATEGORY CODE: QA/AM/FM

ISSUE TITLE: Discrepancy in Maryland data, between WQ and Biomonitoring discrete measurements of chlorophyll (affected parameters are CHLA and PHEA).

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 17 Dec. 1997

STATEMENT OF ISSUE: The discrepancy was revealed in a comparison of results of the 12-year trend analyses conducted for the '97 Re-evaluation. The trend analyses of surface measurements made by MD Dept. of Natural Resources (DNR) and the Academy of Natural Sciences (ANSERC) in the main stem Chesapeake Bay yielded opposite results--no trend or *decreasing* chla concentrations if the DNR data were used, no trend or *increasing* concentrations if ANSERC data were used. Subsequent analyses of these parameters in the upper Bay showed that there is a fairly consistent trend of the ANSERC chla getting larger with respect to the DNR chla over time. The discrepancy was not apparent in the results for the tributaries.

In the main stem and larger Maryland tributaries, ANSERC and DNR collect samples from the same boat either simultaneously or, at the most, within an hour of each other. Both samples are processed by the same method, i.e., the samples are collected and filtered onboard, kept in the same cooler until transported to the lab, and analyzed spectrophotometrically. Routine split comparisons earlier in the Program found no differences in the results. The underlying causes of these differences are subtle and elusive.

Some exploratory analyses have already been conducted. This issue and DAITS #028 are currently (Dec '97) being addressed to some extent by a special split sample experiment (see below).

PROPOSED SOLUTION:
Not yet clear about causes of the discrepancy.

DISCUSSION:

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

PRIORITY RANKING: 5
Chlorophyll is a major parameter in evaluating the response to nutrient reductions. This problem has confounded interpretation of monitoring results for the re-evaluation and made linkages

between WQ and phytoplankton unreliable.

SUBMITTER/RESPONSIBLE PARTY:
Name: Marcia Olson on behalf of AMQAW
Organization: CBPO and the Monitoring Subcommittee

ACTIONS TO DATE: Elgin Perry, independent statistical consultant to the Bay Program, has conducted several exploratory analyses, first using a small hand-entered comparison data set, and then using the full data sets of DNR and ANSERC. The results of this latter analysis are given below in a memo from ESP:

> 11/12/97 [...] Because trend assessments for the two parameters were consistent in the tribs, it was inferred that there was no discrepancy. This seemed to rule out the possibility of instrument drift as an explanation for this discrepancy. Marcia later pointed out that the consistency of trend in the tribs may have resulted from the trends being large enough to overwhelm the bias. This conjecture posed one question that I will address in this note.
>
> Also, in the previous analysis, I had discovered that the bias between the parameters seemed to have a strong seasonal component. This observation raises the question of the bias being associated with water clarity. I include below some results of analyses that address the association of bias with TSS and Secchi.
>
> Bias in the tribs?
>
> The methods used here are the same as methods used earlier. Recall that the difference is computed as (ANSERC - DNR). A positive bias indicates that the ANSERC chla is higher. Also recall that each parameter has been transformed by natural logarithms.
>
> The stations on which the tribs comparison are based are:
>
> if station = 'MLE2.2' (LE2.2)
> or station = 'XDA1177' (RET2.2)
> or station = 'XEA6596' (TF2.3)
> or station = 'XDE5339' (LE1.1)
> or station = 'XED4892' (TF1.7)
> or station = 'PXT0402' (TF1.5)
> or station = 'MET5.2' (ET5.2)
> or station = 'MET5.1' (ET5.1)
> or station = 'MWT5.1'; (WT5.1)
>
> The bias in the tribs and bias in the main stem have one important feature in common: From 1993 to 1996 there is a consistent positive bias (tables below). One notable exception to consistency between the main stem and the tribs is 1987 where the bias is negative in

the main stem and positive in the tribs.

Mean difference by year for Tributaries

		LNDIFF		
YEAR	N	Mean	SD	
1985	88	0.02690113	0.67698762	
1986	137	0.15538591	0.51648938	
1987	123	0.20203364	0.62795148	Mean > .1 is sig here.
1988	134	0.37415622	0.50246652	
1989	129	0.10221772	0.57285573	
1990	135	-0.02758287	0.44239104	
1991	131	0.02986984	0.49877366	
1992	143	-0.05773641	0.63117803	
1993	152	0.29480604	0.52062830	
1994	143	0.22676953	0.51507873	
1995	147	0.25796489	0.49185358	
1996	108	0.31603642	0.53368129	

Mean difference by year for Main stem

		LNDIFF		
YEAR	N	Mean	SD	
1985	66	-0.10370104	0.39745391	
1986	79	-0.08840200	0.58601805	
1987	81	-0.24329881	0.57534532	Mean > .12 is sig here
1988	76	0.18685640	0.46021852	
1989	78	0.16189655	0.51044248	
1990	86	0.17053947	0.53155675	
1991	77	0.21384653	0.50076990	
1992	85	0.18806956	0.62504586	
1993	85	0.55990096	0.55691230	
1994	80	0.30679626	0.63284261	
1995	82	0.20872508	0.51942427	
1996	61	0.28675220	0.49936622	

ANOVA results on lndiff in the tributaries.

Like the main stem, the trend in the bias over years is not consistent over months. Unlike the main stem, there is some evidence of inconsistency over stations. However, when the data are analyzed month-by-month, this station-by-year interaction looks unimportant.

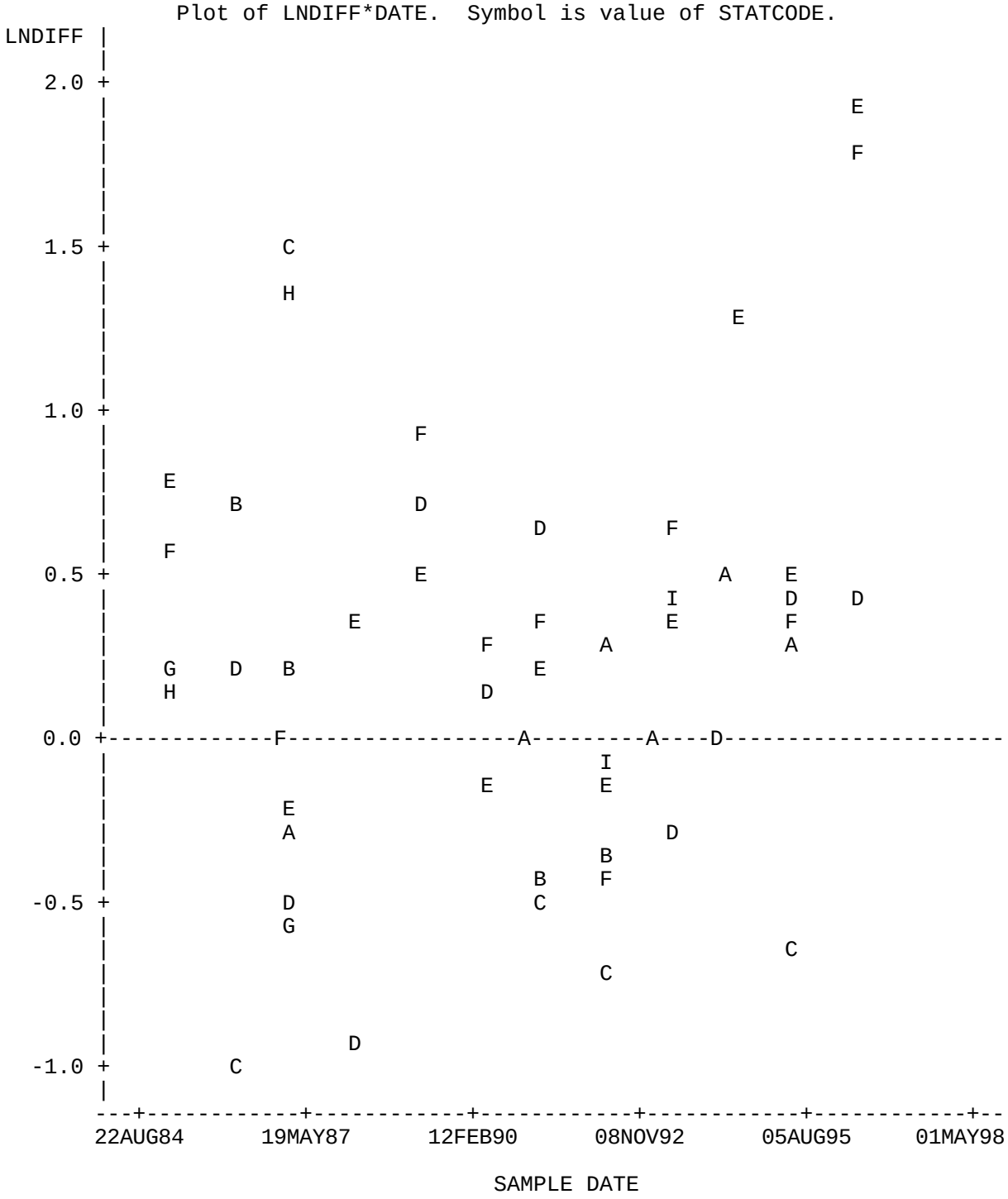
Source	DF	Type III SS	Mean Square	F Value	Pr > F
YEAR	11	29.37686199	2.67062382	11.10	0.0001
MONTH	11	3.34296272	0.30390570	1.26	0.2407
YEAR*MONTH	116	77.39067052	0.66716095	2.77	0.0001
STATION	8	9.16242978	1.14530372	4.76	0.0001
YEAR*STATION	86	29.68780124	0.34520699	1.43	0.0070
MONTH*STATION	86	27.43090430	0.31896400	1.33	0.0284
MONTH=4					
YEAR	11	13.73545866	1.24867806	6.12	0.0001
STATION	8	2.65504797	0.33188100	1.63	0.1321
YEAR*STATION	81	16.44833494	0.20306586	1.00	0.5102
MONTH=5					
YEAR	11	11.03931633	1.00357421	3.66	0.0003
STATION	8	7.12145083	0.89018135	3.24	0.0029
YEAR*STATION	81	20.13374670	0.24856477	0.91	0.6735
MONTH=6					
YEAR	11	9.02967931	0.82087994	2.26	0.0178
STATION	8	2.77735499	0.34716937	0.96	0.4761
YEAR*STATION	86	16.31788499	0.18974285	0.52	0.9986
MONTH=7					
YEAR	11	6.97973654	0.63452150	3.10	0.0014
STATION	8	5.80972858	0.72621607	3.55	0.0013
YEAR*STATION	83	27.49695819	0.33128865	1.62	0.0126
MONTH=8					
YEAR	11	7.05031368	0.64093761	2.15	0.0244
STATION	8	3.84475265	0.48059408	1.61	0.1329
YEAR*STATION	86	24.12125467	0.28047971	0.94	0.6137
MONTH=9					
YEAR	11	10.09663453	0.91787587	5.42	0.0001
STATION	8	5.18345726	0.64793216	3.83	0.0007
YEAR*STATION	84	20.37649256	0.24257729	1.43	0.0498

If we model the trend over years with a linear regression model for each month we obtain the following:

Parameter		slope Estimate	T for H0: Parameter=0	Pr > |T|
TIME*MONTH	1	0.0000877179	1.47	0.1424
	2	0.0001562503	1.45	0.1470
	3	0.0000962573	1.79	0.0742
	4	0.0000829724	2.41	0.0162
	5	-.0000093768	-0.29	0.7704
	6	-.0000583090	-1.78	0.0756
	7	-.0000596587	-1.79	0.0731
	8	-.0000186801	-0.59	0.5569
	9	0.0000760855	2.24	0.0252
	10	0.0001359795	3.07	0.0022
	11	0.0001082489	2.07	0.0383
	12	0.0000992514	2.07	0.0389

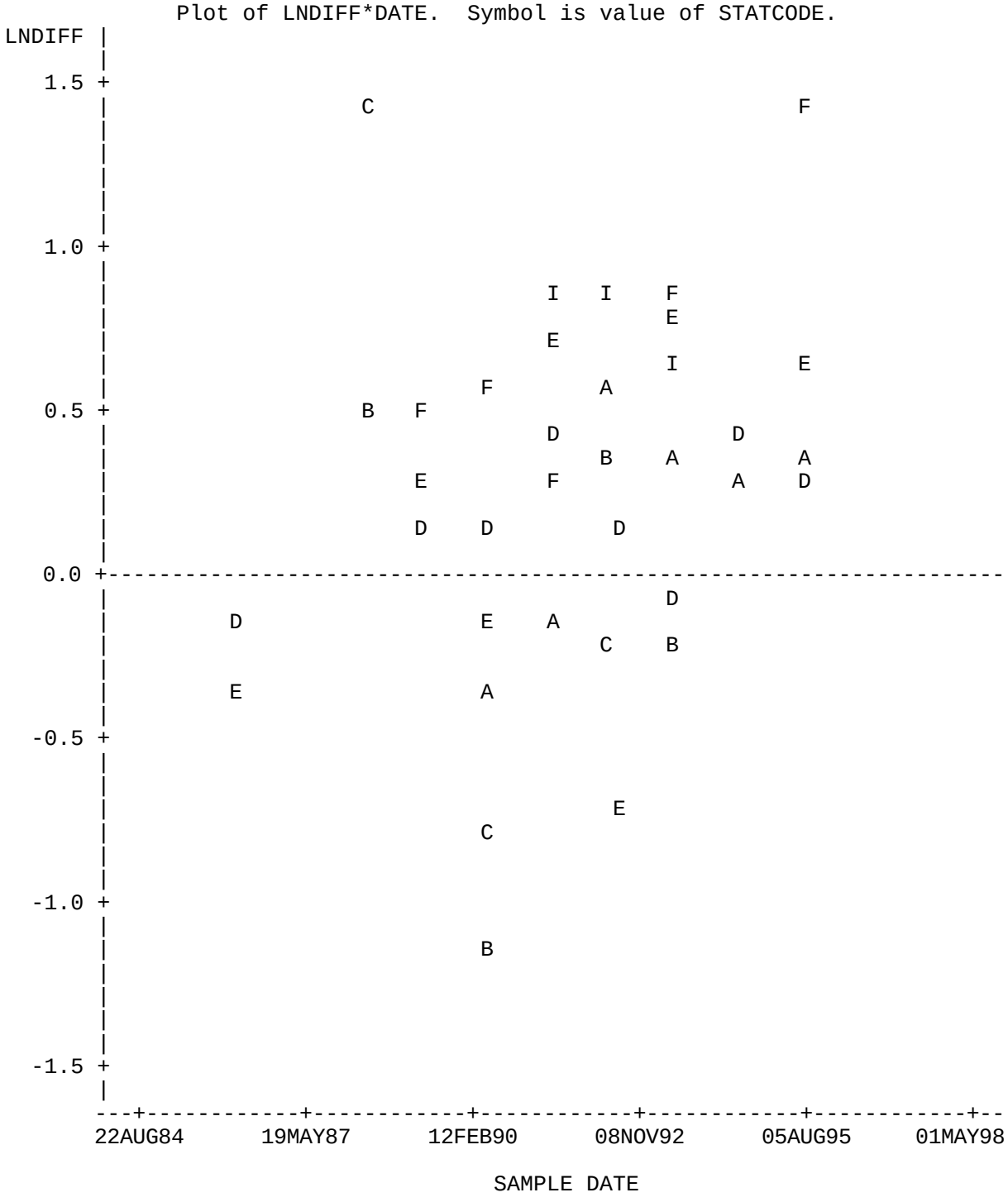
The rule appears to be that the bias is increasing in the fall and winter months and either flat or decreasing in the summer. These results are similar to the main stem (see last note). Here are plots month by month for a visual assessment.

MONTH=1



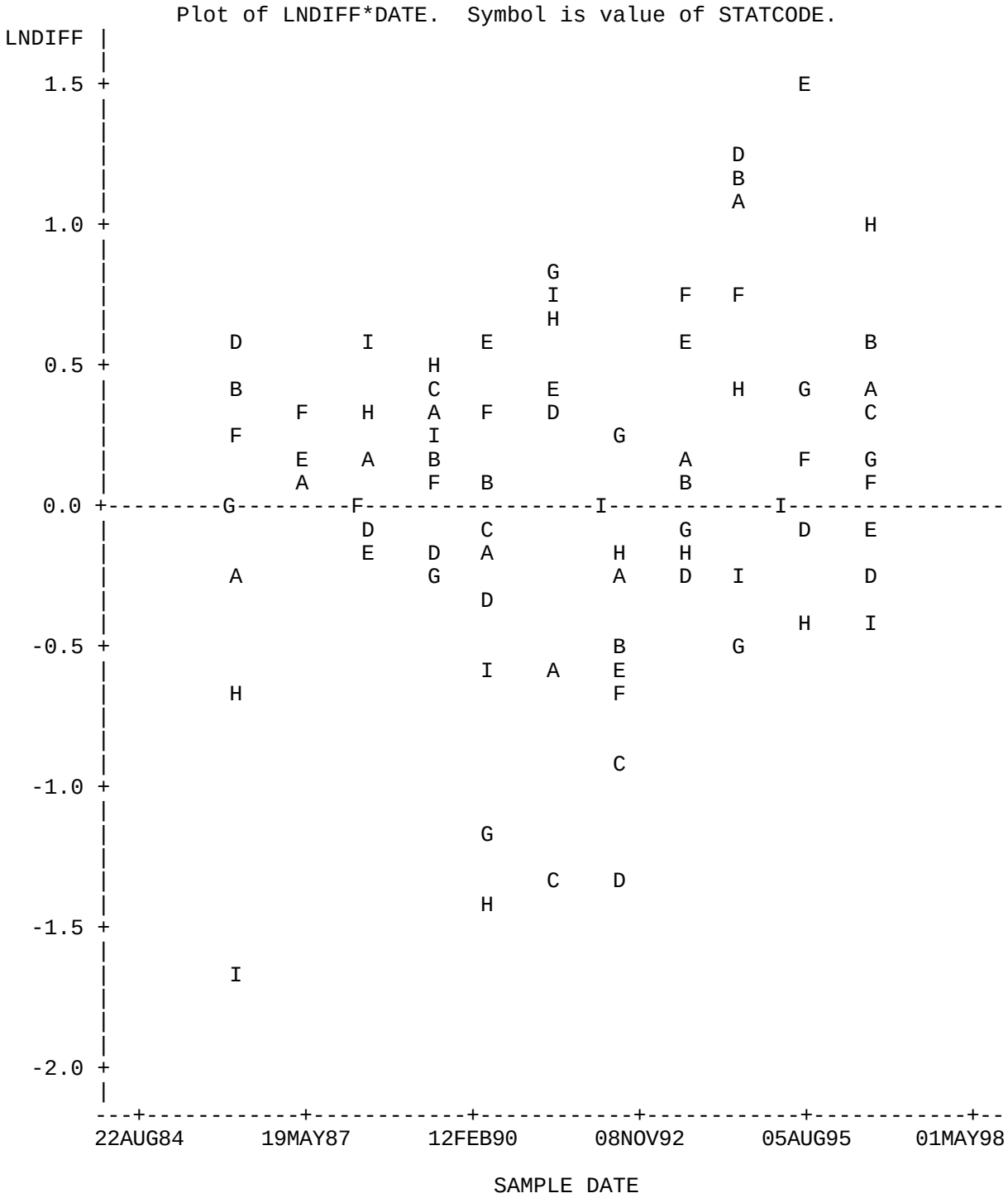
NOTE: 40 obs had missing values. 4 obs hidden. Outliers trimmed at 2.0.

MONTH=2



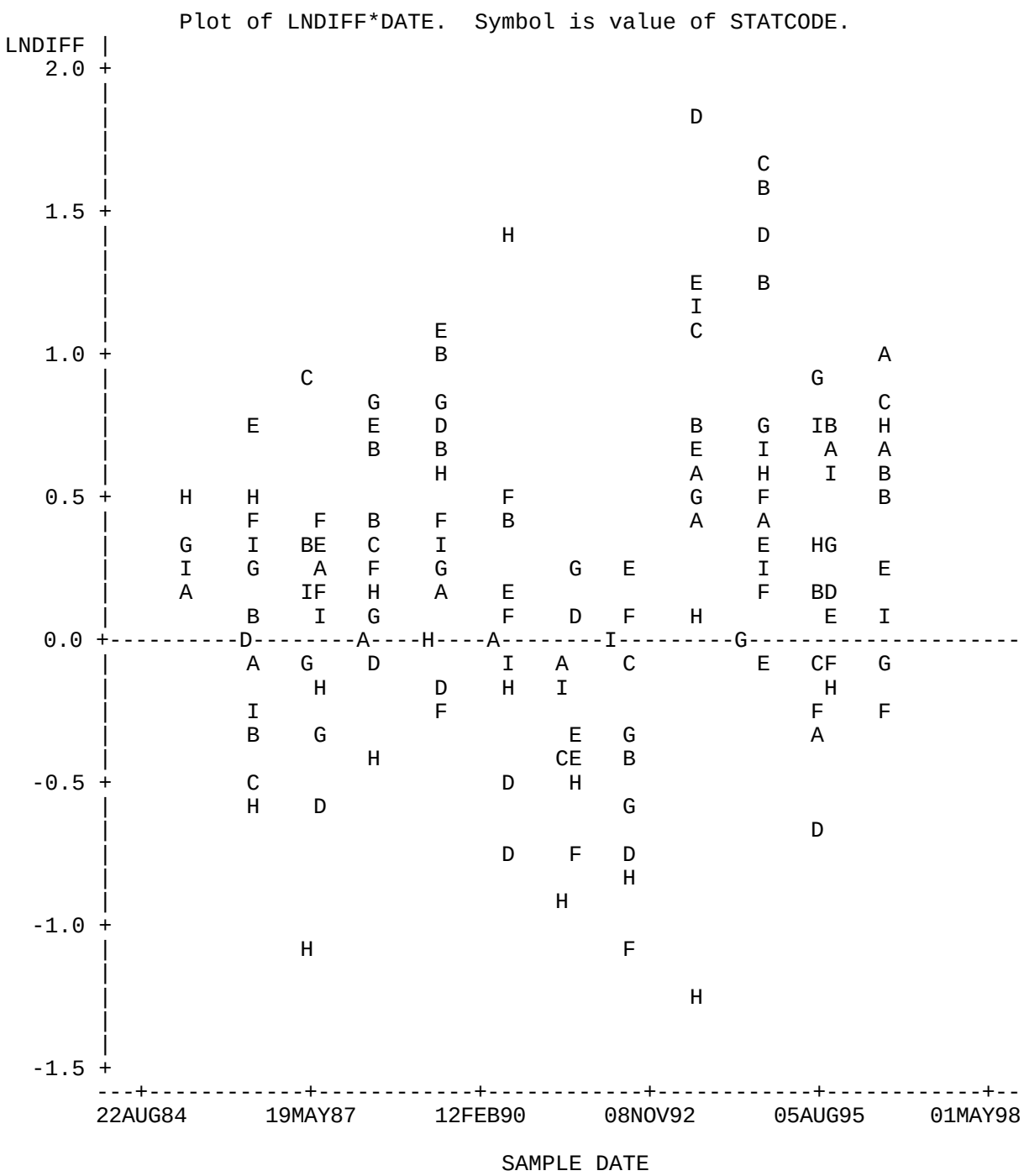
NOTE: 69 obs had missing values. 1 obs hidden. Outliers trimmed at 2.0

MONTH=3



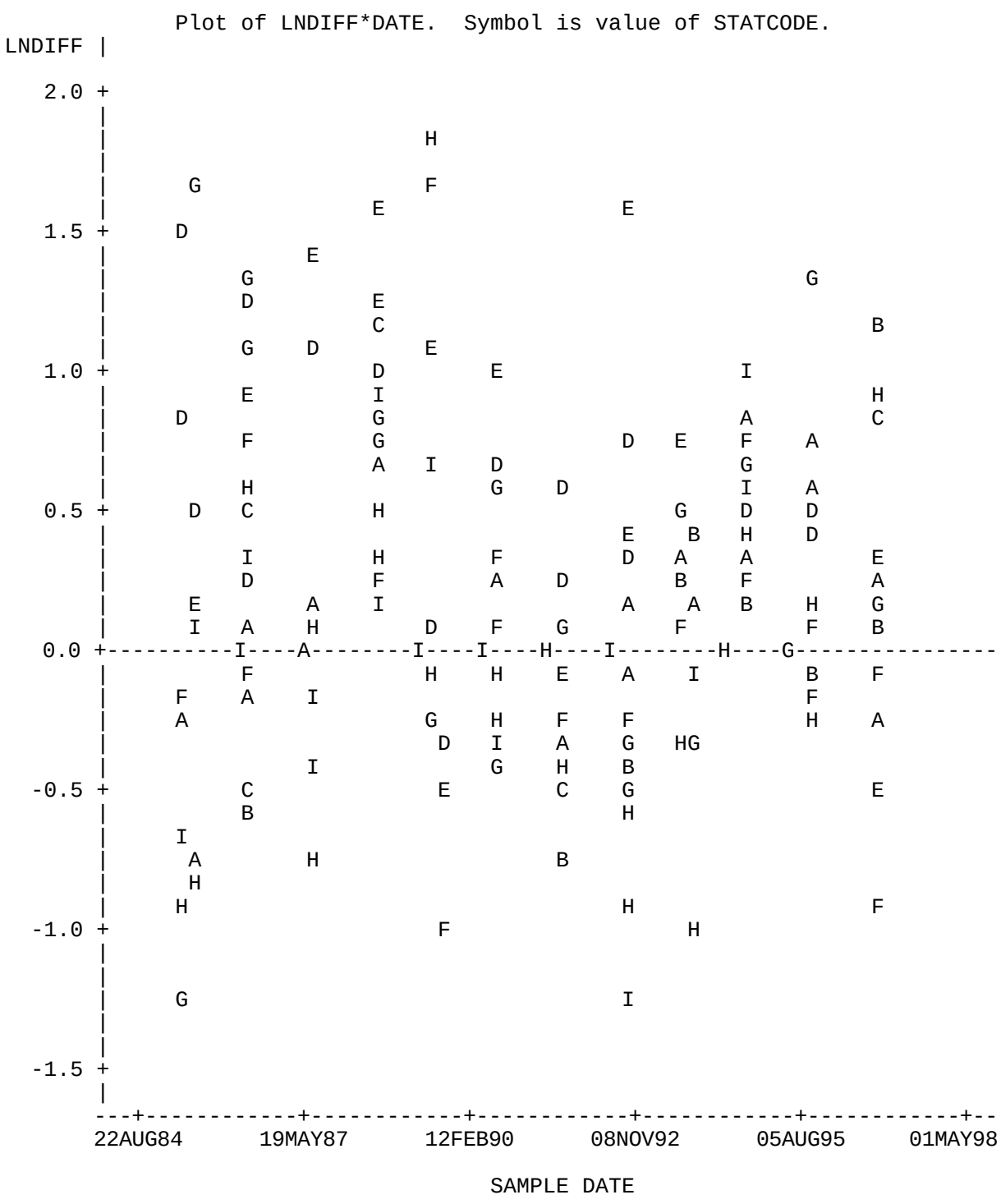
NOTE: 119 obs had missing values. 6 obs hidden. Outliers trimmed at 2.0

MONTH=4



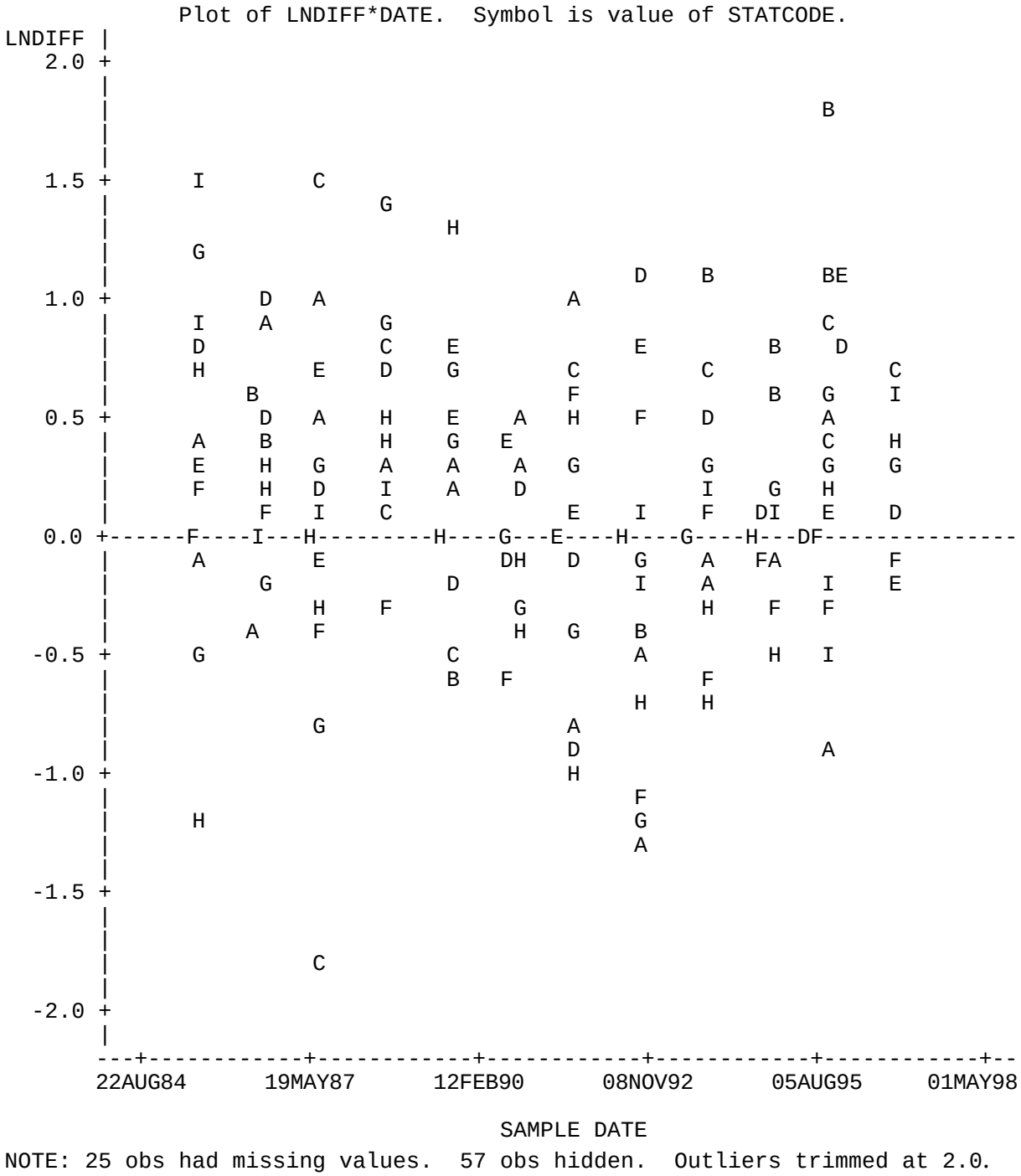
NOTE: 53 obs had missing values. 40 obs hidden. Outliers trimmed at 2.0.

MONTH=5



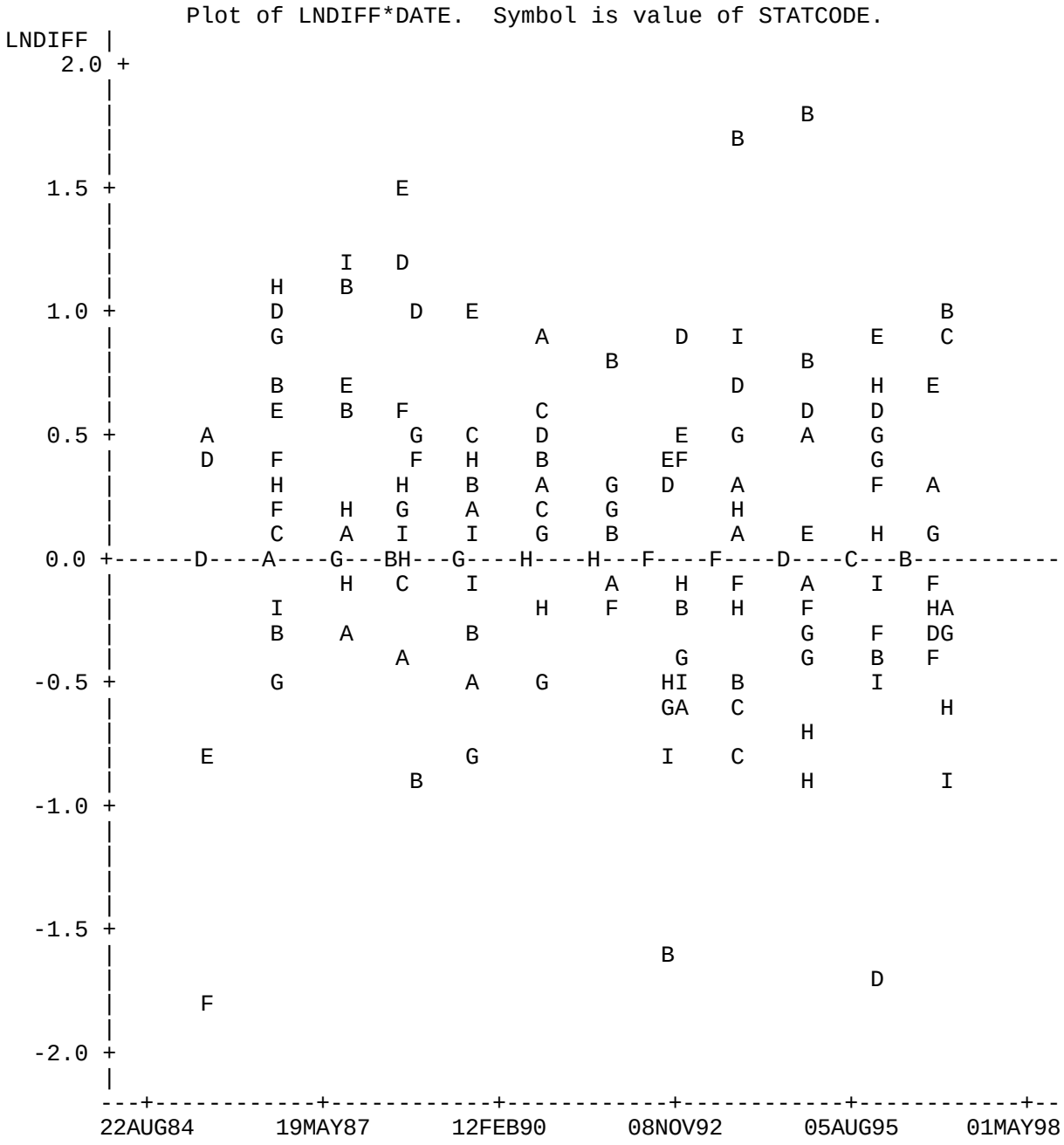
NOTE: 38 obs had missing values. 48 obs hidden. Outliers trimmed at 2.0.

MONTH=6



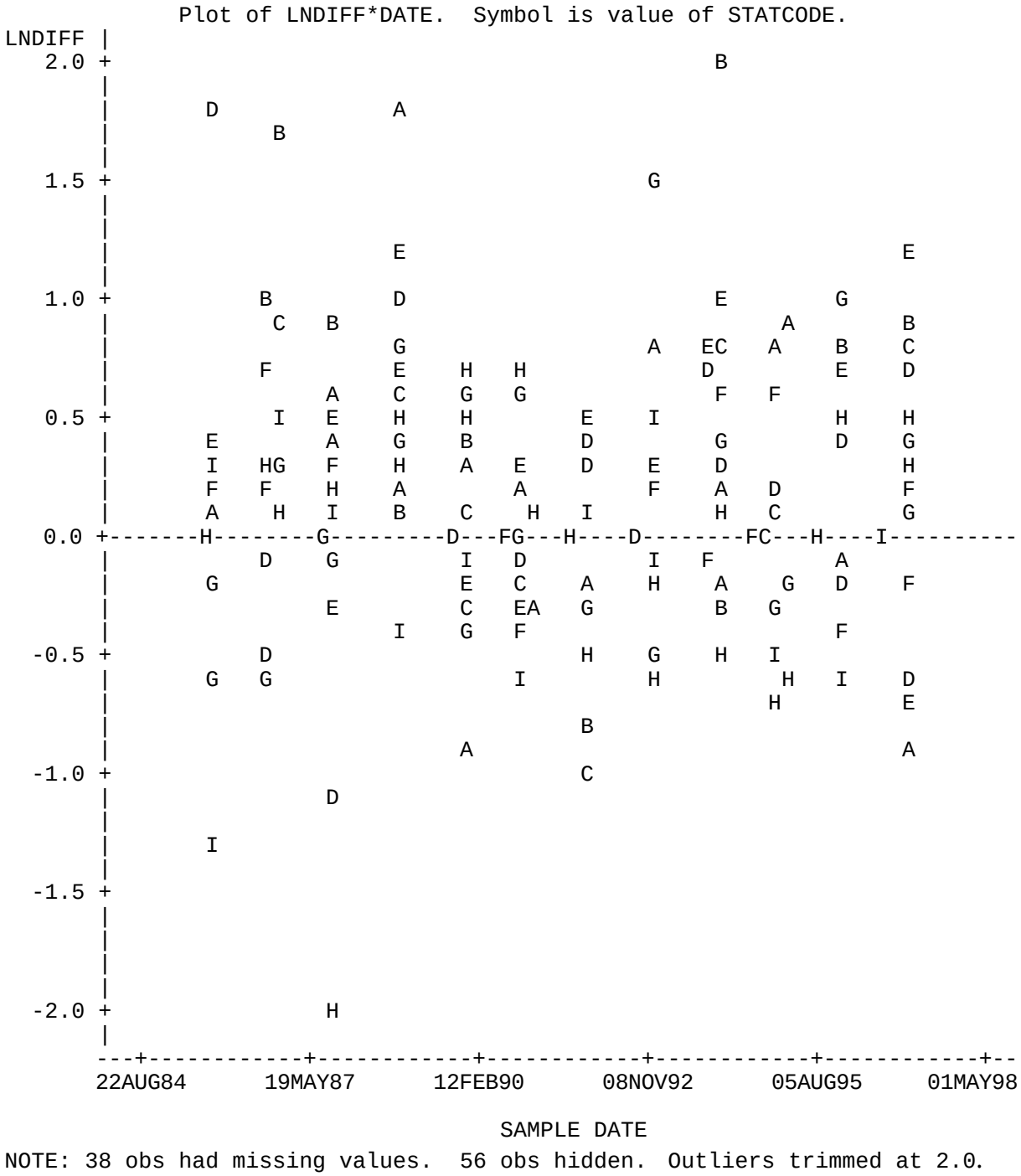
NOTE: 25 obs had missing values. 57 obs hidden. Outliers trimmed at 2.0.

MONTH=7



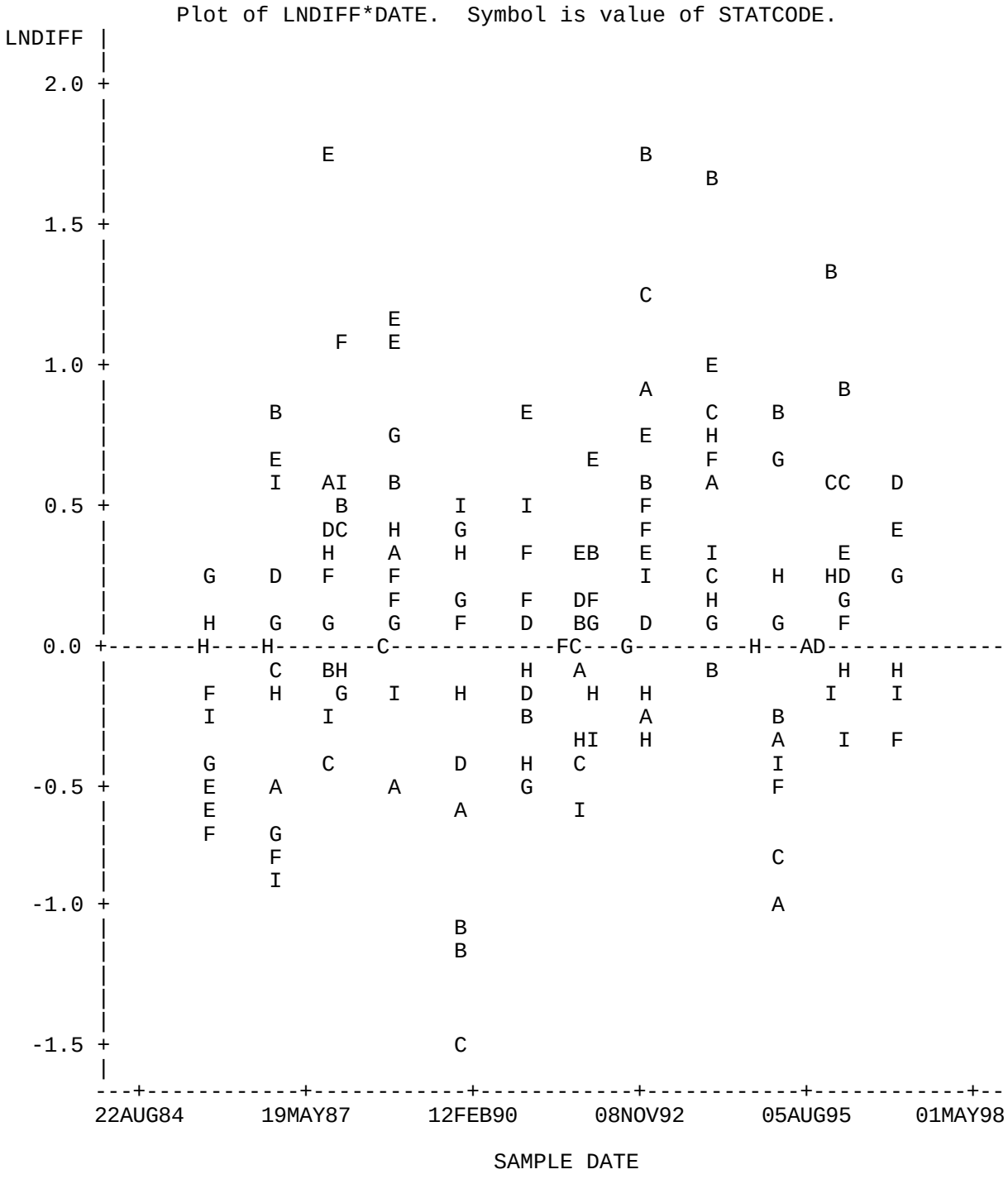
NOTE: 15 obs had missing values. 58 obs hidden. Outliers trimmed at 2.0.

MONTH=8



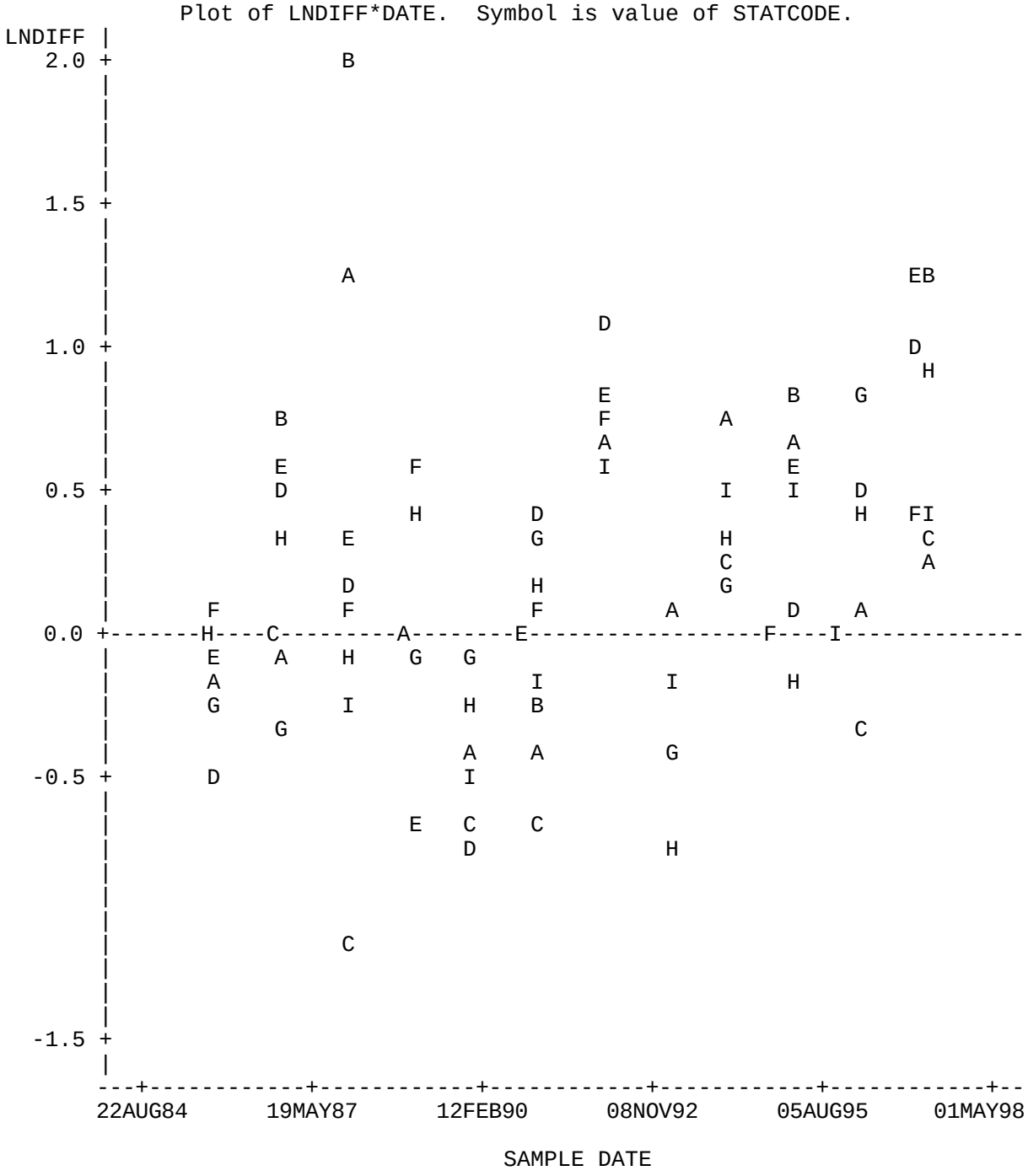
NOTE: 38 obs had missing values. 56 obs hidden. Outliers trimmed at 2.0.

MONTH=9



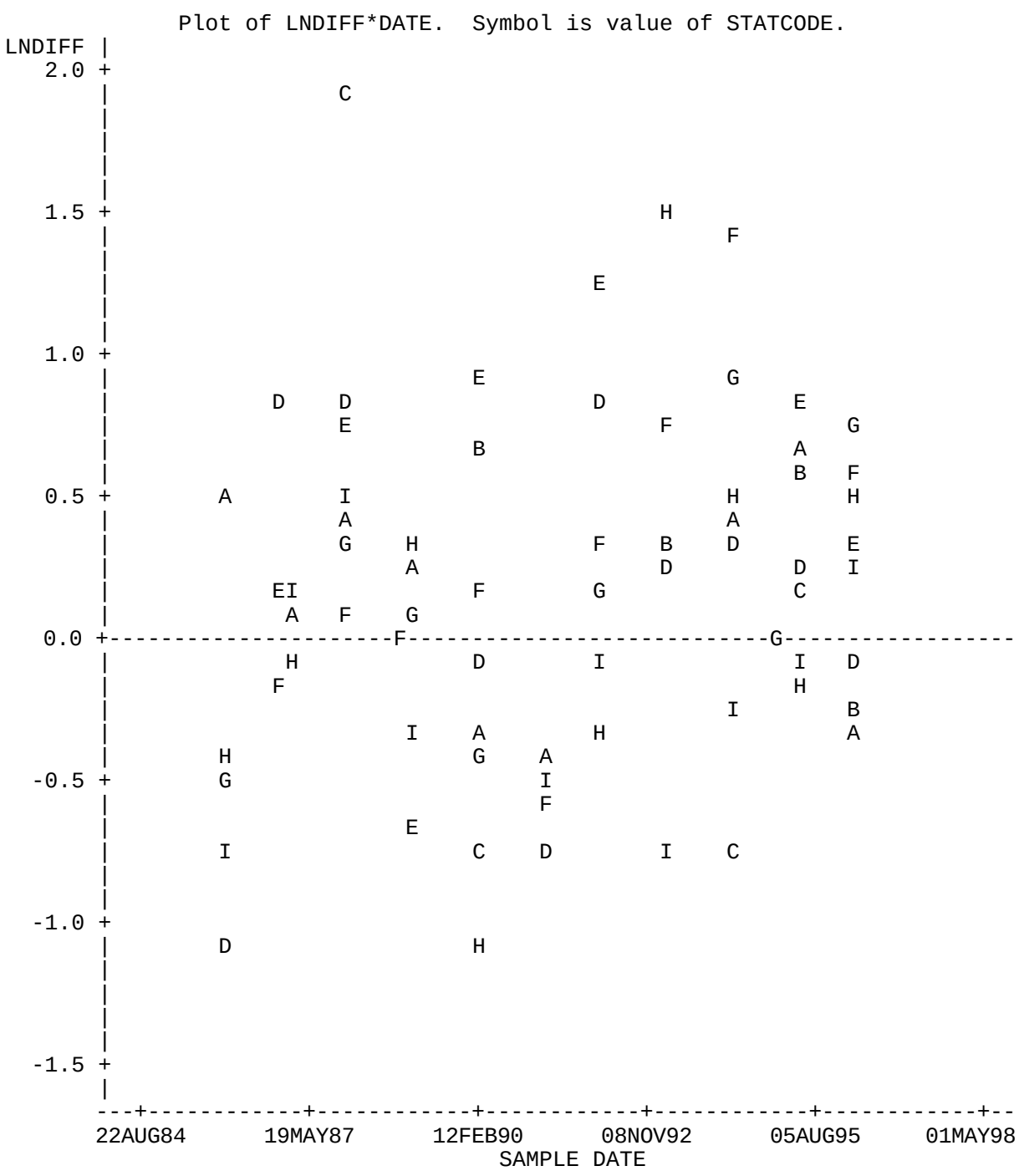
NOTE: 48 obs had missing values. 48 obs hidden. Outliers trimmed at 2.0.

MONTH=10



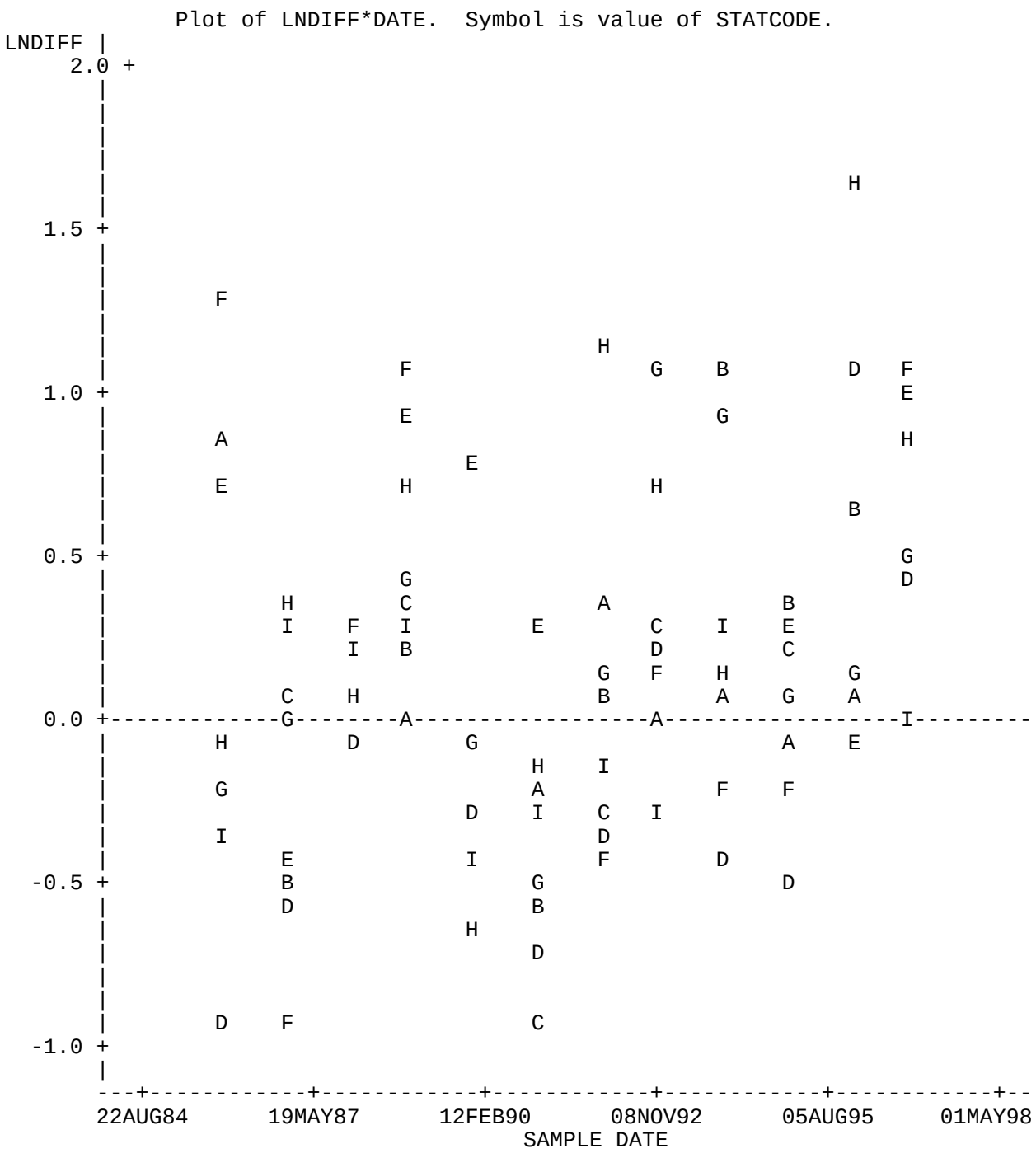
NOTE: 138 obs had missing values. 15 obs hidden. Outliers trimmed at 2.0.

MONTH=11



NOTE: 47 obs had missing values. 9 obs hidden. Outliers trimmed at 2.0.

MONTH=12



NOTE: 22 obs had missing values. 9 obs hidden. Outliers trimmed at 2.0.

Looking at these month-by month plots, I get the impression that there is a short period around 1987-'88 where there is a positive bias and then again in 1992-'96. Looking at these same plots for the mainstem, I don't think I see the '87-'88 blip, except perhaps in the winter months.
Other than that, the results from the mainstem and the tribs are similar.

I think the consistency of the bias over the main stem and the tribs indicates that it is caused by some kind of change in methods or instrument drift. Given that no split sample or cross laboratory validation work has been done, I don't think there is any way to resolve which data more accurately reflects the state of nature. It does appear that the bias is flat in the summer months. Perhaps we should emphasize the summer period in interpretive analysis.

There remains the curious phenomenon that the bias seems to have a seasonal component. Here is what we find when TSS is included in the predictive model. In both the tributaries and the mainstem: Either TSS or Secchi are significant in the type I sums of squares but become non-significant in the type III sums of squares. This suggests that the association of water clarity with the bias is linked to a seasonal trend in the bias. Therefore it cannot be conclusively inferred that water clarity is a causal factor in the bias. It could be that some other seasonal factor is the problem and it is just a coincidence that there is an association of the bias with water clarity. If there is a cause and effect, the relation is that the greater the water clarity, the greater
the bias.

Tributary Analysis

Dependent Variable: LNDIFF

Source	DF	Type I SS	Mean Square	F Value	Pr > F
TSS	1	27.16695908	27.16695908	91.93	0.0001
SECCHI	1	9.51876043	9.51876043	32.21	0.0001
STATION	9	23.91851180	2.65761242	8.99	0.0001
MONTH	11	2.57166085	0.23378735	0.79	0.6493
YEAR	1	1.78833466	1.78833466	6.05	0.0140
YEAR*MONTH	11	11.11673052	1.01061187	3.42	0.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
TSS	1	0.03558421	0.03558421	0.12	0.7286
SECCHI	1	0.12817858	0.12817858	0.43	0.5103
STATION	8	19.21570430	2.40196304	8.13	0.0001
MONTH	11	11.11840440	1.01076404	3.42	0.0001
YEAR	1	4.62728646	4.62728646	15.66	0.0001
YEAR*MONTH	11	11.11673052	1.01061187	3.42	0.0001

Mainstem Analysis

Dependent Variable: LNDIFF

Source	DF	Type I SS	Mean Square	F Value	Pr > F
TSS	1	25.14100982	25.14100982	98.54	0.0001
SECCHI	1	1.42690860	1.42690860	5.59	0.0182
STATION	5	14.09813104	2.81962621	11.05	0.0001
MONTH	11	25.55157244	2.32287022	9.10	0.0001
YEAR	1	22.27173093	22.27173093	87.30	0.0001
YEAR*MONTH	11	13.86853341	1.26077576	4.94	0.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
TSS	1	0.42072916	0.42072916	1.65	0.1994
SECCHI	1	0.82605516	0.82605516	3.24	0.0723
STATION	4	9.95299714	2.48824928	9.75	0.0001
MONTH	11	13.84487745	1.25862522	4.93	0.0001
YEAR	1	25.58471207	25.58471207	100.28	0.0001
YEAR*MONTH	11	13.86853341	1.26077576	4.94	0.0001

Conclusions:

I'm tempted to leave this section blank. After reviewing the mainstem and trib data, I think it is clear that we have a measurement problem. The bias is fairly consistent between the two data sets and across stations. I find the seasonal trend curious. Does anyone else have a conjecture as to why it is there? I can't think of any method that would determine which set of measurements most closely represents the state of nature. Because the summer months appear to have less bias than other months, I think interpretive analysis should focus on those months. The most important conclusion is that we should implement some cross laboratory checks and not let this happen again.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS:

ACTION NUMBER 029.01
Designated Respondent: AMQAW
Action: Establish a split sample experiment to look coarsely at interlab differences in chla determination methods.

Resolution Summary:

ACTION NUMBER 029.02
Desginated Respondent: MMO and ESP
Action: At the 12/5/97 AMQAW meeting, Sally Bowen (MD/DNR) had two suggestions

concerning the issues: 1) If we've only looked at Surface samples, then there may be some value in checking to see if the differences would also show up in the AP or BP or B samples since the surface samples, she says, are not collected from the same pump. ANSERC collects the sample from their own pump that is collecting the phytoplankton sample and it is usually a bit deeper than the DNR sample. Also, she thought their surface sample was collected about 20 minutes after the boat came on station while DNR's sample was taken much sooner. There may be some depth adjustment of the plankters in the interim. This factor could be species and/or month specific for light reasons. The subsurface samples are taken from the same pump and relatively close in time. Sally suggested that a species effect alone could play a role, e.g., mucous types versus diatoms, as you and I have considered, but why would the effect always be in one direction? . She suggested looking at ratios of chl_c/chl_a.

Resolution summary: Funds need to be allocated to support further data analysis.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: (DM) 031

CATEGORY CODE: DS

ISSUE TITLE: SUBMISSION OF TRIBUTARY WATER QUALITY DATA CONSISTENT WITH MAINSTEM DATA

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: NOVEMBER 4, 1994

SUBMITTER/RESPONSIBLE PARTY:
Name: Garland Alston
Organization: MTI
410 Severn Ave
Annapolis, MD 21403

PRIORITY RANKING:

STATEMENT OF ISSUE: Two variables in the December 93 Tributary data submission were renamed. The variable TALK (TOTAL ALKALINITY) was renamed to ALK and BOD (5 DAY BIOLOGICAL OXYGEN DEMAND) was renamed to BOD5. These changes generated errors when the data was processed through the monitoring programs.

PROPOSED SOLUTION(S):

1. Rename the variables ALK and BOD5 back to TALK and BOD so that the existing monitoring programs can recognize the data without causing errors.

2. Make no changes to the existing monitoring programs and have future data submitted with original variable names.

3. A decision should be made by the Data Management and Acquisition Workgroup on weather the current monitoring programs should be altered to accommodate the new variable names.

The author recommends the third option.

INTERIM SOLUTION:
Rename the variables to allow processing. Document data so treated and revise based on DM and AWG decision.

DISCUSSION:

OVERALL SOLUTION/RECOMMENDED ACTIONS:
Refer to Data Management and Acquisitions Workgroup
Document in User's Guide and Data Management Plan Manuals.

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 032

CATEGORY CODE: DM/AM

ISSUE TITLE: Virginia Tributary SI and NO23 data:

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM:
01/Feb/1996

STATEMENT OF ISSUE:
With changes in personnel at both VADEQ and the CBPO Data Center, several issues have remained unresolved for a period of years. In the interim, some analyses may have been affected.

CBP Parameter: total silica **(SI**) (filtered?)

A parameter named DSILICO was submitted in the VA trib data sets for a number of years and renamed to SI to conform to the CBP naming convention. At some point, it was communicated to the data submitter that CBP only accepts directly measured parameters. Since the value submitted was derived by taking the value for SIO2 divided by 2.14 to obtain the elemental concentration, the correspondents erroneously determined that it was a "calculated" parameter and therefore not to be submitted. It was thus missing in the original submission of the 1992 and 1993 data. Later, the parameter SIO2 was submitted separately and divided by 2.14 at CBP to obtain SI. The current method code in the data base is 101. The issues are

- is the analytical method the same as other collectors and is division by 2.14 the simple solution? It is currently assumed to be the same.
- if so, has **all** previous data been correctly adjusted either at the data source or at CBP? It is currently believed to have been correctly adjusted.
- is there a detection-limit issue here?

CBP Parameters: filtered nitrite + nitrate (**NO23**), filtered nitrate (**NO3**)

The parameters required by the CBP are NO23 and NO2 as measured directly; NO3 is obtained by subtraction if desired. The parameters NITRITE and NITRATE were submitted in the VA trib data sets for a number of years and converted to NO2 and NO3 at the CBP Data Center; NO23 was obtained by summation of NO2 and NO3. This is problematic if NO2 and/or NO23 were at or below detection level. After the problem was recognized, NO3 data were not included in the 1992-93 data submission to CBP. The NO3 data were submitted separately at a later date and merged into

the data base. An effort to obtain the NO23 data has been initiated. Unfortunately, NO3 is calculated at the analytical lab, not at VADEQ, and the **original NO23 values prior to 1994 are not readily available or not available at affordable dollar or time cost**. VADEQ has requested and **may obtain the NO23 values for 1994.** The problem is further complicated by the fact that prior to 1994, detection levels were relatively high. The 1994 and current data from a new machine have relatively low detection levels. Sometime in 1997, the lab began to submit NO23 as requested.

An analysis of the data revealed the following statistics for NO2, NO3 and NO23 parameters:

NO23 IN VA TRIB DATA

YEAR	NO2 -N-	PCT BDL	AVG MDL FOR NO2	NO3 -N-	PCT BDL	AVG MDL FOR NO3	NO23 -N-	PCT BDL	AVG MDL FOR NO23
1984	424	61.3	0.010	391	29.7	0.050	0	.	.
1985	1007	64.7	0.010	1005	33.9	0.050	0	.	.
1986	1032	62.4	0.010	1030	32.7	0.050	0	.	.
1987	947	68.2	0.010	947	24.6	0.050	0	.	.
1988	1055	25.3	0.010	1055	34.5	0.040	0	.	.
1989	1143	41.4	0.010	1143	17.8	0.040	0	.	.
1990	1187	49.2	0.010	1187	26.0	0.041	0	.	.
1991	1230	64.8	0.010	1230	24.2	0.041	0	.	.
1992	1156	53.8	0.010	1234	27.6	0.040	0	.	.
1993	1194	62.0	0.010	1194	26.6	0.040	0	.	.
1994	1061	24.8	0.003	1064	13.2	0.007	0	.	.
1995	700	23.0	0.002	700	14.1	0.004	0	.	.
1996	684	12.7	0.002	684	5.6	0.004	499	5.6	0.004

*Note the large number of missing values for NO3 in 1992, when NO3 values were added belatedly to the data set.

The issues are:

- Calculations for NO23, DIN (calculated by NH4 + NO23) and TN when calculated by TKNW + NO23 are compromised when NO2 or NO3 are below detection level;
- NO23 values can possibly be obtained from the lab and submitted to CBP for 1994 and after;
- what are the implications for analyses where NO23 data are not available?
- should monies be budgeted to obtain and computerize the lost NO23 data?

PROPOSED SOLUTION:

VADEQ has agreed to provide NO23 data for 1995 data sets, and seek to obtain the 1994 NO23 data from the laboratory. (This was found to be too expensive and was never completed - RB, 2/1/00)
VADEQ will seek guidance from AMQAW, DAWG whether the benefit of pre-1994 NO23 data are worth special funding costs for retrieval.

DISCUSSION:

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

It is not known whether the new NO23 data from the lab will require hand entry or will be machine-readable, but in either case it will require careful merging with the VADEQ source data sets and subsequent submittal to the CBP.

PRIORITY RANKING: 3
Five point scale where 1 is the lowest priority and 5 is the highest.

SUBMITTER/RESPONSIBLE PARTY:
Name: Marcia Olson
Organization: MSC staff analyst

ACTIONS TO DATE:

2/1/96 Conference call between Rick Hoffman, Mark Bushing and Marcia Olson to define problem and outline resolution. Write up DAITS statement.

3/ 96 SI and NO3 data for 1992 and 1993 were submitted separately by VADEQ and merged at CBP with original data sets. Note that fall line stations are handled separately and were not been processed at this time. Because of mismatching key variables, the merging of these data was not easy. After correcting obvioius errors, it still seemed that there were unusually high number of missing values for SI or NO3.

1/31/00 E-mail from Mike Lane on NO3 questions:
Dear Lowell,

Over the past two weeks I have been in the process of constructing historical
water quality data sets in SAS for use here
by the ODU-PIs and myself for ongoing and future data analysis projects. While
constructing the data sets I have discovered
inconsistencies between the On-line databases and the Static data sets for NO3.
There are numerous instances where there
are missing values in the On-line databases for NO3 i.e. observations for which
a value for NO3 was recorded in the Static data sets
but was not found in the On-line databases. There were also missing values in
the Static data sets i.e. observations for which
a value for NO3 was recorded in the ON-line database but was not found in the
Static data sets. A cursory review suggests that

in instances where the two data sets match with respect to date and location of a sample collection (i.e. no missings in either of the two data sets), the values for NO3 are the same. Note I have NOT checked every case so there could still be additional discrepancies. I did notice that there did not appear to be any values for the Chesapeake Bay Mainstem stations in the ON-line databases for NO3 which seems unlikely. I did my search from 1984 through 1999, marked the All basins box and selected only NO3F as the parameter. Is it possible I missed something while running the query? Or is it expected that data analysts should calculate NO3 from NO23 and NO2 once they have assembled a data set containing those two variables?

In addition to these problems, I have discovered that the Static data sets contain numerous (922) observations for which the value of NO23 is less than that of NO2. This results in negative values for NO3 for these observations since NO3 is calculated by subtracting NO2 from NO23. I would suggest that this problem may have been some kind of transposition error that occurred either during data entry at the collection agencies, data processing at the collection agencies, or data processing error at the EPA. There was no single Agency or source that consistently generated data with this type of error and there did not appear to be any consistency with respect to the station location of date of collection. It does APPEAR to me that NO2 and NO23 have been transposed for the problematic observations but I don't have any direct evidence of that. If you or anyone up at EPA have any insight into the cause of these problems I would appreciate some assistance. Someone may need to consider how these problematic observations have affected status and trend analyses. That is probably a question for DAWG and not you but you may want to discuss it with DAWG members up your way.

To help you in tracking down the solution(s) to this problem, I have attached a couple of SAS listing files that show the discrepancies between the On-line database and the Static data sets (BAY6C.LST) and the negative NO3 values (BAY6B.LST) in a zip file. Please review these and let me know if there is anything I can do to alleviate these problems with the data. Until I resolve these problems, ongoing and future data analysis projects could be delayed. I will update you with any other problems I find. Thank you for your assistance.
(See attached file: bay.zip)

Mike Lane

Applied Marine Research Laboratory
Old Dominion University
Norfolk, VA, 23529

P: (757) 683-4692
F: (757) 683-5293

2/1/00 E-mail responding to Mike Lane on NO3 in the database from Ricky Bahner and Marcia Olson: Dear Mike;

Thank you for your email of 1/31/00 outlining some problems you encountered with NO3. I believe the following will answer your questions. I have also included comments from Marcia Olson.

1. Early in the design stage of the ACCESS database (On-line database), it was decided NOT to include calculated parameters, except for CHLA and PHEO. The Static database did contain calculated parameters such as NO3, therefore you will find them in the Static but not the On-line database, with some exceptions. We have discussed creating a database with calculated parameters, but at this time it does not exist. You as the analyst will need to create this parameter and decide on how you want to deal with below detection values.

2. The exceptions I mentioned in item1 are for tributary data submitted from VADEQ and DCDOH Anacostia data. The following paragraph, sent to me from Marcia, explains the discrepancy for VADEQ NO3 data.

VA tribs submitted only NO2 and NO3 for a number of years. When it was discovered that NO3 was calculated from NO23, we asked that they not submit the NO3, but provide the NO23. The result (just around the time CSC was dismissed) was that neither NO23 or NO3 was provided. (See DAITS issue 32 attached to this memo) DEQ tried to get back the NO23 measurements from the lab and was only partially successful. Then we asked for the NO3 again, so we would at least have something. Mark Bushing provided a separate file with date/time/depth and NO3 values for 1992 and 1993. Many did not mesh because of differences in depths, etc --- I don't recall all the problems. These were added to the Static database where there was a match. When the new data base was in development, we (Peter Legg, Ricky and whoever else was mulling on these things) discussed how to resolve this problem: how to keep only directly measured values in the data base, but keep the NO3's where no NO23 was provided.

We decided to keep the NO3 values from DEQ, where that was all that was submitted, in the On-line database.

A similar thing happened with DC data. DCRA (now DCDOH) submitted NO2 and NO3 until August, 1995 when they began to submit NO23. Therefore you will also find DC stations with NO3 in the On-line database prior to August, 1995. When I started here in 1997, the DC data beginning around 1990 had not been processed and moved into the Static database, and DC had not submitted data beyond 1993. As I

processed these data in late 1998 and 1999, I moved them into the On-line database, rather than trying to maintain them in the Static database.

3. On the issue of negative detection limits, Marcia writes:
I'm not sure about the methods and detection limits of NO23 and NO2, but they are independently measured, and if near the detection limits, they could yield negative numbers when subtracted. It happens with almost all the derived parameters, particularly old POC values when TOC-DOC=POC.. As for the effect of the negative values on trend.... If the issues Mike raises are caused by gross errors, miskeyed values, etc., of course the results are questionable. If we assume the negatives come from lab error around the detection limits of NO23 and NO2, then the negative values ought to be relatively small. Our rule for trend analysis is to raise the directly measured values to a selected detection limit (if they are less than that value), then take half the value. For a calculated parameter like NO3, NO23 and NO2 are censored first, then NO3 is calculated from the adjusted values. I presume the detection limits for NO23 and NO2 are the same, so the result should be zero or close to it in the adjusted trend data set. If NO3 is being treated like a directly measured parameter, which I guess it has to be in the VA trib data set, then the negative values should disappear in the detection-limit censoring process.

4. Additionally mainstem data through June is currently in the On-line database, and I am working to catch up with getting the rest of 1999 processed as quickly as possible. You would not have found data for the latter part of 1999. I will notify you when it is available.

5. I reviewed at random the BAY6C.LST listing you sent and am satisfied that I could explain the questionable data based on my above comments, at least for the values I checked. Thank you for sending the files. As time permits, I will continue to review those lists.

I hope this answers you questions. Please call or email if you have further concerns.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:
Reference appropriate documents as required. To be completed after all actions have been addressed:

RECOMMENDED ACTIONS: (Copy next section for as many actions as needed)

ACTION NUMBER:
This number is an extension of the Issue Number based on Issue Number plus .01, .02 postscript
Example: QA 001.01

1. Designated Respondent:
   (Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 033

CATEGORY CODE: DS = Issue related to Data Submittal

ISSUE TITLE: Below Detection Limit

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 03/14/96

STATEMENT OF ISSUE:

The Monitoring Subcommittee has put forward a formal request to begin submitting Below Detection Limit data, or BDL, with the January 1996 data. With improved statistical techniques, Bay Program statisticians can gain valuable information from the below detection limit values. This information will be used to aid and improve current data analysis projects, which include trend analysis. As a result the Bay Program will be better able to characterize the Chesapeake Bay ecosystem.

PROPOSED SOLUTION:

BDL data is to be submitted to the Bay Program as a separate field. That field will be created by adding **_U** to the parameter name (e.g. parameter_U). This field will contain the actual reading from the instrument. All other fields will remain exactly the same as before. This data structure will aid in limiting access to the below detection limit data. Data requests for the below detection limit values will be fulfilled to authorized personnel only.

DISCUSSION:

Currently laboratories in the Chesapeake Bay Program submit data that are censored at a lower detection limit, called the Method Detection Limit or MDL. Concentrations that are less than this limit are raised to the MDL, and the associated detection limit flag (parameter_D) is set to "<". For example, if the MDL for ammonium (NH4) was 0.003 mg/L, and the measured concentration was 0.002 mg/L, the reported value would be 0.003 mg/L, and the parameter NH4_D would be set to "<". The MDL is calculated by taking 3 times the standard deviation of 7 low-level replicates. Field parameter MDLs are "calibrated accuracy" from the manufacturer. MDLs for calculated parameters are the sum of the MDLs of the components.

Censoring data limits the analysis that can be performed on data. Allowing Chesapeake Bay Program Statisticians access to BDL concentrations will enable them to perform test sensitive analysis that may give better accuracy and reveal trends that were not otherwise noticeable.

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

Data generators need to create new fields for BDLs in field sheets, data set documentation forms (Chesapeake Bay Program) and data documentation forms (non-Chesapeake Bay Program). CBPCC needs to restrict access to the BDLs to authorized personnel only. Water Quality Users Guide and the Data Management Plan need to be updated.

PRIORITY RANKING:

2 (formal request from the Monitoring Subcommittee)

SUBMITTER/RESPONSIBLE PARTY:

Name: David Kimball for Bruce Michael
Organization: CBP/AMQAW

ACTIONS TO DATE:

Formal request from the Monitoring Subcommittee to have BDLs submitted by the data generators. Addition to the Data Management Plan has been approved by AMQAW.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:
Reference appropriate documents as required. To be completed after all actions have been addressed:

RECOMMENDED ACTIONS: (Copy next section for as many actions as needed)

ACTION NUMBER:
This number is an extension of the Issue Number based on Issue Number plus .01, .02 postscript
Example: QA 001.01

1. Designated Respondent:
   (Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 035

CATEGORY CODE:

ISSUE TITLE: VA Optical Density Data Submission

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: February 16, 1999

STATEMENT OF ISSUE:
Old Dominion University has been submitting optical density values for OD480 and OD510 for many years. Optical density values are used to calculate chlorophyll and pheophytin. The values for OD480 and OD510 were measured and sent to the CBP in the late 1980's. They were used at ODU as part of a food web study run by Dr. Birdsong. To the best of our knowledge no one uses these data from the CBP database, and they have never been kept in the BAYSTATS database. They are not the optical densities used to calculate CHLA and PHEO, which are currently kept in the database, nor are they used to calculate trichloromatic a, b, or c, which could be calculated but are not currently kept in the database. These data were part of a special study completed at ODU and were never submitted by other CBP data providers.

PROPOSED SOLUTION:
As we move our CBP data from SAS into a relational database, we propose to keep the values that have been submitted for OD480 and OD510. However we no longer wish to have them submitted to the CBP. ODU working through VADEQ could arrange by mutual agreement to discontinue the collection of these values.

DISCUSSION:

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

PRIORITY RANKING:

SUBMITTER/RESPONSIBLE PARTY:

Name:
Organization:

ACTIONS TO DATE:

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS: (Copy next section for as many actions as needed)

ACTION NUMBER:

1. Designated Respondent:
   (Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

Chesapeake Bay Program Data Analysis Issues Tracking System

Issue Tracking Number:
036

Category Code:
FM = Issue related to field method

Issue Title:
Downward Facing Light Attenuation Probe

Date of Issue Introduction into the System;
5-February-1999

Statement of Issue:
The ODU AMRL and VADEQ plan to eliminate the collection of KD values for the downward facing probe. This probe is used to correct light attenuation calculations for reflected light from the sediment surface.

Proposed Solution:
Unless any objections to this change are received from DAWG members by 8-February-1999, the change to the monitoring regime will be initiated after discussions and confirmation at the Data Management and Acquisition Workgroup

Discussion:
The basis for the change is lack of light penetration to the bottom in all areas currently sampled in the bay. As a result, the is no need to correct for bottom reflected light when making the light attenuation calculations

Sense of the Resources Needed to Respond:
Approval of DAWG, DMAW, AMQAW and the SAV workgroup

Priority Ranking:
4 ■ Would like to have this quickly resolved

Submitter/Responsible Party:
Dave Jasinski for Mike Lane

Actions to Date:

-Peter Bergstrom prepared a consensus statement based on a conference call on 5/7/98 with DMAWG, DAWG, SAV WG and SAV technical synthesis authors. There was agreement that the parameter could be dropped.

-Mike Lane brought up the issue at the January 1999 DAWG meeting. There were no objections.

Overall Resolution Summary of all Actions:

Parameter was dropped from sampling.

Recommended Actions:

Action Number: FM 036.01

1. Designated Respondent:
   (Peter Bergstrom/SAV)
2. Action: Issue needs to be brought before the SAV workgroup
3. Resources Needed:
4. Due Date: Next SAV Workgroup Meeting
5. Action Item Resolution Summary: SAV work group agrees that the parameter can be dropped

Action Number: FM 036.02

1. Designated Respondent:
   AMQAW
2. Action: Issue needs to be brought before the AMQAW workgroup
3. Resources Needed:
4. Due Date: Next AMQAW Meeting
5. Action Item Resolution Summary: All in attendance at the March 25, 1999 meeting agreed that the parameter could be dropped. ODU will stop using the downward facing probe beginning with the April 1999 cruise.

Action Number: FM 036.03

1. Designated Respondent:
   DMAW

2. Action: Issue needs to be brought before the DMAW workgroup
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary: DMAW approved 3/4/99 via email
6.

From:
Rick Hoffman, VADEQ <fahoffman@deq.state.va.us>

To:
R3MD 1.R3CBP(JASINSKI-DAVE)

Date:
3/4/99 9:35am

Subject:
re: Light probe

Dave,
DMAW has no problem with the proposal to drop that parameter. I assume your writing this up as DAITS?

Rick Hoffman
DEQ, Chesapeake Bay Program
P.O. Box 10009
Richmond, VA 23240-0009
Phone: (804)698-4334
Fax: (804)698-4319

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 037

CATEGORY CODE: AM

ISSUE TITLE: Chlorophyll Method Comparison and Revision

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 3/29/99

STATEMENT OF ISSUE: Discrepancies in Virginia tributary chlorophyll data (DAITS 028) and in trends between Maryland DNR and the Academy of Natural Sciences (DAITS 029) prompted an investigation of the analytical methods used by all Chesapeake Bay Program laboratories.

PROPOSED SOLUTION: 1) See if the existing methods produce comparable data through split sample results. 2) Identify significant differences among laboratory procedures, i.e., differences that may affect the resultant data, 3) Look at new methods and 4) Agree upon revisions to the CBP method that all laboratories will follow; estimate affect on historical data.

DISCUSSION: Chlorophyll *a* is a method dependent parameter - results obtained by using one technique can be quite different than results from another. CBP laboratories follow ASTM Method D3731-79 (1979). Samples are filtered, preserved with $MgCO_3$ and frozen. Laboratory staff grind and extract chlorophyll from the filters using 90% acetone, followed by spectrophotometric analysis. To correct for pheophytin interference, the extract is acidified to convert the chlorophyll *a* to pheophytin. Lorenzen's equation is used to subtract the pheophytin from the uncorrected chlorophyll *a*.

New Methods - Recent revisions to chlorophyll methods in the US.PA Marine Methods Manual (1997) and Standard Methods for the Examination of Water and Wastes (1995) have changed some of the method's procedures. These are summarized below.

Change	**EPA Method**	**Standard Methods**
Pheophytin Conversion: 0.003 N instead of 0.03 N HCl	X	X
$MgCO_3$ no longer used for preservative	X	

Sodium bicarbonate no longer added to acetone	X	X
Vacuum filtration ≤ 6 in. Hg.	X	
Add known volume of acetone for grinding & extraction	X	
Extracts may be filtered to remove turbidity interference	X	X
Periodic wavelength check with holium oxide SRM filter	X	

Split Samples - In October 1997, Maryland DNR collected two split samplings for chlorophyll and pheophytin analysis from stations XDE4892 and PXT0402. Eighteen filters containing chlorophyll were collected from each the two stations and sent to 6 laboratories: ODU/AMRL, DCLS, DCRA, VCU, CBL and ANS. The XDE4892 chlorophyll results ranged from 25 (ODU) to 42 µg/L (VCU), with an average value of 34µg/L. Results from PXT0402 ranged from 48 (ODU) to 77 (VCU), with an average value of 66µg/L.

In December 1997, Maryland DNR collected a second split sampling for chlorophyll and pheophytin at station MLE2.3. Twenty-one filters containing chlorophyll were collected and sent to 7 laboratories, the 6 listed above plus DHMH. Sample results ranged from 8.3 µg/L (ODU) to 14 µg/L (CBL), with an average value of 11µg/L chlorophyll.

In April 1998, CBL prepared two sets of chlorophyll blind audit samples. One set was a low level water sample collected off the pier in Solomons, MD. The other set was a high level sample prepared from a culture of mycrocytis??? and the se

Attachment 1 is a tabular/Graphs of these results. Ranking??

In all of the split samplings, ODU reported the lowest values and VCU reported the highest or second highest values. These biases may be indicative of systematic differences in their laboratory procedures.

Method Matrix -

New CBP Method and Individual Laboratory Changes

SENSE OF THE RESOURCES REQUIRED TO RESPOND: $ 4,000 for chlorophyll split samples and data analysis.

PRIORITY RANKING: 1

SUBMITTER/RESPONSIBLE PARTY:

Name: Mary Ellen Ley

Organization: ICPRB/Chesapeake Bay Program

ACTIONS TO DATE:

October 1997 - Chlorophyll Split Samples
December 4, 1997 - Chlorophyll Split Samples
May 1998 - Chlorophyll Blind Audits
April 1998 - Conference Call on Chlorophyll Method Matrix
May 1998- March 1999 - On-site review of each laboratory's procedure.

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS:

RECOMMENDED ACTIONS: (Copy next section for as many actions as needed)

ACTION NUMBER:

1. Designated Respondent:
   (Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 038

CATEGORY CODE: DM, DS

ISSUE TITLE: Light Attenuation Parameter Names and KD Calculation

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: April 30, 2003

STATEMENT OF ISSUE: There are some discrepancies between the parameter names for the PAR readings used to calculate KD in the CBP water quality database and the documentation for those parameters. Because of confusion between the terms downwelling, upwelling, down facing sensor and upward facing sensor, the parameter name EPARU_Z originally intended for the upwelling reading with sensor facing down, was used for upward facing sensor to record downwelling. EPARD_Z now refers to down facing sensor used to record upwelling. Since downwelling values named EPARU_Z have been submitted for some time and data sheets and computer software both at the CBP and data submitter sites, use this parameter name, it was decided to keep the name the same and make the appropriate changes in the documentation. This issue was discussed and agreed upon at the April 24, 2003 Analytical Methods and Quality Assurance Workgroup (AMQAW).

PROPOSED SOLUTION: Continue to use the same parameter names, but correct the documentation in the database methods and parameters tables. This DAITS issue provides documentation on the history of decisions made concerning the naming conventions, the method and calculation used for computing KD in the database as well as other light attenuation issues.

DISCUSSION: In 1992 it was decided to collect and submit photosynthetically active radiation (PAR) from which we could calculate KD. No direction was provided by the CBP for a naming convention to follow in submitting these data. Old Dominion University (ODU) began collecting these data in 1993 and submitting the parameters SAVALUE, UWVALUE, and UDVALUE. Data from other submitters was either not collected pending a naming convention or was collected but not submitted pending a naming convention.

On Nov 3, 1997, the Data Management and Analytical Workgroup (DMAW) made these

recommendations on the following new parameter names for light attenuation:

NEW NAMES	DESCRIPTION	ODU NAMES
IR_OB	Incident radiation, onboard reading	SAVALUE
IR_UP	Incident radiation, up sensor reading	UWVALUE
IR_DOWN	Incident radiation, down sensor reading	UDVALUE
KD	Light attenuation coefficient	KD

Units for the IR parameters would be microeinsteins/m**2/s. KD would have no units since it is a coefficent. Since KD is a calculated value, it would not be stored in the database. Instead, the user interface to the database will provide the formula for calculating KD.

5/1/03 Note: The units were later changed to uM(micromoles) per second per square meter, uM/m**2/s, and it was decided to store KD and other calculated values in the database.

In May, 1998 the Submerged Aquatic Vegetation Workgroup (SAV) chaired by Peter Bergstrom met to discuss the parameter naming issue and the method for calculating KD. The group, which included Chuck Gallegos, SERC, Larry Harding, UMD, Joe Winfield and Irene Weber, ODU, Rick Hoffman VADEQ, and Ricky Bahner, and Peter Legg, CBP, decided on the following names:

EPARD_Z - Downwelling PAR measured underwater (see DEPTH for depth)
EPAR_S - PAR measured in air, on deck or pier (taken at same time)
EPARU_Z - Upwelling PAR measured underwater (see DEPTH for depth)

Other notes from that meeting include:
1. The minimum data needed to calculate KD at a station are two EPARD_Z values at different DEPTH readings;

2. If EPAR_S data are submitted there should be an EPAR_S value for every value of EPARD_Z taken as close as possible in time to the EPARD_Z value at that DEPTH (and EPARU_Z value if that is also submitted).

3. Units should always be uM(micromoles) per second per square meter which are the same as uE (micro Einsteins). uM is used on the latest Li-Cor meter and is the newer name.

4. The sensor used must be a flat cosine quantum sensor (Li-Cor LI-190SA for EPAR_S, LI-192SA for EPARD_Z and EPARU_Z, or equivalent) using the calibration constant for water for the LI-192SA. Underwater sensor points up for EPARD_Z and down for EPARU_Z. These variable names cannot be used for spherical sensor data (LI-193SA).

5. There are no plans to use upwelling data in any calculations.

5/1/03 Note: The upwelling measurement was only submitted by ODU for VA mainstem and Elizabeth River. This was dropped from the sample collection as of March, 1999.

The SAV workgroup also discussed the adjustment of underwater light readings with EPAR_S values before calculating KD. The consensus was to recommend the adjustment if EPAR_S data are available, and to collect and submit EPAR_S data if not now being collected. Note that EPAR_S must be present for every EPARD_Z value used in the KD calculation in order to do the adjustment. The recommended adjustment method (from Larry Harding) is:

1. identify maximum EPAR_S value among the DEPTHS being used in the KD calculation;
2. adjust each EPARD_Z value by multiplying it by (Maximum EPAR_S in that sequence/EPAR_S from that DEPTH); and
3. use the adjusted EPARD_Z values to calculate KD.

This means that if EPAR_S went down between reading 1 and reading 2 of EPARD_Z, this would make the second reading larger (relative to the first) to remove the effect of the drop in ambient light level. Adjusted underwater light data will not be stored in the raw data table in the database. The adjustment will be used as part of the KD calculation.

5/1/03 Note: See Statement of Issue above on the use of the name EPARU_Z for upward facing sensor measuring downwelling instead of EPARD_Z. EPARU_Z is used in the calculation that follows.

The SAV 2-point KD calculation, with adjustment as discussed above, uses the points taken between the most consistent shallowest underwater depth and as close to 1 meter below that as available. In most trib data this will be values from DEPTH = 0.1 and 1.0; in Maryland mainstem data this is usually DEPTH = 0.5 and 1.5; and in Virginia mainstem data is usually DEPTH = 1.0 and 2.0. The 2-point calculation is:

KD = - (LN(EPARU_Z DEEP) - LN (EPARU_Z SHALLOW)) / (DEEP DEPTH - SHALLOW DEPTH)

WHERE:
* SHALLOW DEPTH - shallowest depth with a PAR reading in the first 2 meters of the water column
* DEEP DEPTH - deepest depth with a PAR reading in the first 2 meters of the water column
* EPARU_Z DEEP - PAR reading (upward sensor) at DEEP DEPTH
* EPARU_Z SHALLOW - PAR reading (upward sensor) at SHALLOW DEPTH.

Using this method, KD is not calculated for any sampling event with only one PAR reading in the first 2 meters of the water column, or if EPARU_Z DEEP and/or EPARU_Z SHALLOW are negative.

The measurements of PAR at depth are adjusted to account for the variation in the amount of light reaching the water column using the following formula attributed to Larry Harding:

1. identify maximum EPAR_S value among the DEPTHS being used in the KD calculation,
2. adjust each EPARU_Z value by multiplying it by: (Maximum EPAR_S in that sequence / EPAR_S from that DEPTH); and
3. use the adjusted EPARU_Z values to calculate KD.

Note: EPAR_S must be present for every EPARU_Z value used in the KD calculation in order to do the adjustment. If the required values are not present, the adjustment is not performed.

5/1/03 Note: For online data retrievals from the www.chesapeakebay.net Data Hub, select Light Attenuation for the raw PAR values and Water Quality Data to select the calculated KD values

Two other methods for calculating KD were discussed but never implemented in the database. However, data users could download the raw PAR values and perform these calculations. The first method is the SAV regression which uses EPARU_Z values from the shallowest down to the EPARU_Z value that is the first to fall below 20% of the shallowest EPARD_Z. Take their natural log and regress them on DEPTH with intercept; KD is the slope of the regression times -1. The second method is a Phytoplankton regression which is the same as the SAV regression but uses EPARU_Z down to 1% of the shallowest value (usually as far as light readings are taken).

SENSE OF THE RESOURCES REQUIRED TO RESPOND: 2 hours

PRIORITY RANKING: 3

SUBMITTER/RESPONSIBLE PARTY:

Name: Ricky Bahner, Water Quality Data Manager
Organization: ICPRB at the Chesapeake Bay Program

ACTIONS TO DATE: Corrected the documentation in the database Methods and Parameters tables

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS AND DATE COMPLETED:
Documentation of the Methods and the Parameter tables was completed 5/1/2003.

RECOMMENDED ACTIONS: Correct the documentation

ACTION NUMBER: DM,DS 038.1

1. Designated Respondent: Ricky Bahner, CBP Water Quality Database Manger
2. Action: Correct the title and description fields for EPARU_Z and EPARD_Z in the methods table and the calculation field in the Parameter table. Verified with Mark Lane of Veridyne that the calculation for KD is correct in the database.
3. Resources Needed: 2 hours.
4. Due Date: May 2, 2003
5. Action Item Resolution Summary: Documentation corrected

Chesapeake Bay Program Analysis Issues Tracking System

Issue Tracking Number: 039

Category Code:

Issue Title: Variability in station depth

Date of Issue Introduction into the System: July 21, 2005

Statement of Issue: The total depth at station (TDEPTH) is measured at each sampling event. Variation in that depth measurement is normal, but some stations exhibit more variability than expected, which may be an important consideration for data users.

Water depth can vary greatly due to seasonally extreme tides, persistent winds, and other meteorological causes. Persistent high variability is also observed at stations located at the edge of holes or sills, where small differences in the sampling vessel's position may result in relatively large differences in depth measurements. In other cases, differences are due to unintended or intended-but-undocumented changes in station location. This latter situation was discovered recently for Station LE5.5 and was the impetus for the exploratory investigation of depth variation and submission of the findings to DAITS.

Proposed Solution:
The explanation for station LE5.5 is as follows, as related by Suzanne Doughten (Water Quality Lab. Supervisor, Old Dominion University) to Ricky Bahner (CBPO water quality data manager): " I found an old note dated 9/3/96, that said using DGPS station LE5.5 is located in 6 meters of water. In this note it states that the old work plan had the lat/long for LE5.5 as 36 59 48 and 76 18 12. The new contract that started January 1996 had the station location as 36 59 56 and 76 18 49. This was not discovered until the August cruise, so in September [1996] they switched to the station location listed in the contract.

The resolution is to assign a unique station name to the new (shallower) sampling site to reflect its significantly different location and character and, in the database, to change the name of the station associated with the data collected there since September 1996 from LE5.5 to the new name.

Several other stations need evaluation to determine whether the differences are large enough and the underlying reasons for the large variation in depth warrant a change in station name and site descriptors.

Discussion:
The situation at LE5.5 is perhaps not unique: Station LE5.1 appears to have a step change as well (see figure below). Station CB5.1 was formerly sampled both as part of the Tributary program

(Project=TRIB) and as part of the Mainstem monitoring program (Project=MAIN). The station IDs have the same name, but the station depths are significantly different between projects (see figure). Stations in the upper Patuxent river (TF1.0 – TF1.4) have many missing values for TDEPTH, tdepth appears in 1989, then again in later years. This needs further investigation.
The attached table provides summary statistics for TDEPTH for all tidal stations. The asterisks indicate stations where the standard deviation is => 20% of the mean, as one way to highlight stations with highly variable depths. Note that for station CB5.1, MAIN project CB5.1 appears in the table as station CB5.1A, an arbitrary designation assigned only for this discussion. Most of the other stations exhibiting high variability in total depth probably do so for the other reasons given above, although time series plots of tdepth at some stations suggest systematic change over time, not random variation (see examples below). The particular causes will have to be investigated station by station depending on the user's interest and need.

Sense of the Resources Needed to Respond:

Priority Ranking:

Submitter/Responsible Party: Marcia Olson/Ricky Bahner

Actions to Date: A new station name, LE5.5-W, was created for the relocated LE5.5. All data pertaining to LE5.5 after September 1, 1996 were renamed LE5.5-W. 8/11/2005, R.B.

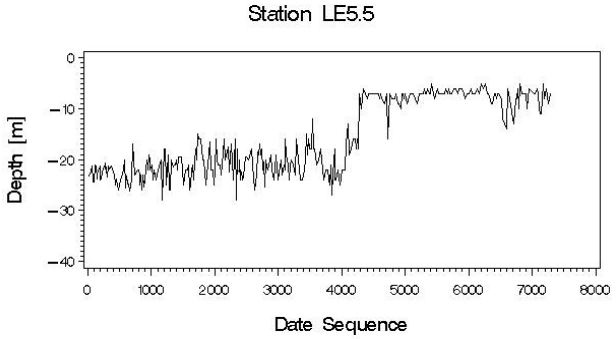
Overall Resolution Summary of all Actions:

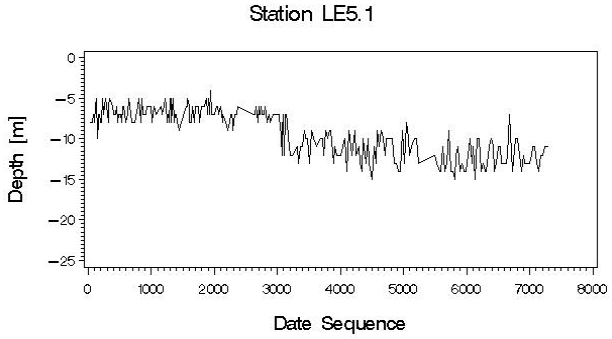
Recommended Actions: Continue to review the attached station list.

Actions Number:
This number is an extension of the Issue Number plus .0n, .0n+1 postscript
Example: QA 001.01

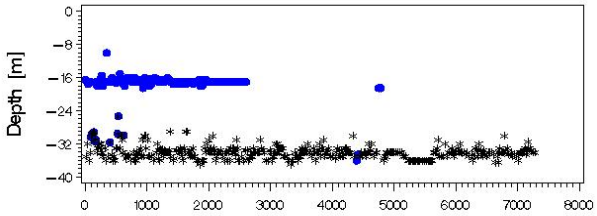
1. Designated Respondent: (Name/Organization and/or Specific Workgroup)
2. Action:
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary:

Example Plots:



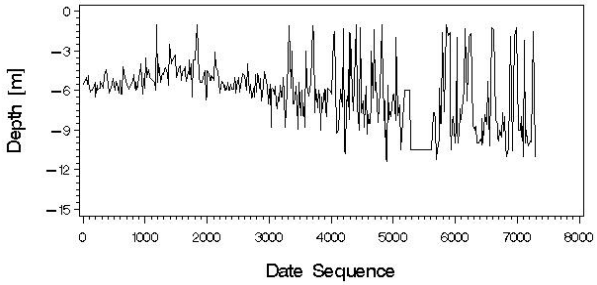


Station CB5.1

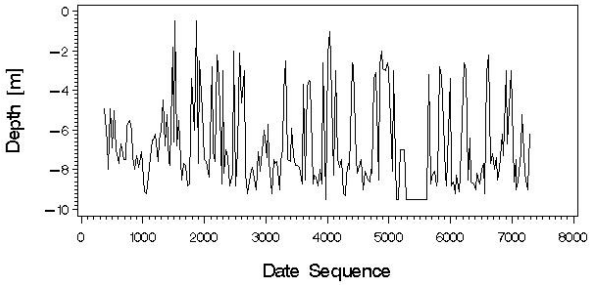


Dot=Trib Star=Main (CB5.1A)

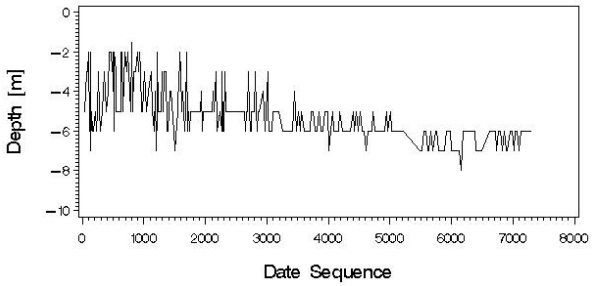
Station ET5.1



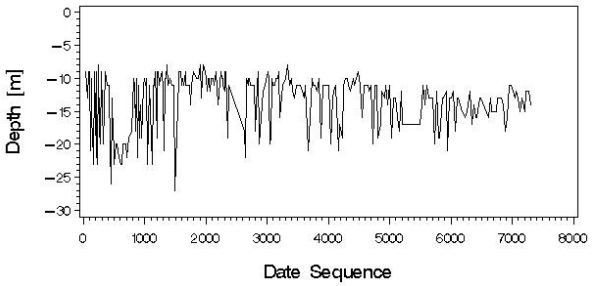
Station ET7.1



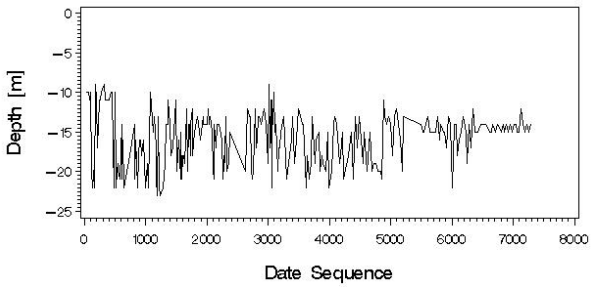
Station LE3.3



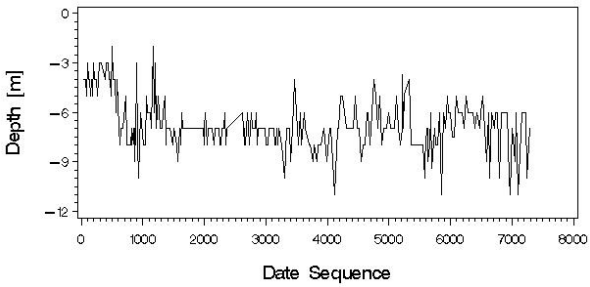
Station LE3.4



Station LE4.3



Station TF4.2



Variability of TDEPTH. (*) indicates stations with std/mean > 20% and number of events (N) > 24

Obs	Flag	Segment	Station	Mode	Median	Mean	STD	Min	P10	Max	N	Flag
1		CB1TF	CB1.1	6.0	6.0	6.1	0.9	4.0	5.0	8.5	346	
2		CB1TF	CB2.1	6.0	6.0	6.1	0.7	3.7	5.5	8.0	382	
3		CB2OH	CB2.2	13.0	12.5	12.4	1.2	1.0	11.0	19.0	352	
4		CB2OH	CB3.1	13.0	13.0	12.9	1.2	8.0	11.5	15.0	352	
5		CB3MH	CB3.2	12.0	12.0	12.1	0.9	8.5	11.0	14.0	354	
6		CB3MH	CB3.3C	25.0	24.5	23.8	2.1	15.5	21.0	27.5	422	
7		CB3MH	CB3.3E	8.0	8.0	8.3	0.7	7.0	7.5	11.0	292	
8		CB3MH	CB3.3W	9.0	9.0	9.0	0.6	7.0	8.0	11.0	292	
9		CB4MH	CB4.1C	33.0	32.0	32.2	1.4	23.0	30.5	35.0	358	
10		CB4MH	CB4.1E	25.0	24.0	23.5	1.9	17.0	21.0	26.5	289	
11		CB4MH	CB4.1W	9.0	9.0	9.3	0.4	8.0	9.0	10.5	289	
12		CB4MH	CB4.2C	27.0	27.0	27.2	1.1	20.5	26.0	29.0	358	
13		CB4MH	CB4.2E	9.0	9.5	9.5	0.9	1.0	9.0	14.0	288	
14		CB4MH	CB4.2W	9.0	9.5	9.4	0.5	8.0	9.0	10.5	291	
15		CB4MH	CB4.3C	27.0	27.0	26.8	1.0	21.0	25.5	29.0	360	
16		CB4MH	CB4.3E	22.0	22.0	22.4	0.8	20.0	21.8	26.0	292	
17		CB4MH	CB4.3W	10.0	10.0	9.8	0.5	8.0	9.0	11.0	291	
18		CB4MH	CB4.4	30.0	30.0	30.2	1.2	27.0	29.0	33.5	360	
19	*	CB5MH	CB5.1	17.0	17.0	18.0	3.9	10.0	16.5	36.0	147	*
20		CB5MH	CB5.1A	34.0	34.0	34.0	1.6	25.3	32.0	37.0	360	
21		CB5MH	CB5.1W	9.0	9.0	9.1	0.3	8.0	9.0	10.0	400	
22		CB5MH	CB5.2	31.0	30.5	30.5	1.0	27.5	29.0	34.0	359	
23		CB5MH	CB5.3	27.0	27.0	26.8	1.1	19.4	25.5	30.0	349	
24		CB5MH	CB5.4	32.0	32.0	32.0	2.2	16.0	30.0	38.0	318	
25		CB5MH	CB5.4W	5.0	5.0	5.2	0.5	4.0	5.0	7.0	321	
26		CB5MH	CB5.5	20.0	18.0	18.4	2.1	14.0	16.0	24.0	322	
27		CB6PH	CB6.1	13.0	13.0	12.8	0.6	11.0	12.0	15.0	329	
28		CB6PH	CB6.2	11.0	11.0	10.9	0.7	10.0	10.0	15.0	326	
29		CB6PH	CB6.3	12.0	12.0	12.2	1.3	8.0	10.0	17.0	326	
30		CB6PH	CB6.4	10.0	10.0	10.3	0.9	8.0	9.0	14.0	328	
31		CB7PH	CB7.1	26.0	25.0	23.8	3.0	13.0	19.0	28.0	320	
32		CB7PH	CB7.1N	33.0	31.0	28.9	5.2	13.0	21.0	37.0	317	
33		CB7PH	CB7.1S	16.0	16.0	15.3	1.5	11.0	13.0	18.0	321	
34		CB7PH	CB7.2	22.0	22.0	21.4	1.8	14.0	19.0	26.0	321	
35		CB7PH	CB7.2E	13.0	13.0	13.2	0.7	10.0	13.0	15.0	321	
36		CB7PH	CB7.3	13.0	13.4	13.6	1.3	8.0	12.0	17.5	328	
37		CB7PH	CB7.3E	20.0	18.0	17.9	3.4	7.0	14.0	28.0	327	
38		CB7PH	CB7.4N	12.0	12.2	12.7	1.6	7.0	11.0	16.0	328	
39		CB7PH	EE3.5	28.0	27.0	26.0	3.8	9.0	21.0	32.0	317	
40		CB8PH	CB7.4	15.0	14.0	14.2	1.4	8.0	12.0	18.0	330	
41		CB8PH	CB8.1	9.0	9.4	9.9	1.7	7.0	8.0	17.0	331	
42		CB8PH	CB8.1E	18.0	17.0	17.0	1.9	12.0	14.0	22.0	331	
43		CB8PH	LE5.5A	3.0	3.0	3.3	0.6	2.0	3.0	4.0	12	
44		CB8PH	LE5.5B	2.0	2.0	2.1	0.3	2.0	2.0	3.0	12	
45		NORTF	ET1.1	3.0	2.8	2.8	0.4	0.5	2.4	4.0	199	
46		C&DOH	ET2.1	13.0	13.2	13.0	1.6	2.2	12.0	15.5	215	
47		BOHOH	ET2.2	3.0	2.8	2.8	0.4	1.7	2.4	4.9	214	
48		ELKOH	ET2.3	12.5	12.4	12.4	0.6	10.6	11.8	14.6	210	
49		SASOH	ET3.1	6.0	5.8	5.8	0.9	2.2	4.7	7.5	227	
50		CHSOH	ET4.1	5.0	5.4	5.4	0.7	3.0	4.7	7.1	343	
51		CHSMH	ET4.2	15.0	14.0	14.0	2.0	6.2	11.8	20.8	343	
52		CHSMH	XGG8251	7.0	5.6	5.5	1.0	0.7	4.2	7.2	223	
53		EASMH	EE1.1	13.0	12.5	12.6	0.7	10.2	12.0	15.0	342	
54	*	CHOOH	ET5.1	6.0	6.0	6.4	2.4	1.0	3.7	11.4	378	*
55		CHOMH2	ET5.2	11.0	12.1	11.9	1.7	3.9	10.2	14.9	380	
56		CHOMH1	EE2.1	8.0	7.7	7.7	0.4	6.4	7.2	10.0	331	
57		LCHMH	EE2.2	14.0	13.0	13.0	1.1	7.2	11.7	15.0	309	
58		FSBMH	EE3.0	7.0	7.2	7.3	0.7	5.2	6.5	9.2	214	
59		NANTF	ET6.1	5.0	5.0	5.0	0.7	1.9	4.3	7.7	227	
60		NANMH	ET6.2	4.0	3.9	3.9	0.5	2.8	3.3	5.0	215	
61	*	WICMH	ET7.1	9.5	7.6	6.8	2.3	0.5	2.9	9.5	219	*
62		MANMH	ET8.1	6.0	5.4	5.3	0.7	3.0	4.1	6.6	214	
63		BIGMH	ET9.1	5.0	5.0	4.9	0.5	3.5	4.3	6.0	217	
64		POCTF	ET10.1	7.0	6.0	5.7	1.1	3.0	4.2	8.5	225	
65		POCMH	EE3.3	4.0	4.0	3.9	0.4	3.0	3.5	5.0	286	
66		POCMH	EE3.4	5.0	5.0	4.8	0.7	3.0	4.0	8.0	310	

Variability of TDEPTH. (*) indicates stations with std/mean > 20% and number of events (N) > 24

Obs	Flag	Segment	Station	Mode	Median	Mean	STD	Min	P10	Max	N	Flag
67		TANMH	EE3.1	13.0	13.2	13.1	0.9	9.8	12.0	14.6	319	
68		TANMH	EE3.2	28.0	27.3	27.1	1.4	18.8	25.6	29.6	303	
69		BSHOH	WT1.1	2.0	2.2	2.3	0.4	1.4	1.9	3.7	208	
70		GUNOH	WT2.1	2.0	1.9	1.9	0.3	1.0	1.5	2.6	212	
71		MIDOH	WT3.1	3.0	3.4	3.4	0.4	2.0	3.0	4.5	214	
72		BACOH	WT4.1	1.5	1.7	1.6	0.3	0.9	1.2	2.2	227	
73		PATMH	WT5.1	16.0	15.5	15.2	1.2	11.0	13.3	17.2	377	
74		MAGMH	WT6.1	6.0	5.6	5.6	0.4	3.9	5.0	7.0	224	
75		SEVMH	WT7.1	10.0	9.5	9.2	1.1	5.0	7.4	11.1	222	
76		SOUMH	WT8.1	9.0	9.0	8.8	1.1	3.4	7.5	11.0	226	
77		RHDMH	WT8.2	2.5	2.6	2.6	0.3	1.8	2.2	4.0	220	
78		WSTMH	WT8.3	3.0	3.4	3.3	0.4	2.2	2.9	4.5	222	
79	*	PAXTF	TF1.3	3.7	3.7	2.9	1.6	0.0	0.0	7.0	66	*
80	*	PAXTF	TF1.4	2.0	2.1	2.0	0.8	0.0	0.9	3.7	196	*
81		PAXTF	TF1.5	11.0	10.9	10.6	0.7	7.5	10.0	12.5	376	
82	*	WBRTF	TF1.2	3.0	3.0	1.9	1.4	0.0	0.0	3.0	44	*
83	*	WBRTF	WXT0001	3.0	0.9	1.2	0.9	0.2	0.5	5.0	172	*
84		PAXOH	TF1.6	6.0	6.0	6.2	0.7	2.3	6.0	11.0	391	
85		PAXOH	TF1.7	3.0	3.0	2.9	0.3	1.6	2.5	4.5	390	
86		PAXMH	LE1.1	12.0	12.0	12.1	0.4	10.0	12.0	13.0	402	
87		PAXMH	LE1.2	17.0	17.0	17.1	0.7	15.0	16.5	19.0	400	
88		PAXMH	LE1.3	23.5	23.5	23.4	0.8	17.0	23.0	29.8	401	
89		PAXMH	LE1.4	15.0	15.0	15.4	1.0	13.0	14.0	18.0	401	
90		PAXMH	RET1.1	11.0	11.0	11.2	0.7	9.5	10.5	14.0	401	
91		POTTF	TF2.1	19.0	19.2	19.1	1.1	12.9	17.7	21.8	365	
92		POTTF	TF2.2	8.2	8.3	8.3	0.5	6.3	7.6	9.3	365	
93		POTTF	TF2.3	13.0	12.7	12.8	0.9	5.0	11.9	15.0	389	
94		POTTF	TF2.4	9.0	8.9	8.9	0.5	7.1	8.4	10.5	372	
95		PISTF	PIS0033	0.0	0.0	0.0	.	0.0	0.0	0.0	1	
96	*	PISTF	XFB1986	1.5	1.5	1.5	0.4	0.5	1.0	2.7	362	*
97		MATTF	MAT0016	7.4	6.9	6.9	0.7	4.3	6.0	8.3	348	
98		POTOH	RET2.1	7.3	7.3	7.4	0.4	6.0	6.9	8.2	369	
99		POTOH	RET2.2	10.0	9.9	10.1	1.5	5.2	8.5	14.5	388	
100		POTOH	RET2.3	9.1	9.1	9.1	0.3	8.5	8.7	10.1	92	
101		POTMH	LE2.2	11.0	11.9	12.0	1.5	9.0	10.2	18.0	382	
102		POTMH	LE2.3	20.0	20.0	20.1	1.0	17.0	19.0	26.2	353	
103		POTMH	RET2.4	15.5	15.6	15.8	1.1	13.0	14.7	19.0	360	
104		RPPTF	TF3.1A	3.0	3.0	3.2	0.5	2.0	3.0	5.0	83	
105	*	RPPTF	TF3.1B	3.0	3.0	3.5	0.8	3.0	3.0	6.0	170	*
106		RPPTF	TF3.1C	4.0	4.0	4.7	1.2	4.0	4.0	6.0	3	
107		RPPTF	TF3.1D	3.0	3.0	3.1	0.3	3.0	3.0	4.0	54	
108	*	RPPTF	TF3.1E	3.0	3.0	3.6	0.8	2.0	3.0	6.0	146	*
109		RPPTF	TF3.2	7.0	7.0	6.6	1.3	4.0	5.0	11.0	255	
110	*	RPPTF	TF3.2A	5.0	6.0	5.8	1.6	3.0	4.0	13.0	118	*
111		RPPOH	TF3.3	7.0	7.0	7.0	1.3	3.0	5.0	12.0	274	
112		RPPMH	LE3.1	6.0	6.0	6.5	0.9	5.0	5.0	12.0	270	
113		RPPMH	LE3.2	14.0	14.0	14.4	1.4	0.0	13.0	19.0	274	
114	*	RPPMH	LE3.4	11.0	12.0	13.3	4.1	8.0	9.0	27.0	273	*
115		RPPMH	LE3.6	10.0	10.0	9.8	0.8	7.0	9.0	14.0	329	
116		RPPMH	LE3.6N	3.0	4.0	3.8	0.8	3.0	3.0	5.0	13	
117		RPPMH	LE3.6S	4.0	4.0	4.1	0.5	3.0	4.0	5.0	13	
118		RPPMH	RET3.1	6.0	6.0	5.7	0.9	3.0	5.0	8.0	281	
119		RPPMH	RET3.2	4.0	5.0	4.7	0.9	3.0	4.0	8.0	277	
120	*	CRRMH	LE3.3	6.0	5.0	5.2	1.3	1.5	3.0	8.0	273	*
121		PIAMH	LE3.7	7.0	7.0	7.2	0.8	4.0	7.0	9.0	328	
122	*	MPNTF	TF4.4	3.0	3.0	3.1	0.9	1.0	2.0	8.0	268	*
123		MPNTF	TF4.4A	6.0	6.0	6.4	0.8	5.0	6.0	8.0	12	
124		MPNOH	RET4.2	11.0	13.0	13.0	2.4	1.7	10.0	18.0	268	
125		PMKTF	TF4.1A	6.0	6.0	5.4	0.9	3.0	5.0	6.0	12	
126	*	PMKTF	TF4.2	7.0	7.0	6.7	1.6	2.0	4.0	11.0	277	*
127		PMKOH	RET4.1	5.0	5.0	5.3	1.0	3.0	4.0	8.0	262	
128		YRKMH	LE4.1	8.0	9.0	8.8	1.1	5.0	8.0	12.0	270	
129		YRKMH	RET4.3	5.0	5.0	5.4	0.7	3.0	5.0	8.0	273	
130	*	YRKPH	LE4.2	13.0	13.0	13.6	2.7	7.0	10.0	19.0	268	*
131	*	YRKPH	LE4.3	14.0	15.0	15.8	3.3	9.0	12.0	23.0	262	*
132		MOBPH	WE4.1	6.0	6.0	5.9	0.6	4.0	5.0	8.0	331	

Variability of TDEPTH. (*) indicates stations with std/mean > 20% and number of events (N) > 24

Obs	Flag	Segment	Station	Mode	Median	Mean	STD	Min	P10	Max	N	Flag
133		MOBPH	WE4.2	13.0	13.0	13.6	1.7	4.0	12.0	19.0	332	
134		MOBPH	WE4.2N	4.0	4.0	4.0	1.4	3.0	3.0	8.0	13	
135		MOBPH	WE4.2S	3.0	3.0	3.4	1.3	2.0	2.0	7.0	13	
136		MOBPH	WE4.3	6.0	6.0	5.6	0.6	4.0	5.0	8.0	330	
137		MOBPH	WE4.4	8.0	7.0	7.0	1.2	2.0	5.0	9.0	329	
138		JMSTF	TF5.2	1.0	2.0	2.6	3.0	1.0	1.0	11.0	10	
139		JMSTF	TF5.2A	9.0	8.0	8.1	1.1	6.0	7.0	11.0	210	
140		JMSTF	TF5.3	11.0	11.0	10.7	1.4	4.0	9.0	14.0	270	
141		JMSTF	TF5.5	9.0	9.0	9.2	1.0	2.0	8.0	13.0	285	
142		JMSTF	TF5.5A	8.0	9.0	8.7	0.9	7.0	8.0	11.0	218	
143		JMSTF	TF5.6	9.0	9.0	9.6	0.9	6.0	9.0	13.0	277	
144		APPTF	TF5.4	7.0	6.0	6.3	1.1	3.0	5.0	9.0	272	
145	*	JMSOH	LE5.1	7.0	8.0	9.1	2.8	4.0	6.0	15.0	272	*
146		JMSOH	RET5.2	9.0	9.0	9.1	1.6	5.0	8.0	15.0	275	
147		JMSOH	TF5.6A	8.0	8.0	7.8	0.4	7.0	7.0	8.0	12	
148		CHKOH	RET5.1	2.0	2.0	2.1	0.4	2.0	2.0	3.0	7	
149	*	CHKOH	RET5.1A	3.0	4.0	3.8	1.0	2.0	3.0	6.0	219	*
150		JMSMH	LE5.2	9.0	9.0	8.6	1.1	4.0	7.0	11.0	273	
151		JMSMH	LE5.3	7.0	7.0	6.8	0.8	4.0	6.0	11.0	273	
152		JMSPH	ELI1	8.0	8.0	8.0	0.0	8.0	8.0	8.0	2	
153		JMSPH	LE5.4	15.0	16.0	15.7	1.3	6.0	14.0	18.0	269	
154	*	JMSPH	LE5.5	7.0	19.3	16.5	7.1	5.0	7.0	28.0	330	*
155		WBEMH	WBB05	5.0	5.0	4.9	0.7	3.0	4.0	6.0	80	
156		WBEMH	WBE1	4.0	4.0	4.4	0.9	3.0	3.0	7.0	190	
157		SBEMH	SBA1	13.0	12.5	12.2	1.4	9.0	10.0	15.0	58	
158		SBEMH	SBC1	12.0	12.0	11.4	1.0	9.0	10.0	14.0	49	
159		SBEMH	SBD1	12.0	12.0	11.8	0.8	10.0	11.0	13.0	49	
160		SBEMH	SBD4	3.0	3.0	3.3	0.4	3.0	3.0	4.0	58	
161		SBEMH	SBE1	.	12.3	12.3	2.5	10.5	10.5	14.0	2	
162		SBEMH	SBE2	12.0	12.0	12.3	1.3	8.0	10.3	15.0	190	
163		SBEMH	SBE3	.	9.3	9.3	1.8	8.0	8.0	10.5	2	
164		SBEMH	SBE4	.	9.8	9.8	2.5	8.0	8.0	11.5	2	
165	*	SBEMH	SBE5	5.0	8.0	8.1	3.1	3.0	4.0	13.0	191	*
166		EBEMH	EBB01	7.0	7.0	6.9	0.8	6.0	6.0	8.0	78	
167		EBEMH	EBE1	8.0	8.5	8.6	0.9	6.0	8.0	12.0	187	
168		EBEMH	EBE1-E	8.0	8.0	8.3	0.6	8.0	8.0	9.0	3	
169		EBEMH	EBE2	.	9.3	9.3	0.4	9.0	9.0	9.5	2	
170		LAFMH	LAF1	6.0	6.0	5.8	0.8	4.0	4.5	6.7	17	
171		LAFMH	LFA01	4.0	4.0	4.1	0.4	3.0	4.0	5.0	80	
172		LAFMH	LFB01	4.0	4.0	4.3	0.5	3.0	4.0	6.0	80	
173		ELIPH	ELD01	7.0	7.0	6.7	0.7	5.0	6.0	8.0	80	
174	*	ELIPH	ELE01	8.0	10.0	10.4	2.3	4.0	8.0	14.0	80	*
175		ELIPH	ELI2	13.0	13.5	13.3	1.6	5.0	12.0	16.0	190	
176		ELIPH	ELI3	.	12.8	12.8	1.1	12.0	12.0	13.5	2	
177		ELIPH	LE5.6	15.0	15.0	15.1	1.0	10.0	14.0	18.0	274	

Chesapeake Bay Program Analysis Issues Tracking System

Issue Tracking Number: 040

Category Code: Field Method, Analytical Method (FM, AM)

Issue Title: Pycnocline Calculation: Different methods for WQ sample collections and for Designated Use boundary delineation.

Date of Issue Introduction into the System: June 2006

Statement of Issue:
There is an inconsistency between the method used to determine the presence and location of a pycnocline for water quality sample collection and analysis for the WQ monitoring program and the method used to define Designated Use boundaries for water quality criteria assessments.

In the Chesapeake Bay and its tributaries, the fresh water originating from land meets the higher density, saline water from the ocean with varying degrees of layering and mixing, resulting in vertical density gradients of varying strengths and sometimes strong layering or stratification. The pycnocline is the region of rapid vertical density change, which can create a barrier to gaseous and chemical exchange between layers. In the case of dissolved oxygen, the barrier essentially isolates the lower layers from oxygenating processes that usually occur at or near the surface. The isolation of the layers from one another can result in very different physical/chemical characteristics between proximate layers. The sampling design of the CBP WQ monitoring program takes this into consideration and collects samples at depths relative to the presence/absence and vertical position of the pycnocline(s) if one or more are present. The criteria for dissolved oxygen also take this into account, and different oxygen criteria apply to different parts of the water column, i.e., to different 'designated uses'. The boundaries of these designated uses are a function of pycnocline depth.

The Monitoring Program sampling protocol uses vertical differences in conductivity to determine pycnocline depth and to locate depths of above-pycnocline (AP) and below-pycnocline (BP) samples for laboratory analysis of nutrients and other constituents. (The step-by-step method for calculating pycnocline depth is given in the attached Appendix.) By this method, conductivity is used as a surrogate for density, and a pycnocline is present if the difference from one depth to the next (at meter increments) exceeds a minimum of 500 umhos/cm and is at least 2 times the average rate of change per meter over the entire water column. The 'density' difference constituting a pycnocline is therefore *a relative, not fixed value,* and the same value at one station may not constitute

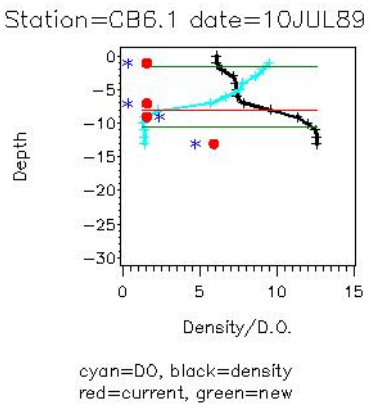
a pycnocline at another station, nor at the same station at a different time with a different vertical density structure.

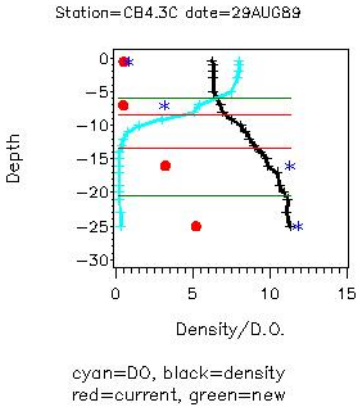
Tom Fisher and colleagues have quibbled with the pycnocline depths as determined by this method. The results are apparently not suitable for their phytoplankton/nutrient limitation work requiring a proper definition of the 'upper mixed layer' (Fisher, et al., 2002, unpublished ms). The CBPO staff working on the Water Quality Model also took issue with the conductivity-based field method. They use the WQ model to examine effects of various nutrient reduction scenarios on criteria attainment, and they believe a density-based calculation is more desirable and defensible for their purposes and for future regulatory applications to criteria attainment assessments. (Designated Uses for dissolved oxygen are based in part on pycnocline depth.) They argue further that the exchange barrier is caused by physical factors, which suggests that the critical density-difference should be a fixed, not relative value.

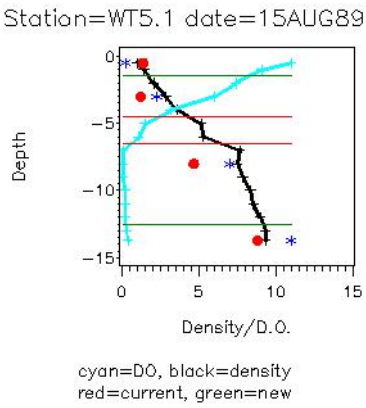
After some exploratory analysis and empirical testing, the following method was adopted for determining Designated Use boundaries: The upper pycnocline is defined as the uppermost depth where the difference in density (designated by sigma_t) from one meter to the next is at least 0.15 kg/m^4. The lower pycnocline is the first encounter, measuring up from the bottom, of a density difference greater than 0.20 kg/m^4 from one depth to the next.

Using this definition, a pycnocline is determined to be present more often than with the other method, and the upper pycnocline tends to be higher in the water column, and the lower pycnocline tends to be lower in the water column than when pycnocline(s) are determined using the relative conductivity method.

Some examples of pycnocline determinations by the two methods are below ('current' indicates field conductivity method, 'new' is the fixed density method):







Reference:
Fisher, T. R.; A.B. Gustafson; H.L. Berndt; L.Walstadt; L.W. Haas; and S. MacIntyre. Submitted to *Estuaries* 2002*, The Upper Mixed Layer of Chesapeake Bay, USA* (not accepted for publication).

Proposed Solution:

Continue investigation to find a definition and method of calculating pycnocline depth that will serve both the Water Quality monitoring objectives and the regulatory requirements for clearly and consistently defining Designated Uses.

Discussion:

A presentation of this issue was made to TMAW in February 2004. The group made no recommendation to resolve the difference, but perhaps they did not appreciate the potential consequences of collecting nutrient samples at depths unconnected to Designated Use boundaries. It may be that the fixed-depth method is more desirable, but that the threshold values should be changed. The Gang-of-n analytical group looked at many examples and was not convinced that one method was consistently better than the other in selecting the depth that best described the layer boundaries.

Sense of the Resources Needed to Respond:

Priority Ranking:

Submitter/Responsible Party: Marcia Olson

Actions to Date:

Overall Resolution Summary of all Actions:

Recommended Actions:

Actions Number:
This number is an extension of the Issue Number plus .0n, .0n+1 postscript
Example: QA 001.01

1. Designated Respondent:
   (Name/Organization and/or Specific Workgroup)
2. Action:
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary:

APPENDIX

A. Field method -- Determination of pycnocline depth using conductivity

- On station, find average change in conductivity per meter through water column: change/m = (cond(bot) - cond(sur))/total depth;
- Establish threshold: threshold=(change/m) x 2. Note: Must be => 500 or no pycnocline exists;
- From surface, find first instance where change from one meter to next exceeds threshold. Upper pycnocline depth is half way between those two depths.
- Do the same from the bottom to find lower pycnocline, if one exists;
- AP and BP samples are collected 1 m above upper pycnocline and 1 m below lower pycnocline, respectively. If no lower pycnocline, then the BP sample is collected 1 m below the upper pycnocline. (If no pycnocline exists, then AP and BP samples arcollected at 1/3 and 2/3 depth of water column.)

B. Fixed threshold method –

1) Calculation of sigma_t (wtemp=water temperature in deg C):

```
sigo   =-0.069+((1.47808*((salinity-0.03)/1.805))
       -(0.00157*(((salinity-0.03)/1.805)**2))
       +(0.0000398*(((salinity-0.03)/1.805)**3)));
tsum   =(-1*(((wtemp-3.98)**2)/503.57))*((wtemp+283)
       /(wtemp+67.26));
sa     =((10**-3)*wtemp)*(4.7867-(0.098185*wtemp)
       +(0.0010843*(wtemp**2)));
sb     =((10**-6)*wtemp)*(18.030-(0.8164*wtemp)
       +(0.01667*(wtemp**2)));
Sigma_t=tsum+((sigo+0.1324)*(1-sa+sb*(sigo-0.1324)))
```

2) Determination of upper and lower pycnocline depths

- On station, use fixed value of 0.1 as the difference in sigma_t that is sufficient to constitute a barrier to define the lower boundary of the surface mixed layer

- Use fixed value of 0.2 as the difference in density to define the upper boundary of the bottom mixed layer.

Chesapeake Bay Program Analysis Issues Tracking System

Issue Tracking Number:041

Category Code: Analytical Methods (AM)

Issue Title:

Analytical Method Changes in Total Nitrogen Measurements for the Virginia Tributaries

Date of Issue Introduction into the System;

Entered into DAITS in November 2006

Statement of Issue:

The Virginia Department of Environmental Quality has conducted water quality monitoring within the tidal portions of the Virginia tributaries from 1984 through the present as part of the Chesapeake Bay Agreement of 1983 (USEPA Chesapeake Bay Program, 1983). Ambient total nitrogen (TN) concentrations were initially calculated as the sum of total Kjeldahl nitrogen (TKN) and filtered nitrite-nitrate (NO_{23}) concentrations (referred to as the Old method). In 1995, the method used for TN calculations was changed to the summation of particulate nitrogen (PN) and total dissolved nitrogen (TDN) (referred to as the New method). See Figure 1 for a summary of the differences between methodologies. Appendix A provides a time line of events and a listing of additional documentation associated with the effort to characterize the effects of the method change and attempts made to correct it. The New method was adopted to avoid the necessity of calculating any parameters by subtraction, since calculations by subtraction were determined to be less accurate and often yield negative values. The New method was also deemed to be more accurate in estuarine waters than the Kjeldahl nitrogen method developed originally for freshwater.

Examination of scatterplots of data collected in the lower estuarine portions of the Virginia tributaries indicated that concentrations of TN experienced a large step reduction in magnitude and variability in 1995 immediately following the adoption of the New method. This reduction may be due solely to the change in TN methodologies rather than natural phenomena, management actions or some combination thereof and could result in a misinterpretation of statistical results, in particular, those produced by long term trend analysis. If the method change did result in the downward step trend observed in the data, trend analysis might detect false negative trends in this parameter resulting in the misinterpretation that water quality conditions had improved.

As a result of these observations the Chesapeake Bay Program Data Analysis Workgroup (now the Tidal Monitoring and Assessment Workgroup or TMAW) recommended the data be assessed to determine whether or not a real bias existed and, if such a bias existed, whether or not a correction factor could be developed to adjust the data making both pre-method and post-method change data statistically comparable.

An intervention analysis was conducted to determine if the change in methodologies accounted for the observed step change in the TN data (Perry, 2005a; see Appendix B). To test the hypothesis that there was a step trend in the data while controlling for the effects of other potentially confounding factors, a parametric model was developed which included terms for long term trends, seasonality, flow effects, temperature effects, and autoregression, as well as, a dummy variable term used to represent the advent of the intervention i.e. the method change.

Results of the intervention analysis were mixed although a preponderance of the evidence indicated that the method change resulted in a positive change in TN which contrasted with previous observations suggesting a negative step trend. A significant negative intervention effect was observed at only two out of 63 stations. In general, the magnitude of the method change effect decreased moving downstream from freshwater stations in both the York River and James River although this pattern was not observed for data collected in the Rappahannock River. Quantification of the magnitude of the method change was not attempted with the monitoring data but was instead conducted using data collected during a DEQ split sample project designed specifically for that purpose.

An initial series of screening and descriptive analyses were conducted on the DEQ split sample project data (see Appendix C). Results indicated that overall there was a significant difference between Old and New methods and the Old Method was biased high relative to the New Method; however, plots of the bias (difference between Old and New method measurements) against the mean of the two methods revealed two distinct groups of values. Plots indicated that the Old method was biased low relative to the New method for most tidal freshwater and oligohaline stations collected primarily by DEQ's Piedmont and Northern regional offices (PRO and NRO) but was biased high relative to the New method at higher salinity stations collected primarily by DEQ's Tidewater regional office (TRO).

Additional assessments were made exclusively on data collected by TRO in an attempt to isolate the grouping effect. Plots of the bias for the TRO data indicated that the groups corresponded roughly to two separate collection years (2002 and 2003). For both years, the Old method data were biased high relative to the New method data but the bias for data collected in 2002 was in general much higher than for 2003. Additional graphical and correlation analysis indicated the difference between years was the result of the high TKNW values obtained during 2003 and that salinity, total suspended solids, and flow rates may have influenced these high values. Further analysis of the split sample data was recommended along with an attempt to use these data for developing a correction factor.

Split sample data were examined by calculating the difference between the log-transformed Old and New methods and relating this difference (lnDiff) to various parameters in an attempt to explain it (Perry, 2005b; see Appendix D). An attempt was made to assess the relationship between lnDiff and the concentration of TN being measured. This was accomplished by correlating (Spearman's coefficient) the mean of the two methods (log-transformed) for each observation (lnTNmean) with lnDiff. In addition, the degree of association between lnDiff and date, distance from the Chesapeake Bay mainstem and several environmental variables including conductivity, salinity, temperature, pH, dissolved oxygen, total suspended solids, and with and was assessed using Spearman's correlation coefficients. Results indicated that lnDiff was positively correlated with lnTNmean indicating that as TN concentrations increase there was an increase in the difference between methods. Results indicated that lnDiff (1) increased with distance from the Chesapeake Bay mainstem; (2) showed a positive association with date of collection; and (3) was correlated with several environmental variables in directions that reflect a longitudinal gradient in the estuary. Total nitrogen values typically decrease moving down the estuary. Given the positive relationship between TN concentration and lnDiff, lnDiff should have decreased moving downstream; however, the opposite was observed suggesting that other factors influenced the magnitude of lnDiff.

Stepwise regression analysis was used to selected the most important parameters affecting lnDiff. Date of collection was eliminated from this analysis because date had a positive association with the longitudinal gradient indicating that in general upstream samples tended to be collected at later dates. Stepwise analysis using the split sample data resulted in the selection of four parameters as important predictors of lnDiff including lnTNmean, conductivity, total suspended solids and water temperature in decreasing level of importance. A method adjustment equation was developed from this regression and applied to the monitoring data to determine if the applied adjustment reduced the number of step trends detected. Application of this adjustment resulted in only a small reduction the number of step trends detected by intervention analysis indicating that this adjustment factor did not correct the data adequately.

As a result, an adjustment factor model based on the results of the intervention analysis was developed. In this case, the station regression coefficients (log-transformed) for the Step trend term in the intervention model were themselves used in a regression analysis using log transformed values of the station specific mean log transformed TN values and mean scaled specific conductance. The resulting regression equation provided an estimate of a correction factor that can be applied to the Old method data based on station mean values of log transformed TN and scaled specific conductance. Equation 3 in Appendix D provides the appropriate formulae for applying this correction factor. The validity of the correction factor was evaluated by applying it to the Old method data and then rerunning the intervention analysis to determine if the step trend effects were removed. Application of this correction factor substantially reduced the number of station specific step trends observed indicating it reliably adjusted the Old method data. Based on the results of this study is was recommended that the Old method data remain in the database and that the correction factor only be applied when comparisons of the Old and New method data are required.

Proposed Solution:

It is recommended that the original data remain in the data base. Adjustments to the TN data need to be implemented only if analyses include comparisons of data collected using both the Old and New methods. Adjustments should be made using Equation 3 as described in Perry (2005b) and would be applied only to those data collected prior to the method change. Long-term trend analysis of TN for the Virginia tributaries should be conducted using the "blocked" seasonal Kendall approach (Gilbert, 1987) with the pre-method (1985 through 1993) and post-method change (1995 through 2004) periods set up as the two time blocks. The PROBLEM code field in the CBP Water Quality Database table WQ_DATA (see USEPA, 2004) should be updated to indicate that a DAITS issue exists for this parameter and to refer all users to this document for resolution of analytical problems.

Sense of the Resources Needed to Respond:

The resources required to update the PROBLEM code in the CBP database should not be more than several hours of database programming time. Future analysis of these data may require additional resources than might be anticipated if the step trend were not present; however, a direct estimate of the resources required is dependent.

Proposed Priority Ranking:

This issue has been partially resolved since the "blocked" Seasonal Kendall approach has been implemented for trend analysis of Virginia TN data. However, the PROBLEM code field in the CBP database needs to be updated and the priority ranking for this task should be high.

Submitter/Responsible Party:

Mr. Frederick A. Hoffman
Chesapeake Bay Program
Virginia Department of Environmental Quality
629 East Main Street
Richmond, Virginia 23230

Actions to Date:

Use of the blocked Seasonal Kendall trend test has been implemented for all Virginia tributary monitoring stations.

Recommended Actions:

1. Actions Number:

Not Applicable

2. Designated Respondent:

Tami Huber
CBP Water Quality Database Manager
410 Severn Ave, Suite 109
Annapolis, MD 21403
(410) 267-5700 or
1 (800) YOUR BAY

3. Action:

Update of CBP database records to include CBP Problem code entry for all TN concentrations in the database collected prior to 1994.

4. Resources Needed:

Unknown.

5. Due Date:

Not Applicable.

6. Action Item Resolution Summary:

Not Applicable.

Literature Cited:

Perry, E, 2005a. Assessment of 1994 Methods Change for Total Nitrogen using Intervention Analysis. Report to the Department of Environmental Quality. Richmond VA. 14 pp.

Perry, E, 2005b. Assessment of 1994 Methods Change for Total Nitrogen using Split Sample Data. Report to the Department of Environmental Quality. Richmond VA. 13 pp.

Gilbert, R.O. 1987. Statistical methods for environmental pollution monitoring. Van Nostrand Reinhold Co., New York, pp. 320.

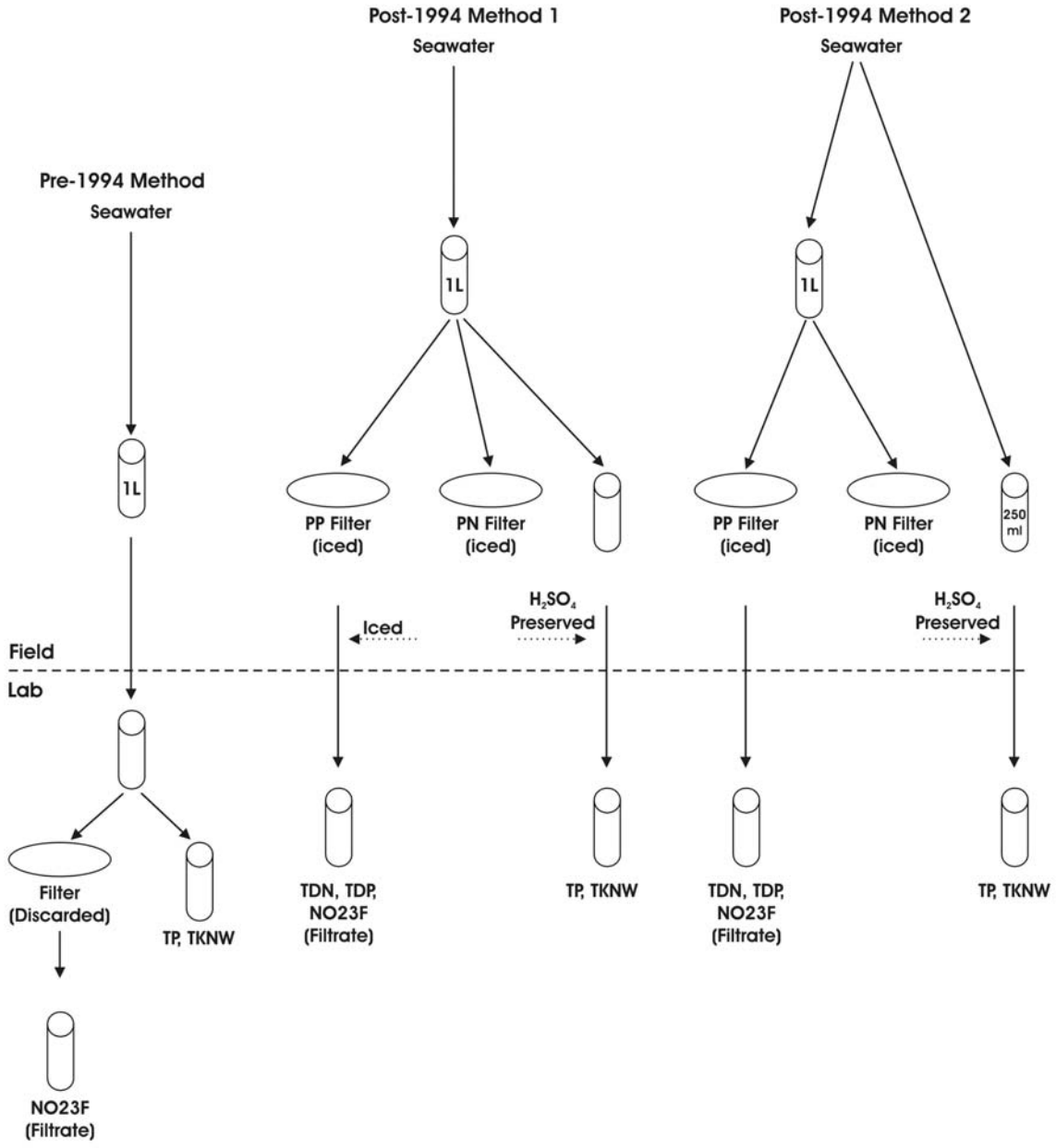


Figure 1. Summary of differences between total nitrogen and total phosphorus methodologies prior to and after 1994.

Appendix A. Timeline and Additional Documentation of Issues Related to Method Changes for Total Phosphorus and Total Nitrogen Determinations

Timeline and Additional Documentation of Issues Related to Method Changes for Total Phosphorus and Total Nitrogen Determinations

July 1984 – November 1993. Total phosphorus (TP) is directly measured by VADCLS using EPA method 365.4 a colorimetric, automated, block digestion using an acid persulfate for the digestion.VADCLS utilized a Technicon AA II instrument for analysis. EPA 365.4 was later found by DCLS to overestimate TP in samples with salinities greater than 5 ppt. (1997; refer to memo from Loretta Kirk). This method was also utilized January 1995 – November 1995 at select sites (TF3.1A, TF3.1D, TF4.1A and TF4.4A only).

Prior to 1994 TN concentrations were calculated as the sum of total Kjeldahl nitrogen (TKN) and filtered nitrate-nitrates ($NO_{23)}$ concentrations (referred to as the Old method). TKNW was determined using EPA method 351.2 (Colorimetric, Semi-Automated Block Digestion) and NO23F by EPA method 353.2 (Colorimetric, Automated Cadmium Reduction). Unpreserved whole water samples were collected in the field and delivered to the lab for analysis.

January 1994 – December 1994. TN is calculated by using particulate nitrogen (PN) and total dissolved nitrogen (TDN) results analyzed by VIMS. VIMS utilized a SKALAR instrument and EPA method 365.2 and an alkaline persulfate digestion. Note: these data are not utilized for status and trend purposes and were not included in the analysis to determine the cause of the observed step trend in the TN and TP data. TP is calculated by using particulate phosphorus (PP) and total dissolved phosphorus (TDP) results analyzed by VIMS. VIMS utilized a SKALAR instrument and EPA method 365.1 for PP and TDP determinations utilizing an alkaline digestion.

February 1995 onward. TP is calculated using PP and TDP results analyzed by VADCLS using a SKALAR instrument using EPA method 365.1 for both PP and TDP. The method uses an alkaline persulfate digestion. TN is calculated using PN and TDN results analyzed by VADCLS with a SKALAR instrument using the EPA method.

2002. During trend analysis Marcia Olson discovers anomalies in TN and TP for Virginia Tributaries that point to step trends in 1995. DEQ initiates data analysis by ODU to determine if a possible correction factor may be applied. In October 2002 DEQ begins the collection of additional samples so that directly measured TP can be compared to TDN+PP.

October 2003. DEQ completes the collection of samples for the TN/TP method comparison.

2004. ODU concludes they are unable to determine a single correction factor for DEQ's tributary TP data. DEQ enlists the aid of Elgin Perry, a consultant to the Chesapeake Bay Program in Annapolis to further examine the data.

Table 1. Available Memos/Data files for TP/TN analyses. Abbreviations include the following: CBPO for the EPA Chesapeake Bay Program Office, DCLS for the Virginia Department of Consolidated Laboratory Services, DEQ CO for Virginia Department of Environmental Quality Central Office, MD CBL for Maryland Chesapeake Bay Laboratory, and ODU for Old Dominion University.

Date/Author	**Format and Locations**	**Title/Subject**	**Issue**	**Summary**
Unknown	Hardcopy on file at (DEQCO)	TN/TP component comparison studies summary	TN/TP step trend documentation summary	Summary of memos/data mentioned below and questions regarding how they relate/compare to step trend demonstrated by data
03-10-1990 Rick Hoffman (DEQCO)	Hardcopy on file at (DEQCO)	Request for copy of final report for instrument comparison between Skalar San Plus and Technicon AA II	A preliminary report for the method comparison dated 01-13-94 had been received and is attached to the request for the final report. The preliminary findings indicated for Orthophosphate and Nitrate plus Nitrite there was a significant difference between results based on instrument change	The SKALAR instrument was capable of detecting results in the lower range (3 decimal places) while the Technicon was only capable of detecting 2 decimal places.
04-19-1990 Steve Sokolowski (ODU)	Hardcopy on file at (DEQCO)	Pre-proposal submitted to the Chesapeake Bay Program to evaluate the effects of matrix interferences on analytical results for Phosphate-P in Aqueous Chesapeake Bay Samples	Underestimates of orthophosphate and dissolved phosphate and overestimates of total phosphate concentrations that increase with increasing concentrations.	Bias demonstrated a site effect and appeared to demonstrate spatial and temporal effects.
01-21-1992 Peter Bergstrom (CBPO)	Hardcopy on file at (DEQCO)	QA data relevant to TN ocean boundary definition	Differences observed between ODU and VIMS TN data	Data differences observed in ODU/VIMS data as described in DAITS Issue #10 were found to be related to TKNW differences. Differences varied by station.
1994	Electronic and hardcopy on file (DEQCO)	Lltp instrument comp.csv; NH4F instrument comp.csv; NO2F instrument comp.csv; NO23F instrument comp.csv; PO4F instrument comp.csv; PP VIMS vs DCLS.csv; TDN VIMS vs DCLS.csv; TDP VIMS vs DCLS.csv	Split sample data for instrument comparison studies summarized in aforementioned reports.	
09-26-1996 Christopher D'Elia MDCBL	Hardcopy on file (DEQCO /MDCBL)	Total Kjeldahl Nitrogen - Total Persulfate nitrogen method comparison	Report on the comparison of EPA 351.2 and EPA 365.2 methods for determination of TN and PN to Alkaline persulfate method EPA 353.2	EPA 353.2 had not yet been approved as an EPA methodology for the determination of TN and TP. Results indicated a poor comparison of results between 351.2 and 353.2 that was spurious. When 351.2 was modified slightly as utilized by ODU, results between the two methods were comparable.

Table 1. Continued. Abbreviations include the following: CBPO for the EPA Chesapeake Bay Program Office, DCLS for the Virginia Department of Consolidated Laboratory Services, DEQ CO for Virginia Department of Environmental Quality Central Office, MD CBL for Maryland Chesapeake Bay Laboratory, and ODU for Old Dominion University.

Date/Author	**Format/ locations**	**Title/Subject**	**Issue**	**Summary**
08-29-1997 Chris Gennings and Denise Toney	Hardcopy on file (DEQCO)	Evaluation of Water Samples	Final copy of DCLS instrument comparison study for SKALAR and Technicon AA II	All the studied parameters showed significant differences between instruments when a Wilcoxin paired t-test is used. Data were compared for equivalency. Orthophosphate, Particulate Phosphorus, Ammonia Nitrogen and Nitrite Nitrogen failed to show equivalence.
10-22-1997 Loretta Kirk DCLS	Hardcopy on file (DEQCO)	Total Phosphorus Method Changes	Salinity interference with TP method 365.4	DCLS institutes method change for all TP samples with salinities greater than 5 ppt due to higher than expected sample results and spike recoveries.
01-07-2004	Electronic file (DEQCO)	9495 lab change comparison data.xls	File contains all Pfiesteria data (PF), Chesapeake Bay River Input Monitoring data (RIM) and Tributary Monitoring data (CB) collected between 1998 and 2003. Where a comparison can be made between old and new TP/TN methods.	
05-10-2004 Mike Lane (ODU)	Electronic file (DEQCO and ODU)	Method Correction Analyses.ppt	Powerpoint presentation to describe TP/TN step trend issue and initial analyses of data to determine if a correction factor can be found	Analyses inconclusive – no one correction factor can be applied. Trends appear to be site influenced.
07-06-2006 Mike Lane (ODU)	Electronic file (DEQCO and ODU)	TP_Correction3.ppt	Powerpoint presentation to describe TP method adjustment analysis by ODU	Analyses inconclusive – no one correction factor can be applied. Trends appear to be site influenced.
07-08-2006 Mike Lane (ODU)	Electronic file (DEQCO and ODU)	TN_Correction2.ppt	Powerpoint presentation to describe TN method adjustment analysis by ODU	Analyses inconclusive – no one correction factor can be applied. Trends appear to be site influenced
07-14-2005	Electronic file (DEQCO)	Method change data2.zip	Zip file sent to Elgin Perry for analysis contains the following files: 9495 method comparison data4.xls –pfiesteria, RIM and DEQ CBP data allowing comparison of TN/TP old and new methods. Instrument and VIMS comparison data.xls – data comparison performed by DCLS when switching methods/ instruments in 1994. VADCLS CSSP columnar4.xls – AMQAW split sample data allowing comparison between TP old replicates and TP new replicates. CBP VNTP data. xls – DEQ's CBP non-tidal network data for TN/TP method comparison.	

Appendix B – Assessment of 1994 Methods Change for Total Nitrogen using Intervention Analysis

Assessment of 1994 Methods Change for Total Nitrogen using Intervention Analysis.

submitted to

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by

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Introduction

This report addresses the apparent change of estimated total nitrogen (TN) concentration that occurs coincident with a change in the methods for assaying TN in three Virginia Tributaries to the Chesapeake Bay. The results presented here are based on intervention analysis the TN concentrations collected as part of routine monitoring at individual Chesapeake Bay Program stations. The intervention analysis attempts to identify a step change in the time series of the TN data for each station. Additional split sample data addressing the methods change have been collected and these data will be addressed in a subsequent report.

Background

In 1994, the Virginia Department of Environmental Quality which oversees the tidal monitoring of nutrients in these Virginia tributaries implemented the TDN+PN method to replace the TKNW+NO23F method for the assay of TN. Sometime after this change was implemented, it became apparent when viewing a time series plot (Figure 1.) of TN concentration for stations in the lower James River, that the concentration of TN appeared to take a step down at the time of the methods change. This result is of particular concern because the long term trends analysis will show that TN concentration is improving (decreasing) and this favorable conclusion may in fact be false. It is possible that a large part of the decrease in TN is an artifact due to the change in analytical methods.

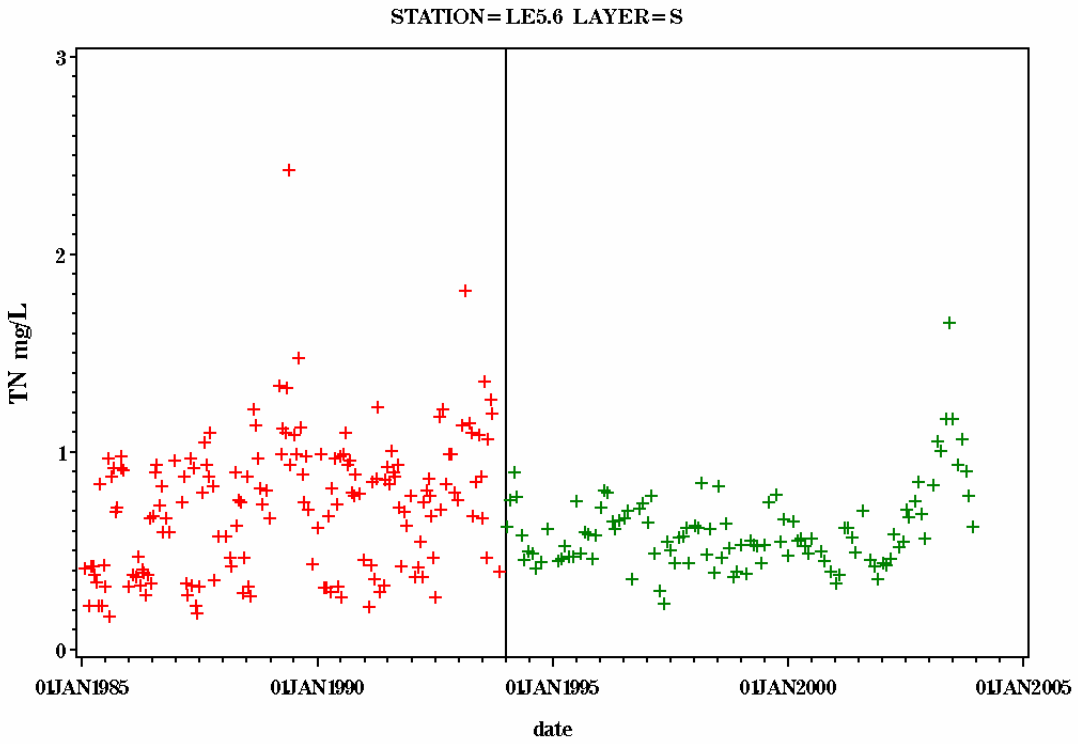


Figure 1. Time series plot of total nitrogen concentration for a station in the James River lower estuary. The vertical bar indicates the point of the methods change. Pre method change data are in red; post method change data are in green.

To assess the magnitude of the apparent change in TN that may be caused by the method change, DEQ implemented a split sample program using the two methods in recent years. The results of analysis of this split sample data is confusing when juxtaposed with the results from the monitoring data. This report does not address these data.

This report is the first in a series that will re-examine this issue. This first report examines only the routine monitoring data for the Rappahannock, York, and James rivers. The analysis addresses the question of whether or not there is a step trend in the data for each time series. A time series of data exist for the surface and bottom at most stations. The individual analyses of each time series are presented in Appendix A. Summaries of these analyses are presented in the body of the report.

Data Management

The data used for this analysis were downloaded from the CIMS website. DEQ provided a list of 47 stations to consider. Of the 47, four, TF3.1, TF3.1A, TF3.1C, and TF3.1D do not appear in the CIMS data base. Seven of the 47 do not have data before 1994 (Table 1.).
Table 1. Stations that lack pre-methods change data.

station	first date	last date
TF3.2A	11JAN1994	04DEC2003
EBB01	22JAN1998	18DEC2003
ELD01	22JAN1998	18DEC2003
ELE01	22JAN1998	18DEC2003
LFA01	22JAN1998	18DEC2003
LFB01	22JAN1998	18DEC2003
WBB05	22JAN1998	18DEC2003

Other stations, TF4.0P , TF4.0M, TF5.0J, TF5.0A, and TF5.2, appear to have wide data gaps near the time of the methods change and these have been excluded from this analysis.

Flow data from the Mattaponi is missing for the period 01OCT1987 to 30AUG1989. These data were imputed using a regression of the existing Mattaponi data against the Pamonkey, James at Appomattox, and Rappahannock at Fredericksburg. Predictions from this 3 term regression model for the period 01OCT1987 to 30AUG1989 are used to estimate Mattaponi flow for that period.

For the year 1994, data for the Virginia Tributaries were collected by VIMS. These data were excluded from this analysis.

After the data exclusions noted above, 32 stations remain. All but one of these 32 stations have surface and bottom data resulting in 63 time series that were analyzed.

Model Building

In order to test hypotheses concerning the step trend in the data and at the same time control for other potentially confounding factors, a parametric model was developed for this analysis. This model builds on the basic intervention model and adds terms for long term trends, seasonality, flow effects, temperature effects, and autoregression. In this section, we discuss how each of these terms are introduced in the model and illustrate the effect of each set of terms on model prediction. Estimation is done using the AUTOREG procedure of the SAS software system. The basic intervention model is designed to estimate a time series for which some intervention, in this case a change of analytical methods, causes a shift in the mean response. Estimation for this model is typically done by introducing a binary independent variable which takes the value 0 for observations collected before the intervention and the value 1 for observations collected after the intervention. In the analysis, the intervention variable is called MC for Methods Change. The regression coefficient for MC estimates the shift in the mean at the point of the intervention (e.g.Figure 2).

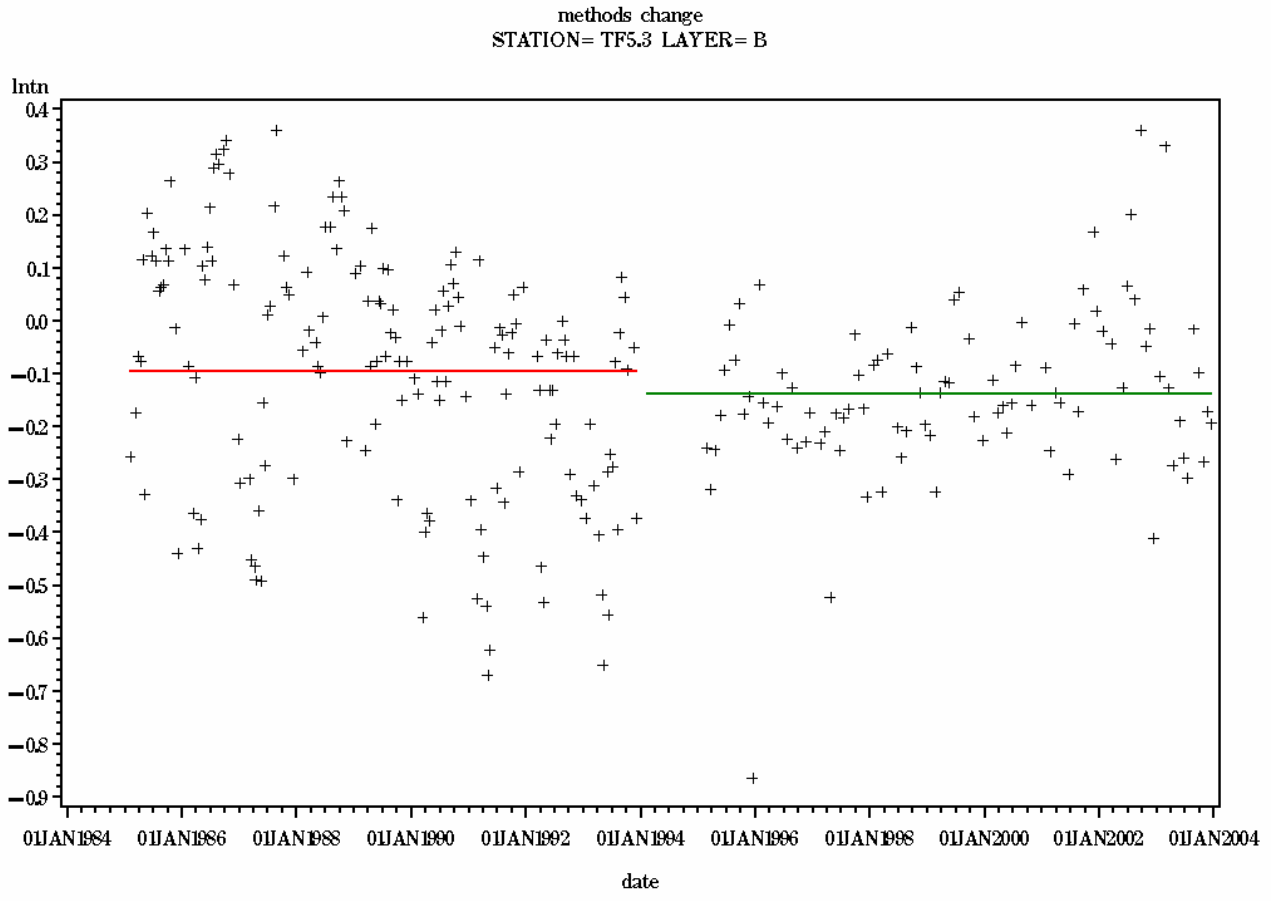


Figure2. Basic intervention model fit for a time series of log(TN) data from a tidal fresh station on the James River. Before method change predictions are in red, and post method change predictions are in green.

Long term trends are introduced to the model by adding year as an independent variable. Year is scaled to be centered at 1994 (cyear) so that the intercept of the model in the mean response just before the methods change. The product of the cyear and MC is also introduced as an independent variable to allow for a change in the slope of the trend between the periods before and after the methods change. To see the effect of adding these trend variables to the intervention model, see figure 3.

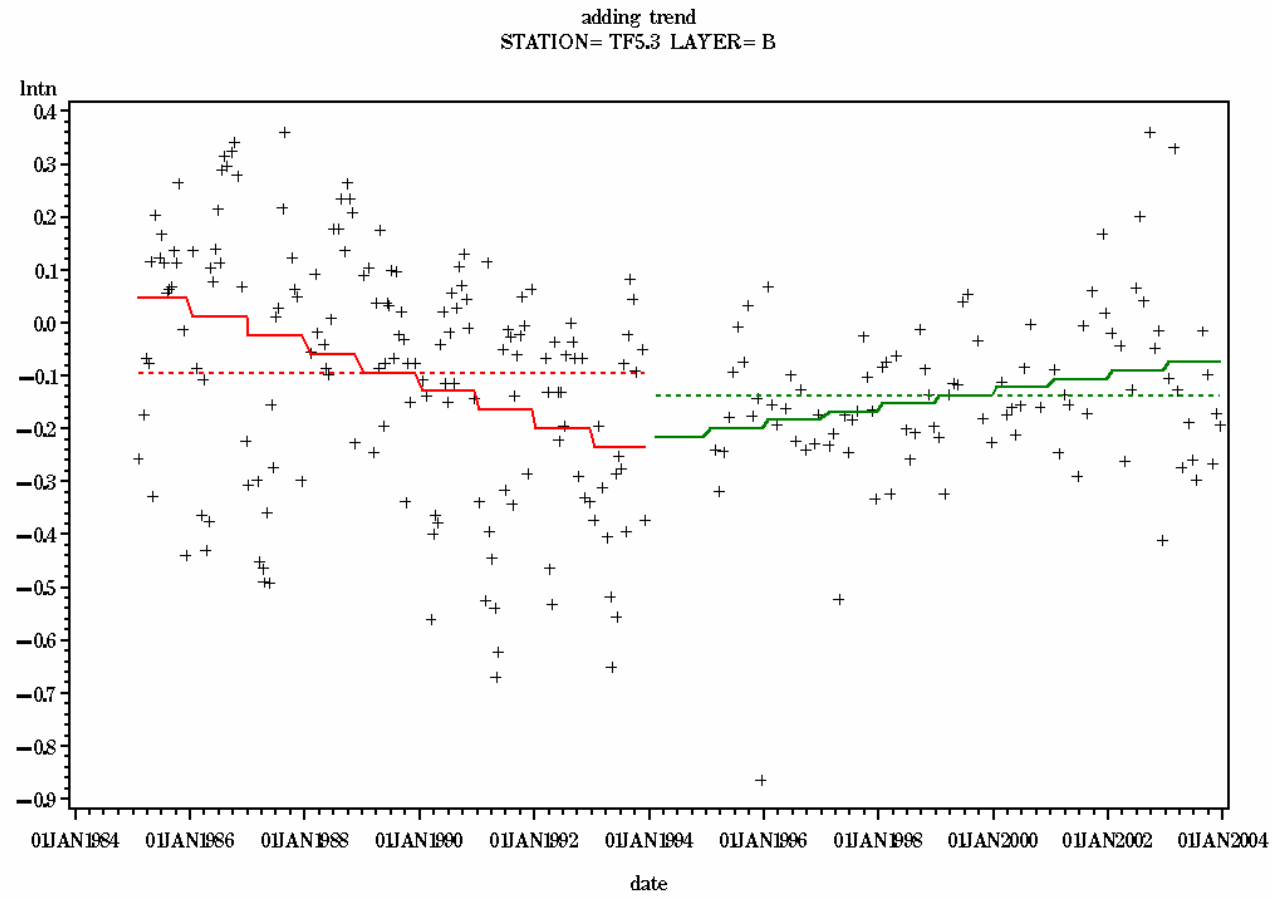


Figure 3. Model fit showing the addition of long term trends to the basic intervention model are shown in solid lines. The model fit with just the intervention term is shown by dashed lines.

Seasonality is added to the model by introducing a dummy variable (0 or 1) for each month. The coefficients for these variables are constrained to sum to zero so that each coefficient estimates the shift in TN mean for each month relative to the annual average. To see the effect of adding these variables, see figure 4.

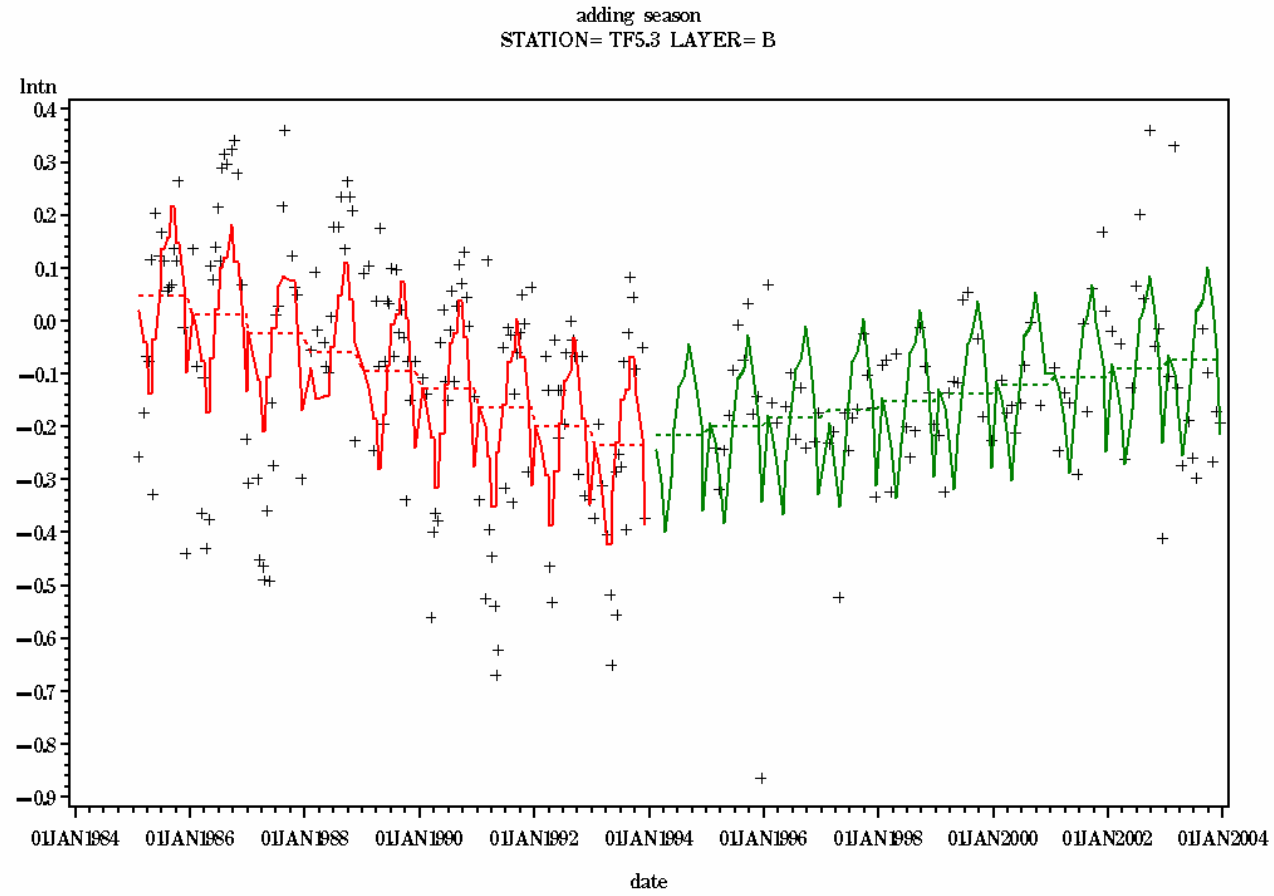


Figure 4. Model fit with the addition of seasonality shown in solid lines. Previous model shown in dashed lines.

Flow is known to effect many estuarine processes at various degrees of lag. For this analysis, the log of flow was first seasonally adjusted by subtracting monthly means and then smoothed with a 10 day moving average. Lag variables of this smoothed flow were created with lags of 10 to 150 days by 10 day intervals. Stepwise regression was used to select the lagged flow variables that were the best predictors of the log(TN) response. This regression was done so that the intervention term, the trend terms, and the seasonality terms were forced into the model before the flow terms were selected. (Figure 5).

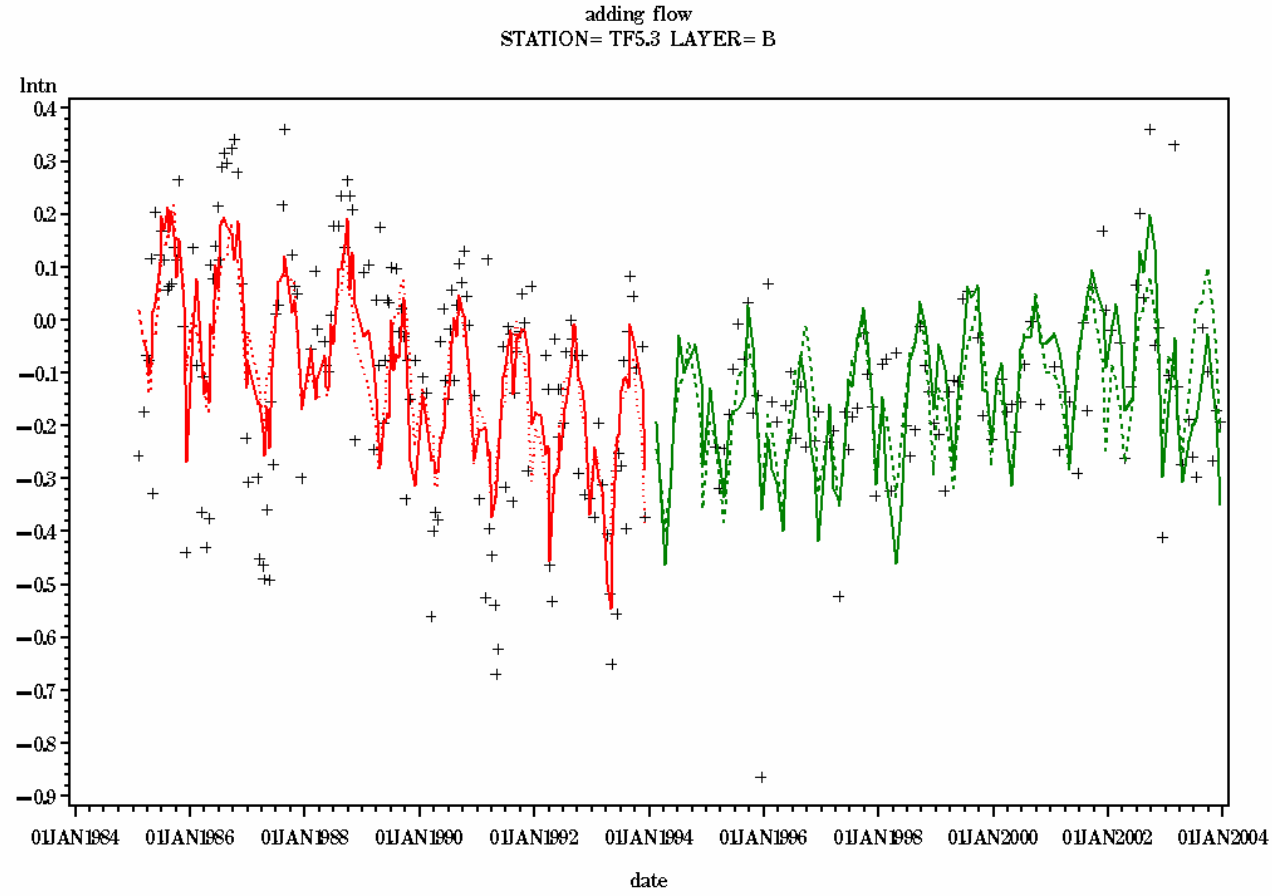


Figure 5. Model fit adding flow terms to the previous model. Previous model shown as dashed lines.

The final model adds seasonally adjusted water temperature and a first order autoregressive term (Figure 6.).

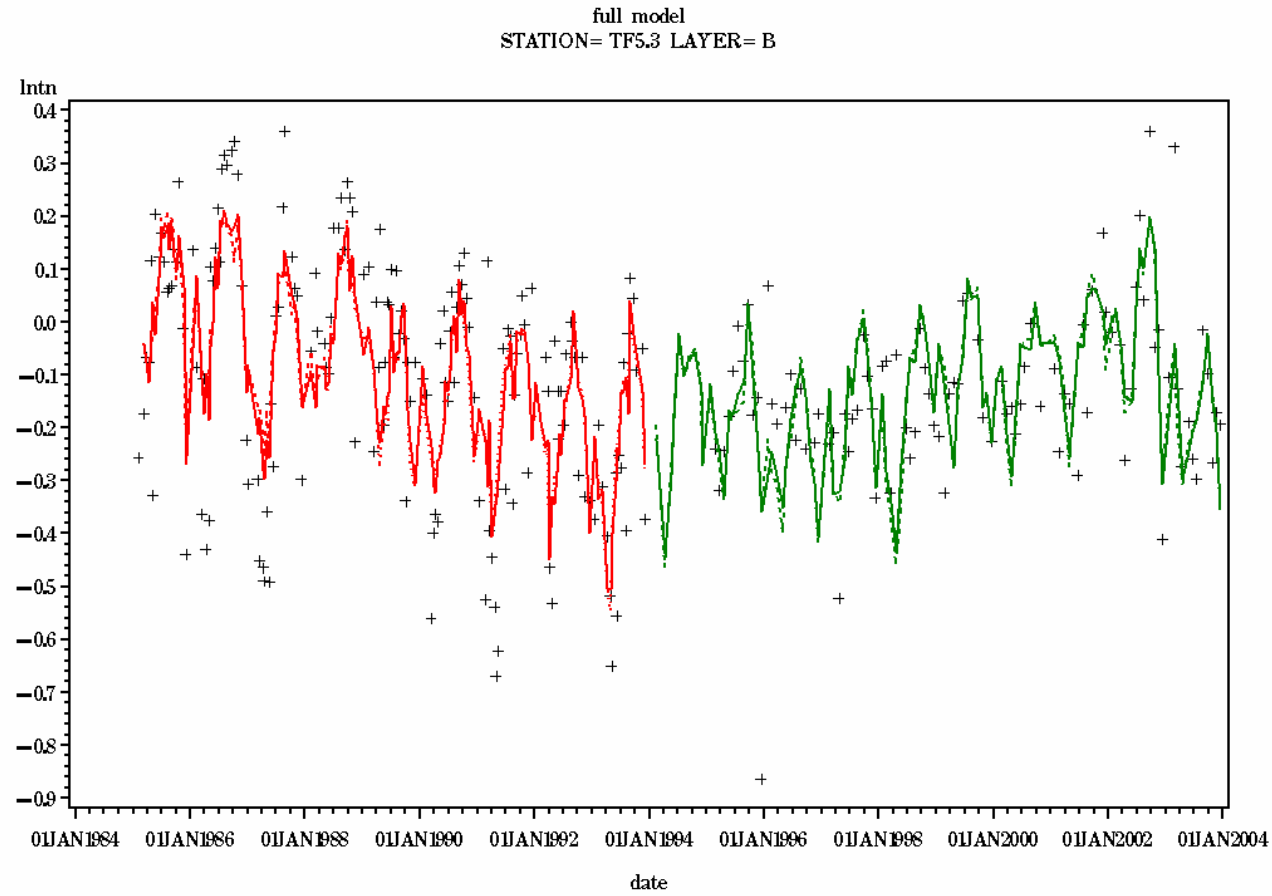


Figure 6. Model fit showing the effect of adding water temperature and autoregressive lag 1 terms. Previous model fit shown in dashed lines.

Results

An illustration of the final model fit along with all parameter estimates for the final model of each of the 63 time series can be found in appendix A. In general it appears that the model does a good job of capturing the character of the data. If for example the trend term (cyear) is statistically significant, the trend is apparent in the data. Similarly for the method change parameter (MC).

In addition we summarize below some overview statistics for the direction and magnitude of the methods change effect. Table 2 shows the number of positive and negative estimates for the effect of the methods change and the proportion of those that are statistically significant ($p < 0.05$).

Table 2. Frequency of positive and negative step trend estimates base on the 63 cases analyzed and the frequency of statistically significant step trend estimates.

Direction of step change	not significant	significant $p < 0.05$	Total
decrease	10	2	12
increase	26	25	51
Total	36	27	63

Of the 63 cases, 51 are found to have a positive step trend indicating that post method change TN is higher than pre method change TN. Of these 51, 25 or nearly half are statistically significant. Of the 12 cases that show a negative strep trend, only two are statistically significant.

To assess the relation of the step trend to salinity gradients, for each tributary a graph is prepared showing the upstream - downstream gradient of the step trend estimates.

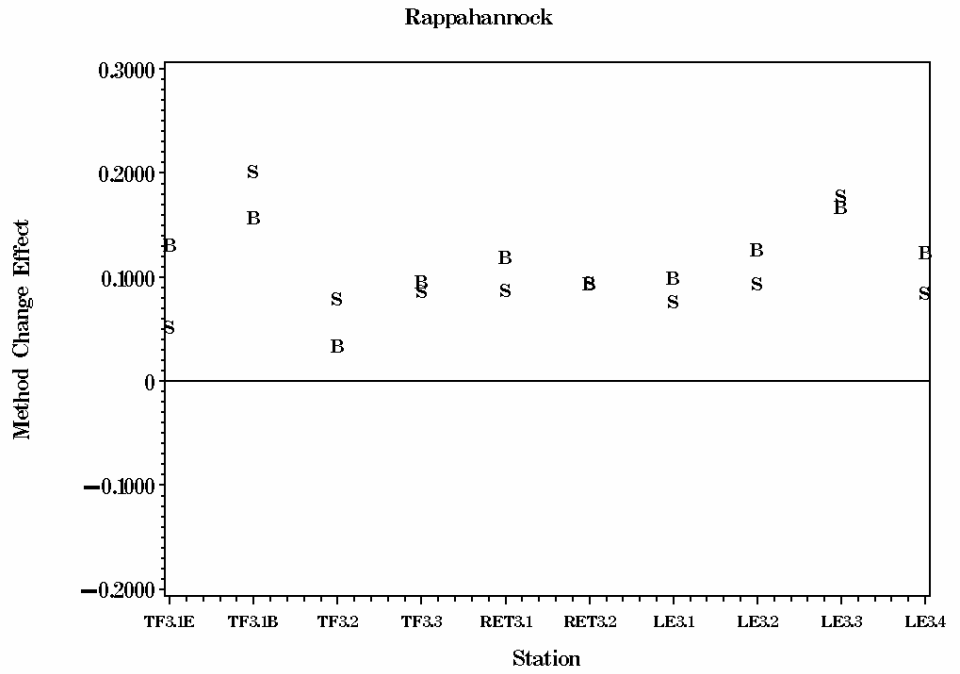


Figure 7. Plot of method change estimate versus stations in order from upstream to downstream for the Rappahannock River. Surface and Bottom are shown by S and B.

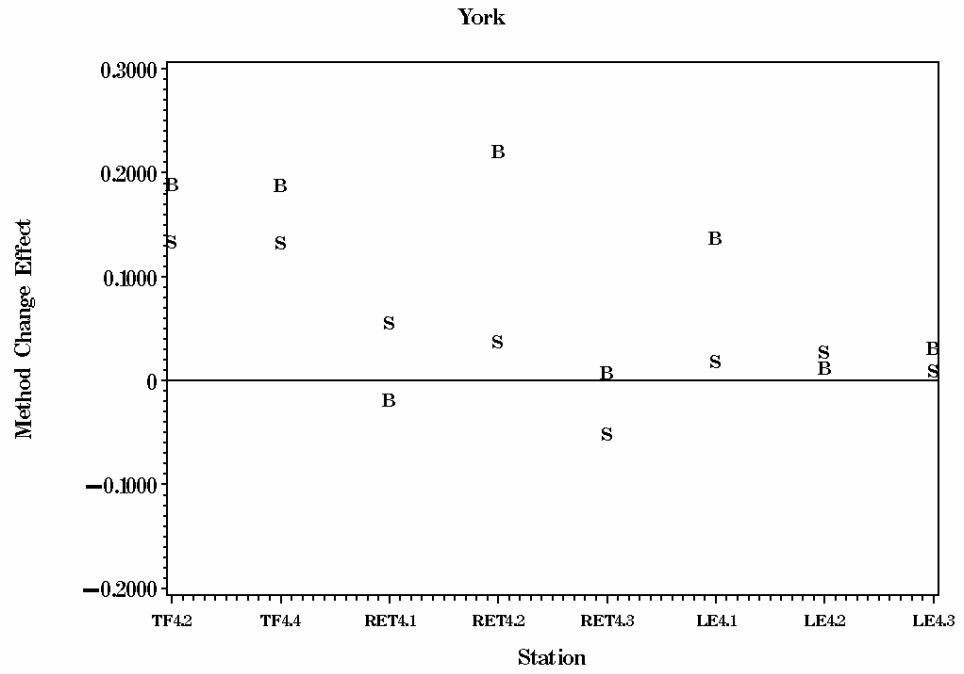


Figure 8. Plot of methods change versus station in order from upstream to downstream for the York River. Surface and Bottom are shown by S and B.

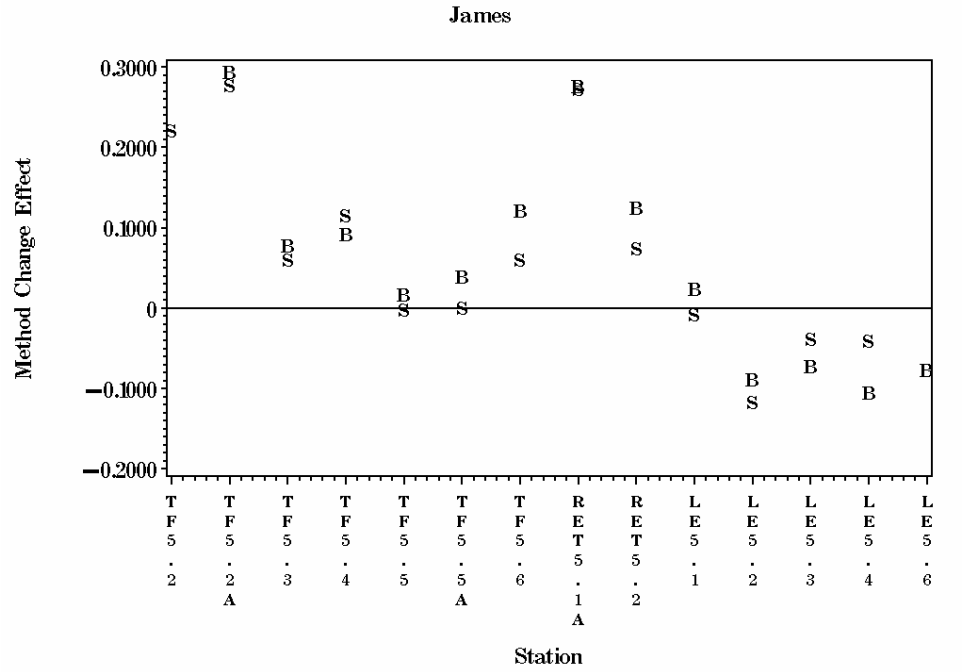


Figure 9. Plot of the method change estimate versus stations in order from upstream to downstream for the James River. Surface and Bottom are shown by S and B.

Discussion

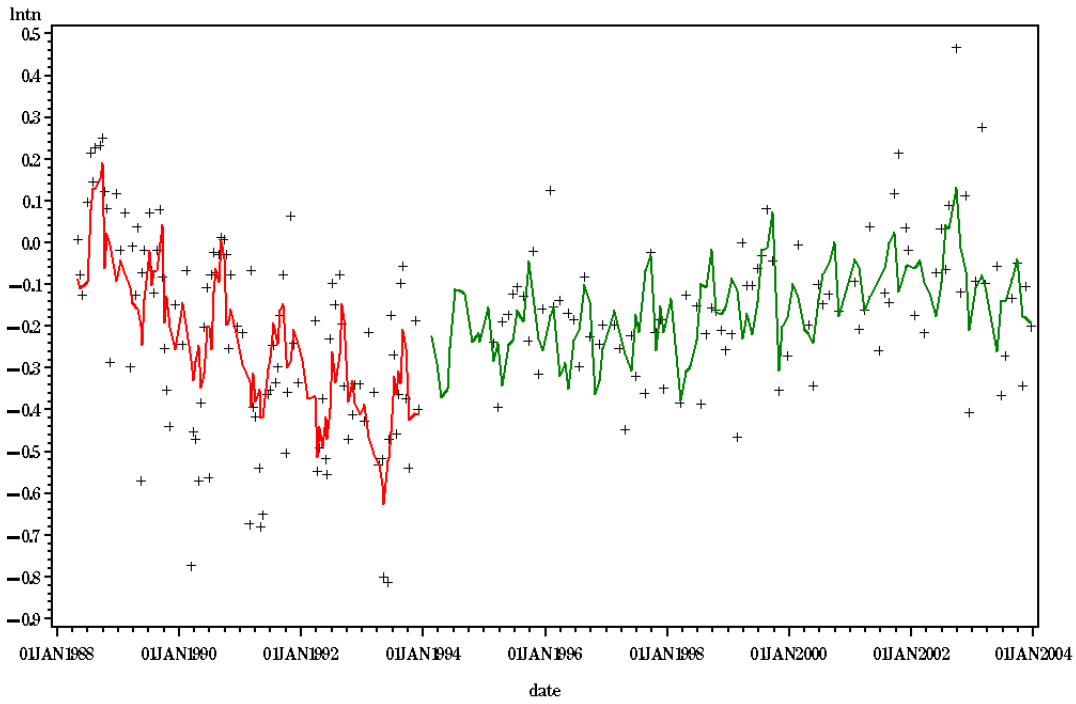
The variety of results that are obtained by this analysis is surprising. Some cases show an almost seamless transition from the old method to the new method (see RET4.1 B in appendix A). Other stations appear to show a step up (see TF4.1 B), and other appear to show a step down (LE5.6 S). Because there is a variety of results with some clearly contradictory, we rely on a weight of evidence overview to reach conclusions about the average method change effect.

Most cases (51 of 63 or 81%) the effect estimate for the methods change indicates a positive step change in TN. Of the 51, 25 are statistically significant. On the other hand, 12 cases show a decreasing step change and only two of these are statistically significant. These results weight heavily toward the conclusion that the methods change leads to a increase in the estimate of TN.

Examining the plots of the method change estimate versus river gradient, it is clear that most of the negative estimates of the method change effect occur in the lower James. This clustering of the negative results suggests that they are not independent. Possibly some other phenomenon caused a decrease in TN in the lower James at about the same time as the method change. The York River also shows a decreasing effect of the method change moving from upriver to downriver, but the effect does not become clearly negative as it does in the James. There appears to be no trend for the method change parameter estimate in the Rappahannock. While it is important to estimate the magnitude of the method change effect, we will not attempt that task with the monitoring data, but will rely on the split sample data for that estimate.

Appendix A

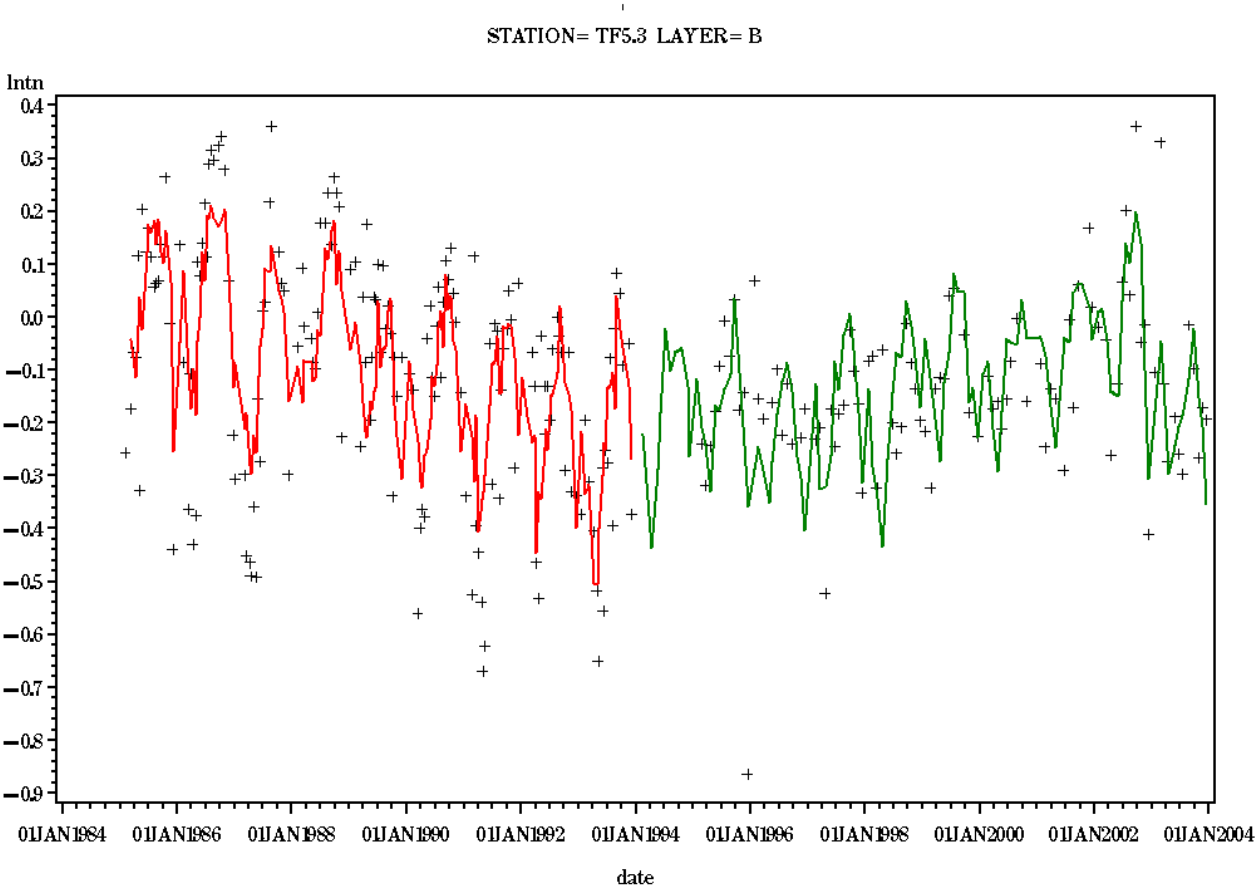
On each page of this appendix are the results on the intervention analysis of the TN time series at one station x layer combination. The results include a graph showing the time series of the data and the model fit before (red) and after (green) the methods change. Below the graph are the parameter estimates for the model with standard errors and p-values. Of particular interest is the MC (method change) parameter. A positive value for this estimate indicates a step up; a negative value indicates a step down.



Tributary	Station	Layer
James	TF5.2A	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.5154	0.0400	-12.87	<.0001
jan	0.0286	0.0494	0.58	0.5631
feb	0.0088	0.0471	0.19	0.8522
mar	-0.0724	0.0397	-1.82	0.0699
apr	-0.0756	0.0391	-1.93	0.0549
may	-0.1148	0.0362	-3.17	0.0018
jun	-0.0251	0.0351	-0.72	0.4749
jul	0.0644	0.0360	1.79	0.0750
aug	0.0964	0.0350	2.76	0.0065
sep	0.1588	0.0359	4.43	<.0001
oct	-0.0220	0.0369	-0.60	0.5521
nov	-0.0108	0.0404	-0.27	0.7894
dec	-0.0364	0.0401	-0.91	0.3654
rtemp	0.0025	0.0049	0.51	0.6087
cyear	-0.0817	0.0105	-7.74	<.0001
mc	0.2943	0.0564	5.22	<.0001
mc_cyear	0.0943	0.0129	7.30	<.0001
flow40	-0.1339	0.0392	-3.42	0.0008
AR1	-0.0960	0.0752	-1.28	0.1058

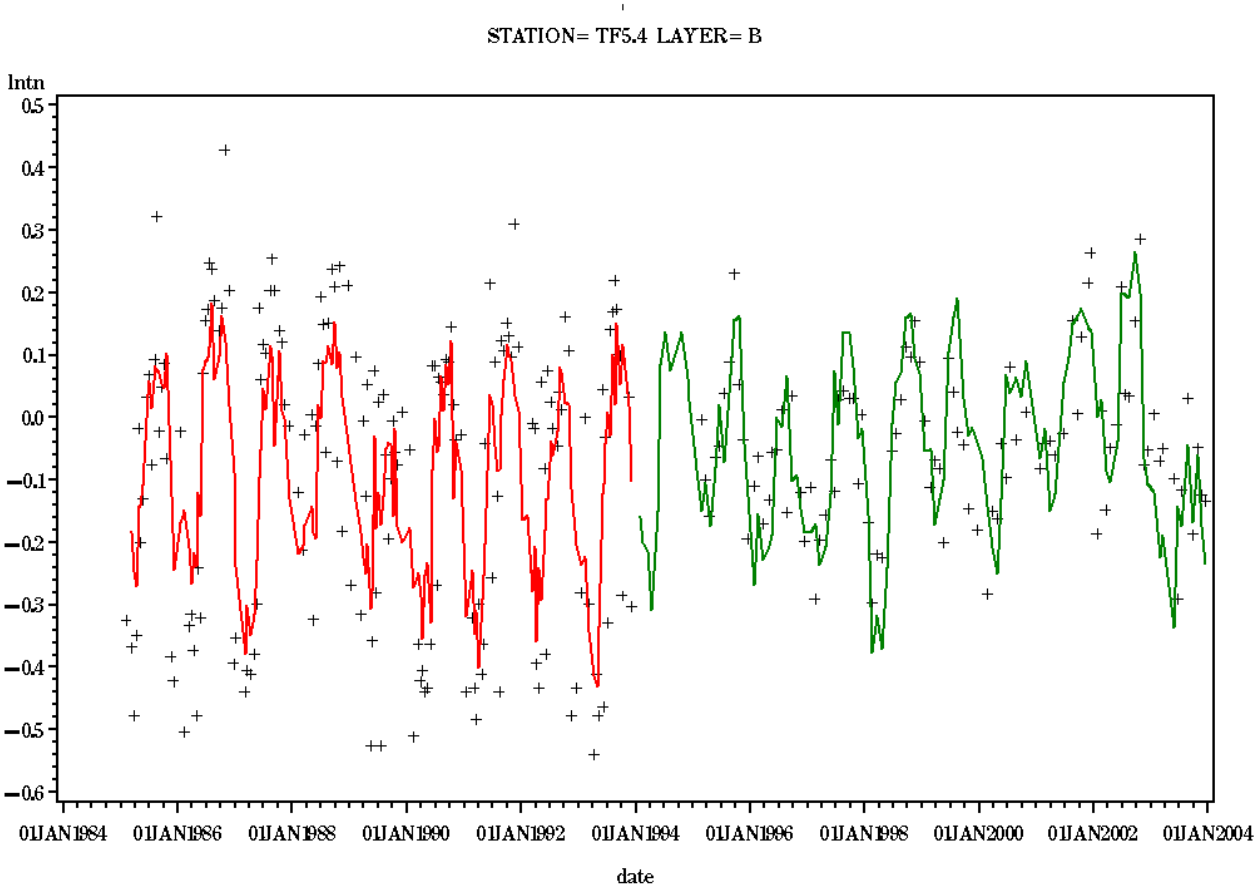
Root MSE = 0.1579 Total R-Square = 0.4980



Tributary	Station	Layer
James	TF5.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2577	0.0311	-8.28	<.0001
jan	0.0087	0.0409	0.21	0.8322
feb	-0.0044	0.0381	-0.12	0.9071
mar	-0.0972	0.0304	-3.19	0.0016
apr	-0.1654	0.0313	-5.28	<.0001
may	-0.0909	0.0309	-2.94	0.0036
jun	0.0134	0.0292	0.46	0.6461
jul	0.0944	0.0310	3.04	0.0026
aug	0.0902	0.0306	2.95	0.0035
sep	0.1638	0.0321	5.10	<.0001
oct	0.0936	0.0318	2.94	0.0036
nov	0.0250	0.0352	0.71	0.4775
dec	-0.1313	0.0358	-3.67	0.0003
rtemp	0.0055	0.0039	1.42	0.1573
cyear	-0.0336	0.0056	-6.04	<.0001
mc	0.0786	0.0505	1.56	0.1211
mc_cyear	0.0417	0.0092	4.55	<.0001
flow30	-0.0784	0.0314	-2.50	0.0131
flow40	-0.0819	0.0350	-2.34	0.0202
flow10	-0.0598	0.0320	-1.87	0.0628
AR1	-0.1654	0.0643	-2.57	0.0077

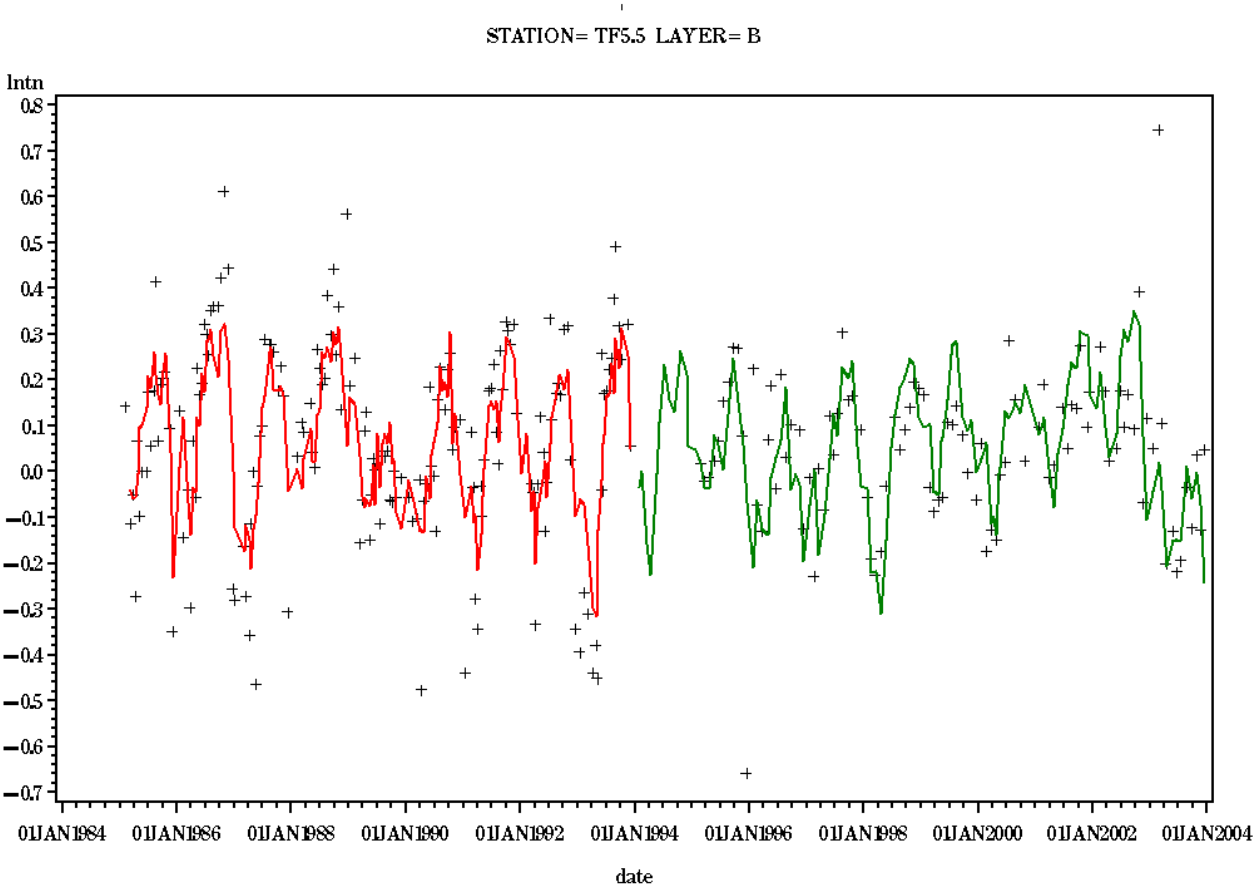
Root MSE = 0.1506 Total R-Square = 0.5206



Tributary	Station	Layer
James	TF5.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1196	0.0270	-4.43	<.0001
jan	-0.0669	0.0377	-1.77	0.0774
feb	-0.0879	0.0357	-2.46	0.0144
mar	-0.1550	0.0278	-5.57	<.0001
apr	-0.1839	0.0297	-6.20	<.0001
may	-0.1239	0.0287	-4.31	<.0001
jun	0.0712	0.0272	2.61	0.0095
jul	0.0890	0.0290	3.07	0.0024
aug	0.1228	0.0280	4.38	<.0001
sep	0.1416	0.0294	4.81	<.0001
oct	0.1492	0.0285	5.24	<.0001
nov	0.0467	0.0339	1.38	0.1693
dec	-0.0031	0.0341	-0.09	0.9286
rtemp	0.0060	0.0039	1.54	0.1239
cyear	-0.0042	0.0049	-0.87	0.3870
mc	0.0922	0.0437	2.11	0.0360
mc_cyear	-0.0010	0.0080	-0.13	0.8995
flow0	-0.1122	0.0323	-3.48	0.0006
flow40	-0.1084	0.0315	-3.44	0.0007
flow10	-0.0706	0.0325	-2.17	0.0308
AR1	-0.0708	0.0643	-1.10	0.1398

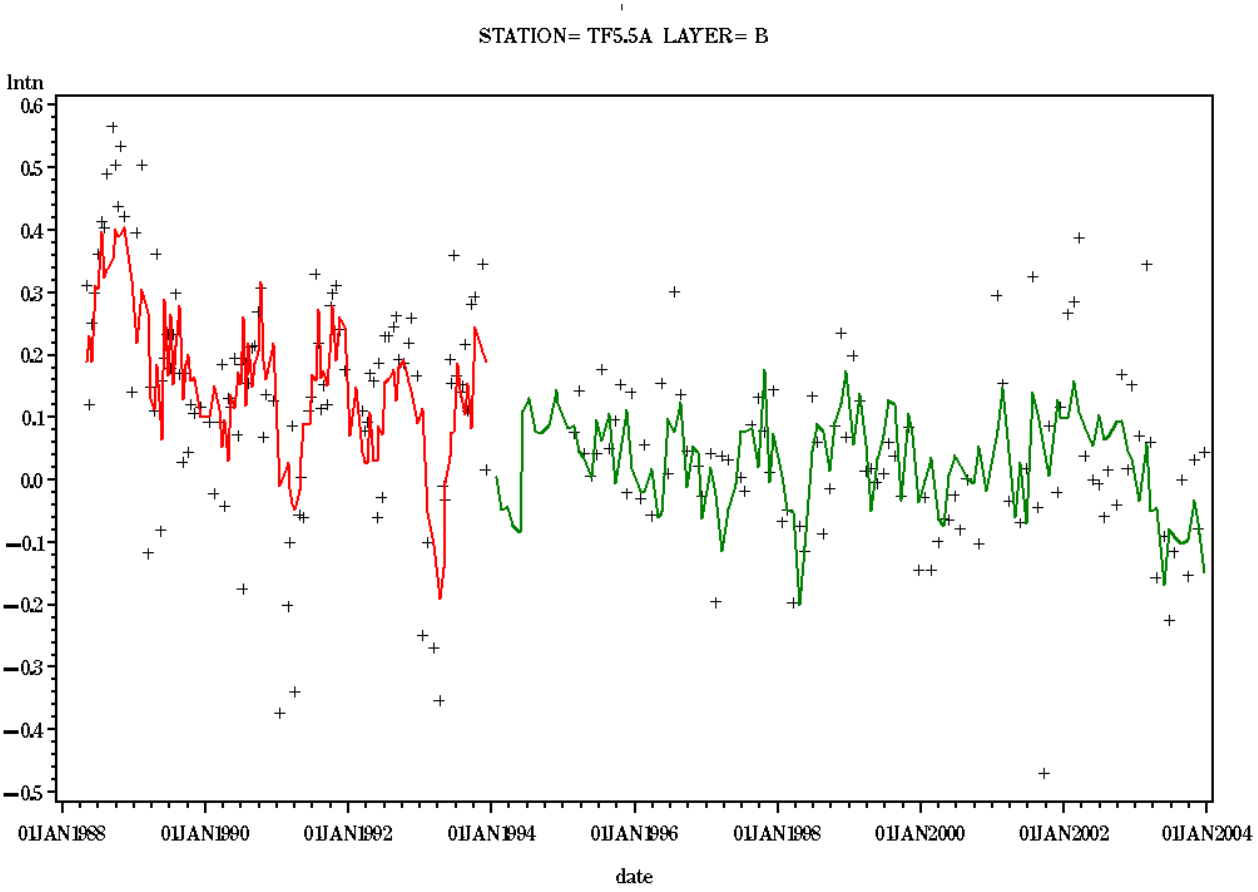
Root MSE = 0.1441 Total R-Square = 0.5408



Tributary	Station	Layer
James	TF5.5	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	0.0569	0.0280	2.03	0.0434
jan	-0.0580	0.0376	-1.55	0.1236
feb	-0.0255	0.0354	-0.72	0.4726
mar	-0.1439	0.0280	-5.14	<.0001
apr	-0.1745	0.0288	-6.06	<.0001
may	-0.0697	0.0285	-2.45	0.0150
jun	0.0165	0.0280	0.59	0.5566
jul	0.0795	0.0286	2.79	0.0058
aug	0.1147	0.0286	4.00	<.0001
sep	0.1096	0.0296	3.71	0.0003
oct	0.1508	0.0292	5.16	<.0001
nov	0.0834	0.0345	2.42	0.0163
dec	-0.0828	0.0332	-2.50	0.0133
rtemp	0.0035	0.0041	0.86	0.3913
cyear	-0.0020	0.0050	-0.41	0.6842
mc	0.0180	0.0454	0.40	0.6913
mc_cyear	-0.0036	0.0082	-0.44	0.6627
flow10	-0.1191	0.0340	-3.50	0.0005
flow40	-0.0878	0.0339	-2.59	0.0102
flow0	-0.0643	0.0321	-2.00	0.0465
flow30	-0.0696	0.0299	-2.33	0.0207
AR1	-0.1049	0.0641	-1.64	0.0559

Root MSE = 0.1436 Total R-Square = 0.5362



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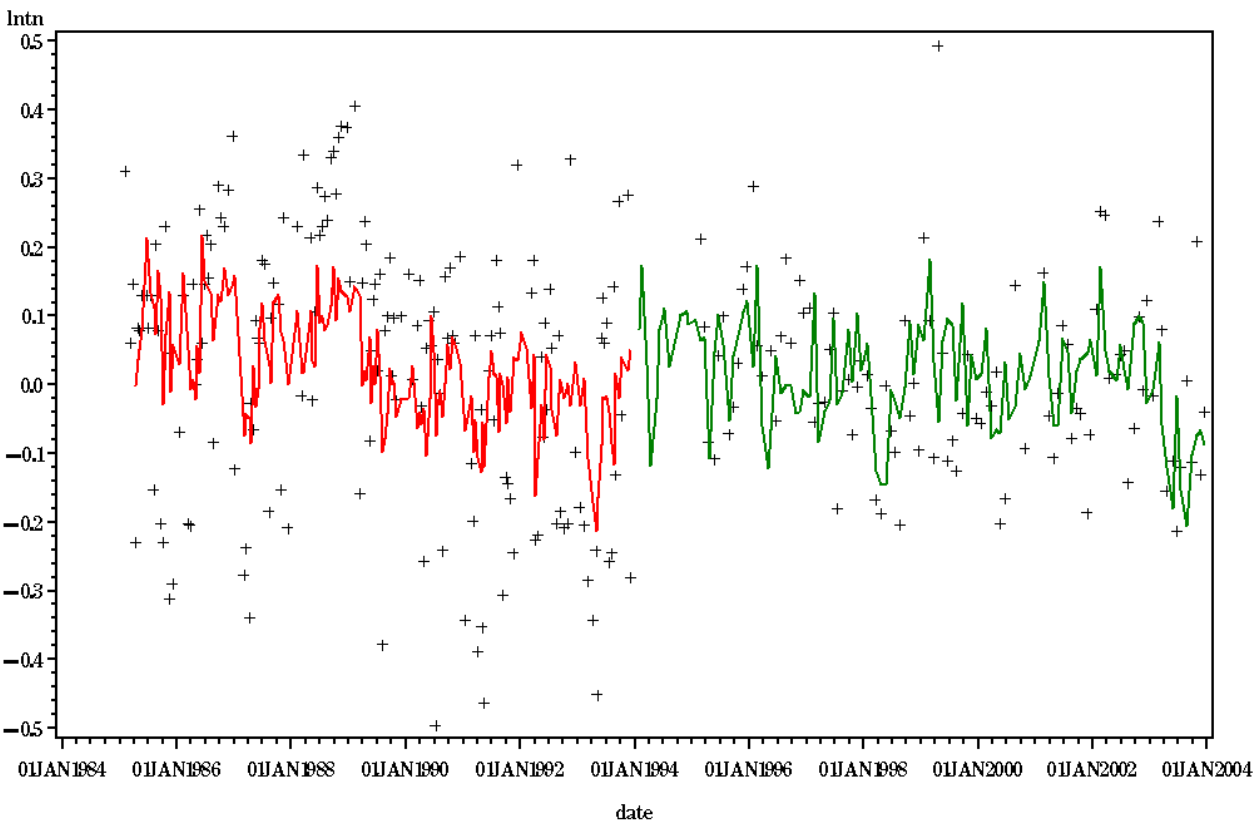
Tributary	Station	Layer
James	TF5.5A	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	0.0245	0.0405	0.60	0.5463
jan	-0.0064	0.0353	-0.18	0.8557
feb	-0.0044	0.0341	-0.13	0.8970
mar	-0.0575	0.0310	-1.85	0.0652
apr	-0.0959	0.0323	-2.97	0.0033
may	-0.0706	0.0304	-2.33	0.0211
jun	0.0153	0.0292	0.52	0.6009
jul	0.0568	0.0298	1.91	0.0583
aug	0.0379	0.0298	1.27	0.2059
sep	0.0067	0.0306	0.22	0.8262
oct	0.0753	0.0314	2.40	0.0173
nov	0.0386	0.0337	1.14	0.2538
dec	0.0042	0.0333	0.13	0.8996
rtemp	0.0050	0.0043	1.17	0.2417
cyear	-0.0393	0.0106	-3.70	0.0003
mc	0.0402	0.0564	0.71	0.4770
mc_cyear	0.0305	0.0127	2.40	0.0175
flow80	-0.0908	0.0302	-3.01	0.0030
flow10	-0.0946	0.0303	-3.12	0.0021
AR1	-0.2907	0.0698	-4.17	0.0001

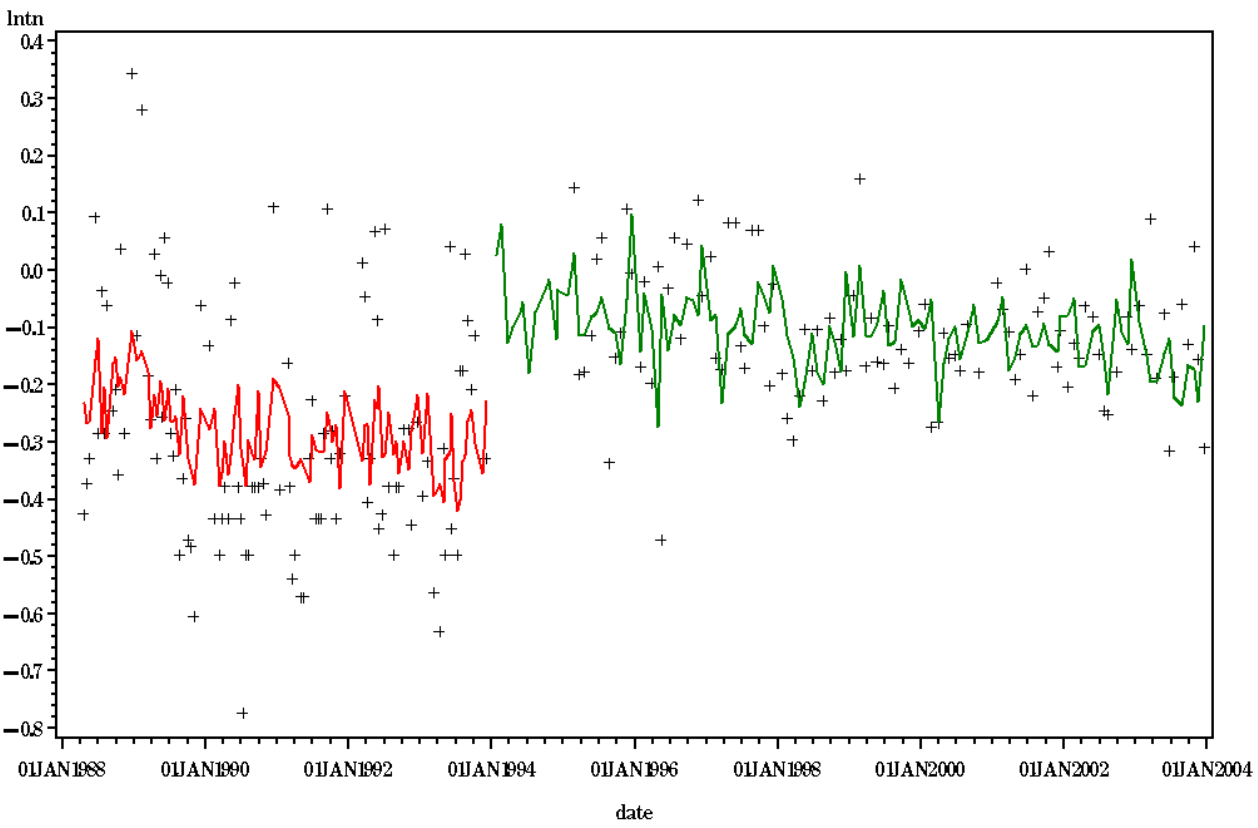
Root MSE = 0.1290 Total R-Square = 0.4790



Tributary	Station	Layer
James	TF5.6	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0491	0.0319	-1.54	0.1244
jan	0.0140	0.0421	0.33	0.7390
feb	0.0857	0.0398	2.15	0.0324
mar	-0.0433	0.0327	-1.32	0.1872
apr	-0.0771	0.0331	-2.33	0.0206
may	-0.0585	0.0314	-1.86	0.0642
jun	0.0469	0.0310	1.51	0.1318
jul	0.0159	0.0329	0.48	0.6287
aug	-0.0453	0.0319	-1.42	0.1572
sep	0.0165	0.0334	0.49	0.6222
oct	0.0150	0.0331	0.45	0.6502
nov	0.0170	0.0366	0.46	0.6427
dec	0.0130	0.0371	0.35	0.7264
rtemp	-0.0040	0.0052	-0.78	0.4388
cyear	-0.0161	0.0057	-2.80	0.0055
mc	0.1224	0.0513	2.39	0.0177
mc_cyear	0.0026	0.0094	0.27	0.7847
flow40	-0.1270	0.0347	-3.66	0.0003
flow90	-0.0710	0.0327	-2.17	0.0307
AR1	-0.1161	0.0636	-1.83	0.0389

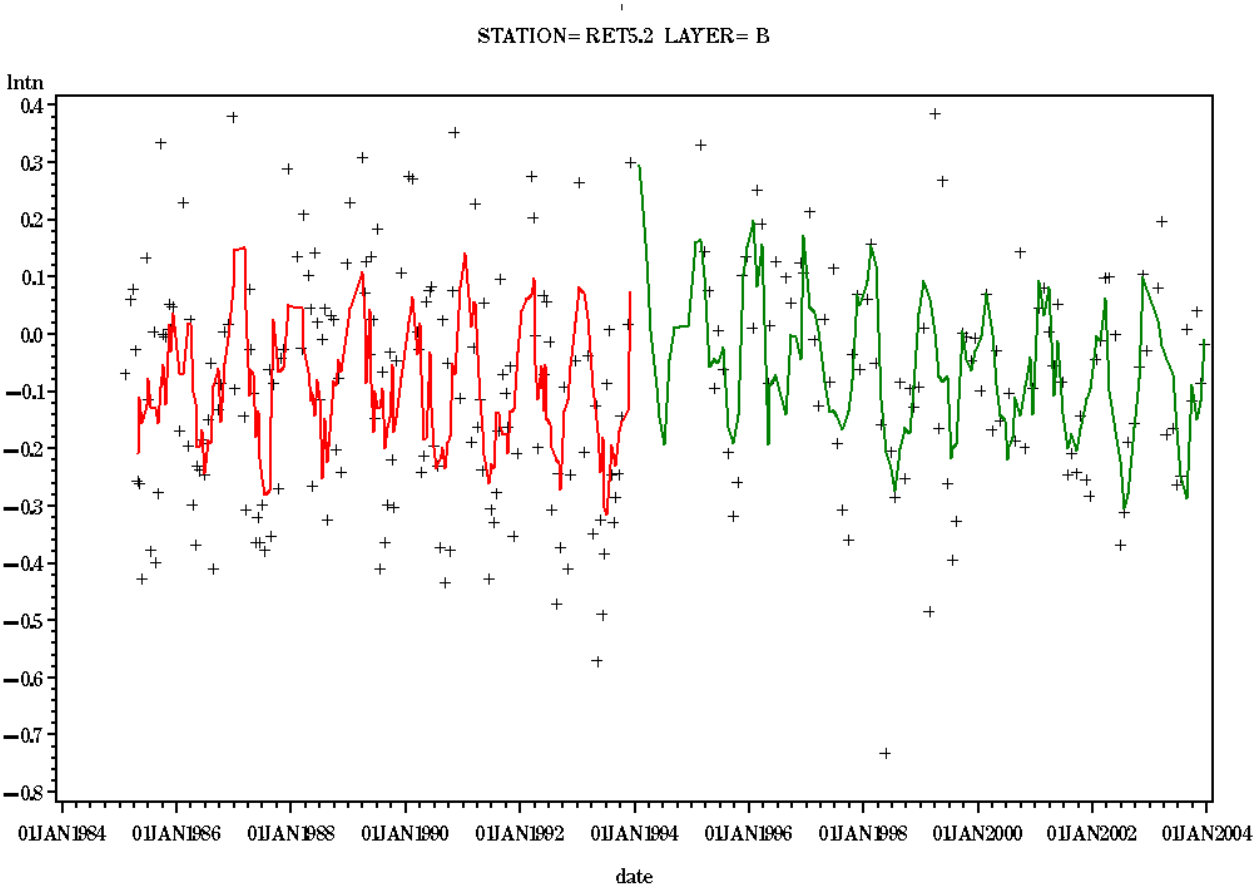
Root MSE = 0.1621 Total R-Square = 0.2149



Tributary	Station	Layer
James	RET5.1A	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3234	0.0411	-7.87	<.0001
jan	0.0300	0.0430	0.70	0.4862
feb	0.0611	0.0414	1.47	0.1420
mar	-0.0609	0.0367	-1.66	0.0987
apr	-0.0433	0.0356	-1.21	0.2263
may	-0.0098	0.0351	-0.28	0.7795
jun	0.0118	0.0339	0.35	0.7274
jul	-0.0291	0.0351	-0.83	0.4078
aug	-0.0315	0.0350	-0.90	0.3692
sep	0.0357	0.0360	0.99	0.3229
oct	-0.0106	0.0369	-0.29	0.7745
nov	-0.0277	0.0403	-0.69	0.4925
dec	0.0743	0.0400	1.86	0.0650
rtemp	-0.0098	0.0054	-1.82	0.0703
cyear	-0.0148	0.0107	-1.38	0.1680
mc	0.2770	0.0563	4.92	<.0001
mc_cyear	0.0018	0.0130	0.14	0.8896
flow100	-0.0990	0.0340	-2.91	0.0041
AR1	-0.1296	0.0717	-1.81	0.0405

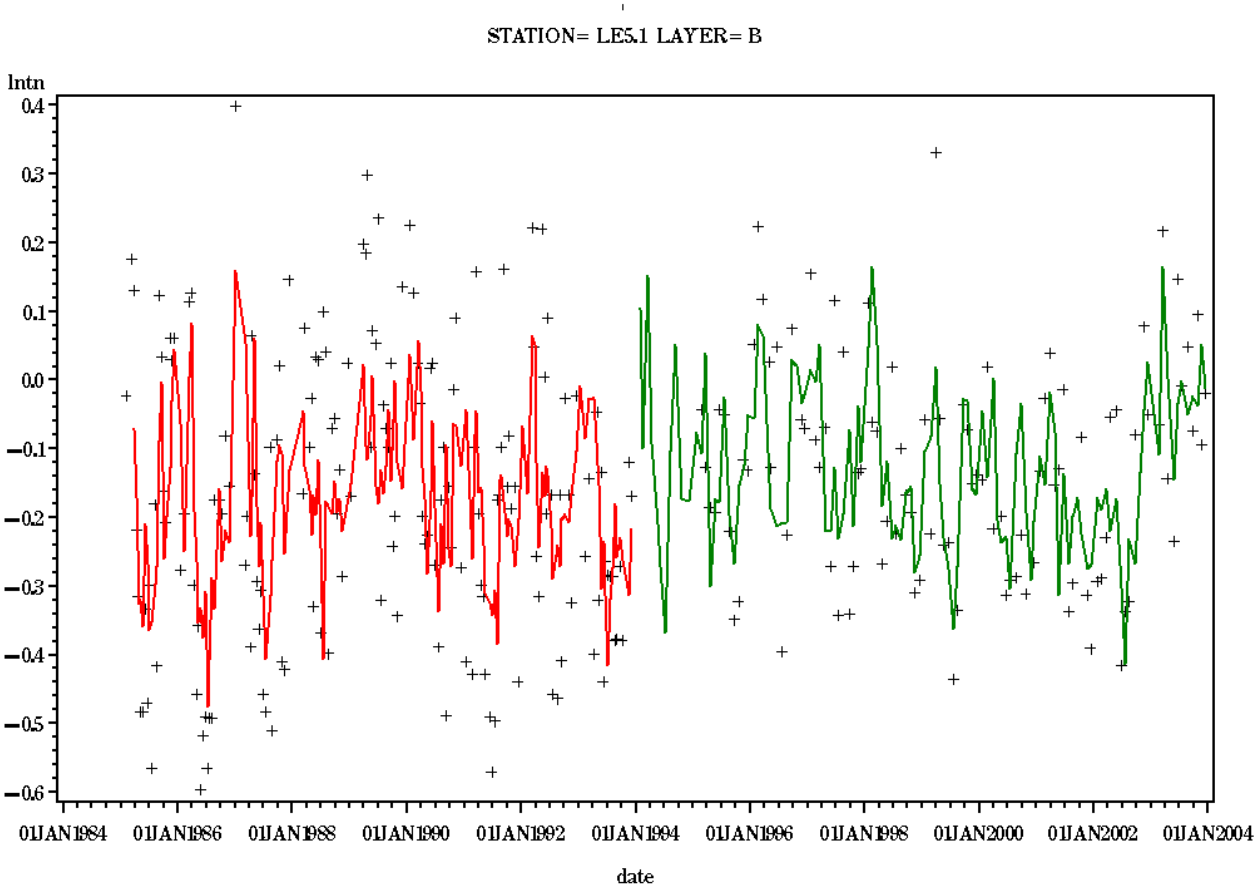
Root MSE = 0.1578 Total R-Square = 0.3415



Tributary	Station	Layer
James	RET5.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0929	0.0341	-2.72	0.0070
jan	0.1265	0.0458	2.76	0.0061
feb	0.1321	0.0427	3.09	0.0022
mar	0.1230	0.0346	3.55	0.0005
apr	-0.0161	0.0338	-0.48	0.6347
may	-0.0538	0.0327	-1.64	0.1016
jun	-0.0813	0.0335	-2.43	0.0159
jul	-0.1236	0.0354	-3.49	0.0006
aug	-0.0935	0.0335	-2.79	0.0057
sep	-0.0621	0.0342	-1.82	0.0706
oct	-0.0548	0.0344	-1.59	0.1129
nov	0.0232	0.0373	0.62	0.5336
dec	0.0803	0.0388	2.07	0.0395
rtemp	-0.0113	0.0054	-2.08	0.0382
cyear	-0.0038	0.0061	-0.62	0.5368
mc	0.1255	0.0536	2.34	0.0199
mc_cyear	-0.0157	0.0099	-1.58	0.1152
flow0	0.1261	0.0330	3.83	0.0002
flow150	-0.0978	0.0341	-2.87	0.0045
flow70	-0.0768	0.0355	-2.17	0.0314
AR1	-0.1192	0.0642	-1.86	0.0367

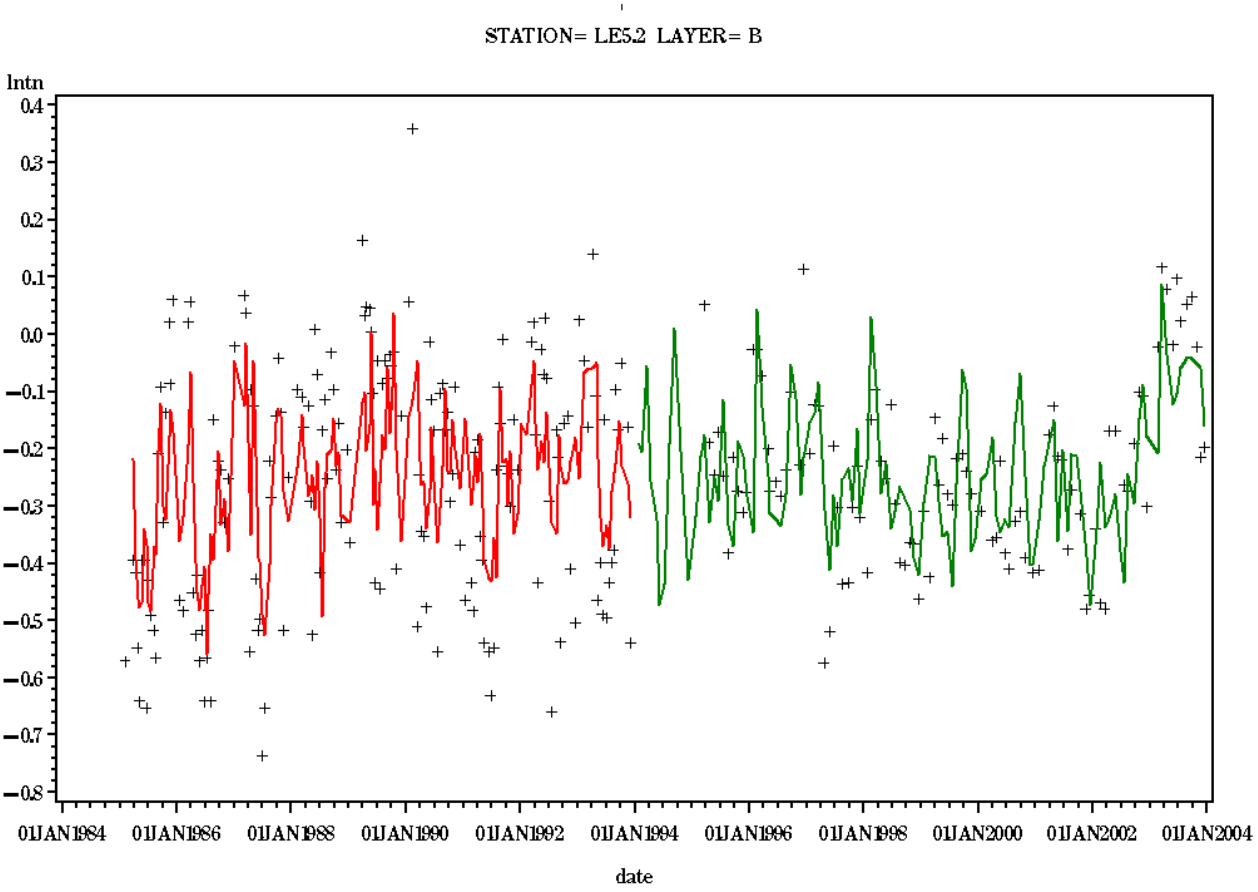
Root MSE = 0.1688 Total R-Square = 0.3081



Tributary	Station	Layer
James	LE5.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1694	0.0353	-4.80	<.0001
jan	0.1184	0.0430	2.75	0.0064
feb	0.0580	0.0415	1.40	0.1639
mar	0.1580	0.0326	4.85	<.0001
apr	-0.0099	0.0328	-0.30	0.7624
may	-0.0652	0.0316	-2.07	0.0398
jun	-0.0698	0.0318	-2.19	0.0293
jul	-0.1488	0.0329	-4.52	<.0001
aug	-0.0530	0.0323	-1.64	0.1023
sep	0.0225	0.0337	0.67	0.5056
oct	-0.0047	0.0334	-0.14	0.8890
nov	-0.0408	0.0357	-1.14	0.2544
dec	0.0353	0.0376	0.94	0.3495
rtemp	-0.0081	0.0052	-1.56	0.1199
cyear	-0.0007	0.0062	-0.11	0.9108
mc	0.0243	0.0561	0.43	0.6656
mc_cyear	0.0048	0.0101	0.47	0.6366
flow10	0.1570	0.0349	4.51	<.0001
flow20	0.1131	0.0386	2.93	0.0037
flow80	-0.0643	0.0337	-1.91	0.0573
AR1	-0.2215	0.0628	-3.53	0.0007

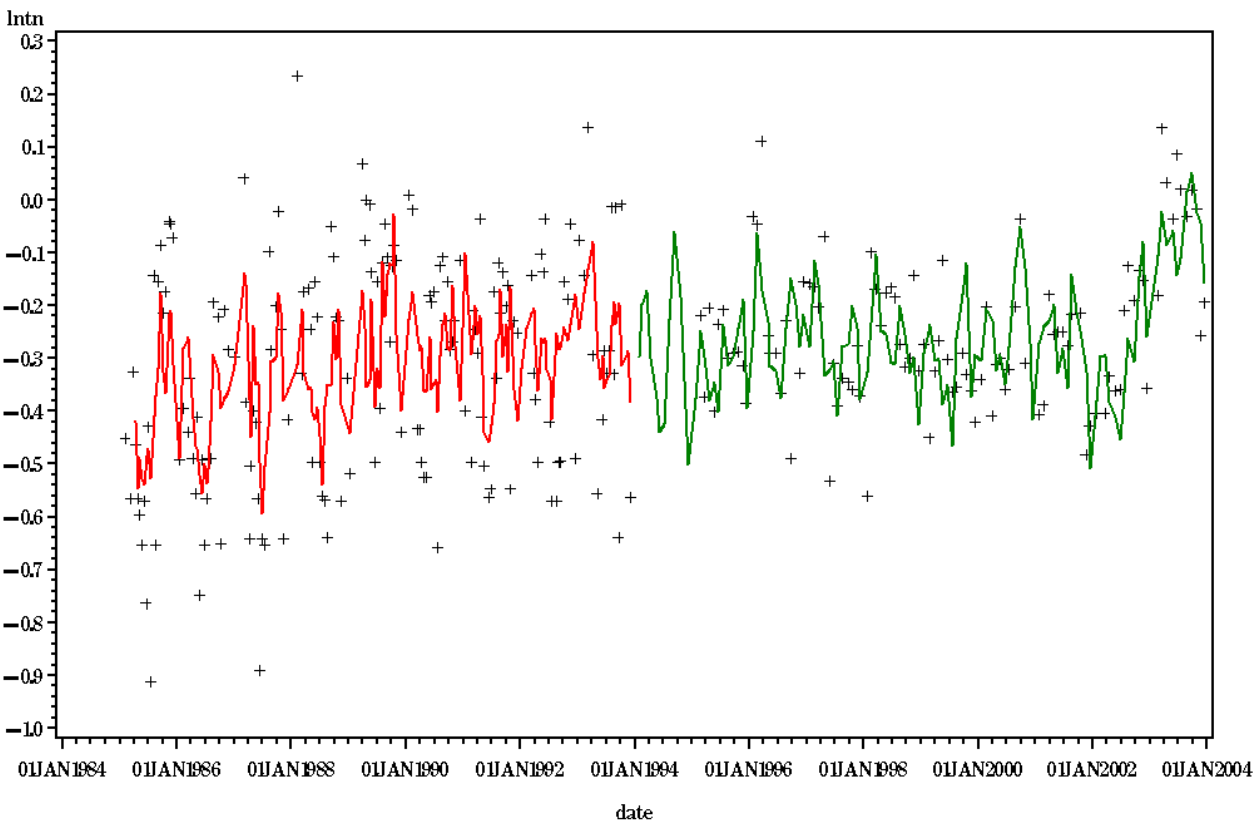
Root MSE = 0.1589 Total R-Square = 0.3795



Tributary	Station	Layer
James	LE5.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1938	0.0366	-5.30	<.0001
jan	0.0164	0.0405	0.41	0.6855
feb	0.0736	0.0431	1.71	0.0893
mar	0.1137	0.0321	3.54	0.0005
apr	-0.0083	0.0318	-0.26	0.7945
may	-0.0464	0.0312	-1.49	0.1385
jun	-0.0805	0.0319	-2.52	0.0123
jul	-0.1130	0.0325	-3.48	0.0006
aug	0.0043	0.0321	0.13	0.8929
sep	0.0724	0.0332	2.18	0.0304
oct	0.0425	0.0324	1.31	0.1911
nov	-0.0383	0.0349	-1.10	0.2733
dec	-0.0365	0.0376	-0.97	0.3324
rtemp	-0.0071	0.0051	-1.39	0.1645
cyear	0.0111	0.0065	1.71	0.0892
mc	-0.0875	0.0587	-1.49	0.1374
mc_cyear	-0.0023	0.0107	-0.22	0.8282
flow10	0.1221	0.0332	3.67	0.0003
flow20	0.1537	0.0372	4.13	<.0001
flow70	-0.0889	0.0324	-2.74	0.0065
AR1	-0.2750	0.0619	-4.44	<.0001

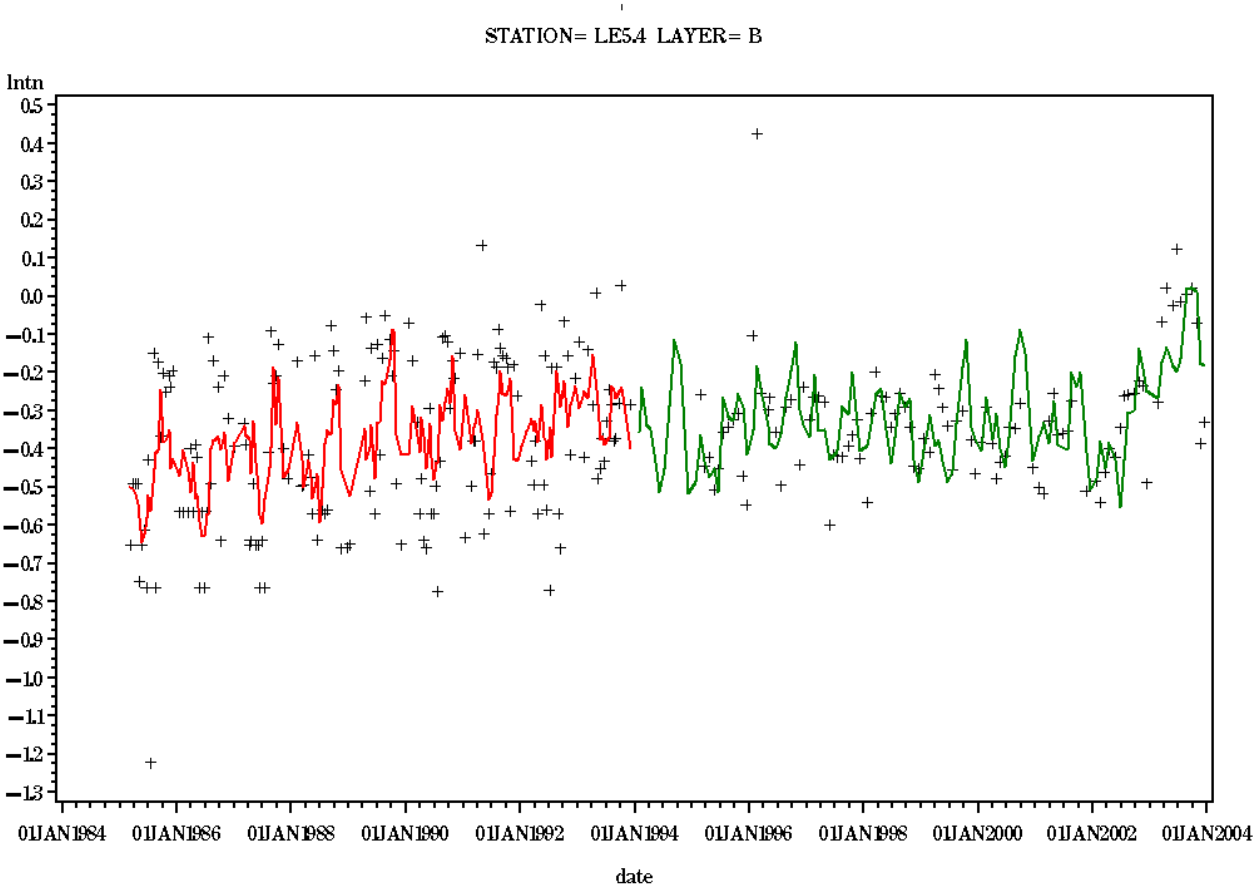
Root MSE = 0.1546 Total R-Square = 0.4050



Tributary	Station	Layer
James	LE5.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2431	0.0343	-7.09	<.0001
jan	-0.0190	0.0428	-0.44	0.6578
feb	0.0783	0.0439	1.78	0.0760
mar	0.0802	0.0335	2.39	0.0175
apr	-0.0267	0.0330	-0.81	0.4182
may	-0.0638	0.0319	-2.00	0.0466
jun	-0.0954	0.0324	-2.95	0.0035
jul	-0.0915	0.0331	-2.77	0.0061
aug	0.0439	0.0325	1.35	0.1784
sep	0.0798	0.0338	2.36	0.0190
oct	0.0692	0.0329	2.10	0.0364
nov	0.0180	0.0369	0.49	0.6257
dec	-0.0730	0.0396	-1.84	0.0663
rtemp	-0.0083	0.0058	-1.44	0.1521
cyear	0.0132	0.0061	2.18	0.0302
mc	-0.0717	0.0535	-1.34	0.1811
mc_cyear	-0.0006	0.0097	-0.06	0.9528
flow20	0.1500	0.0379	3.96	0.0001
flow90	0.0858	0.0331	2.59	0.0102
flow70	-0.0740	0.0349	-2.12	0.0350
flow0	0.0924	0.0358	2.58	0.0105
AR1	-0.1496	0.0644	-2.32	0.0135

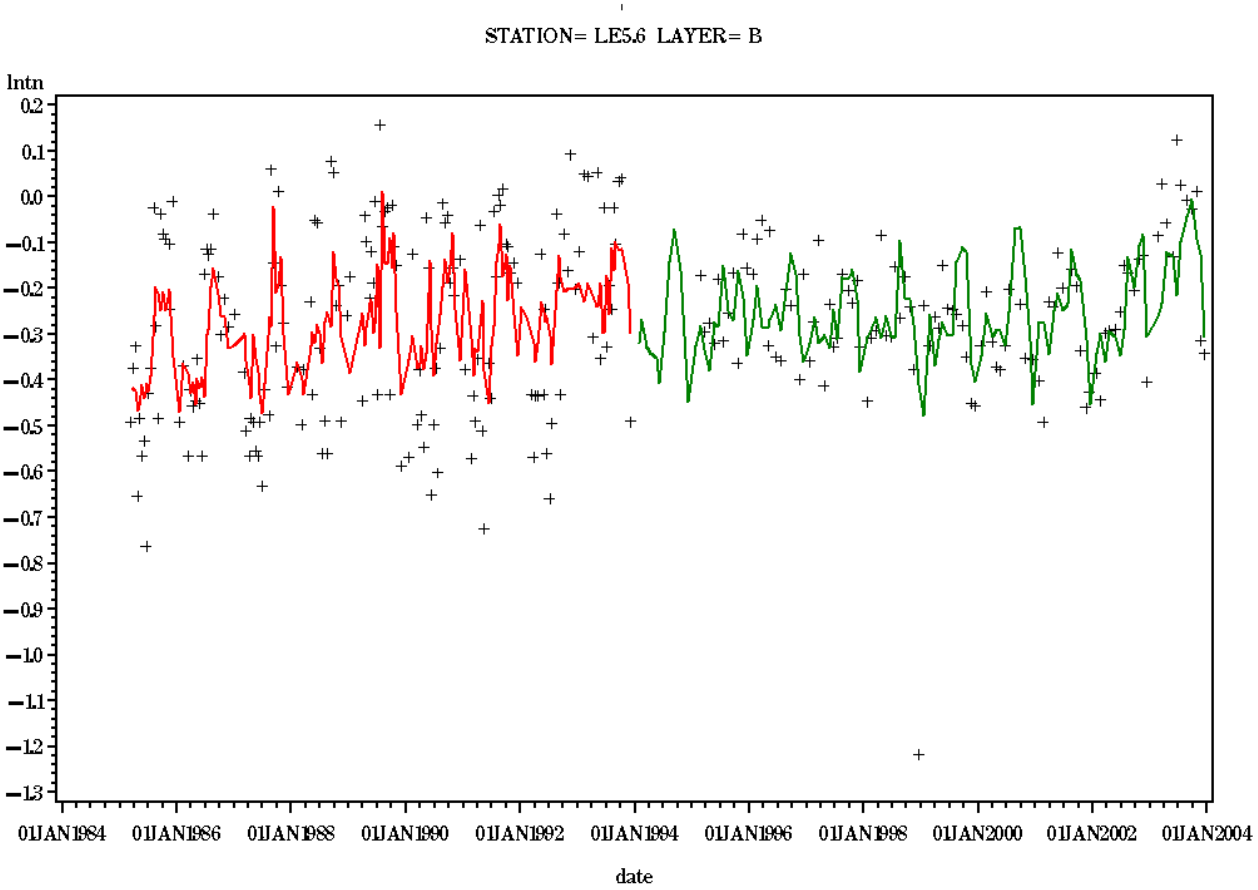
Root MSE = 0.1622 Total R-Square = 0.3599



Tributary	Station	Layer
James	LE5.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2809	0.0333	-8.44	<.0001
jan	-0.0482	0.0446	-1.08	0.2802
feb	0.0355	0.0442	0.80	0.4228
mar	-0.0095	0.0342	-0.28	0.7819
apr	0.0022	0.0338	0.07	0.9475
may	-0.0697	0.0325	-2.14	0.0330
jun	-0.1211	0.0329	-3.68	0.0003
jul	-0.0582	0.0337	-1.73	0.0857
aug	0.0774	0.0334	2.32	0.0212
sep	0.1102	0.0351	3.14	0.0019
oct	0.1415	0.0368	3.84	0.0002
nov	-0.0073	0.0385	-0.19	0.8489
dec	-0.0529	0.0414	-1.28	0.2025
rtemp	-0.0104	0.0057	-1.81	0.0715
cyear	0.0192	0.0059	3.27	0.0012
mc	-0.1044	0.0531	-1.97	0.0505
mc_cyear	-0.0049	0.0094	-0.52	0.6065
flow20	0.1338	0.0393	3.40	0.0008
flow0	0.0892	0.0338	2.64	0.0088
AR1	-0.1120	0.0643	-1.74	0.0458

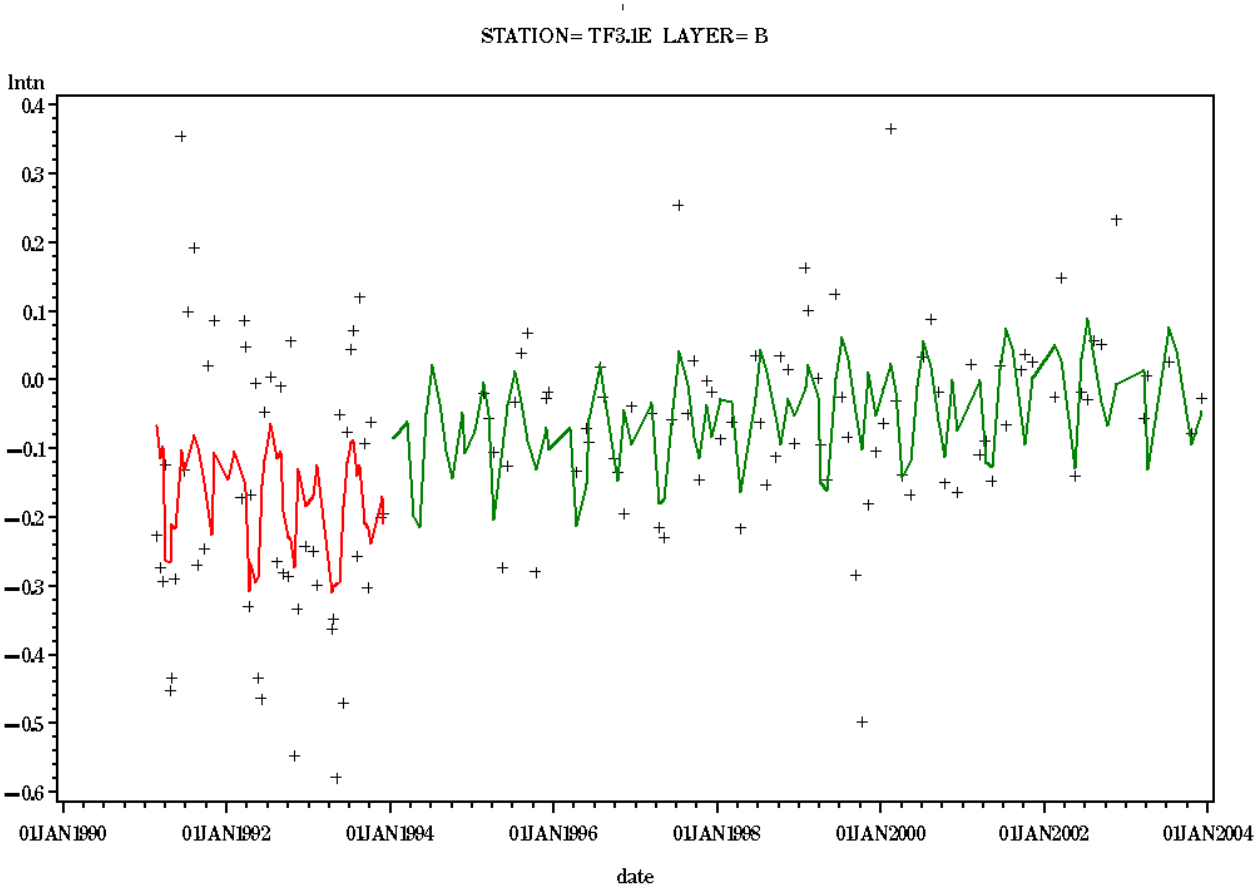
Root MSE = 0.1694 Total R-Square = 0.3435



Tributary	Station	Layer
James	LE5.6	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2038	0.0387	-5.27	<.0001
jan	-0.0538	0.0441	-1.22	0.2237
feb	-0.0074	0.0436	-0.17	0.8657
mar	-0.0576	0.0345	-1.67	0.0963
apr	-0.0607	0.0360	-1.69	0.0929
may	-0.0246	0.0334	-0.74	0.4620
jun	-0.0422	0.0339	-1.24	0.2152
jul	-0.0068	0.0352	-0.19	0.8461
aug	0.1217	0.0351	3.46	0.0006
sep	0.1128	0.0346	3.26	0.0013
oct	0.1002	0.0348	2.88	0.0043
nov	0.0241	0.0384	0.63	0.5312
dec	-0.1058	0.0397	-2.67	0.0082
rtemp	-0.0012	0.0055	-0.22	0.8246
cyear	0.0156	0.0068	2.28	0.0233
mc	-0.0762	0.0607	-1.26	0.2106
mc_cyear	-0.0103	0.0109	-0.94	0.3459
flow20	0.0733	0.0391	1.88	0.0618
flow70	-0.0839	0.0358	-2.35	0.0198
flow0	0.0849	0.0341	2.49	0.0135
AR1	-0.2331	0.0626	-3.72	0.0004

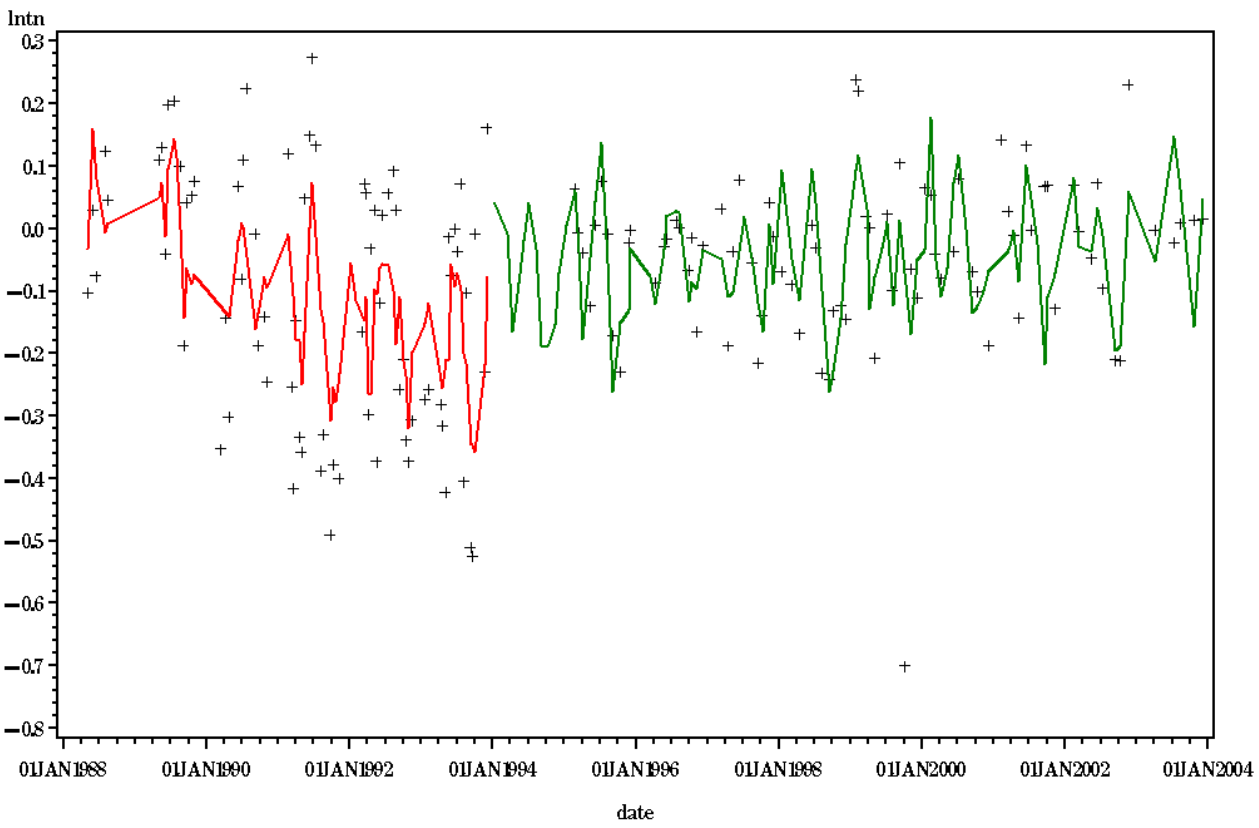
Root MSE = 0.1681 Total R-Square = 0.2957



Tributary	Station	Layer
Rappahannock	TF3.1E	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2168	0.0542	-4.00	0.0001
jan	0.0193	0.0704	0.27	0.7849
feb	0.0669	0.0577	1.16	0.2485
mar	0.0257	0.0405	0.63	0.5273
apr	-0.1160	0.0377	-3.07	0.0026
may	-0.1054	0.0433	-2.44	0.0163
jun	0.0304	0.0401	0.76	0.4507
jul	0.1004	0.0421	2.39	0.0187
aug	0.0566	0.0418	1.36	0.1780
sep	-0.0174	0.0418	-0.42	0.6786
oct	-0.0632	0.0403	-1.57	0.1192
nov	0.0260	0.0457	0.57	0.5699
dec	-0.0233	0.0481	-0.48	0.6290
rtemp	0.0051	0.0058	0.89	0.3766
cyear	-0.0259	0.0262	-0.99	0.3256
mc	0.1320	0.0643	2.05	0.0424
mc_cyear	0.0340	0.0272	1.25	0.2138
AR1	0.0584	0.0939	0.62	0.2693

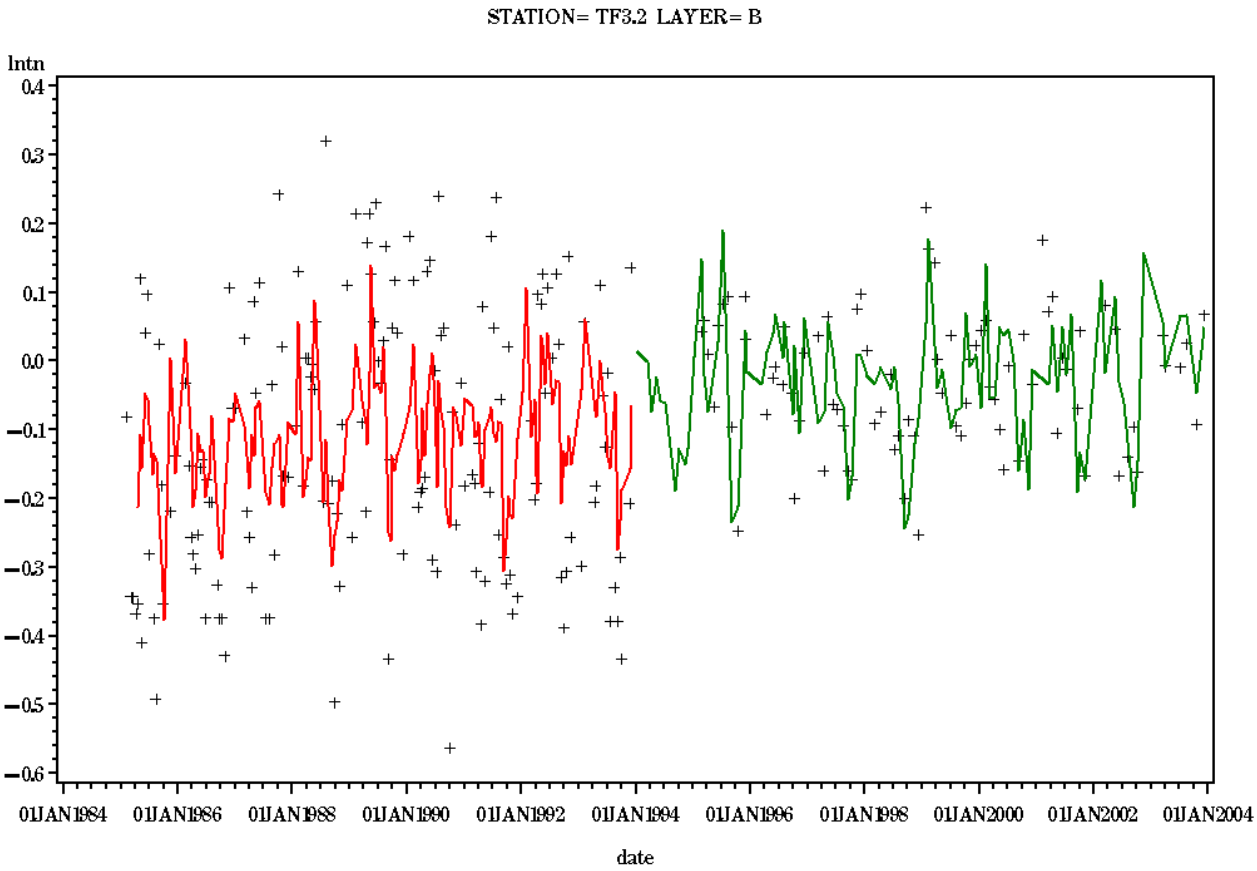
Root MSE = 0.1494 Total R-Square = 0.3151



Tributary	Station	Layer
Rappahannock	TF3.1B	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2216	0.0414	-5.35	<.0001
jan	0.0539	0.0648	0.83	0.4069
feb	0.1452	0.0529	2.75	0.0069
mar	0.0100	0.0400	0.25	0.8027
apr	-0.0862	0.0351	-2.45	0.0154
may	-0.0231	0.0390	-0.59	0.5543
jun	0.0918	0.0347	2.65	0.0092
jul	0.0864	0.0379	2.28	0.0242
aug	-0.0055	0.0368	-0.15	0.8805
sep	-0.1128	0.0352	-3.21	0.0017
oct	-0.1119	0.0346	-3.24	0.0015
nov	-0.0459	0.0384	-1.20	0.2342
dec	-0.0020	0.0467	-0.04	0.9666
rtemp	0.0015	0.0060	0.25	0.8043
cyear	-0.0422	0.0126	-3.34	0.0011
mc	0.1581	0.0578	2.74	0.0071
mc_cyear	0.0497	0.0147	3.37	0.0010
flow0	0.1565	0.0400	3.91	0.0001
flow30	-0.0762	0.0320	-2.38	0.0188
AR1	-0.1703	0.0864	-1.97	0.0290

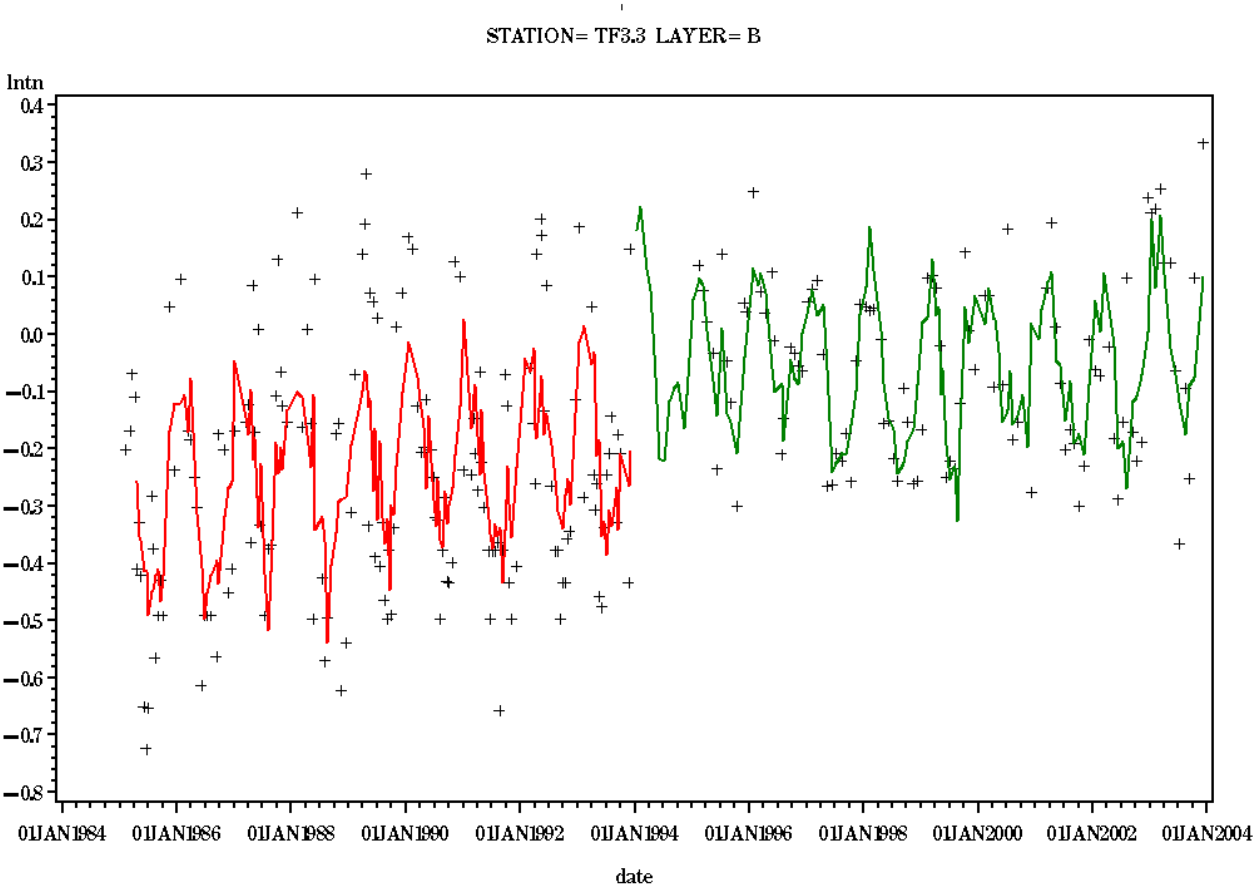
Root MSE = 0.1389 Total R-Square = 0.4272



Tributary	Station	Layer
Rappahannock	TF3.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0676	0.0273	-2.47	0.0142
jan	0.0156	0.0466	0.33	0.7382
feb	0.1585	0.0466	3.40	0.0008
mar	-0.0084	0.0313	-0.27	0.7896
apr	-0.0309	0.0284	-1.09	0.2785
may	0.0619	0.0313	1.98	0.0492
jun	0.0504	0.0300	1.68	0.0947
jul	0.0069	0.0309	0.22	0.8235
aug	-0.0049	0.0306	-0.16	0.8736
sep	-0.1317	0.0310	-4.25	<.0001
oct	-0.0857	0.0284	-3.02	0.0029
nov	-0.0401	0.0369	-1.09	0.2779
dec	0.0084	0.0370	0.23	0.8212
rtemp	-0.0096	0.0045	-2.12	0.0352
cyear	0.0070	0.0050	1.40	0.1641
mc	0.0343	0.0446	0.77	0.4435
mc_cyear	-0.0029	0.0087	-0.33	0.7398
flow0	0.0822	0.0364	2.26	0.0250
flow40	-0.0639	0.0273	-2.34	0.0200
flow10	0.0835	0.0337	2.48	0.0141
flow100	-0.0568	0.0285	-1.99	0.0474
AR1	0.0196	0.0690	0.28	0.3889

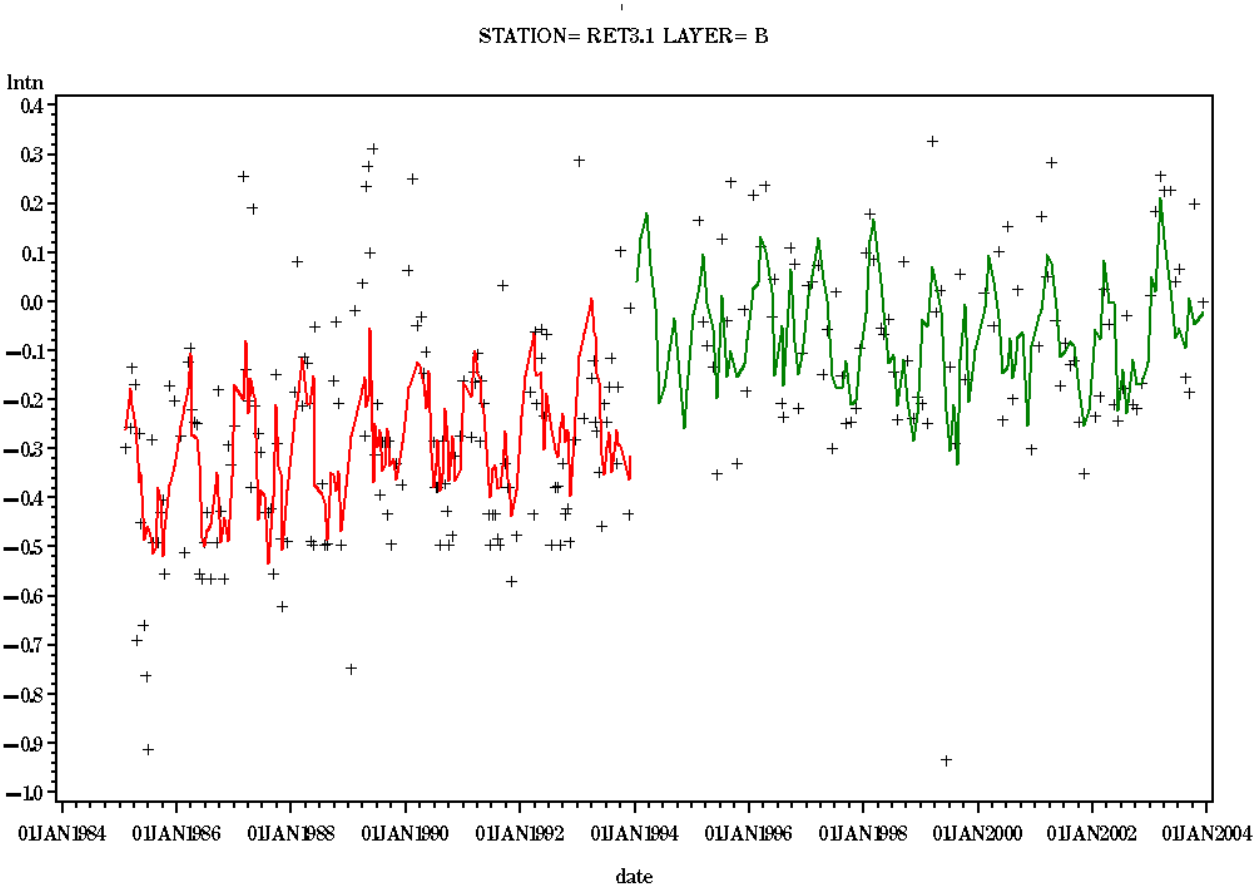
Root MSE = 0.1481 Total R-Square = 0.3265



Tributary	Station	Layer
Rappahannock	TF3.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1616	0.0373	-4.33	<.0001
jan	0.1490	0.0429	3.48	0.0006
feb	0.1303	0.0467	2.79	0.0057
mar	0.1455	0.0354	4.12	<.0001
apr	0.0820	0.0335	2.45	0.0150
may	-0.0001	0.0343	-0.00	0.9982
jun	-0.0837	0.0326	-2.57	0.0110
jul	-0.0983	0.0338	-2.91	0.0040
aug	-0.1472	0.0328	-4.49	<.0001
sep	-0.1103	0.0334	-3.30	0.0011
oct	-0.0718	0.0337	-2.13	0.0339
nov	-0.0431	0.0376	-1.14	0.2536
dec	0.0475	0.0375	1.27	0.2070
rtemp	-0.0040	0.0047	-0.85	0.3980
cyear	0.0142	0.0069	2.06	0.0407
mc	0.0966	0.0585	1.65	0.0999
mc_cyear	-0.0114	0.0108	-1.06	0.2916
flow10	0.1204	0.0269	4.47	<.0001
flow100	-0.0661	0.0311	-2.12	0.0349
AR1	-0.2441	0.0651	-3.75	0.0004

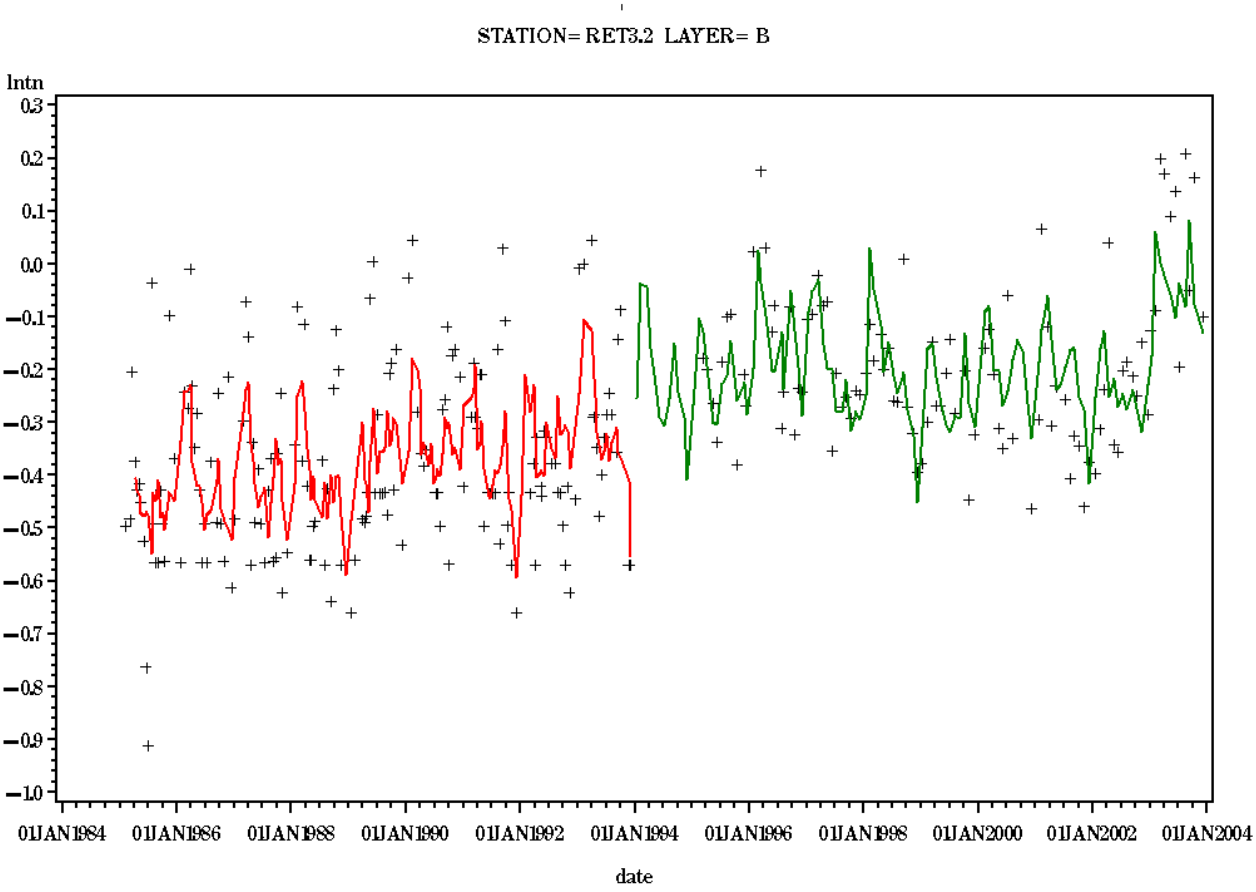
Root MSE = 0.1584 Total R-Square = 0.5221



Tributary	Station	Layer
Rappahannock	RET3.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2052	0.0340	-6.04	<.0001
jan	0.0815	0.0430	1.89	0.0595
feb	0.0931	0.0448	2.08	0.0387
mar	0.1754	0.0347	5.05	<.0001
apr	0.1096	0.0332	3.31	0.0011
may	0.0636	0.0351	1.81	0.0717
jun	-0.0902	0.0340	-2.65	0.0086
jul	-0.0522	0.0351	-1.49	0.1385
aug	-0.1143	0.0347	-3.29	0.0011
sep	-0.0121	0.0336	-0.36	0.7194
oct	-0.0668	0.0342	-1.96	0.0517
nov	-0.1355	0.0417	-3.25	0.0013
dec	-0.0520	0.0445	-1.17	0.2436
rtemp	-0.0081	0.0053	-1.53	0.1275
cyear	0.0169	0.0060	2.83	0.0051
mc	0.1195	0.0538	2.22	0.0274
mc_cyear	-0.0132	0.0096	-1.37	0.1729
flow10	0.1108	0.0274	4.04	<.0001
AR1	-0.1145	0.0649	-1.76	0.0441

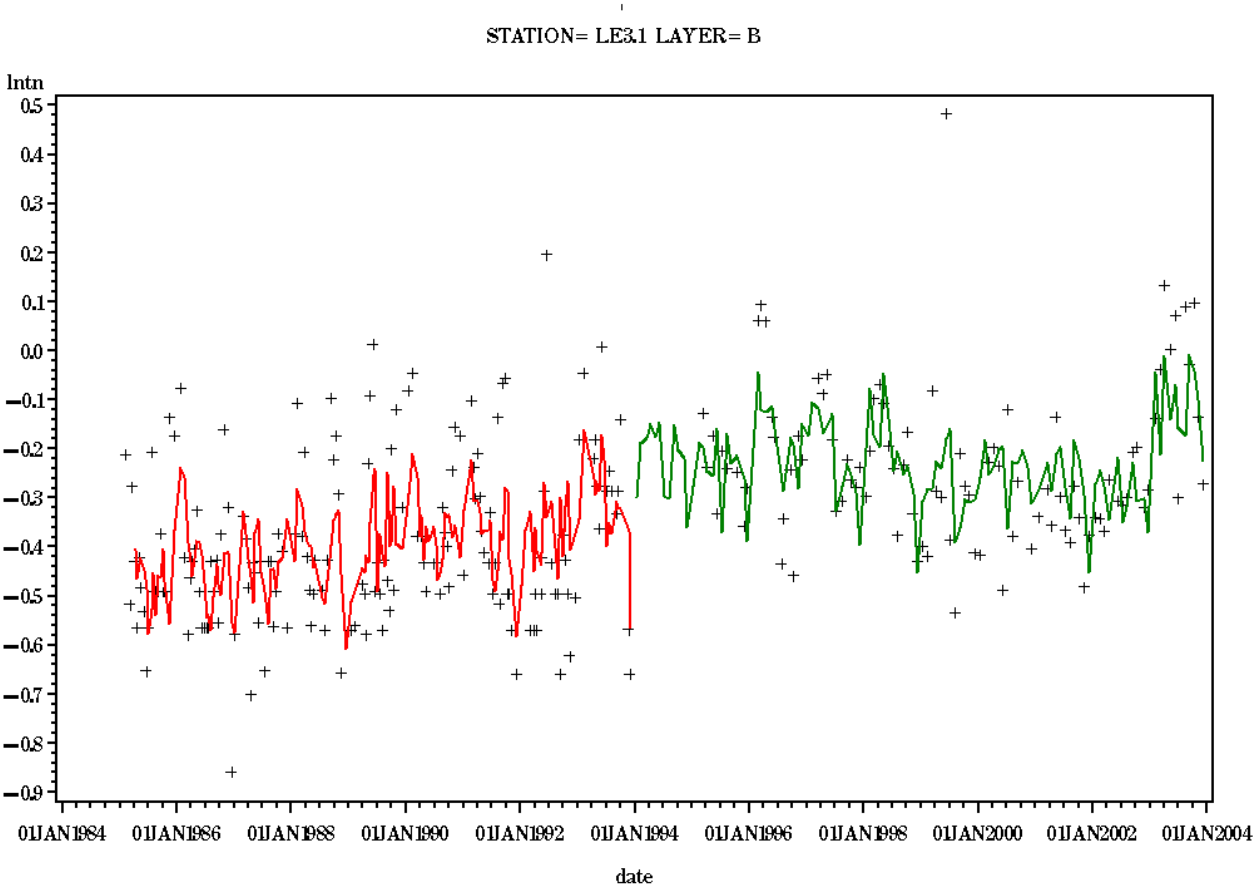
Root MSE = 0.1710 Total R-Square = 0.4847



Tributary	Station	Layer
Rappahannock	RET3.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3394	0.0304	-11.18	<.0001
jan	-0.0091	0.0364	-0.25	0.8039
feb	0.1252	0.0393	3.19	0.0016
mar	0.1370	0.0299	4.59	<.0001
apr	0.0259	0.0283	0.91	0.3622
may	-0.0233	0.0294	-0.79	0.4298
jun	-0.0388	0.0302	-1.29	0.1997
jul	-0.0323	0.0298	-1.08	0.2806
aug	-0.0375	0.0290	-1.29	0.1979
sep	0.0333	0.0294	1.13	0.2595
oct	-0.0127	0.0291	-0.44	0.6628
nov	-0.0489	0.0345	-1.42	0.1578
dec	-0.1188	0.0341	-3.48	0.0006
rtemp	-0.0026	0.0042	-0.64	0.5249
cyear	0.0064	0.0055	1.17	0.2437
mc	0.0947	0.0477	1.98	0.0485
mc_cyear	0.0049	0.0088	0.56	0.5763
flow30	0.0748	0.0256	2.92	0.0039
flow80	0.0510	0.0248	2.06	0.0407
flow10	0.0558	0.0251	2.23	0.0269
AR1	-0.1462	0.0648	-2.26	0.0158

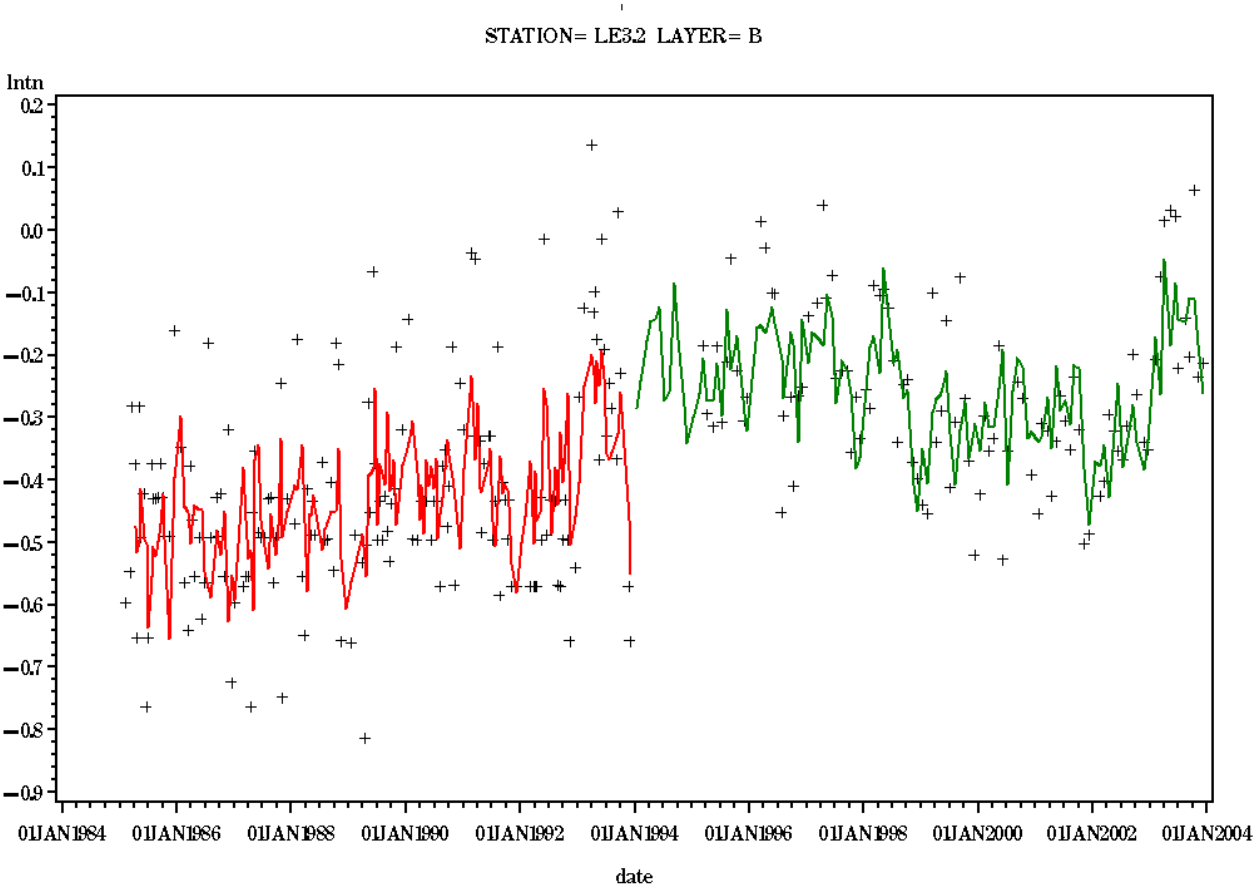
Root MSE = 0.1443 Total R-Square = 0.4618



Tributary	Station	Layer
Rappahannock	LE3.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3453	0.0356	-9.70	<.0001
jan	-0.0122	0.0415	-0.29	0.7687
feb	0.0973	0.0432	2.25	0.0254
mar	0.0447	0.0319	1.40	0.1622
apr	0.0140	0.0298	0.47	0.6394
may	0.0212	0.0315	0.67	0.5027
jun	0.0455	0.0306	1.49	0.1382
jul	-0.0610	0.0312	-1.95	0.0519
aug	-0.0586	0.0302	-1.94	0.0537
sep	0.0189	0.0304	0.62	0.5356
oct	0.0260	0.0311	0.84	0.4038
nov	-0.0275	0.0339	-0.81	0.4187
dec	-0.1082	0.0349	-3.10	0.0022
rtemp	-0.0058	0.0052	-1.11	0.2678
cyear	0.0099	0.0063	1.56	0.1206
mc	0.0997	0.0572	1.74	0.0827
mc_cyear	-0.0058	0.0102	-0.57	0.5689
flow40	0.0651	0.0258	2.52	0.0123
flow90	0.0868	0.0247	3.51	0.0005
AR1	-0.2670	0.0634	-4.21	0.0001

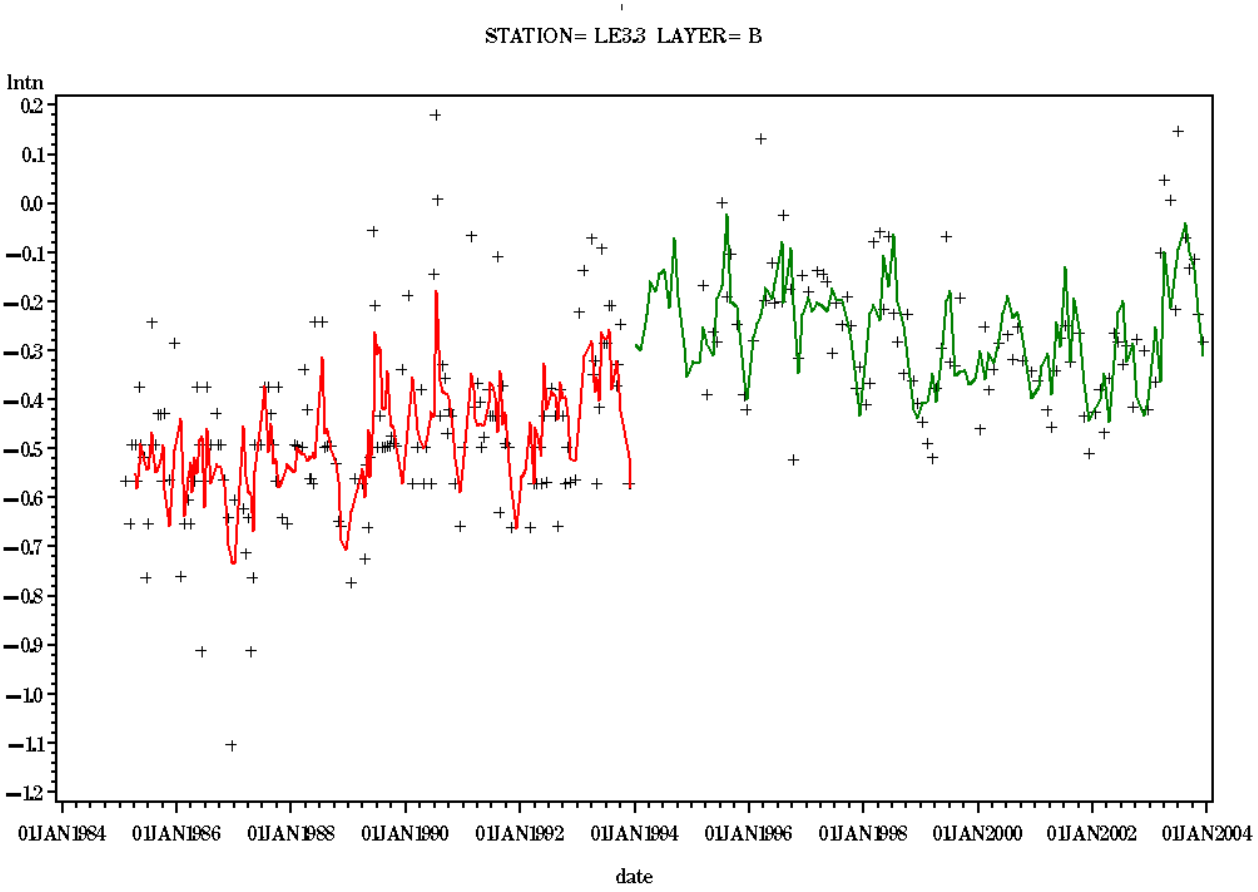
Root MSE = 0.1468 Total R-Square = 0.4227



Tributary	Station	Layer
Rappahannock	LE3.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3684	0.0317	-11.62	<.0001
jan	-0.0194	0.0358	-0.54	0.5879
feb	0.0305	0.0360	0.85	0.3982
mar	0.0353	0.0273	1.29	0.1971
apr	-0.0044	0.0259	-0.17	0.8662
may	0.0345	0.0278	1.24	0.2169
jun	0.0570	0.0265	2.16	0.0322
jul	-0.0289	0.0273	-1.06	0.2914
aug	-0.0142	0.0273	-0.52	0.6035
sep	0.0313	0.0262	1.20	0.2331
oct	0.0415	0.0263	1.58	0.1163
nov	-0.0815	0.0295	-2.77	0.0061
dec	-0.0817	0.0296	-2.76	0.0062
rtemp	-0.0085	0.0046	-1.86	0.0638
cyear	0.0135	0.0057	2.36	0.0190
mc	0.1268	0.0510	2.49	0.0136
mc_cyear	-0.0159	0.0091	-1.74	0.0834
flow40	0.0990	0.0219	4.53	<.0001
flow90	0.0720	0.0213	3.38	0.0008
AR1	-0.2993	0.0621	-4.82	<.0001

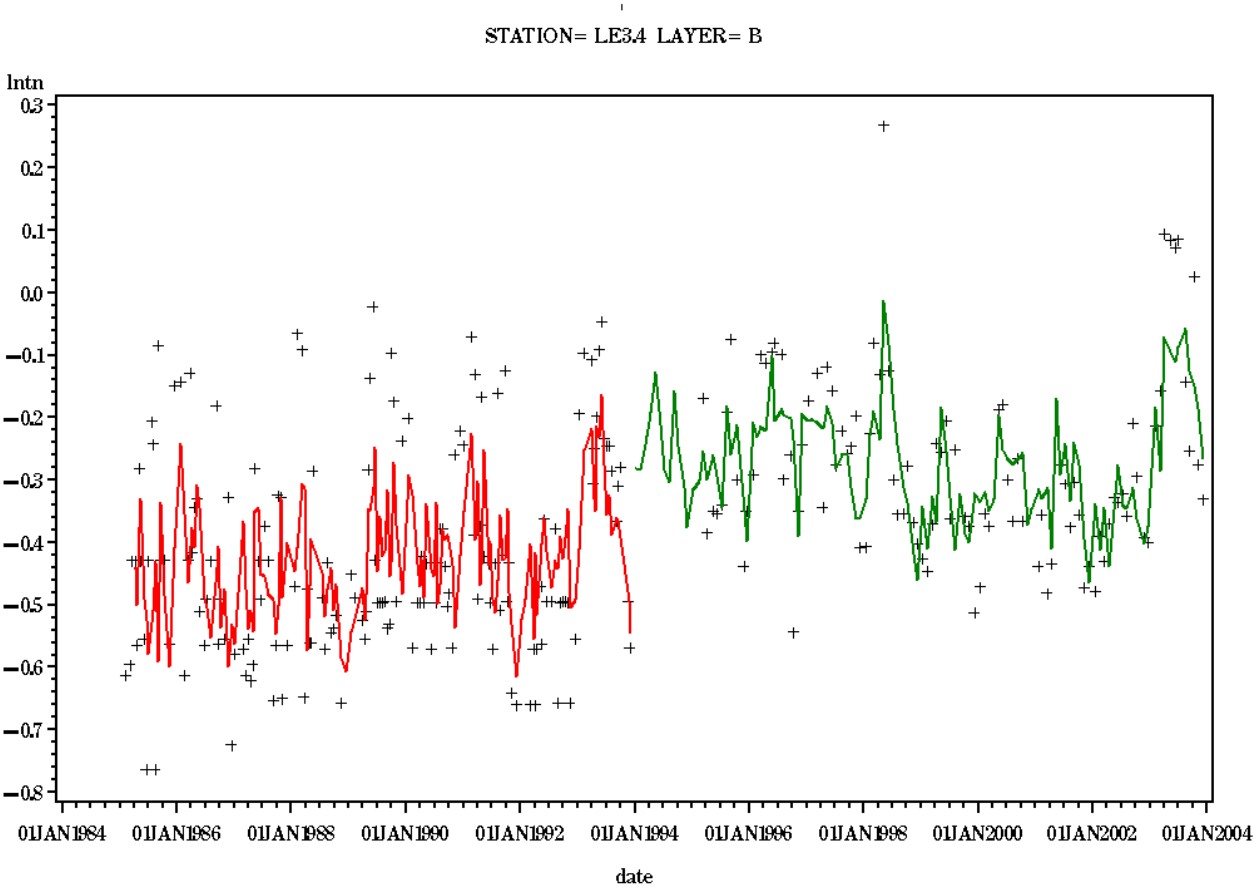
Root MSE = 0.1275 Total R-Square = 0.5026



Tributary	Station	Layer
Rappahannock	LE3.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4122	0.0314	-13.14	<.0001
jan	-0.0493	0.0340	-1.45	0.1482
feb	-0.0159	0.0382	-0.42	0.6778
mar	0.0031	0.0277	0.11	0.9121
apr	-0.0206	0.0262	-0.79	0.4316
may	0.0058	0.0279	0.21	0.8347
jun	0.0640	0.0276	2.32	0.0212
jul	0.1259	0.0276	4.56	<.0001
aug	0.0411	0.0270	1.52	0.1293
sep	0.0479	0.0273	1.76	0.0800
oct	0.0108	0.0275	0.39	0.6958
nov	-0.0897	0.0308	-2.91	0.0039
dec	-0.1231	0.0319	-3.86	0.0001
rtemp	0.0031	0.0043	0.72	0.4700
cyear	0.0151	0.0056	2.70	0.0075
mc	0.1679	0.0499	3.36	0.0009
mc_cyear	-0.0189	0.0090	-2.11	0.0360
flow40	0.1006	0.0227	4.43	<.0001
flow90	0.0602	0.0223	2.70	0.0075
AR1	-0.2704	0.0635	-4.26	<.0001

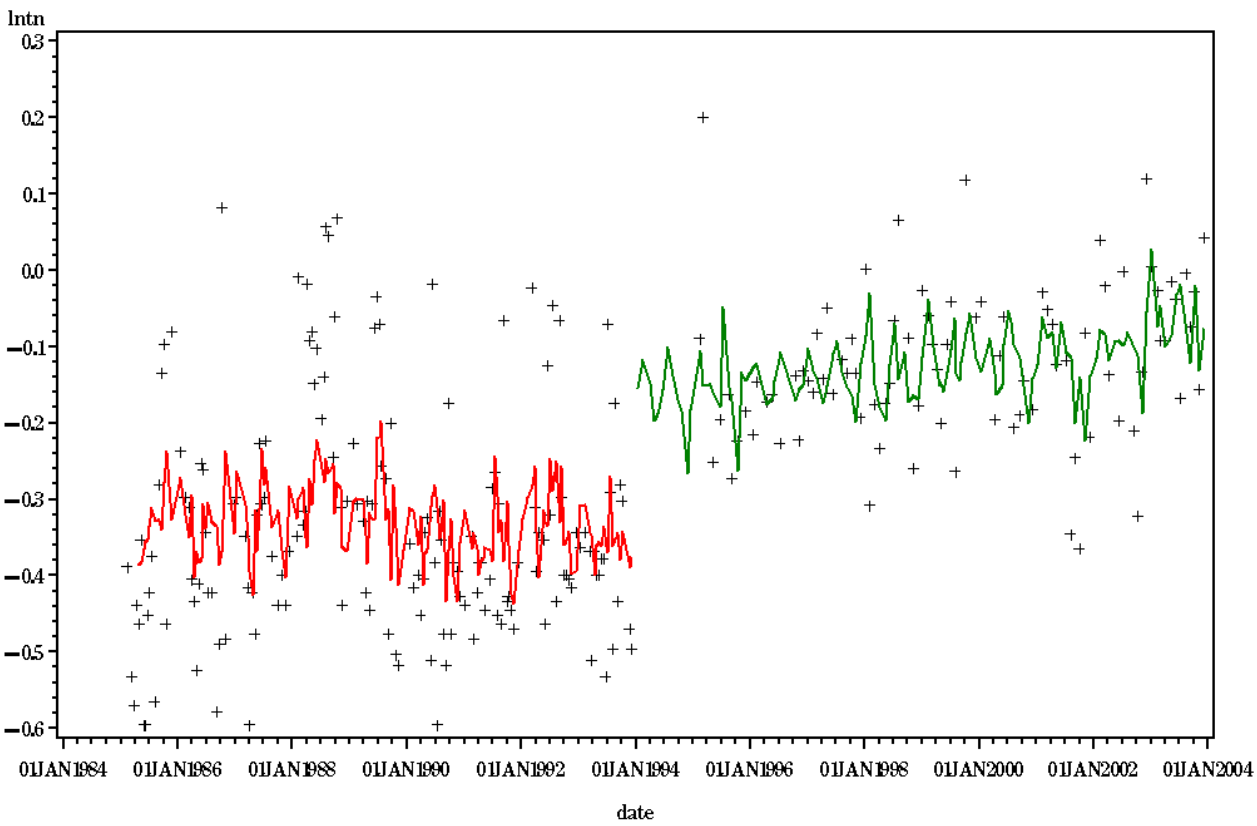
Root MSE = 0.1299 Total R-Square = 0.5705



Tributary	Station	Layer
Rappahannock	LE3.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4057	0.0354	-11.47	<.0001
jan	-0.0024	0.0344	-0.07	0.9450
feb	0.0302	0.0381	0.79	0.4286
mar	0.0236	0.0290	0.81	0.4160
apr	-0.0112	0.0284	-0.40	0.6931
may	0.0938	0.0302	3.11	0.0021
jun	0.0311	0.0293	1.06	0.2894
jul	0.0003	0.0295	0.01	0.9907
aug	-0.0182	0.0290	-0.63	0.5295
sep	0.0127	0.0286	0.44	0.6586
oct	0.0093	0.0288	0.32	0.7459
nov	-0.0831	0.0314	-2.64	0.0088
dec	-0.0861	0.0323	-2.66	0.0083
rtemp	-0.0059	0.0049	-1.21	0.2281
cyear	0.0047	0.0064	0.74	0.4600
mc	0.1244	0.0562	2.21	0.0280
mc_cyear	-0.0026	0.0101	-0.26	0.7955
flow40	0.0907	0.0240	3.78	0.0002
flow90	0.0804	0.0227	3.54	0.0005
AR1	-0.3296	0.0620	-5.32	<.0001

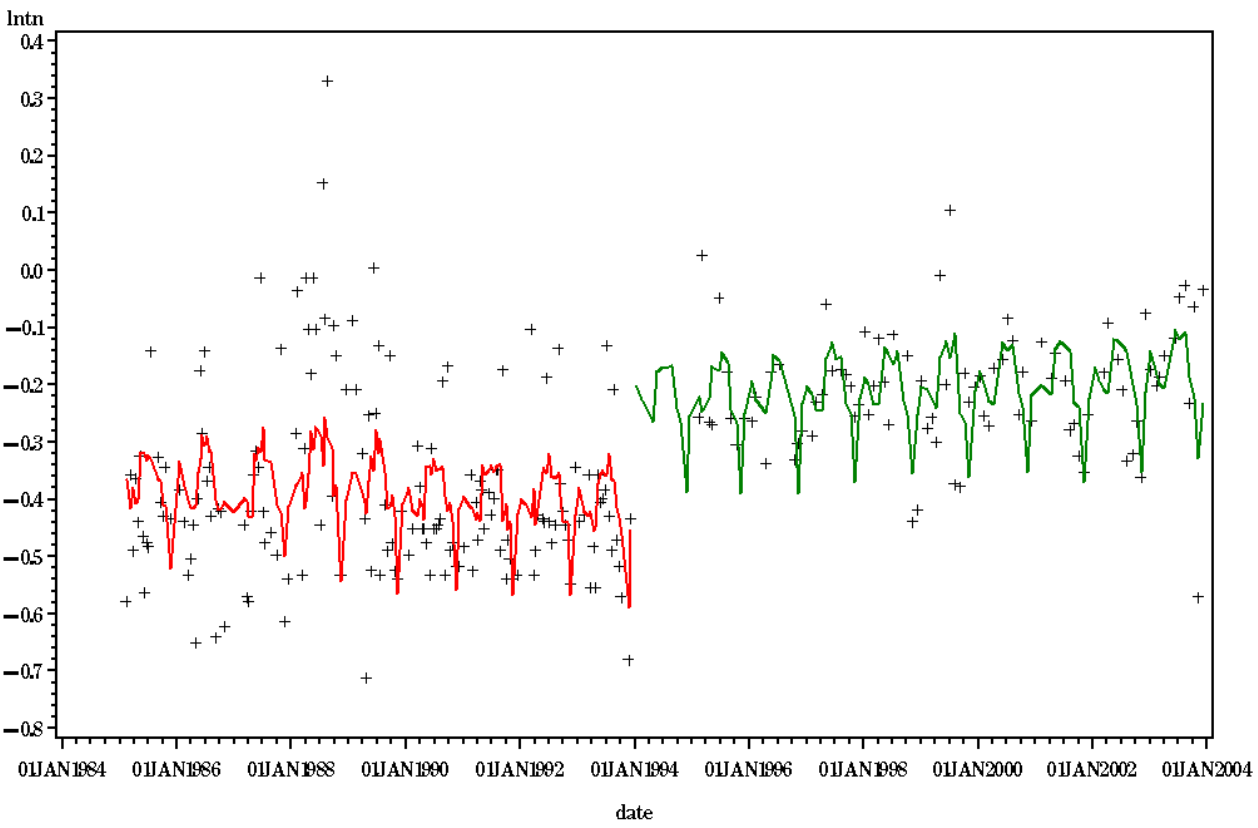
Root MSE = 0.1355 Total R-Square = 0.4493



Tributary	Station	Layer
York	TF4.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3450	0.0296	-11.64	<.0001
jan	0.0203	0.0339	0.60	0.5511
feb	0.0351	0.0330	1.06	0.2887
mar	0.0091	0.0286	0.32	0.7514
apr	-0.0413	0.0275	-1.51	0.1337
may	-0.0168	0.0287	-0.59	0.5579
jun	0.0124	0.0276	0.45	0.6548
jul	0.0513	0.0288	1.78	0.0759
aug	0.0105	0.0290	0.36	0.7169
sep	-0.0052	0.0300	-0.17	0.8635
oct	-0.0117	0.0269	-0.43	0.6644
nov	-0.0480	0.0322	-1.49	0.1372
dec	-0.0156	0.0314	-0.50	0.6196
rtemp	-0.0006	0.0033	-0.17	0.8630
cyear	-0.0024	0.0055	-0.43	0.6659
mc	0.1892	0.0500	3.78	0.0002
mc_cyear	0.0097	0.0090	1.07	0.2853
flow10	0.0593	0.0222	2.67	0.0081
flow150	-0.0437	0.0245	-1.78	0.0761
AR1	-0.2439	0.0651	-3.75	0.0004

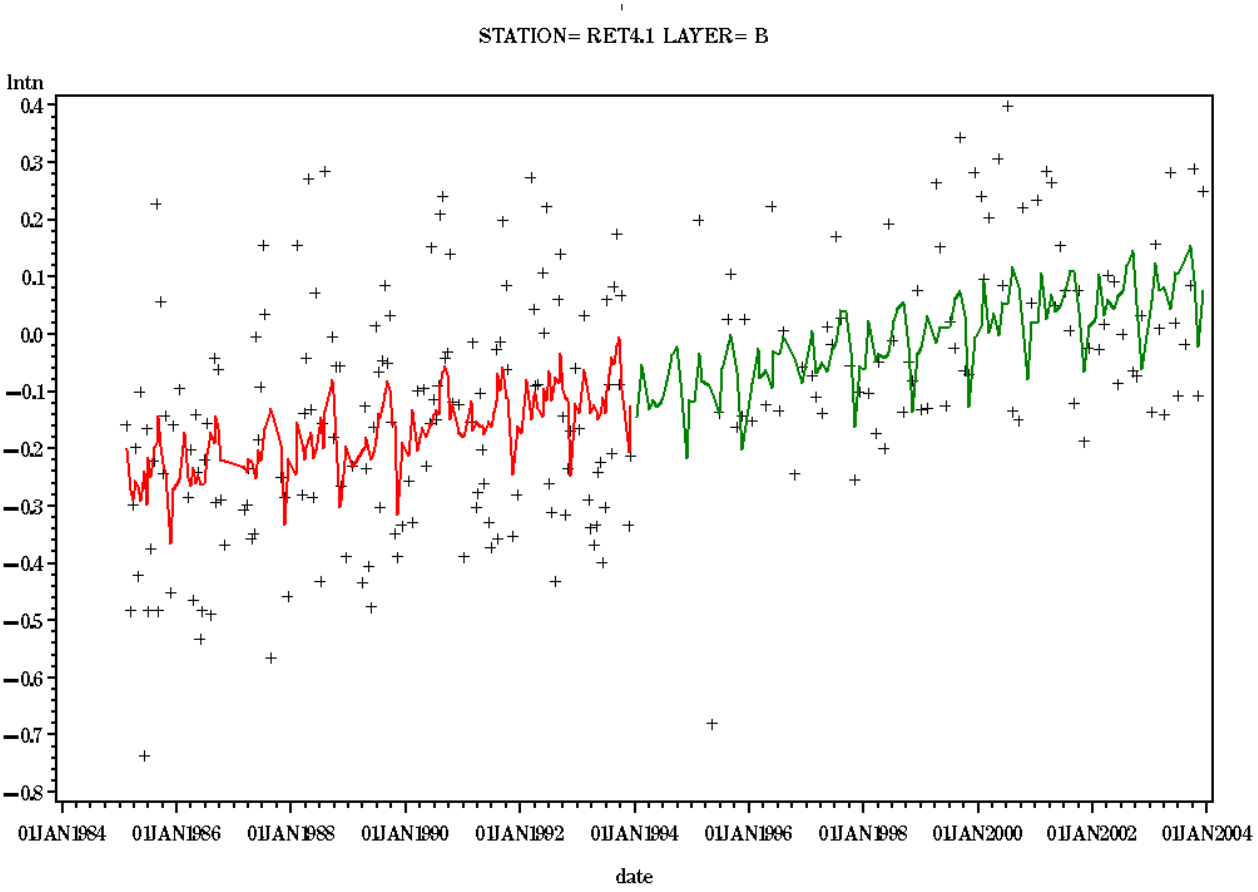
Root MSE = 0.1310 Total R-Square = 0.4450



Tributary	Station	Layer
York	TF4.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4210	0.0273	-15.42	<.0001
jan	0.0222	0.0388	0.57	0.5670
feb	0.0014	0.0336	0.04	0.9666
mar	-0.0172	0.0283	-0.61	0.5443
apr	-0.0278	0.0273	-1.02	0.3080
may	0.0557	0.0296	1.88	0.0613
jun	0.0684	0.0280	2.44	0.0153
jul	0.0641	0.0280	2.29	0.0229
aug	0.0640	0.0305	2.10	0.0372
sep	-0.0128	0.0299	-0.43	0.6682
oct	-0.0355	0.0272	-1.31	0.1927
nov	-0.1585	0.0328	-4.82	<.0001
dec	-0.0240	0.0328	-0.73	0.4645
rtemp	-0.0012	0.0033	-0.37	0.7087
cyear	-0.0057	0.0050	-1.16	0.2486
mc	0.1891	0.0464	4.07	<.0001
mc_cyear	0.0109	0.0082	1.32	0.1867
AR1	-0.1331	0.0654	-2.04	0.0253

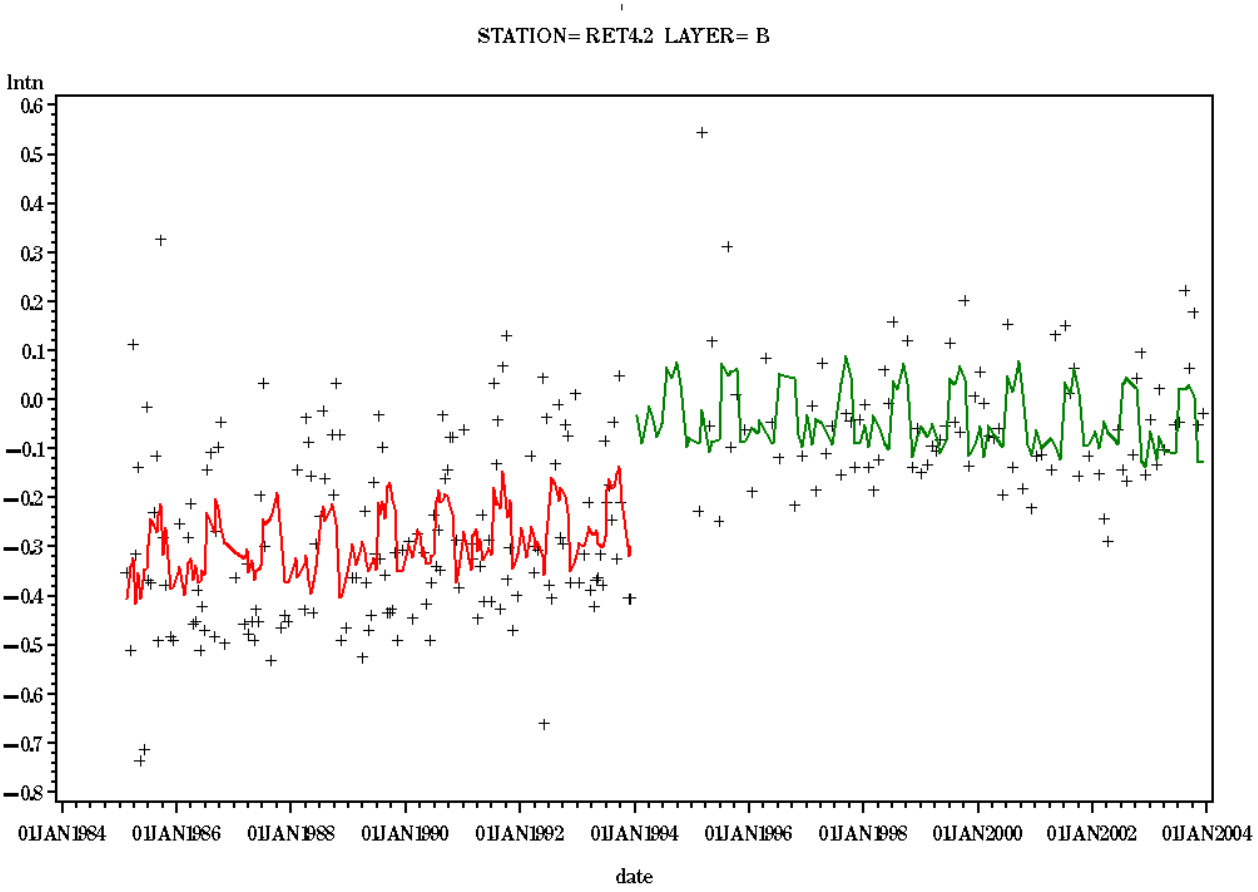
Root MSE = 0.1382 Total R-Square = 0.3796



Tributary	Station	Layer
York	RET4.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0849	0.0338	-2.51	0.0127
jan	-0.0359	0.0533	-0.67	0.5016
feb	0.0427	0.0490	0.87	0.3852
mar	-0.0216	0.0380	-0.57	0.5707
apr	-0.0059	0.0366	-0.16	0.8727
may	-0.0239	0.0363	-0.66	0.5106
jun	-0.0038	0.0354	-0.11	0.9150
jul	0.0221	0.0365	0.61	0.5457
aug	0.0638	0.0372	1.71	0.0880
sep	0.0782	0.0387	2.02	0.0443
oct	0.0125	0.0356	0.35	0.7268
nov	-0.1169	0.0442	-2.64	0.0088
dec	-0.0113	0.0439	-0.26	0.7979
rtemp	-0.0022	0.0058	-0.37	0.7090
cyear	0.0186	0.0060	3.08	0.0023
mc	-0.0180	0.0592	-0.30	0.7617
mc_cyear	0.0025	0.0103	0.25	0.8052
AR1	-0.0822	0.0666	-1.23	0.1134

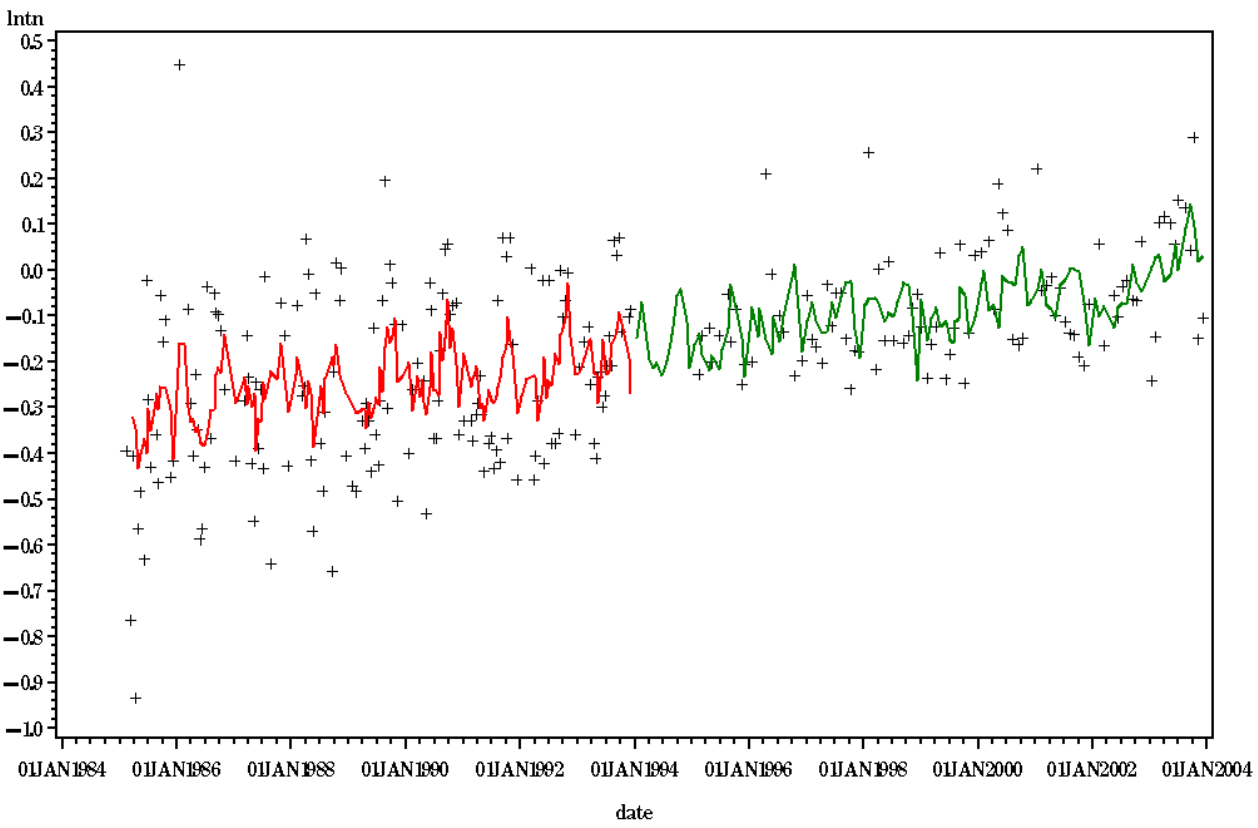
Root MSE = 0.1801 Total R-Square = 0.2934



Tributary	Station	Layer
York	RET4.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2444	0.0246	-9.93	<.0001
jan	-0.0130	0.0430	-0.30	0.7626
feb	-0.0554	0.0402	-1.38	0.1699
mar	-0.0025	0.0317	-0.08	0.9371
apr	-0.0299	0.0292	-1.02	0.3067
may	-0.0529	0.0329	-1.61	0.1099
jun	-0.0430	0.0296	-1.45	0.1473
jul	0.0826	0.0302	2.74	0.0067
aug	0.0710	0.0308	2.30	0.0222
sep	0.1027	0.0336	3.06	0.0025
oct	0.0643	0.0293	2.20	0.0291
nov	-0.0662	0.0396	-1.67	0.0959
dec	-0.0577	0.0368	-1.57	0.1182
rtemp	0.0036	0.0051	0.71	0.4796
cyear	0.0102	0.0044	2.30	0.0221
mc	0.2214	0.0440	5.03	<.0001
mc_cyear	-0.0139	0.0077	-1.81	0.0720
AR1	0.0936	0.0664	1.41	0.0843

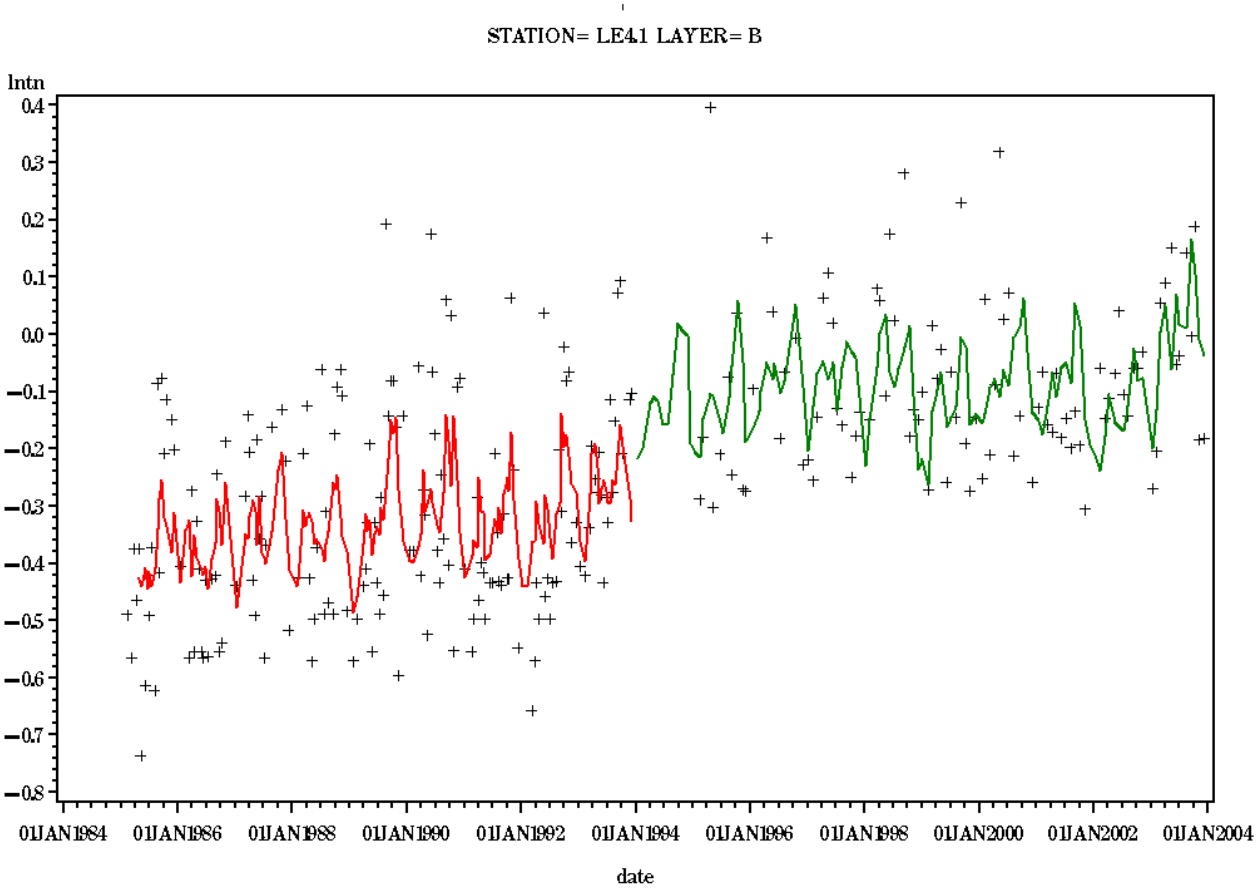
Root MSE = 0.1565 Total R-Square = 0.4315



Tributary	Station	Layer
York	RET4.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1771	0.0314	-5.64	<.0001
jan	0.0039	0.0442	0.09	0.9305
feb	0.0051	0.0443	0.12	0.9082
mar	-0.0126	0.0334	-0.38	0.7065
apr	-0.0361	0.0325	-1.11	0.2677
may	-0.0607	0.0328	-1.85	0.0660
jun	-0.0294	0.0325	-0.90	0.3671
jul	-0.0252	0.0326	-0.77	0.4403
aug	0.0183	0.0336	0.55	0.5859
sep	0.0824	0.0343	2.40	0.0171
oct	0.0860	0.0317	2.71	0.0072
nov	0.0231	0.0404	0.57	0.5686
dec	-0.0548	0.0396	-1.38	0.1681
rtemp	-0.0105	0.0050	-2.10	0.0366
cyear	0.0149	0.0057	2.61	0.0097
mc	0.0087	0.0520	0.17	0.8671
mc_cyear	0.0047	0.0093	0.51	0.6138
flow70	0.0700	0.0270	2.59	0.0102
AR1	-0.1014	0.0657	-1.54	0.0668

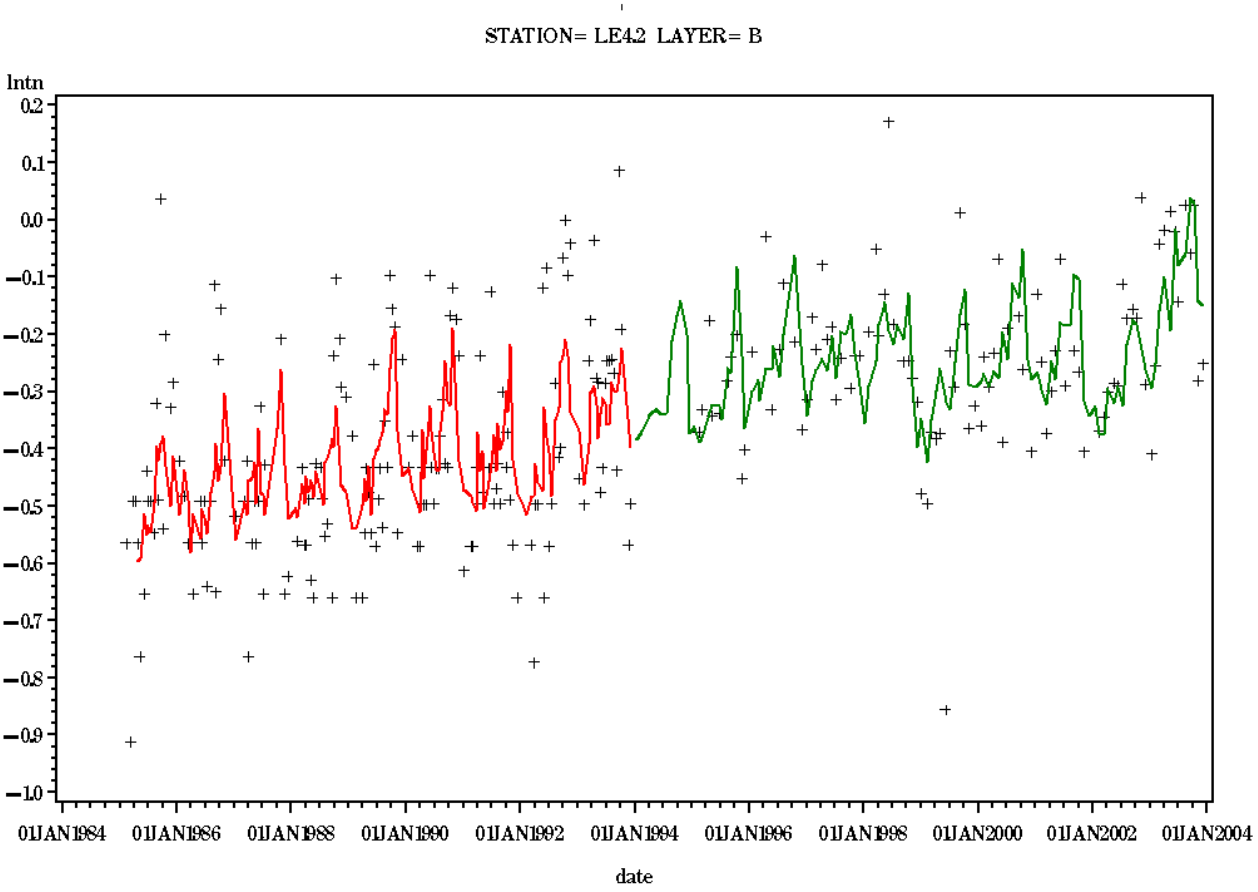
Root MSE = 0.1626 Total R-Square = 0.3461



Tributary	Station	Layer
York	LE4.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2723	0.0285	-9.55	<.0001
jan	-0.0952	0.0433	-2.20	0.0287
feb	-0.0786	0.0421	-1.87	0.0632
mar	-0.0184	0.0330	-0.56	0.5782
apr	0.0320	0.0308	1.04	0.3003
may	-0.0125	0.0318	-0.39	0.6959
jun	-0.0064	0.0308	-0.21	0.8370
jul	-0.0371	0.0316	-1.18	0.2408
aug	0.0173	0.0313	0.55	0.5825
sep	0.1098	0.0340	3.23	0.0014
oct	0.1041	0.0313	3.33	0.0010
nov	0.0194	0.0379	0.51	0.6088
dec	-0.0344	0.0391	-0.88	0.3798
rtemp	-0.0072	0.0051	-1.41	0.1590
cyear	0.0128	0.0053	2.43	0.0159
mc	0.1381	0.0483	2.86	0.0047
mc_cyear	-0.0019	0.0087	-0.22	0.8252
flow100	0.0759	0.0276	2.75	0.0065
flow0	0.0461	0.0253	1.82	0.0693
AR1	-0.0371	0.0657	-0.56	0.2884

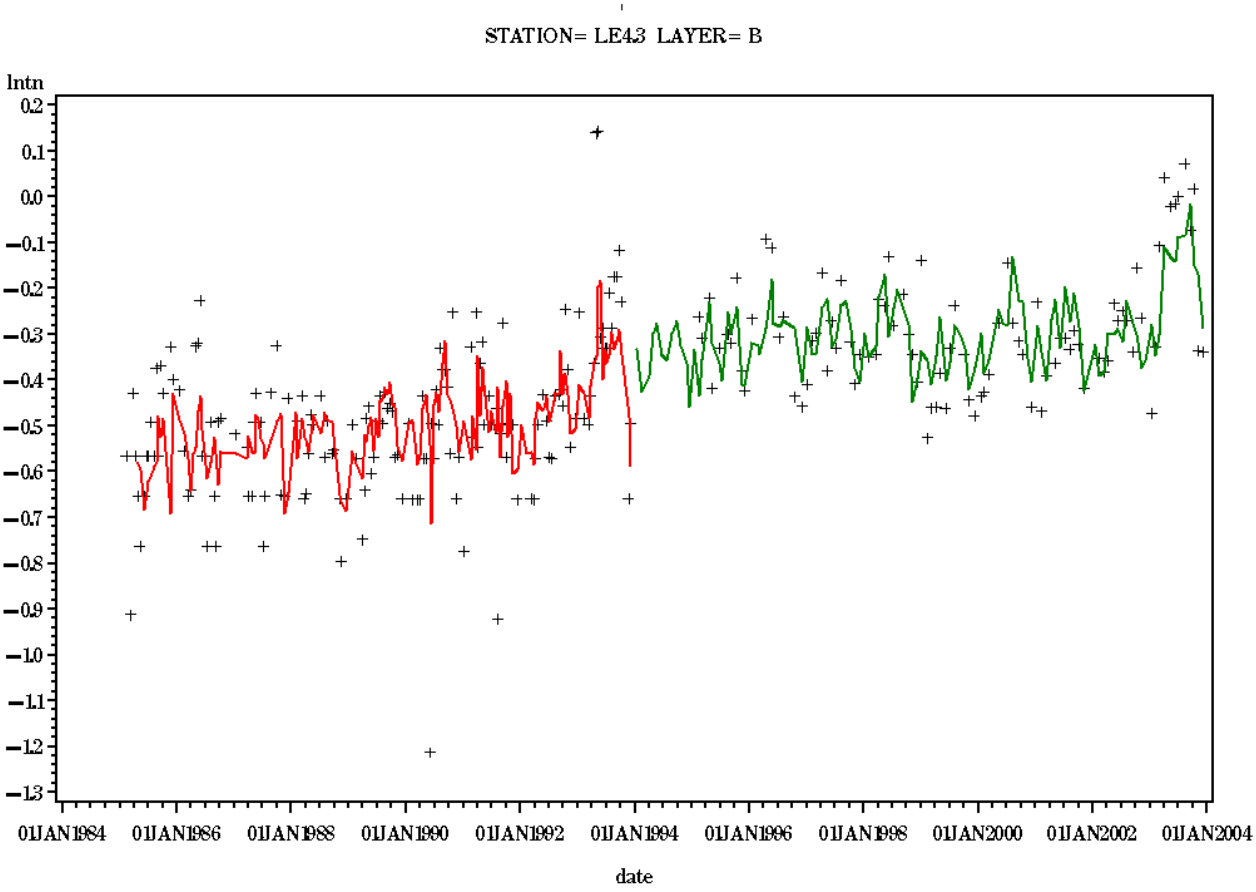
Root MSE = 0.1595 Total R-Square = 0.4455



Tributary	Station	Layer
York	LE4.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3369	0.0267	-12.63	<.0001
jan	-0.0647	0.0387	-1.67	0.0961
feb	-0.0683	0.0363	-1.88	0.0612
mar	-0.0663	0.0293	-2.26	0.0247
apr	-0.0104	0.0283	-0.37	0.7135
may	-0.0373	0.0292	-1.28	0.2035
jun	0.0088	0.0279	0.31	0.7536
jul	-0.0328	0.0286	-1.15	0.2515
aug	0.0553	0.0302	1.83	0.0682
sep	0.0946	0.0307	3.08	0.0023
oct	0.1386	0.0277	5.00	<.0001
nov	0.0092	0.0340	0.27	0.7874
dec	-0.0267	0.0351	-0.76	0.4479
rtemp	-0.0085	0.0050	-1.69	0.0922
cyear	0.0186	0.0049	3.78	0.0002
mc	0.0133	0.0448	0.30	0.7675
mc_cyear	-0.0003	0.0080	-0.04	0.9694
flow0	0.0613	0.0231	2.66	0.0084
flow100	0.0745	0.0244	3.06	0.0025
AR1	-0.0672	0.0659	-1.02	0.1582

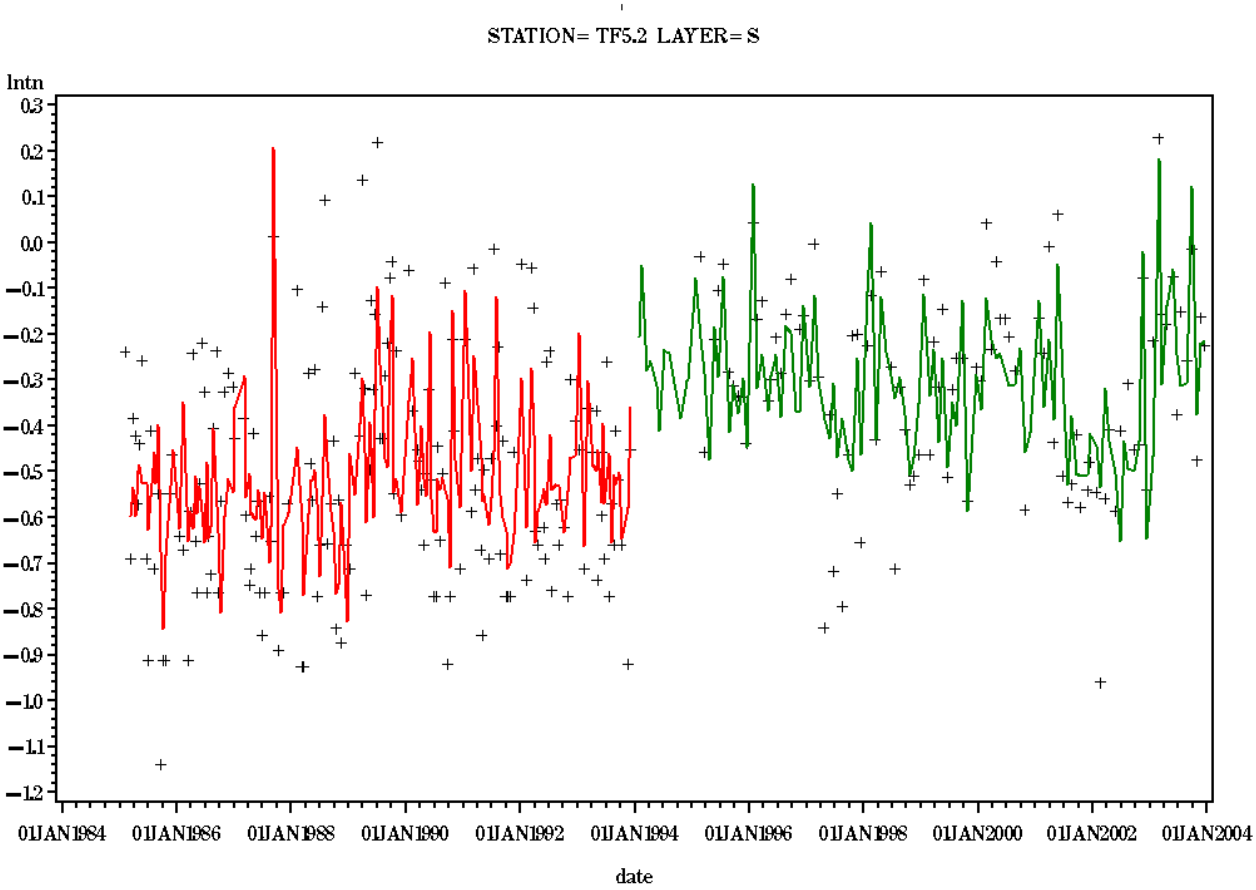
Root MSE = 0.1432 Total R-Square = 0.4525



Tributary	Station	Layer
York	LE4.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4031	0.0313	-12.87	<.0001
jan	0.0084	0.0346	0.24	0.8096
feb	-0.0487	0.0324	-1.50	0.1350
mar	-0.0539	0.0281	-1.92	0.0566
apr	0.0391	0.0280	1.39	0.1648
may	0.0499	0.0273	1.83	0.0692
jun	-0.0006	0.0291	-0.02	0.9837
jul	-0.0025	0.0280	-0.09	0.9279
aug	0.0673	0.0272	2.47	0.0142
sep	0.0711	0.0289	2.46	0.0148
oct	0.0378	0.0274	1.38	0.1692
nov	-0.0894	0.0307	-2.91	0.0040
dec	-0.0784	0.0319	-2.46	0.0147
rtemp	0.0012	0.0045	0.26	0.7970
cyear	0.0220	0.0058	3.77	0.0002
mc	0.0323	0.0519	0.62	0.5339
mc_cyear	-0.0059	0.0093	-0.63	0.5291
flow150	0.0753	0.0234	3.21	0.0015
flow40	0.0460	0.0227	2.03	0.0435
AR1	-0.3044	0.0644	-4.73	<.0001

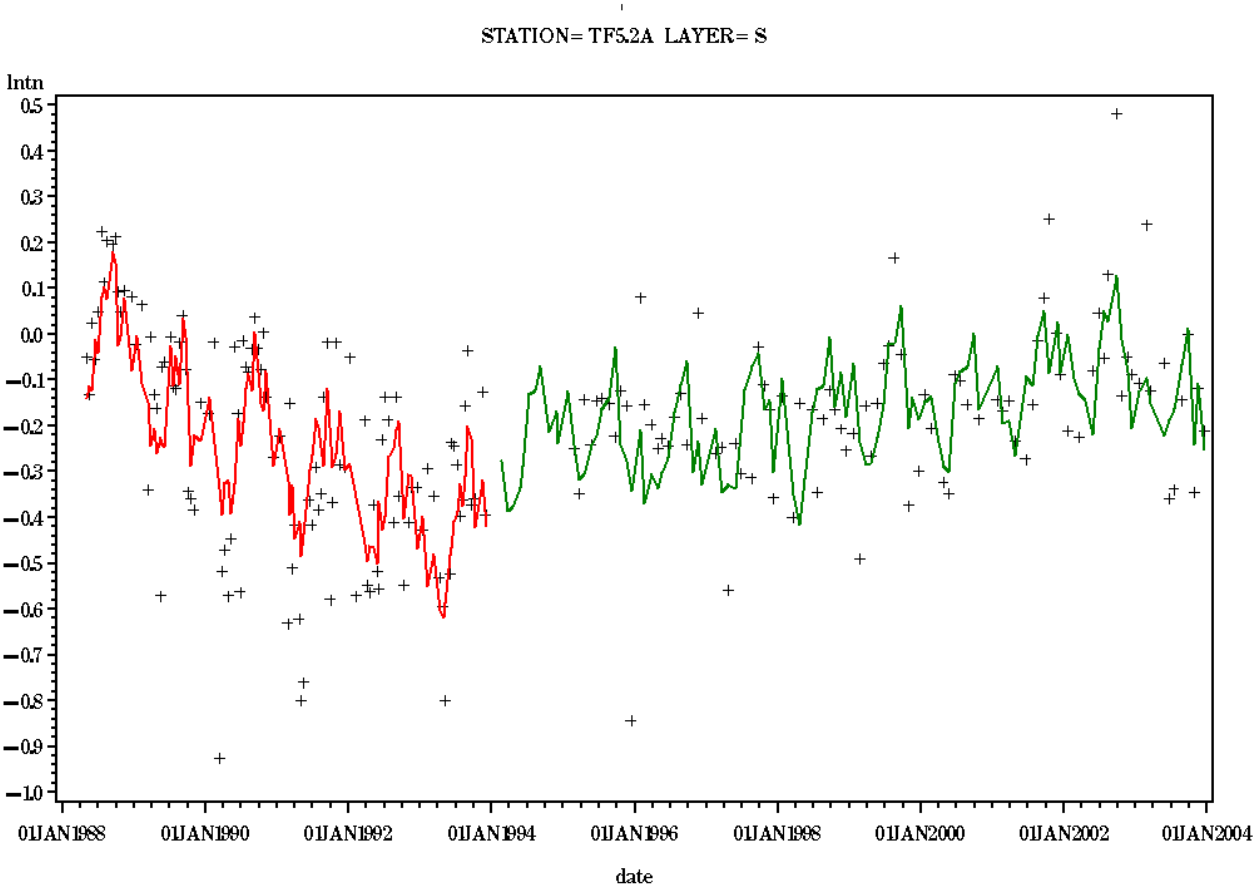
Root MSE = 0.1277 Total R-Square = 0.5497



Tributary	Station	Layer
James	TF5.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4888	0.0393	-12.44	<.0001
jan	0.0782	0.0451	1.74	0.0839
feb	0.0484	0.0437	1.11	0.2695
mar	0.0362	0.0368	0.98	0.3267
apr	0.0074	0.0383	0.19	0.8473
may	0.0324	0.0383	0.85	0.3985
jun	-0.0326	0.0362	-0.90	0.3693
jul	0.0071	0.0383	0.19	0.8531
aug	0.0061	0.0376	0.16	0.8720
sep	0.0098	0.0387	0.25	0.8008
oct	-0.1347	0.0375	-3.59	0.0004
nov	-0.0001	0.0441	-0.00	0.9982
dec	-0.0581	0.0437	-1.33	0.1845
rtemp	0.0099	0.0042	2.33	0.0205
cyear	0.0020	0.0071	0.28	0.7790
mc	0.2220	0.0634	3.50	0.0006
mc_cyear	-0.0114	0.0114	-1.00	0.3182
flow0	0.4265	0.0363	11.75	<.0001
flow40	-0.0727	0.0428	-1.70	0.0912
flow30	-0.0867	0.0371	-2.34	0.0201
AR1	-0.1899	0.0631	-3.01	0.0026

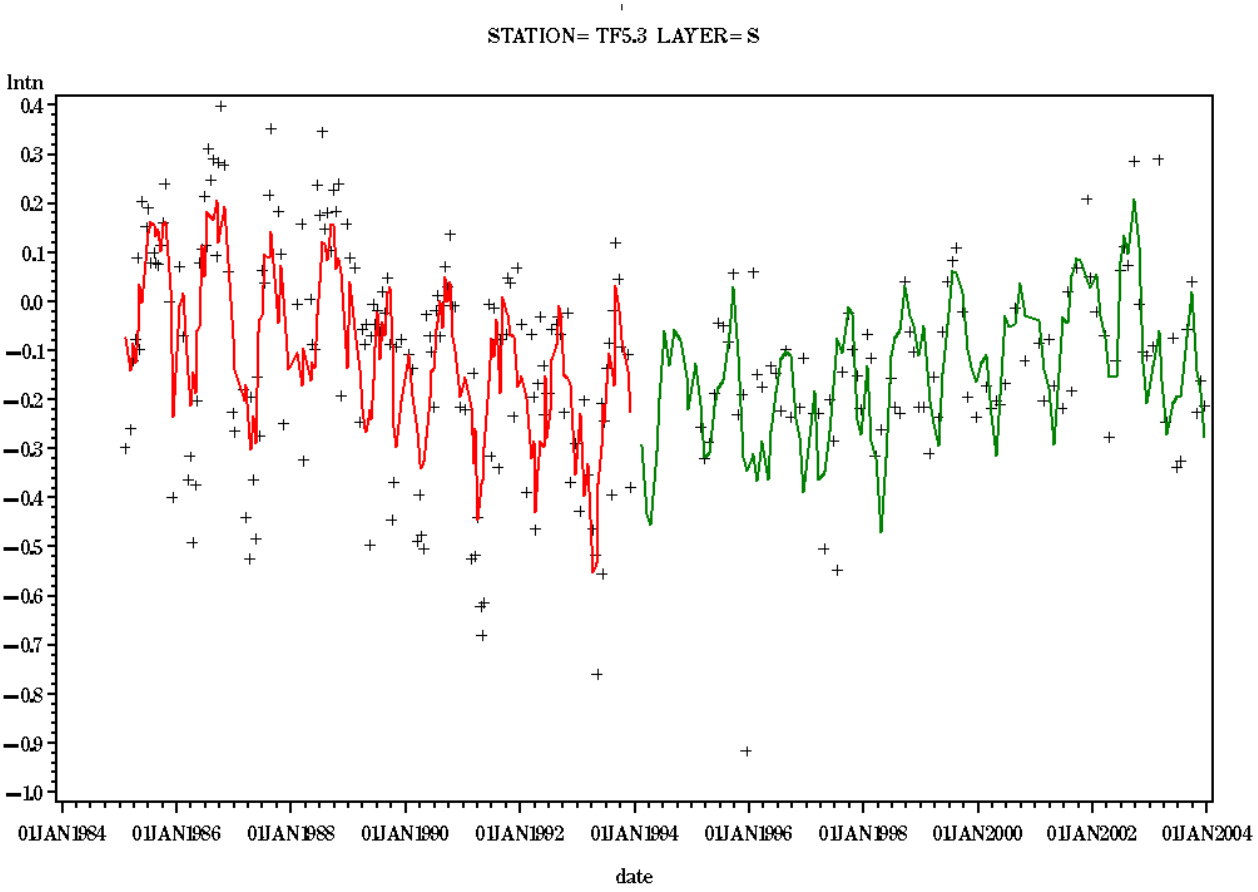
Root MSE = 0.1847 Total R-Square = 0.5188



Tributary	Station	Layer
James	TF5.2A	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.5099	0.0407	-12.53	<.0001
jan	0.0493	0.0435	1.13	0.2587
feb	-0.0320	0.0452	-0.71	0.4798
mar	-0.0988	0.0387	-2.55	0.0115
apr	-0.1117	0.0388	-2.88	0.0044
may	-0.1139	0.0366	-3.11	0.0022
jun	-0.0090	0.0356	-0.25	0.7998
jul	0.0651	0.0362	1.80	0.0742
aug	0.0889	0.0354	2.51	0.0128
sep	0.1642	0.0363	4.52	<.0001
oct	-0.0079	0.0363	-0.22	0.8285
nov	0.0579	0.0407	1.42	0.1561
dec	-0.0520	0.0403	-1.29	0.1985
rtemp	0.0029	0.0046	0.64	0.5216
cyear	-0.0776	0.0107	-7.24	<.0001
mc	0.2781	0.0570	4.88	<.0001
mc_cyear	0.0912	0.0130	7.02	<.0001
flow30	-0.1285	0.0341	-3.77	0.0002
AR1	-0.1222	0.0736	-1.66	0.0536

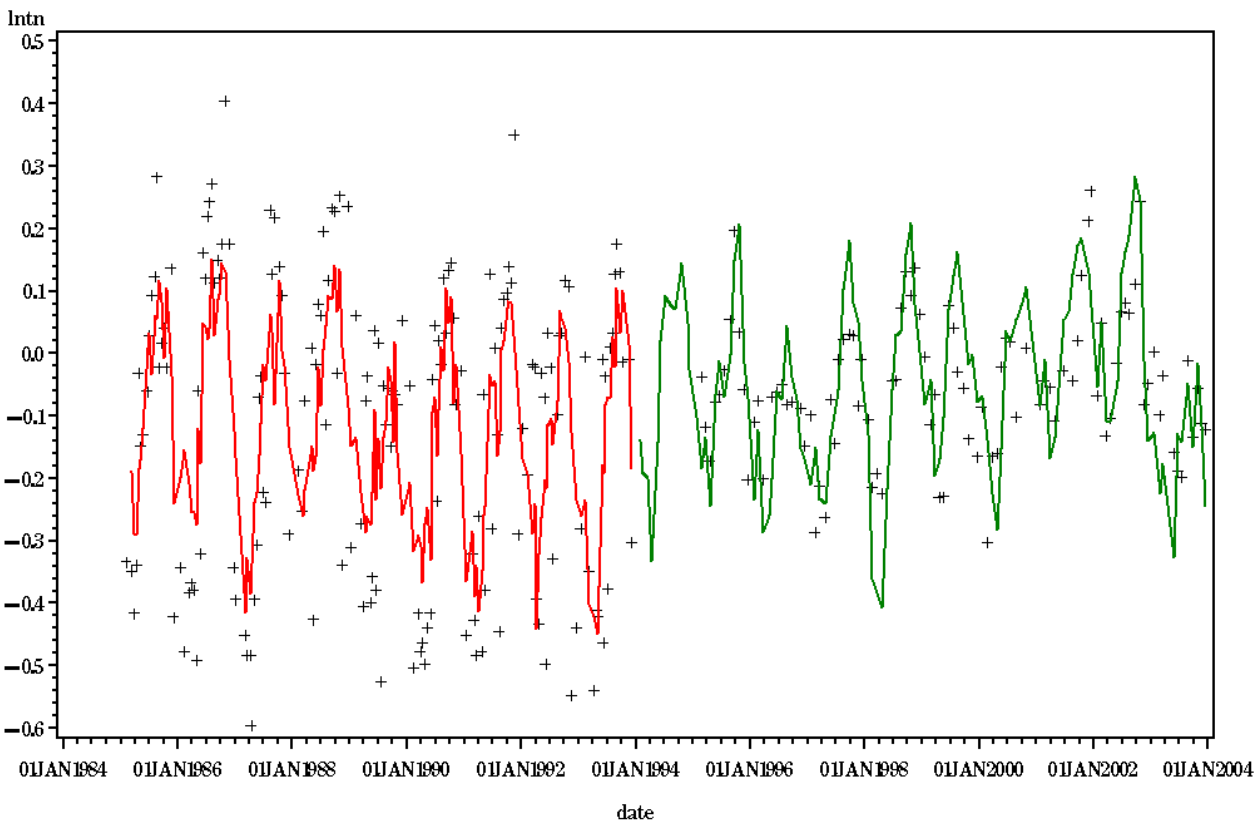
Root MSE = 0.1591 Total R-Square = 0.5103



Tributary	Station	Layer
James	TF5.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2656	0.0308	-8.61	<.0001
jan	0.0201	0.0400	0.50	0.6148
feb	-0.0455	0.0362	-1.26	0.2099
mar	-0.1246	0.0308	-4.05	<.0001
apr	-0.1831	0.0316	-5.80	<.0001
may	-0.0904	0.0311	-2.90	0.0040
jun	0.0252	0.0301	0.84	0.4025
jul	0.0878	0.0313	2.80	0.0055
aug	0.0962	0.0304	3.17	0.0017
sep	0.1664	0.0319	5.21	<.0001
oct	0.0892	0.0314	2.84	0.0049
nov	0.0279	0.0356	0.79	0.4330
dec	-0.0693	0.0364	-1.91	0.0578
rtemp	0.0051	0.0036	1.44	0.1525
cyear	-0.0332	0.0055	-6.03	<.0001
mc	0.0607	0.0505	1.20	0.2302
mc_cyear	0.0464	0.0091	5.11	<.0001
flow30	-0.1179	0.0303	-3.89	0.0001
flow10	-0.0839	0.0319	-2.63	0.0090
AR1	-0.1638	0.0635	-2.58	0.0076

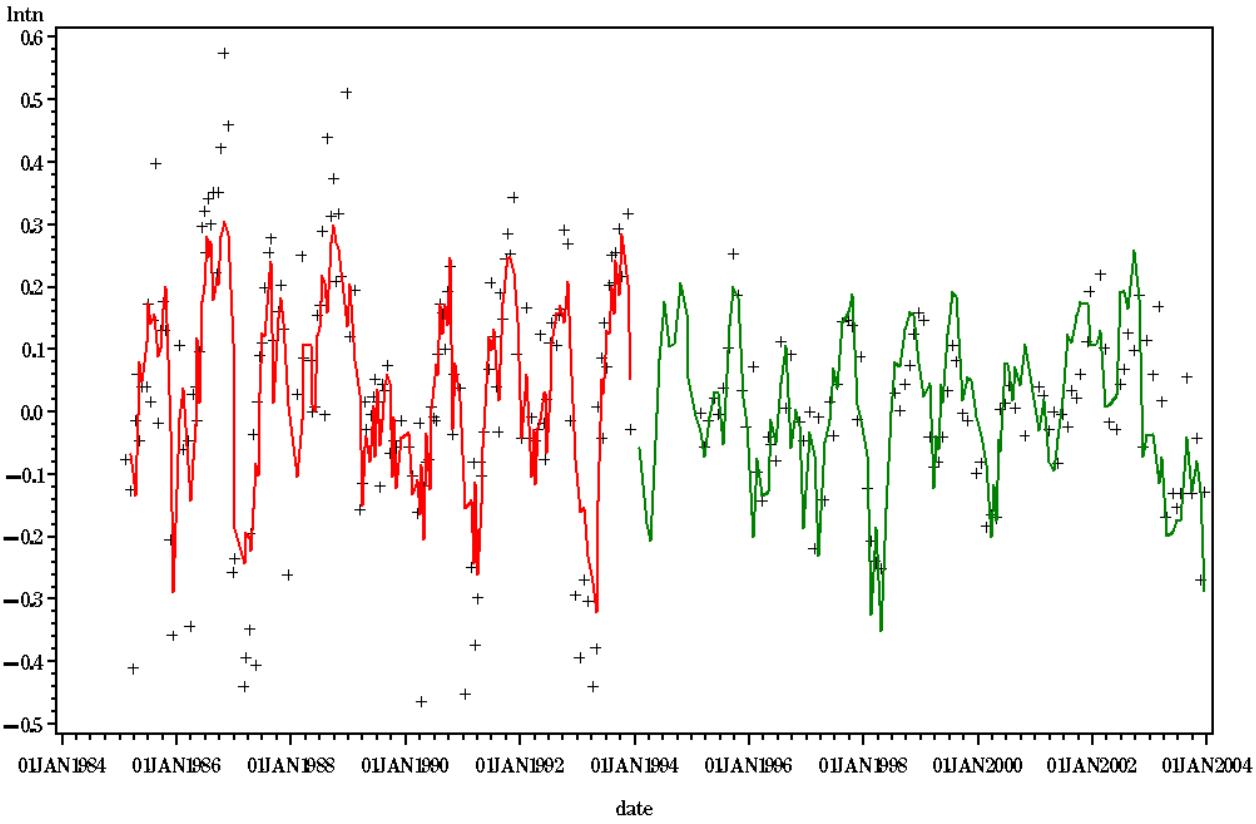
Root MSE = 0.1525 Total R-Square = 0.5243



Tributary	Station	Layer
James	TF5.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1595	0.0235	-6.79	<.0001
jan	-0.0723	0.0344	-2.10	0.0367
feb	-0.0635	0.0335	-1.90	0.0591
mar	-0.1658	0.0264	-6.27	<.0001
apr	-0.1949	0.0286	-6.82	<.0001
may	-0.1108	0.0270	-4.10	<.0001
jun	0.0487	0.0261	1.87	0.0631
jul	0.0644	0.0274	2.35	0.0197
aug	0.1084	0.0265	4.09	<.0001
sep	0.1709	0.0279	6.12	<.0001
oct	0.1789	0.0269	6.65	<.0001
nov	0.0611	0.0322	1.90	0.0590
dec	-0.0251	0.0323	-0.78	0.4381
rtemp	0.0035	0.0036	0.97	0.3331
cyear	-0.0069	0.0043	-1.61	0.1091
mc	0.1163	0.0387	3.00	0.0030
mc_cyear	0.0036	0.0070	0.51	0.6110
flow40	-0.1545	0.0294	-5.25	<.0001
flow0	-0.1176	0.0269	-4.37	<.0001
AR1	0.0189	0.0640	0.30	0.3847

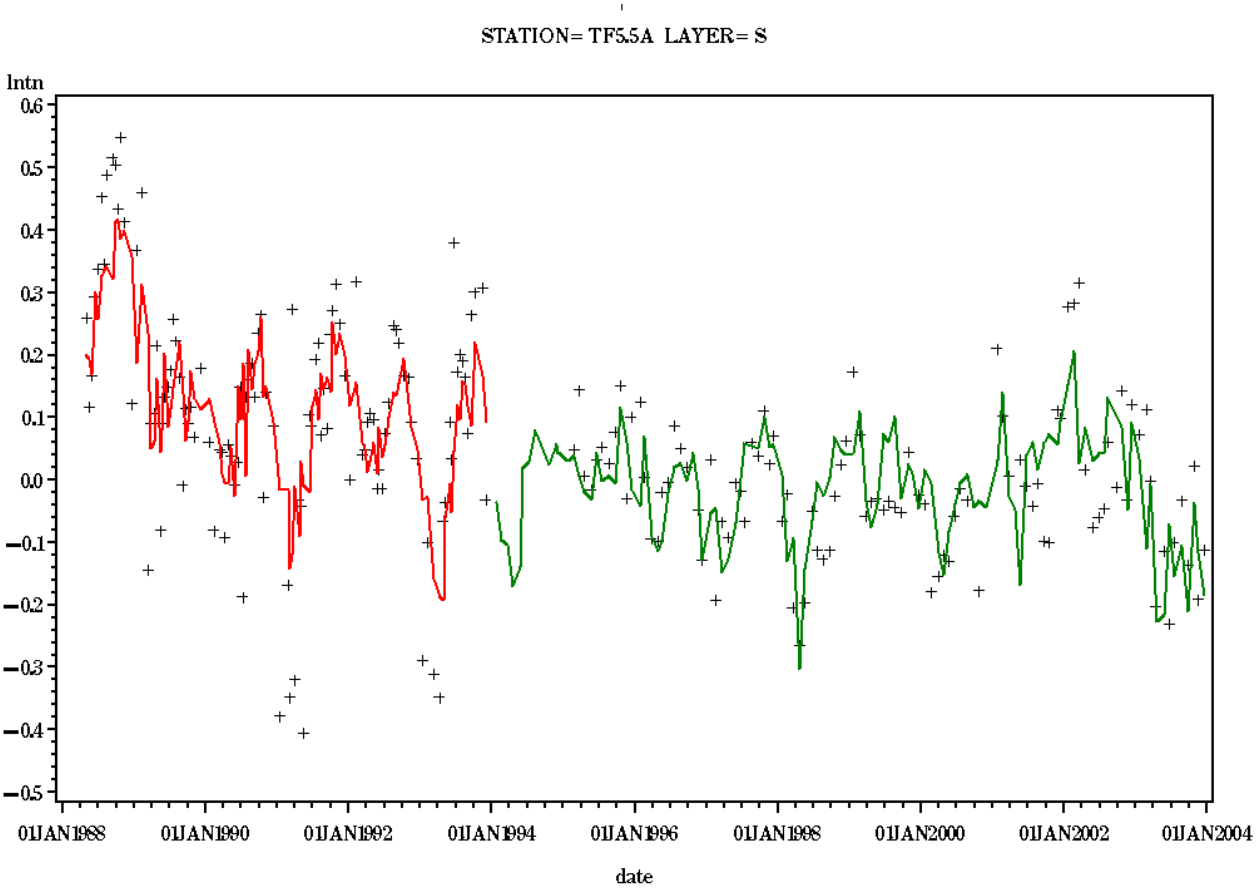
Root MSE = 0.1397 Total R-Square = 0.5599



Tributary	Station	Layer
James	TF5.5	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	0.0413	0.0280	1.48	0.1412
jan	-0.0485	0.0283	-1.72	0.0874
feb	-0.0596	0.0267	-2.23	0.0265
mar	-0.1449	0.0231	-6.28	<.0001
apr	-0.1379	0.0240	-5.75	<.0001
may	-0.0578	0.0238	-2.43	0.0157
jun	0.0185	0.0234	0.79	0.4297
jul	0.0713	0.0236	3.03	0.0027
aug	0.0851	0.0237	3.59	0.0004
sep	0.1008	0.0240	4.21	<.0001
oct	0.1288	0.0236	5.46	<.0001
nov	0.0667	0.0265	2.52	0.0123
dec	-0.0226	0.0260	-0.87	0.3857
rtemp	-0.0016	0.0032	-0.51	0.6111
cyear	0.0005	0.0050	0.11	0.9150
mc	-0.0017	0.0450	-0.04	0.9701
mc_cyear	-0.0092	0.0081	-1.14	0.2573
flow0	-0.1325	0.0237	-5.60	<.0001
flow10	-0.0891	0.0250	-3.56	0.0004
flow40	-0.0506	0.0253	-2.00	0.0467
flow30	-0.0671	0.0226	-2.97	0.0032
AR1	-0.3217	0.0605	-5.32	<.0001

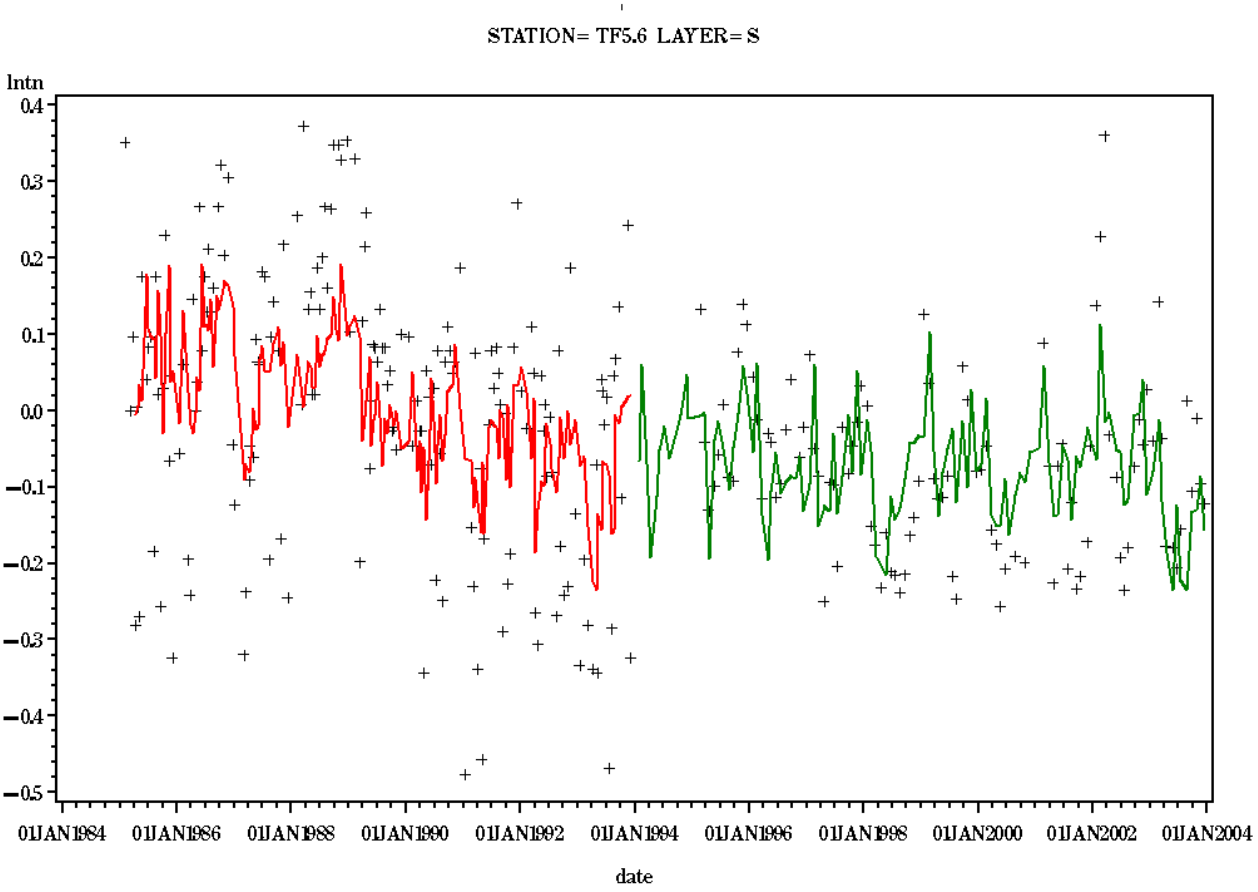
Root MSE = 0.1119 Total R-Square = 0.6362



Tributary	Station	Layer
James	TF5.5A	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0003	0.0380	-0.01	0.9927
jan	0.0255	0.0312	0.82	0.4155
feb	0.0181	0.0303	0.60	0.5508
mar	-0.0632	0.0285	-2.22	0.0274
apr	-0.1186	0.0287	-4.13	<.0001
may	-0.0882	0.0271	-3.26	0.0013
jun	0.0012	0.0276	0.04	0.9643
jul	0.0189	0.0273	0.69	0.4905
aug	0.0437	0.0274	1.60	0.1123
sep	0.0329	0.0282	1.17	0.2449
oct	0.0828	0.0280	2.96	0.0035
nov	0.0251	0.0305	0.82	0.4117
dec	0.0218	0.0300	0.73	0.4689
rtemp	-0.0012	0.0038	-0.33	0.7454
cyear	-0.0370	0.0100	-3.70	0.0003
mc	0.0009	0.0528	0.02	0.9866
mc_cyear	0.0335	0.0120	2.80	0.0056
flow0	-0.1116	0.0267	-4.18	<.0001
flow50	-0.0699	0.0257	-2.72	0.0072
flow80	-0.0663	0.0272	-2.43	0.0159
AR1	-0.3182	0.0686	-4.64	<.0001

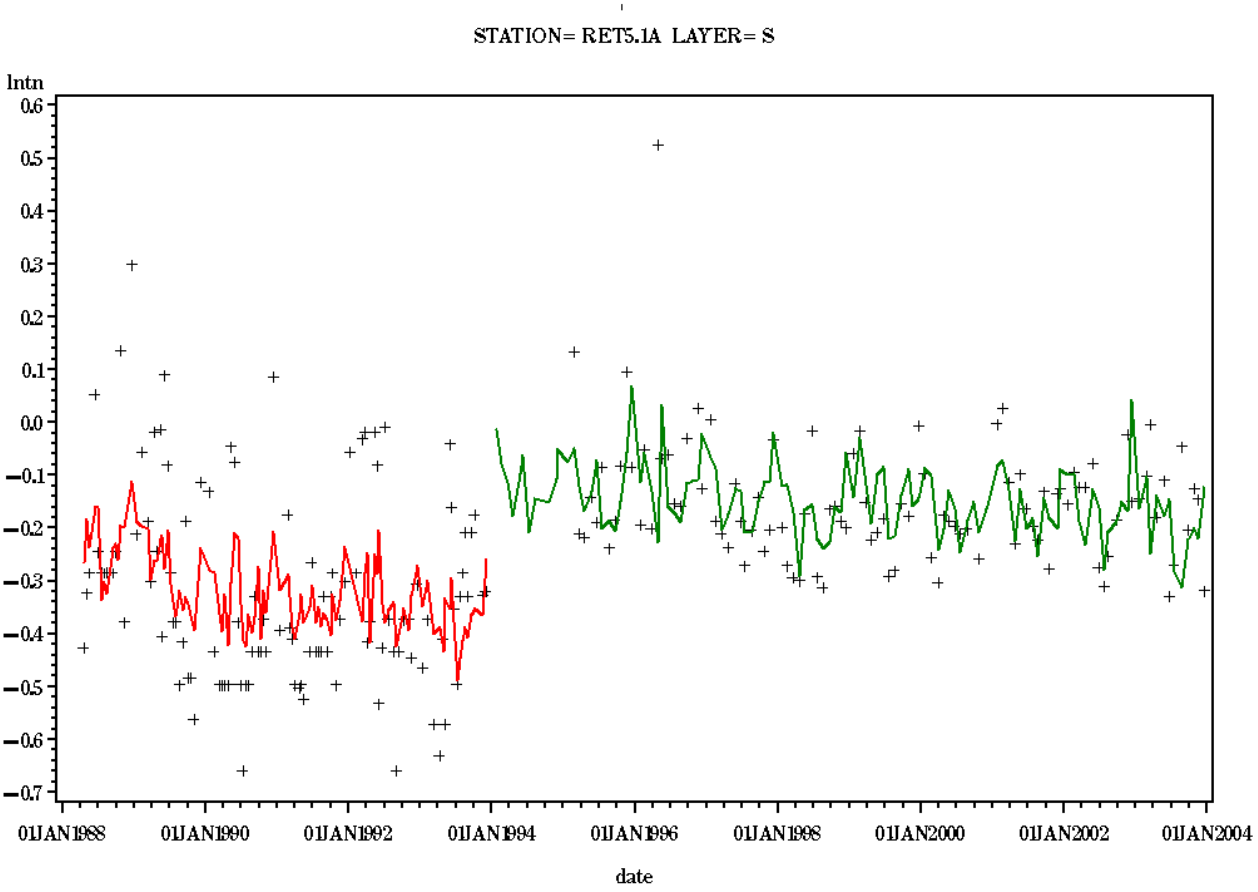
Root MSE = 0.1176 Total R-Square = 0.5632



Tributary	Station	Layer
James	TF5.6	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0877	0.0309	-2.83	0.0050
jan	0.0068	0.0362	0.19	0.8504
feb	0.0838	0.0344	2.44	0.0155
mar	-0.0360	0.0298	-1.21	0.2276
apr	-0.0766	0.0290	-2.64	0.0088
may	-0.0502	0.0287	-1.75	0.0818
jun	0.0161	0.0284	0.57	0.5709
jul	-0.0088	0.0300	-0.29	0.7708
aug	-0.0324	0.0295	-1.10	0.2725
sep	0.0167	0.0304	0.55	0.5837
oct	0.0145	0.0299	0.48	0.6292
nov	0.0630	0.0329	1.92	0.0565
dec	0.0032	0.0331	0.10	0.9236
rtemp	-0.0002	0.0044	-0.05	0.9630
cyear	-0.0200	0.0056	-3.56	0.0004
mc	0.0613	0.0495	1.24	0.2169
mc_cyear	0.0096	0.0091	1.06	0.2914
flow40	-0.0904	0.0309	-2.93	0.0037
flow90	-0.0721	0.0291	-2.48	0.0139
AR1	-0.2039	0.0623	-3.27	0.0013

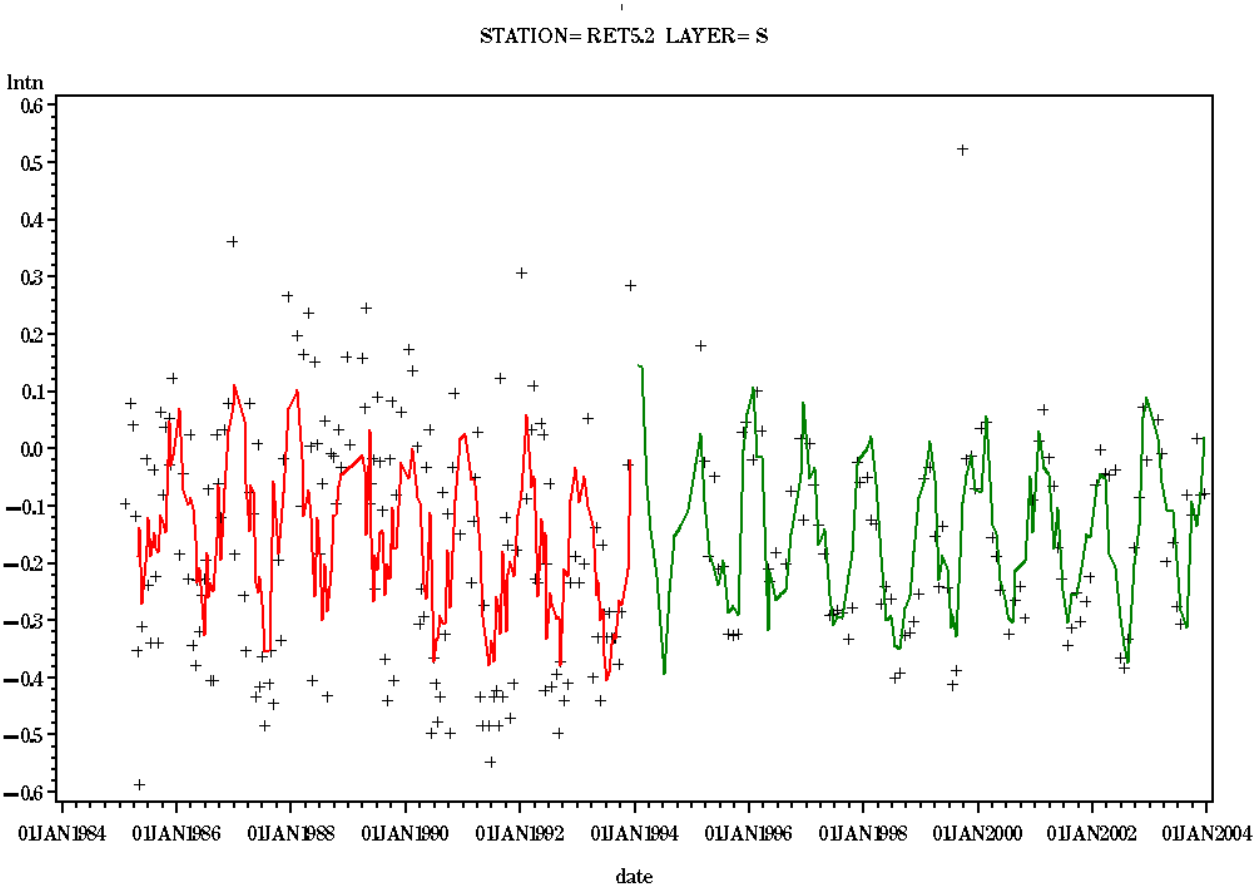
Root MSE = 0.1446 Total R-Square = 0.2983



Tributary	Station	Layer
James	RET5.1A	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3797	0.0386	-9.82	<.0001
jan	0.0395	0.0388	1.02	0.3110
feb	0.0599	0.0375	1.60	0.1120
mar	-0.0281	0.0333	-0.84	0.3999
apr	-0.0406	0.0319	-1.27	0.2043
may	0.0277	0.0319	0.87	0.3872
jun	0.0294	0.0311	0.95	0.3453
jul	-0.0692	0.0320	-2.17	0.0315
aug	-0.0577	0.0319	-1.81	0.0723
sep	-0.0228	0.0328	-0.69	0.4886
oct	-0.0157	0.0343	-0.46	0.6475
nov	-0.0194	0.0366	-0.53	0.5969
dec	0.0971	0.0361	2.69	0.0078
rtemp	-0.0133	0.0048	-2.75	0.0065
cyear	-0.0205	0.0101	-2.02	0.0451
mc	0.2727	0.0532	5.13	<.0001
mc_cyear	0.0112	0.0121	0.93	0.3541
flow80	-0.0718	0.0313	-2.29	0.0229
AR1	-0.1677	0.0713	-2.35	0.0127

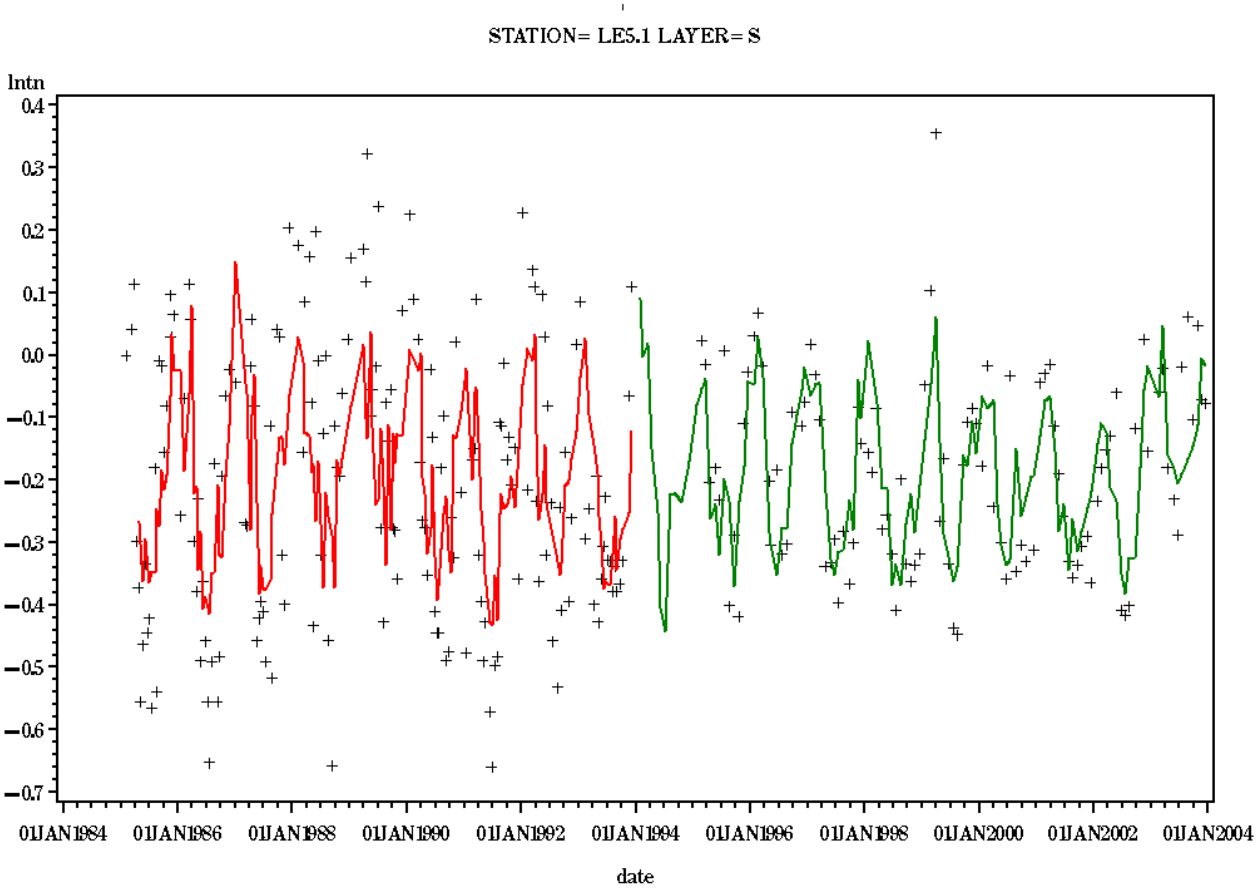
Root MSE = 0.1427 Total R-Square = 0.4007



Tributary	Station	Layer
James	RET5.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2061	0.0328	-6.28	<.0001
jan	0.1237	0.0406	3.05	0.0026
feb	0.1571	0.0381	4.12	<.0001
mar	0.0797	0.0325	2.45	0.0148
apr	-0.0062	0.0317	-0.19	0.8457
may	-0.0560	0.0305	-1.83	0.0678
jun	-0.1163	0.0316	-3.69	0.0003
jul	-0.1391	0.0323	-4.30	<.0001
aug	-0.1262	0.0314	-4.02	<.0001
sep	-0.0524	0.0317	-1.65	0.0994
oct	-0.0522	0.0323	-1.62	0.1073
nov	0.0724	0.0347	2.09	0.0381
dec	0.1156	0.0359	3.22	0.0015
rtemp	-0.0159	0.0049	-3.23	0.0014
cyear	-0.0139	0.0059	-2.34	0.0202
mc	0.0753	0.0528	1.42	0.1556
mc_cyear	0.0104	0.0096	1.09	0.2786
flow150	-0.1047	0.0310	-3.38	0.0008
flow0	0.1016	0.0301	3.38	0.0008
AR1	-0.1817	0.0627	-2.90	0.0035

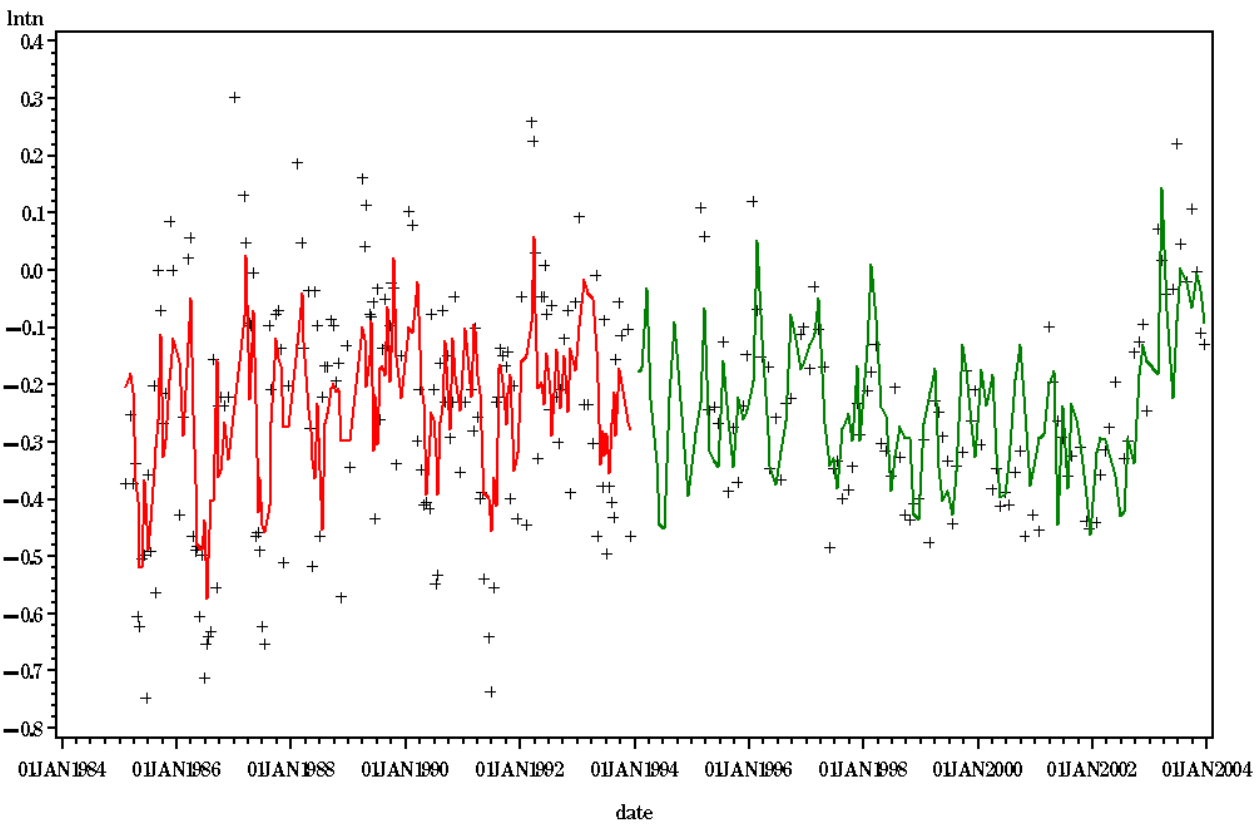
Root MSE = 0.1567 Total R-Square = 0.3786



Tributary	Station	Layer
James	LE5.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1965	0.0363	-5.41	<.0001
jan	0.1369	0.0399	3.43	0.0007
feb	0.1497	0.0389	3.85	0.0002
mar	0.1461	0.0337	4.34	<.0001
apr	-0.0037	0.0336	-0.11	0.9119
may	-0.0627	0.0319	-1.97	0.0505
jun	-0.1461	0.0323	-4.53	<.0001
jul	-0.1458	0.0329	-4.43	<.0001
aug	-0.0914	0.0327	-2.80	0.0055
sep	-0.0666	0.0329	-2.03	0.0439
oct	-0.0343	0.0339	-1.01	0.3118
nov	0.0258	0.0358	0.72	0.4719
dec	0.0922	0.0377	2.45	0.0151
rtemp	-0.0087	0.0052	-1.68	0.0951
cyear	-0.0022	0.0066	-0.34	0.7363
mc	-0.0077	0.0584	-0.13	0.8954
mc_cyear	0.0068	0.0106	0.64	0.5256
flow10	0.1459	0.0309	4.72	<.0001
flow150	-0.0590	0.0316	-1.87	0.0629
AR1	-0.2544	0.0615	-4.13	0.0001

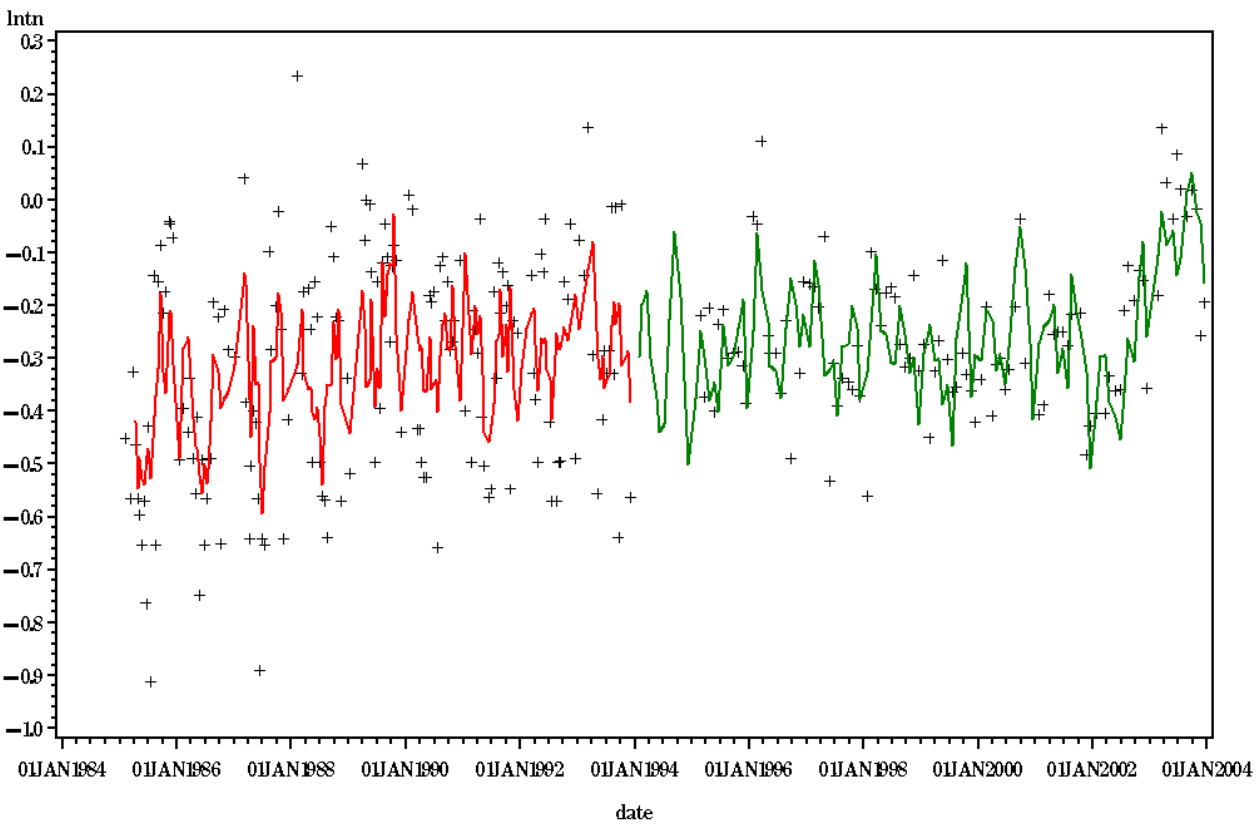
Root MSE = 0.1598 Total R-Square = 0.3929



Tributary	Station	Layer
James	LE5.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1714	0.0352	-4.87	<.0001
jan	0.0606	0.0399	1.52	0.1297
feb	0.0836	0.0380	2.20	0.0286
mar	0.1421	0.0312	4.55	<.0001
apr	0.0089	0.0311	0.29	0.7754
may	-0.0934	0.0306	-3.05	0.0025
jun	-0.1102	0.0313	-3.53	0.0005
jul	-0.1052	0.0315	-3.34	0.0010
aug	-0.0132	0.0313	-0.42	0.6741
sep	0.0408	0.0322	1.27	0.2058
oct	0.0290	0.0317	0.92	0.3604
nov	-0.0259	0.0348	-0.74	0.4574
dec	-0.0172	0.0359	-0.48	0.6331
rtemp	-0.0106	0.0048	-2.19	0.0291
cyear	0.0124	0.0063	1.99	0.0481
mc	-0.1163	0.0570	-2.04	0.0423
mc_cyear	-0.0023	0.0102	-0.22	0.8244
flow10	0.1383	0.0329	4.20	<.0001
flow20	0.1086	0.0364	2.99	0.0031
AR1	-0.2771	0.0610	-4.54	<.0001

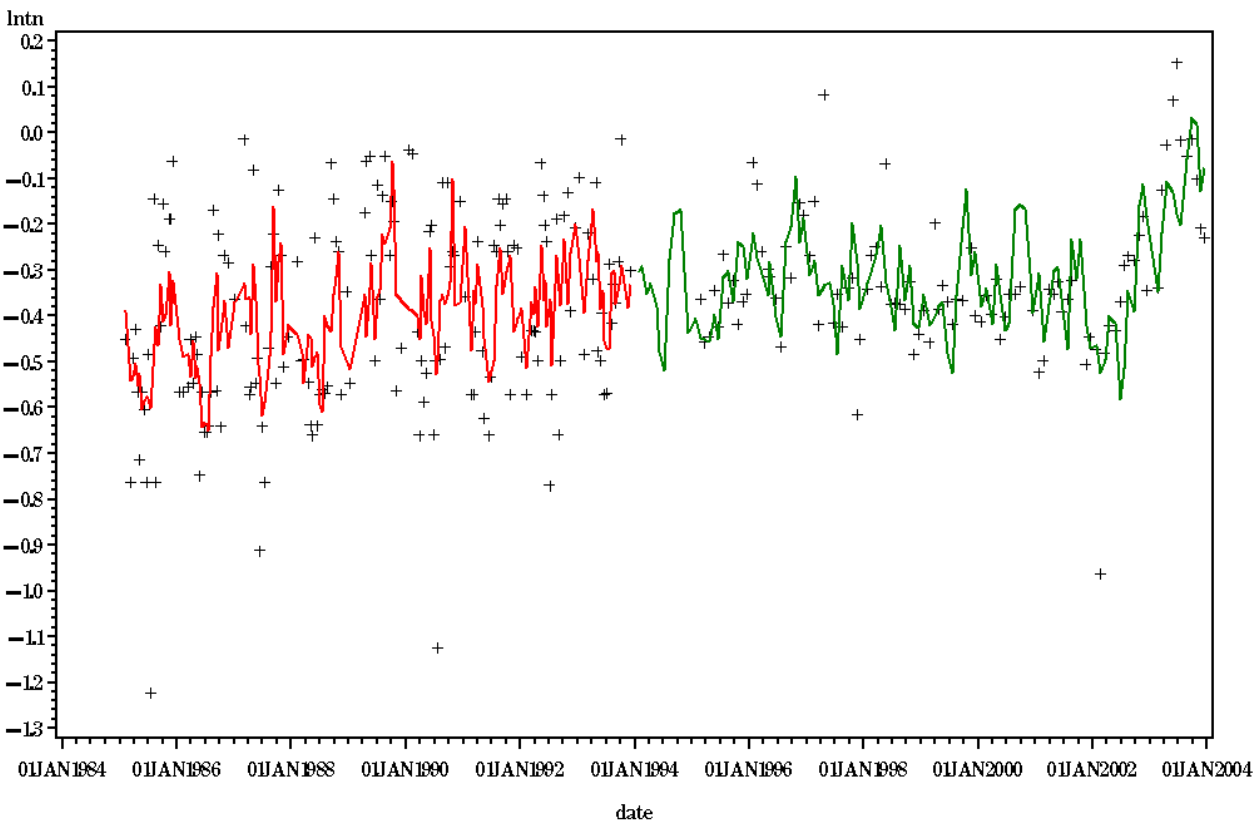
Root MSE = 0.1520 Total R-Square = 0.4332



Tributary	Station	Layer
James	LE5.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3063	0.0347	-8.84	<.0001
jan	0.0591	0.0454	1.30	0.1935
feb	0.0579	0.0444	1.30	0.1933
mar	0.1060	0.0354	3.00	0.0030
apr	-0.0220	0.0341	-0.65	0.5195
may	-0.0589	0.0332	-1.78	0.0771
jun	-0.1450	0.0341	-4.25	<.0001
jul	-0.1194	0.0344	-3.48	0.0006
aug	0.0182	0.0341	0.53	0.5938
sep	0.0366	0.0351	1.04	0.2981
oct	0.0952	0.0345	2.76	0.0063
nov	0.0071	0.0379	0.19	0.8526
dec	-0.0348	0.0417	-0.84	0.4045
rtemp	-0.0032	0.0058	-0.55	0.5800
cyear	-0.0024	0.0063	-0.39	0.6977
mc	-0.0379	0.0559	-0.68	0.4977
mc_cyear	0.0156	0.0101	1.55	0.1230
flow20	0.1672	0.0394	4.24	<.0001
flow0	0.1392	0.0369	3.77	0.0002
flow90	0.0747	0.0341	2.19	0.0294
AR1	-0.1573	0.0634	-2.48	0.0094

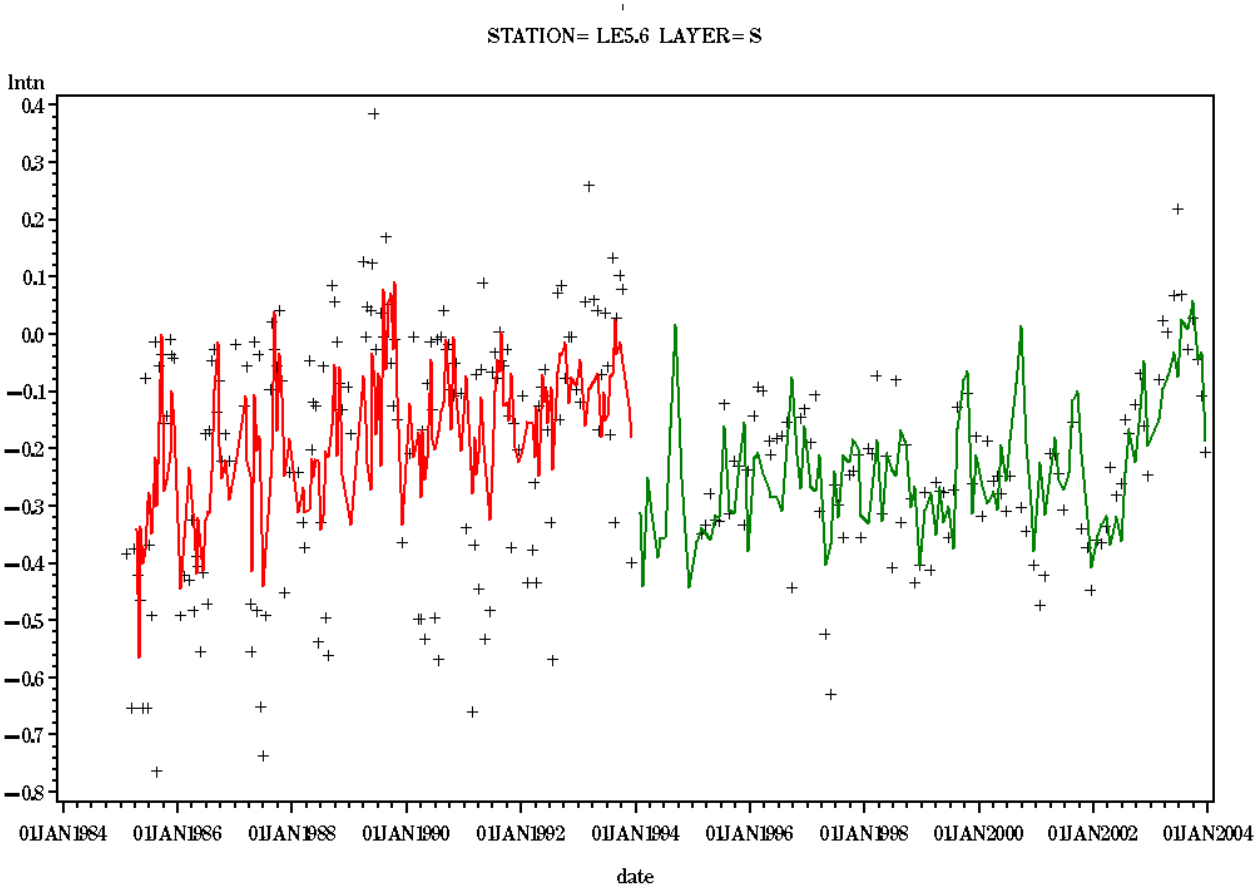
Root MSE = 0.1709 Total R-Square = 0.3617



Tributary	Station	Layer
James	LE5.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3219	0.0318	-10.14	<.0001
jan	-0.0086	0.0419	-0.21	0.8371
feb	-0.0530	0.0401	-1.32	0.1875
mar	-0.0253	0.0333	-0.76	0.4478
apr	0.0154	0.0328	0.47	0.6386
may	-0.0158	0.0322	-0.49	0.6239
jun	-0.0946	0.0320	-2.96	0.0034
jul	-0.1088	0.0327	-3.32	0.0010
aug	0.0651	0.0324	2.01	0.0457
sep	0.0566	0.0335	1.69	0.0923
oct	0.1313	0.0351	3.74	0.0002
nov	0.0247	0.0374	0.66	0.5098
dec	0.0129	0.0391	0.33	0.7411
rtemp	-0.0116	0.0059	-1.96	0.0511
cyear	0.0150	0.0056	2.68	0.0079
mc	-0.0398	0.0514	-0.77	0.4402
mc_cyear	-0.0048	0.0091	-0.53	0.5964
flow0	0.1568	0.0324	4.83	<.0001
flow20	0.1118	0.0379	2.95	0.0035
AR1	-0.1115	0.0636	-1.75	0.0450

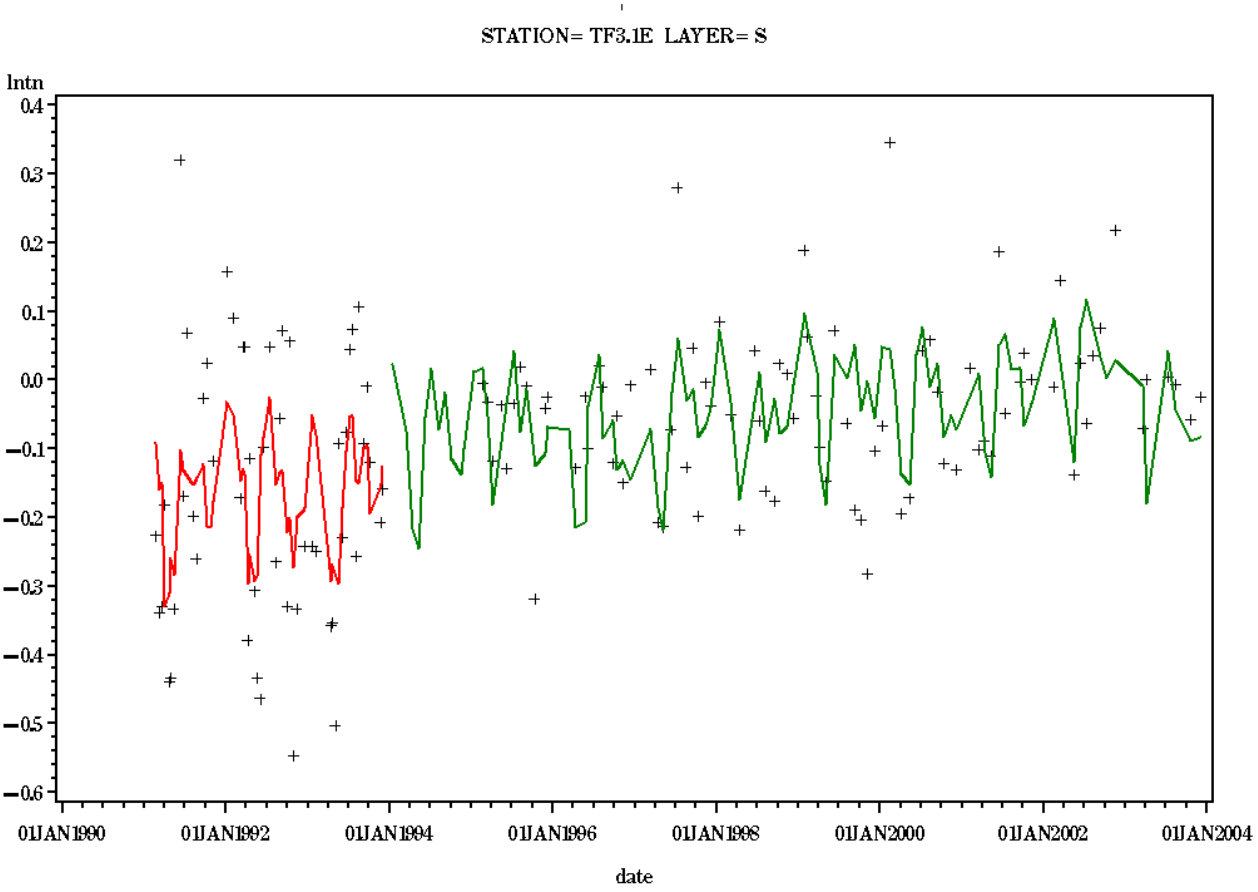
Root MSE = 0.1649 Total R-Square = 0.3707



Tributary	Station	Layer
James	LE5.6	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.0749	0.0329	-2.27	0.0239
jan	-0.0428	0.0416	-1.03	0.3041
feb	-0.0332	0.0410	-0.81	0.4180
mar	-0.0088	0.0335	-0.26	0.7917
apr	-0.0708	0.0328	-2.16	0.0317
may	-0.0429	0.0314	-1.37	0.1723
jun	-0.0452	0.0319	-1.42	0.1579
jul	-0.0138	0.0337	-0.41	0.6818
aug	0.0761	0.0330	2.30	0.0221
sep	0.1368	0.0334	4.09	<.0001
oct	0.0722	0.0328	2.20	0.0287
nov	0.0177	0.0369	0.48	0.6327
dec	-0.0452	0.0385	-1.17	0.2416
rtemp	-0.0060	0.0058	-1.03	0.3018
cyear	0.0209	0.0059	3.55	0.0005
mc	-0.2356	0.0524	-4.50	<.0001
mc_cyear	-0.0059	0.0095	-0.62	0.5362
flow20	0.1505	0.0379	3.97	<.0001
flow90	0.1412	0.0374	3.77	0.0002
flow80	-0.1125	0.0429	-2.62	0.0093
flow0	0.0880	0.0340	2.59	0.0101
flow70	-0.0684	0.0373	-1.83	0.0679
AR1	-0.1360	0.0640	-2.13	0.0209

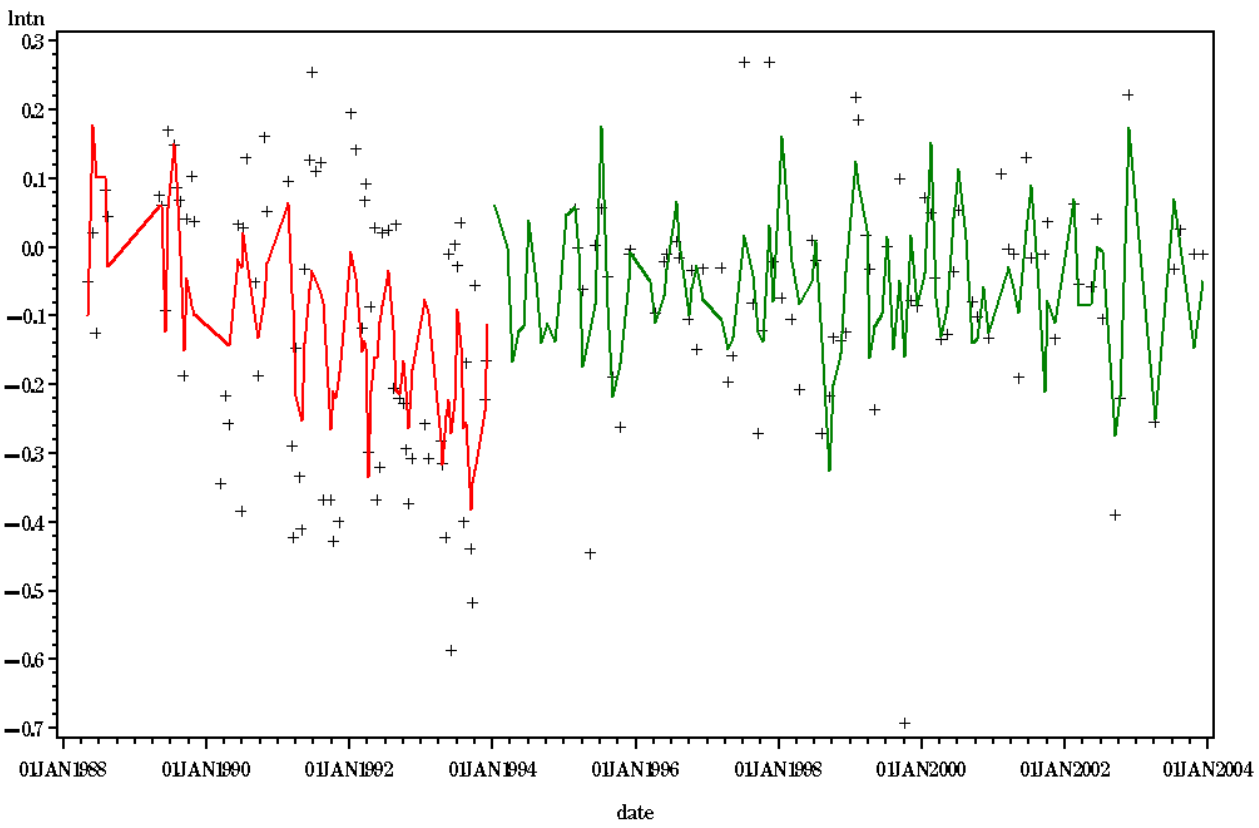
Root MSE = 0.1625 Total R-Square = 0.3612



Tributary	Station	Layer
Rappahannock	TF3.1E	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1279	0.0503	-2.54	0.0124
jan	0.0916	0.0571	1.61	0.1112
feb	0.0710	0.0488	1.46	0.1484
mar	0.0073	0.0379	0.19	0.8482
apr	-0.1256	0.0341	-3.68	0.0004
may	-0.1456	0.0391	-3.72	0.0003
jun	0.0496	0.0365	1.36	0.1772
jul	0.1003	0.0394	2.54	0.0124
aug	0.0068	0.0364	0.19	0.8529
sep	0.0391	0.0376	1.04	0.3003
oct	-0.0509	0.0363	-1.40	0.1636
nov	-0.0273	0.0415	-0.66	0.5114
dec	-0.0162	0.0434	-0.37	0.7101
rtemp	0.0043	0.0053	0.82	0.4161
cyear	0.0125	0.0243	0.51	0.6097
mc	0.0523	0.0595	0.88	0.3813
mc_cyear	-0.0049	0.0252	-0.19	0.8463
flow90	-0.0569	0.0307	-1.86	0.0659
AR1	0.0302	0.0940	0.32	0.3752

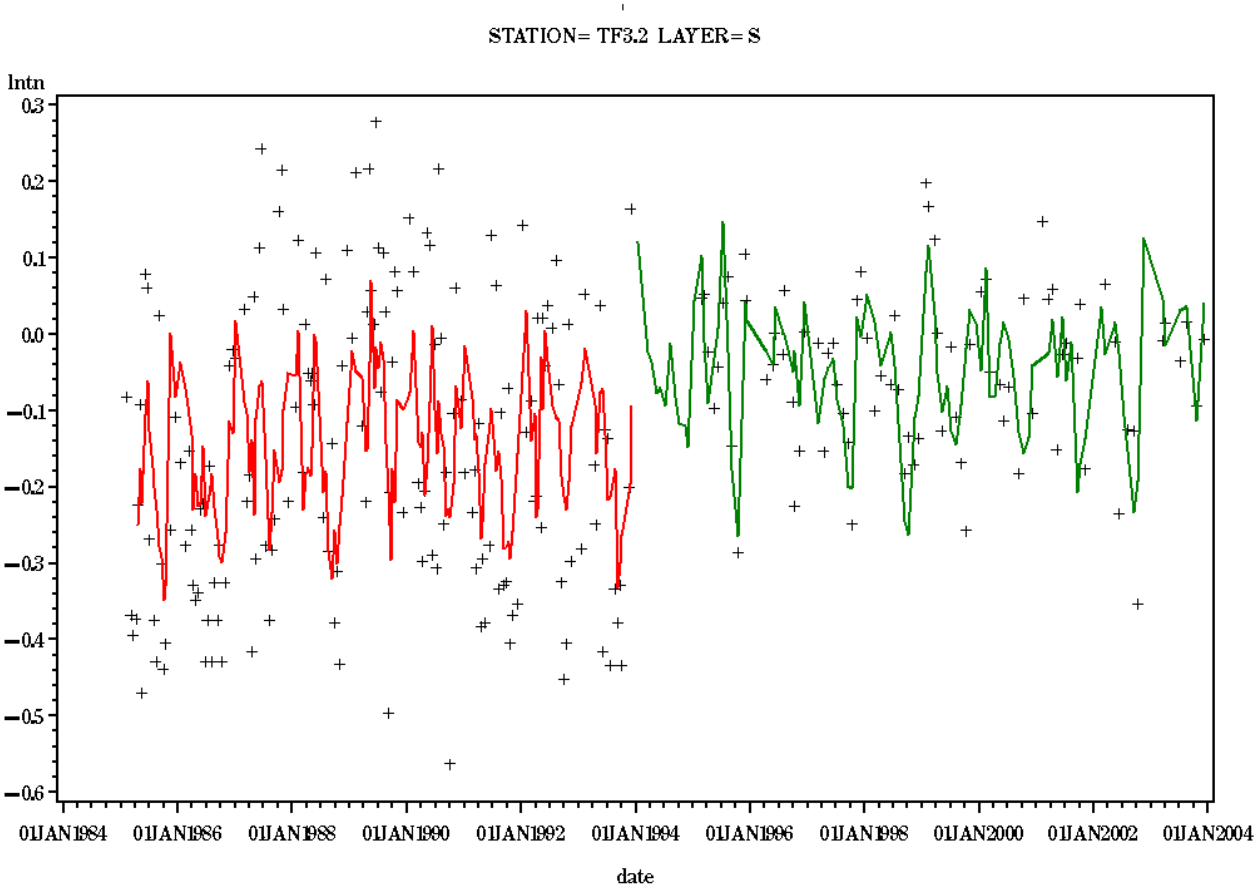
Root MSE = 0.1346 Total R-Square = 0.4012



Tributary	Station	Layer
Rappahannock	TF3.1B	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2561	0.0366	-7.00	<.0001
jan	0.1102	0.0620	1.78	0.0779
feb	0.1495	0.0531	2.82	0.0056
mar	0.0031	0.0408	0.08	0.9394
apr	-0.1109	0.0355	-3.12	0.0022
may	-0.0681	0.0388	-1.75	0.0820
jun	0.0289	0.0346	0.83	0.4057
jul	0.1080	0.0377	2.86	0.0049
aug	-0.0041	0.0377	-0.11	0.9134
sep	-0.1238	0.0359	-3.45	0.0008
oct	-0.0876	0.0354	-2.47	0.0147
nov	0.0010	0.0405	0.02	0.9802
dec	-0.0062	0.0492	-0.13	0.9001
rtemp	0.0017	0.0062	0.27	0.7860
cyear	-0.0558	0.0113	-4.92	<.0001
mc	0.2023	0.0517	3.91	0.0001
mc_cyear	0.0570	0.0132	4.31	<.0001
flow0	0.1313	0.0413	3.18	0.0018
flow90	-0.0962	0.0350	-2.75	0.0069
flow50	0.0874	0.0375	2.33	0.0212
flow30	-0.0767	0.0365	-2.10	0.0374
AR1	-0.0270	0.0870	-0.31	0.3794

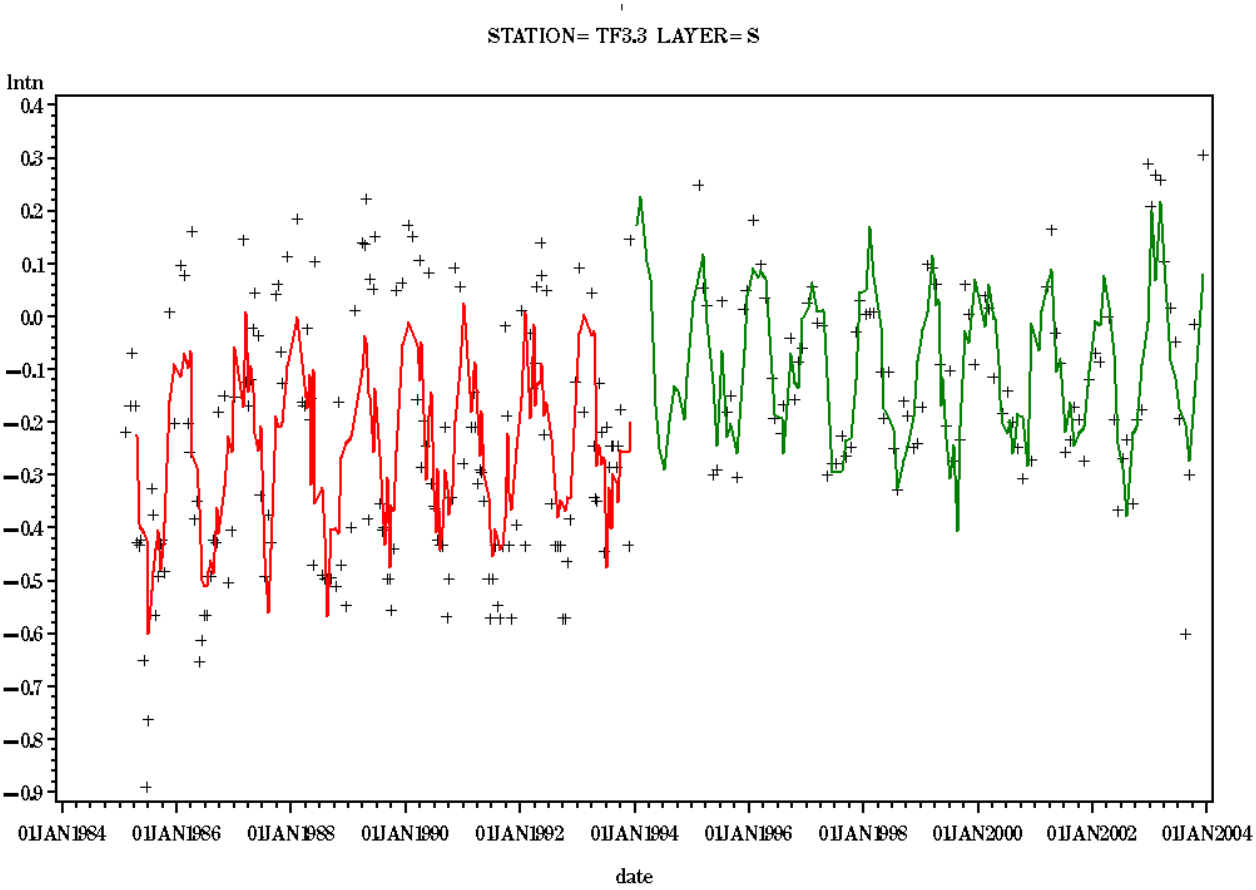
Root MSE = 0.1442 Total R-Square = 0.4301



Tributary	Station	Layer
Rappahannock	TF3.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1209	0.0297	-4.07	<.0001
jan	0.0850	0.0421	2.02	0.0449
feb	0.1232	0.0442	2.79	0.0058
mar	0.0134	0.0321	0.42	0.6770
apr	-0.0390	0.0299	-1.30	0.1945
may	0.0049	0.0322	0.15	0.8794
jun	0.0593	0.0305	1.94	0.0532
jul	0.0042	0.0322	0.13	0.8960
aug	-0.0471	0.0311	-1.51	0.1316
sep	-0.1140	0.0311	-3.67	0.0003
oct	-0.1121	0.0288	-3.89	0.0001
nov	0.0034	0.0367	0.09	0.9261
dec	0.0187	0.0377	0.50	0.6204
rtemp	-0.0060	0.0045	-1.35	0.1795
cyear	0.0026	0.0055	0.48	0.6347
mc	0.0799	0.0494	1.62	0.1070
mc_cyear	-0.0008	0.0096	-0.08	0.9368
flow0	0.0826	0.0353	2.34	0.0203
flow150	-0.0885	0.0288	-3.08	0.0024
flow10	0.0677	0.0331	2.05	0.0416
AR1	-0.0940	0.0679	-1.38	0.0882

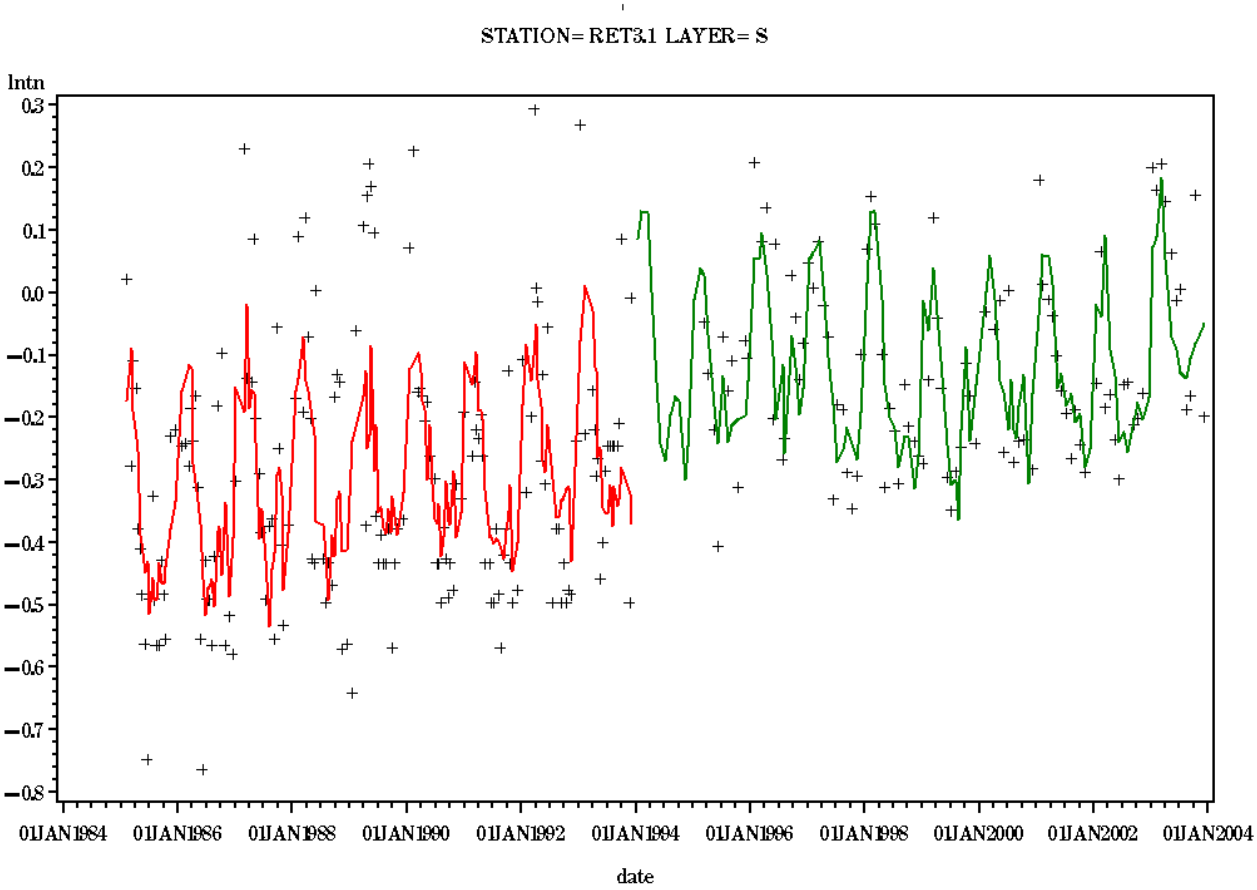
Root MSE = 0.1489 Total R-Square = 0.3436



Tributary	Station	Layer
Rappahannock	TF3.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1881	0.0395	-4.77	<.0001
jan	0.1580	0.0410	3.86	0.0001
feb	0.1546	0.0422	3.67	0.0003
mar	0.1677	0.0342	4.90	<.0001
apr	0.1074	0.0327	3.28	0.0012
may	-0.0169	0.0337	-0.50	0.6178
jun	-0.0799	0.0330	-2.42	0.0162
jul	-0.1287	0.0340	-3.79	0.0002
aug	-0.1926	0.0325	-5.93	<.0001
sep	-0.1169	0.0330	-3.55	0.0005
oct	-0.0930	0.0328	-2.84	0.0049
nov	-0.0376	0.0373	-1.01	0.3133
dec	0.0778	0.0362	2.15	0.0329
rtemp	-0.0030	0.0046	-0.66	0.5103
cyear	0.0106	0.0072	1.46	0.1444
mc	0.0872	0.0629	1.39	0.1670
mc_cyear	-0.0091	0.0115	-0.79	0.4291
flow10	0.1252	0.0267	4.69	<.0001
flow150	-0.0690	0.0307	-2.25	0.0257
AR1	-0.3210	0.0614	-5.23	<.0001

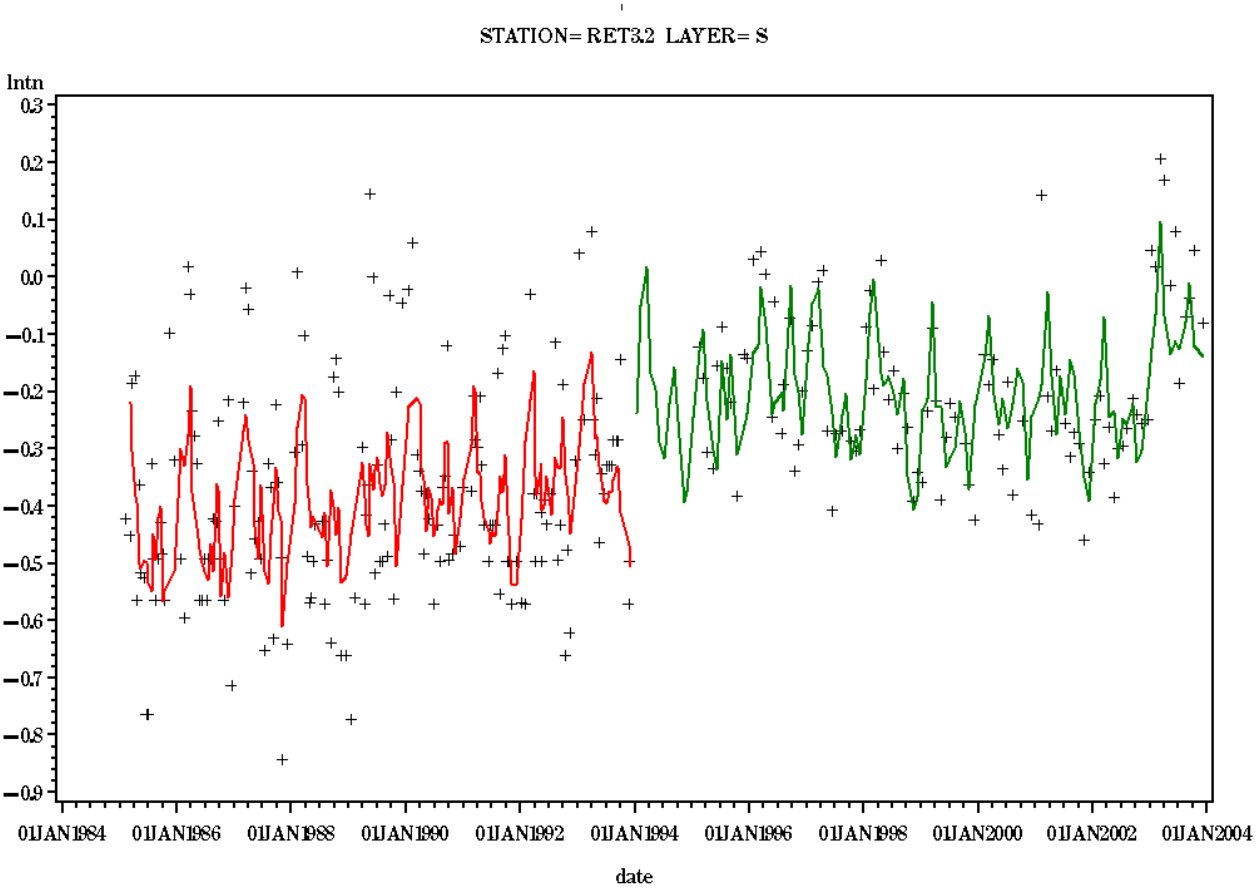
Root MSE = 0.1570 Total R-Square = 0.5546



Tributary	Station	Layer
Rappahannock	RET3.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2340	0.0312	-7.49	<.0001
jan	0.1477	0.0348	4.25	<.0001
feb	0.1611	0.0386	4.18	<.0001
mar	0.1962	0.0293	6.69	<.0001
apr	0.1043	0.0285	3.65	0.0003
may	-0.0033	0.0296	-0.11	0.9105
jun	-0.0695	0.0292	-2.38	0.0181
jul	-0.0886	0.0296	-3.00	0.0030
aug	-0.1312	0.0286	-4.59	<.0001
sep	-0.0730	0.0289	-2.53	0.0120
oct	-0.0549	0.0287	-1.91	0.0570
nov	-0.1241	0.0338	-3.68	0.0003
dec	-0.0648	0.0346	-1.87	0.0625
rtemp	-0.0060	0.0042	-1.44	0.1521
cyear	0.0114	0.0055	2.06	0.0407
mc	0.0882	0.0508	1.73	0.0842
mc_cyear	-0.0054	0.0091	-0.59	0.5546
flow10	0.0923	0.0235	3.93	0.0001
AR1	-0.2250	0.0624	-3.61	0.0006

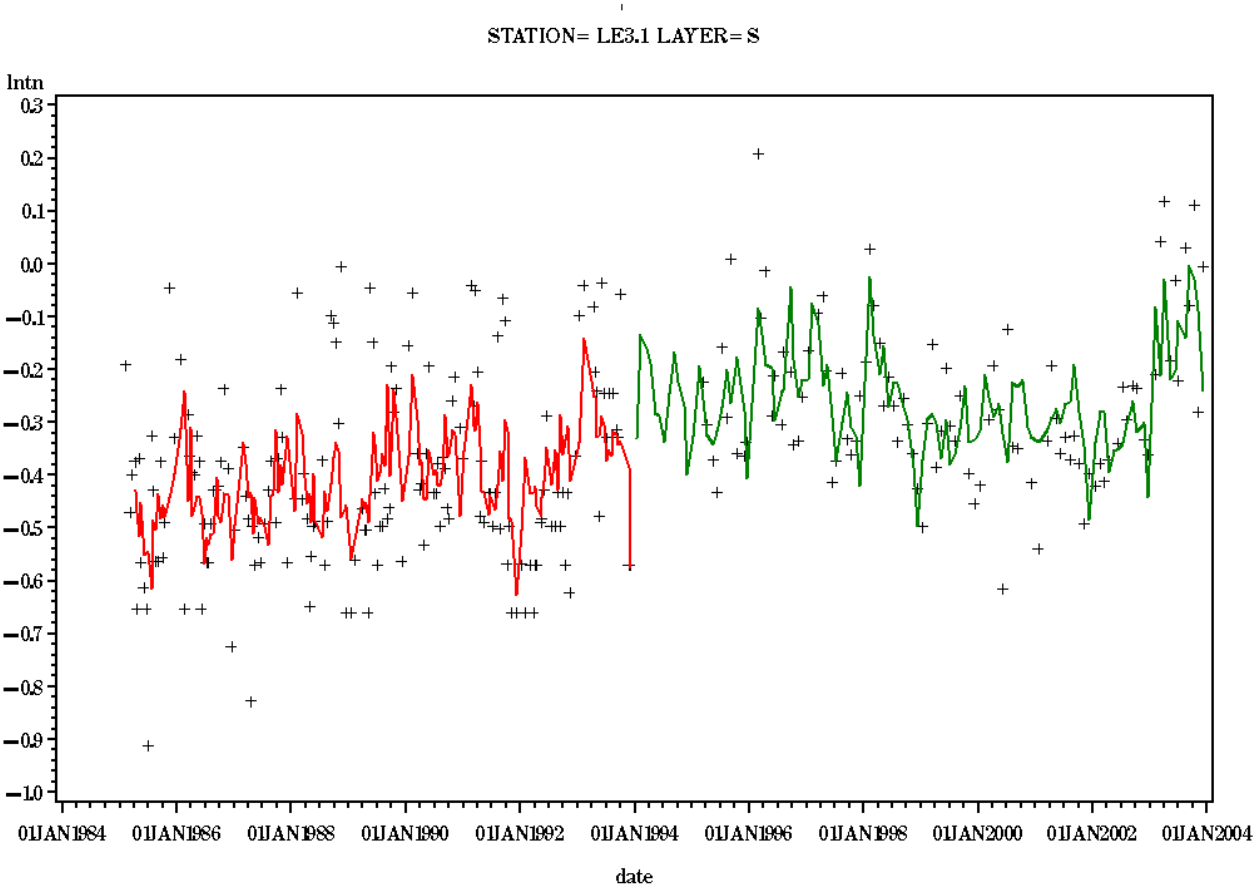
Root MSE = 0.1429 Total R-Square = 0.5542



Tributary	Station	Layer
Rappahannock	RET3.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3415	0.0287	-11.90	<.0001
jan	0.0302	0.0349	0.87	0.3868
feb	0.0924	0.0374	2.47	0.0141
mar	0.1687	0.0282	5.98	<.0001
apr	0.0335	0.0280	1.20	0.2326
may	-0.0201	0.0288	-0.70	0.4853
jun	-0.0444	0.0293	-1.52	0.1305
jul	-0.0490	0.0292	-1.68	0.0941
aug	-0.0302	0.0280	-1.08	0.2816
sep	0.0571	0.0297	1.92	0.0557
oct	-0.0445	0.0282	-1.57	0.1167
nov	-0.1124	0.0349	-3.22	0.0015
dec	-0.0813	0.0329	-2.47	0.0141
rtemp	-0.0103	0.0043	-2.39	0.0177
cyear	0.0092	0.0052	1.79	0.0750
mc	0.0953	0.0461	2.07	0.0396
mc_cyear	0.0005	0.0085	0.06	0.9541
flow10	0.0702	0.0242	2.91	0.0040
flow60	0.0712	0.0236	3.01	0.0029
AR1	-0.1416	0.0634	-2.23	0.0165

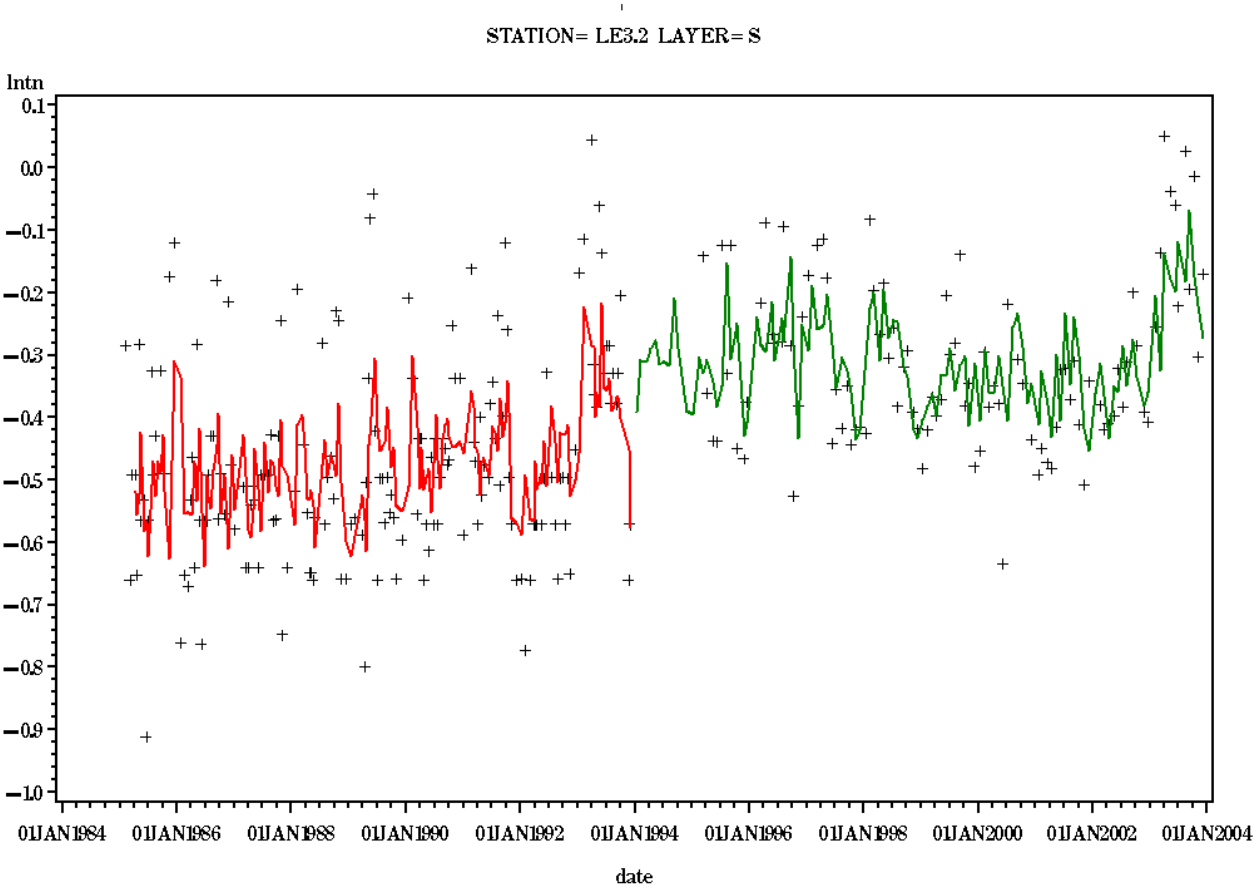
Root MSE = 0.1434 Total R-Square = 0.4865



Tributary	Station	Layer
Rappahannock	LE3.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3624	0.0334	-10.84	<.0001
jan	-0.0166	0.0375	-0.44	0.6578
feb	0.1182	0.0403	2.94	0.0037
mar	0.0549	0.0307	1.79	0.0751
apr	0.0042	0.0290	0.14	0.8862
may	-0.0238	0.0303	-0.79	0.4326
jun	-0.0388	0.0297	-1.31	0.1923
jul	-0.0345	0.0300	-1.15	0.2511
aug	-0.0231	0.0291	-0.79	0.4278
sep	0.0469	0.0290	1.62	0.1071
oct	0.0367	0.0305	1.20	0.2303
nov	-0.0231	0.0333	-0.69	0.4891
dec	-0.1009	0.0331	-3.05	0.0025
rtemp	-0.0042	0.0046	-0.91	0.3661
cyear	0.0083	0.0060	1.38	0.1685
mc	0.0767	0.0540	1.42	0.1570
mc_cyear	-0.0028	0.0097	-0.29	0.7713
flow90	0.0878	0.0239	3.68	0.0003
flow10	0.0746	0.0248	3.01	0.0029
flow40	0.0383	0.0253	1.51	0.1314
AR1	-0.2563	0.0625	-4.10	0.0001

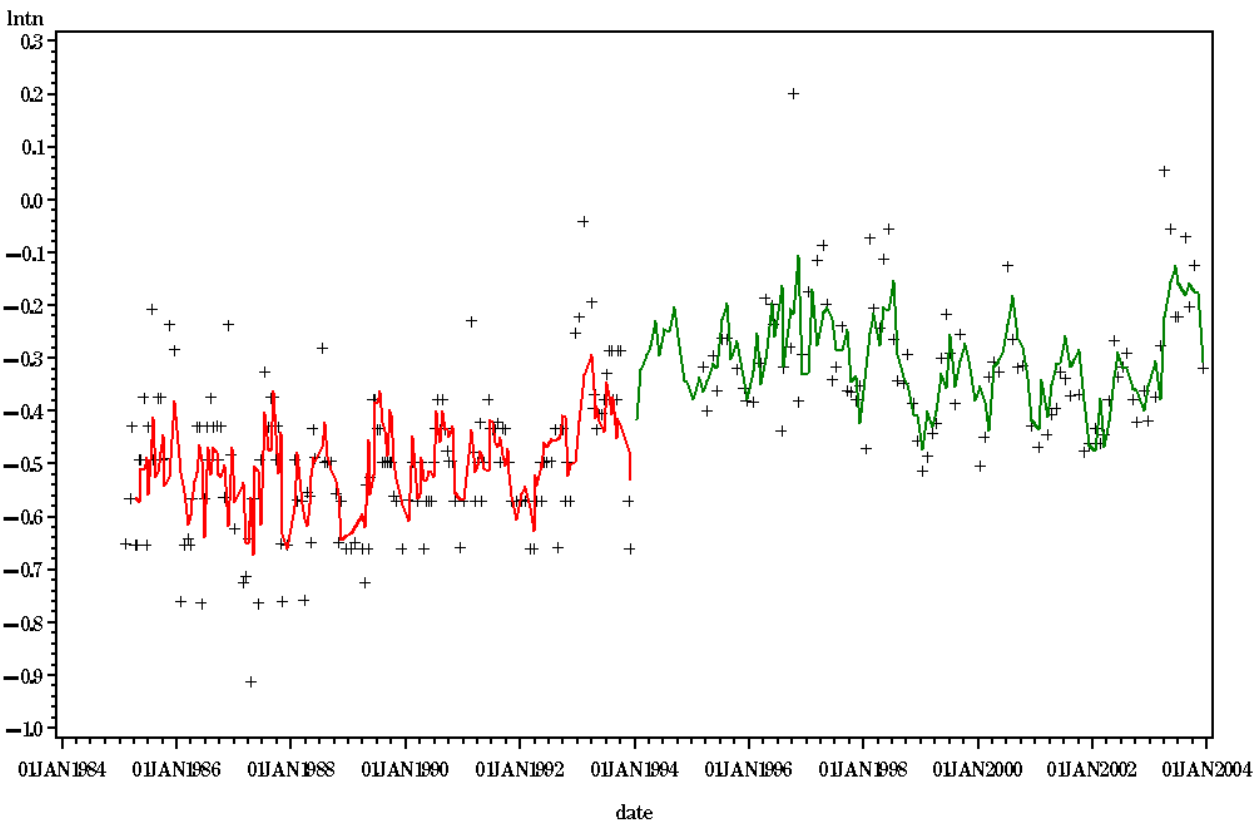
Root MSE = 0.1436 Total R-Square = 0.4126



Tributary	Station	Layer
Rappahannock	LE3.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4286	0.0361	-11.87	<.0001
jan	-0.0466	0.0364	-1.28	0.2011
feb	0.0568	0.0365	1.56	0.1206
mar	0.0093	0.0293	0.32	0.7513
apr	-0.0252	0.0280	-0.90	0.3687
may	0.0127	0.0287	0.44	0.6572
jun	-0.0162	0.0286	-0.57	0.5708
jul	0.0311	0.0290	1.07	0.2847
aug	0.0141	0.0289	0.49	0.6257
sep	0.0495	0.0282	1.76	0.0803
oct	0.0269	0.0284	0.95	0.3443
nov	-0.0641	0.0312	-2.05	0.0411
dec	-0.0484	0.0306	-1.58	0.1155
rtemp	-0.0044	0.0044	-1.00	0.3191
cyear	0.0088	0.0065	1.35	0.1782
mc	0.0940	0.0592	1.59	0.1135
mc_cyear	-0.0032	0.0105	-0.30	0.7621
flow40	0.0620	0.0231	2.68	0.0079
flow90	0.0577	0.0222	2.59	0.0100
AR1	-0.3695	0.0594	-6.22	<.0001

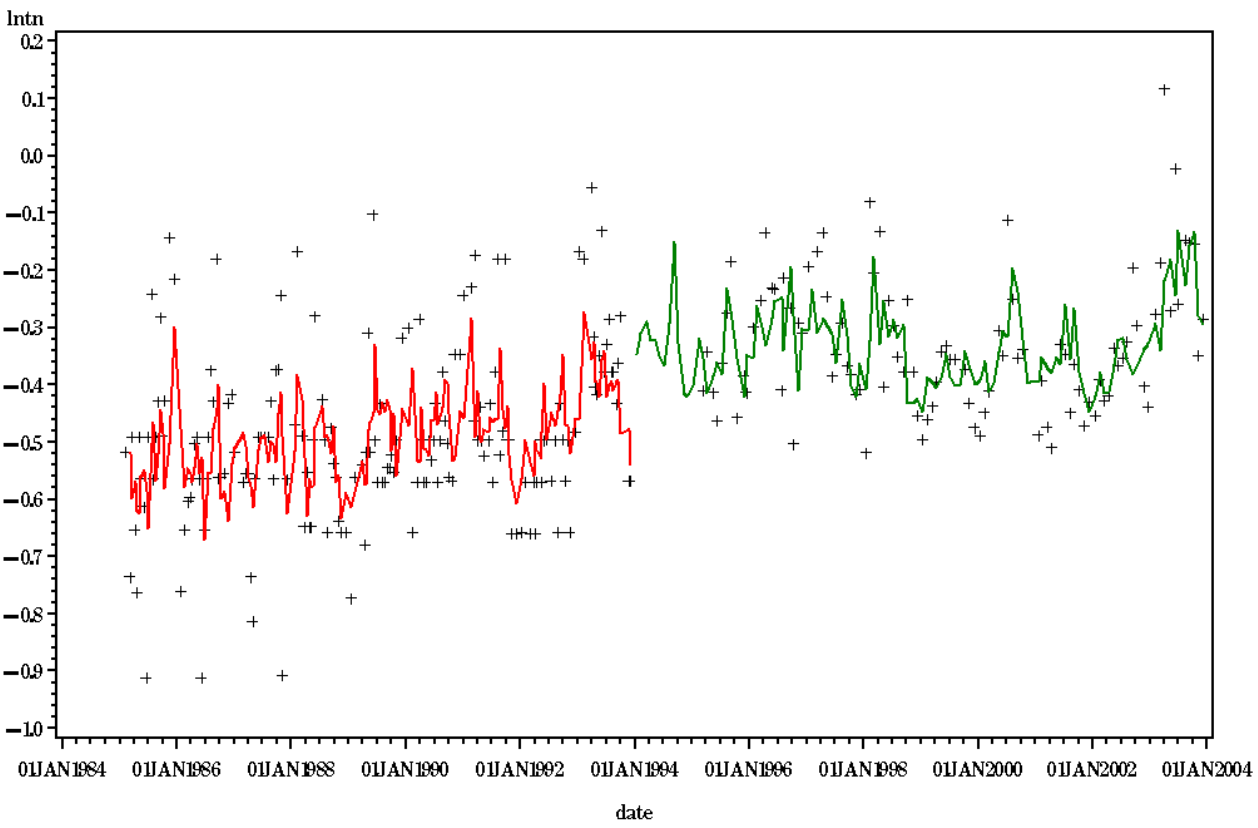
Root MSE = 0.1347 Total R-Square = 0.4269



Tributary	Station	Layer
Rappahannock	LE3.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4813	0.0296	-16.24	<.0001
jan	-0.0673	0.0266	-2.52	0.0122
feb	0.0116	0.0293	0.40	0.6925
mar	-0.0499	0.0228	-2.19	0.0297
apr	-0.0197	0.0223	-0.88	0.3774
may	0.0192	0.0225	0.85	0.3948
jun	0.0159	0.0229	0.69	0.4878
jul	0.0639	0.0229	2.79	0.0057
aug	0.0426	0.0222	1.92	0.0562
sep	0.0368	0.0233	1.58	0.1146
oct	0.0350	0.0227	1.54	0.1250
nov	-0.0279	0.0256	-1.09	0.2769
dec	-0.0602	0.0245	-2.46	0.0148
rtemp	0.0018	0.0032	0.57	0.5680
cyear	0.0043	0.0054	0.79	0.4280
mc	0.1787	0.0479	3.73	0.0002
mc_cyear	-0.0039	0.0087	-0.45	0.6525
flow40	0.0480	0.0188	2.55	0.0114
flow0	0.0658	0.0207	3.17	0.0017
flow100	0.0370	0.0198	1.87	0.0632
AR1	-0.3994	0.0595	-6.71	<.0001

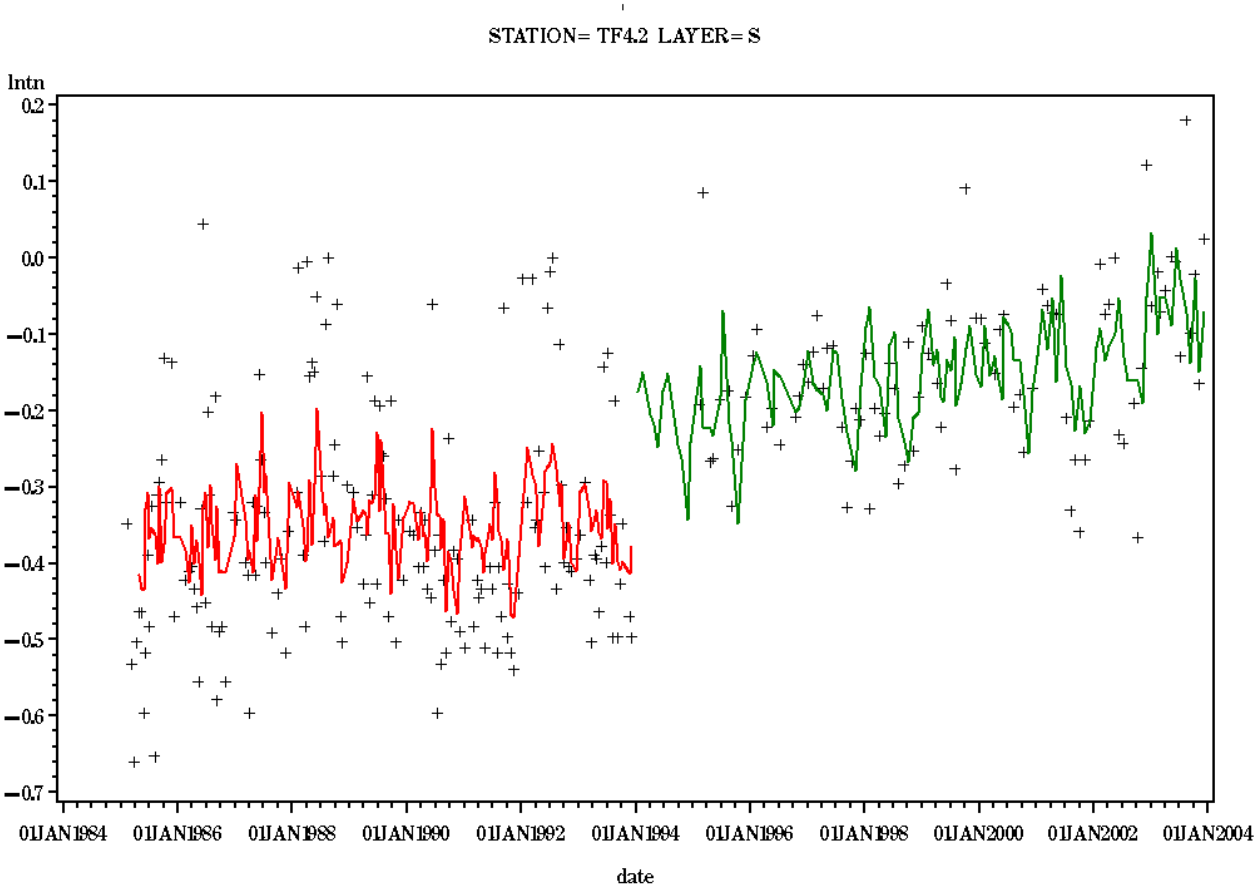
Root MSE = 0.1044 Total R-Square = 0.5986



Tributary	Station	Layer
Rappahannock	LE3.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4399	0.0313	-14.06	<.0001
jan	-0.0253	0.0307	-0.82	0.4110
feb	0.0366	0.0336	1.09	0.2773
mar	-0.0000	0.0259	-0.00	0.9997
apr	-0.0320	0.0261	-1.22	0.2219
may	-0.0123	0.0274	-0.45	0.6533
jun	0.0169	0.0261	0.65	0.5168
jul	0.0220	0.0266	0.83	0.4078
aug	0.0266	0.0258	1.03	0.3040
sep	0.0612	0.0263	2.33	0.0207
oct	-0.0004	0.0260	-0.02	0.9873
nov	-0.0589	0.0289	-2.04	0.0428
dec	-0.0345	0.0290	-1.19	0.2348
rtemp	-0.0022	0.0042	-0.53	0.5988
cyear	0.0103	0.0056	1.84	0.0674
mc	0.0854	0.0511	1.67	0.0957
mc_cyear	-0.0053	0.0091	-0.58	0.5610
flow40	0.0610	0.0221	2.75	0.0063
flow20	0.0675	0.0233	2.90	0.0041
AR1	-0.3247	0.0602	-5.40	<.0001

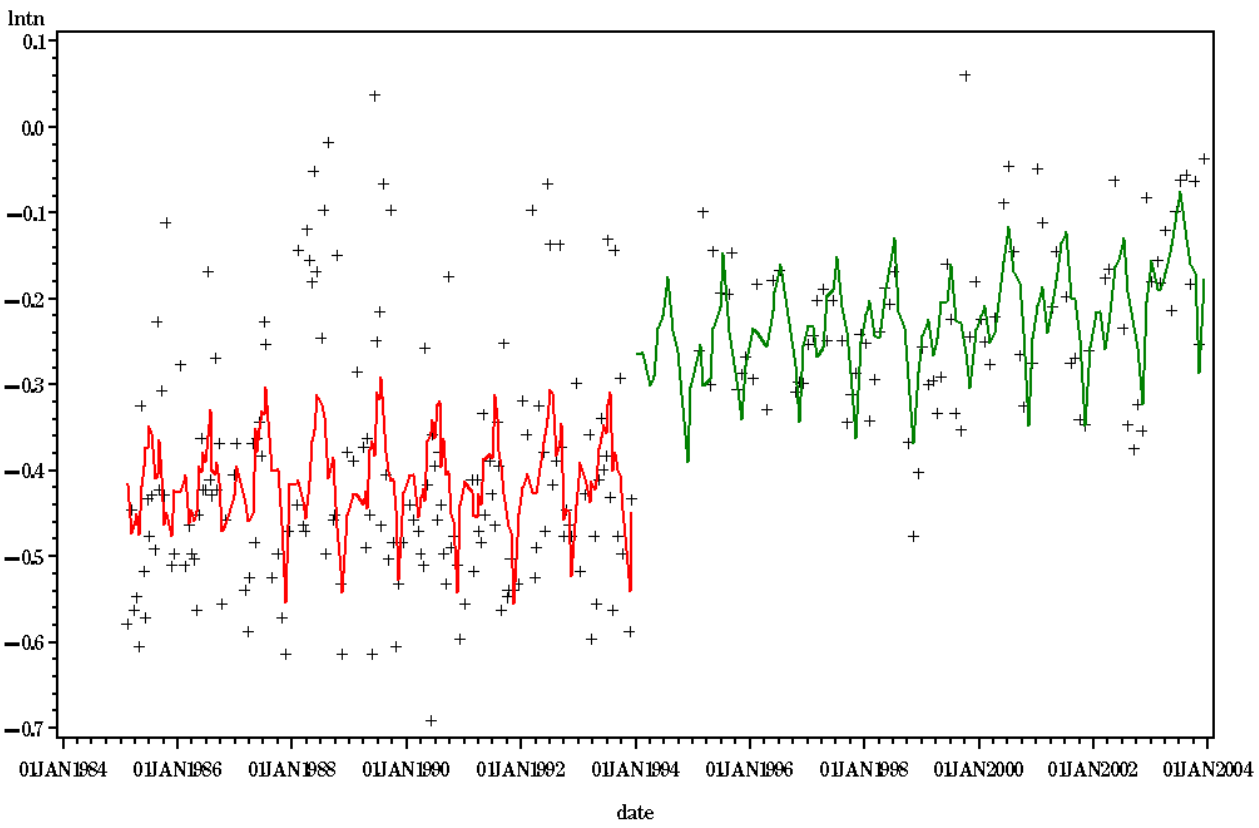
Root MSE = 0.1252 Total R-Square = 0.4374



Tributary	Station	Layer
York	TF4.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3403	0.0251	-13.54	<.0001
jan	0.0311	0.0314	0.99	0.3234
feb	0.0422	0.0296	1.43	0.1550
mar	0.0015	0.0267	0.06	0.9559
apr	-0.0118	0.0250	-0.47	0.6372
may	-0.0200	0.0261	-0.77	0.4433
jun	0.0531	0.0256	2.08	0.0388
jul	0.0493	0.0264	1.87	0.0632
aug	-0.0037	0.0263	-0.14	0.8873
sep	-0.0280	0.0273	-1.02	0.3066
oct	-0.0357	0.0251	-1.42	0.1560
nov	-0.0571	0.0306	-1.86	0.0636
dec	-0.0208	0.0281	-0.74	0.4592
rtemp	-0.0015	0.0031	-0.49	0.6262
cyear	0.0031	0.0046	0.67	0.5015
mc	0.1346	0.0429	3.14	0.0019
mc_cyear	0.0088	0.0077	1.13	0.2576
flow10	0.0829	0.0209	3.96	<.0001
flow100	-0.0569	0.0223	-2.55	0.0113
AR1	-0.1628	0.0646	-2.52	0.0087

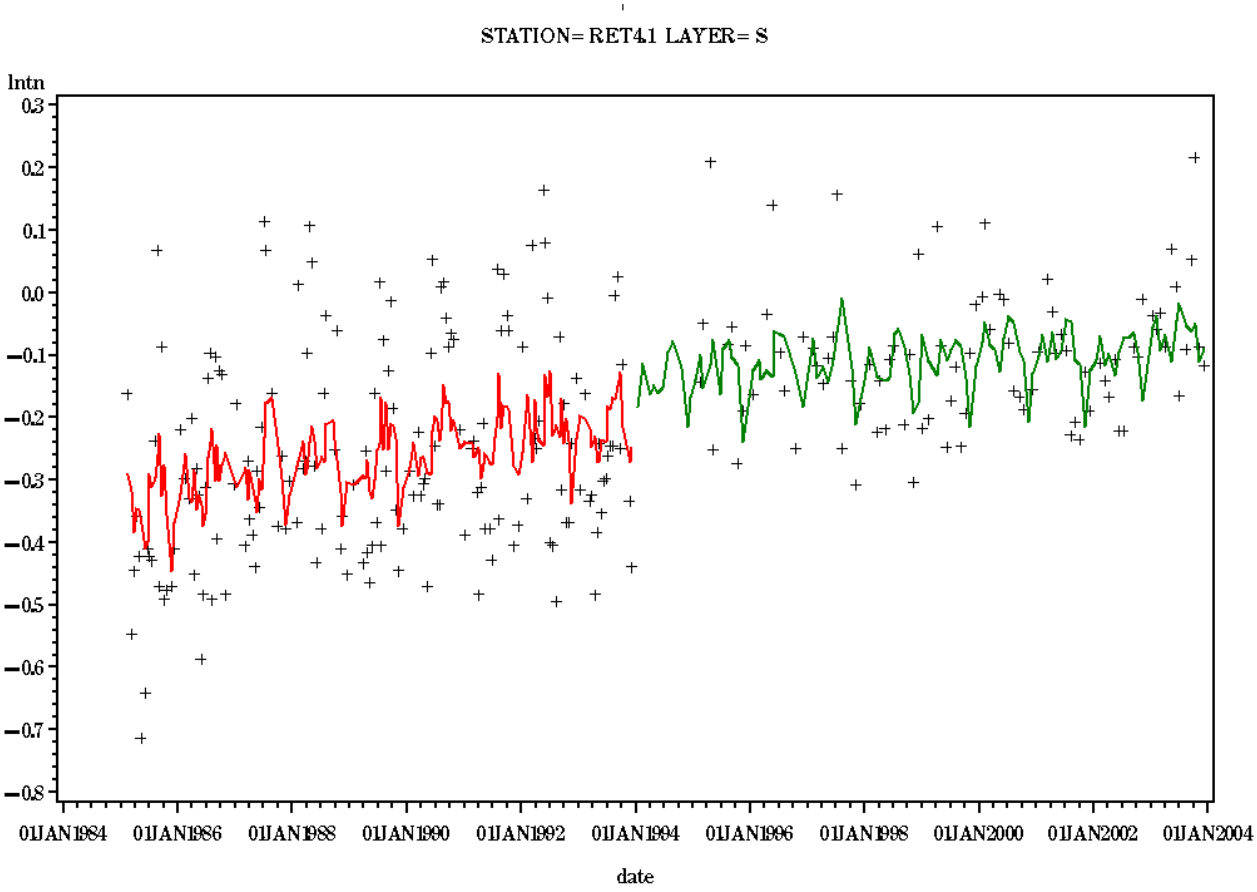
Root MSE = 0.1250 Total R-Square = 0.4693



Tributary	Station	Layer
York	TF4.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4050	0.0213	-19.05	<.0001
jan	0.0034	0.0288	0.12	0.9072
feb	0.0063	0.0280	0.22	0.8232
mar	-0.0307	0.0237	-1.30	0.1960
apr	-0.0228	0.0229	-1.00	0.3205
may	0.0348	0.0237	1.47	0.1430
jun	0.0545	0.0245	2.23	0.0268
jul	0.0902	0.0235	3.84	0.0002
aug	0.0288	0.0242	1.19	0.2344
sep	0.0150	0.0252	0.60	0.5521
oct	-0.0377	0.0229	-1.65	0.1003
nov	-0.1180	0.0273	-4.32	<.0001
dec	-0.0237	0.0265	-0.90	0.3709
rtemp	-0.0010	0.0028	-0.37	0.7145
cyear	0.0022	0.0038	0.57	0.5691
mc	0.1336	0.0364	3.68	0.0003
mc_cyear	0.0079	0.0064	1.23	0.2181
flow10	0.0341	0.0184	1.86	0.0647
AR1	-0.0689	0.0644	-1.07	0.1466

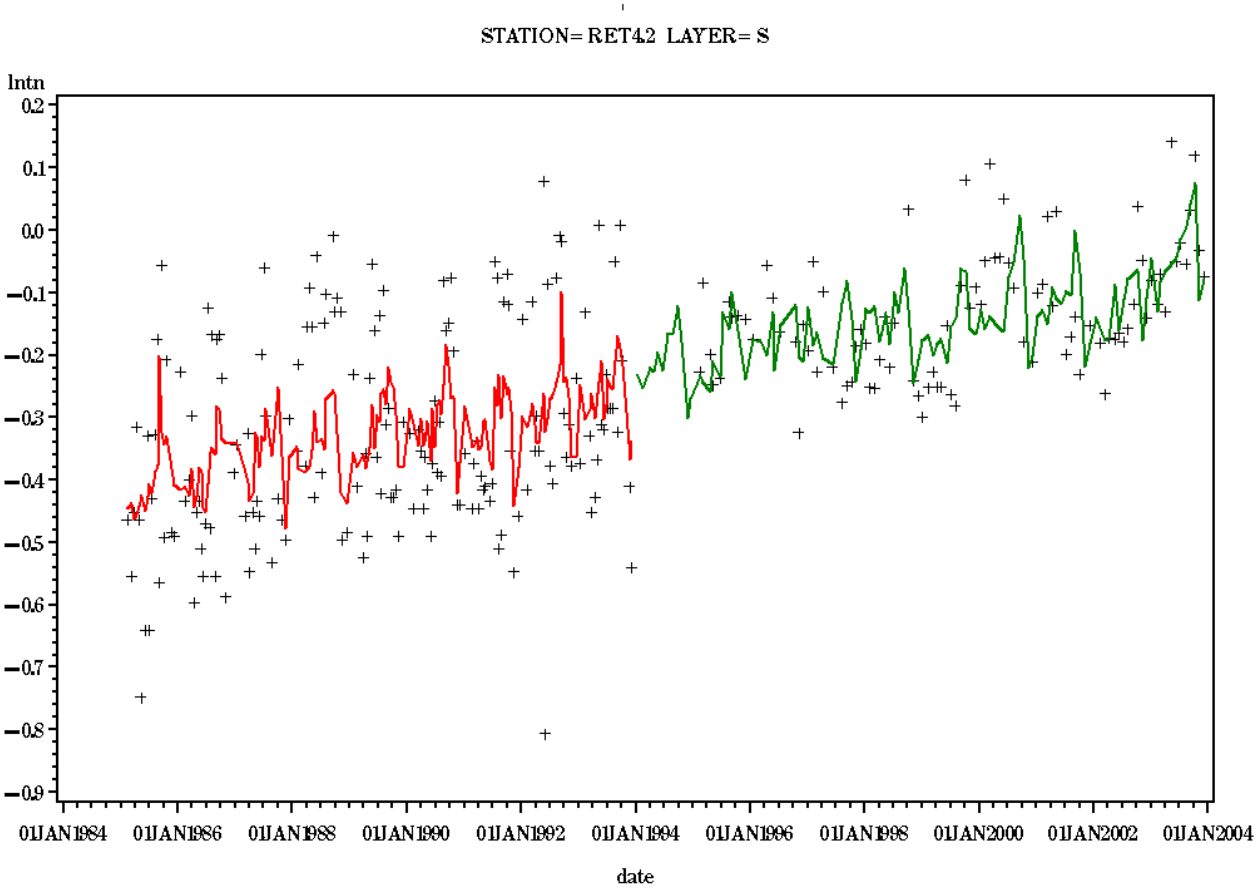
Root MSE = 0.1182 Total R-Square = 0.4479



Tributary	Station	Layer
York	RET4.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1938	0.0307	-6.30	<.0001
jan	-0.0074	0.0373	-0.20	0.8426
feb	0.0271	0.0362	0.75	0.4543
mar	-0.0167	0.0301	-0.55	0.5798
apr	-0.0029	0.0293	-0.10	0.9216
may	-0.0246	0.0299	-0.82	0.4109
jun	-0.0071	0.0300	-0.24	0.8133
jul	0.0441	0.0297	1.48	0.1393
aug	0.0577	0.0307	1.88	0.0614
sep	0.0332	0.0315	1.05	0.2944
oct	0.0100	0.0292	0.34	0.7315
nov	-0.0827	0.0354	-2.34	0.0204
dec	-0.0308	0.0350	-0.88	0.3797
rtemp	-0.0021	0.0046	-0.47	0.6414
cyear	0.0147	0.0055	2.67	0.0080
mc	0.0564	0.0531	1.06	0.2891
mc_cyear	-0.0088	0.0093	-0.95	0.3455
AR1	-0.2124	0.0640	-3.32	0.0012

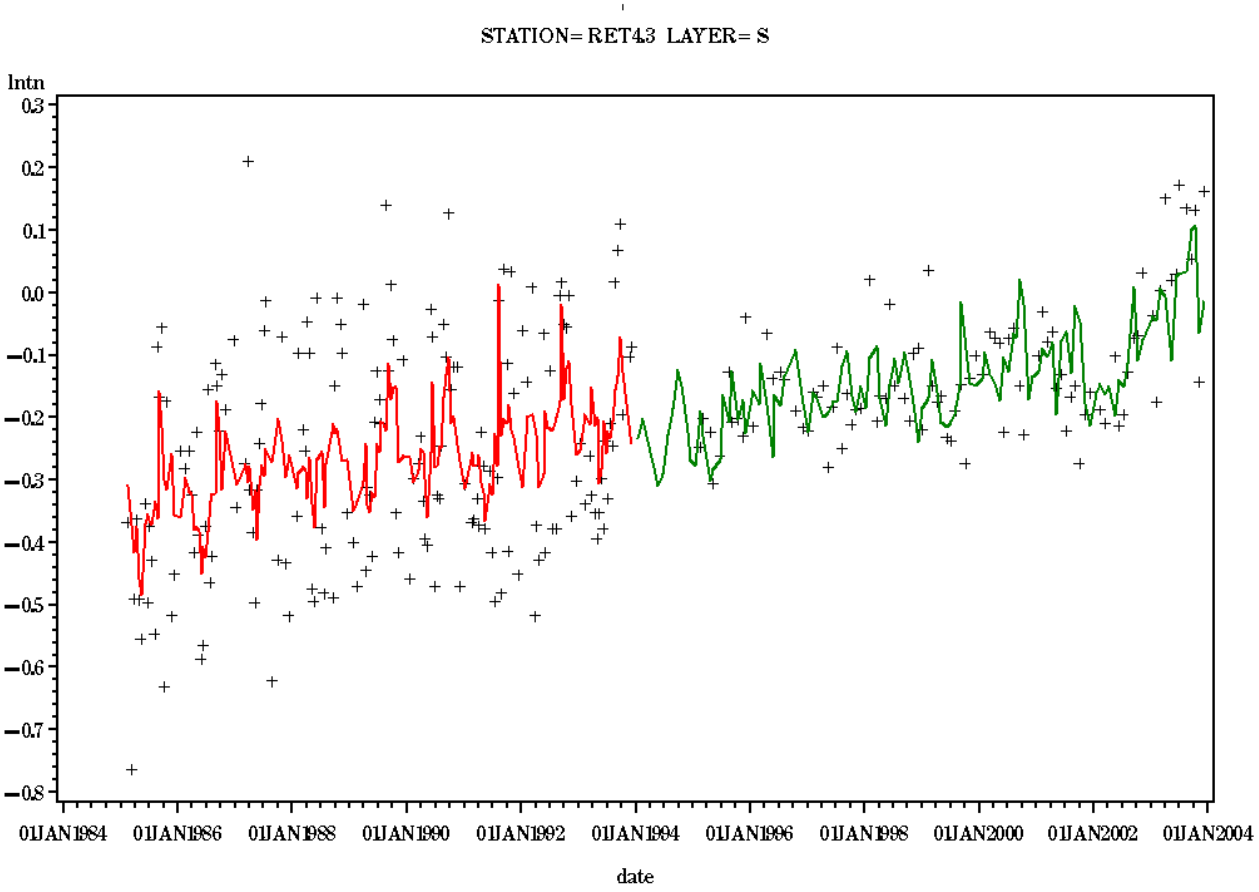
Root MSE = 0.1444 Total R-Square = 0.3210



Tributary	Station	Layer
York	RET4.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2510	0.0240	-10.45	<.0001
jan	0.0002	0.0327	0.01	0.9950
feb	-0.0252	0.0318	-0.79	0.4282
mar	-0.0236	0.0268	-0.88	0.3800
apr	-0.0423	0.0256	-1.65	0.1001
may	0.0123	0.0279	0.44	0.6609
jun	-0.0292	0.0266	-1.10	0.2728
jul	0.0276	0.0267	1.04	0.3010
aug	0.0408	0.0274	1.49	0.1384
sep	0.1100	0.0293	3.76	0.0002
oct	0.0516	0.0260	1.99	0.0479
nov	-0.0749	0.0328	-2.29	0.0232
dec	-0.0473	0.0309	-1.53	0.1278
rtemp	0.0035	0.0043	0.83	0.4067
cyear	0.0171	0.0043	3.95	0.0001
mc	0.0382	0.0418	0.91	0.3618
mc_cyear	-0.0012	0.0073	-0.17	0.8680
flow10	0.0653	0.0207	3.15	0.0018
AR1	-0.0679	0.0648	-1.05	0.1516

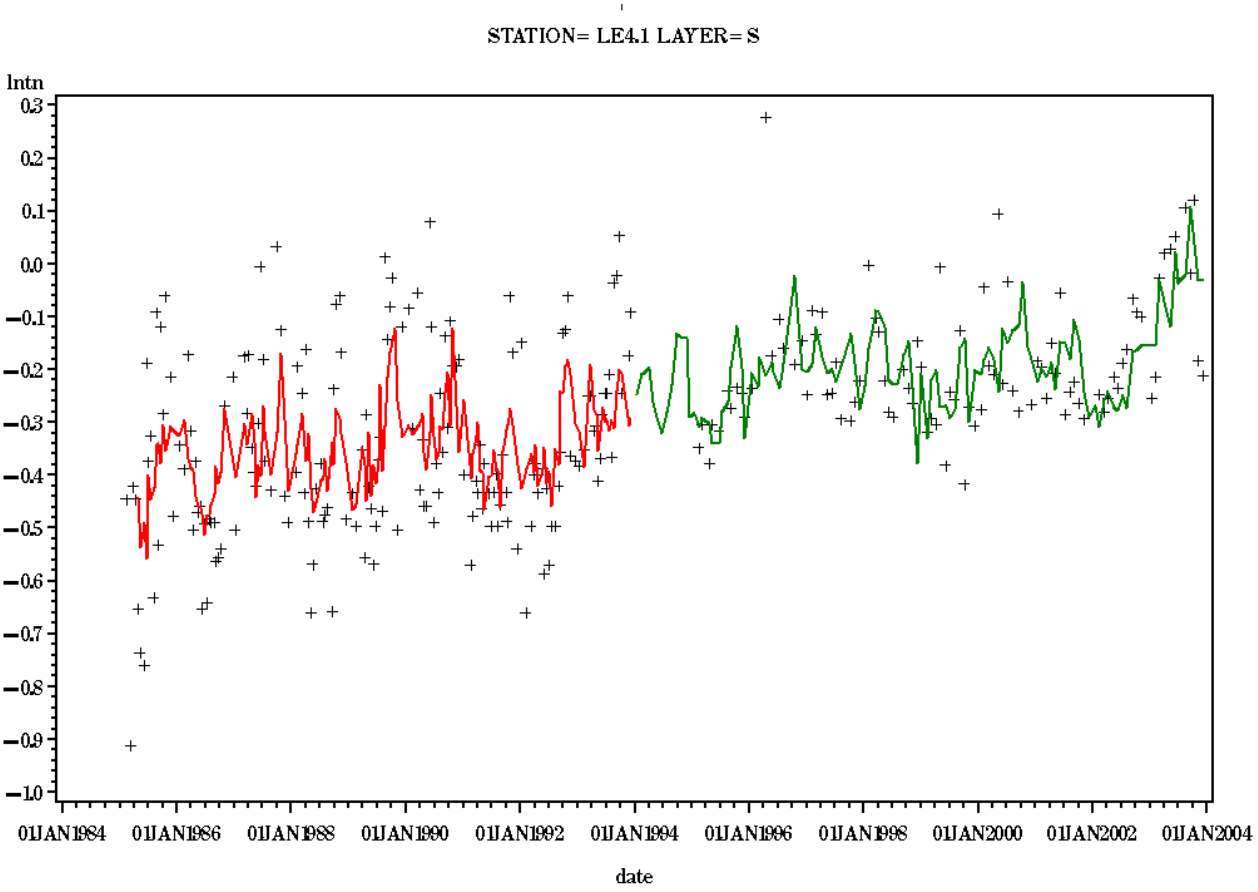
Root MSE = 0.1341 Total R-Square = 0.4385



Tributary	Station	Layer
York	RET4.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.1786	0.0267	-6.70	<.0001
jan	-0.0372	0.0350	-1.06	0.2882
feb	0.0023	0.0340	0.07	0.9467
mar	-0.0014	0.0279	-0.05	0.9587
apr	-0.0366	0.0277	-1.32	0.1871
may	-0.0862	0.0283	-3.05	0.0025
jun	-0.0240	0.0280	-0.86	0.3918
jul	-0.0013	0.0277	-0.05	0.9639
aug	0.0319	0.0288	1.11	0.2692
sep	0.1069	0.0288	3.71	0.0003
oct	0.0616	0.0273	2.25	0.0252
nov	0.0012	0.0331	0.04	0.9714
dec	-0.0170	0.0339	-0.50	0.6160
rtemp	-0.0094	0.0035	-2.68	0.0080
cyear	0.0183	0.0048	3.81	0.0002
mc	-0.0510	0.0452	-1.13	0.2594
mc_cyear	0.0017	0.0080	0.21	0.8342
flow10	0.0722	0.0221	3.27	0.0013
AR1	-0.1241	0.0641	-1.94	0.0311

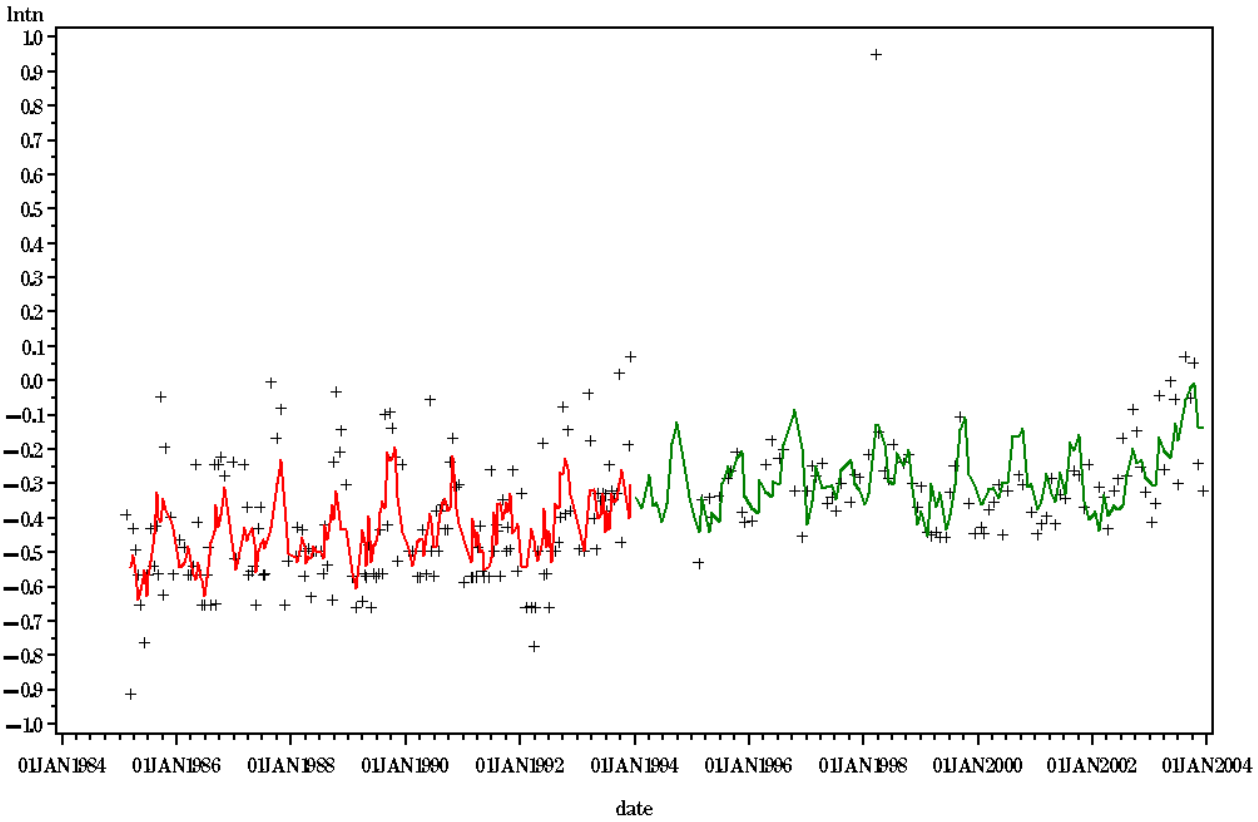
Root MSE = 0.1396 Total R-Square = 0.3734



Tributary	Station	Layer
York	LE4.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.2926	0.0287	-10.19	<.0001
jan	-0.0221	0.0348	-0.64	0.5258
feb	-0.0309	0.0339	-0.91	0.3637
mar	0.0081	0.0291	0.28	0.7824
apr	-0.0011	0.0278	-0.04	0.9695
may	-0.0538	0.0285	-1.89	0.0603
jun	-0.0395	0.0280	-1.41	0.1593
jul	-0.0324	0.0282	-1.15	0.2519
aug	-0.0135	0.0284	-0.48	0.6345
sep	0.0672	0.0299	2.25	0.0255
oct	0.0950	0.0286	3.32	0.0010
nov	0.0432	0.0334	1.29	0.1970
dec	-0.0201	0.0338	-0.59	0.5532
rtemp	-0.0067	0.0043	-1.56	0.1196
cyear	0.0118	0.0053	2.23	0.0268
mc	0.0193	0.0487	0.40	0.6921
mc_cyear	0.0077	0.0087	0.88	0.3796
flow0	0.0635	0.0236	2.69	0.0077
flow70	0.0657	0.0248	2.64	0.0088
flow100	0.0456	0.0250	1.82	0.0702
AR1	-0.1882	0.0639	-2.94	0.0031

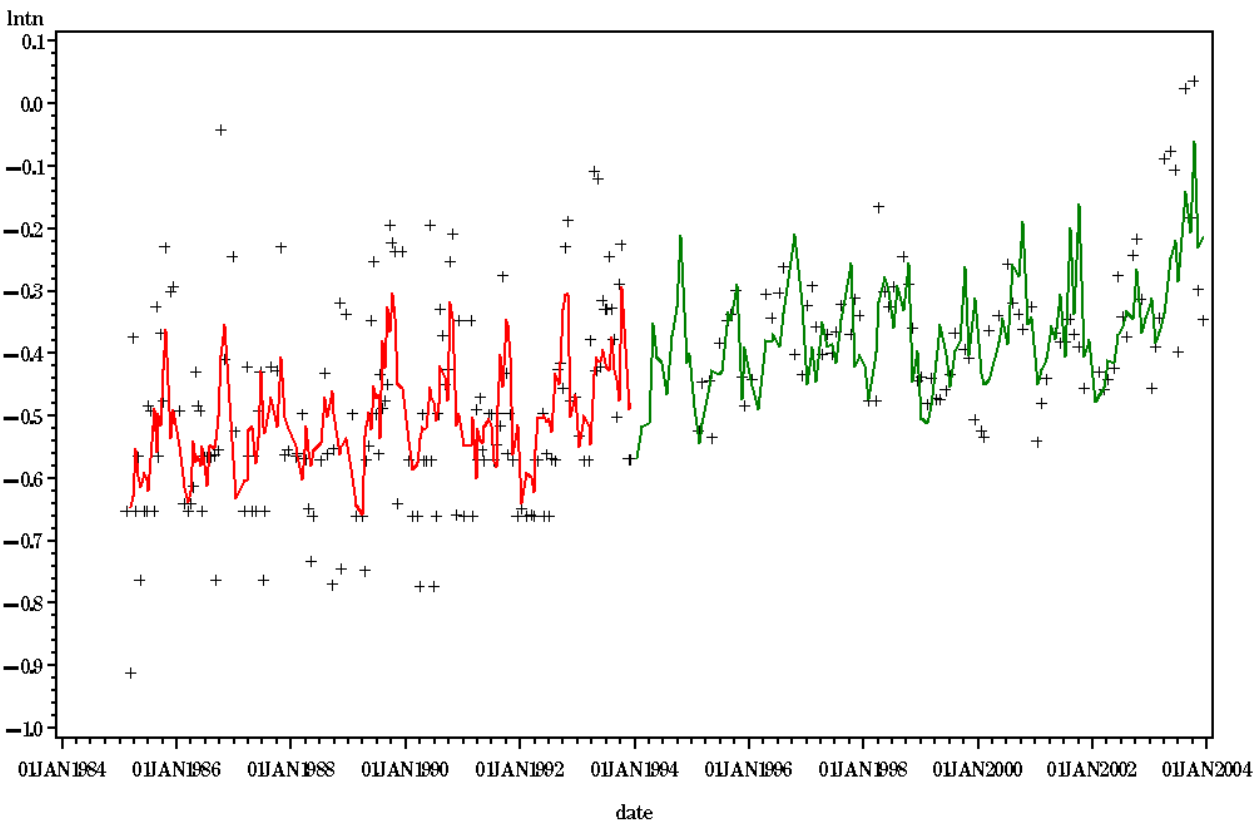
Root MSE = 0.1387 Total R-Square = 0.4247



Tributary	Station	Layer
York	LE4.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.3707	0.0295	-12.56	<.0001
jan	-0.0778	0.0383	-2.03	0.0433
feb	-0.0928	0.0374	-2.48	0.0138
mar	-0.0043	0.0306	-0.14	0.8892
apr	-0.0461	0.0297	-1.55	0.1220
may	-0.0551	0.0310	-1.77	0.0774
jun	-0.0464	0.0303	-1.53	0.1269
jul	-0.0334	0.0303	-1.10	0.2718
aug	0.0622	0.0320	1.94	0.0532
sep	0.1136	0.0324	3.51	0.0005
oct	0.1311	0.0306	4.29	<.0001
nov	0.0427	0.0364	1.17	0.2416
dec	0.0063	0.0362	0.17	0.8630
rtemp	-0.0082	0.0051	-1.60	0.1109
cyear	0.0145	0.0053	2.73	0.0068
mc	0.0286	0.0500	0.57	0.5680
mc_cyear	-0.0006	0.0088	-0.06	0.9488
flow0	0.0879	0.0250	3.52	0.0005
flow50	0.0555	0.0266	2.09	0.0379
AR1	-0.1263	0.0640	-1.97	0.0289

Root MSE = 0.1531 Total R-Square = 0.3963



Tributary	Station	Layer
York	LE4.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.4548	0.0210	-21.63	<.0001
jan	-0.0738	0.0295	-2.50	0.0131
feb	-0.0886	0.0287	-3.08	0.0023
mar	-0.0848	0.0231	-3.67	0.0003
apr	-0.0118	0.0232	-0.51	0.6129
may	-0.0135	0.0235	-0.58	0.5654
jun	0.0101	0.0237	0.43	0.6699
jul	-0.0196	0.0236	-0.83	0.4072
aug	0.0537	0.0231	2.32	0.0210
sep	0.0509	0.0250	2.04	0.0429
oct	0.1513	0.0232	6.52	<.0001
nov	-0.0010	0.0282	-0.04	0.9710
dec	0.0271	0.0287	0.95	0.3448
rtemp	-0.0007	0.0041	-0.16	0.8692
cyear	0.0115	0.0038	3.00	0.0030
mc	0.0098	0.0360	0.27	0.7856
mc_cyear	0.0056	0.0064	0.88	0.3786
flow60	0.0558	0.0218	2.56	0.0111
flow50	0.0638	0.0217	2.94	0.0036
AR1	-0.0630	0.0652	-0.97	0.1711

Root MSE = 0.1173 Total R-Square = 0.4814

Appendix C – 07/08/06 Presentation to TMAW

Total Nitrogen

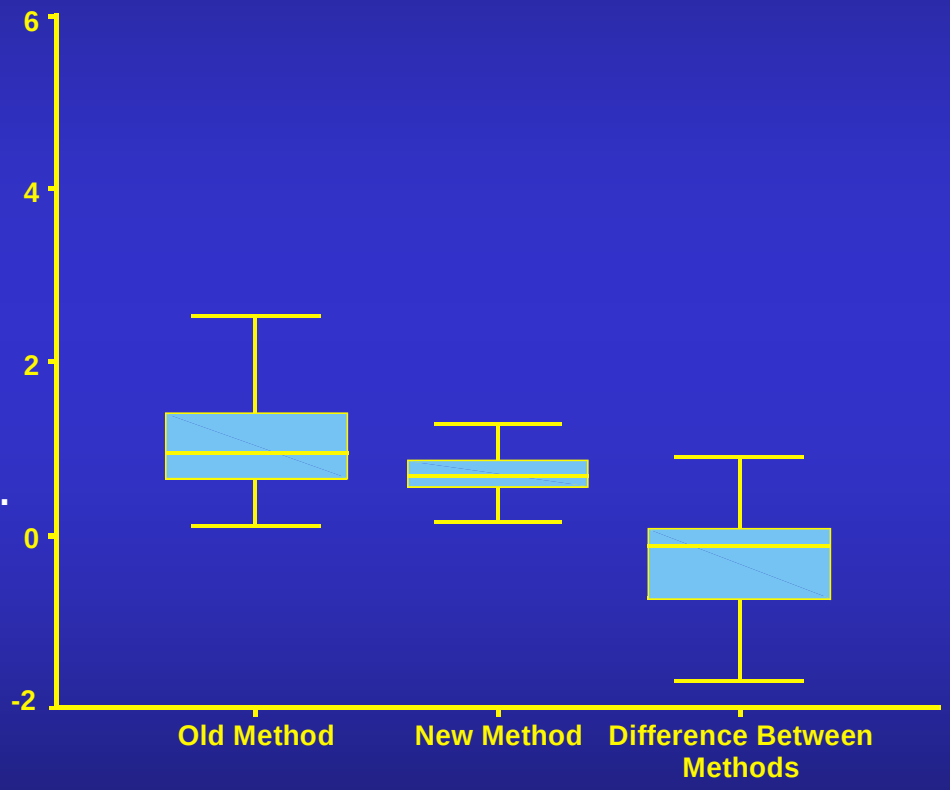
TN - Paired Comparisons

- **Mean difference between methods significantly different from zero:**

  Student's t
  t value =-26.66; Prob. >| t | <0.0001,

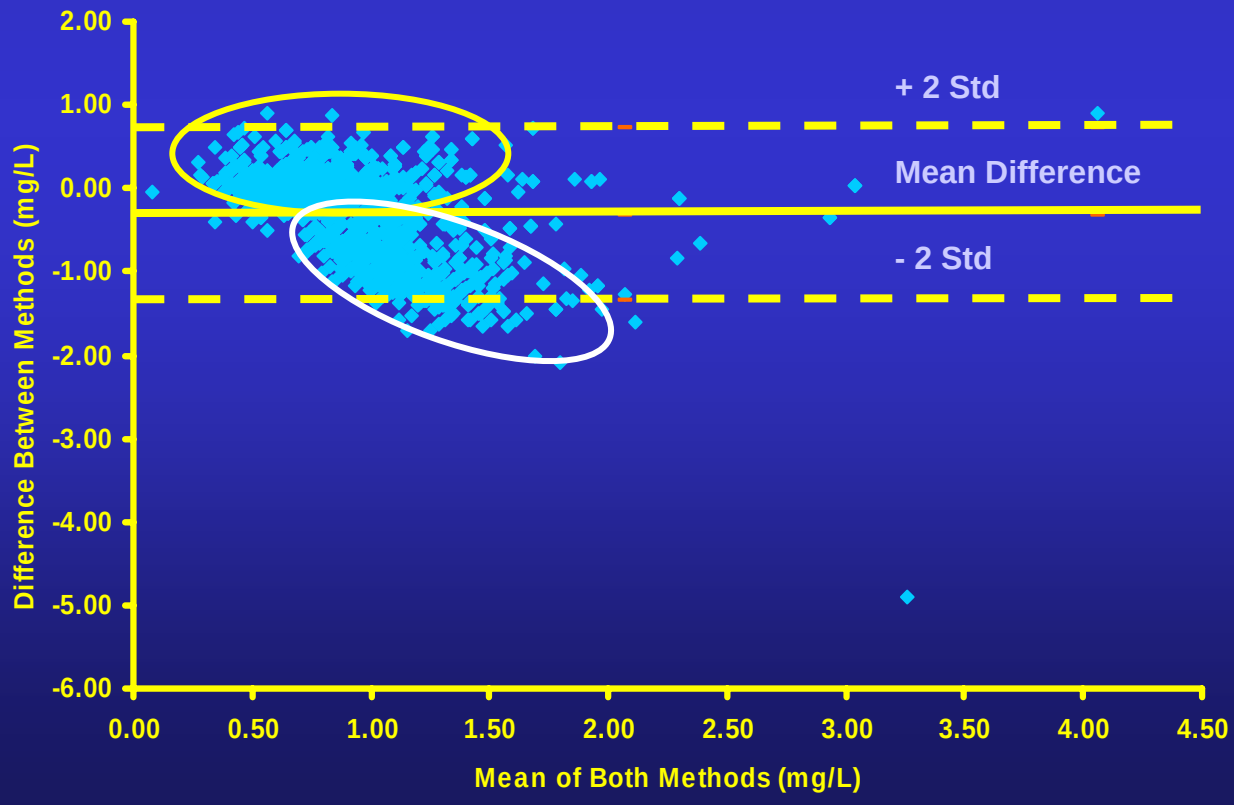
  Wilcoxon Rank Sum
  S value =-500812; Prob. >|S| <0.0001.

- **Nearly 75% of differences <= 0.00.**



TN - Screening Analyses

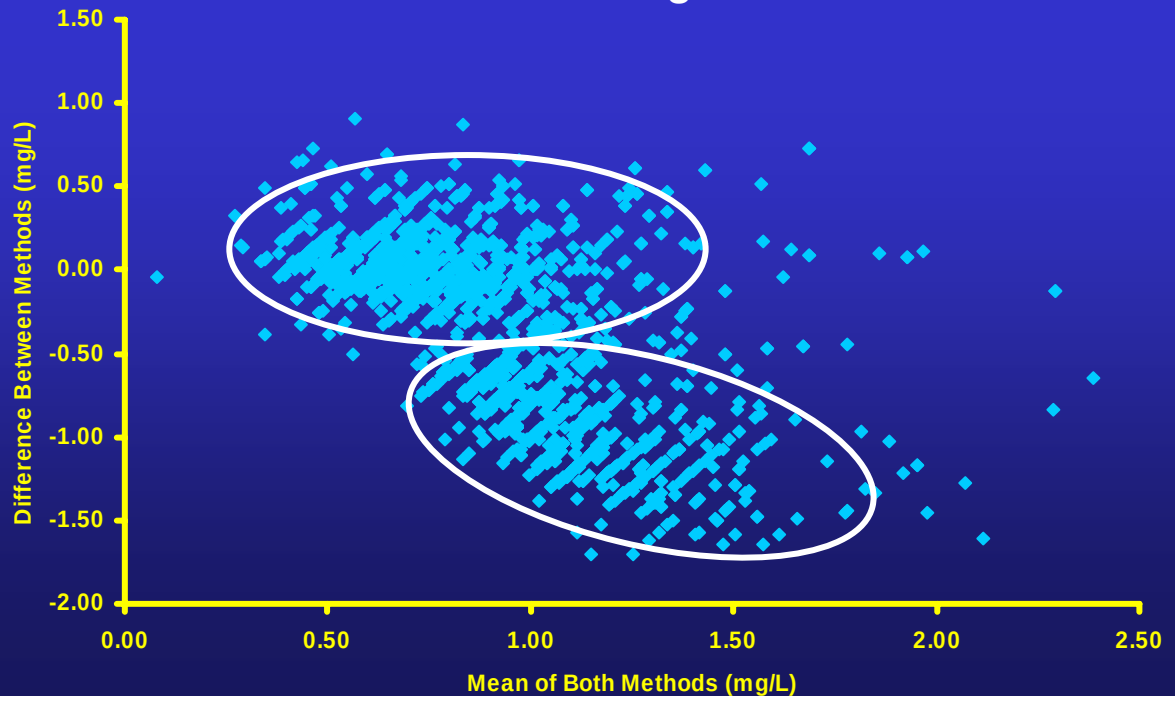
- Mean difference between methods: -0.32±0.52.
- Old TN Method biased high relative to New TN Method up to mg/L.
- There were two distinct groups of values for the differences.



TN – Screening Analyses

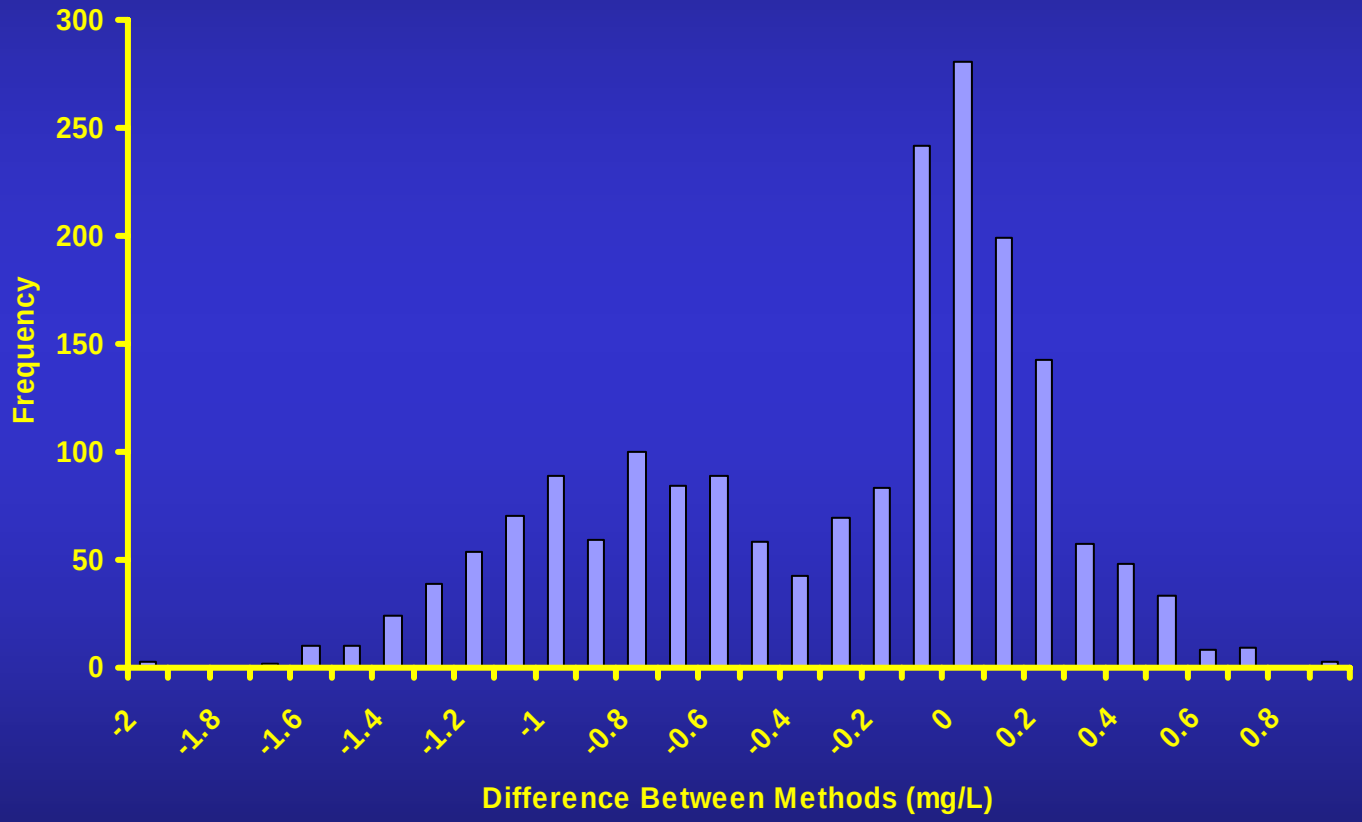
- **First group of differences**
  - **Mean: 0.00 mg/L**
  - **Range: –0.50 to 0.80 mg/L**
  - **Range constant regardless of mean conc.**

- **Second group of differences**
  - **Mean: -1.00 mg/L**
  - **Range: -0.50 to –2.00**
  - **Difference decreases with increasing mean conc.**



TN - Screening Analyses

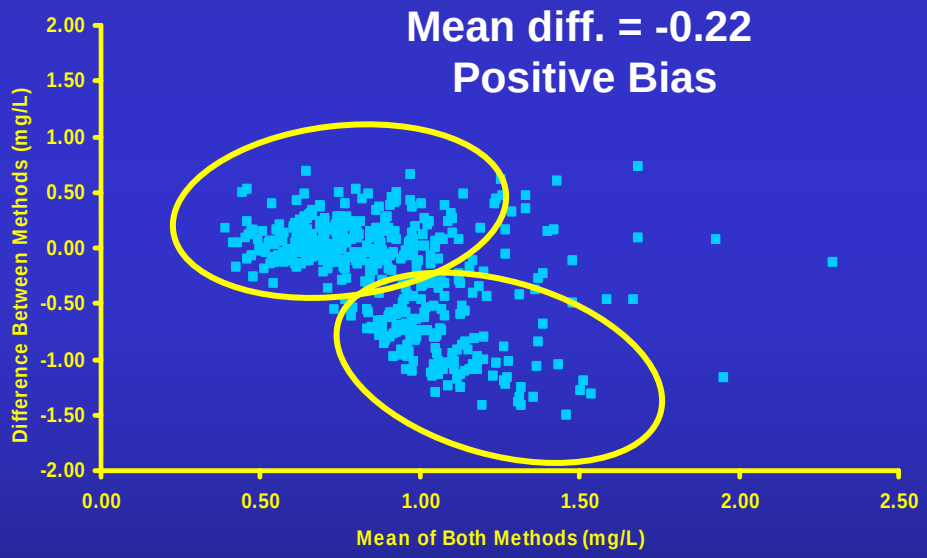
- **Frequency histogram confirms two groups in bias.**



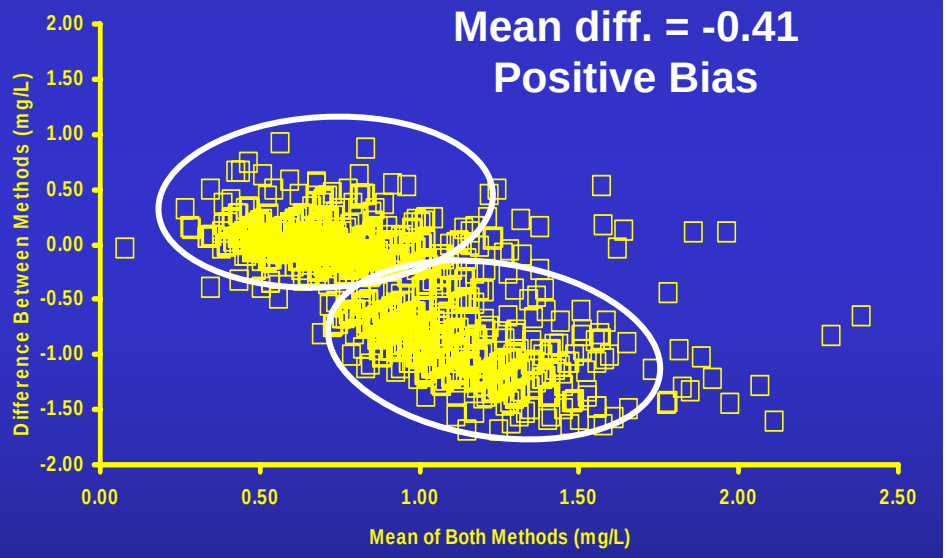
TN – Monitoring Program Effect

- Is the Monitoring Program source of groups?
- Two groups persist in both programs.

CBP

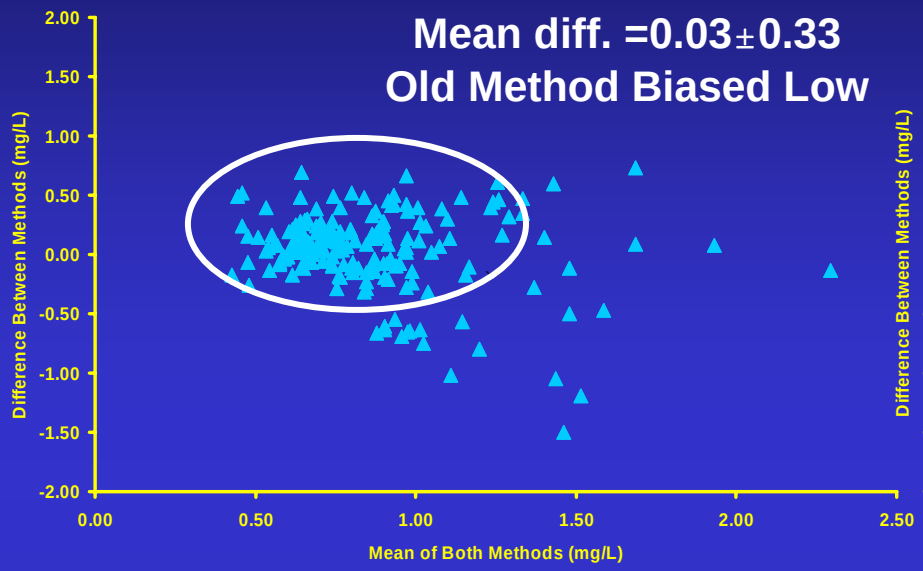


Pfiesteria

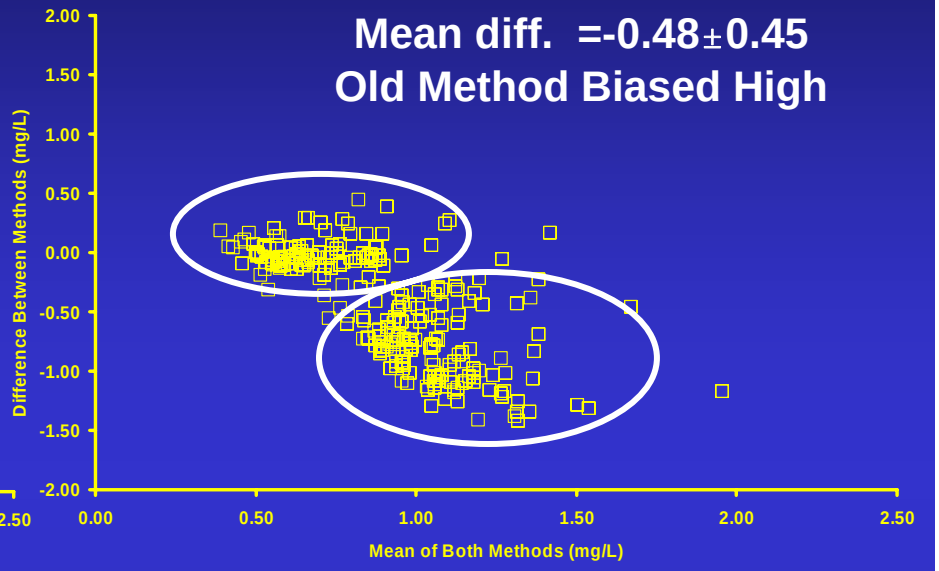


TN – Collection Agency Effect (CBP)

PRO

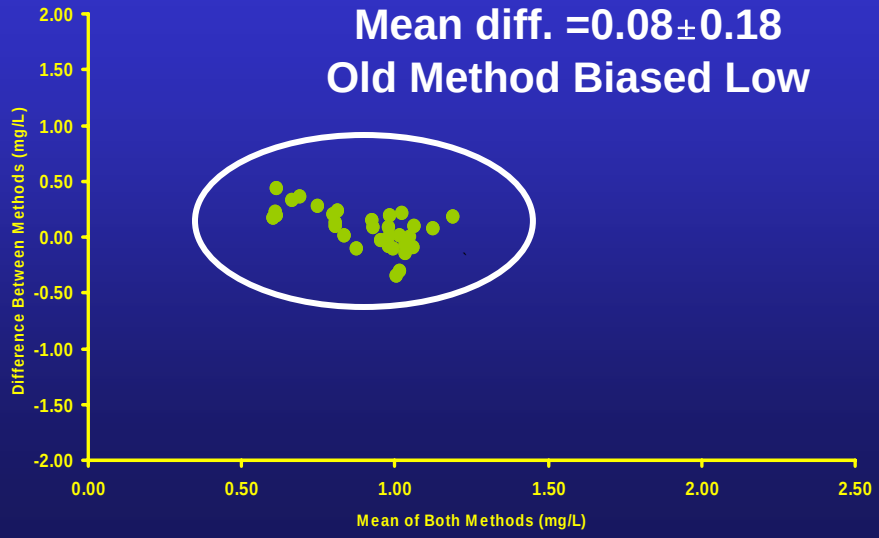


TRO



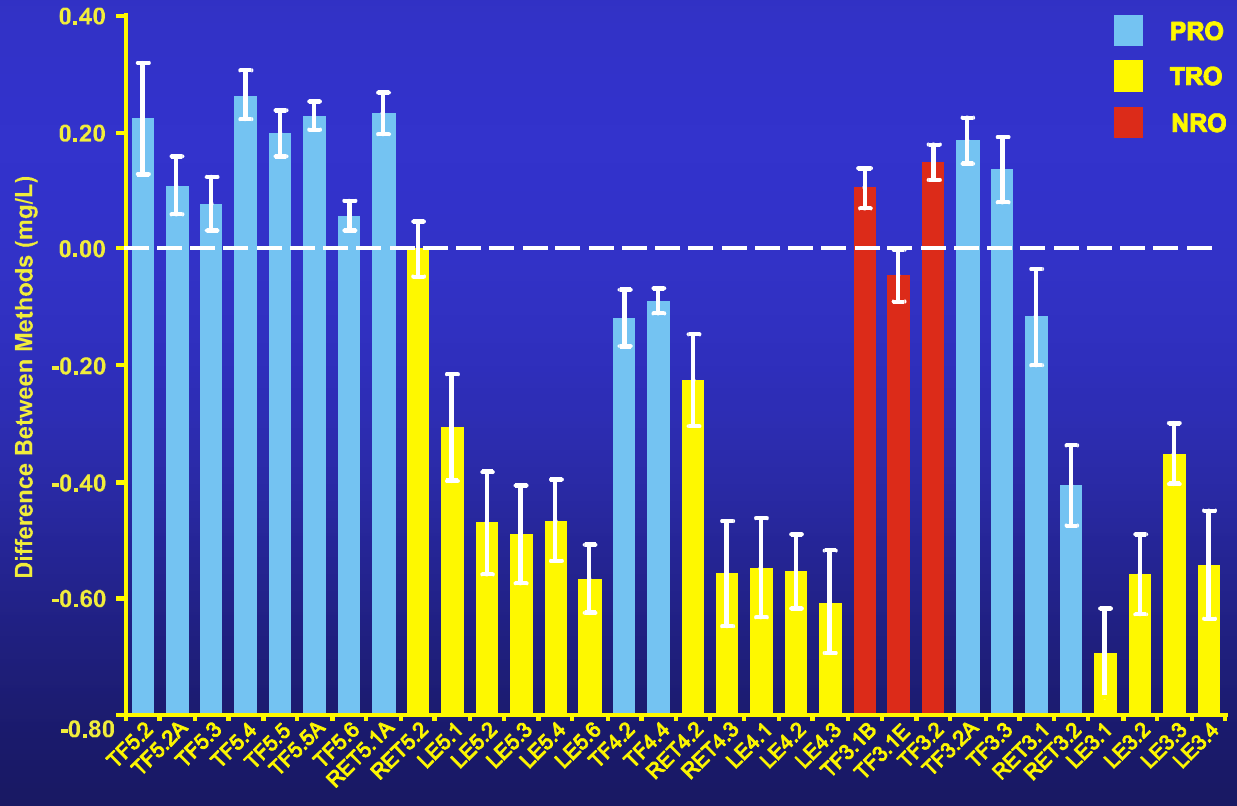
- Was collection agency (PRO, TRO, NRO) responsible?
- Grouping persists in TRO data with Old Method biased high.
- Grouping disappears in PRO data but now Old Method biased low.
- Grouping disappears in NRO data but now Old Method biased low.

NRO



TN – Spatial Effects on Bias (CBP)

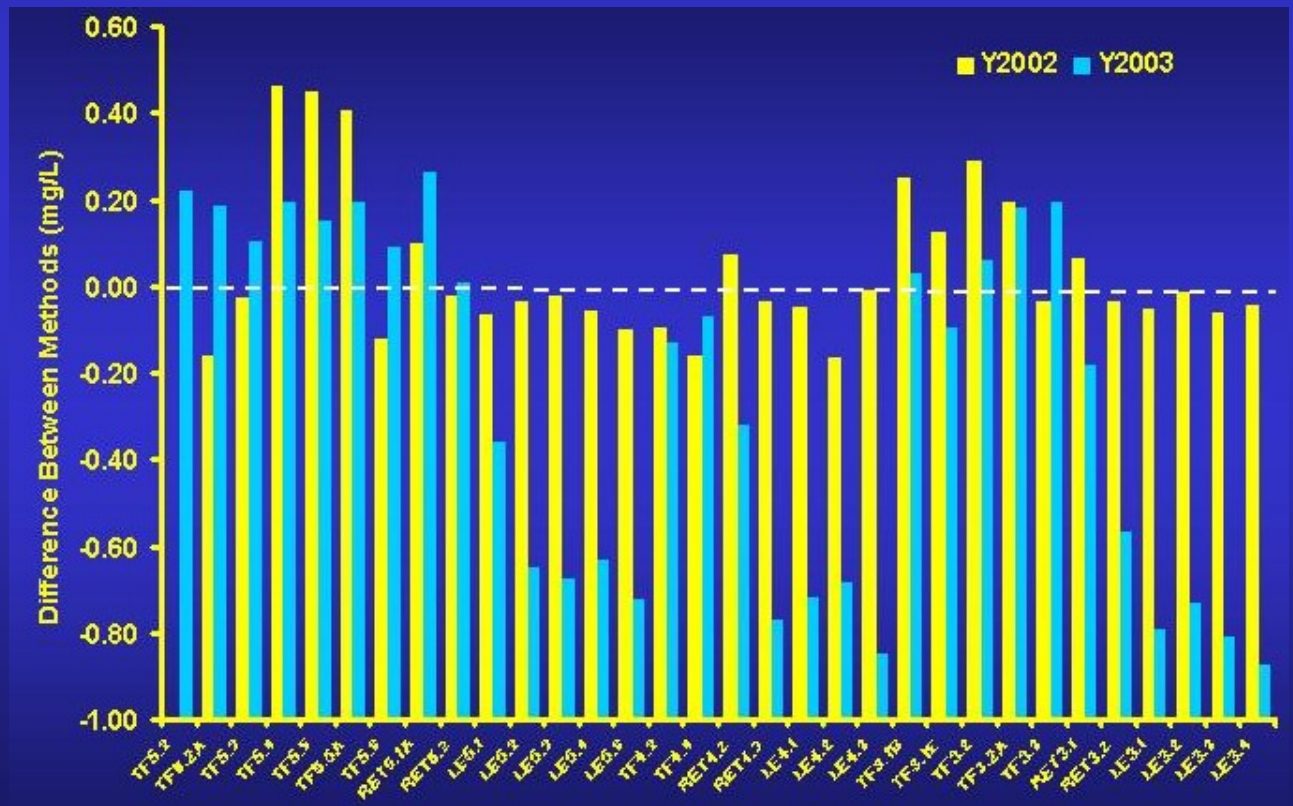
- Negative bias at most Tidal Fresh and Oligohaline stations.
- PRO and NRO responsible for collection at most of these stations.
- Positive bias at higher salinity (mostly TRO) stations.



TN – Spatial and Temporal Effects (CBP)

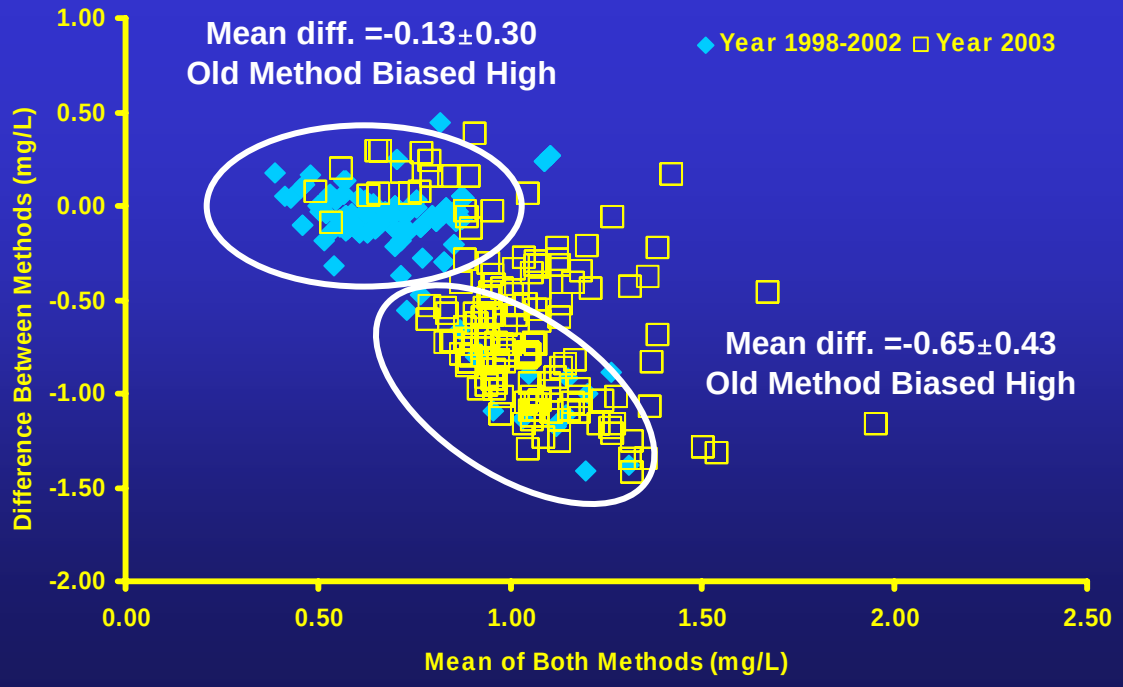
- **Difference Between Methods substantially higher during 2002.**

- **Spatial pattern with respect to salinity persists between years but bias was closer to 0.00 mg/l during 2002 for higher salinity stations.**



TN – Temporal Effects (CBP - TRO)

- Two groups observed appear to be two different time periods.
- Old Method is biased high for both time periods.
- Mean difference for data prior to 2003 is significantly higher (T-test).
- What was the cause of this difference?



TN – Environmental Effects (CBP - TRO)

	Date	Month	Salinity	Salinity^2	Temperature
Difference	-0.71;<0.01	-0.11;0.02	-0.12;0.01	-0.26;<0.01	-0.20;<0.01
	Depth	pH	CHL a	TSS	PC
Difference	-0.08;0.07	-0.08;<0.09	-0.22;<0.01	0.16;<0.01	0.13;<0.01

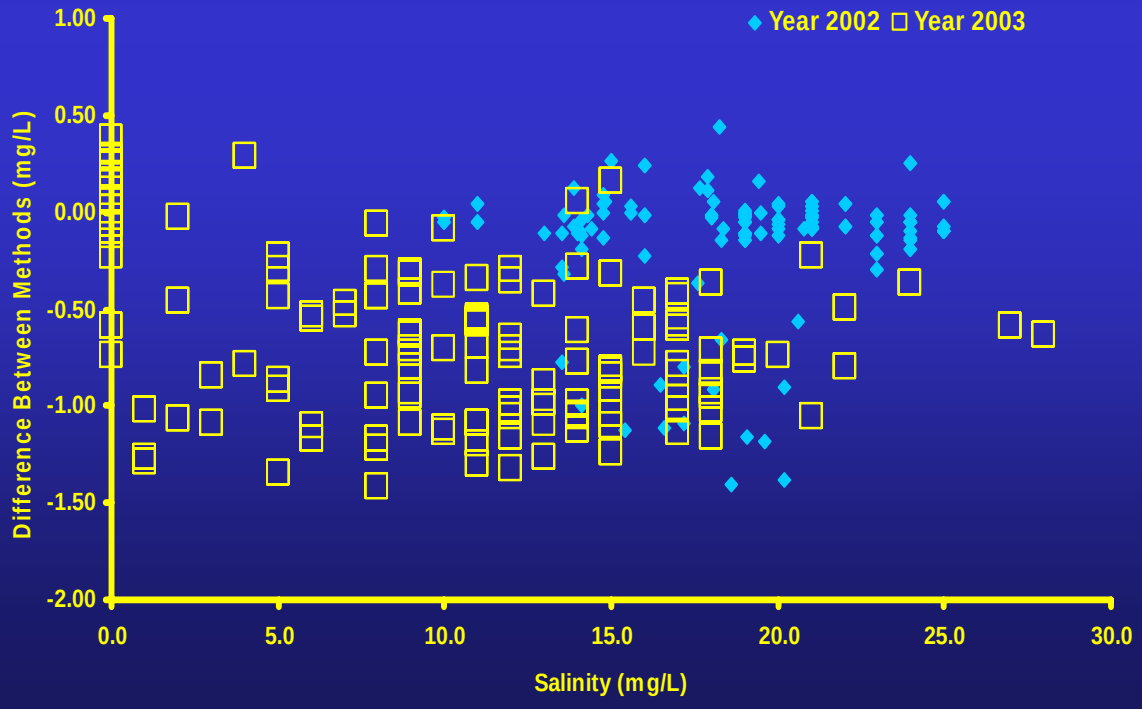
Shown are Pearson's |R| and associated p values. All correlations based on > 400 observations except CHL a (221).

- Several significant correlations but none entirely explain the patterns observed.

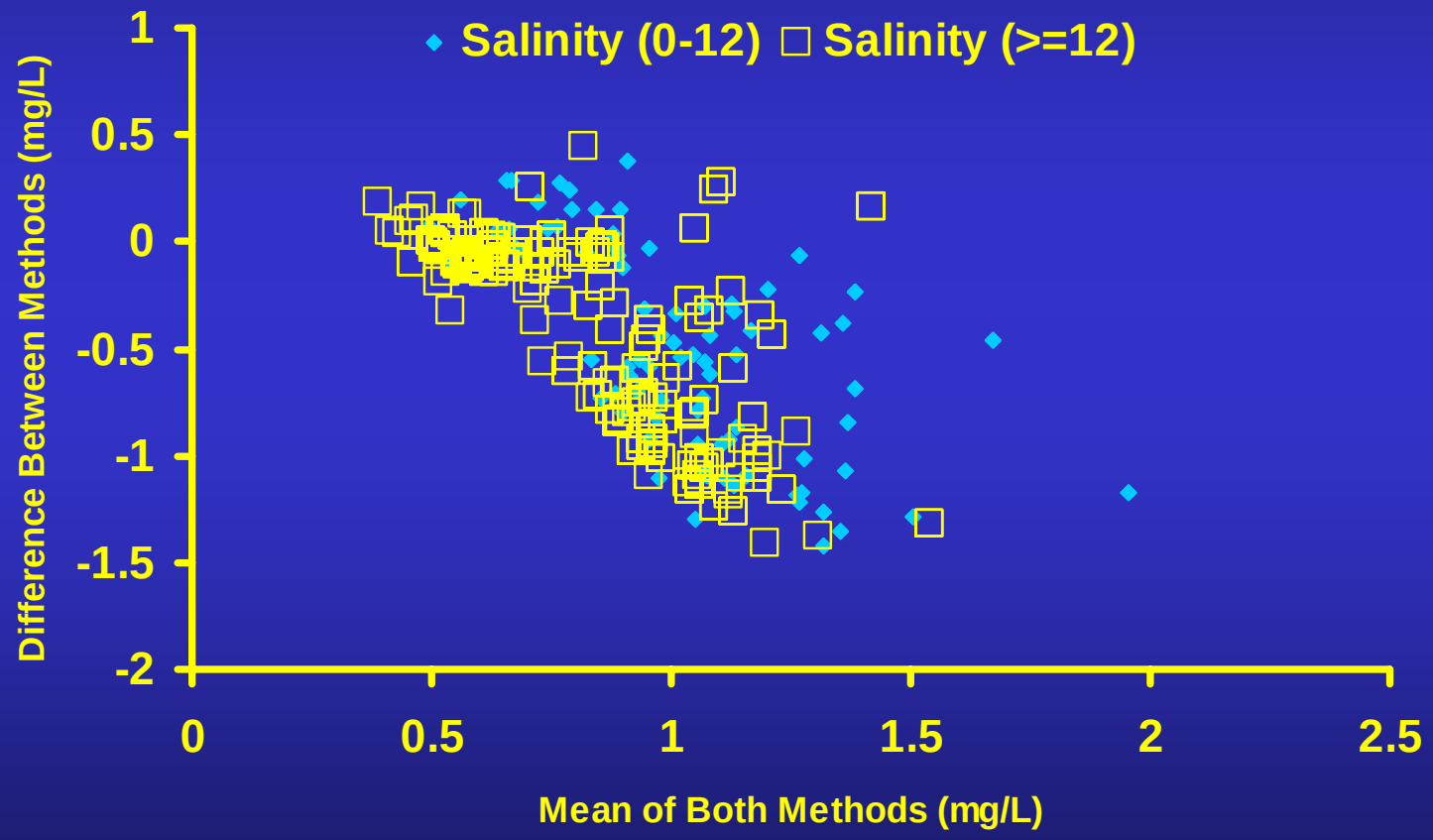
- Other potential predictors?

TN – Environmental Effects (CBP - TRO)

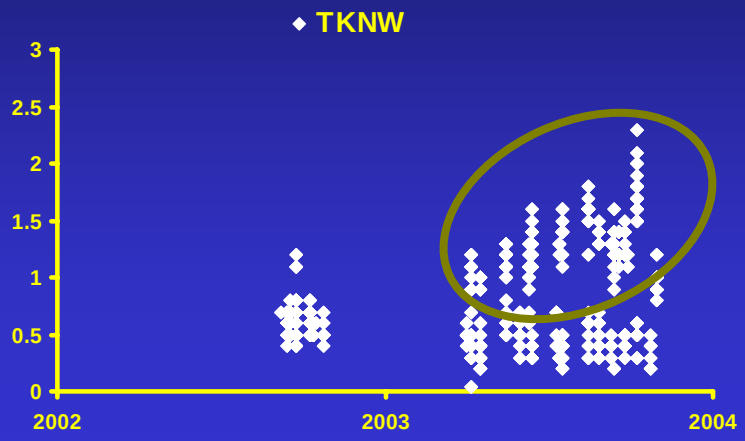
- Prior to 2003, difference was much higher even in high salinities.
- For 2003, values of difference at 0 salinities were higher.
- Overall significant but slight correlation with salinity (|R|=-0.12;0.01).
- For 2003, significant but slight correlation with salinity (|R|=-0.37;0.01).

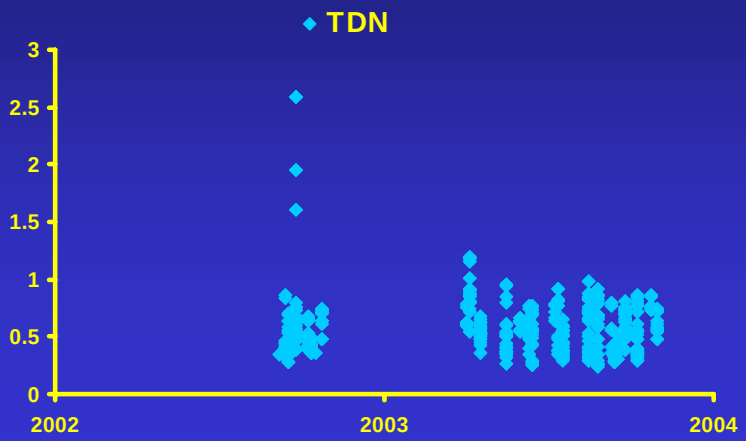


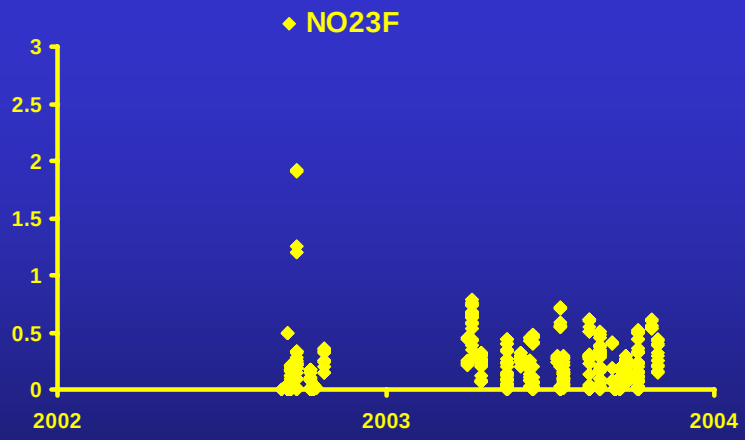
TN – Environmental Effects (CBP - TRO)

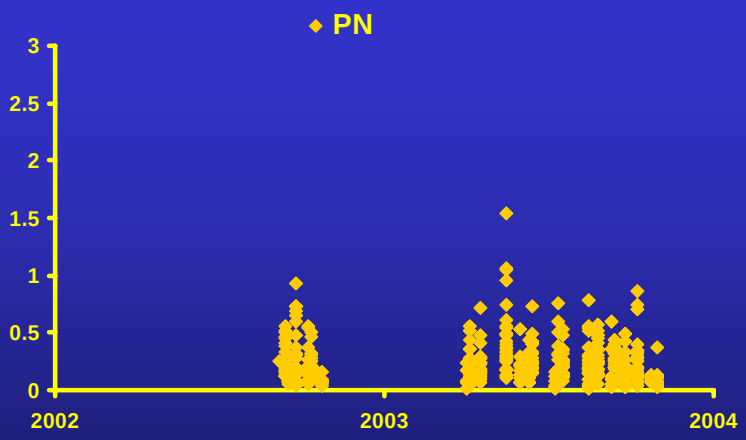


TN – Component Variables (CBP – TRO)



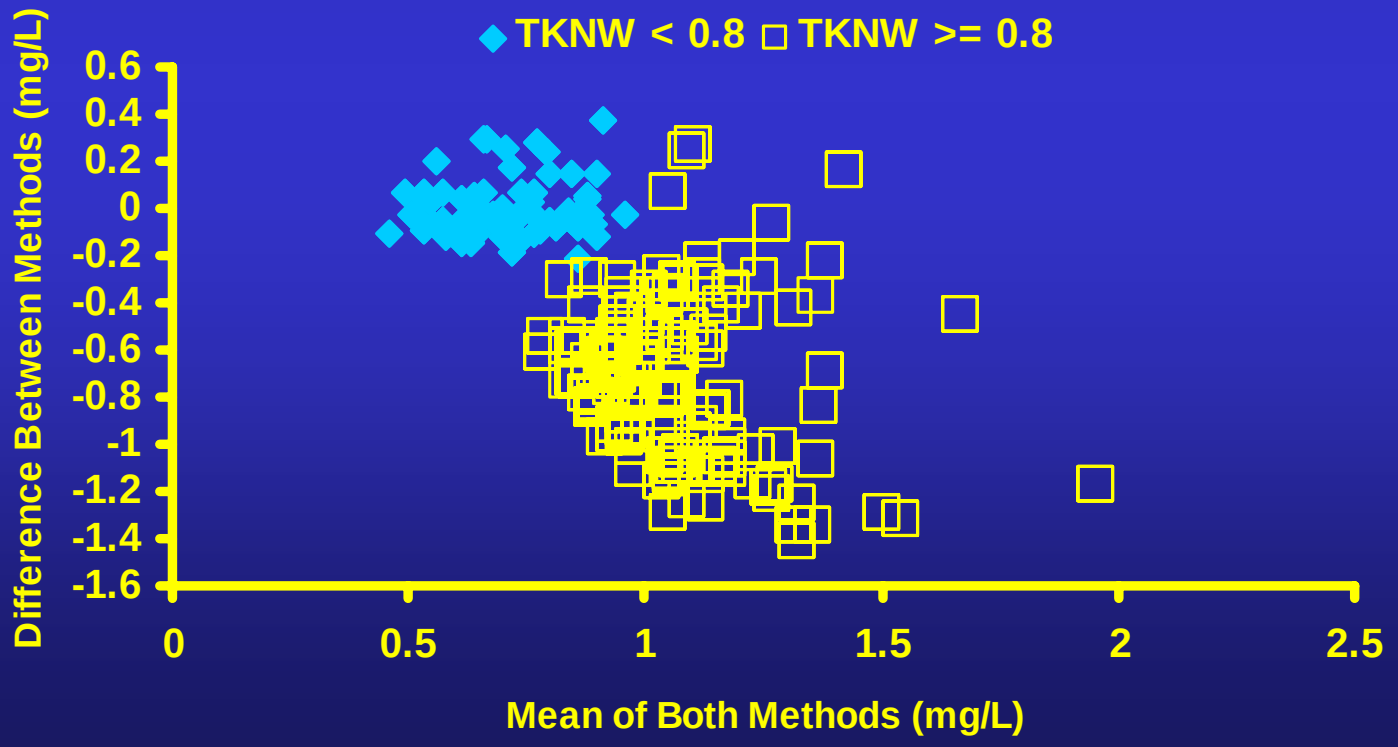




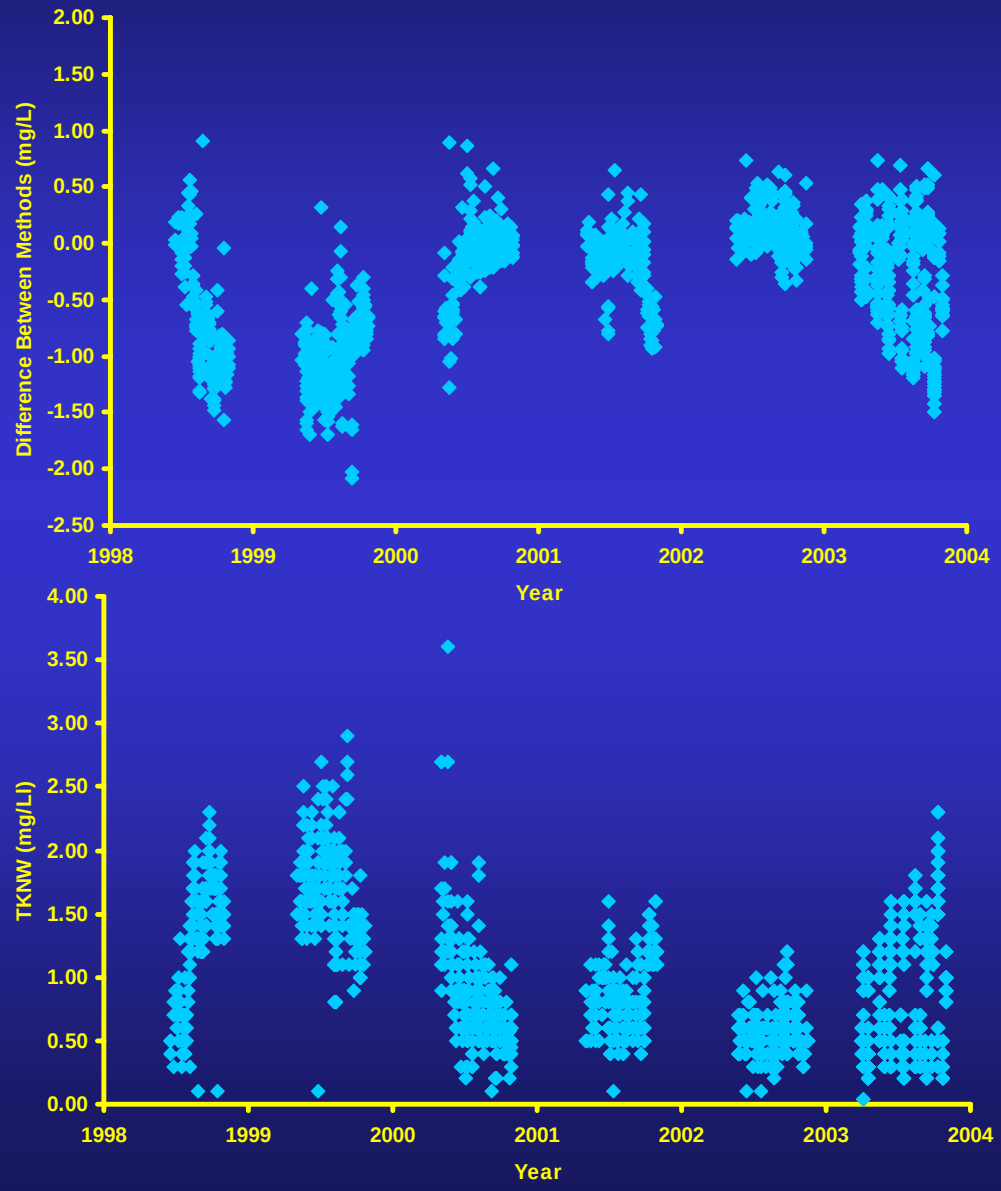


TN – Component Variables (CBP - TRO)

- Plots of component variables indicate TKNW as problem.
- Plot of bias confirms this observation.
- Correlation analysis of TKNW with various predictors reveals only weak relationships (max |R|=0.31 with CHLA).

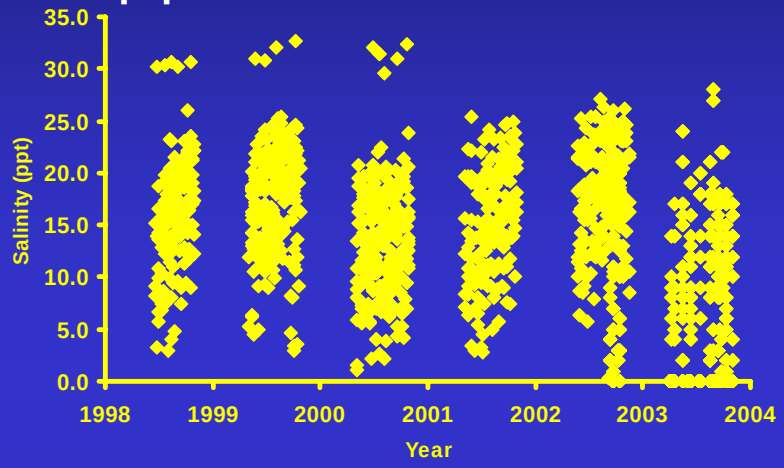


TN – Component Variables (All Data)

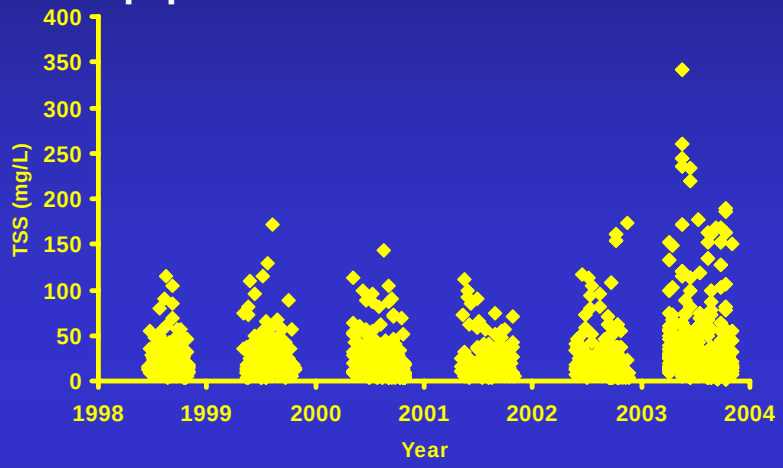


TN – Environmental Effects (All Data)

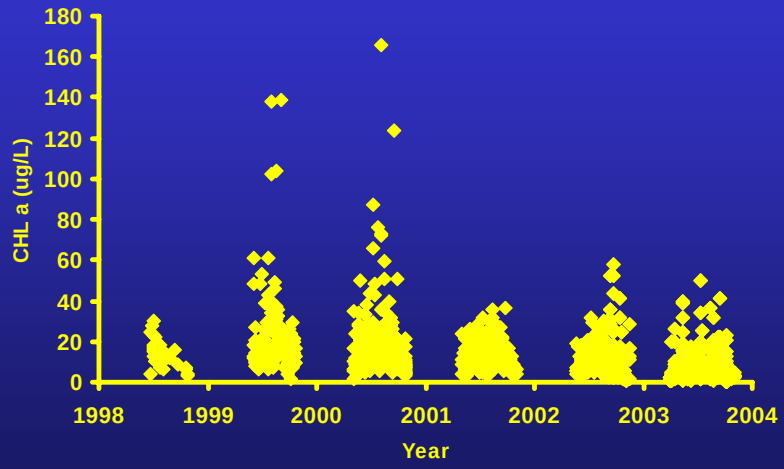
|R| = 0.25



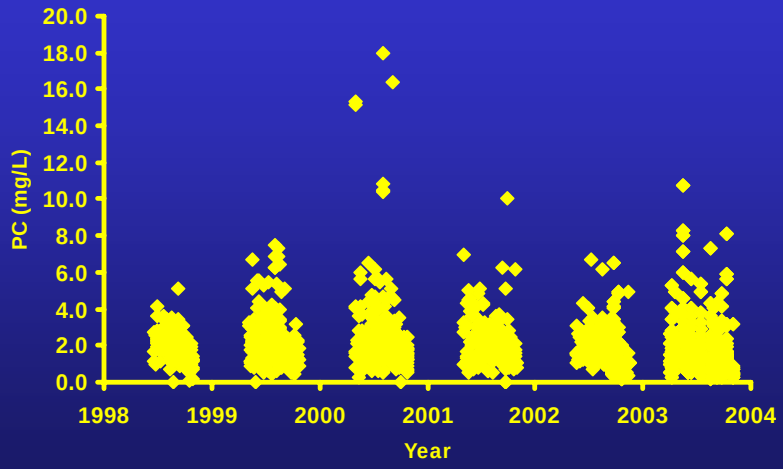
|R| = NS



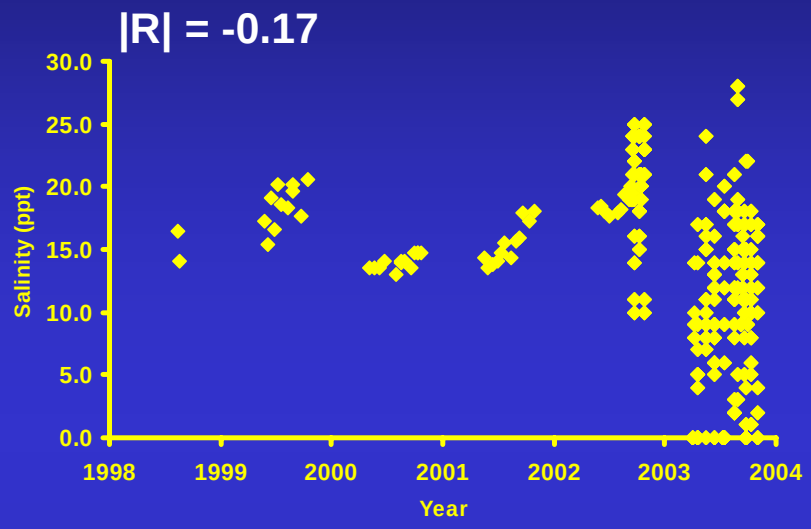
|R| = 0.29

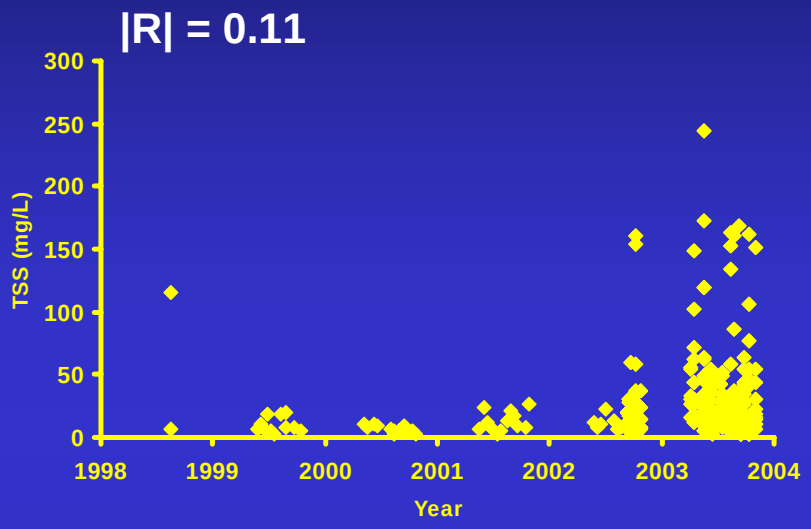


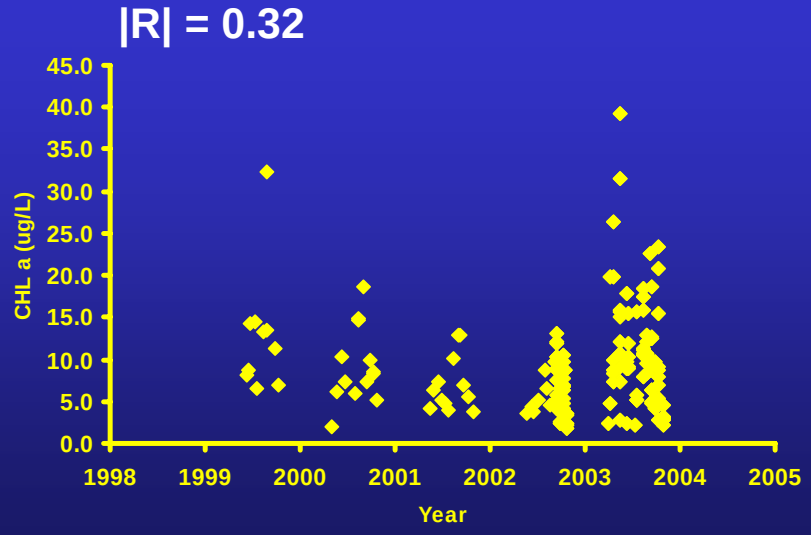
|R| = 0.08

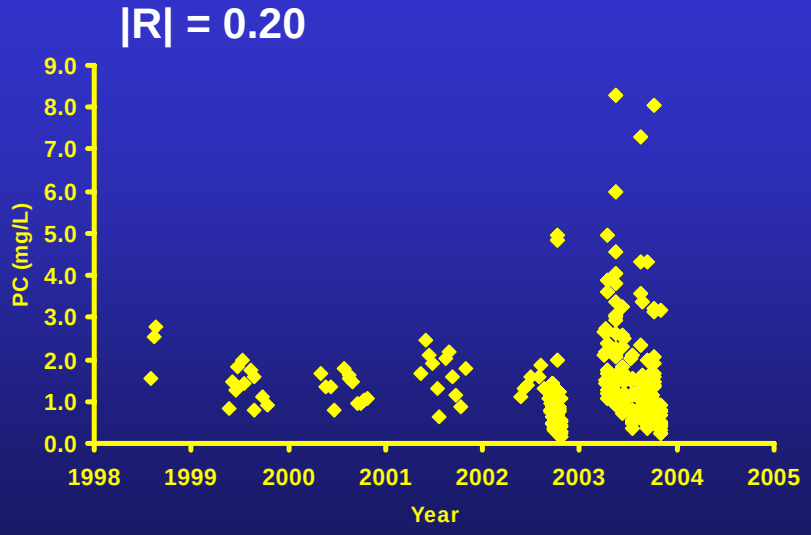


TN – Environmental Effects (CBP - TRO)









TN - Conclusions

- **Significant difference between methods.**
- **Overall Old Method biased high relative to the New Method; however, there are two groups of values.**
- **Groups were significantly different with the difference between methods for the 2003 data being much lower than prior years data.**
- **For the CBP data:**
  - **Biased low for most Tidal Fresh/Oligohaline stations (PRO and NRO data),**
  - **Biased high for TRO data but mean difference at around 0.00 mg/L prior to 2003 for most TRO stations.**

TN - Conclusions

- Data for Tidal/Freshwater Oligohaline stations are not appropriate for method correction analysis.
- For the TRO data, two groups are two time periods: 1998 through 2002 and 2003.
- Higher TKNW concentrations during 2003.
- Salinity, TSS and/or flow may be a factor(s) in this difference.

TN - Conclusions

- Correction factors could be possible for the TRO data but which data do we use?
  - TRO Only?
  - CBP - TRO Only?
  - Select based on TKNW values?
  - Use one time period or another?
  - Correct by station?
- Changes in instrumentation are still at issue with these data.
  - Do we ignore them?
- Are there additional analytical approaches that might be useful for exploring these data?

TN - Recommendations

- **Use Blocked Seasonal Kendall until questions are answered.**
- **No other recommendations…**

Appendix D - Assessment of 1994 Methods Change for Total Nitrogen using Split Sample Data

Assessment of 1994 Methods Change for Total Nitrogen using Split Sample Data.

submitted to

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by

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Introduction

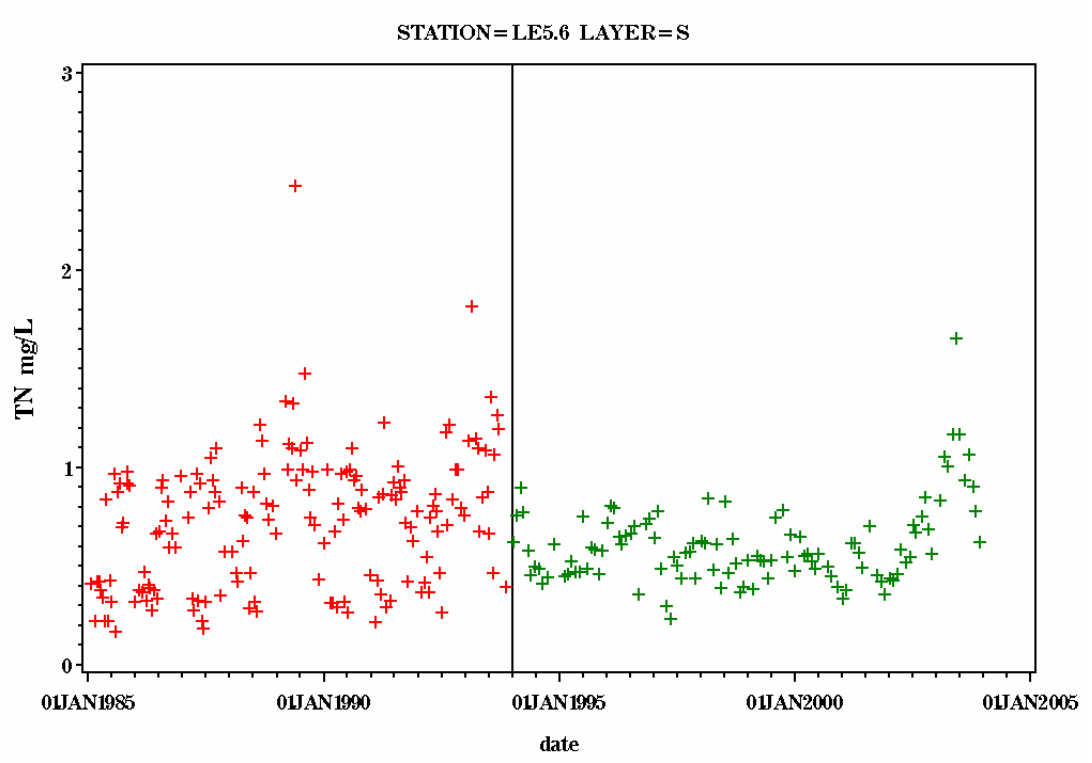
This report addresses the apparent change of estimated total nitrogen (TN) concentration that occurs coincident with a change in the methods for assaying TN in three Virginia Tributaries to the Chesapeake Bay. The first results presented here are based on split sample data that were collected several years after the methods change occurred. It is found that adjustment factors based on the split sample results do not adequately resolve the step trends that have been demonstrated in the monitoring data. Additional results are presented that explore development of an adjustment factor by modeling the steps estimated by the intervention analyses that were performed as part of this effort and reported in an earlier report. This second approach to adjusting for the methods change does resolve many of the step trends observed in the monitoring time series.

Background

In 1994, the Virginia Department of Environmental Quality which oversees the tidal monitoring of nutrients in these Virginia tributaries implemented the TDN+PN method to replace the TKNW+NO23F method for the assay of TN. Sometime after this change was implemented, it became apparent when viewing a time series plot (Figure 1.) of TN concentration for stations in the lower James River, that the concentration of TN appeared to take a step down at the time of the methods change. This result is of particular concern because the long term trends analysis will show that TN concentration is improving (decreasing) and this favorable conclusion may in fact be false. It is possible that a large part of the decrease in TN is an artifact due to the change in analytical methods.

To assess the magnitude of the apparent change in TN that may be caused by the method change, DEQ implemented a split sample program using the two methods FRO 1998-2004. This report addresses the results of analyses of the split sample program data and explores the development of an adjustment factor based on the split sample data. Finding that adjustment factors do not resolve the step trends that have been demonstrated in the monitoring time series data, additional analyses and results are presented base on modeling the step trend terms of the intervention analysis. This approach is shown to perform better in terms of removing step trends from the data. However, one must me cautioned that to some extent this approach is more like treating the symptoms of a problem than treating the cause. The risk is that if the step trend is caused by something other than the methods change, for example a management action, then this approach will remove the step trend when in fact it would be desirable to leave it in the data record.

Figure 1. Time series plot of total nitrogen concentration for a station in the James River lower estuary. The vertical bar indicates the point of the methods change. Pre method change data are in red; post method change data are in green.



Methods

The methods employed for the analysis of the TN split sample data are similar to those used for the TP data. They are reiterated here for completeness. The data were pre-screened by DEQ to remove observations with detection limit or other problems. Using these pre-screened data, variables for TN measured by the old method and the new method were created as TNOLD and TNNEW. The difference was computed as TNDIFF = TNNEW-TNOLD. It follows that a positive difference would indicate a step up between the old and new methods while a negative difference would indicate a step down.

```
tndiff = tnnew - tnold;
lntnnew = log(tnnew);
lntnold = log(tnold);
lntndiff = lntnnew - lntnold;
```

Because water quality parameters typically follow a log-normal distribution, these variables were also transformed by logarithms and the difference was computed as LNTNDIFF = log(TNNEW) - log(TNOLD). This difference variable is better suited to statistical methods that assume normality. Note that this mathematical expression equates to the logarithm of the ratio of

TNNEW to TNOLD. That is LNTNDIFF = log(TNNEW) - log(TNOLD) = log(TNNEW/ TNOLD).

To check if the log difference between the methods might be affected by other water quality constituents, correlation analysis and graphical assessment of association was done for the following variables: mean (of the two methods) of logarithm of TN, specific conductance, water temperature, pH, dissolved oxygen, logarithm of total suspended solids, program office, DEQ_program, distance from the Chesapeake Bay, and date of collection (Table 1).

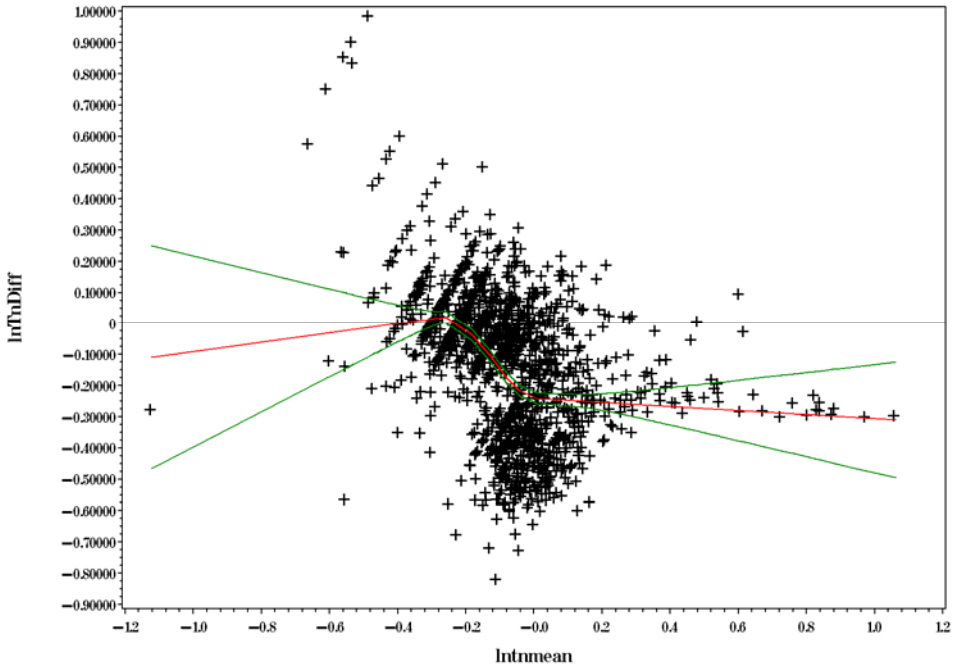
Table 1. Spearman Correlation coefficients between the LNTNDIFF variable and selected water quality variables:

Water Quality Variable	statistic	Pearson correlation /p-value	Spearman Correlation /p-value
lntnmean	correlation	-0.38393	-0.45976
	p-value	<.0001	<.0001
SpCond	correlation	-0.17993	-0.16555
	p-value	<.0001	<.0001
Salinity	correlation	-0.22589	-0.22318
	p-value	<.0001	<.0001
WTemp	correlation	0.08478	0.15009
	p-value	0.0018	<.0001
PH	correlation	-0.17581	-0.18186
	p-value	<.0001	<.0001
DO	correlation	0.01893	0.01436
	p-value	0.4860	0.5974
lntss	correlation	0.18189	0.19134
	p-value	<.0001	<.0001
Date	correlation	0.34513	0.29029
	p-value	<.0001	<.0001
BKM	correlation	0.13717	0.18527
	p-value	<.0001	<.0001

There are associations of the LNTNDIFF variable with 6 of the water quality variables as well as spatial and temporal trends. The method difference has a negative association with Mean TN, Specific Conductance, Salinity, and pH. The method difference has a positive association with water temperature and total suspended solids. There appears to be a trend of increasing difference with date and a trend of increasing difference with distance from the Bay (BKM). Greater detail about these associations can be discerned in the corresponding scatter plots.

For all the variables shown in table 1. we examine the relation between the method difference and each variable graphically.

Figure 1. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus the mean of the logarithms of the methods (abscissa).



The strong association of the lnTNdiff variable with the lnTNmean variable presents a conundrum. It appears that lnTNmean is the best single predictor of the difference between the two methods. However, for adjusting the previously collected old method data, this mean of the two methods is not available for computing an adjustment factor. It would seem reasonable to simply substitute the lnTNold for the mean, but this creates a problem with independence.

If pairs of variables, say x and y, are generated at random, then the mean of x and y will be uncorrelated with the difference of x and y. However, the difference will be highly correlated with either x or y. That is, if the difference is computed as x-y, then a high deviation in x will lead to a high difference and a low deviation in x will lead to a low difference. Clearly x and x-y are positively correlated. Conversely y and x-y are negatively correlated. Because of this, a regression of lnTNdiff against lnTNold will be influenced by both the inherent relation of lnTNdiff to the lnTNmean, but also by this spurious correlation between a deviation in TNold and of the difference between TNnew and TNold.

Figure 2. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus specific conductivity (abscissa).

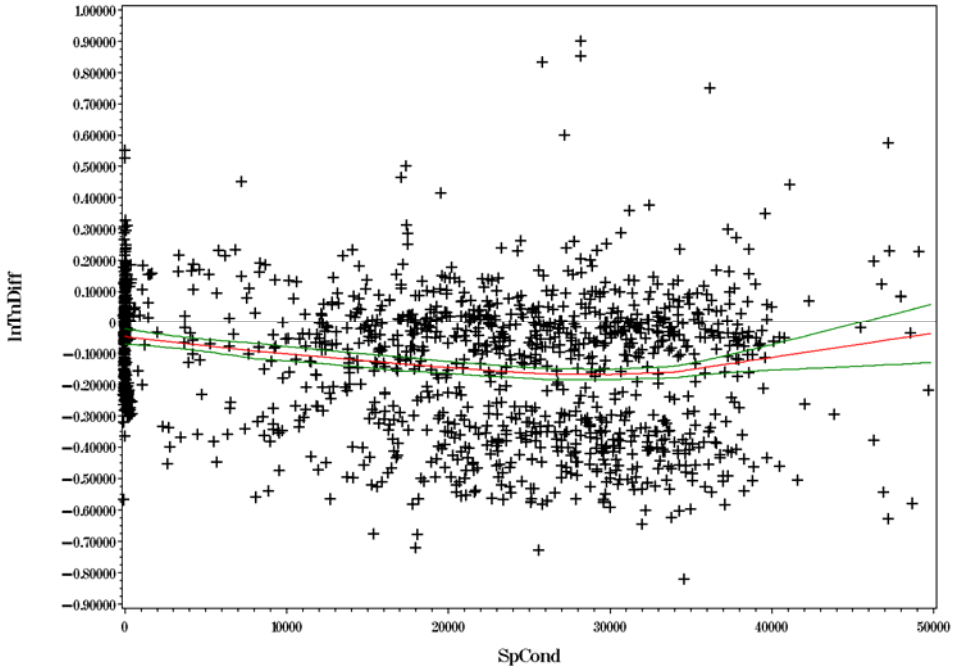


Figure 3. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus salinity (abscissa).

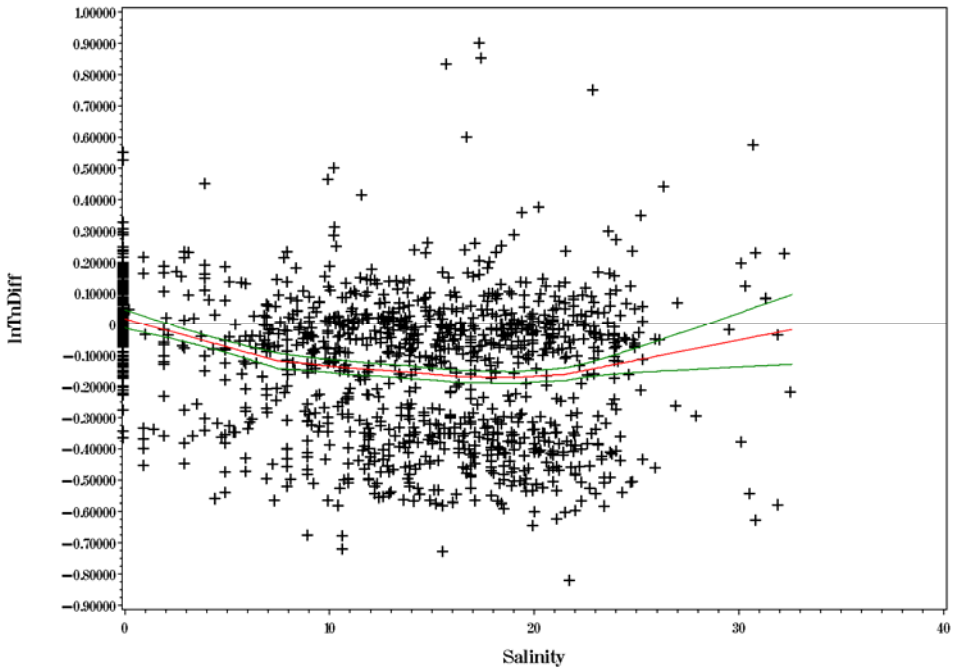


Figure 4. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus water temperature (abscissa).

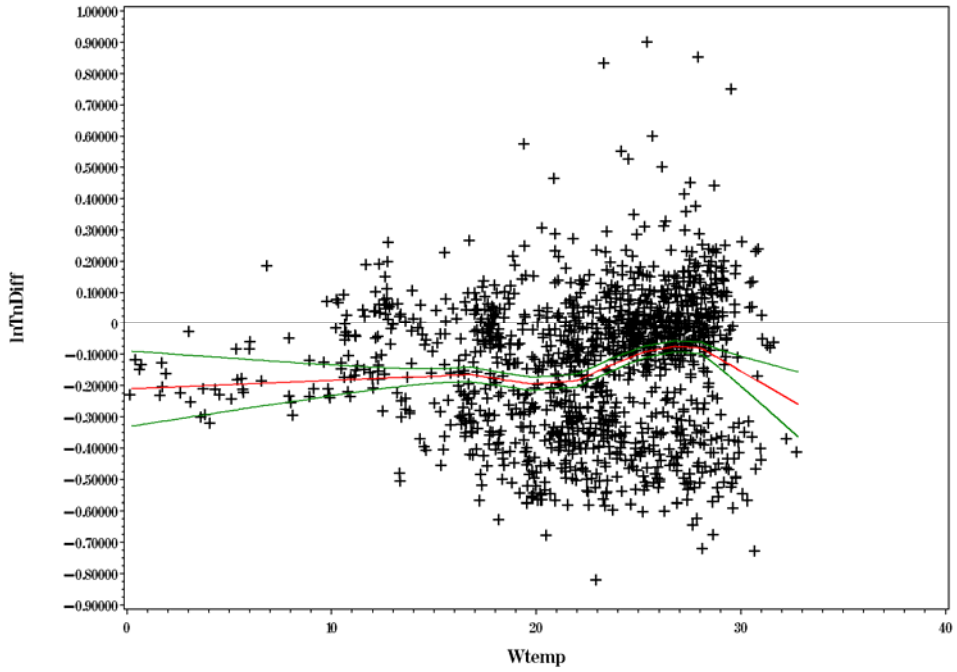


Figure 5. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus pH (abscissa).

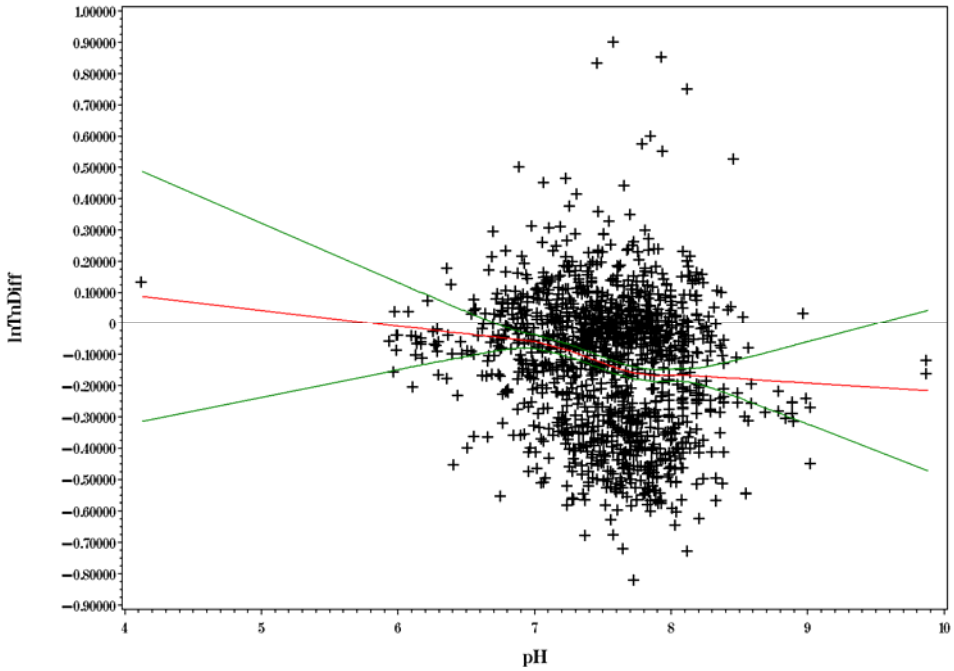


Figure 6. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus logarithm of TSS (abscissa).

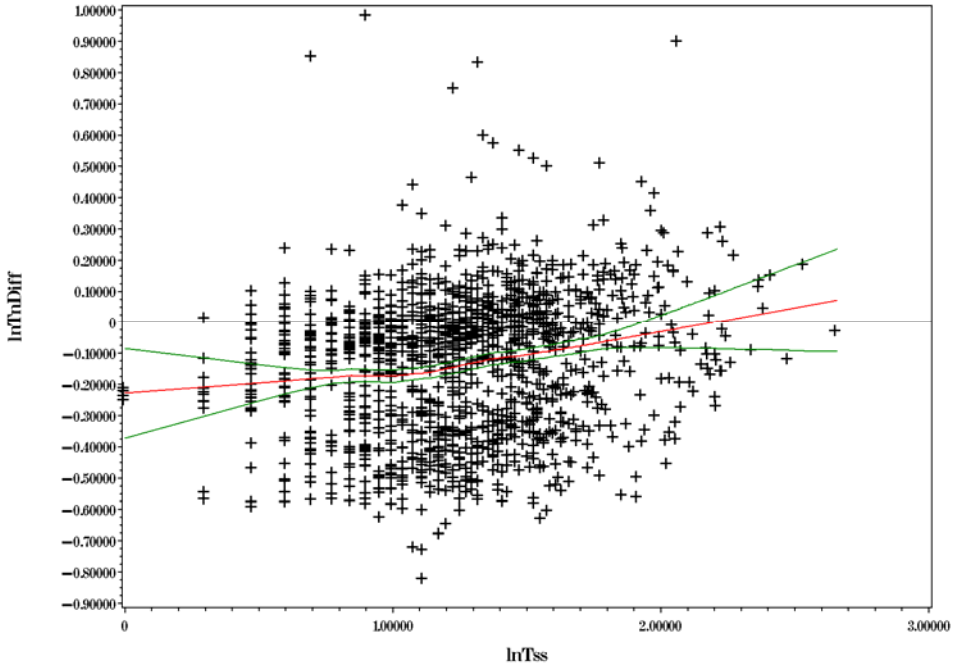


Figure 7. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus date (abscissa).

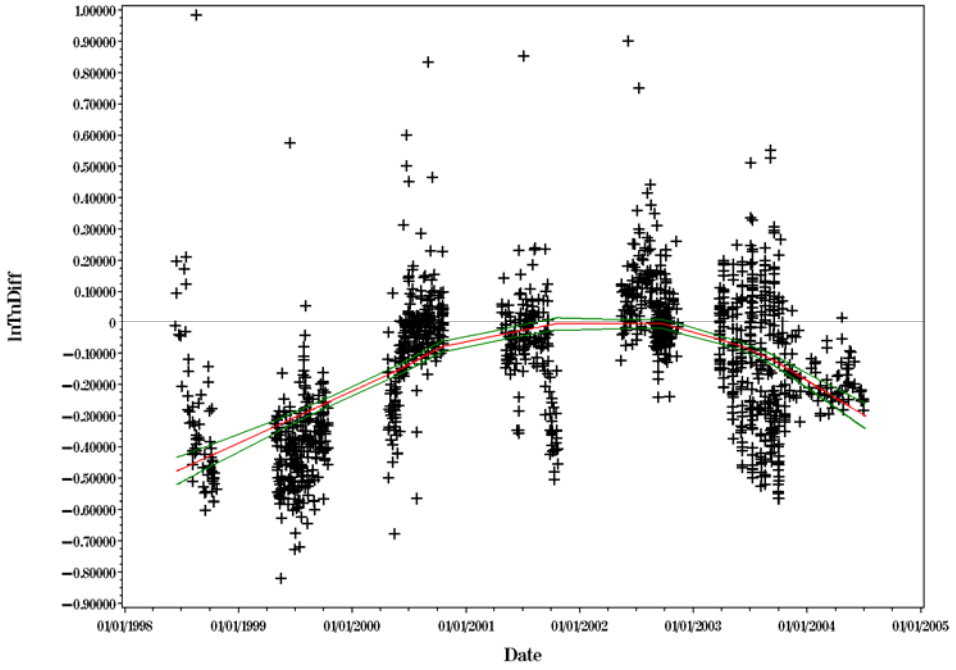
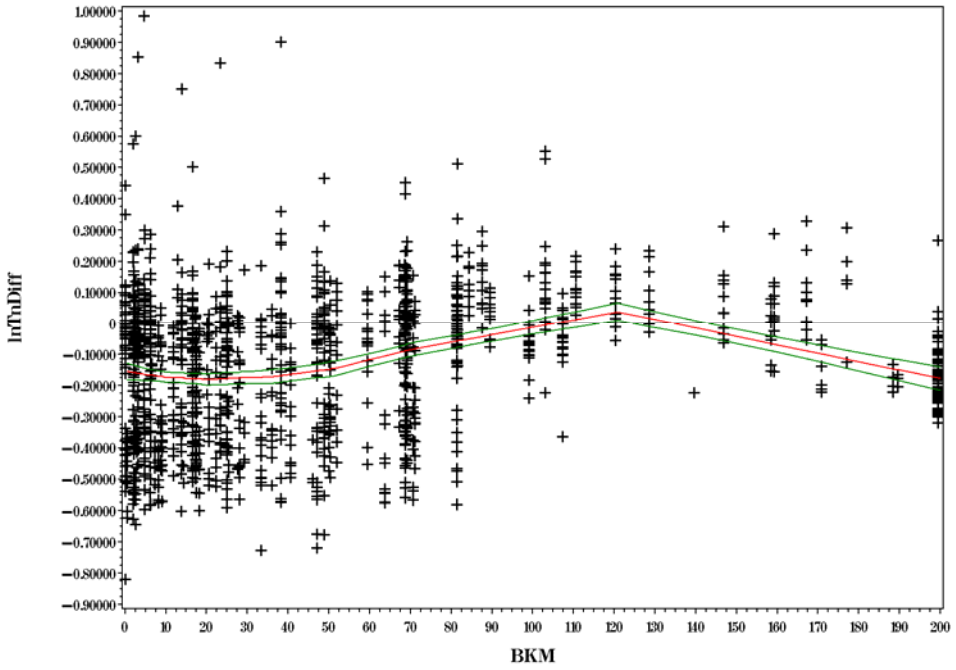


Figure 8. Scatter plot and LOESS regression line for the difference between the logarithms of the methods (ordinate) versus Kilometers from Bay (abscissa) (note BKM is truncated at 200).



Many of the other relationships shown in figures 2-7 can be explained in terms of longitudinal gradient in the estuary. The lnTNdiff variable shows a pattern of being near zero upstream and becoming increasingly negative as one moves toward the bay (fig 8). Other variables including specific conductance, salinity, logarithm of TSS, and pH are known to have longitudinal gradients and this relation was confirmed graphically for these data. Oddly, owing to non-random sampling, even date has an apparent longitudinal gradient for these data with later samples tending to be collected more upstream.

Note that the association shown between lnTNdiff and lnTNmean (fig 1) and lnTNdiff and distance from the Bay (fig 8) seem contradictory. It appears that as lnTNmean decreases, than the difference tends to increase toward zero (fig 1). It is well known and confirmed for these data that lnTNmean tends to decrease as one moves down the estuary. Based on fig 1, one would predict that lnTNdiff would increase toward zero as one moves down the estuary. However, we find that the opposite is true (fig 8). This suggests that at least two forces are at work in determining the magnitude of the difference between the two methods.

Because many water quality parameters appear to have an association with the methods difference variable and with each other, stepwise regression is used to select the important predictors and eliminate redundancy among the potential predictor variables caused by similarity in longitudinal gradient. Because date in not available as a predictor variable and the artificial longitudinal pattern of sampling dates might have caused a spurious association, date is not included in this stepwise regression.

The selected variables are:

Table 2a. Summary of Stepwise Selection results where independent variables are water quality variables found in Table 1. and the dependent variable is the logarithm of the difference between the TN measurement by the two methods.

Dependent Variable: lntndiff

Step	Variable Entered	Partial R-Square	Model R-Square	F Value	Pr > F
1	lntnmean	0.1941	0.1941	293.57	<.0001
2	S_SpCond	0.1192	0.3132	211.33	<.0001
3	lntss	0.0672	0.3804	131.91	<.0001
4	WTemp	0.0097	0.3901	19.37	<.0001
5	BKM	0.0046	0.3947	9.19	0.0025
6	DO	0.0016	0.3963	3.31	0.0693

Table 2b. Final regression estimates for first four variables selected by the stepwise regression procedure.

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	-0.28005	0.02587	-10.82	<.0001
lntnmean	1	-0.61523	0.02858	-21.53	<.0001
S_SpCond	1	-0.00571	0.00042252	-13.52	<.0001
lntss	1	0.12859	0.01315	9.78	<.0001
WTemp	1	0.00266	0.00097711	2.73	0.0065

These regression estimates lead to the following formula for computing the adjustment factor.

Equation 1.

lnaf1 = -0.28005 - 0.61523(lntn) - 0.00571(S_SpCond) + 0.12859(lntss) + 0.00266(WTemp)
lntn_aj1 = lntn + lnaf1;

where lnaf1 = logarithm of adjustment factor 1,
lntn = logarithm of TN,
S_spcond = Scaled Specific conductance = spcond/1000,
lntss = logarithm of TSS,
WTemp = water temperature, and
lntn_aj1 = logarithm of TN adjusted by method 1.

where lnaf is the logarithm of the adjustment factor and lntn_aj1 is the logarithm of adjusted TN using this first method. When this adjustment algorithm (adjustment 1) is applied to the time series data from the Bay program and the data are reexamined for step trends, the results are a slight improvement on the un-adjusted data (compare table 3a and 3b).

Table 3a. The frequency of the directions and statistical significance of the estimated step trends from the intervention analysis when no adjustment is applied to the old method data.

Direction of step change	not significant	significant $p < 0.05$	Total
decrease	10	2	12
increase	26	25	51
Total	36	27	63

Table 3b. The frequency of the directions and statistical significance of the estimated step trends from the intervention analysis when adjustment 1 is applied to the old method data.

Direction of step change	not significant	significant $p < 0.05$	Total
decrease	7	1	8
increase	36	19	55
Total	43	20	63

As a result of the adjustment, the number of step changes that are statistically significant is reduced from 27 to 20. However, we will show that better improvement is possible with adjustments developed below.

As with the TP adjustment, in addition to analyses of the split sample data, we consider developing a model for the step change estimates from the intervention analyses. For the step change data, the best predictive model includes independent variables lnTNmean and specific conductance. The variables lnTNmean and salinity work nearly as well. The resulting adjustment equation is:

Equation 2.

lnaf2 = 0.04533 - 0.46769(lntn) - 0.00812(S_spcond);
lntn_aj2 = lntn + lnaf2;

where lnaf2 = logarithm of adjustment factor 2,
lntn = logarithm of TN,
S_spcond = Scaled Specific conductance = spcond/1000, and
lntn_aj2 = logarithm of TN adjusted by method 2.

There are two ways to apply equation 2. One is to compute the adjustment for each sample using the logarithm of TN and the Specific Conductance that are collected with that sample (adjustment 2). Using this approach, the results of intervention analysis on the adjusted data are:

Table 3c. The frequency of the directions and statistical significance of the estimate step trends from the intervention analysis when adjustment 2 is applied to the old method data.

Direction of step change	not significant	significant $p < 0.05$	Total
decrease	27	8	35
increase	18	10	28
Total	45	18	63

The number of significant step changes is reduced for 27 in the unadjusted data to 18 using this second adjustment(compare table 3c and 3a).

A second way to use equation 2 leads to a third approach for the adjustment. That is to compute the adjustment factor using the mean levels of the independent variables for each station (adjustment 3). By using long term means, one might hope to reduce the influence of the spurious correlation described above. The equation becomes:

Equation 3.

lnaf3 = 0.04533 - 0.46769(mn_lntn) - 0.00812(mn_S_spcond);
lntn_aj3 = lntn + lnaf3;

where lnaf3 = logarithm of adjustment factor 3,
lntn = mean over time of logarithm of TN,
S_spcond = mean over time of Scaled Specific conductance = spcond/1000, and
lntn_aj3 = logarithm of TN adjusted by method 3.

Using this adjustment approach, the results of intervention analysis on the adjusted data are:

Table 3d. The frequency of the directions and statistical significance of the estimate step trends from the intervention analysis when no adjustment is applied to the old method data.

Direction of step change	not significant	significant $p < 0.05$	Total
decrease	26	5	31
increase	28	4	32
Total	54	9	63

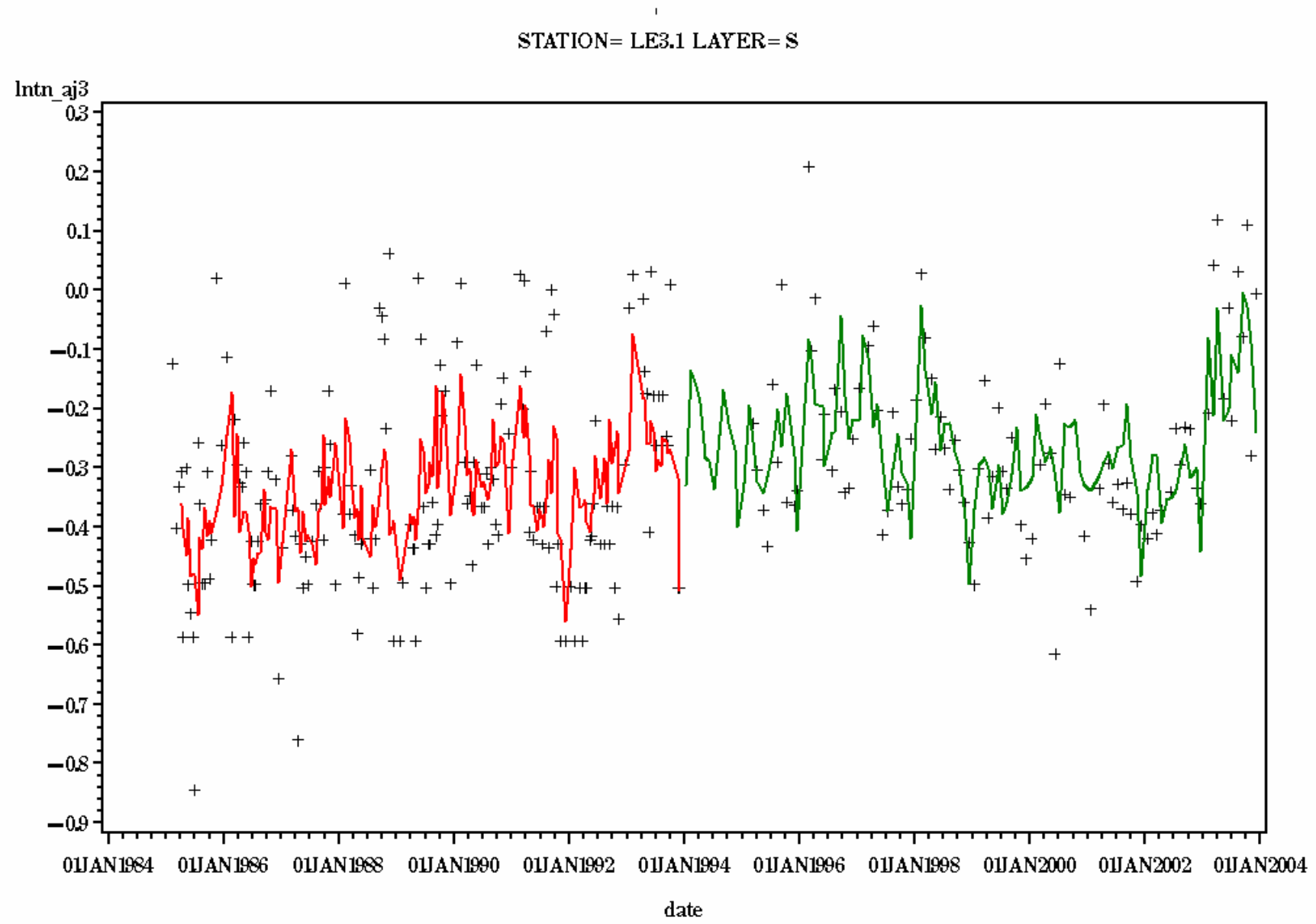
This third adjustment strategy leaves only 9 cases where the step change is significant which is the greatest improvement achieved (compare table 3d and 3a). In table 3d the distribution of positive and negative step is about equal in all columns.

The adjustment factor based on Equation 3 using the mean level of each independent variable at a station removes most of the step trends that were observed in the TN data time series data.

Thus it seems reasonable to apply this adjustment if data analysis or a comparison of data involves data measured under both the new and old methods. If data analysis does not entail a comparison of data from the two methods, it is better to leave the data unadjusted. Therefore it is recommended that the original data remain in the data base and the adjustment be implemented as needed.

Graphical Appendix to Analysis of Assessment of 1994 Methods Change for Total Nitrogen using Split Sample Data.

These figures show the time series of data at each CBP station after the data processed by the Old method have been adjusted using the third adjustment procedure presented in the report. These figures can be compared to those in the Appendix of the Intervention analysis report to assess the effect of the adjustment.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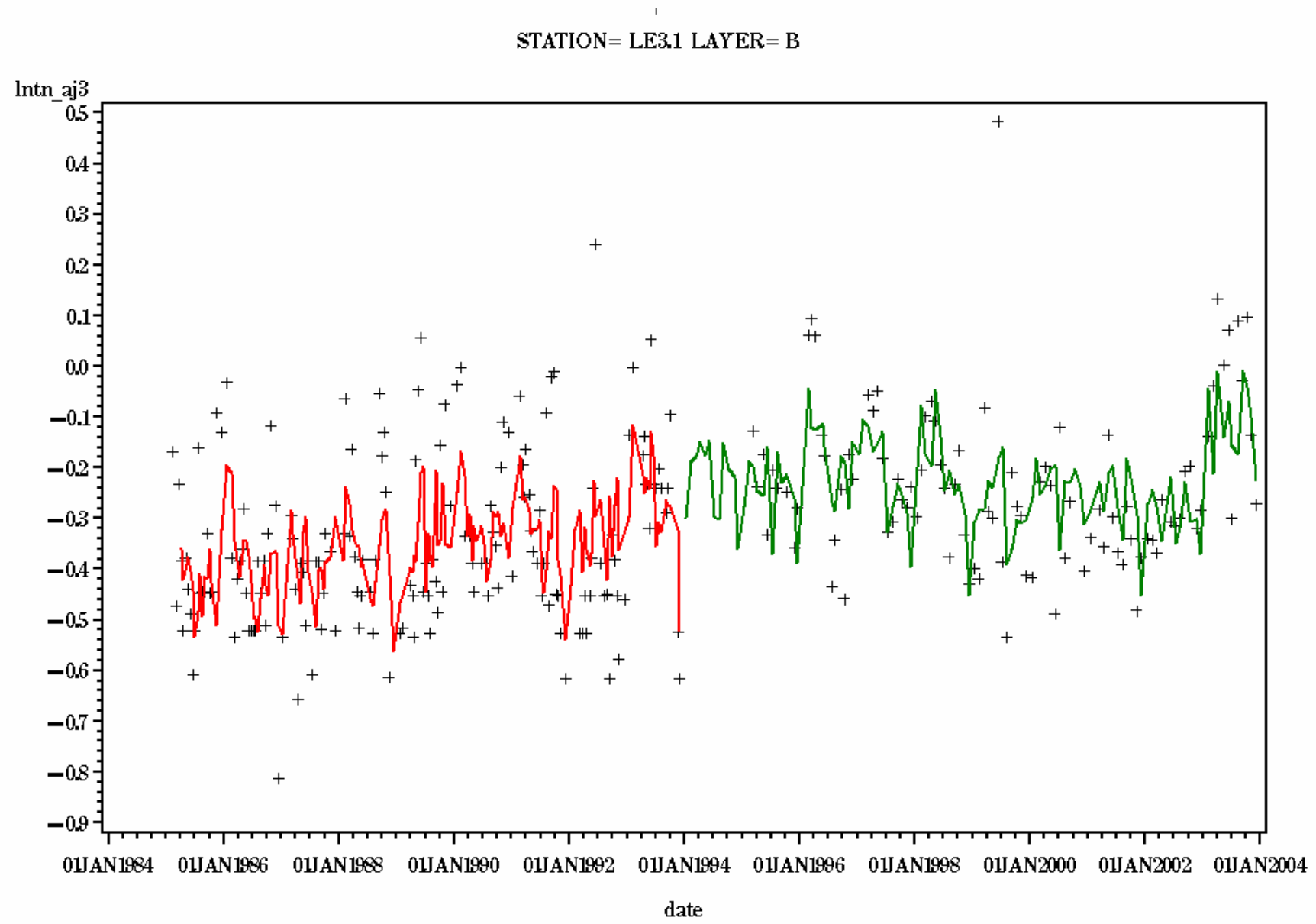
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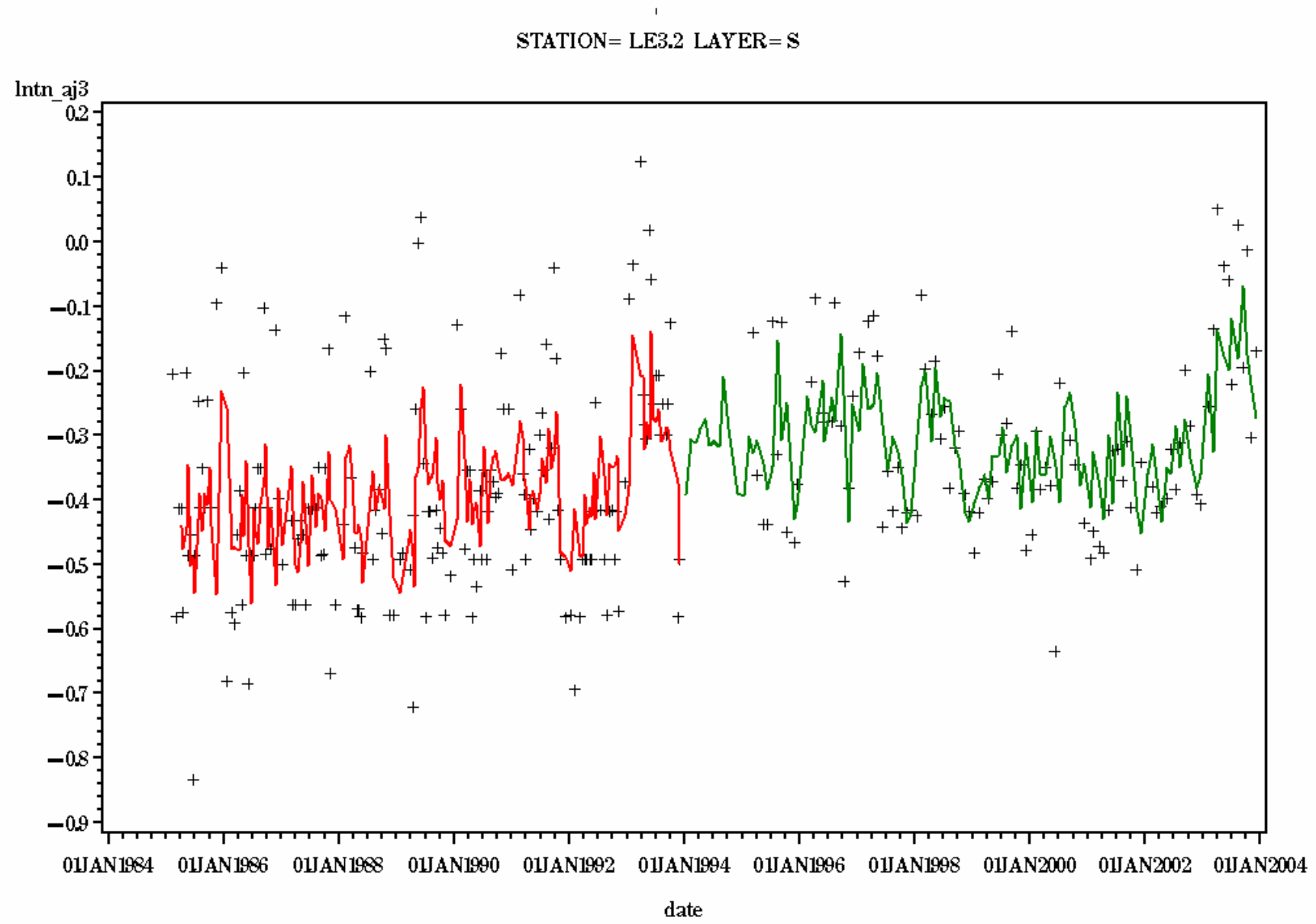
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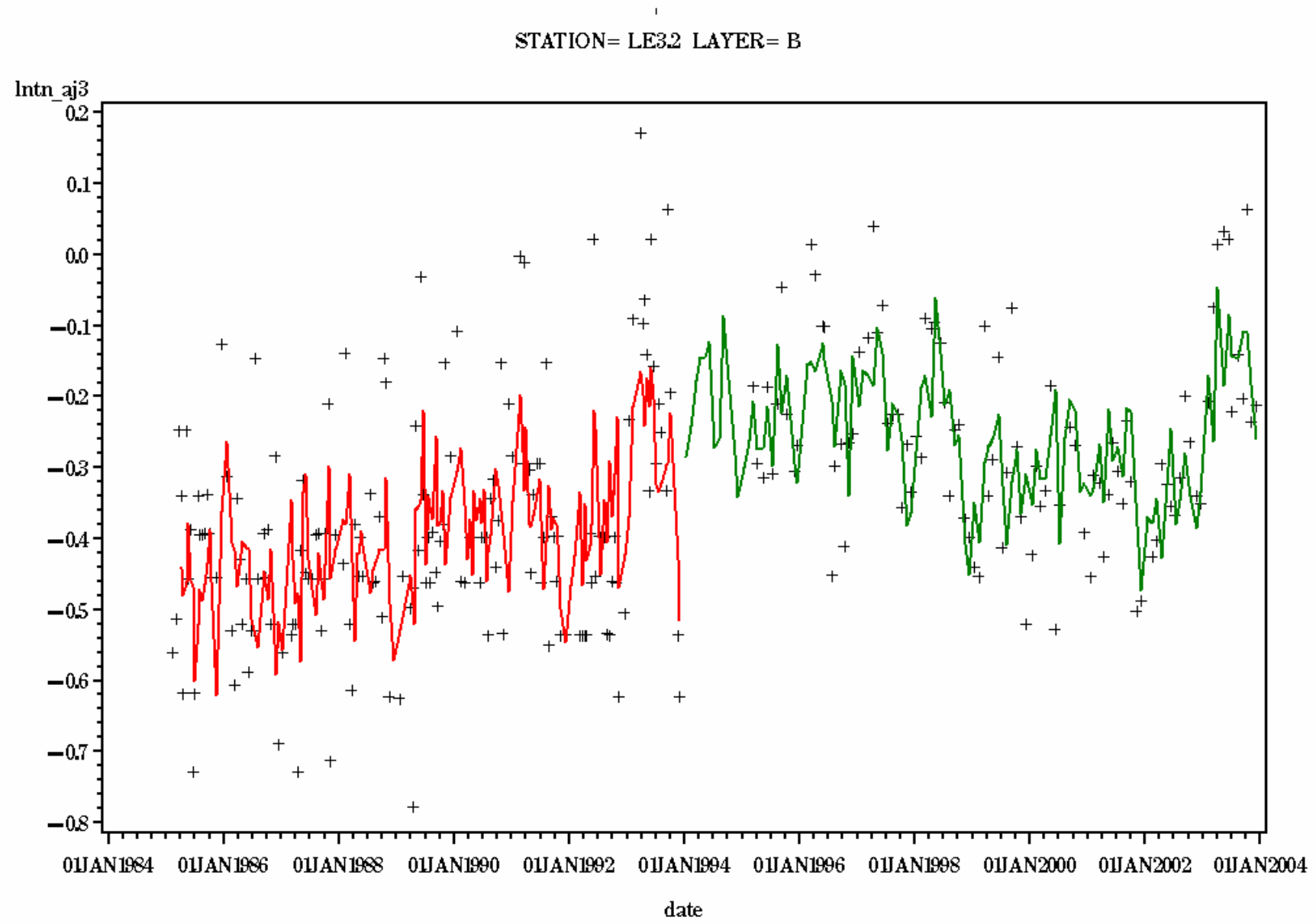
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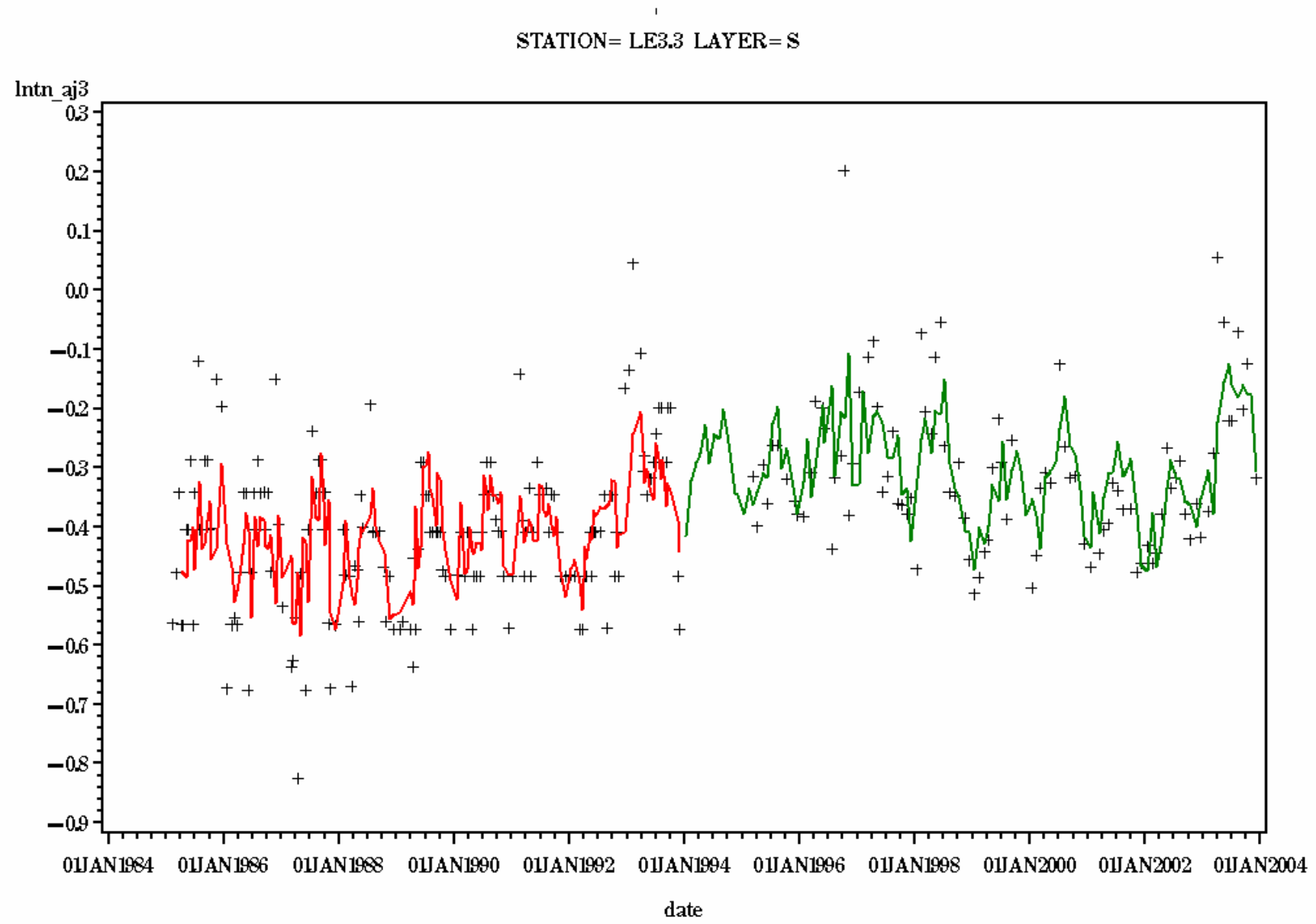
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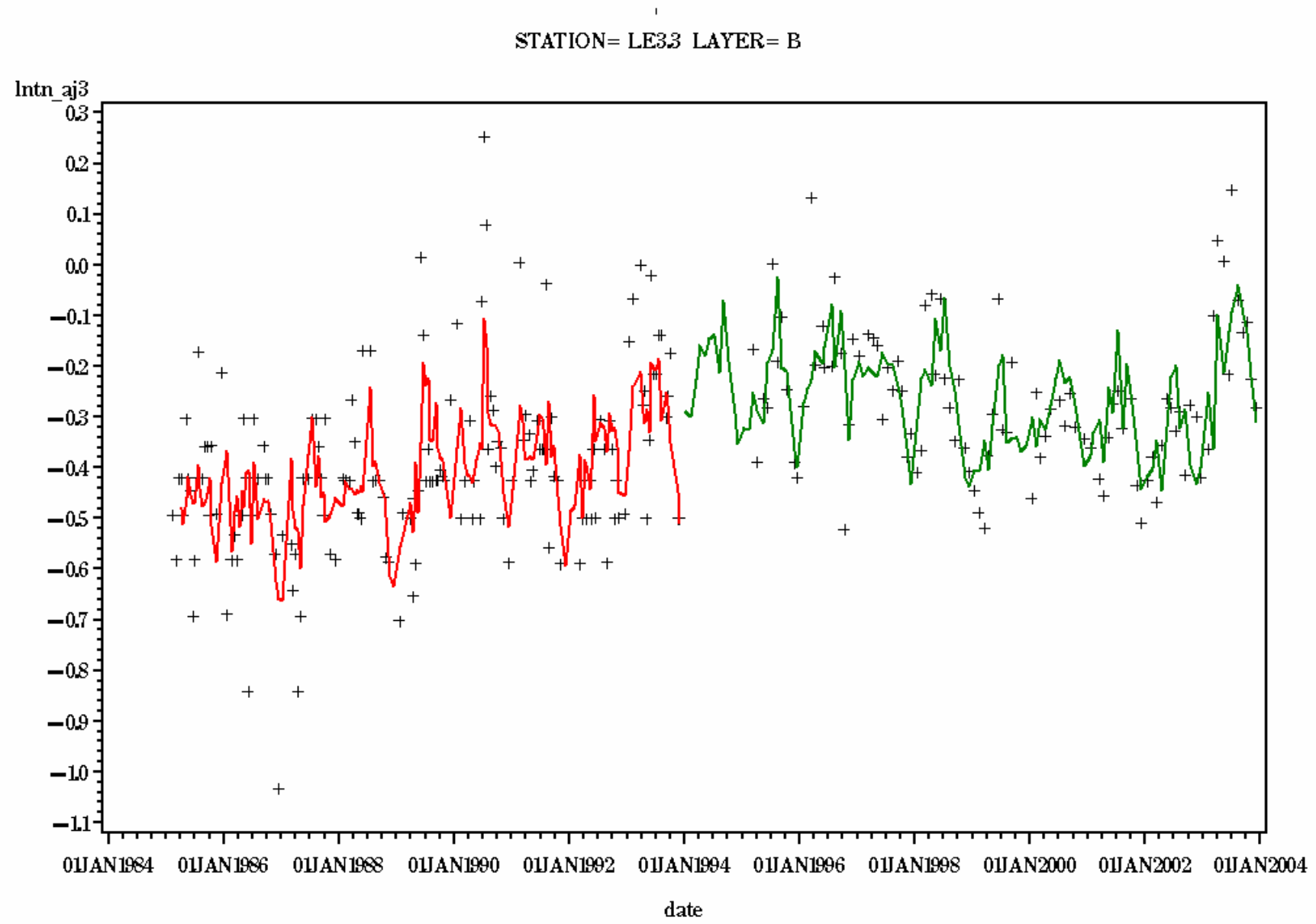
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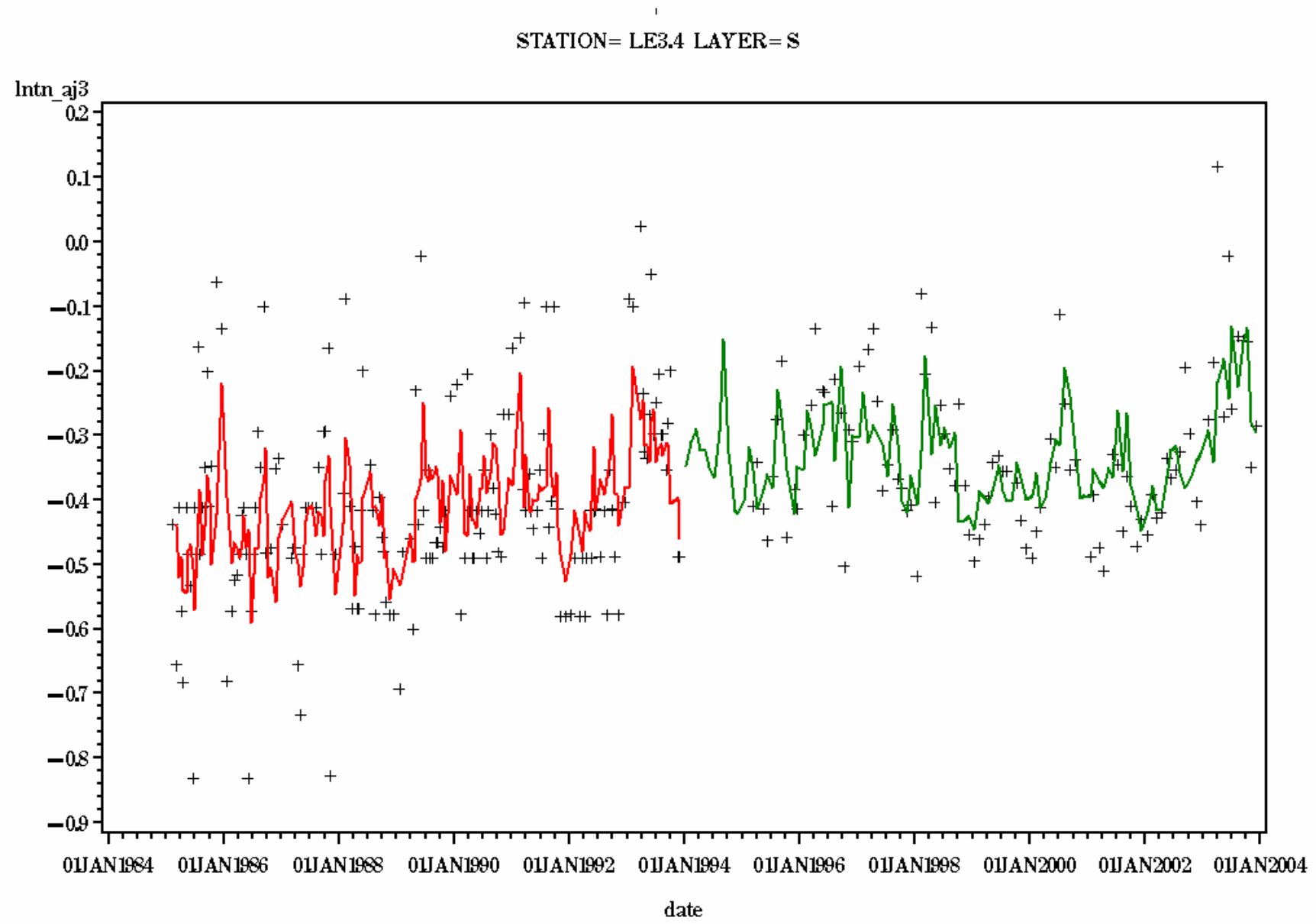
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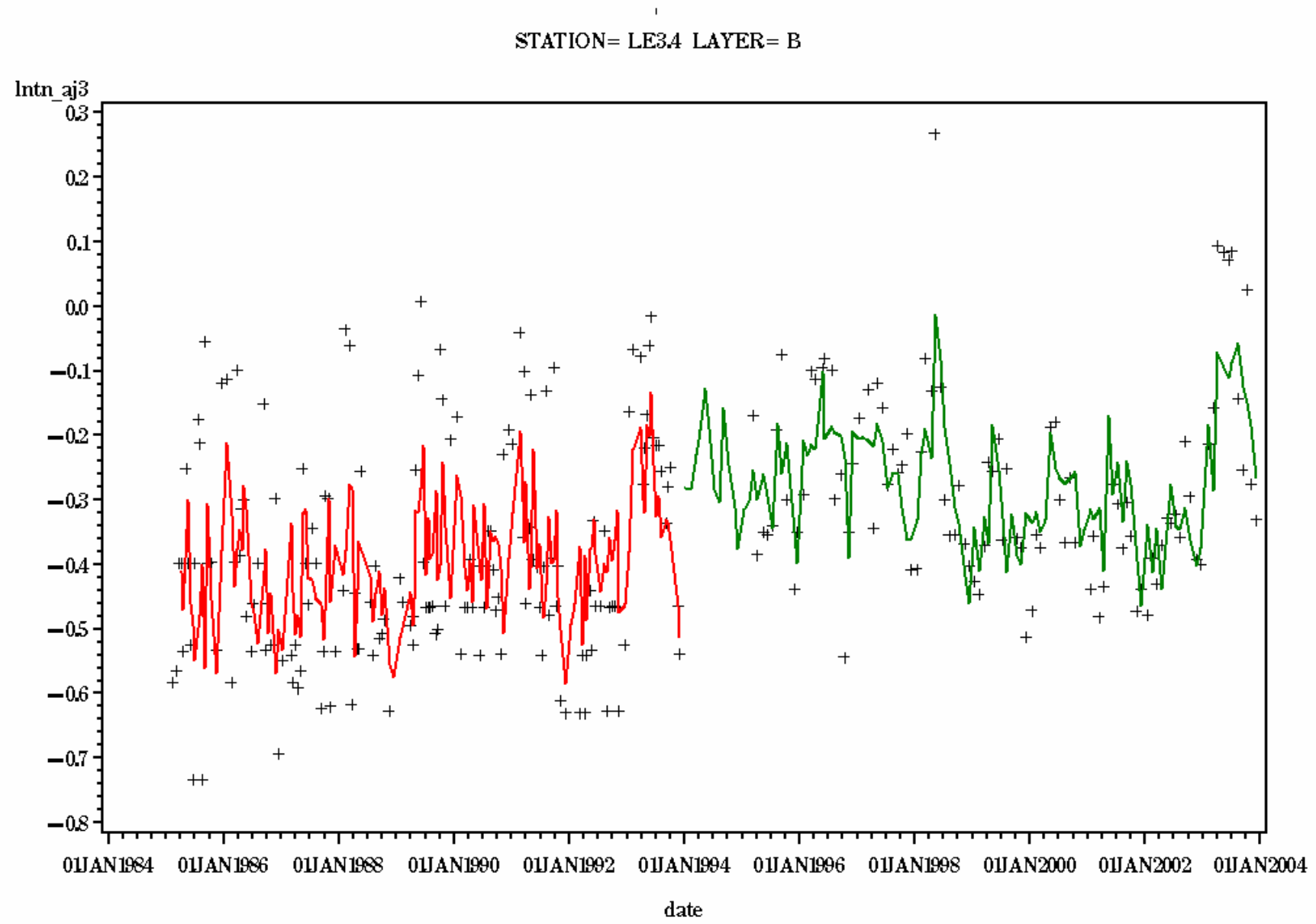
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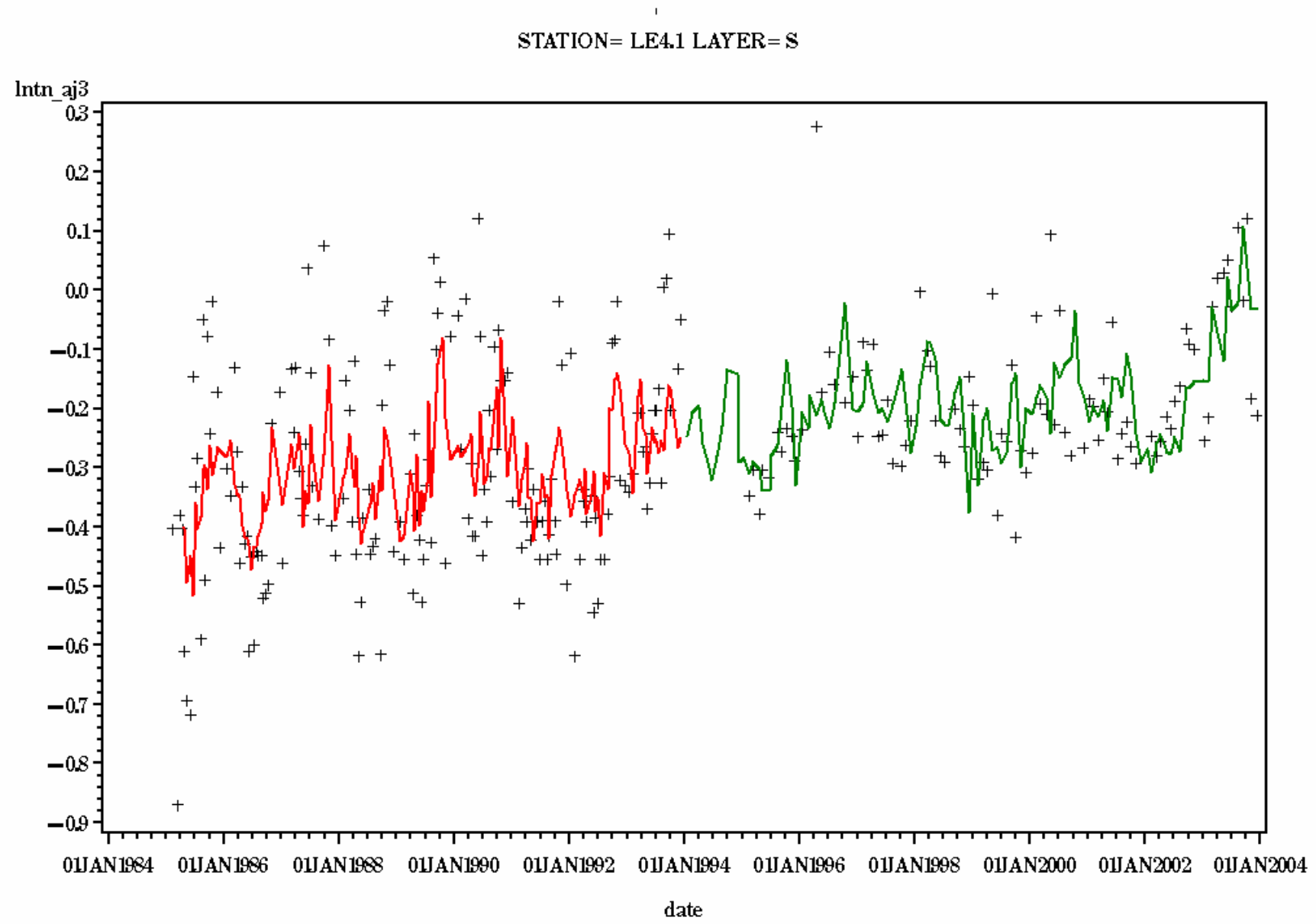
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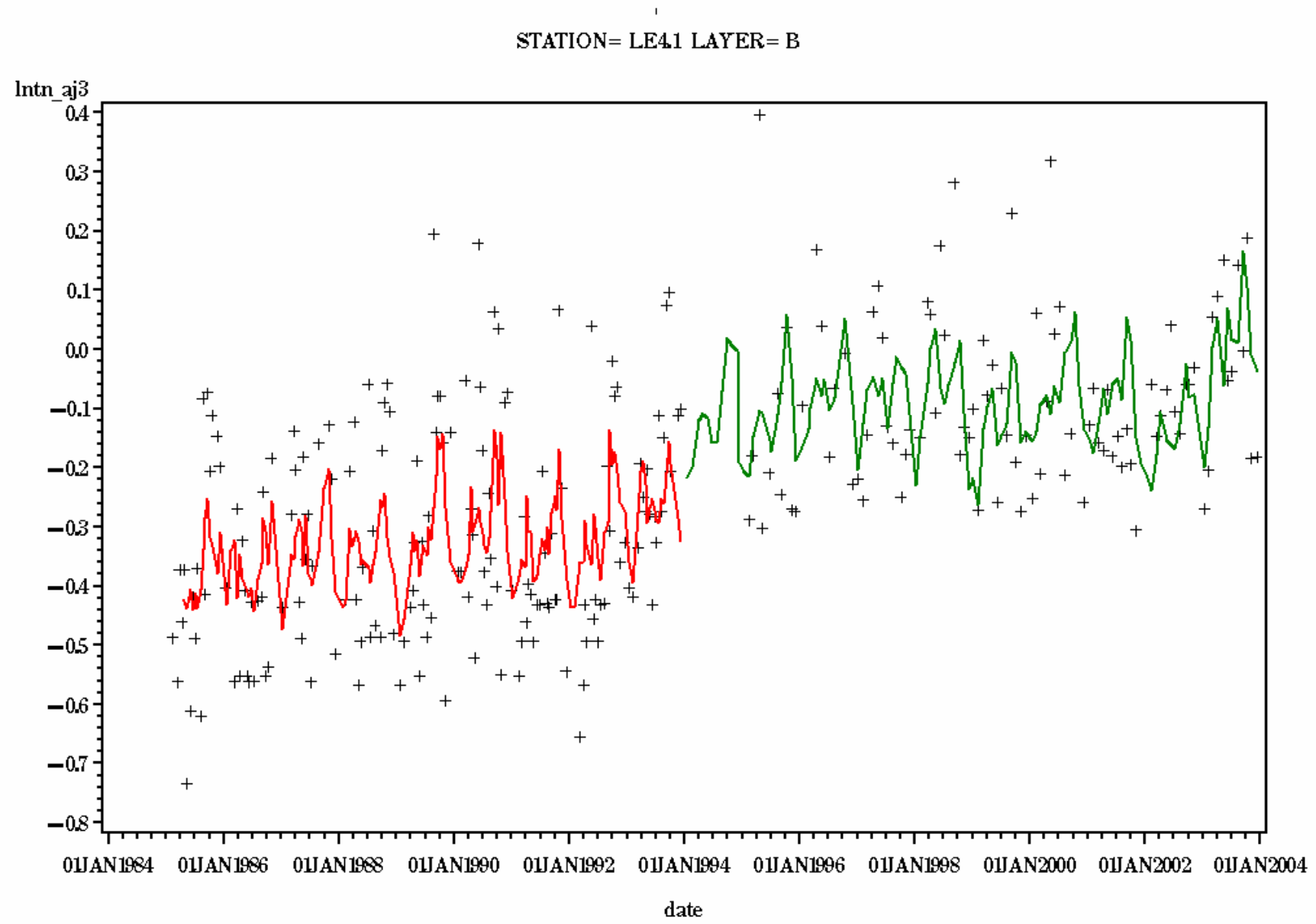
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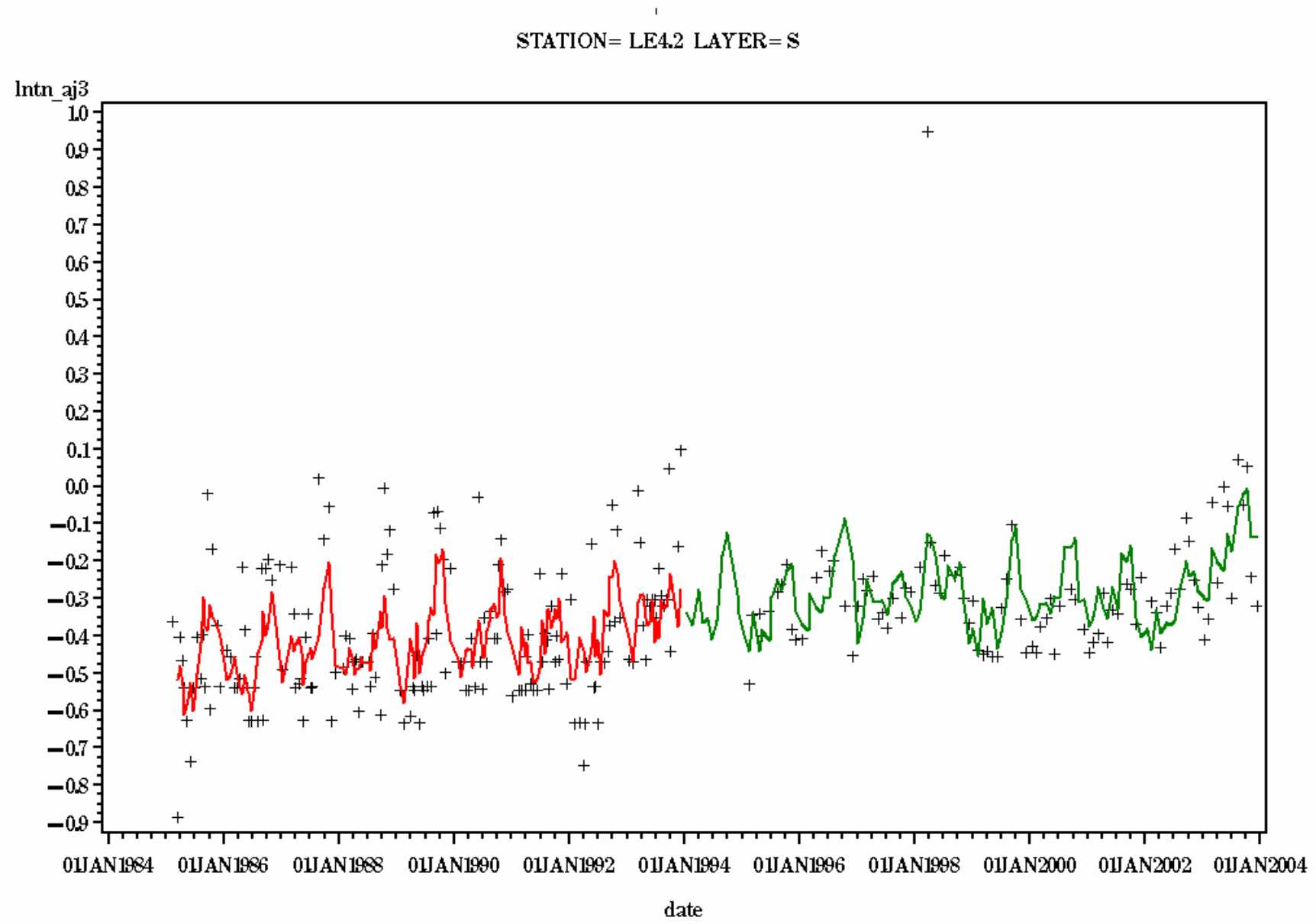
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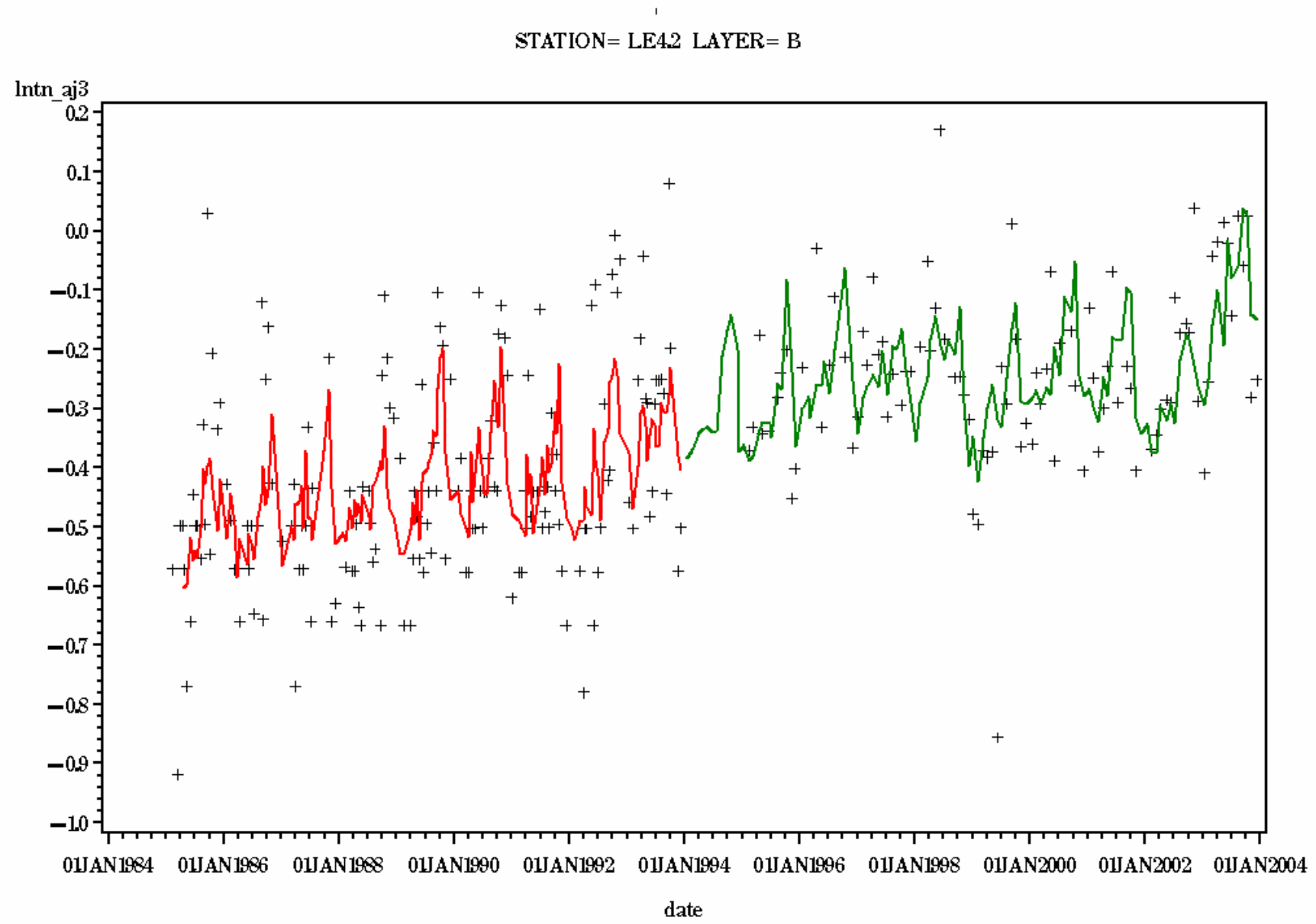
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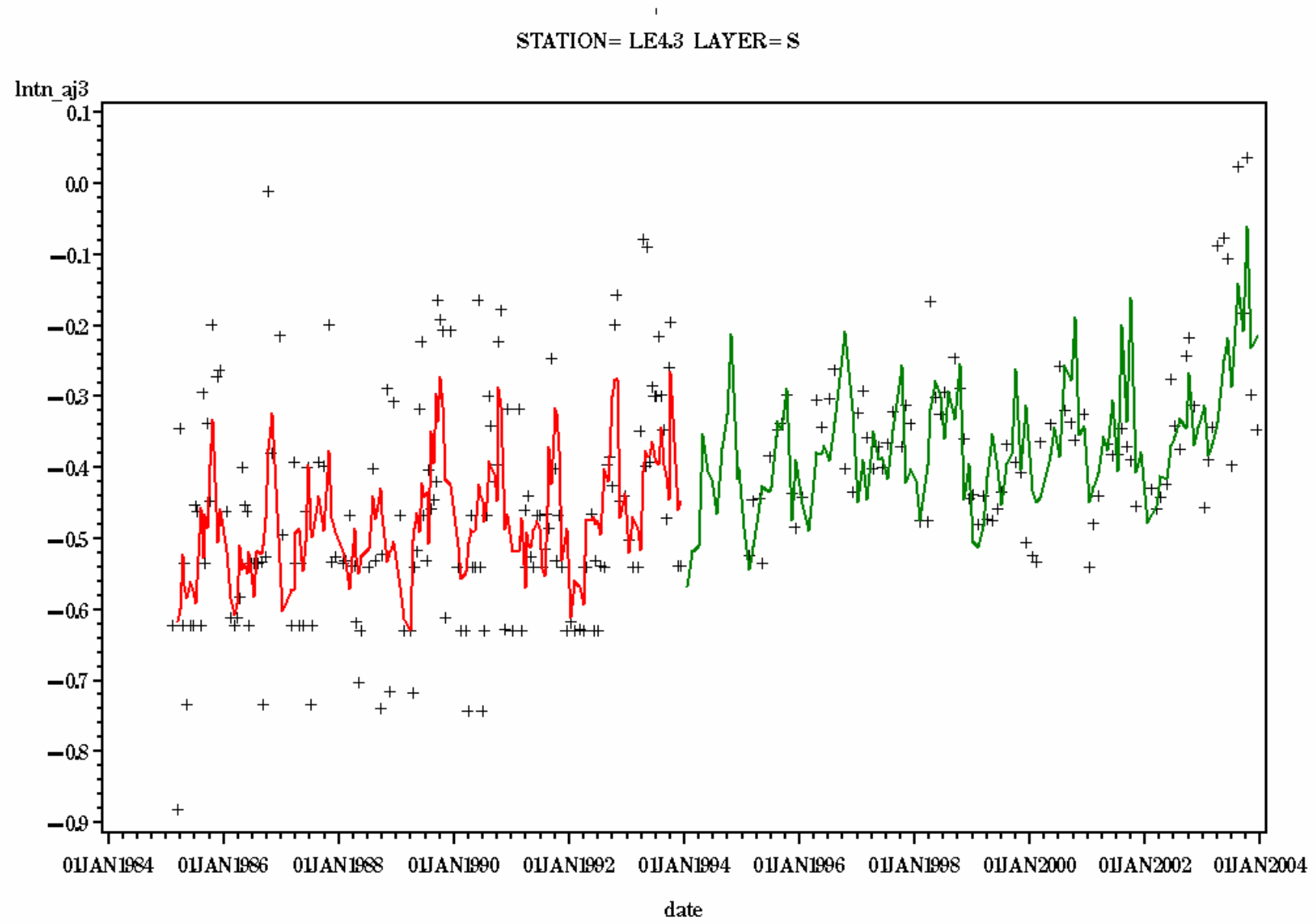
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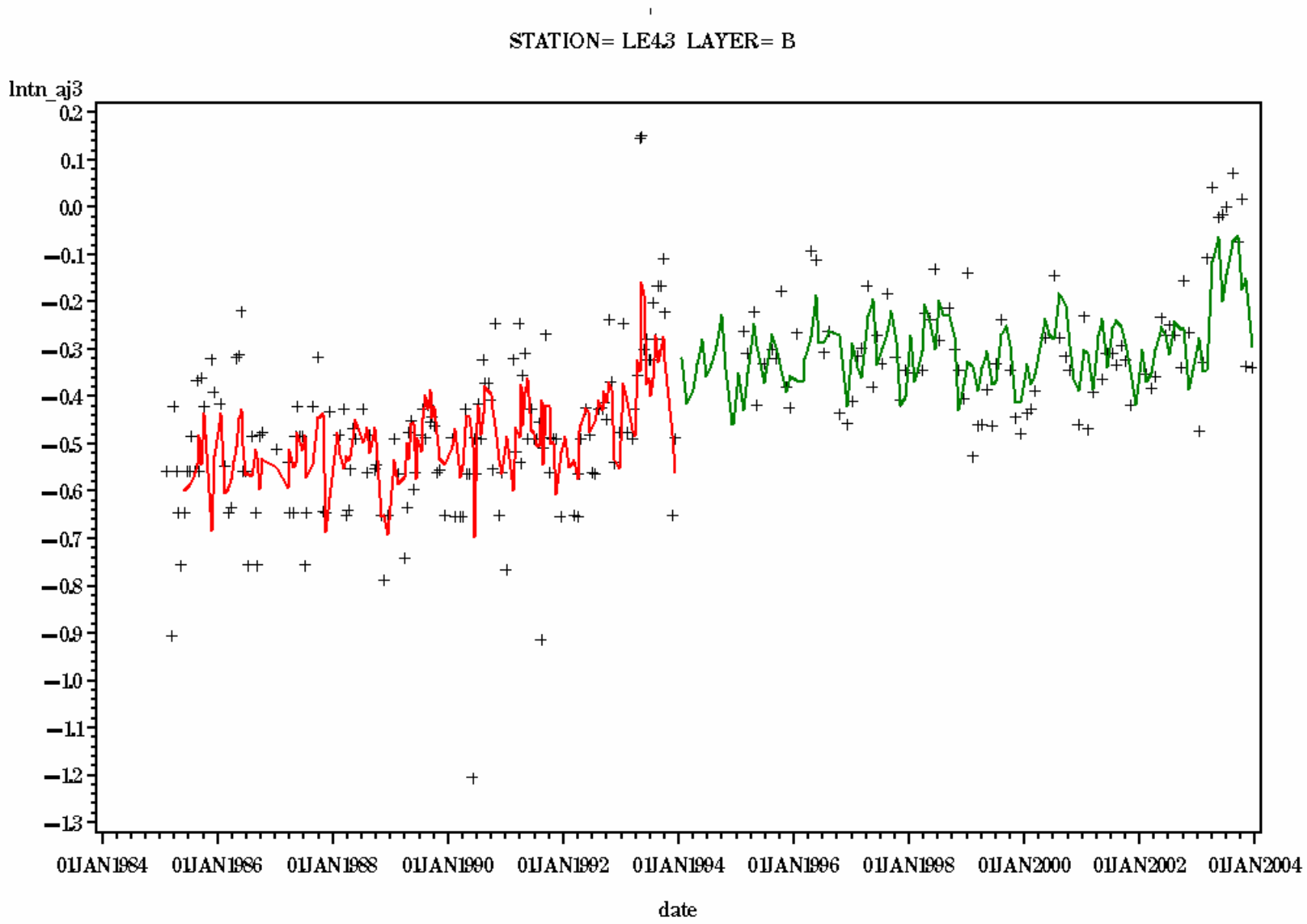
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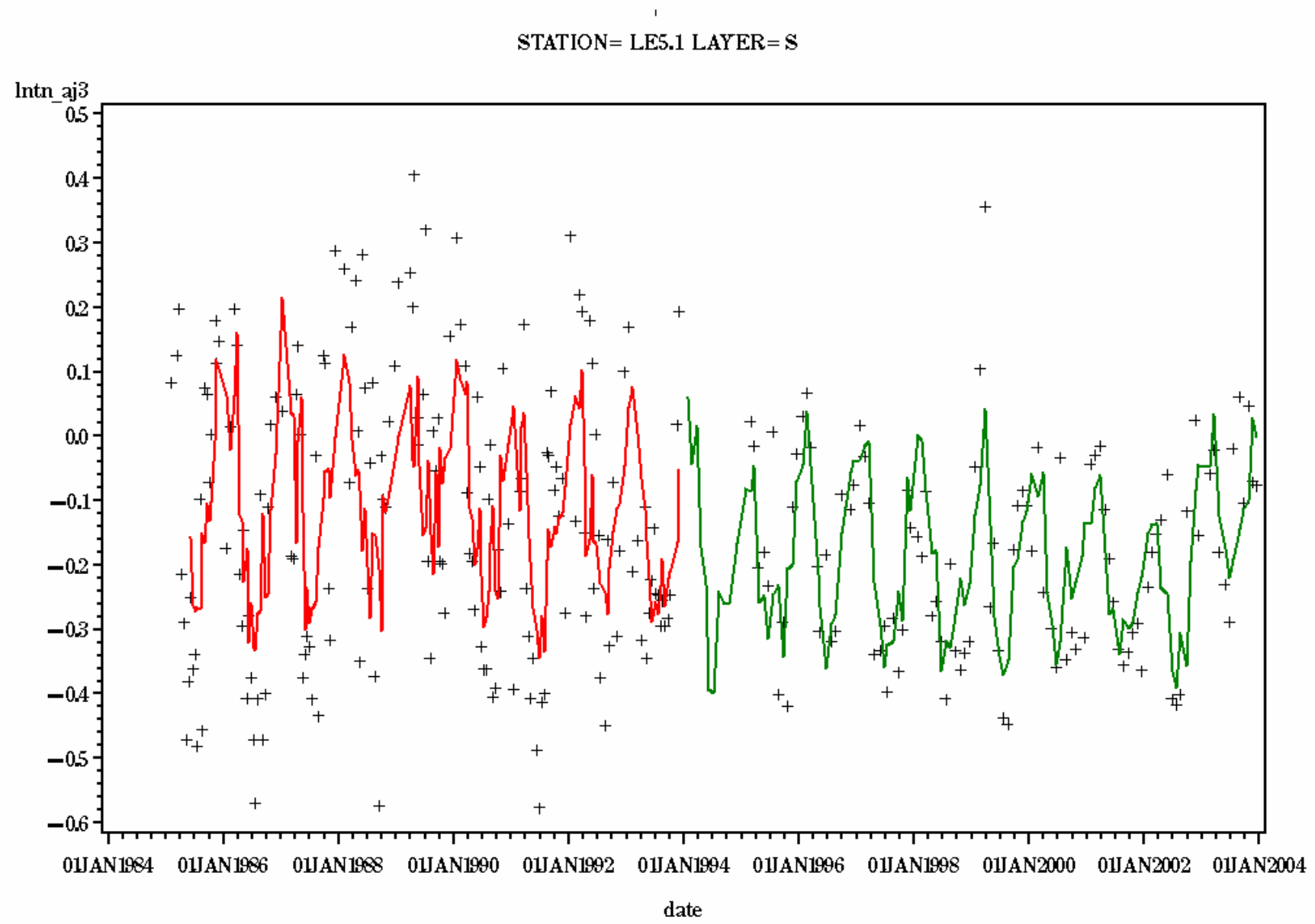
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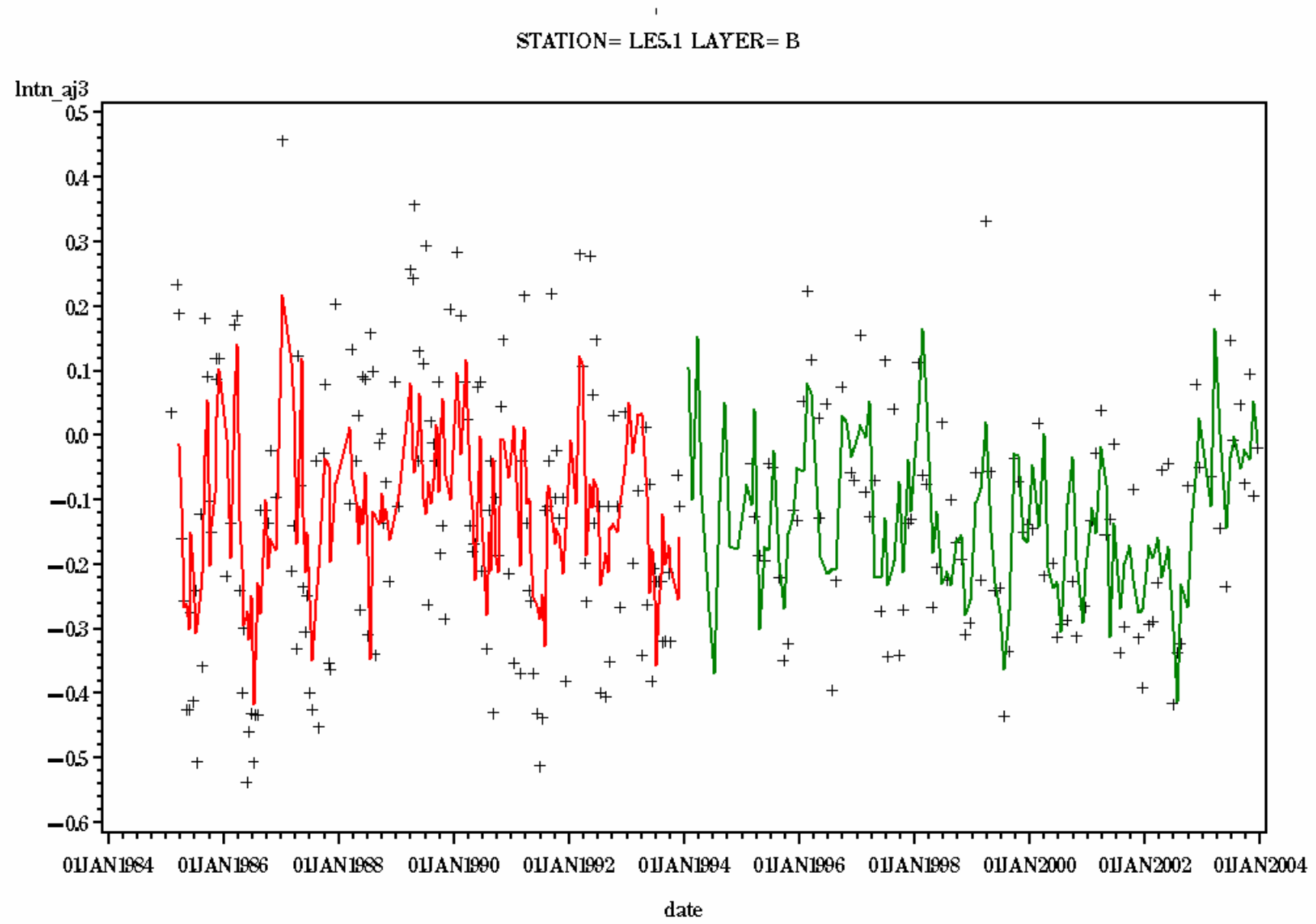
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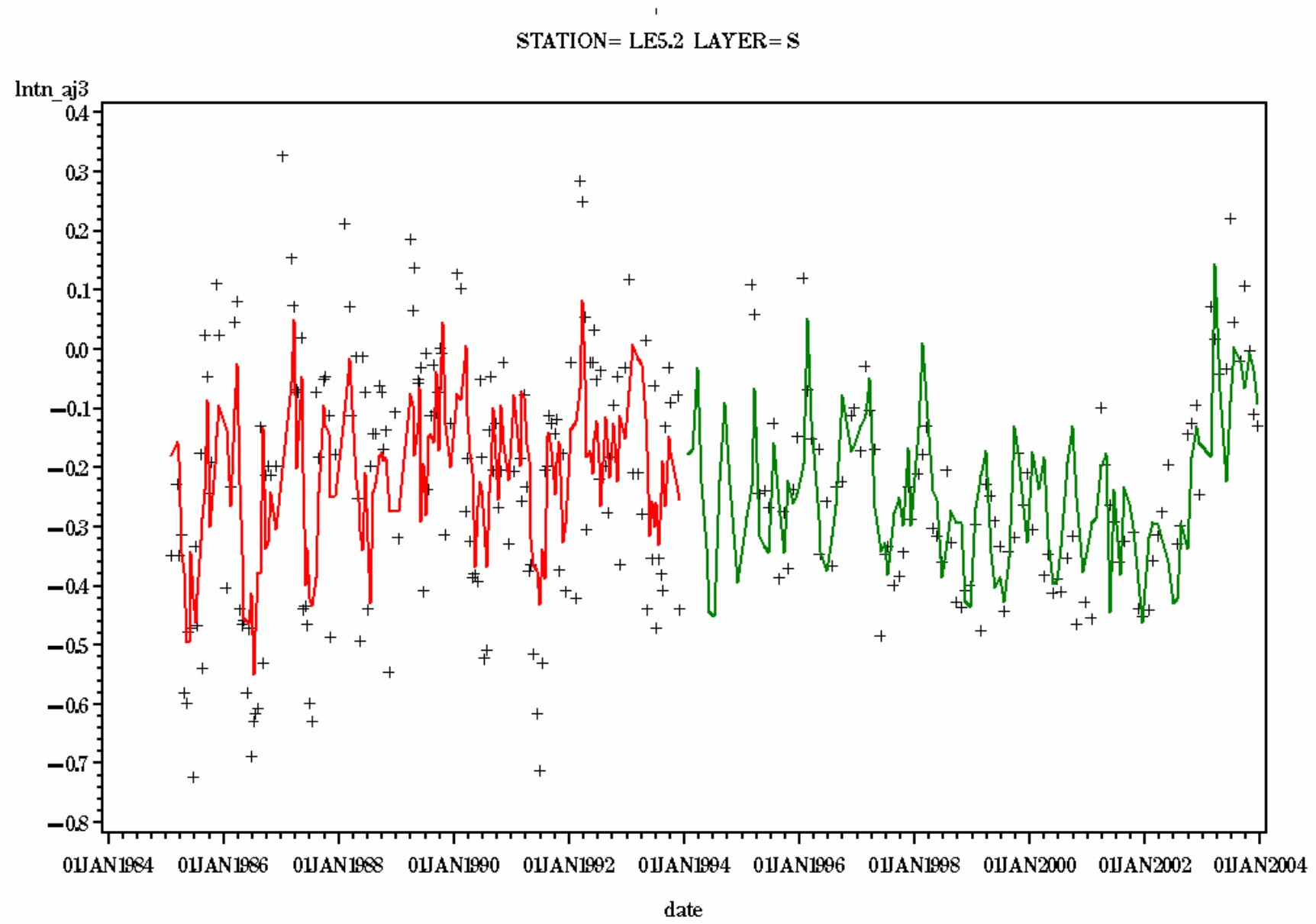
STATION= LE5.2 LAYER= S
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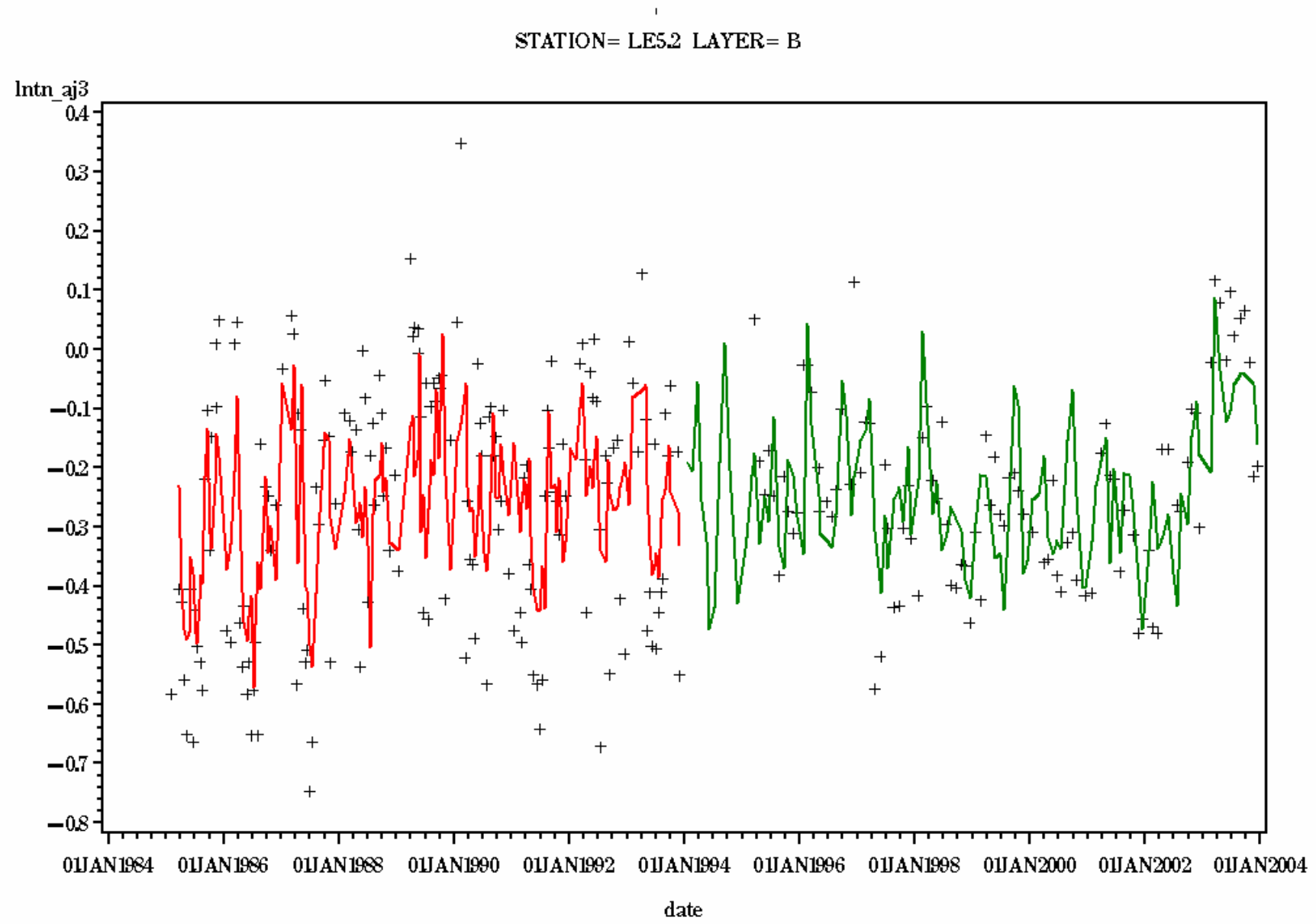
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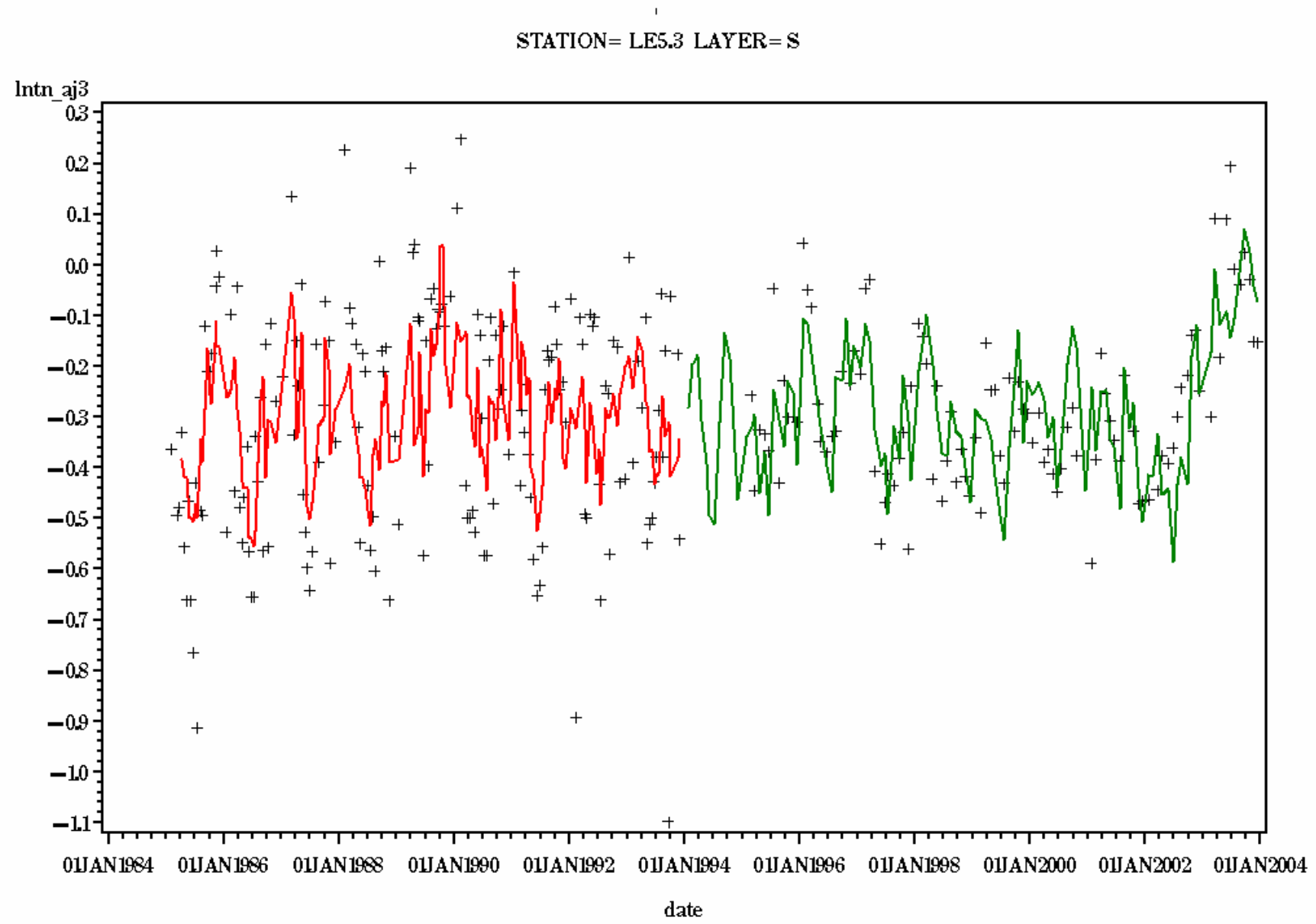
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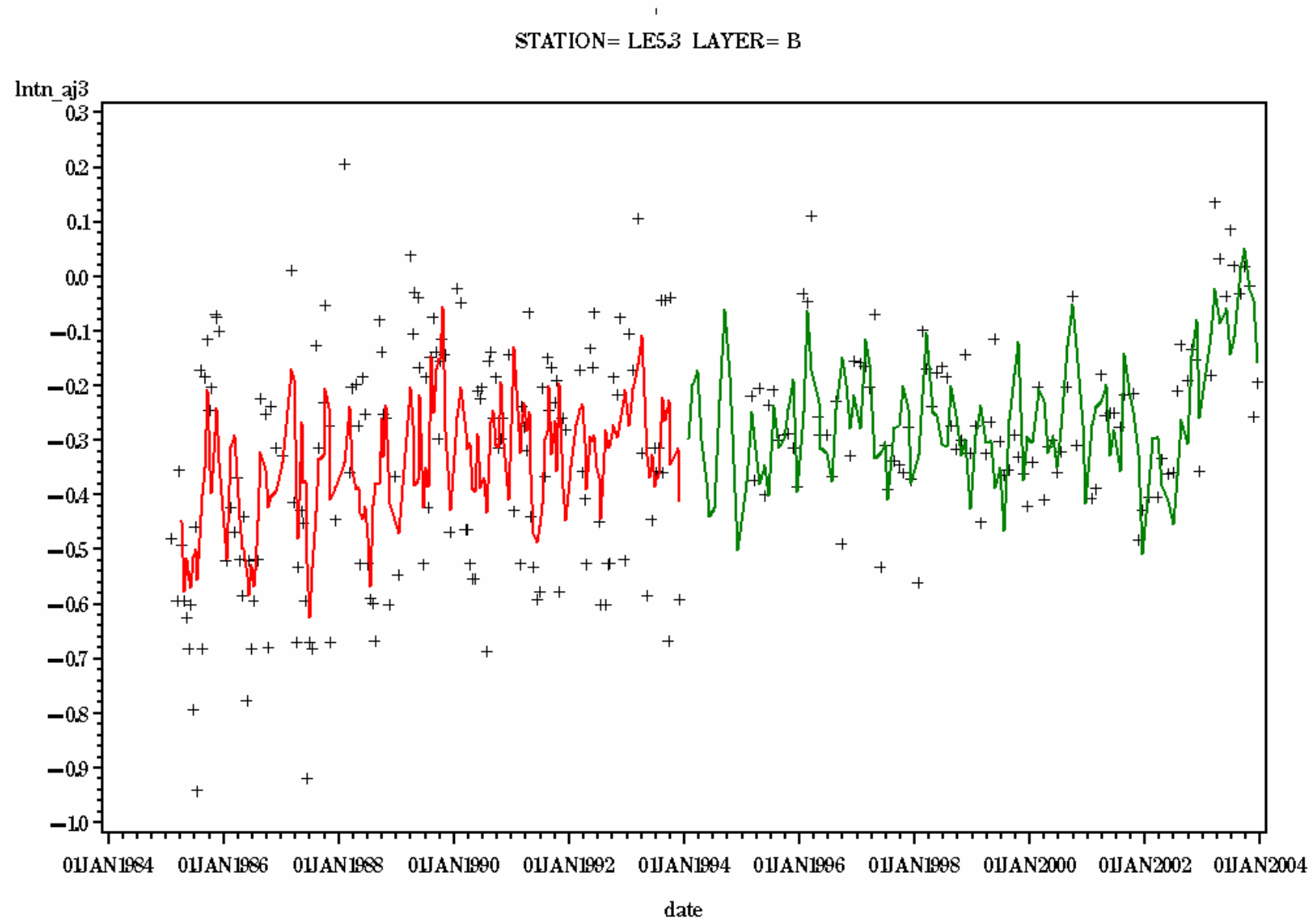
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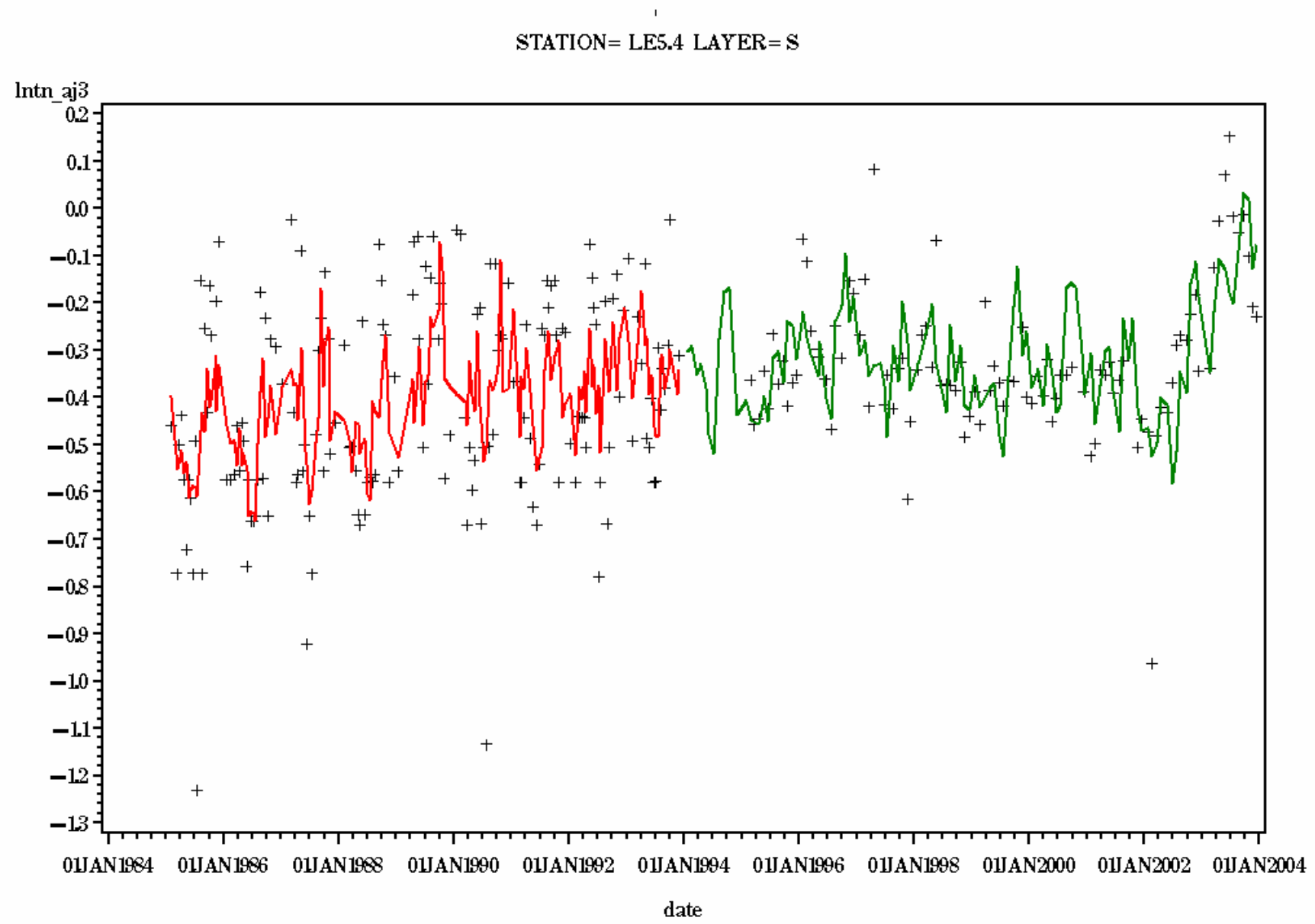
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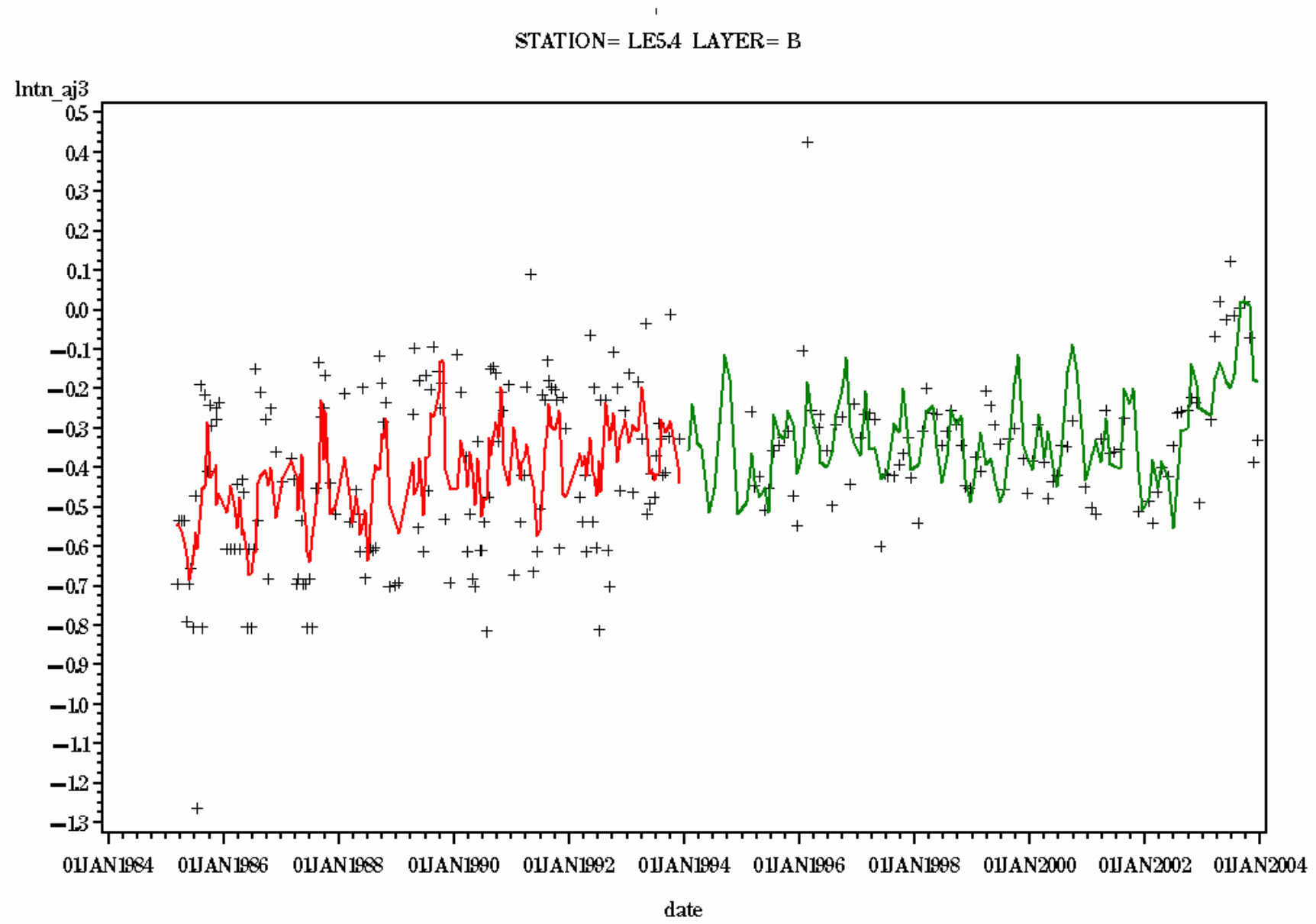
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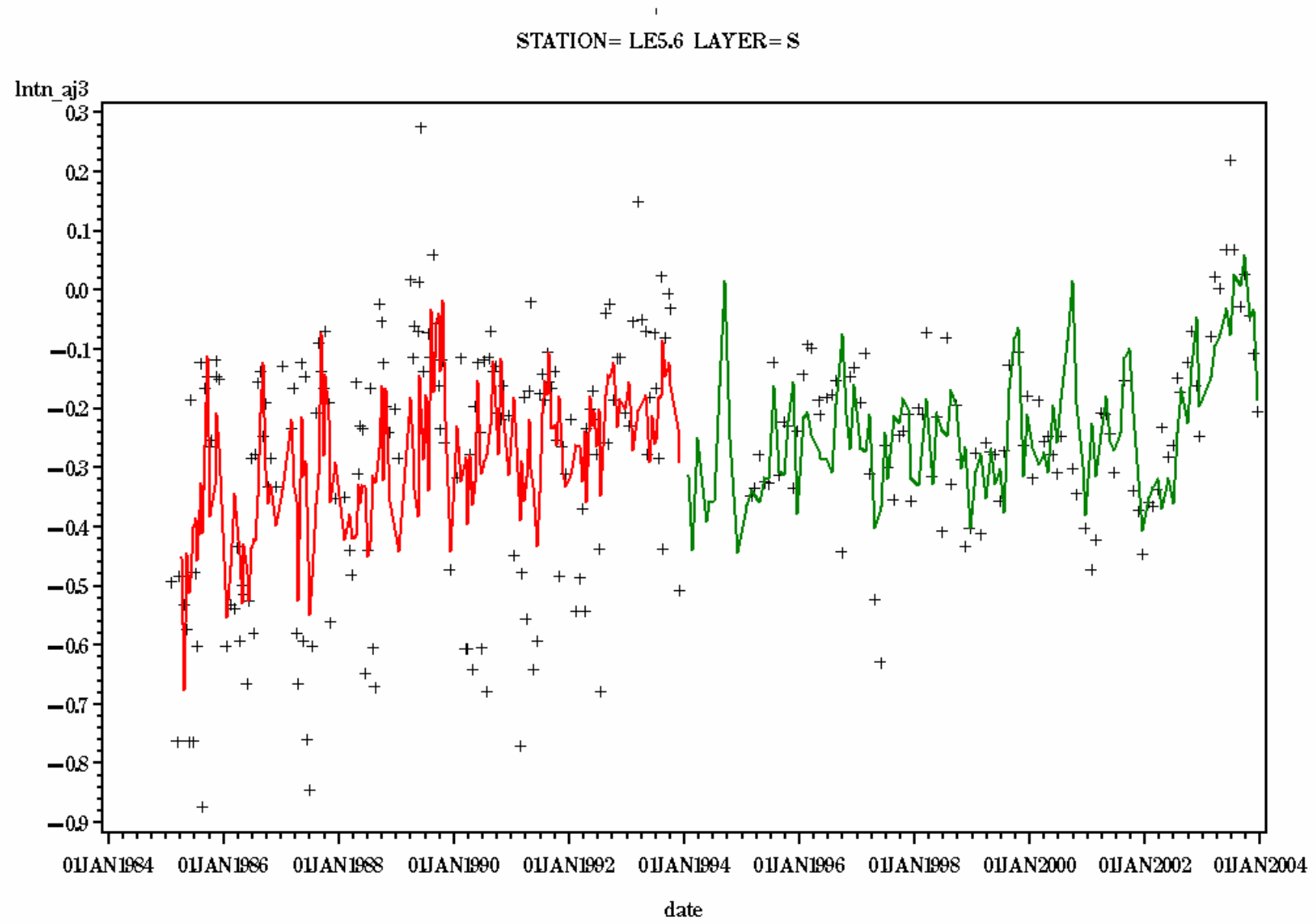
STATION= LE5.6 LAYER= S
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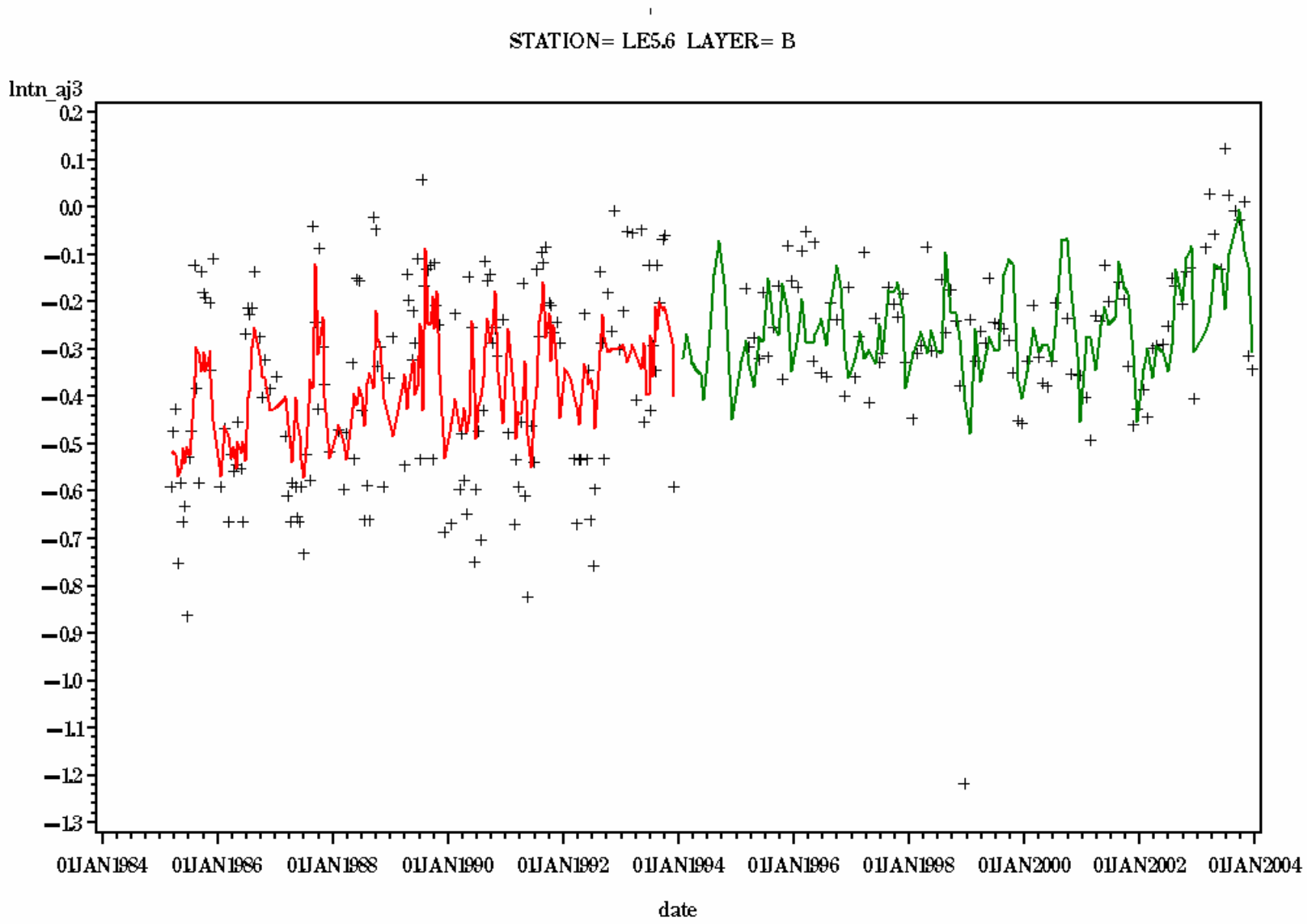
STATION= LE5.6 LAYER= B
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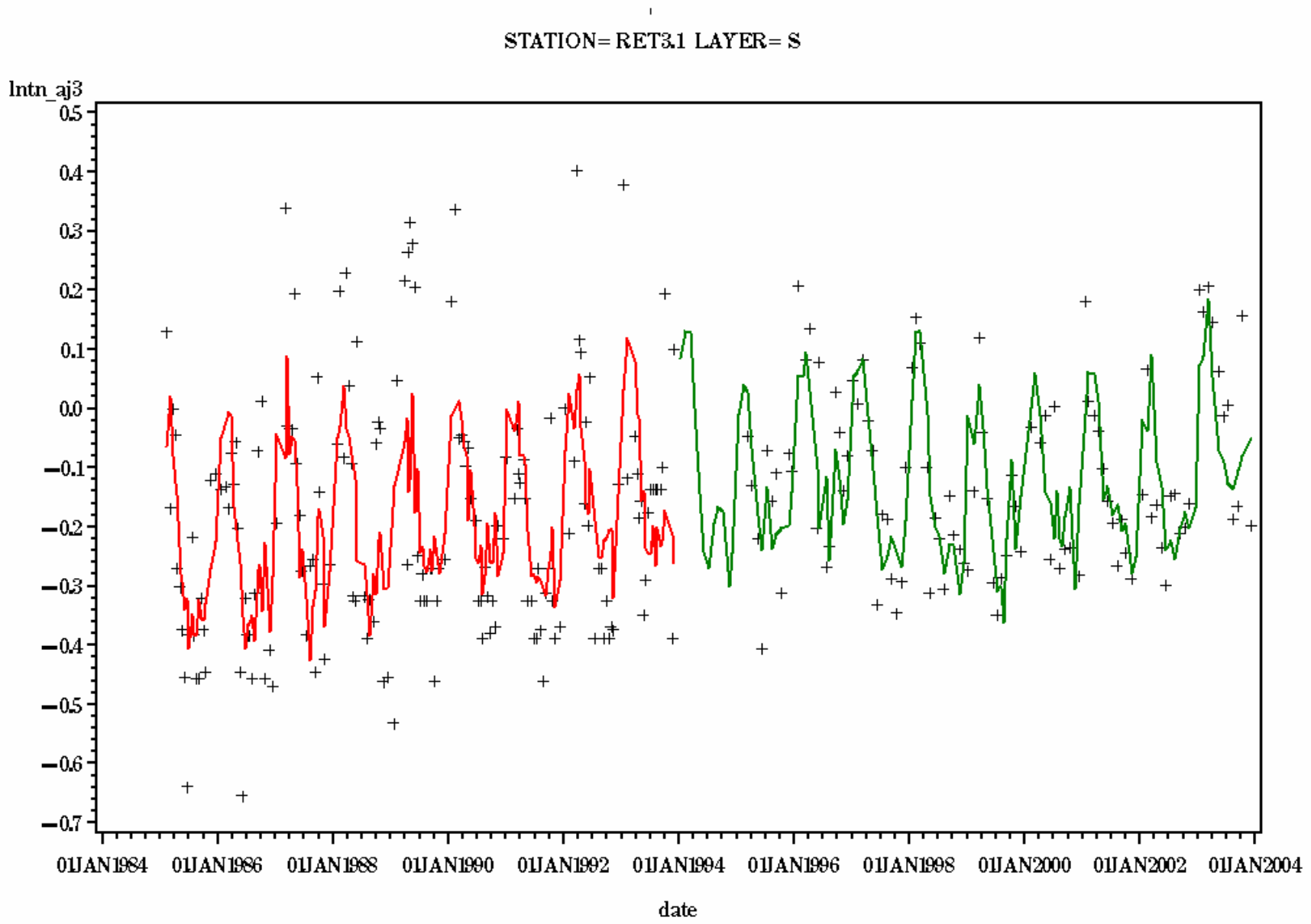
STATION= RET3.1 LAYER= S
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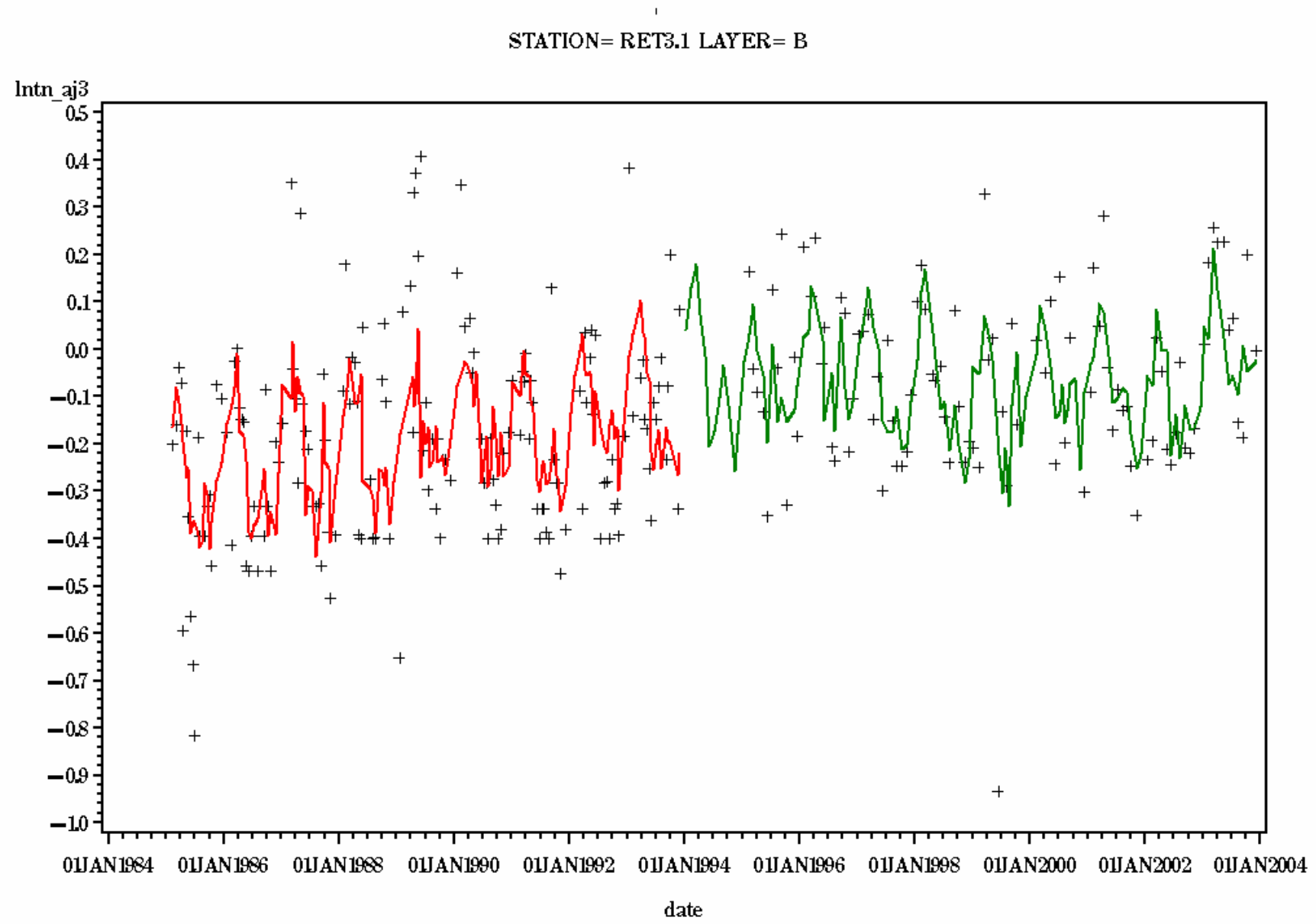
STATION= RET3.1 LAYER= B
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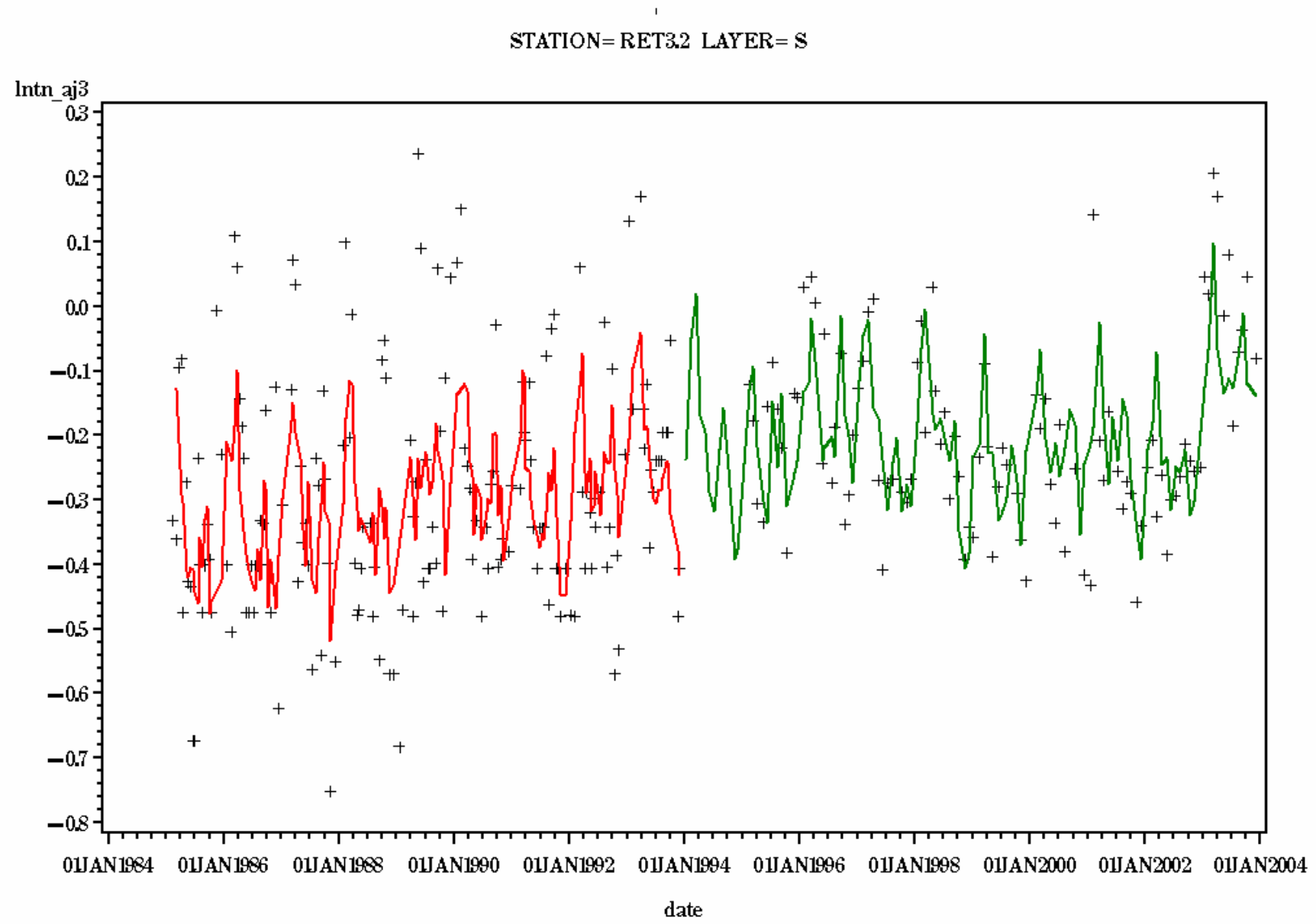
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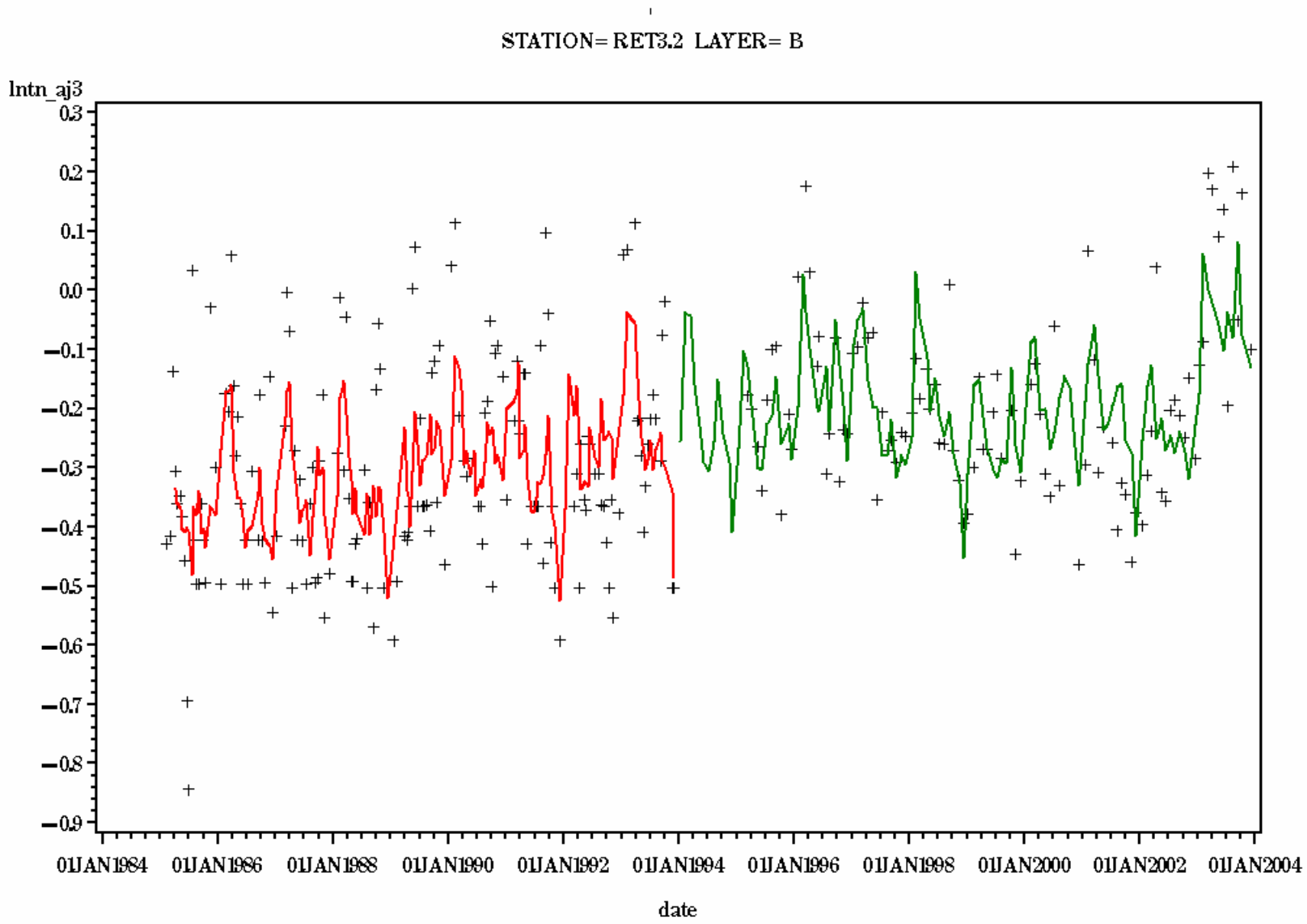
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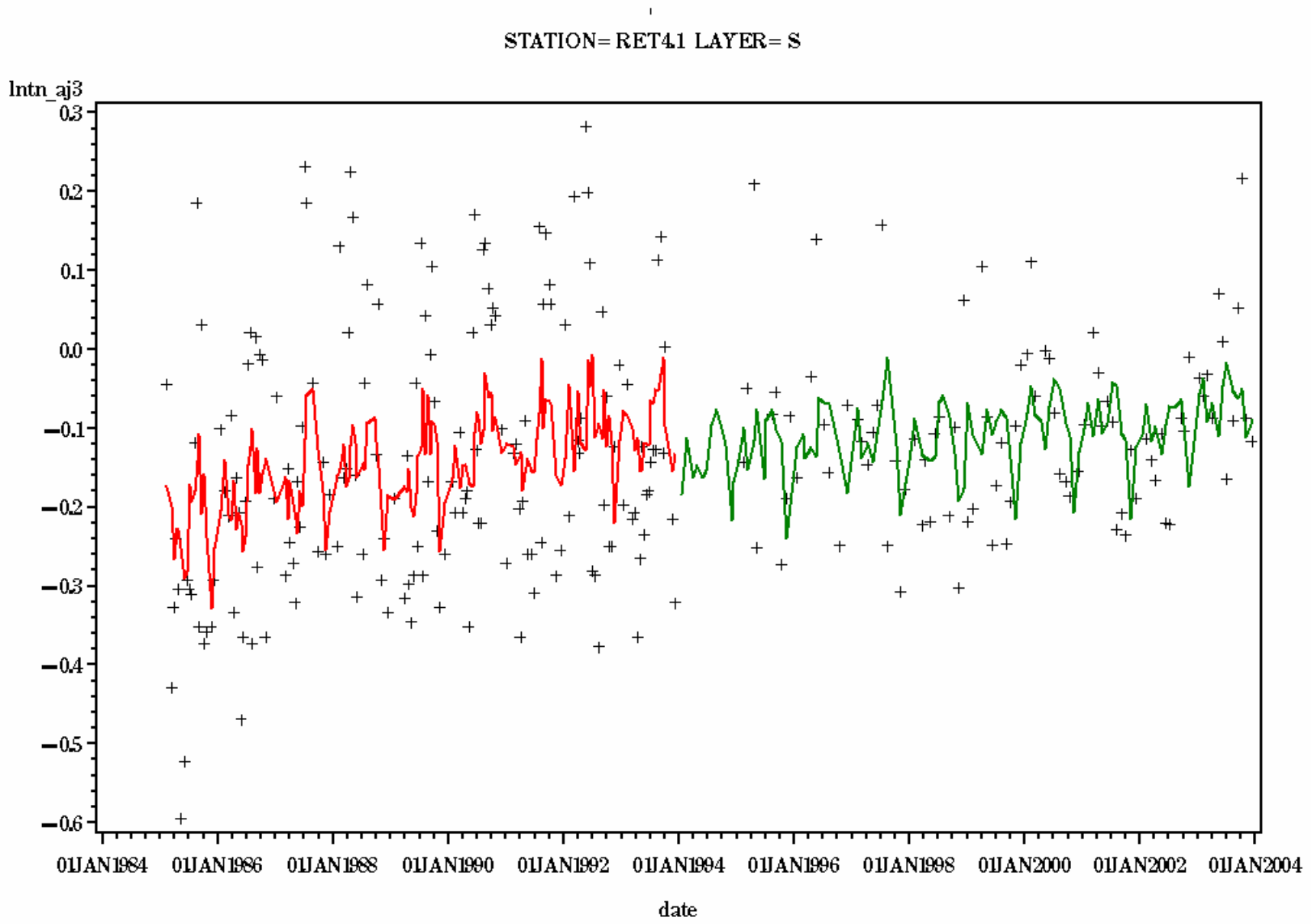
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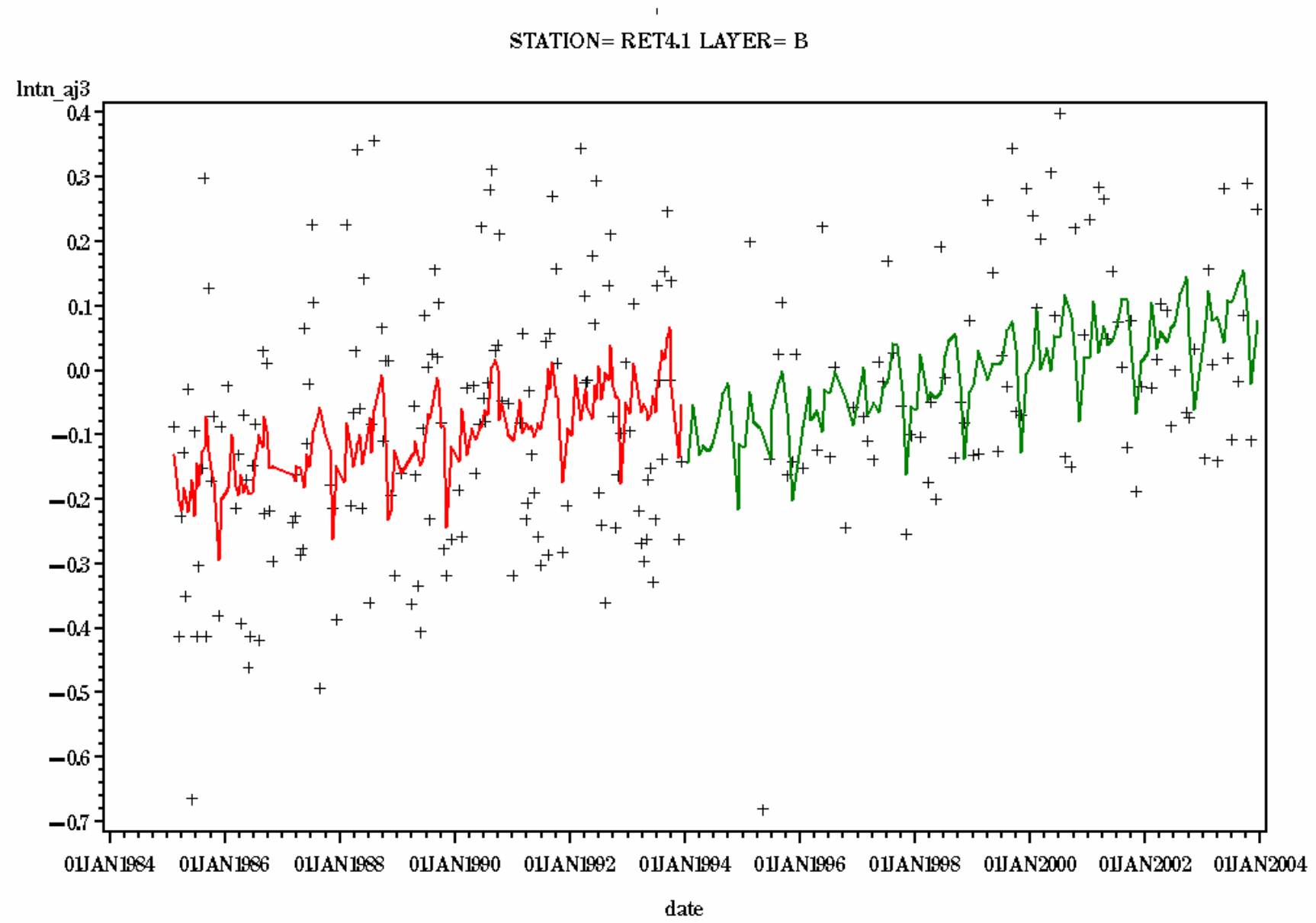
STATION= RET4.1 LAYER= B
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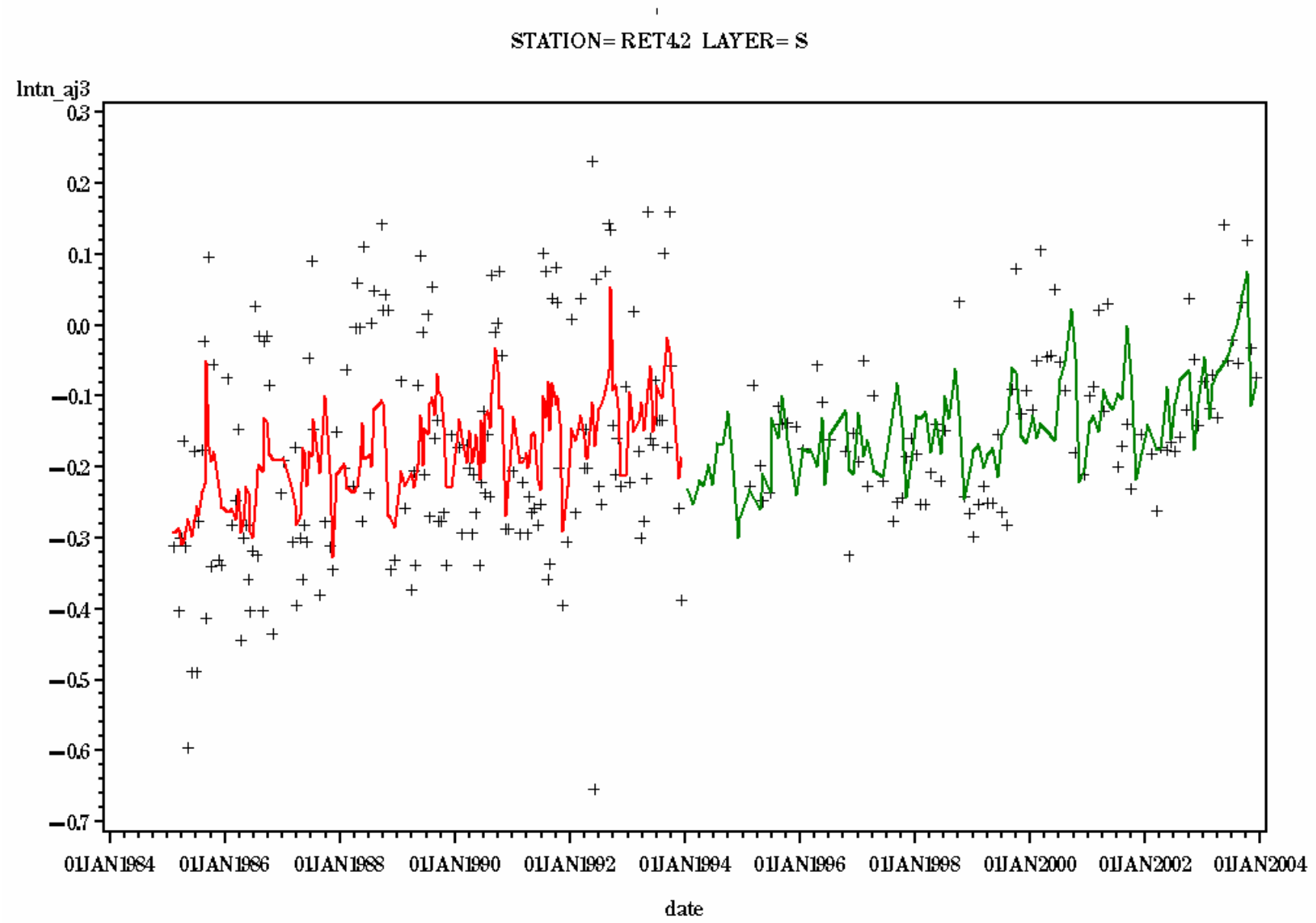
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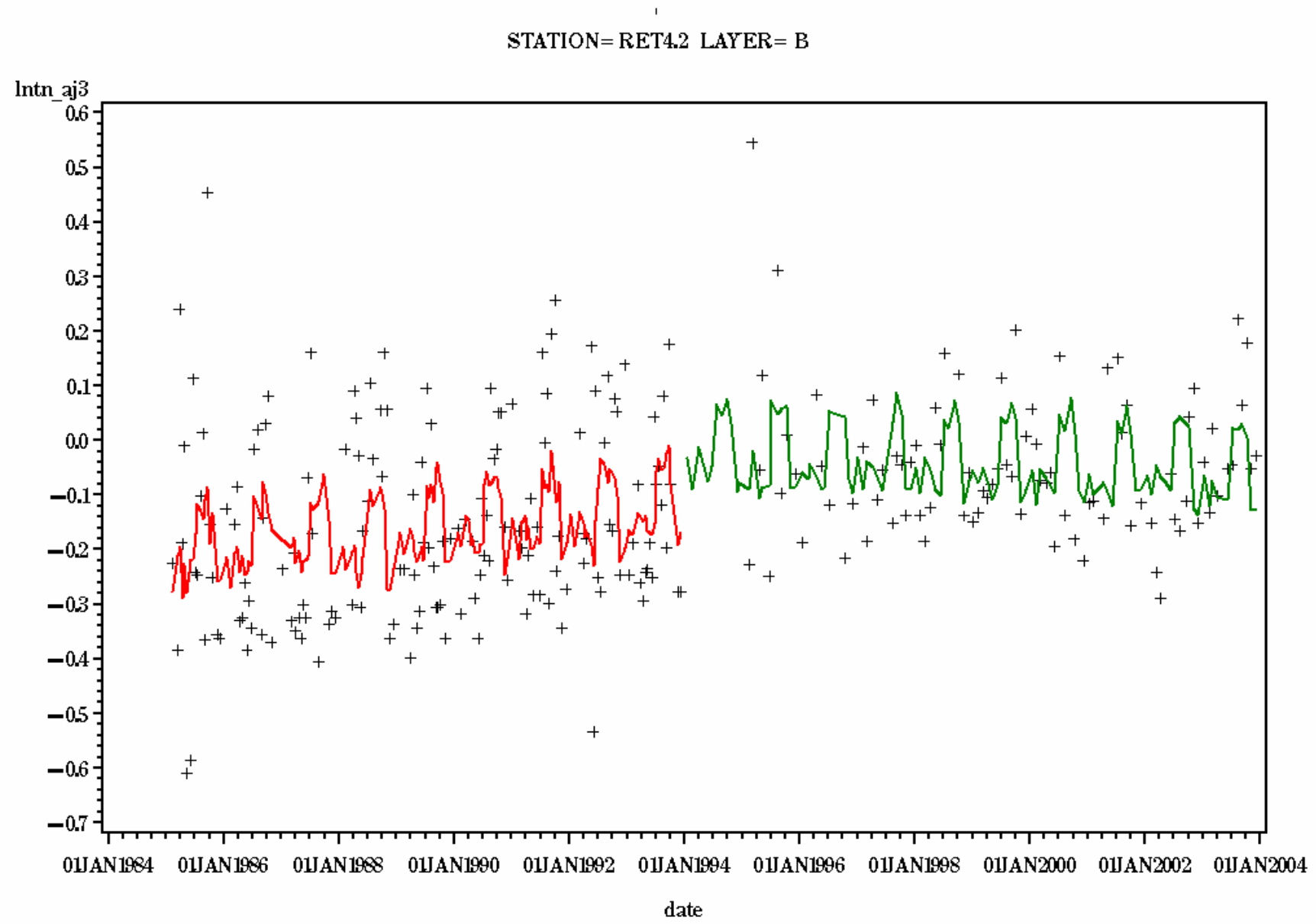
STATION= RET4.2 LAYER= B
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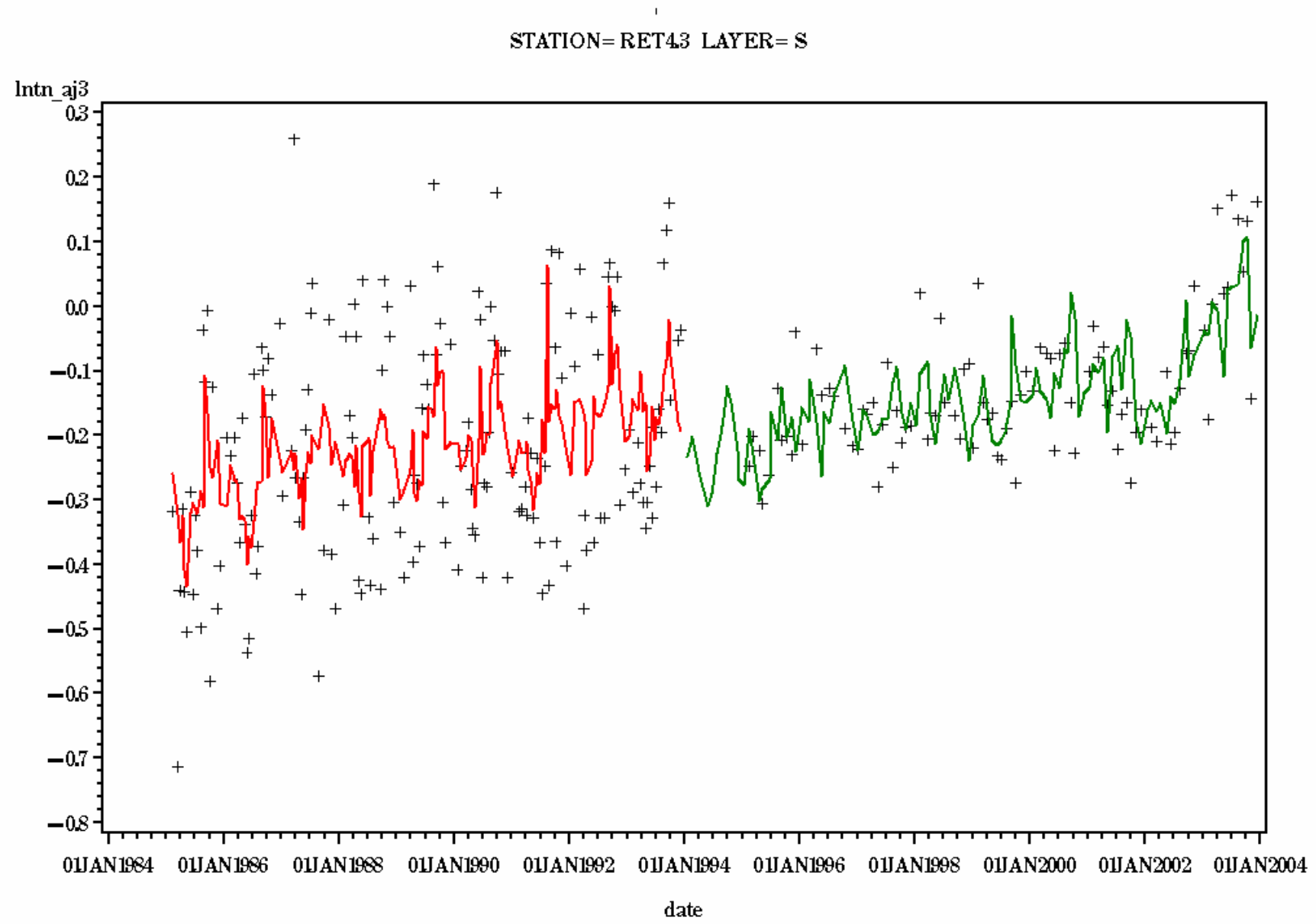
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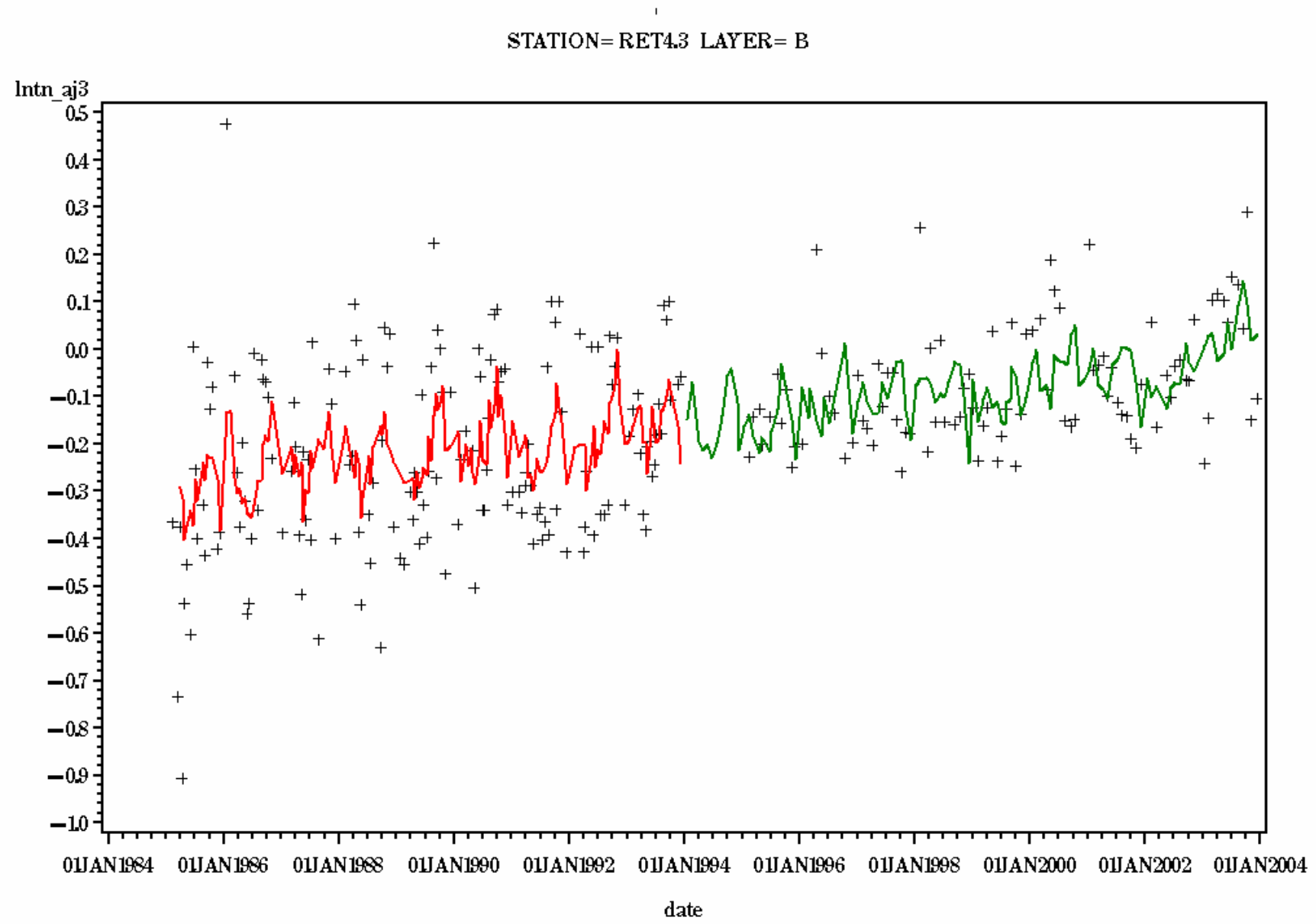
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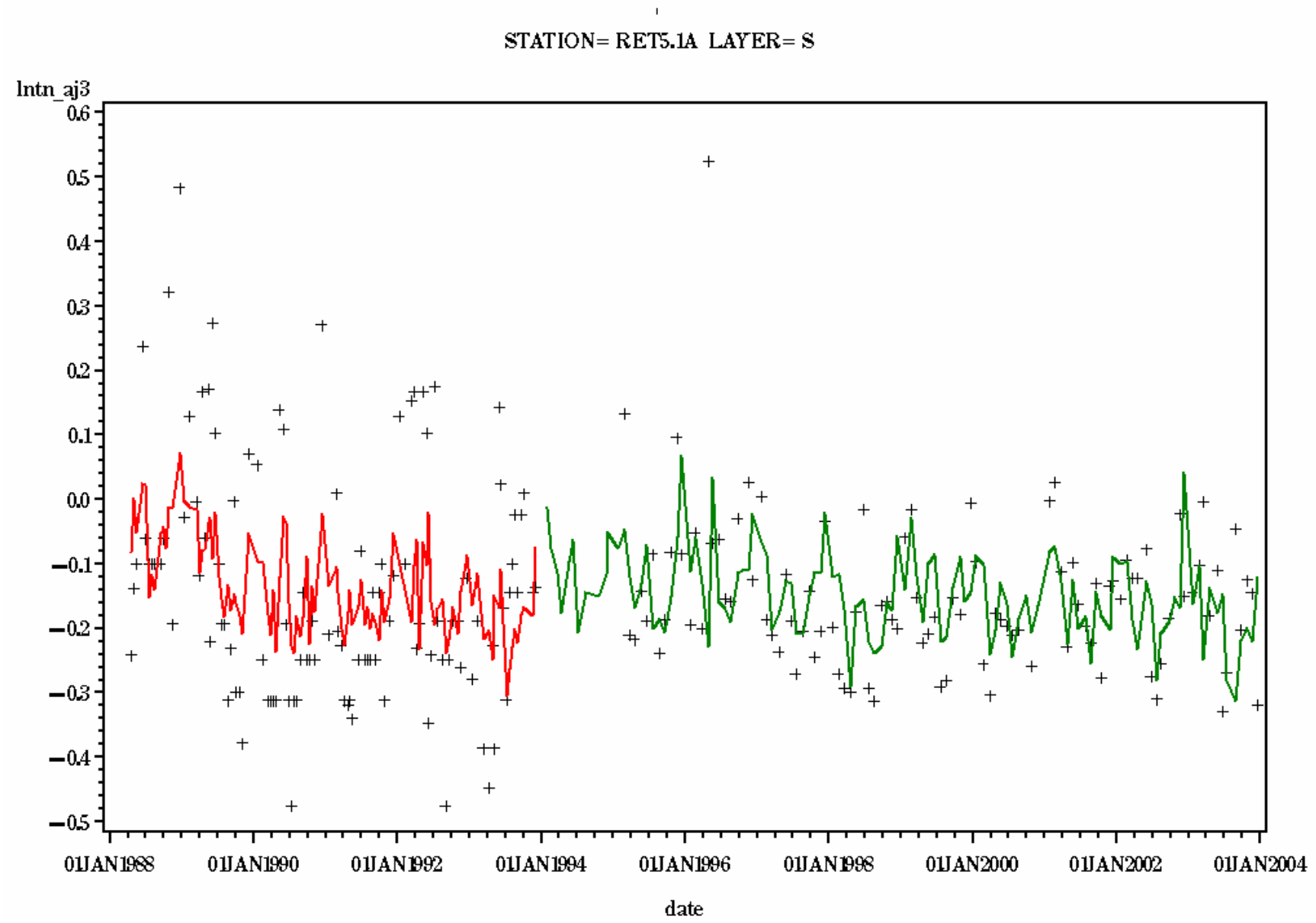
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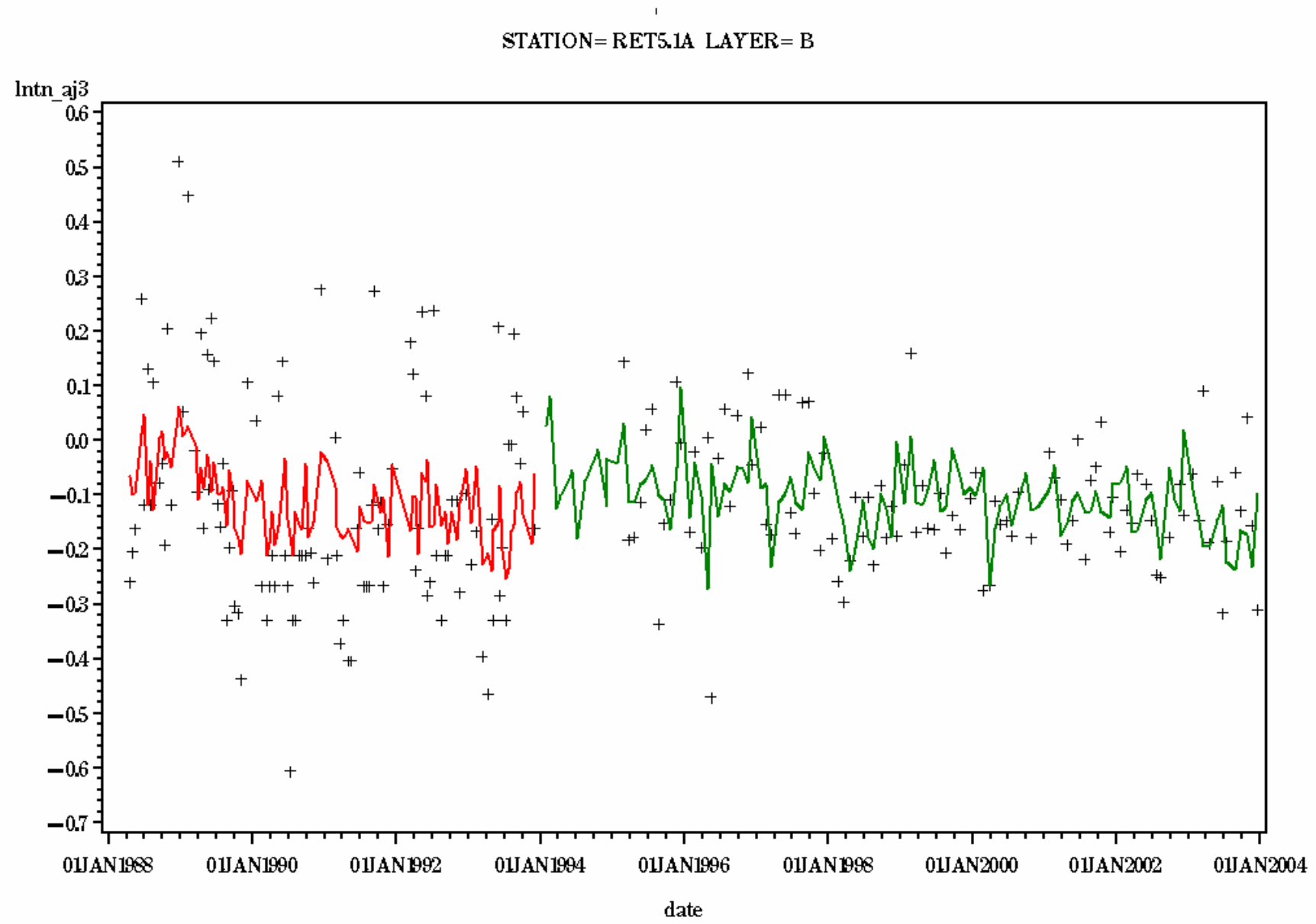
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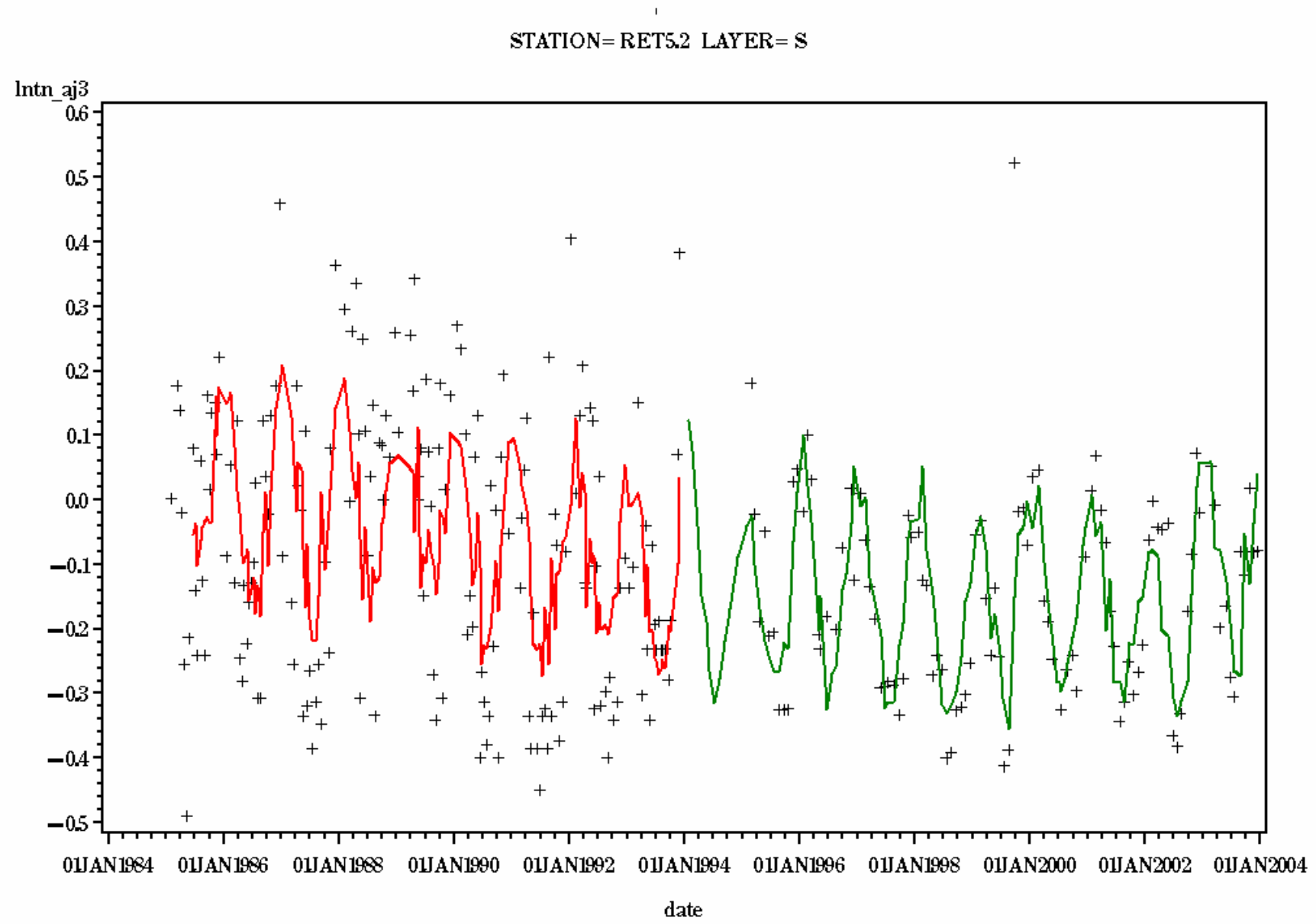
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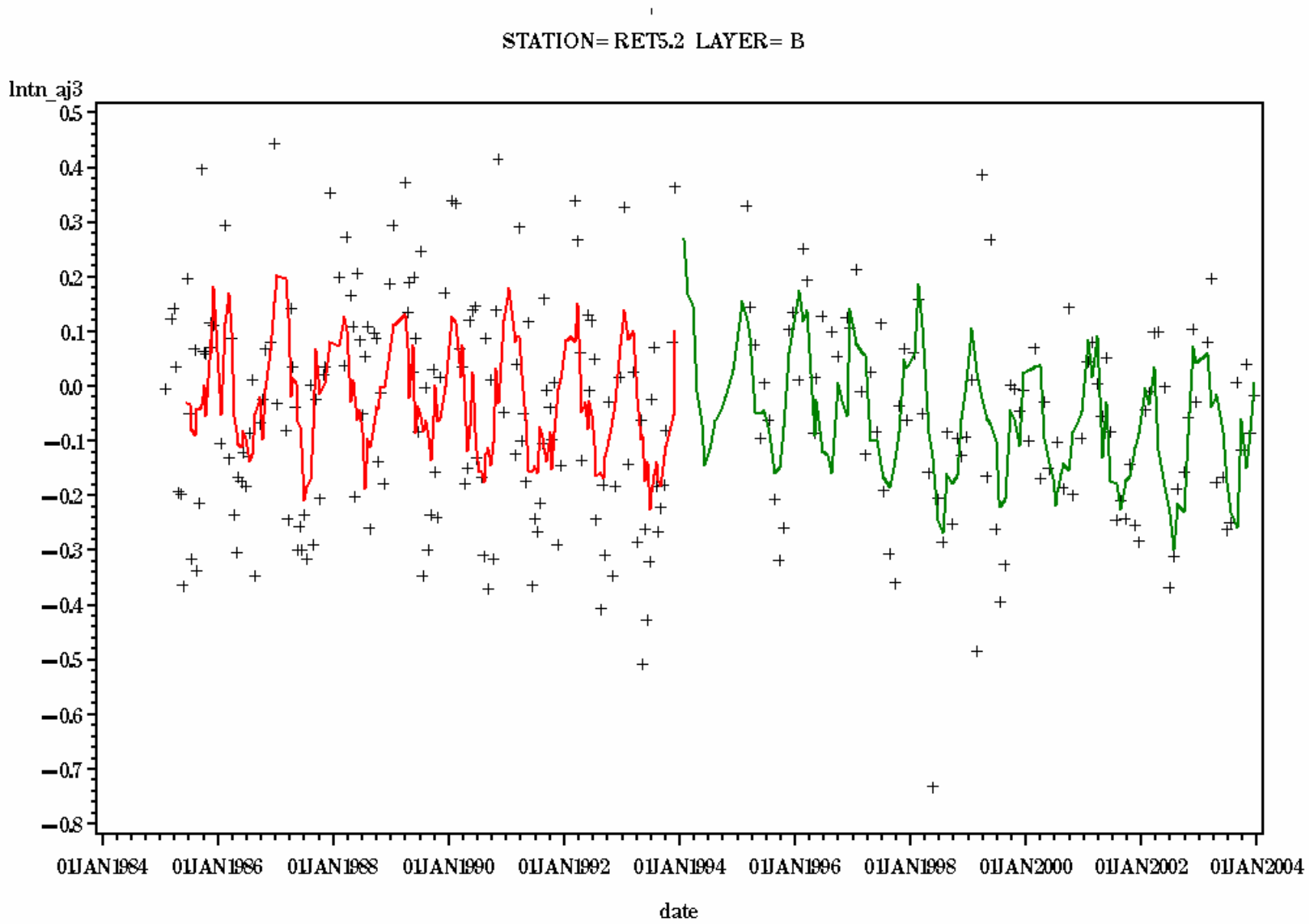
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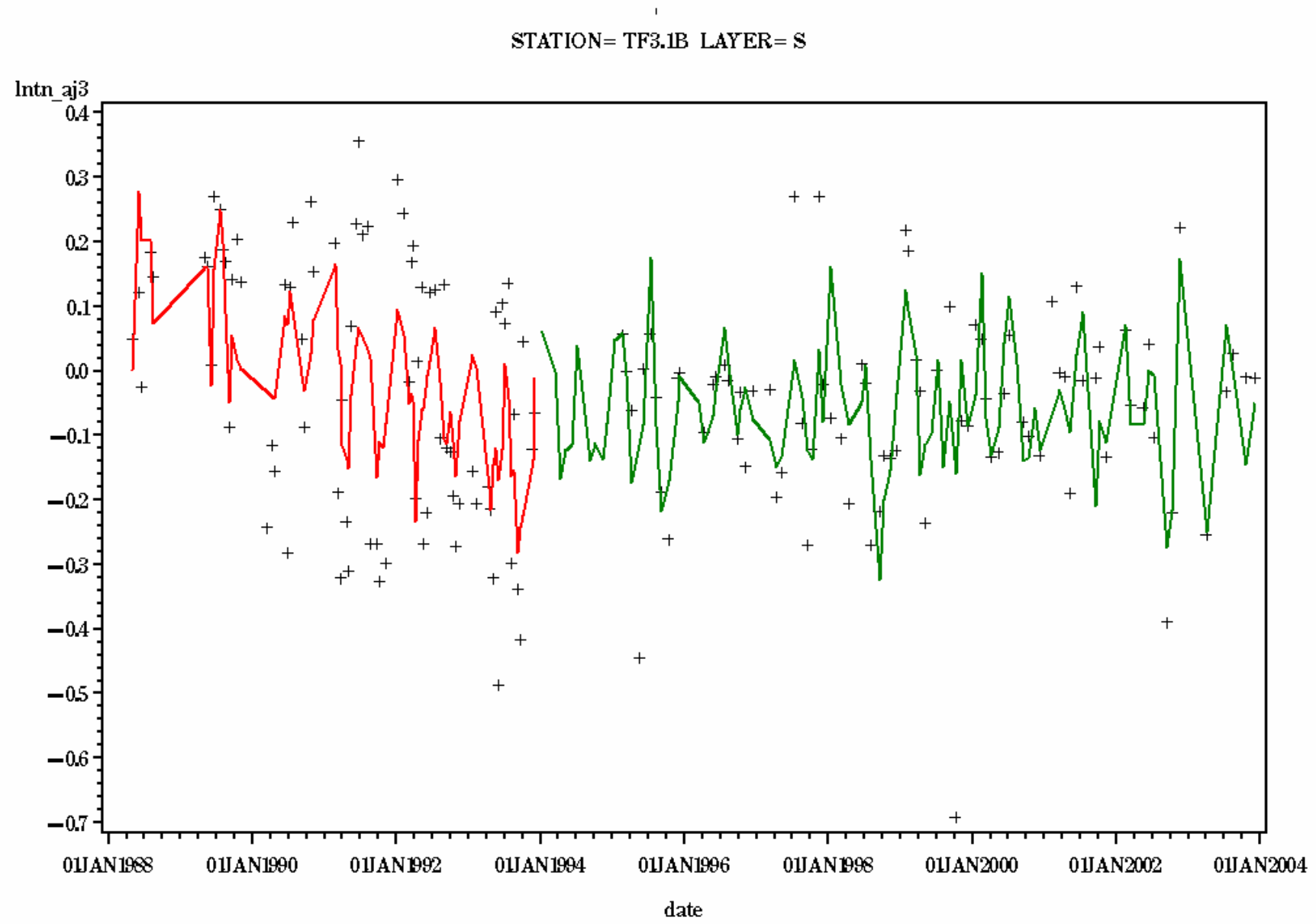
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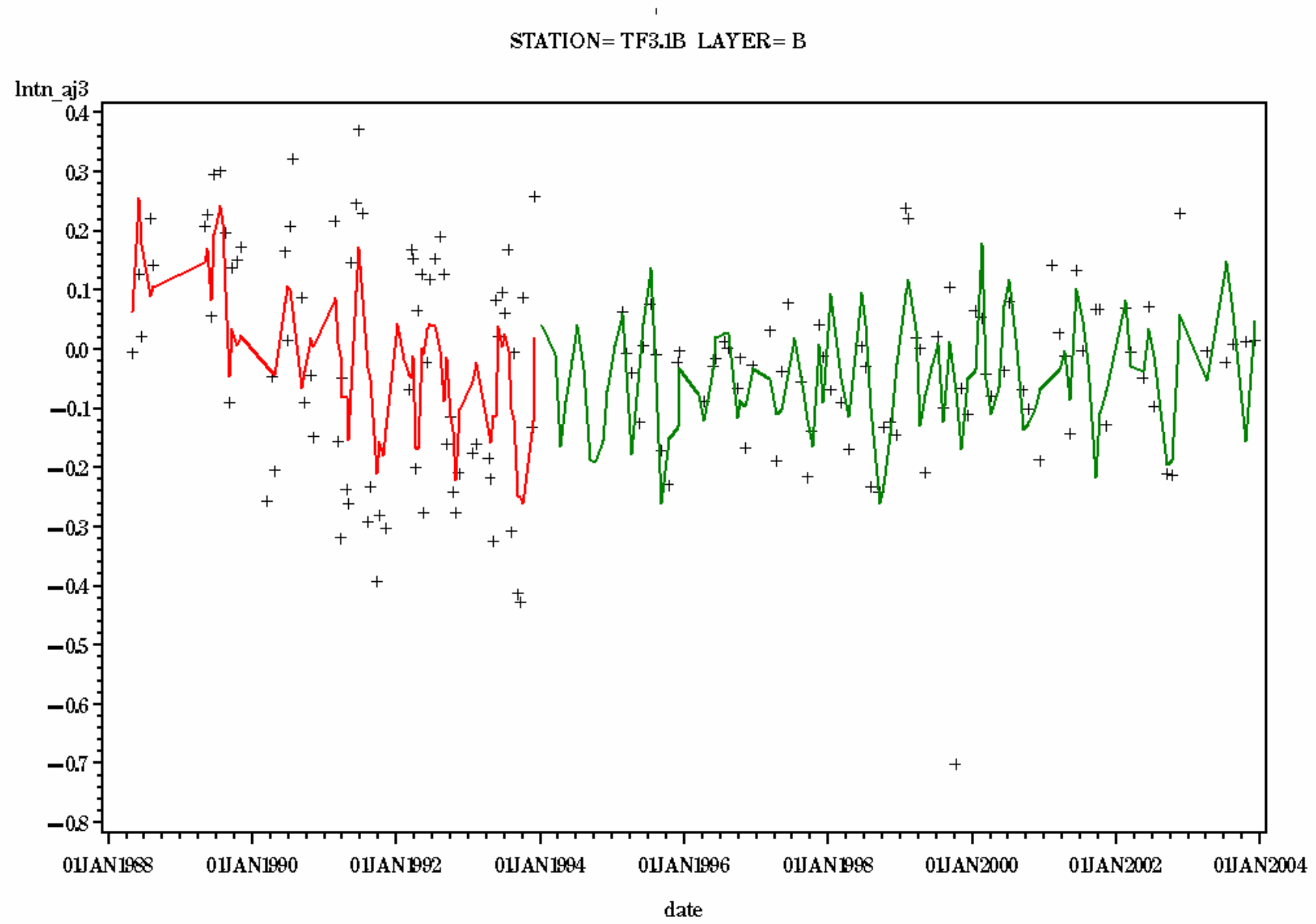
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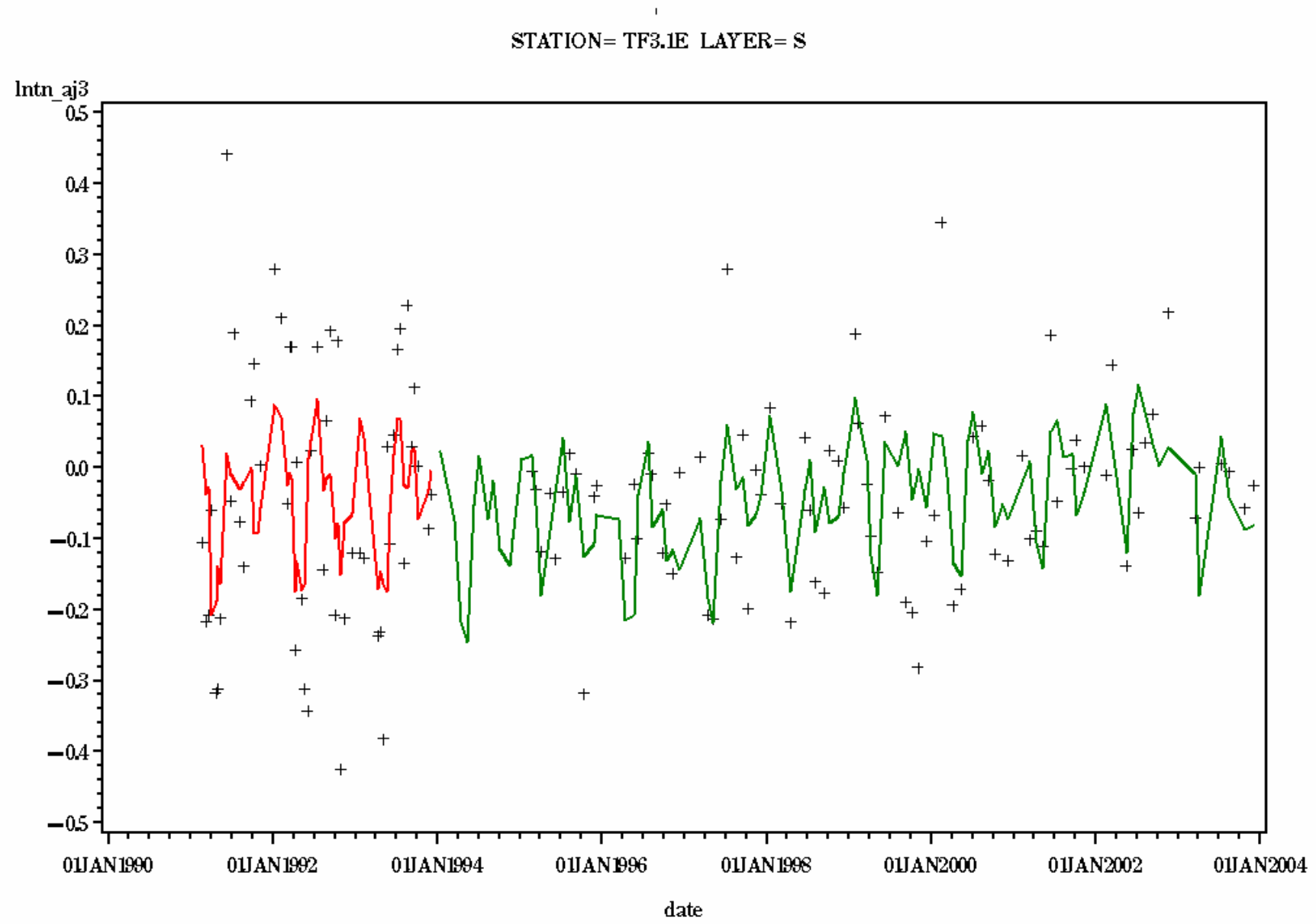
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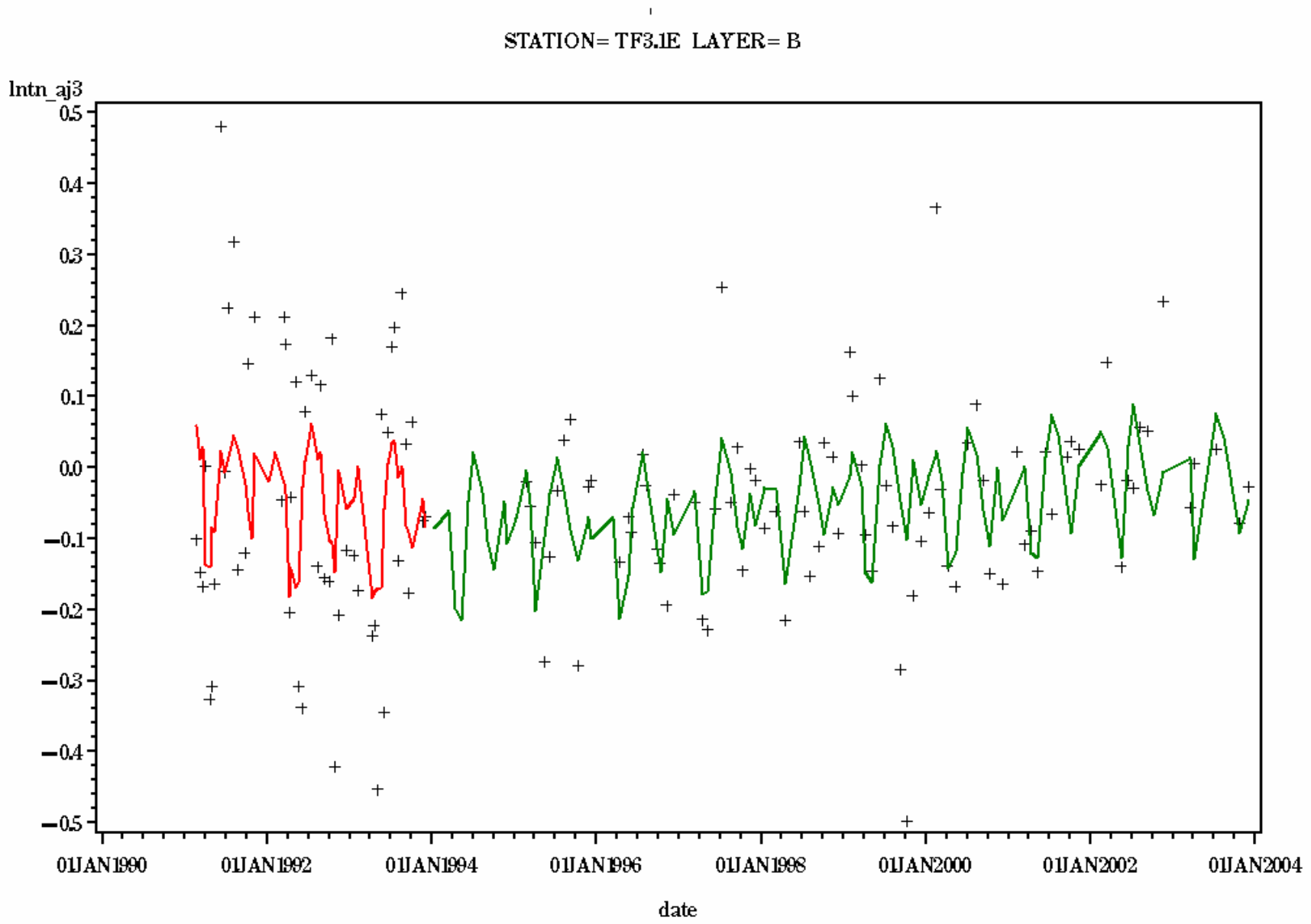
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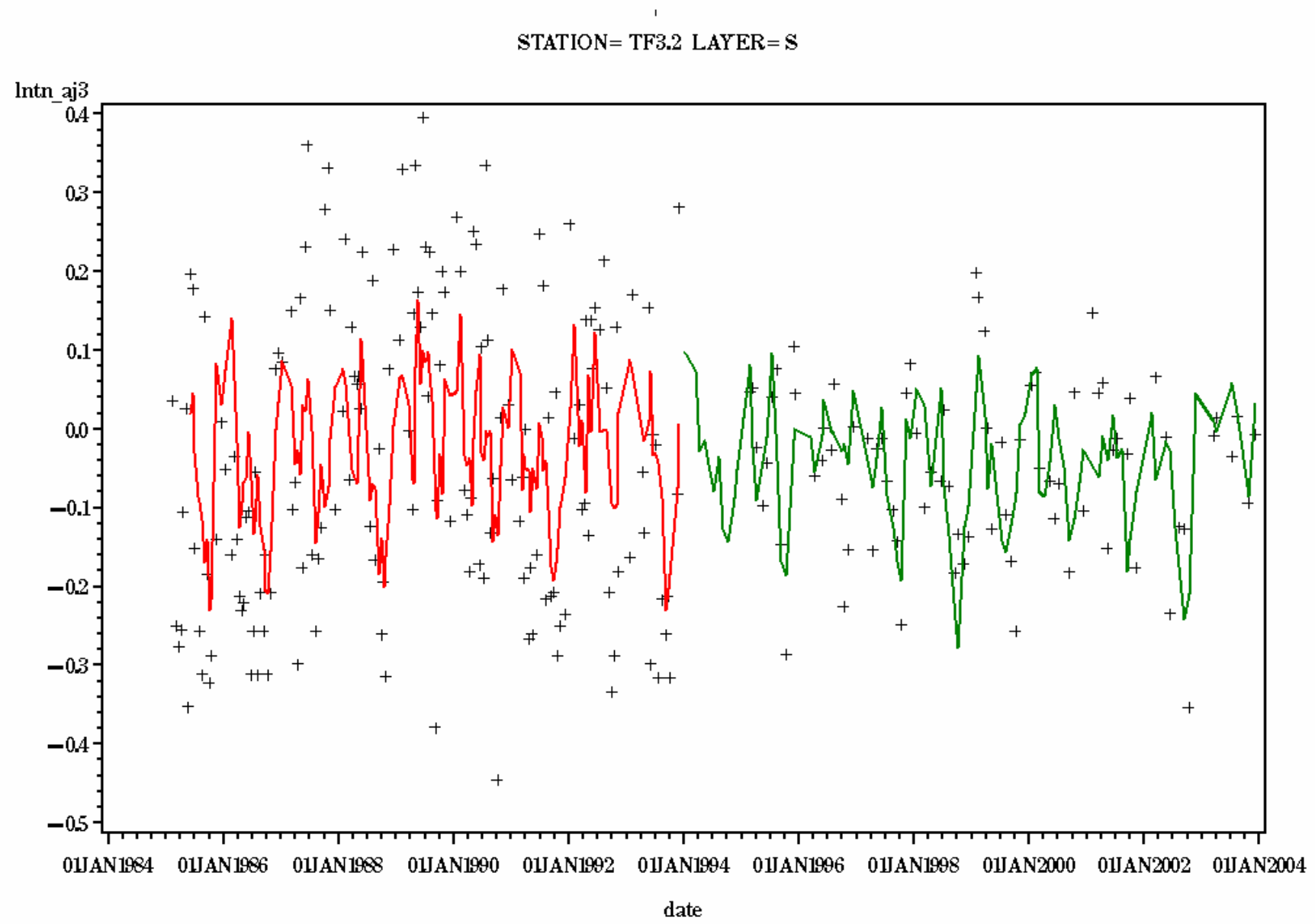
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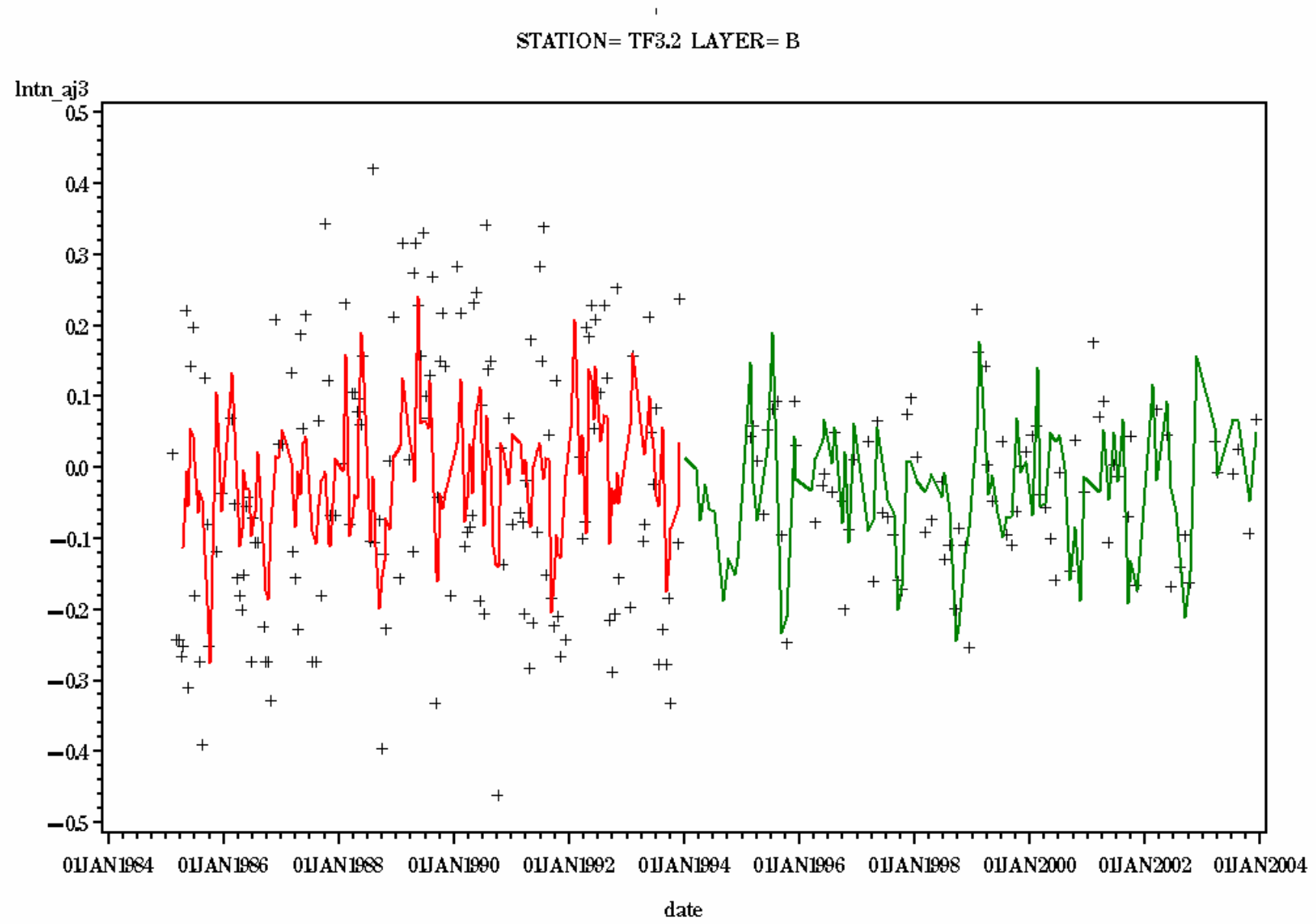
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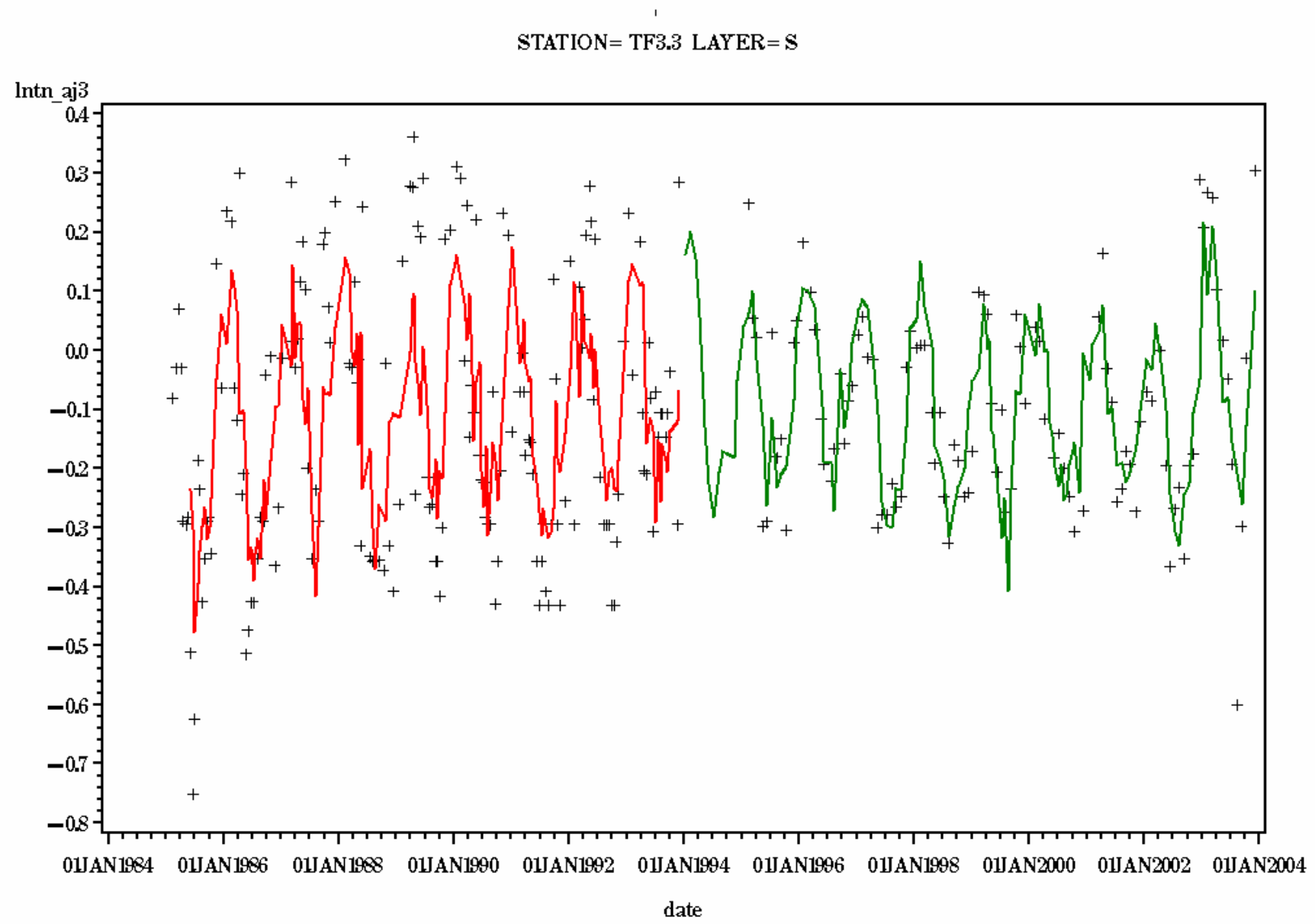
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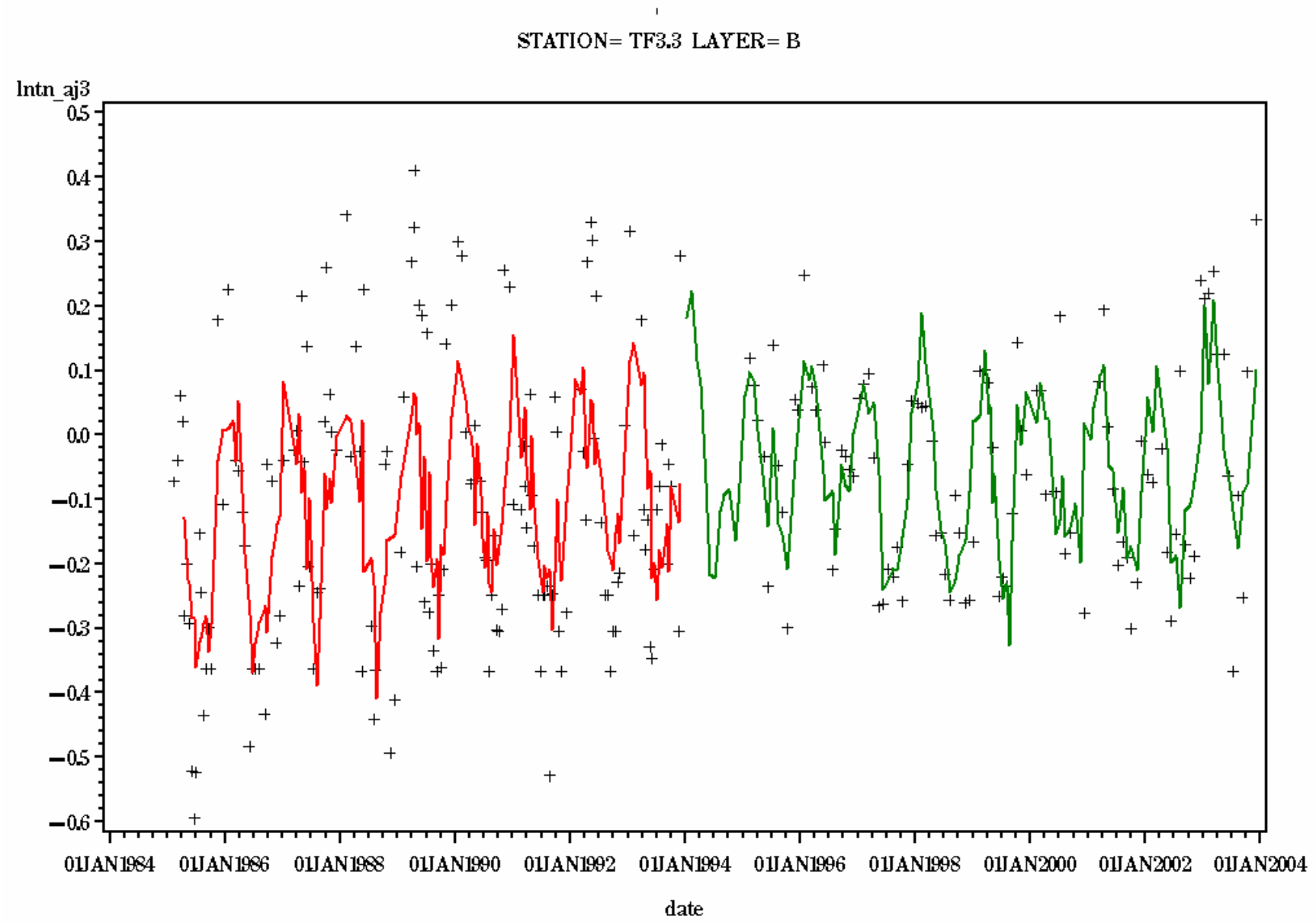
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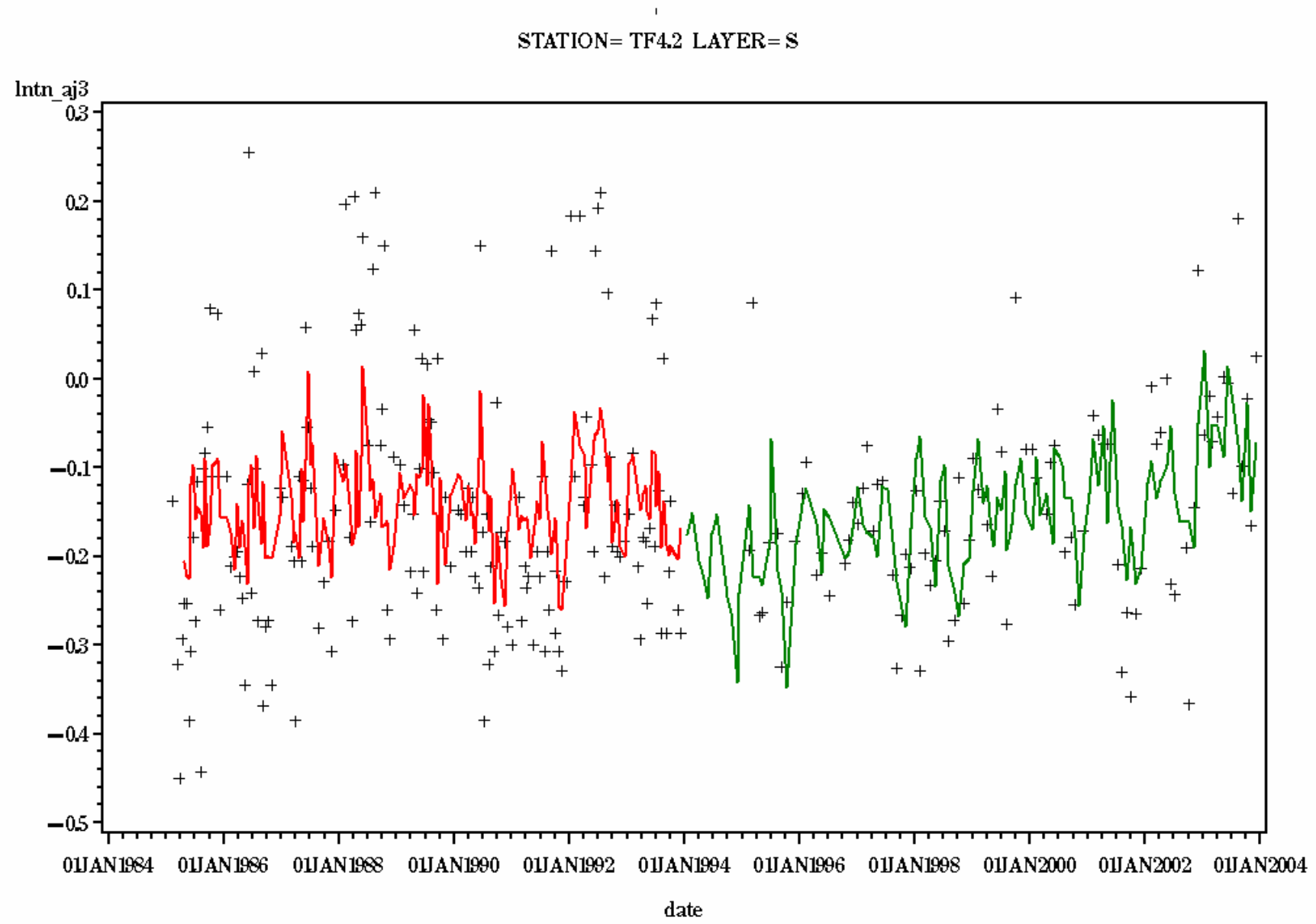
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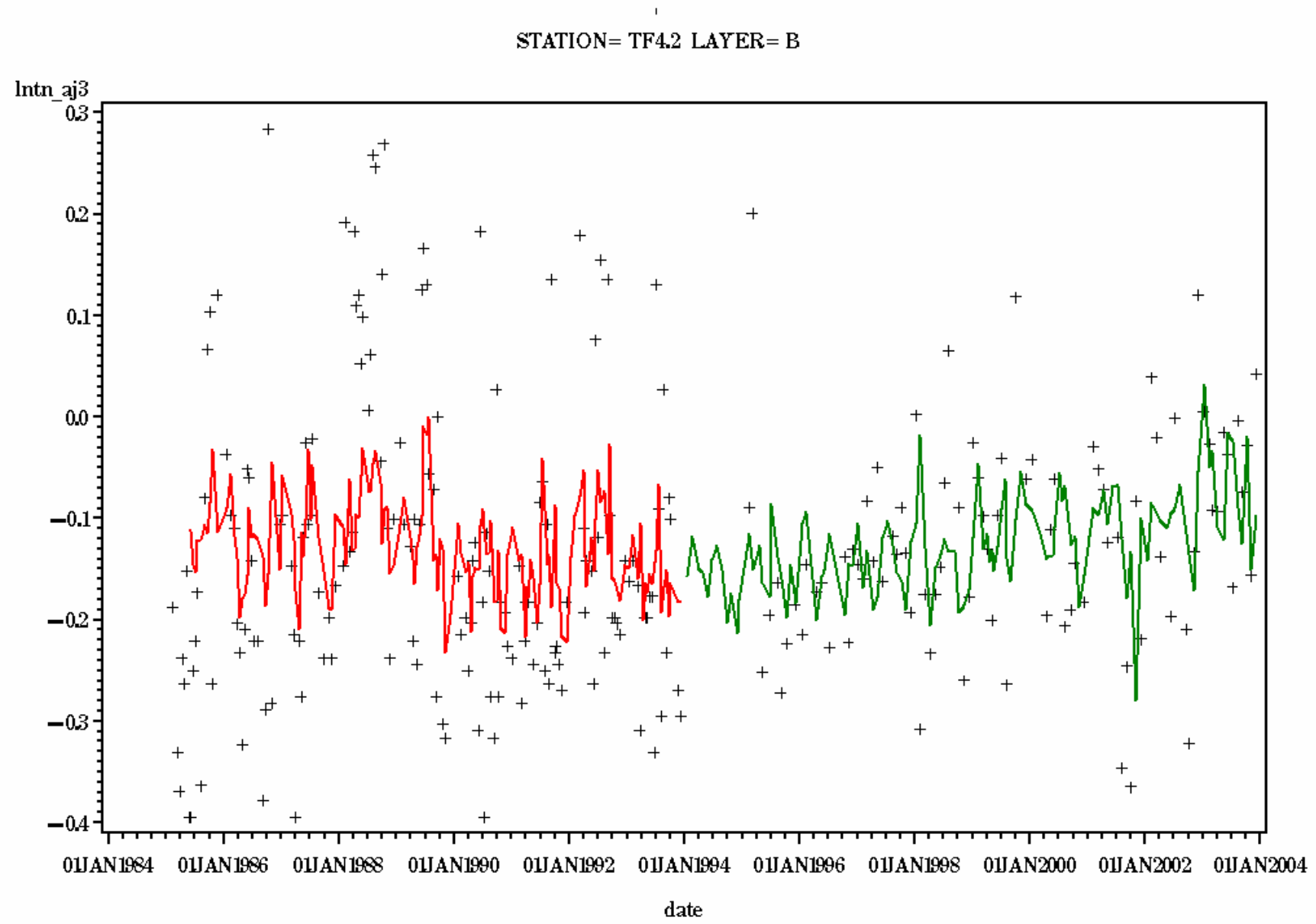
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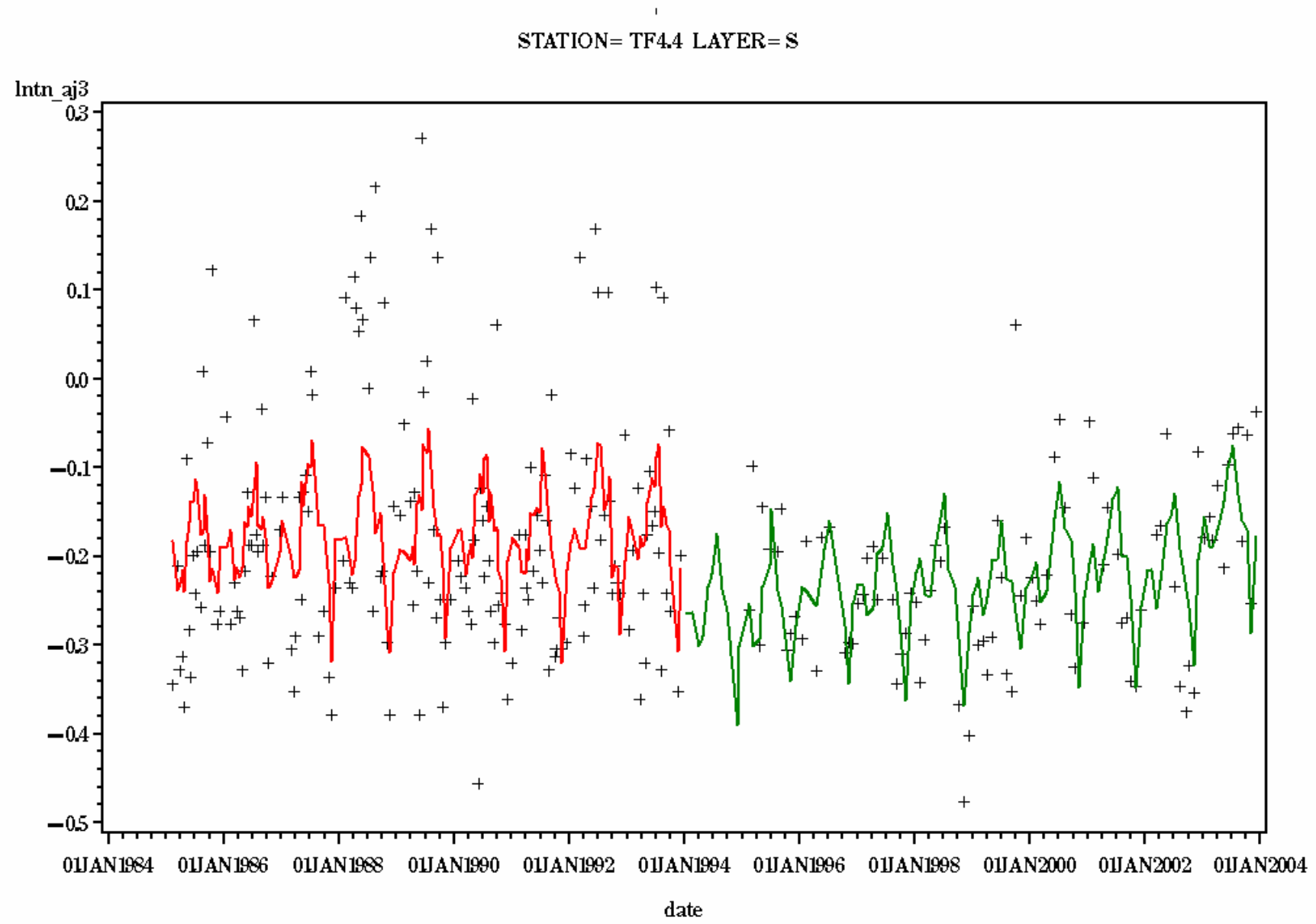
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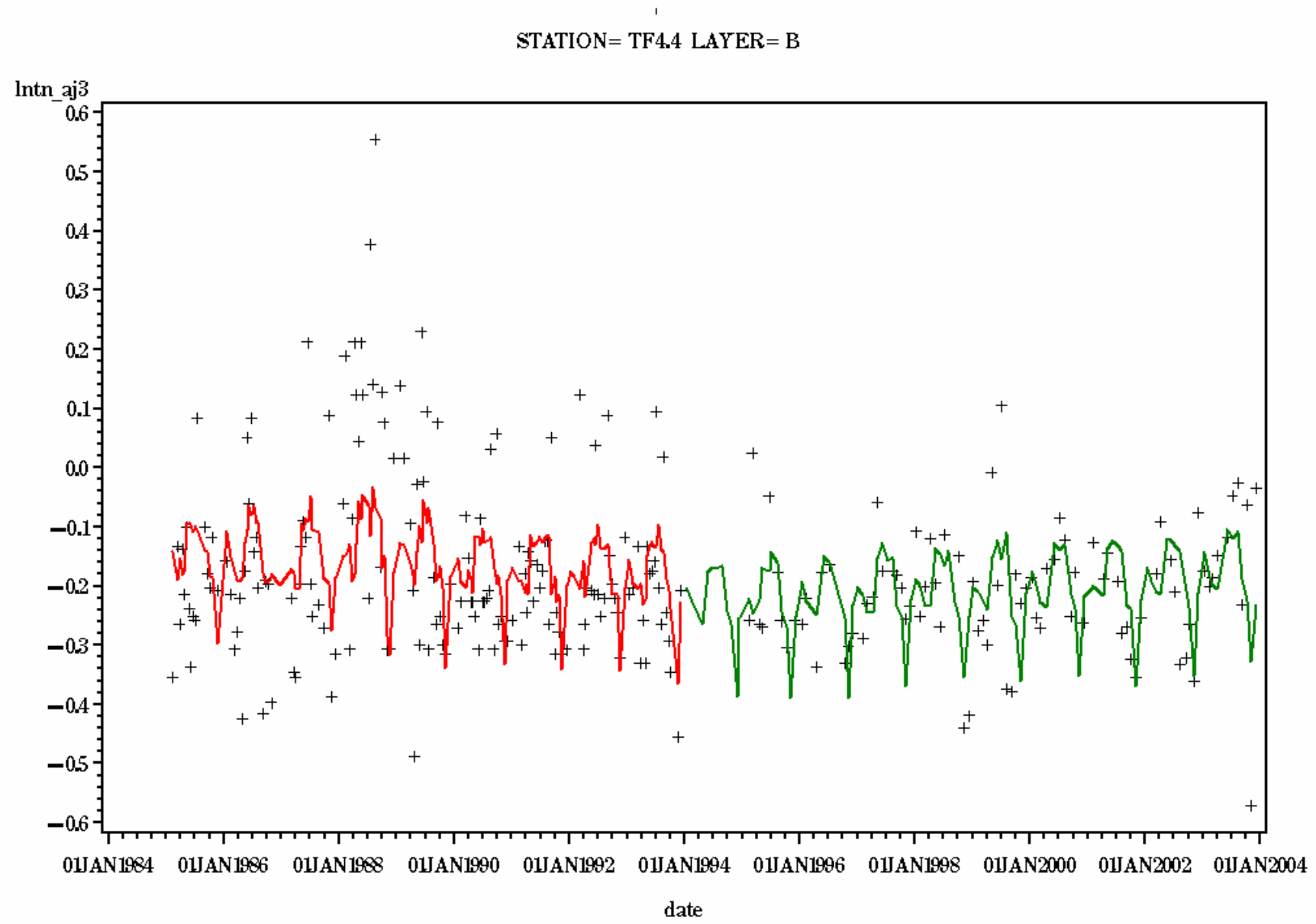
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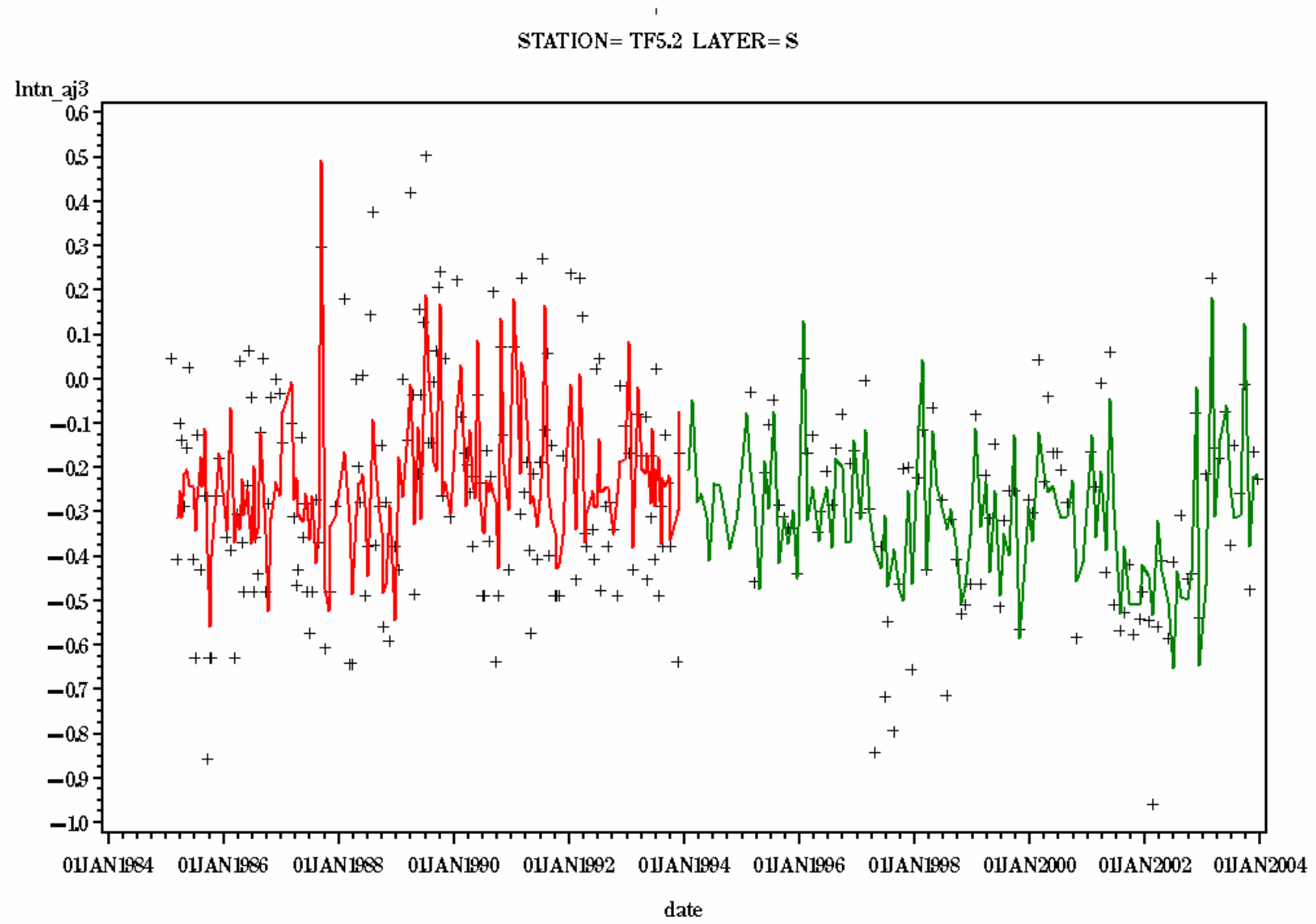
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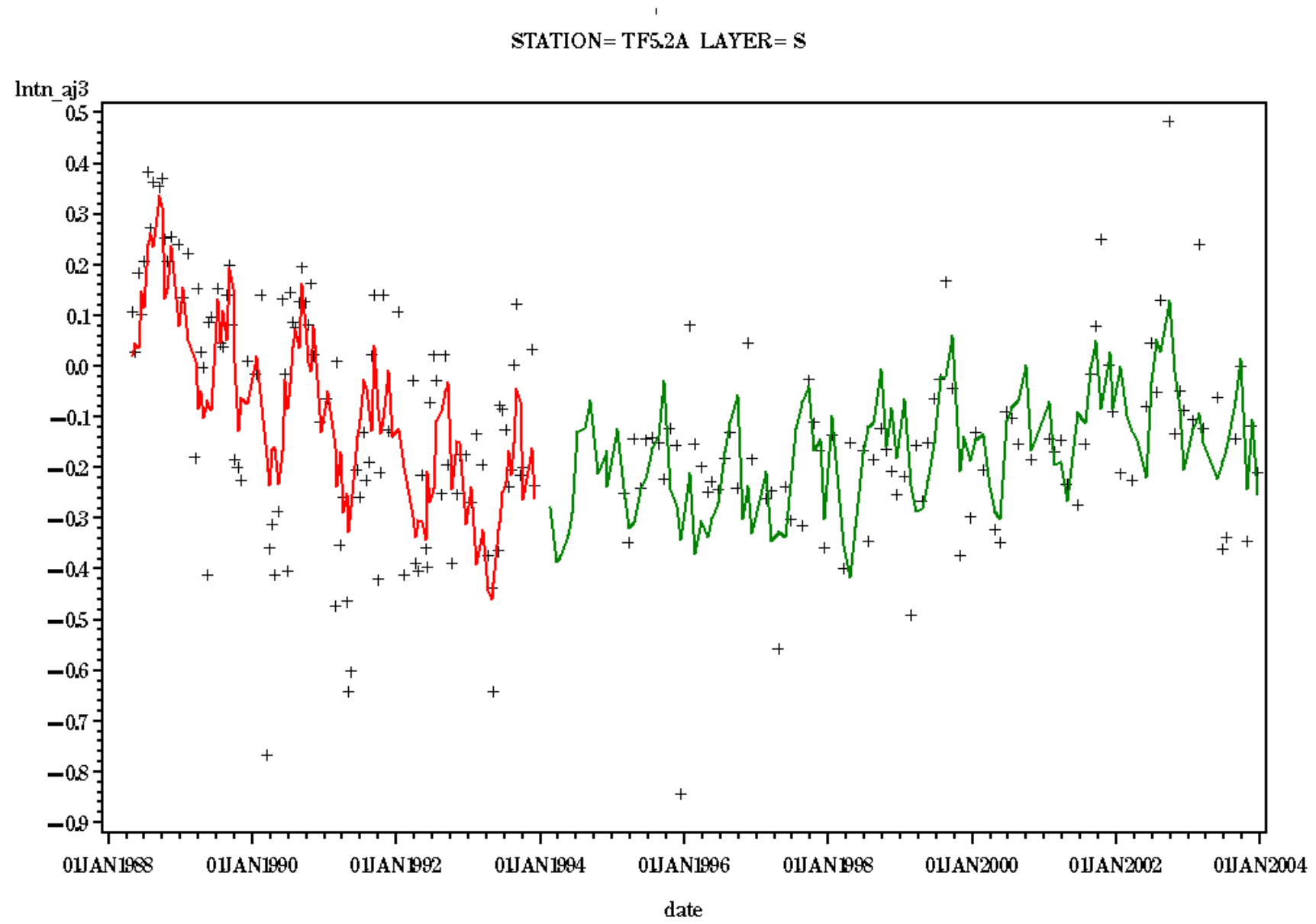
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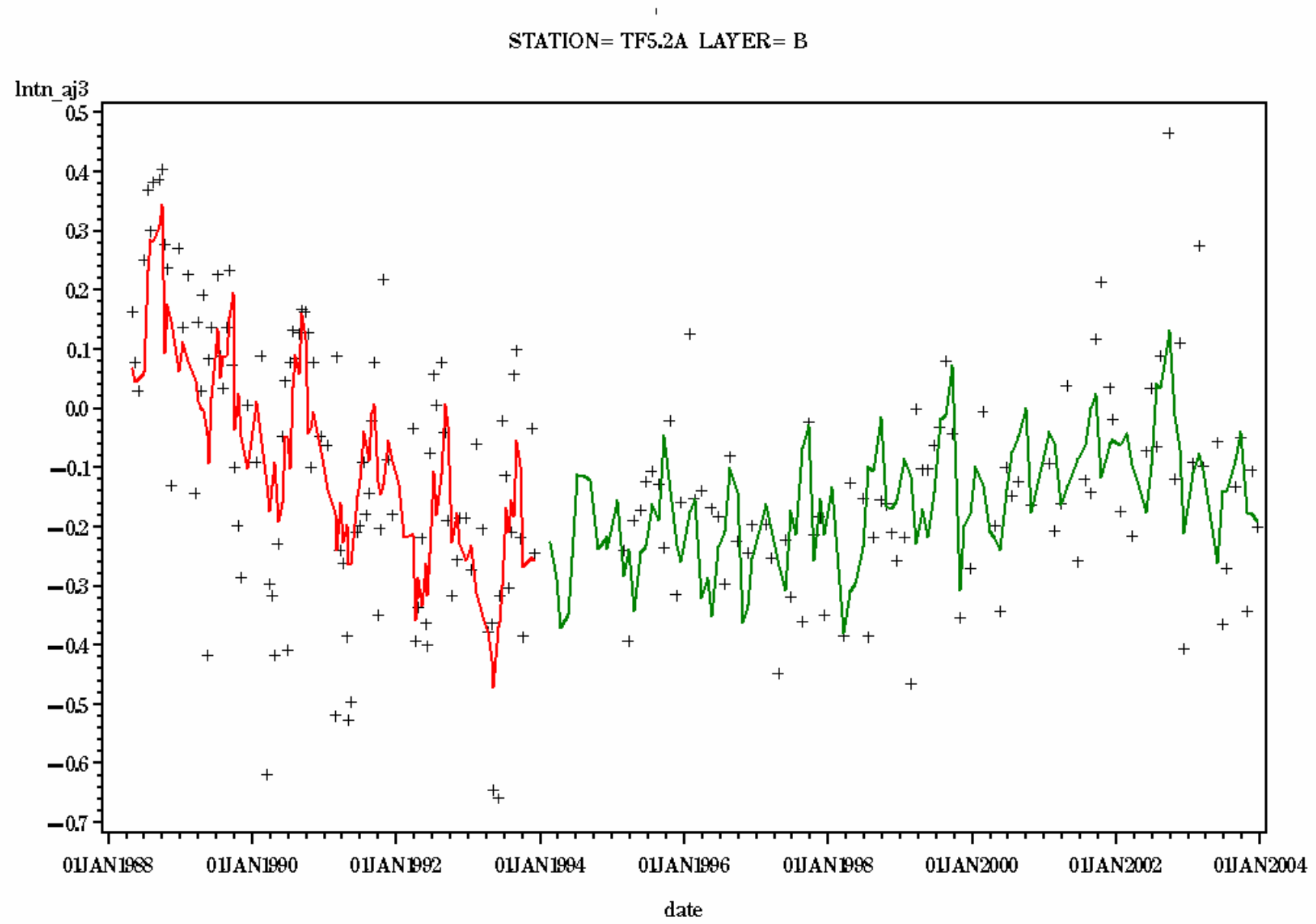
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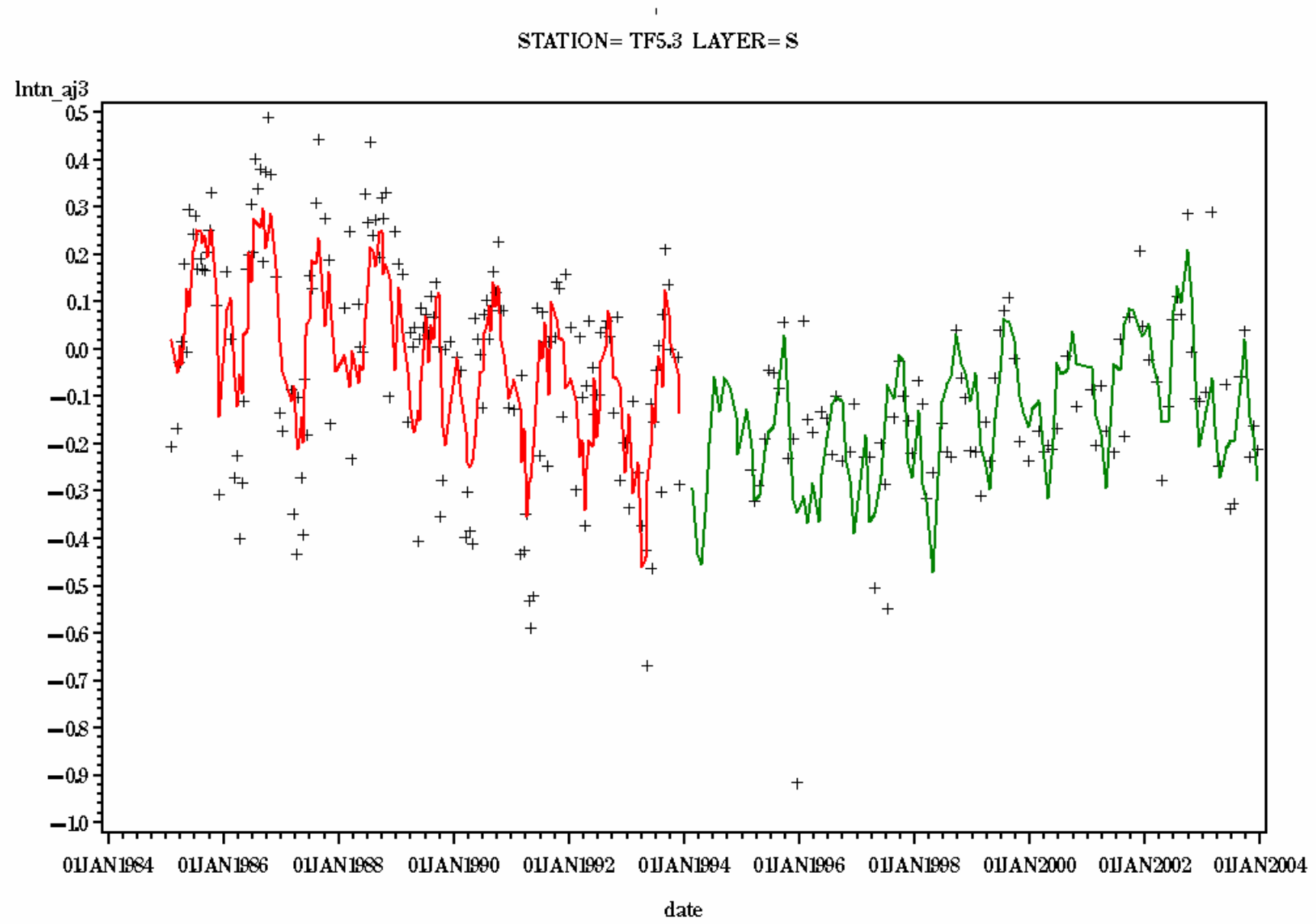
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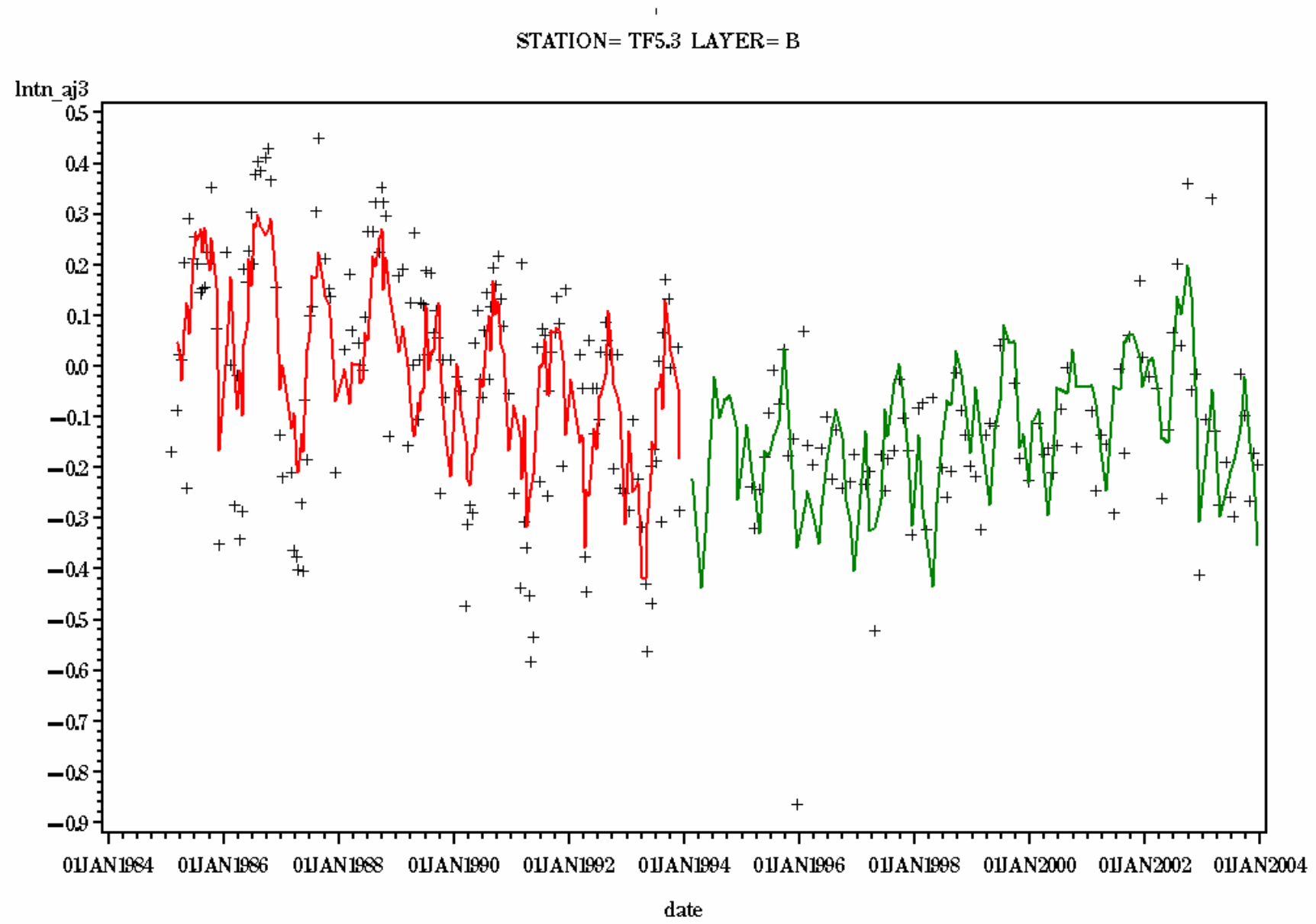
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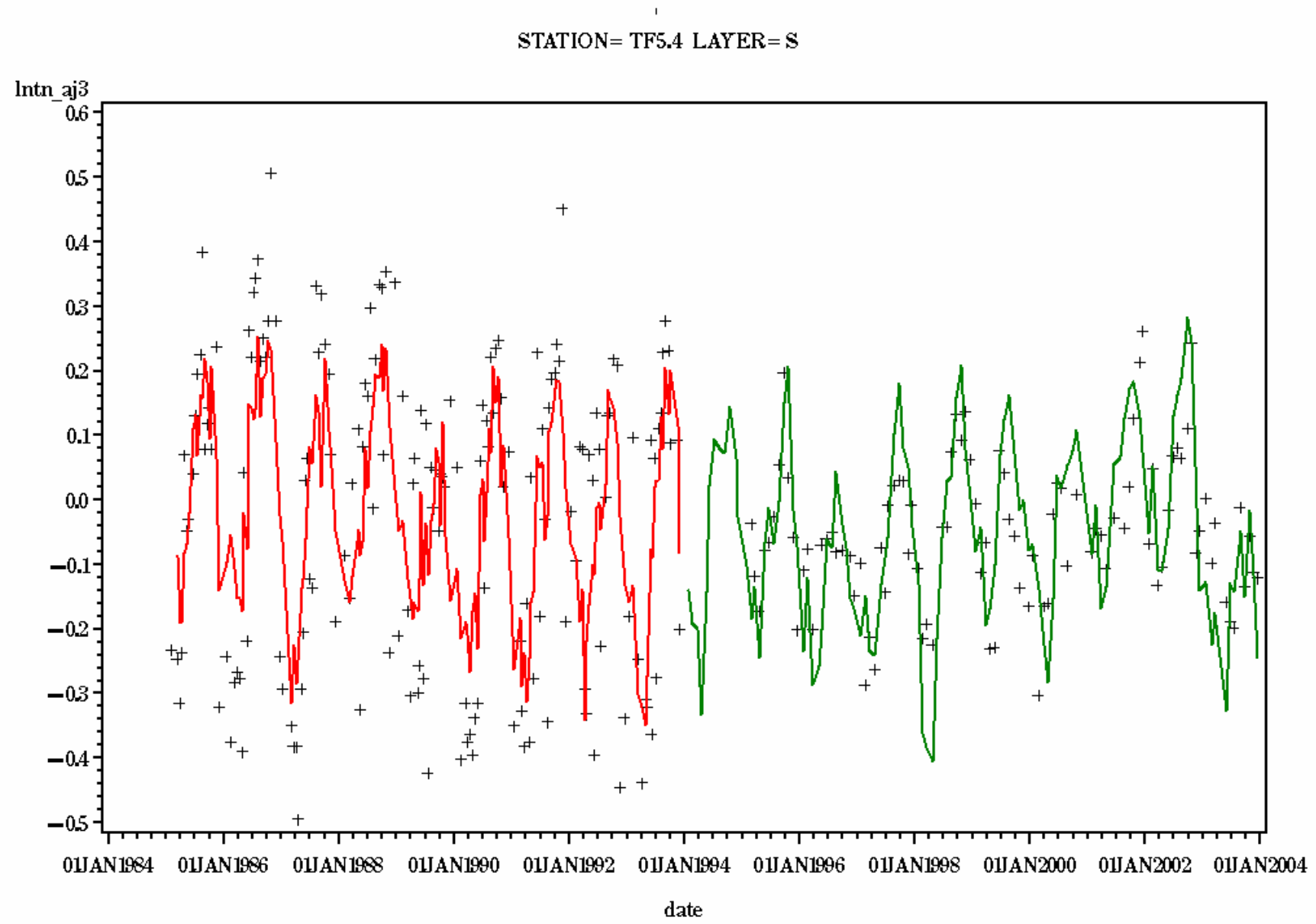
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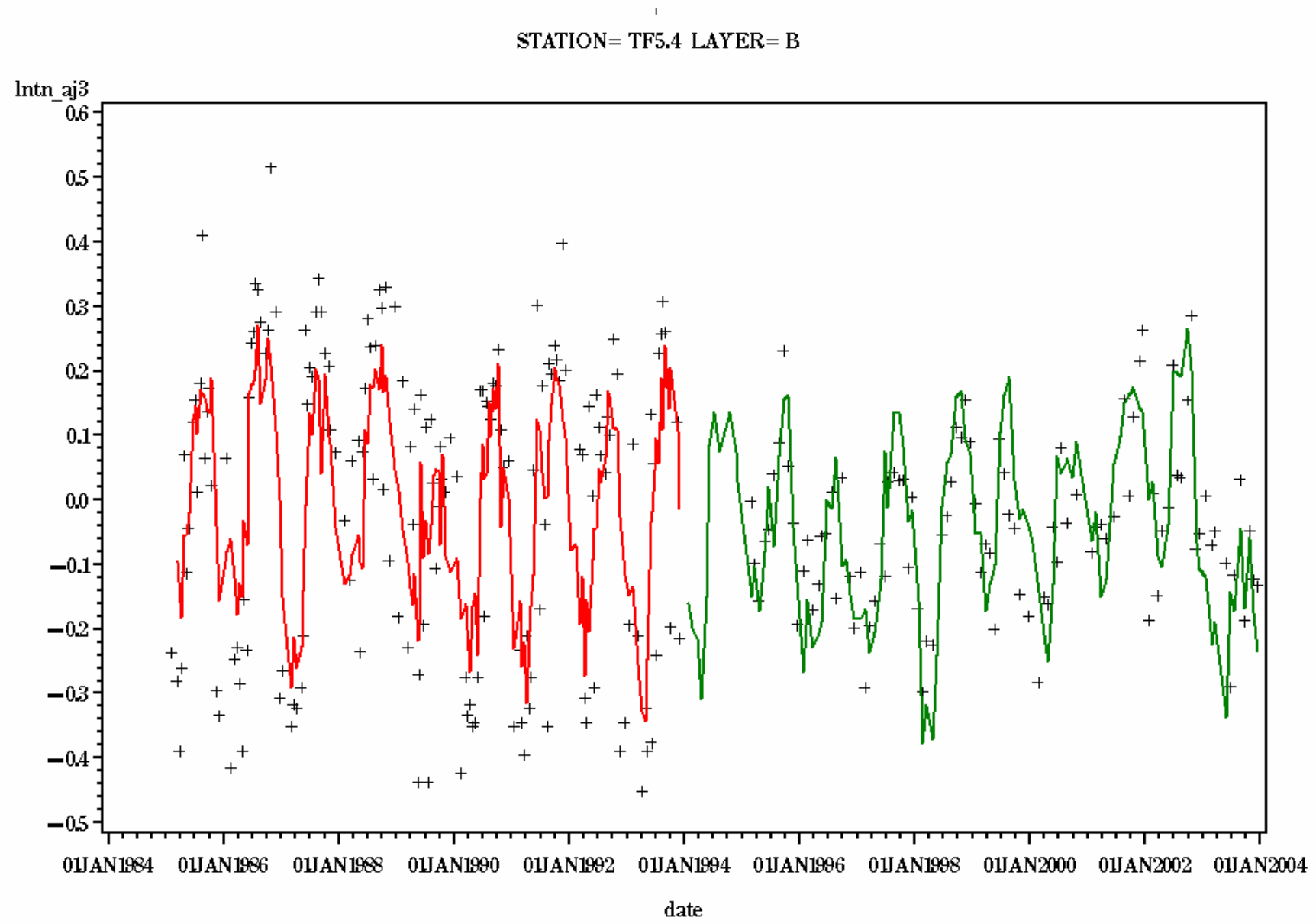
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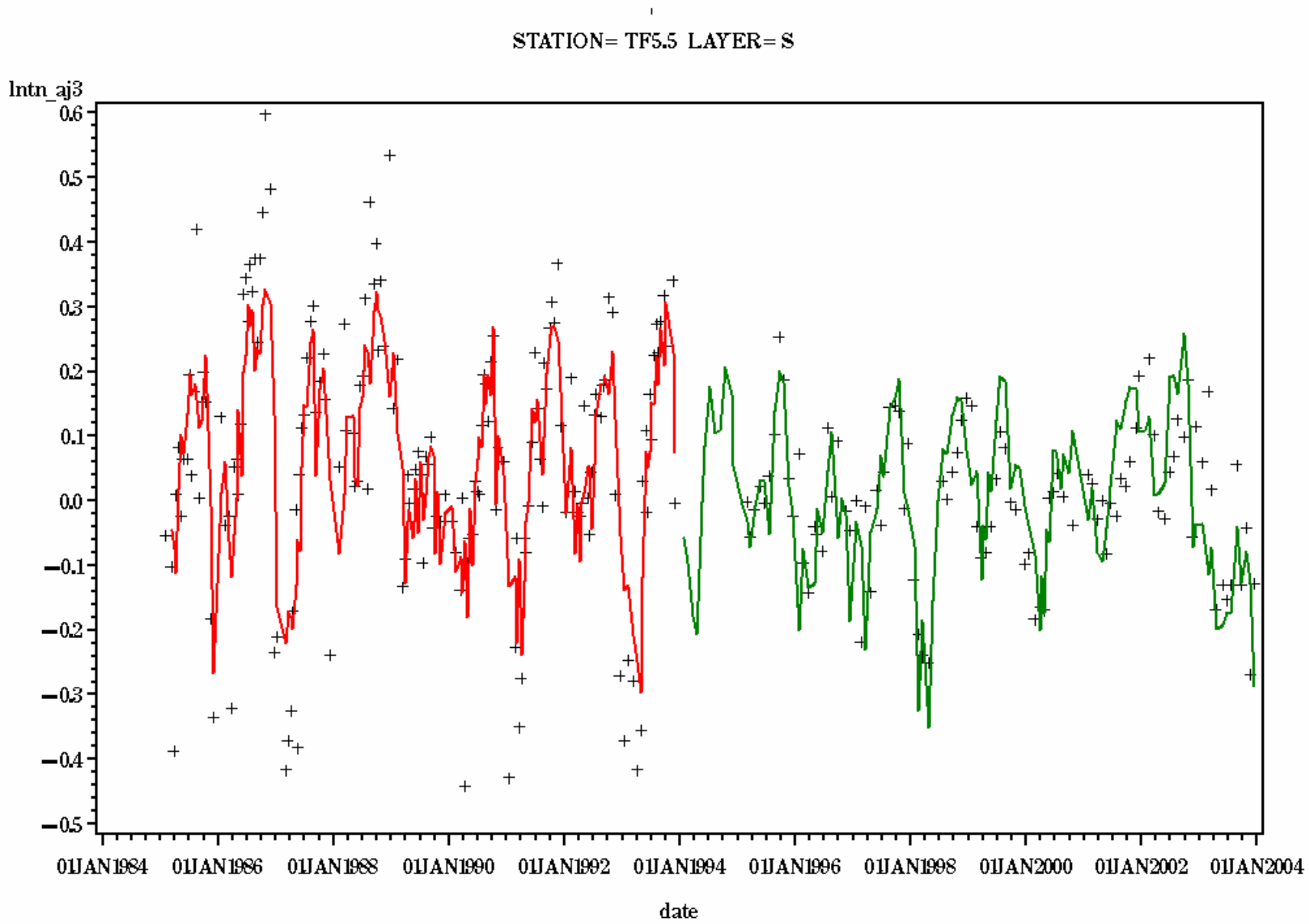
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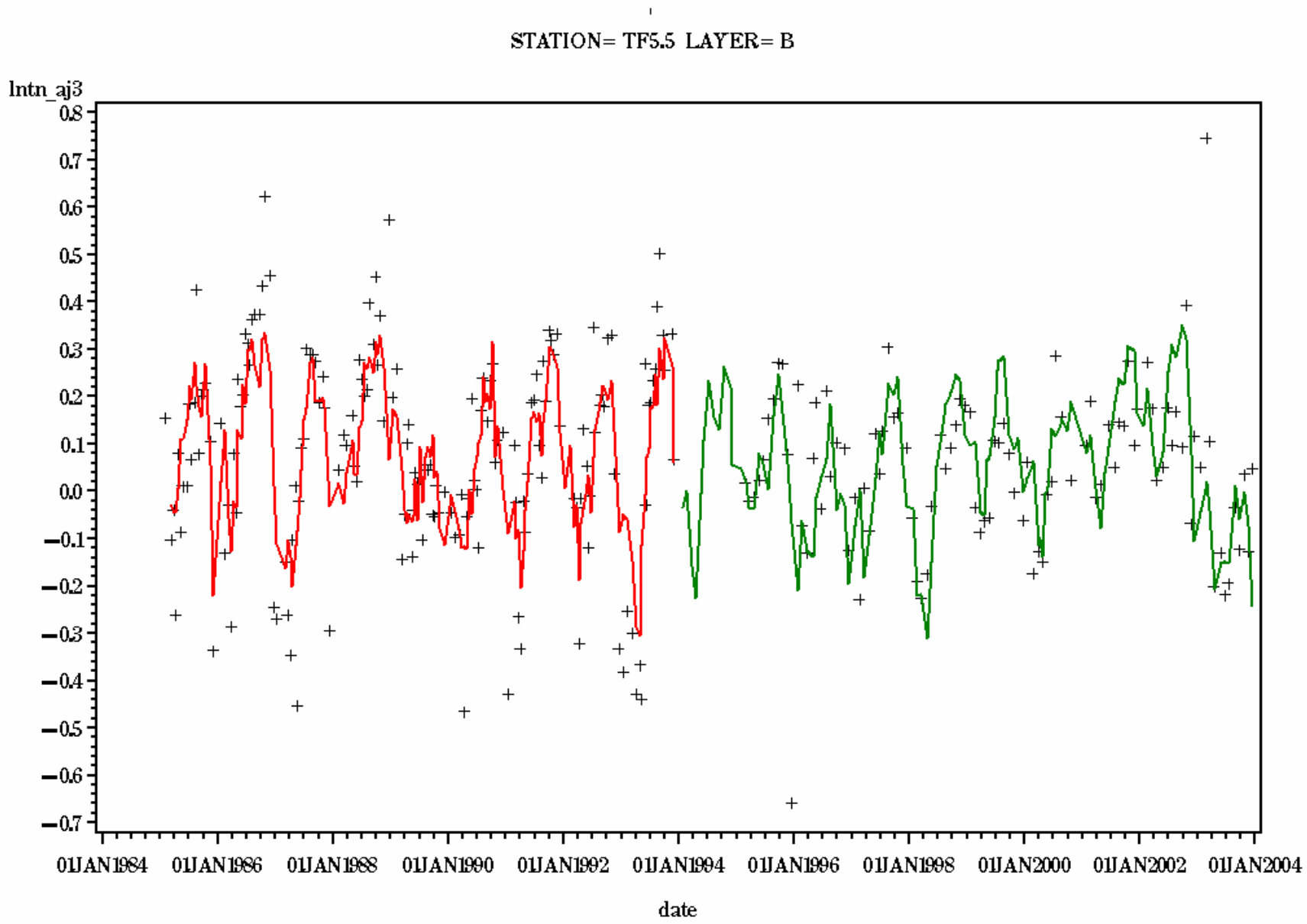
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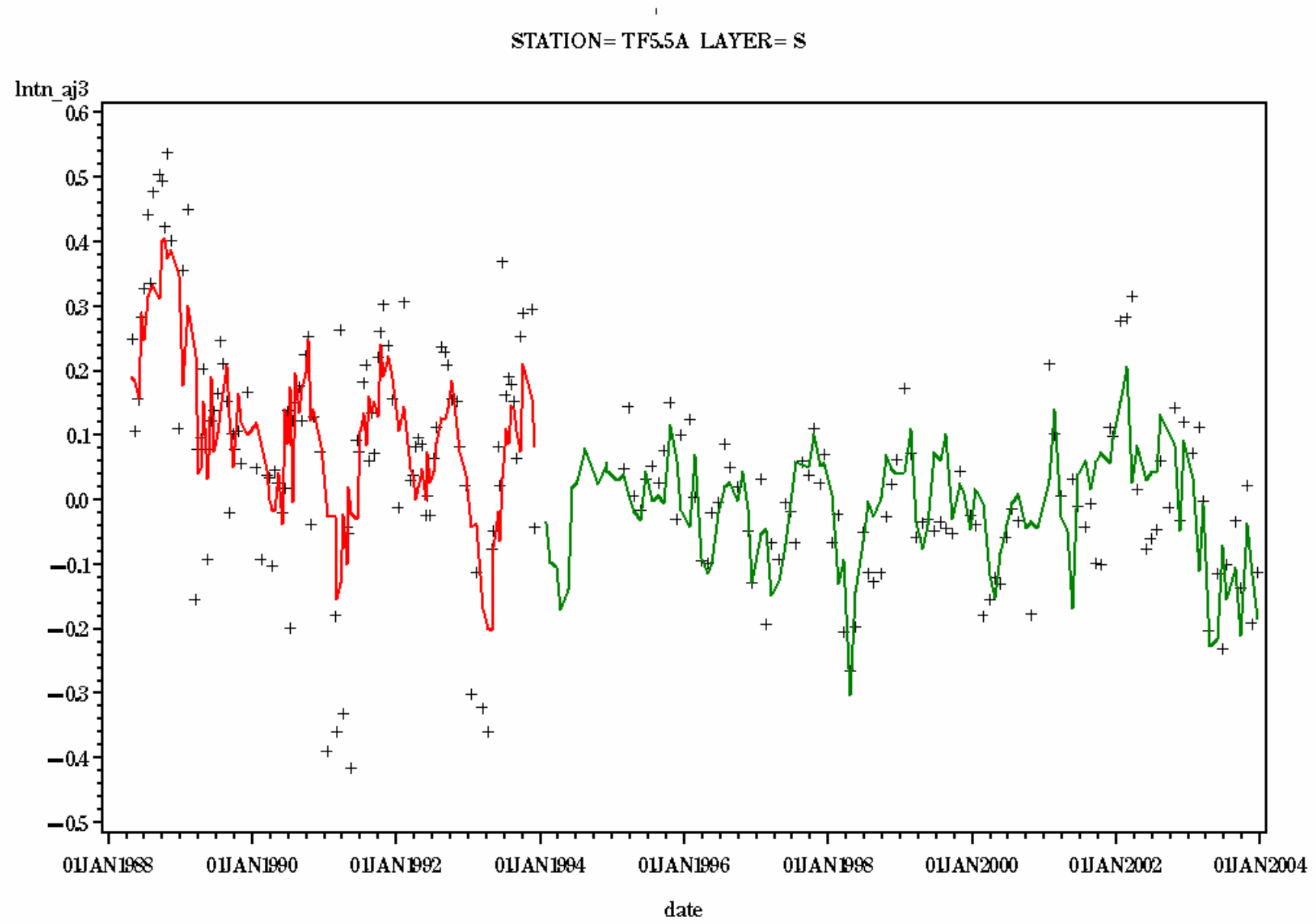
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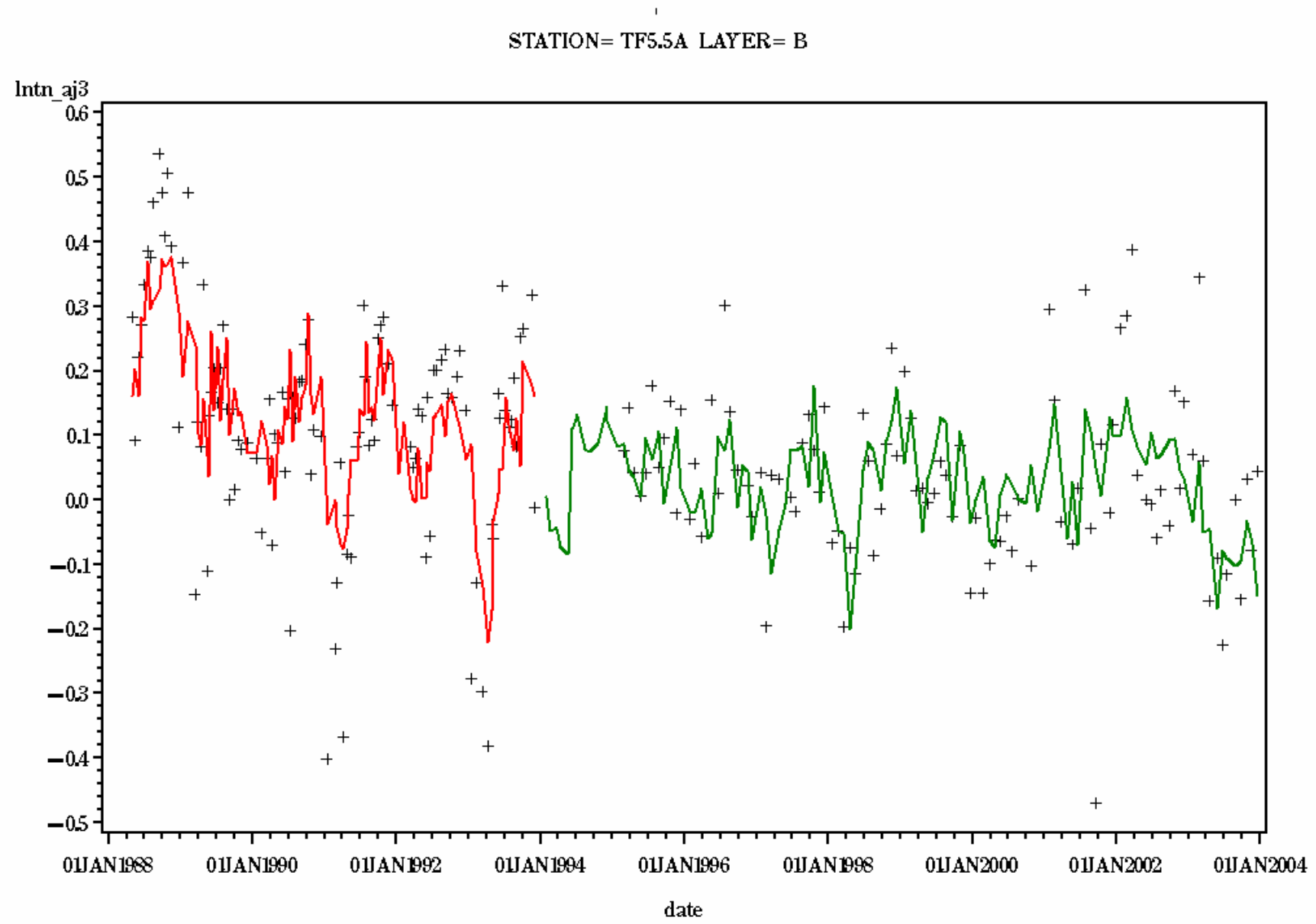
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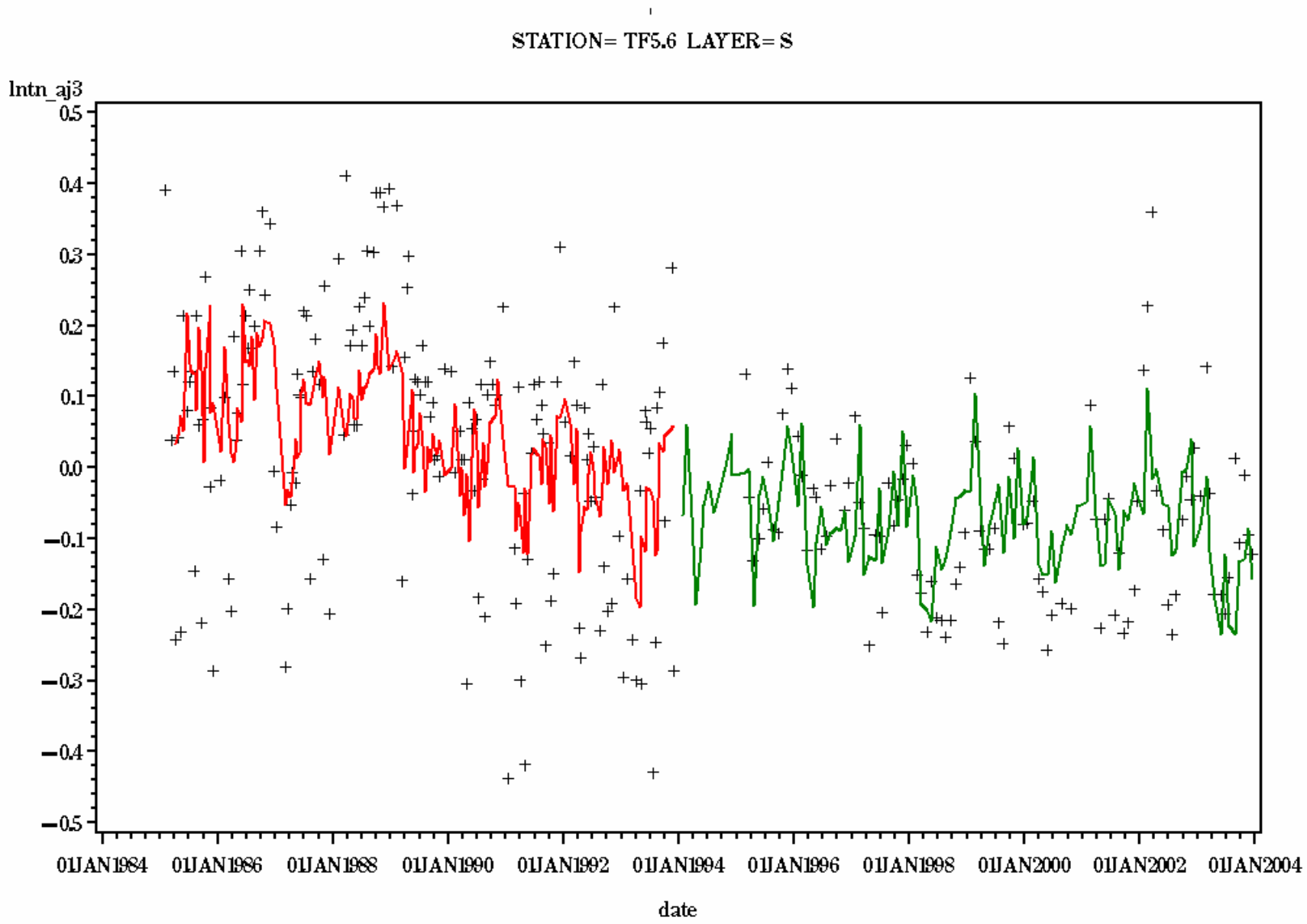
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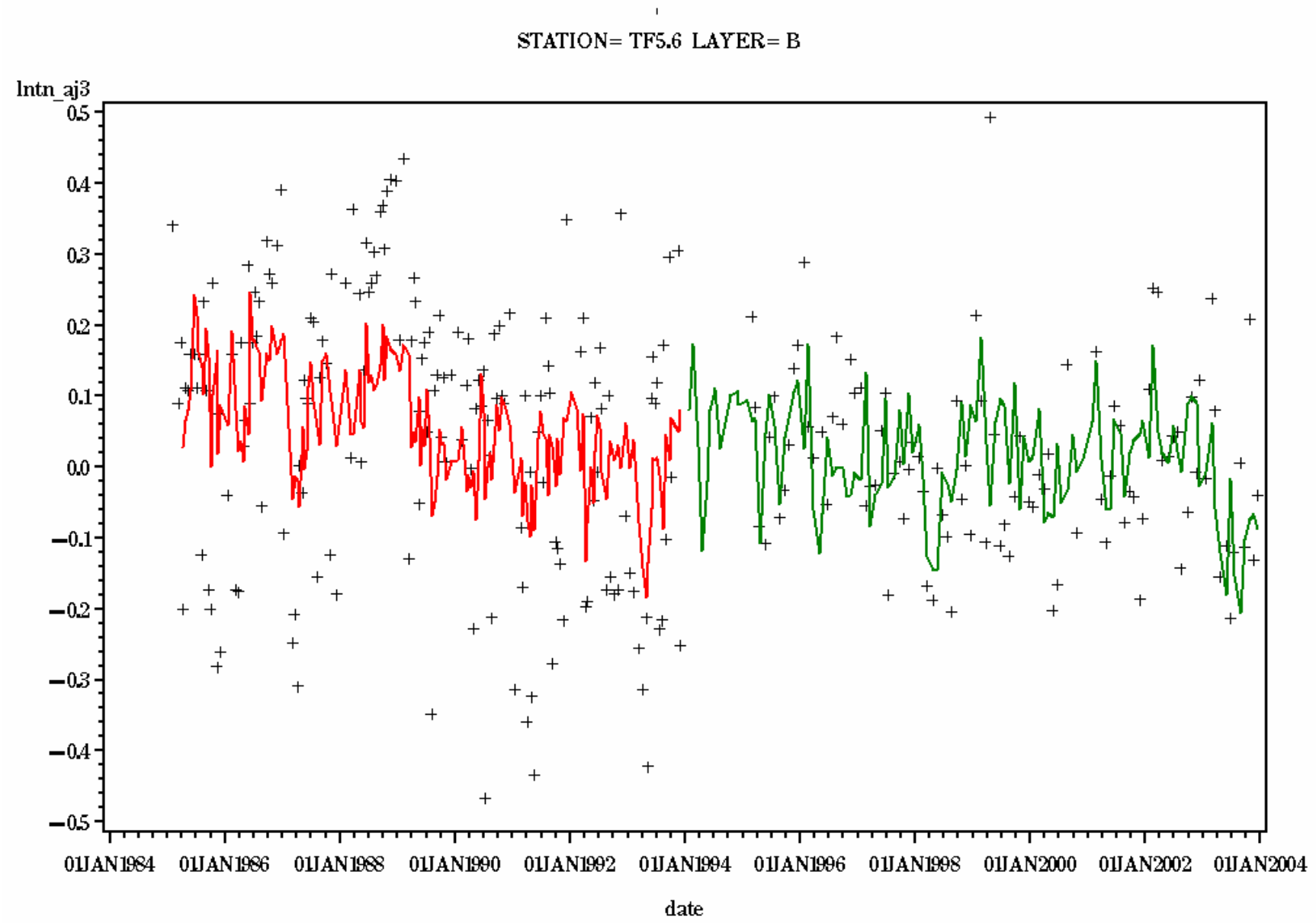
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date

Chesapeake Bay Program Analysis Issues Tracking System

Issue Tracking Number:042

Category Code: Analytical Methods (AM)

Issue Title:

Analytical Method Changes in Total Phosphorus Measurements for the Virginia Tributaries

Date of Issue Introduction into the System;

Entered into DAITS in September 2006

Statement of Issue:

The Virginia Department of Environmental Quality (DEQ) conducts water quality monitoring within the tidal portions of the Virginia tributaries from 1984 through the present as part of the Chesapeake Bay Agreement of 1983 (USEPA Chesapeake Bay Program, 1983). One of the most important parameters measured by the monitoring program is total phosphorus (TP). TP is the concentration of both inorganic and organic compounds in the water column which contain phosphorus measured in mg/L. High levels of TP are considered to be detrimental to living resources either as a source of nutrients for excessive phytoplankton growth or as a source of excessive bacterial decomposition that can increase the incidence and extent of anoxic or hypoxic events. See Figure 1 for a summary of the differences between methodologies. Appendix A provides a time line of events and a listing of additional documentation associated with the effort to characterize the effects of the method change and attempts made to correct it.

Prior to 1994, TP was directly measured by VADCLS using EPA method 365.4 a colorimetric, automated, block digestion. All analyses were performed by Virginia's Division of Consolidated Laboratory Services (DCLS) using an acid persulfate digestion and a Technicon AA II auto-analyzer (the Old method). In 1994, Virginia tributary water quality parameters were measured by the Virginia Institute of Marine Science (VIMS). VIMS calculated TP as the sum of particulate phosphorus (PP) and total dissolved phosphorus (TDP). Both parameters were measured using EPA method 365.1 using an alkaline digestion and a SKALAR auto-analyzer. In February 1995, DCLS resumed analysis of tributary water quality samples and adopted the VIMS methodology (the New method) based on recommendations from an internal study by the DCLS which found that the Old method overestimated TP in samples with salinities greater than five ppt. See Figure 1 for a summary of the differences between methodologies. Appendix A provides a list time line of events and a listing of additional documented associated with the effort to characterized the effects of the method changes and attempts made to correct it.

Examination of scatterplots of data collected in the lower estuarine portions of the Virginia tributaries indicated that concentrations of TP experienced a large step reduction in magnitude and variability in 1995 immediately following the adoption of the New method. This reduction may be due solely to the change in TP methodologies rather than natural phenomena, management actions or some combination thereof and could result in a misinterpretation of statistical results, in particular, those produced by long term trend analysis. If the method change did result in the downward step trend observed in the data, trend analysis might detect false negative trends in this parameter resulting in the misinterpretation that water quality conditions had improved.

An intervention analysis was conducted to determine if the change in methodologies accounted for the observed step change in the TP data (Perry, 2005a; see Appendix B). To test the hypothesis that there was a step trend in the data while controlling for the effects of other potentially confounding factors, a parametric model was developed which included terms for long term trends, seasonality, flow effects, temperature effects, and autoregression, as well as, a dummy variable term used to represent the advent of the intervention i.e. the method change.

Results of the intervention analysis indicated that there was a significant negative step trend in TP at 65% of the sites associated with the implementation of the New method (Perry, 2005a; See Appendix B). A significant positive intervention effect was observed at only two out of 63 stations. These results support the hypothesis that a change in analytical methods may have resulted in a negative step trend in the TP data. Plots of the station specific regression coefficients for the method change term against salinity show that stations with positive values for the coefficients i.e. those having a positive step trend were found primarily in the tidal freshwater portions of the James River and Rappahannock River while elsewhere the effect of the step trend was negative.

Examination of the pre- and post-method change trend results indicated that the slope of the trend effect was lower after the method change than the slope before the method change and in many cases the trend direction shifted from increasing prior to the method change to decreasing during the post-method change period. This strongly suggests that some other factor that influenced TP concentrations occurred at roughly the same time as the method change, e.g. a management action like the phosphate ban (Perry, 2005a). The strong correspondence of the method change effect and trend effects suggests that the assumed method change effect may be an artifact of the trends in the data. Analysis of data collected during a DEQ split sample project designed specifically for the purpose of examining the method change effects was carried out to clarify these issues.

An initial set of graphical and statistical analyses conducted on the split sample data indicated that although the methods were significantly different from each other, the Old method was biased low relative to the New method (see Appendix C). This observation conflicts with the step trends observed in the historical data. The bias in the Old method showed no consistent spatial pattern although there was a slight increase in bias during 2003. An examination of the effects of environmental factors yielded no explanation for the difference between the bias observed in the split sample data and the apparent bias in the historical data that resulted in the step trends but it did

reveal that the New method has a higher correlation to total suspended solids (TSS) than the Old method. The increase in bias during 2003 was probably due to changes in TSS concentrations and it appears that the New method responds more accurately to changes in TSS than the Old method. Despite these problems, an attempt was made to develop a correction factor for converting the Old method TP data to New Method data.

Split sample data were further examined by calculating the difference between the log-transformed Old and New methods and relating this difference (lnDiff) to various parameters in an attempt to explain it (Perry, 2005b; see Appendix D). The effects of various predicator variables such as mean log transformed TP concentrations for both methods, date of collection, distance from the Chesapeake Bay main stem, and several environmental variables including conductivity, salinity, temperature, pH, dissolved oxygen, and total suspended solids were assessed using correlation and stepwise regression analysis. Results of these analyses indicated that salinity and log transformed total suspended solids (lnTSS) concentrations were the most important predictors of lnDiff.

An attempt was made to develop a correction factor for TP by regressing lnDiff with salinity and lnTSS. The resulting regression equation was used to adjust the Old method data and intervention analysis was rerun on the adjusted data to determine the validity of the correction factor developed but the results obtained showed little improvement in the number of step trends detected associated with the method change. Additional graphical analysis indicated that the method difference measured by the monitoring program was different from that measured during the split sample program. As a result, an adjustment factor model based on the results of the original intervention analysis of the monitoring data was developed.

In this case, the station regression coefficients (log-transformed) for the Step trend term in the intervention model were themselves regressed against station specific mean log transformed TSS values and mean salinity values. The resulting regression equation provided an estimate of a correction factor that can be applied to the Old method data based on the station mean values of log transformed TSS and salinity. Equation 2 in Appendix D provides the appropriate formulae for applying this correction factor. The validity of the correction factor was evaluated by applying it to the Old method data and then rerunning the intervention analysis to determine if the step trend effects were removed. Application of this correction factor substantially reduced the number of station specific step trends observed indicating it reliably adjusted the Old method data. Based on the results of this study, it was recommended that the Old method data remain in the database and that the correction factor only be applied when comparisons of the Old and New method data are required.

Proposed Solution:

It is recommended that the original data remain in the database. Adjustments to the TP data need to be implemented only if analyses include comparisons of data collected using both the Old and New methods. Adjustments should be made using Equation 2 as described in Perry (2005b) and would be applied only to those data collected prior to the method change. Long-term trend analysis of TP for the Virginia tributaries should be conducted using the "blocked" seasonal Kendall approach (Gilbert, 1987) with the pre-method (1985 through 1993) and post-method change (1995 through 2004) periods set up as the time blocks. The PROBLEM code field in the CBP Water Quality Database table WQ_DATA should be updated to indicate that a DAITS issue exists for this parameter and to refer all users to this document for resolution of analytical problems.

Sense of the Resources Needed to Respond:

The resources required to update the PROBLEM code in the CBP database should not be more than several hours of database programming time. Future analysis of these data may require additional resources than might be anticipated if the step trend were not present; however, a direct estimate of the resources required is dependent on the analyses attempted.

Proposed Priority Ranking:

This issue has been partially resolved since the "blocked" Seasonal Kendall approach has been implemented for trend analysis of Virginia TP data. However, the PROBLEM code field in the CBP database needs to be updated and the priority ranking for this task should be high.

Submitter/Responsible Party:

Mr. Frederick A. Hoffman
Chesapeake Bay Program
Virginia Department of Environmental Quality
629 East Main Street
Richmond, Virginia 23230

Actions to Date:

Use of the blocked Seasonal Kendall trend test has been implemented for all Virginia tributary monitoring stations.

Recommended Actions:

1. Actions Number:

Not Applicable

2. Designated Respondent:

Tami Huber
CBP Water Quality Database Manager
410 Severn Ave, Suite 109
Annapolis, MD 21403
(410) 267-5700 or
1 (800) YOUR BAY

3. Action:

Update of CBP database records to include CBP Problem code entry for all TP concentrations in the database collected prior to 1994.

4. Resources Needed:

Unknown.

5. Due Date:

Not Applicable.

Literature Cited:

Perry, E, 2005a. Assessment of 1994 Methods Change for Total Phosphorus using Intervention Analysis. Report to the Department of Environmental Quality. Richmond VA. 7 pp.

Perry, E, 2005b. Assessment of 1994 Methods Change for Total Phosphorus using Split Sample Data. Report to the Department of Environmental Quality. Richmond VA. 13 pp.

Gilbert, R.O. 1987. Statistical methods for environmental pollution monitoring. Van Nostrand Reinhold Co., New York, pp. 320.

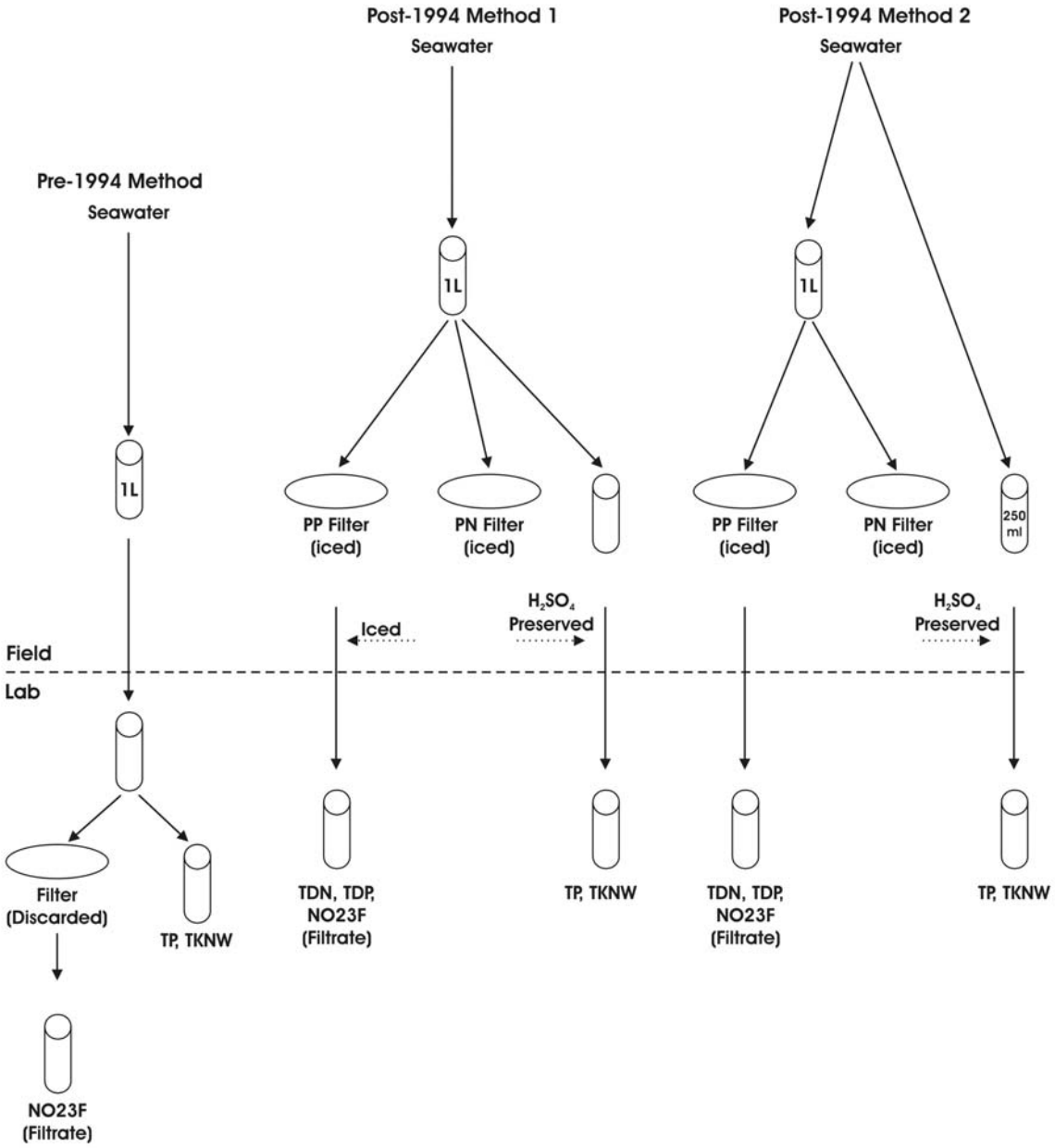

Figure 1. Summary of differences between total nitrogen and total phosphorus methodologies prior to and after 1994.

Appendix A. Timeline and Additional Documentation of Issues Related to Method Changes for Total Phosphorus and Total Nitrogen Determinations

Timeline and Additional Documentation of Issues Related to Method Changes for Total Phosphorus and Total Nitrogen Determinations

July 1984 – November 1993. Total phosphorus (TP) is directly measured by VADCLS using EPA method 365.4 a colorimetric, automated, block digestion using an acid persulfate for the digestion.VADCLS utilized a Technicon AA II instrument for analysis. EPA 365.4 was later found by DCLS to overestimate TP in samples with salinities greater than 5 ppt. (1997; refer to memo from Loretta Kirk). This method was also utilized January 1995 – November 1995 at select sites (TF3.1A, TF3.1D, TF4.1A and TF4.4A only).

Prior to 1994 TN concentrations were calculated as the sum of total Kjeldahl nitrogen (TKN) and filtered nitrate-nitrates ($NO_{23)}$ concentrations (referred to as the Old method). TKNW was determined using EPA method 351.2 (Colorimetric, Semi-Automated Block Digestion) and NO23F by EPA method 353.2 (Colorimetric, Automated Cadmium Reduction). Unpreserved whole water samples were collected in the field and delivered to the lab for analysis.

January 1994 – December 1994. TN is calculated by using particulate nitrogen (PN) and total dissolved nitrogen (TDN) results analyzed by VIMS. VIMS utilized a SKALAR instrument and EPA method 365.2 and an alkaline persulfate digestion. Note: these data are not utilized for status and trend purposes and were not included in the analysis to determine the cause of the observed step trend in the TN and TP data. TP is calculated by using particulate phosphorus (PP) and total dissolved phosphorus (TDP) results analyzed by VIMS. VIMS utilized a SKALAR instrument and EPA method 365.1 for PP and TDP determinations utilizing an alkaline digestion.

February 1995 onward. TP is calculated using PP and TDP results analyzed by VADCLS using a SKALAR instrument using EPA method 365.1 for both PP and TDP. The method uses an alkaline persulfate digestion. TN is calculated using PN and TDN results analyzed by VADCLS with a SKALAR instrument using the EPA method.

2002. During trend analysis Marcia Olson discovers anomalies in TN and TP for Virginia Tributaries that point to step trends in 1995. DEQ initiates data analysis by ODU to determine if a possible correction factor may be applied. In October 2002 DEQ begins the collection of additional samples so that directly measured TP can be compared to TDN+PP.

October 2003. DEQ completes the collection of samples for the TN/TP method comparison.

2004. ODU concludes they are unable to determine a single correction factor for DEQ's tributary TP data. DEQ enlists the aid of Elgin Perry, a consultant to the Chesapeake Bay Program in Annapolis to further examine the data.

Table 1. Available Memos/Data files for TP/TN analyses. Abbreviations include the following: CBPO for the EPA Chesapeake Bay Program Office, DCLS for the Virginia Department of Consolidated Laboratory Services, DEQ CO for Virginia Department of Environmental Quality Central Office, MD CBL for Maryland Chesapeake Bay Laboratory, and ODU for Old Dominion University.

Date/Author	**Format and Locations**	**Title/Subject**	**Issue**	**Summary**
Unknown	Hardcopy on file at (DEQCO)	TN/TP component comparison studies summary	TN/TP step trend documentation summary	Summary of memos/data mentioned below and questions regarding how they relate/compare to step trend demonstrated by data
03-10-1990 Rick Hoffman (DEQCO)	Hardcopy on file at (DEQCO)	Request for copy of final report for instrument comparison between Skalar San Plus and Technicon AA II	A preliminary report for the method comparison dated 01-13-94 had been received and is attached to the request for the final report. The preliminary findings indicated for Orthophosphate and Nitrate plus Nitrite there was a significant difference between results based on instrument change	The SKALAR instrument was capable of detecting results in the lower range (3 decimal places) while the Technicon was only capable of detecting 2 decimal places.
04-19-1990 Steve Sokolowski (ODU)	Hardcopy on file at (DEQCO)	Pre-proposal submitted to the Chesapeake Bay Program to evaluate the effects of matrix interferences on analytical results for Phosphate-P in Aqueous Chesapeake Bay Samples	Underestimates of orthophosphate and dissolved phosphate and overestimates of total phosphate concentrations that increase with increasing concentrations.	Bias demonstrated a site effect and appeared to demonstrate spatial and temporal effects.
01-21-1992 Peter Bergstrom (CBPO)	Hardcopy on file at (DEQCO)	QA data relevant to TN ocean boundary definition	Differences observed between ODU and VIMS TN data	Data differences observed in ODU/VIMS data as described in DAITS Issue #10 were found to be related to TKNW differences. Differences varied by station.
1994	Electronic and hardcopy on file (DEQCO)	Lltp instrument comp.csv; NH4F instrument comp.csv; NO2F instrument comp.csv; NO23F instrument comp.csv; PO4F instrument comp.csv; PP VIMS vs DCLS.csv; TDN VIMS vs DCLS.csv; TDP VIMS vs DCLS.csv	Split sample data for instrument comparison studies summarized in aforementioned reports.	
09-26-1996 Christopher D'Elia MDCBL	Hardcopy on file (DEQCO /MDCBL)	Total Kjeldahl Nitrogen - Total Persulfate nitrogen method comparison	Report on the comparison of EPA 351.2 and EPA 365.2 methods for determination of TN and PN to Alkaline persulfate method EPA 353.2	EPA 353.2 had not yet been approved as an EPA methodology for the determination of TN and TP. Results indicated a poor comparison of results between 351.2 and 353.2 that was spurious. When 351.2 was modified slightly as utilized by ODU, results between the two methods were comparable.

Table 1. Continued. Abbreviations include the following: CBPO for the EPA Chesapeake Bay Program Office, DCLS for the Virginia Department of Consolidated Laboratory Services, DEQ CO for Virginia Department of Environmental Quality Central Office, MD CBL for Maryland Chesapeake Bay Laboratory, and ODU for Old Dominion University.

Date/Author	**Format/ locations**	**Title/Subject**	**Issue**	**Summary**
08-29-1997 Chris Gennings and Denise Toney	Hardcopy on file (DEQCO)	Evaluation of Water Samples	Final copy of DCLS instrument comparison study for SKALAR and Technicon AA II	All the studied parameters showed significant differences between instruments when a Wilcoxin paired t-test is used. Data were compared for equivalency. Orthophosphate, Particulate Phosphorus, Ammonia Nitrogen and Nitrite Nitrogen failed to show equivalence.
10-22-1997 Loretta Kirk DCLS	Hardcopy on file (DEQCO)	Total Phosphorus Method Changes	Salinity interference with TP method 365.4	DCLS institutes method change for all TP samples with salinities greater than 5 ppt due to higher than expected sample results and spike recoveries.
01-07-2004	Electronic file (DEQCO)	9495 lab change comparison data.xls	File contains all Pfiesteria data (PF), Chesapeake Bay River Input Monitoring data (RIM) and Tributary Monitoring data (CB) collected between 1998 and 2003. Where a comparison can be made between old and new TP/TN methods.	
05-10-2004 Mike Lane (ODU)	Electronic file (DEQCO and ODU)	Method Correction Analyses.ppt	Powerpoint presentation to describe TP/TN step trend issue and initial analyses of data to determine if a correction factor can be found	Analyses inconclusive – no one correction factor can be applied. Trends appear to be site influenced.
07-06-2006 Mike Lane (ODU)	Electronic file (DEQCO and ODU)	TP_Correction3.ppt	Powerpoint presentation to describe TP method adjustment analysis by ODU	Analyses inconclusive – no one correction factor can be applied. Trends appear to be site influenced.
07-08-2006 Mike Lane (ODU)	Electronic file (DEQCO and ODU)	TN_Correction2.ppt	Powerpoint presentation to describe TN method adjustment analysis by ODU	Analyses inconclusive – no one correction factor can be applied. Trends appear to be site influenced
07-14-2005	Electronic file (DEQCO)	Method change data2.zip	Zip file sent to Elgin Perry for analysis contains the following files: 9495 method comparison data4.xls –pfiesteria, RIM and DEQ CBP data allowing comparison of TN/TP old and new methods. Instrument and VIMS comparison data.xls – data comparison performed by DCLS when switching methods/ instruments in 1994. VADCLS CSSP columnar4.xls – AMQAW split sample data allowing comparison between TP old replicates and TP new replicates. CBP VNTP data. xls – DEQ's CBP non-tidal network data for TN/TP method comparison.	

Appendix B - Assessment of 1994 Methods Change for Total Phosphorus using Intervention Analysis

Assessment of 1994 Methods Change for Total Phosphorus using Intervention Analysis.

submitted to

Rick Hoffman
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by

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Statistics Consultant
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Huntingtown, MD. 20639

Introduction

This report addresses the apparent change of estimated total phosphorus (TP) concentration that occurs coincident with a change in the methods for assaying TP in three Virginia Tributaries to the Chesapeake Bay. The results presented here are based on intervention analysis the TP. The methods and presentation parallel those for TN.

Background

The 1994 methods change discussed for TN also affects the measurement of TP. As with TN, sometime after this change was implemented, it became apparent when viewing a time series plot (Figure 1.) of TP concentration for stations in the lower James River, that the concentration of TP appeared to take a step down at the time of the methods change. As with TN, this result is of particular concern because the long-term trend analysis will show that TP concentration is improving (decreasing) and this favorable conclusion may in fact be false. It is possible that a large part of the decrease in TP is an artifact due to the change in analytical methods.

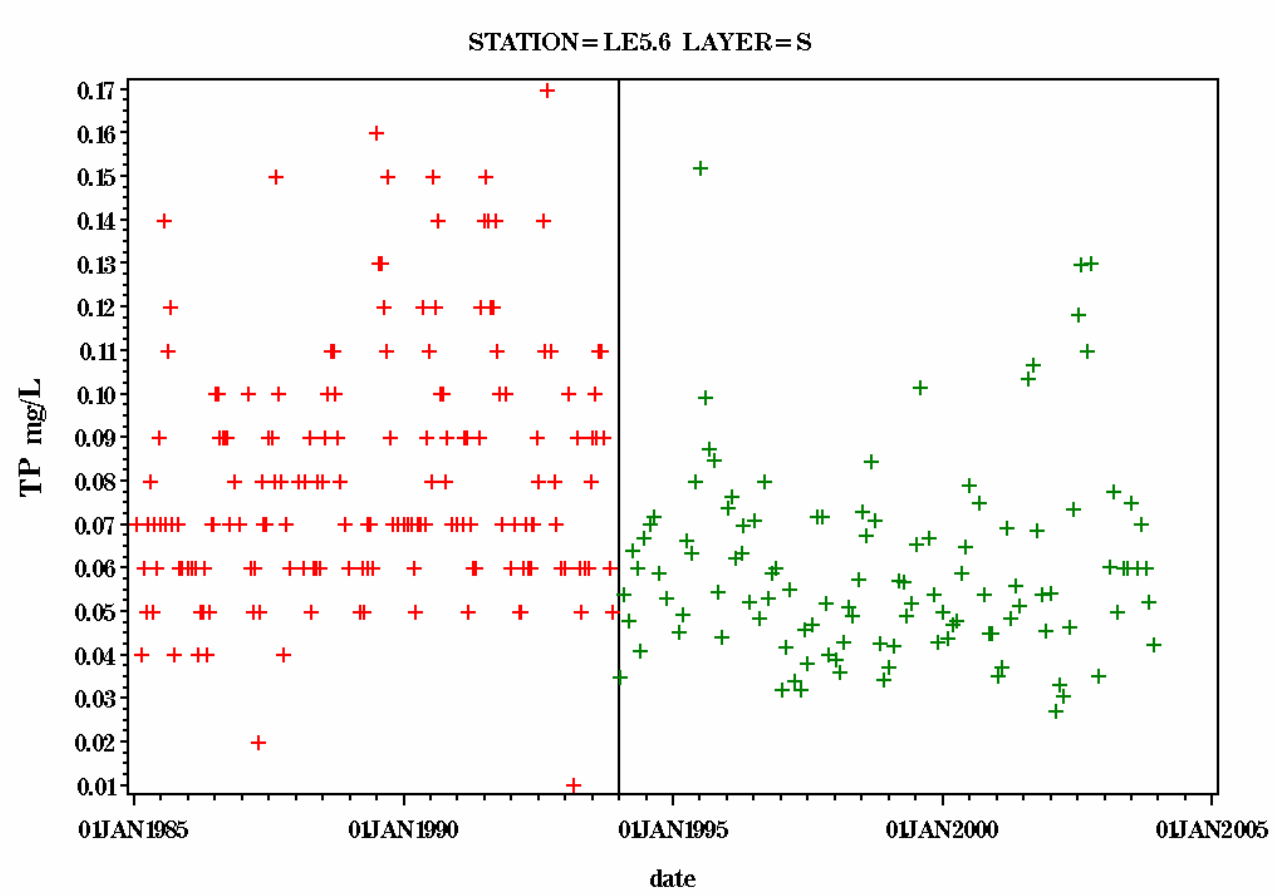


Figure 1. Time series plot of total phosphorus concentration for a station in the James River lower estuary. The vertical bar indicates the point of the methods change. Pre-method change data are in red; post method change data are in green.

Data Management and Model Building

The data management and model building for TP is the same as that for TN.

Results

An illustration of the final model fit along with all parameter estimates for the final model of each of the 63 time series can be found in appendix B. In general it appears that the model does a good job of capturing the character of the data. If for example the trend term (cyear) is statistically significant, the trend is apparent in the data. Similarly for the method change parameter (MC).

In addition we summarize below some overview statistics for the direction and magnitude of the methods change effect. Table 2 shows the number of positive and negative estimates for the effect of the methods change and the proportion of those that are statistically significant ($p < 0.05$).

Table 1. Frequency of positive and negative step trend estimates base on the 63 cases analyzed and the frequency of statistically significant step trend estimates.

Direction of step change	not significant	significant $p < 0.05$	Total
decrease	19	35	54
increase	7	2	9
Total	26	37	63

Of the 63 cases, 54 are found to have a negative step trend indicating that post method change TP is lower than pre method change TP. Of these 54, 35 or 65% are statistically significant. Of the 9 cases that show a positive strep trend, only two are statistically significant.

To assess the relation of the step trend to salinity gradients, for each tributary a graph is prepared showing the upstream - downstream gradient of the step trend estimates.

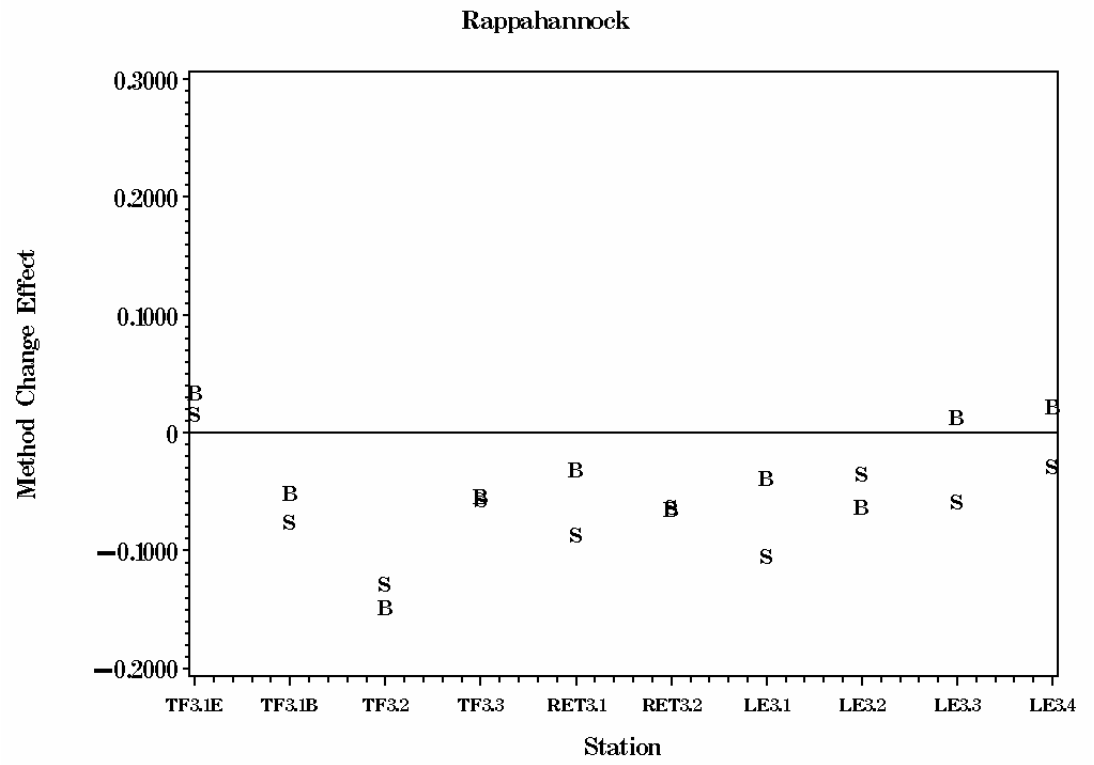


Figure 7. Plot of method change estimate versus stations in order from upstream to downstream for the Rappahannock River. Surface and Bottom are shown by S and B.

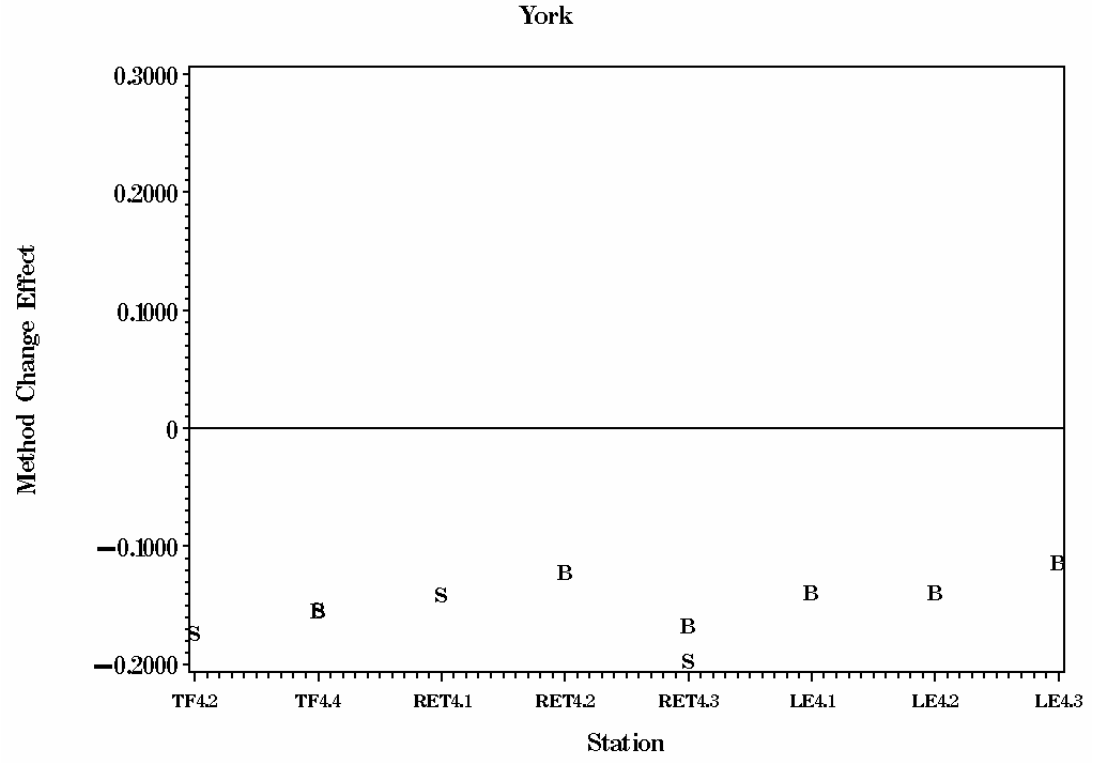


Figure 8. Plot of methods change versus station in order from upstream to downstream for the York River. Surface and Bottom are shown by S and B.

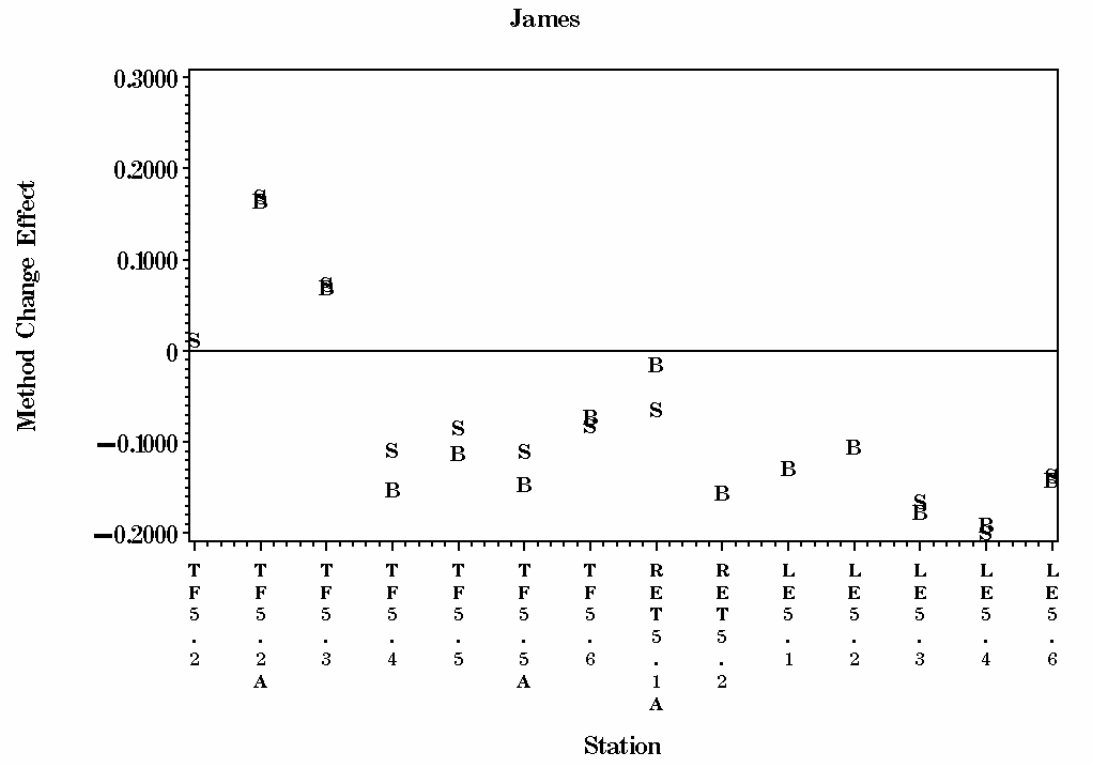


Figure 9. Plot of the method change estimate versus stations in order from upstream to downstream for the James River. Surface and Bottom are shown by S and B.

Another feature of the TP data worth noting in results, is the number of times that trend for the early period appears to differ trend the trend in the later period (table 2).

Table 2. Frequency of direction and significance of the change in trend between the periods before and after the methods change for TP concentration.

Direction of Trend Change	Not Significant	Significant $p < 0.05$	Total
Decrease	19	35	54
Increase	5	4	9
Total	24	39	63

In a large majority of cases the slope of trend after the methods change is lower (decrease) than the slope before the methods change. In many cases, (e.g.) the change is a reversal such that the slope is increasing before the methods change and decreasing after the methods change. Another result of note is the strong correlation between the methods change direction and the trend change direction (table 3.). In all but two cases, the step method change direction is that same as trend change direction.

Table 3. Frequency of direction of step trend compared to frequency of direction of the change in trend.

Effect and Direction	Methods Change Decrease	Methods Change Increase	Total
Trend decrease	53	1	54
Trend increase	1	8	9
Total	54	9	63

Discussion

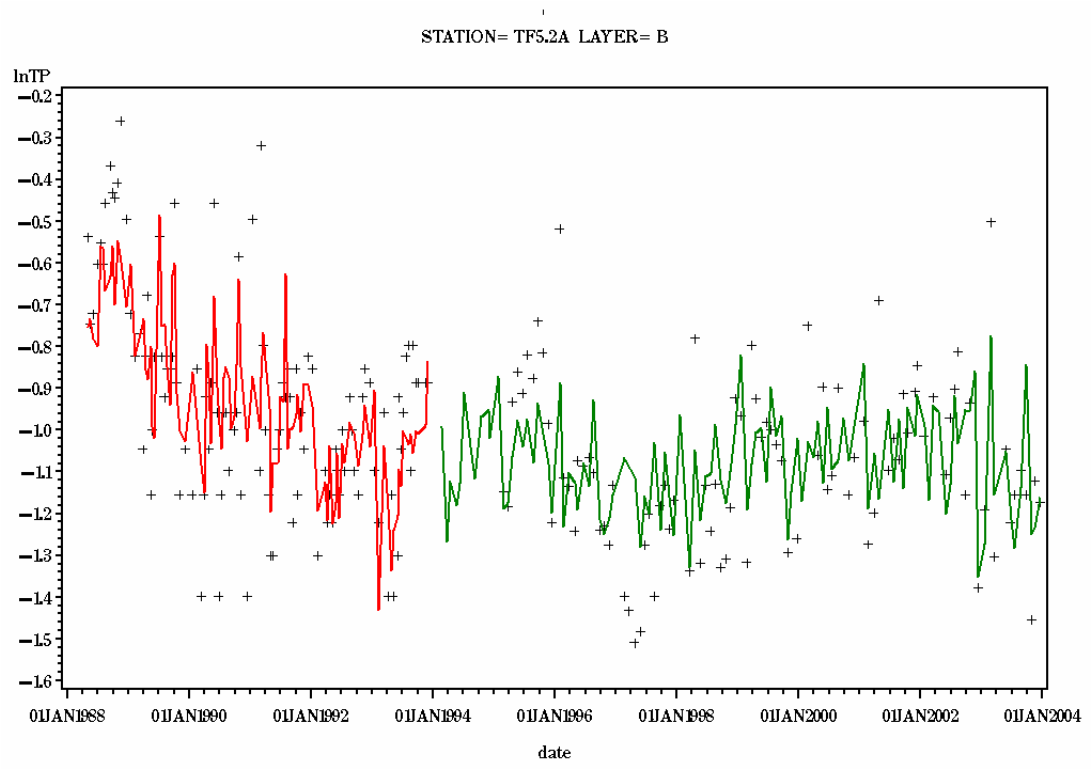
The results for TP are generally more consistent than those for TN in that the large majority of cases show a step down in TP concentration at the point of transition from the old method to the new method. However, in the tidal fresh region of the James (TF5.2A and TF5.3) and Rappahannock (TF3.1A), there are cases with a positive step. Thus one might infer some association of the methods change effect and salinity. But these positive step changes are also associated with features of the trend change as discussed below.

Another prevalant feature of the TP data is that the trends for the pre and post methods change periods differ. This change of trend is strong evidence that some management practice that affects the TP concentration was implemented at about the same time as the methods change. If the change in methods affected the estimated mean, the resulting data would show a step change at the time of the change in methods, but the trends before and after the change in methods should be roughly parallel. The fact that the slope also changes, suggests that some other factor which affects TP concentration has also changed. In order for intervention analysis to correctly estimate a bias due to change in methods, there is an assumption that other factors remain the same for the two periods. Therefore it is possible, that what appear to be methods change effects in these data are in fact artifacts due to the influence of the factor that changed the slope. The strong correlation between methods change estimates and the trend change estimates tends to support this idea that methods change estimates may be artifacts.

At first glance these data seem to support the conjecture that there is a negative shift in the mean TP the occurs at the time of the methods change. However, it is also apparent that other factors affecting TP changed at about the same time as the methods change. Therefore it would be premature to conclude that the methods change caused a negative shift in the mean based on these data.

Appendix A

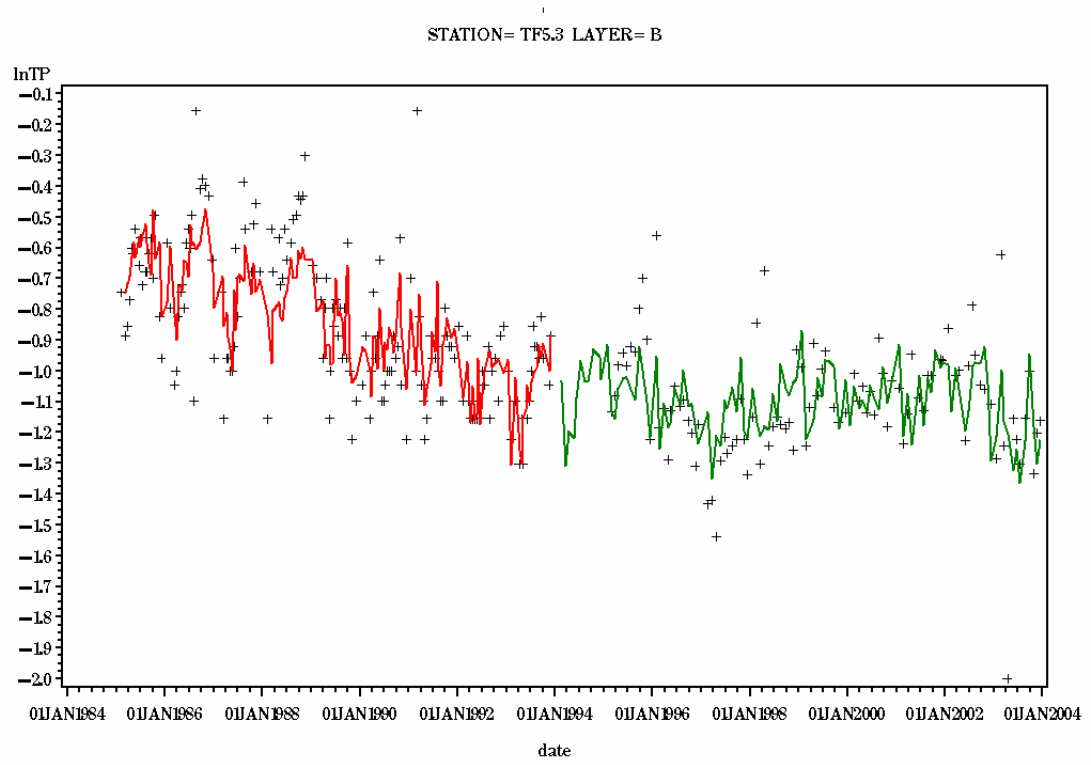
On each page of this appendix are the results on the intervention analysis TP time series at one station x layer combination. The results include a graph showing the time series of the data and the model fit before (red) and after (green) the methods change. Below the graph are the parameter estimates for the model with standard errors and p-values. Of particular interest is the MC (method change) parameter. A positive value for this estimate indicates a step up; a negative value indicates a step down.



Tributary	Station	Layer
James	TF5.2A	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1983	0.0557	-21.50	<.0001
jan	0.0528	0.0529	1.00	0.3190
feb	-0.0698	0.0502	-1.39	0.1663
mar	-0.0811	0.0454	-1.79	0.0756
apr	0.0433	0.0444	0.98	0.3301
may	-0.0555	0.0414	-1.34	0.1813
jun	-0.0306	0.0405	-0.76	0.4508
jul	0.0554	0.0408	1.36	0.1755
aug	0.0510	0.0406	1.25	0.2114
sep	0.0195	0.0417	0.47	0.6396
oct	0.0066	0.0417	0.16	0.8750
nov	0.0515	0.0475	1.09	0.2793
dec	-0.0432	0.0453	-0.95	0.3418
rtemp	0.0072	0.0055	1.30	0.1962
cyear	-0.0814	0.0148	-5.51	<.0001
mc	0.1653	0.0780	2.12	0.0356
mc_cyear	0.0712	0.0179	3.98	0.0001
flow30	-0.1460	0.0430	-3.40	0.0008
flow0	0.3053	0.0476	6.41	<.0001
flow10	-0.1601	0.0485	-3.30	0.0012
flow40	-0.1038	0.0475	-2.19	0.0301
AR1	-0.2990	0.0717	-4.17	0.0001

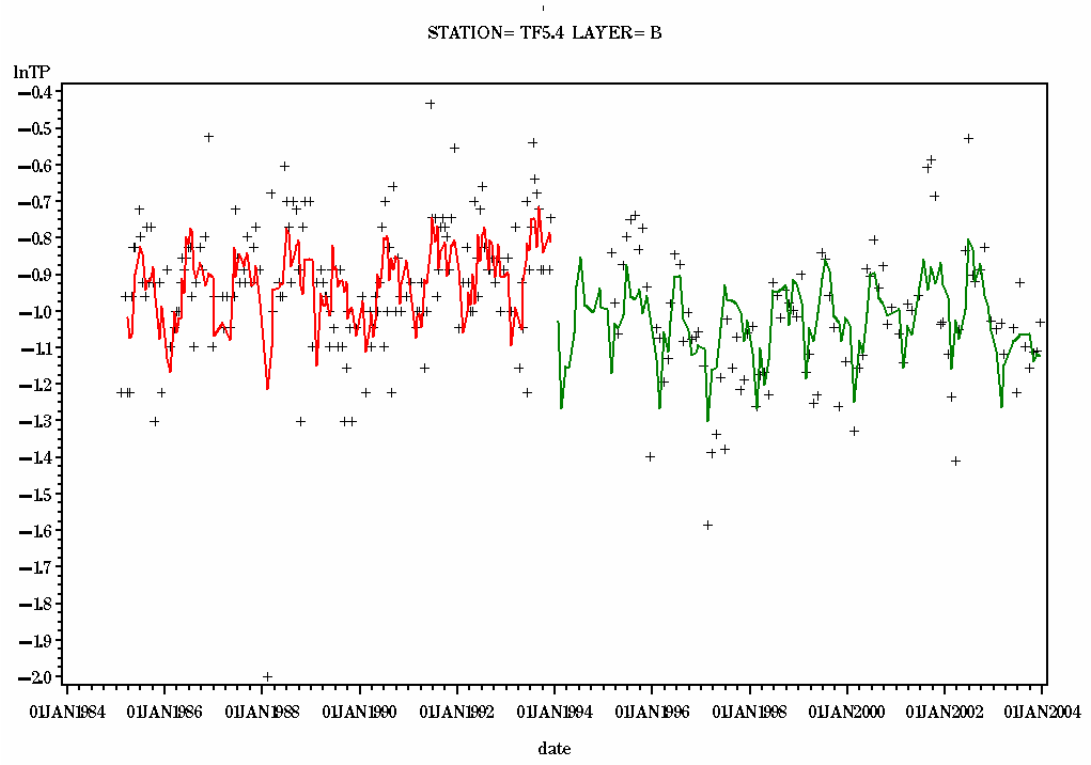
Root MSE = 0.1746 Total R-Square = 0.5425



Tributary	Station	Layer
James	TF5.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1079	0.0369	-30.03	<.0001
jan	0.0446	0.0432	1.03	0.3021
feb	-0.0812	0.0405	-2.00	0.0462
mar	-0.0651	0.0339	-1.92	0.0555
apr	-0.0449	0.0341	-1.32	0.1897
may	-0.0671	0.0338	-1.99	0.0481
jun	-0.0007	0.0327	-0.02	0.9832
jul	0.0215	0.0345	0.62	0.5332
aug	0.0426	0.0341	1.25	0.2125
sep	0.0625	0.0350	1.79	0.0752
oct	0.0747	0.0347	2.15	0.0324
nov	0.0471	0.0400	1.18	0.2392
dec	-0.0341	0.0393	-0.87	0.3857
rtemp	0.0063	0.0043	1.45	0.1477
cyear	-0.0556	0.0067	-8.30	<.0001
mc	0.0699	0.0598	1.17	0.2435
mc_cyear	0.0419	0.0107	3.91	0.0001
flow30	-0.1343	0.0329	-4.08	<.0001
flow10	-0.1494	0.0388	-3.84	0.0002
flow0	0.2111	0.0412	5.12	<.0001
flow50	-0.0813	0.0343	-2.37	0.0185
AR1	-0.2376	0.0628	-3.78	0.0003

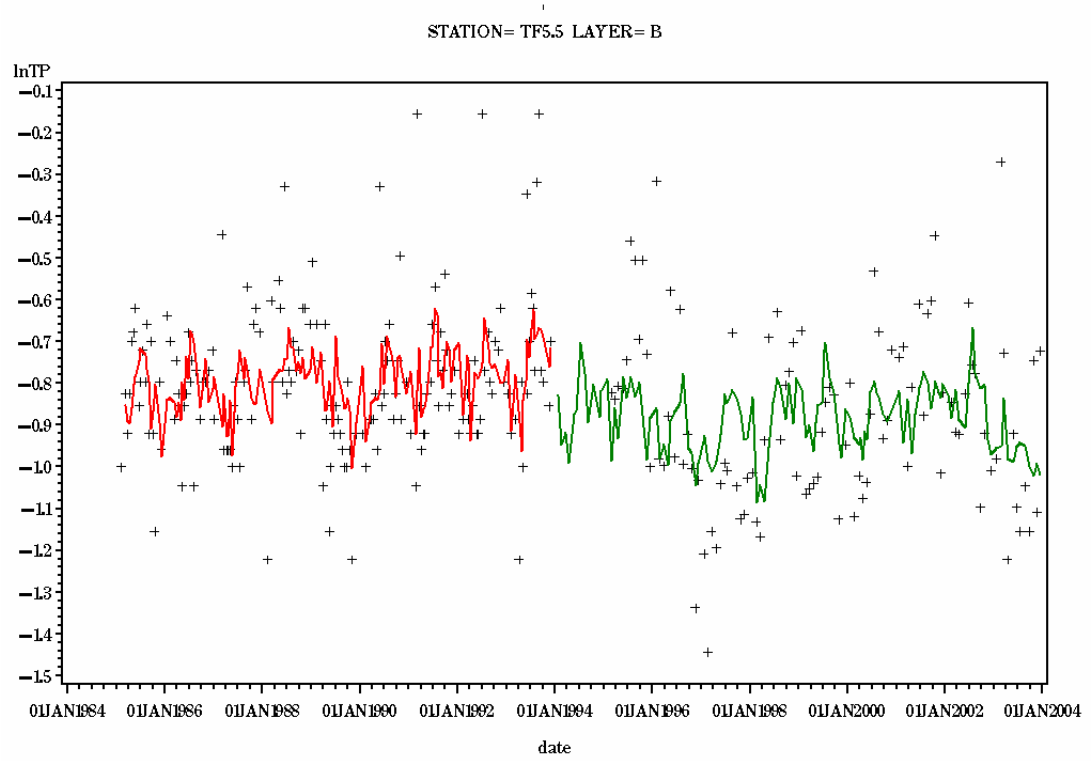
Root MSE = 0.1647 Total R-Square = 0.6177



Tributary	Station	Layer
James	TF5.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8605	0.0300	-28.67	<.0001
jan	-0.0153	0.0387	-0.39	0.6935
feb	-0.2031	0.0365	-5.57	<.0001
mar	-0.0771	0.0304	-2.54	0.0118
apr	-0.0928	0.0319	-2.91	0.0039
may	-0.0041	0.0303	-0.14	0.8927
jun	0.1018	0.0293	3.47	0.0006
jul	0.1154	0.0312	3.70	0.0003
aug	0.0601	0.0303	1.98	0.0488
sep	0.0666	0.0310	2.15	0.0325
oct	0.0052	0.0301	0.17	0.8627
nov	0.0319	0.0368	0.87	0.3863
dec	0.0113	0.0362	0.31	0.7545
rtemp	0.0056	0.0040	1.39	0.1657
cyear	0.0131	0.0054	2.40	0.0171
mc	-0.1509	0.0480	-3.14	0.0019
mc_cyear	-0.0176	0.0089	-1.99	0.0481
flow10	-0.0967	0.0294	-3.29	0.0012
flow70	-0.0772	0.0309	-2.50	0.0130
AR1	-0.1208	0.0634	-1.90	0.0332

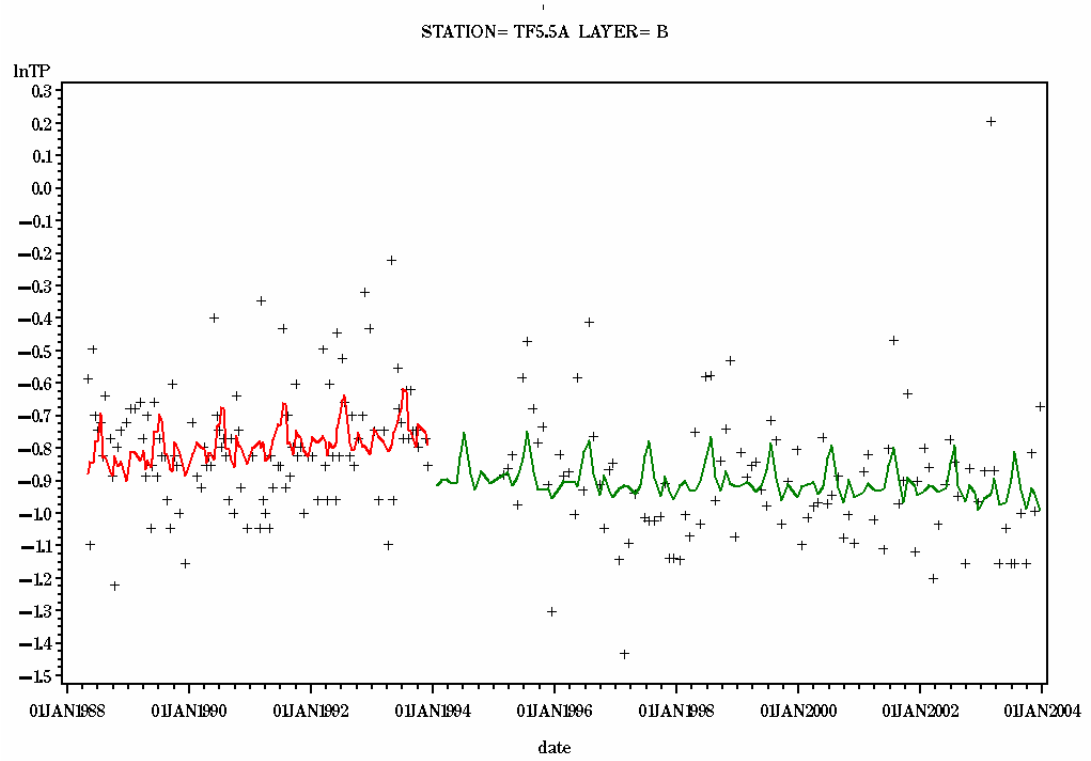
Root MSE = 0.1535 Total R-Square = 0.3714



Tributary	Station	Layer
James	TF5.5	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.7413	0.0350	-21.18	<.0001
jan	0.0249	0.0454	0.55	0.5837
feb	-0.0732	0.0429	-1.70	0.0895
mar	-0.0320	0.0354	-0.90	0.3664
apr	-0.0661	0.0363	-1.82	0.0694
may	-0.0207	0.0358	-0.58	0.5628
jun	0.0296	0.0352	0.84	0.4012
jul	0.1032	0.0360	2.86	0.0045
aug	0.0562	0.0361	1.56	0.1207
sep	0.0011	0.0365	0.03	0.9763
oct	0.0227	0.0362	0.63	0.5305
nov	-0.0457	0.0430	-1.06	0.2882
dec	0.0000	0.0416	0.00	0.9999
rtemp	0.0006	0.0050	0.12	0.9046
cyear	0.0110	0.0063	1.75	0.0821
mc	-0.1119	0.0566	-1.98	0.0490
mc_cyear	-0.0184	0.0104	-1.76	0.0792
flow40	-0.0843	0.0411	-2.05	0.0413
flow30	-0.0884	0.0361	-2.45	0.0150
AR1	-0.1168	0.0632	-1.85	0.0373

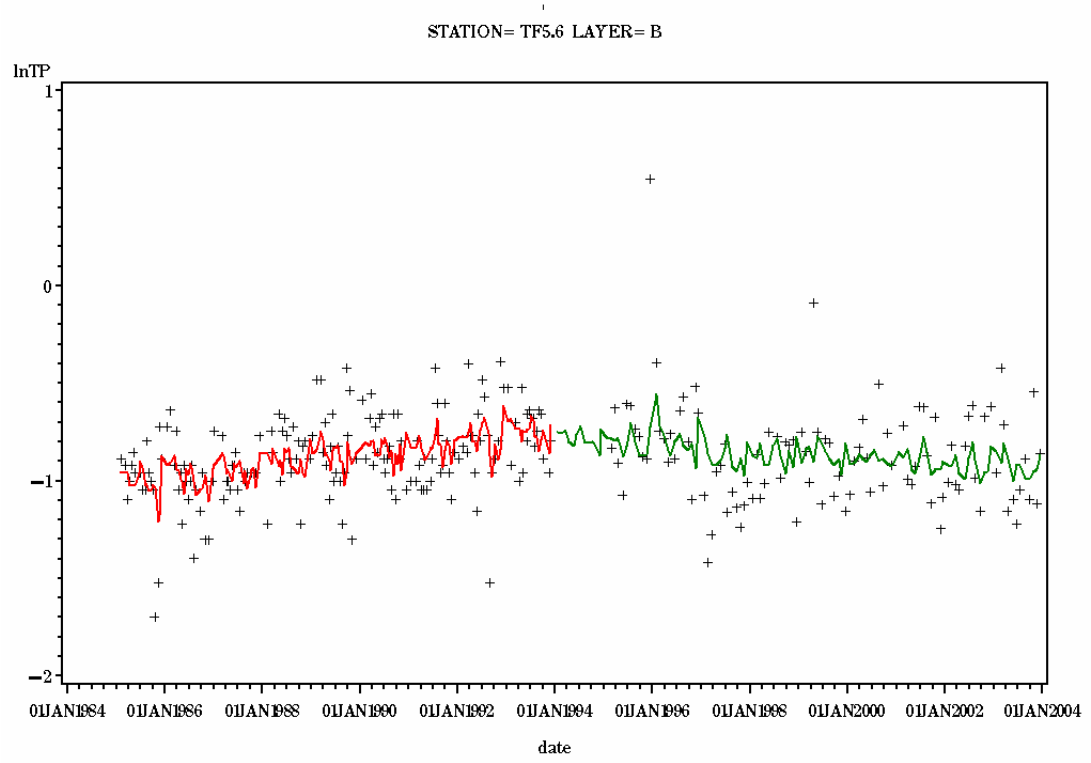
Root MSE = 0.1811 Total R-Square = 0.2141



Tributary	Station	Layer
James	TF5.5A	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.7357	0.0442	-16.64	<.0001
jan	-0.0130	0.0507	-0.26	0.7974
feb	-0.0040	0.0490	-0.08	0.9347
mar	-0.0075	0.0438	-0.17	0.8645
apr	-0.0321	0.0441	-0.73	0.4665
may	-0.0194	0.0422	-0.46	0.6461
jun	0.0554	0.0403	1.37	0.1707
jul	0.1219	0.0419	2.91	0.0040
aug	0.0025	0.0419	0.06	0.9523
sep	-0.0461	0.0419	-1.10	0.2723
oct	0.0142	0.0430	0.33	0.7414
nov	-0.0203	0.0490	-0.41	0.6797
dec	-0.0515	0.0489	-1.05	0.2933
rtemp	0.0056	0.0061	0.90	0.3667
cyear	0.0157	0.0117	1.35	0.1796
mc	-0.1450	0.0619	-2.34	0.0201
mc_cyear	-0.0207	0.0140	-1.47	0.1423
AR1	-0.0314	0.0716	-0.44	0.3322

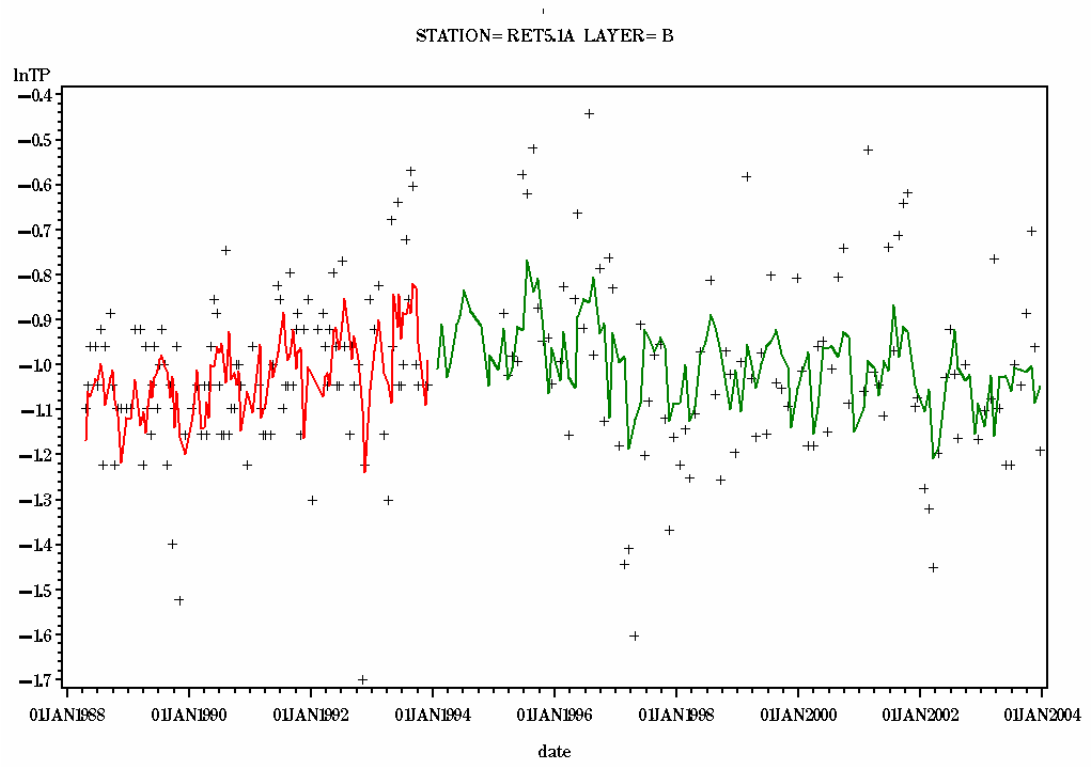
Root MSE = 0.1929 Total R-Square = 0.1590



Tributary	Station	Layer
James	TF5.6	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.7165	0.0445	-16.09	<.0001
jan	0.0346	0.0545	0.63	0.5264
feb	0.0231	0.0499	0.46	0.6433
mar	0.0378	0.0431	0.88	0.3806
apr	-0.0049	0.0441	-0.11	0.9116
may	-0.0405	0.0428	-0.95	0.3440
jun	0.0152	0.0431	0.35	0.7240
jul	0.0692	0.0448	1.54	0.1236
aug	-0.0161	0.0433	-0.37	0.7096
sep	-0.0821	0.0444	-1.85	0.0657
oct	-0.0178	0.0441	-0.40	0.6859
nov	-0.0841	0.0494	-1.70	0.0896
dec	0.0657	0.0498	1.32	0.1885
rtemp	-0.0053	0.0066	-0.80	0.4270
cyear	0.0322	0.0079	4.05	<.0001
mc	-0.0717	0.0723	-0.99	0.3224
mc_cyear	-0.0481	0.0128	-3.74	0.0002
AR1	-0.1768	0.0619	-2.86	0.0038

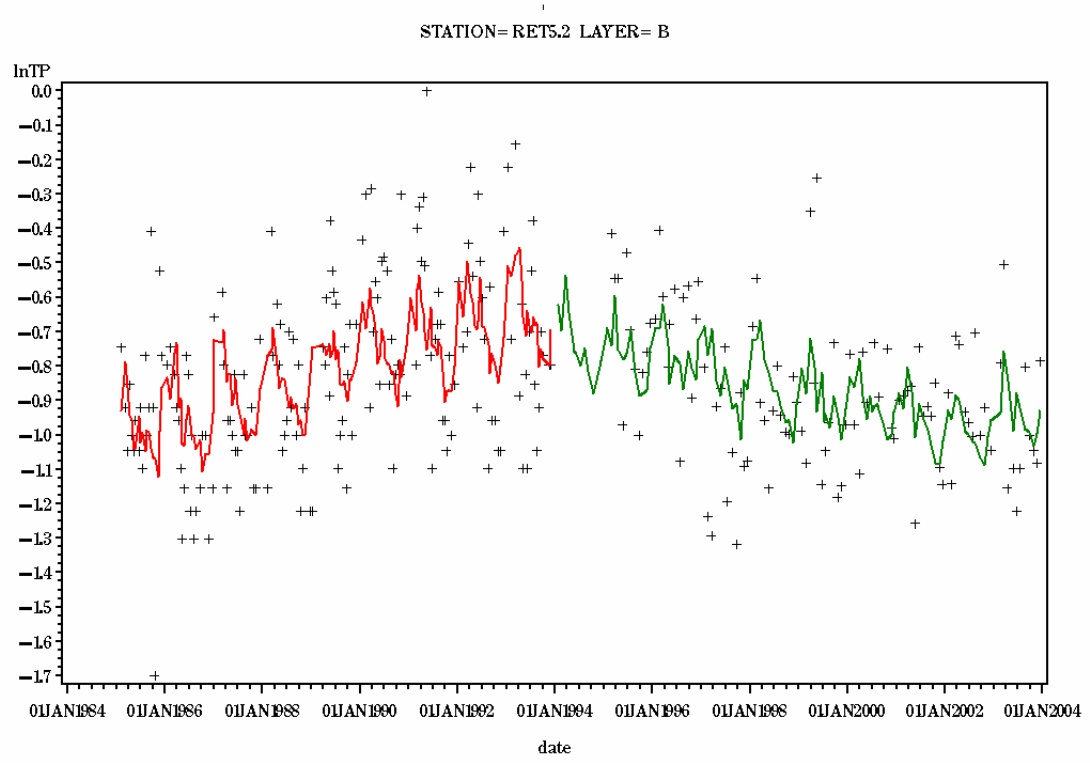
Root MSE = 0.2180 Total R-Square = 0.1654



Tributary	Station	Layer
James	RET5.1A	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9258	0.0514	-18.01	<.0001
jan	-0.0571	0.0477	-1.20	0.2331
feb	0.0321	0.0460	0.70	0.4862
mar	-0.0875	0.0413	-2.12	0.0354
apr	-0.0600	0.0404	-1.49	0.1388
may	0.0291	0.0399	0.73	0.4659
jun	0.0464	0.0398	1.17	0.2452
jul	0.1037	0.0399	2.60	0.0101
aug	0.0588	0.0398	1.48	0.1413
sep	0.0539	0.0398	1.35	0.1775
oct	0.0266	0.0408	0.65	0.5156
nov	-0.1060	0.0465	-2.28	0.0236
dec	-0.0399	0.0444	-0.90	0.3693
rtemp	0.0000	0.0060	0.01	0.9955
cyear	0.0302	0.0134	2.25	0.0258
mc	-0.0144	0.0711	-0.20	0.8397
mc_cyear	-0.0435	0.0160	-2.72	0.0070
AR1	-0.2415	0.0700	-3.45	0.0008

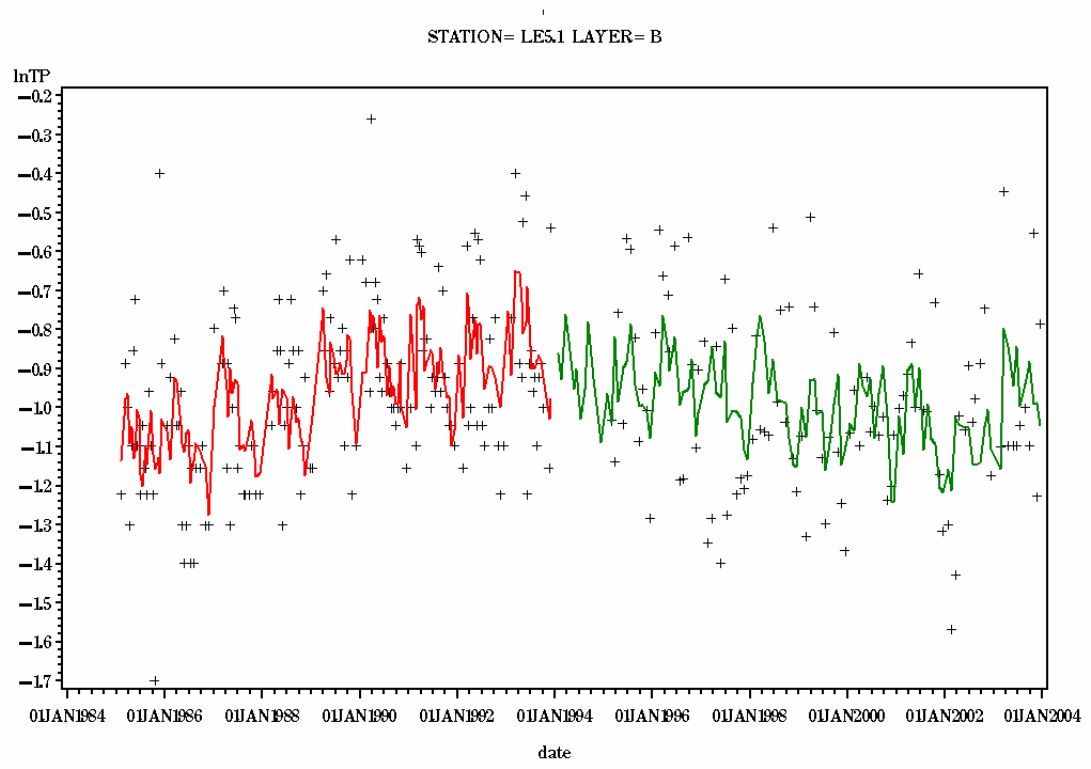
Root MSE = 0.1749 Total R-Square = 0.2118



Tributary	Station	Layer
James	RET5.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.6018	0.0420	-14.32	<.0001
jan	0.0997	0.0566	1.76	0.0793
feb	0.0554	0.0515	1.08	0.2826
mar	0.1556	0.0431	3.61	0.0004
apr	0.0672	0.0426	1.58	0.1161
may	-0.0241	0.0421	-0.57	0.5672
jun	0.0218	0.0429	0.51	0.6124
jul	-0.0204	0.0446	-0.46	0.6475
aug	-0.0441	0.0427	-1.03	0.3031
sep	-0.0772	0.0448	-1.72	0.0859
oct	-0.1113	0.0432	-2.58	0.0106
nov	-0.1170	0.0492	-2.38	0.0183
dec	-0.0056	0.0500	-0.11	0.9112
rtemp	-0.0039	0.0067	-0.58	0.5630
cyear	0.0417	0.0075	5.57	<.0001
mc	-0.1546	0.0670	-2.31	0.0218
mc_cyear	-0.0652	0.0121	-5.37	<.0001
flow10	0.1055	0.0406	2.60	0.0099
AR1	-0.1104	0.0632	-1.75	0.0455

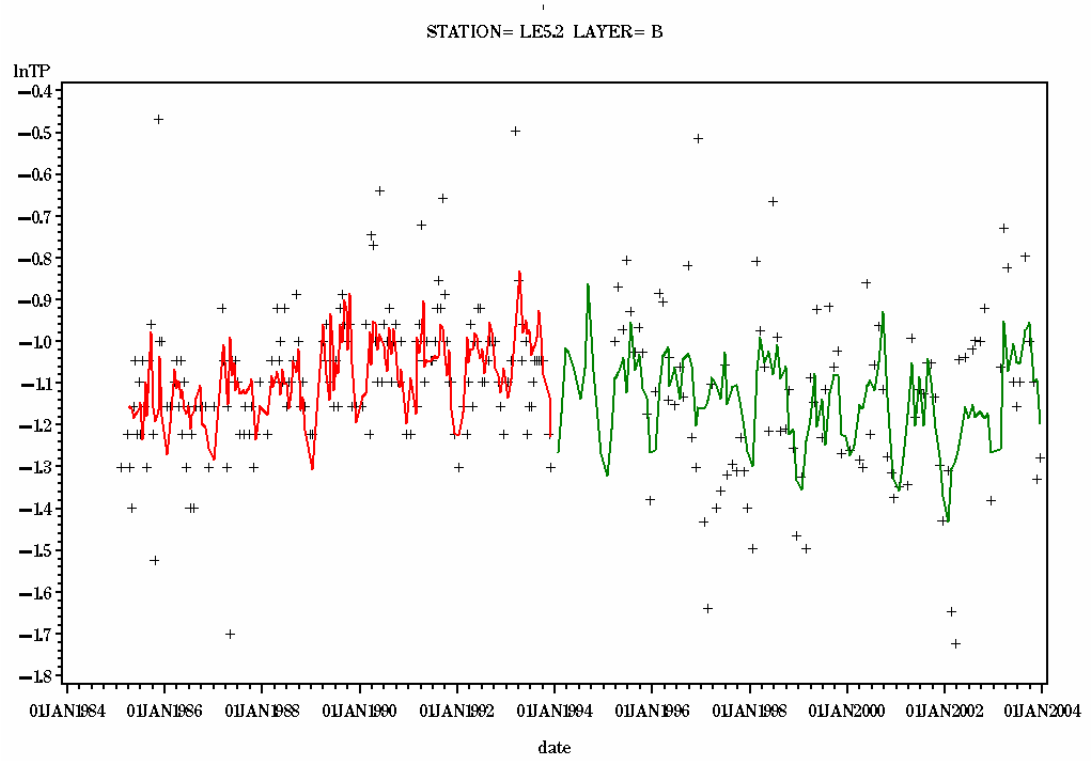
Root MSE = 0.2181 Total R-Square = 0.2937



Tributary	Station	Layer
James	LE5.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8121	0.0376	-21.59	<.0001
jan	0.0247	0.0522	0.47	0.6362
feb	-0.0607	0.0483	-1.26	0.2103
mar	0.1458	0.0390	3.73	0.0002
apr	0.0840	0.0395	2.13	0.0344
may	0.0143	0.0377	0.38	0.7055
jun	0.0827	0.0382	2.16	0.0315
jul	-0.0452	0.0398	-1.14	0.2568
aug	-0.0065	0.0388	-0.17	0.8668
sep	0.0109	0.0407	0.27	0.7890
oct	-0.0195	0.0386	-0.51	0.6136
nov	-0.1137	0.0446	-2.55	0.0114
dec	-0.1168	0.0470	-2.49	0.0135
rtemp	0.0060	0.0063	0.95	0.3437
cyear	0.0305	0.0067	4.56	<.0001
mc	-0.1280	0.0601	-2.13	0.0343
mc_cyear	-0.0408	0.0108	-3.78	0.0002
flow20	0.1381	0.0445	3.10	0.0022
flow0	0.0886	0.0416	2.13	0.0341
AR1	-0.0979	0.0633	-1.55	0.0663

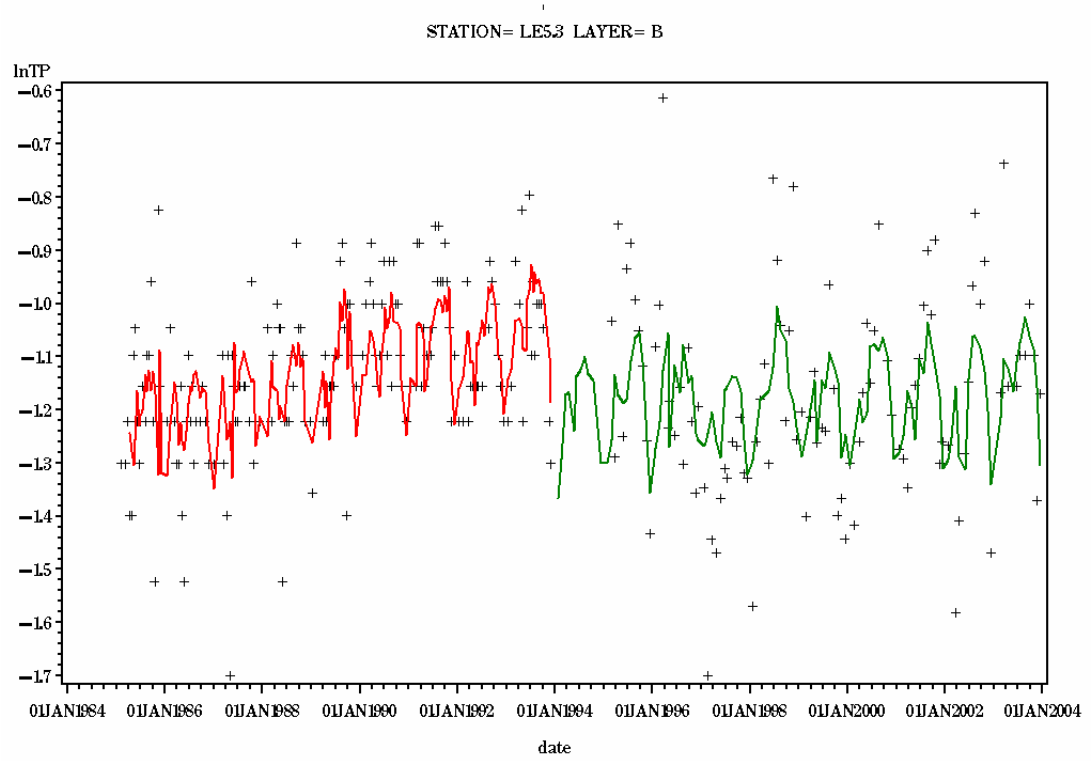
Root MSE = 0.1981 Total R-Square = 0.2906



Tributary	Station	Layer
James	LE5.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0203	0.0305	-33.42	<.0001
jan	-0.1239	0.0400	-3.10	0.0022
feb	-0.0632	0.0428	-1.48	0.1410
mar	0.0594	0.0325	1.83	0.0684
apr	0.0467	0.0311	1.50	0.1345
may	0.0320	0.0303	1.06	0.2921
jun	0.0232	0.0309	0.75	0.4534
jul	0.0130	0.0320	0.41	0.6854
aug	0.0493	0.0311	1.59	0.1135
sep	0.1063	0.0320	3.32	0.0010
oct	0.0084	0.0310	0.27	0.7870
nov	-0.0498	0.0348	-1.43	0.1539
dec	-0.1015	0.0385	-2.64	0.0089
rtemp	0.0032	0.0051	0.62	0.5332
cyear	0.0150	0.0055	2.72	0.0069
mc	-0.1044	0.0494	-2.11	0.0356
mc_cyear	-0.0186	0.0090	-2.08	0.0387
flow20	0.1480	0.0332	4.45	<.0001
flow90	0.0721	0.0310	2.32	0.0209
AR1	-0.1170	0.0634	-1.84	0.0375

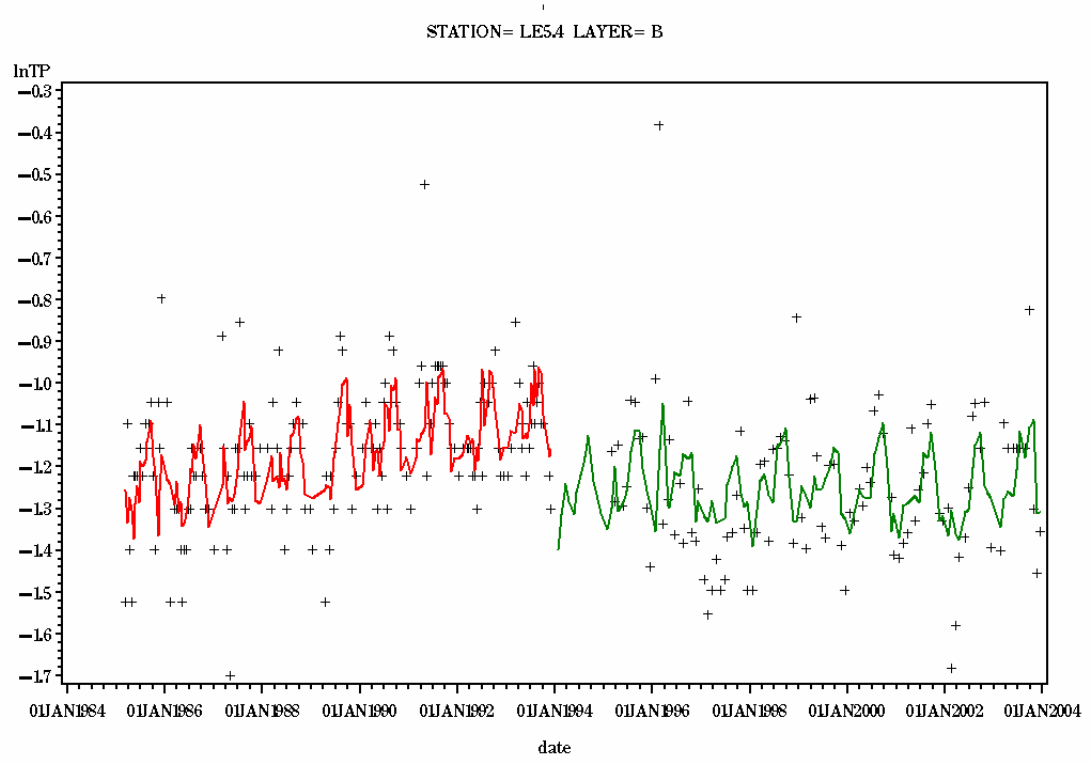
Root MSE = 0.1583 Total R-Square = 0.2955



Tributary	Station	Layer
James	LE5.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0244	0.0299	-34.22	<.0001
jan	-0.1053	0.0359	-2.94	0.0036
feb	-0.0583	0.0372	-1.57	0.1187
mar	0.0300	0.0298	1.01	0.3147
apr	-0.0105	0.0287	-0.37	0.7138
may	-0.0597	0.0283	-2.11	0.0361
jun	0.0347	0.0287	1.21	0.2278
jul	0.0639	0.0294	2.17	0.0307
aug	0.0966	0.0286	3.37	0.0009
sep	0.0854	0.0300	2.85	0.0047
oct	0.0628	0.0285	2.20	0.0287
nov	-0.0311	0.0317	-0.98	0.3275
dec	-0.1085	0.0347	-3.12	0.0020
rtemp	0.0048	0.0049	0.98	0.3293
cyear	0.0234	0.0054	4.34	<.0001
mc	-0.1766	0.0478	-3.69	0.0003
mc_cyear	-0.0189	0.0086	-2.20	0.0290
flow90	0.0753	0.0276	2.73	0.0069
AR1	-0.1799	0.0630	-2.86	0.0039

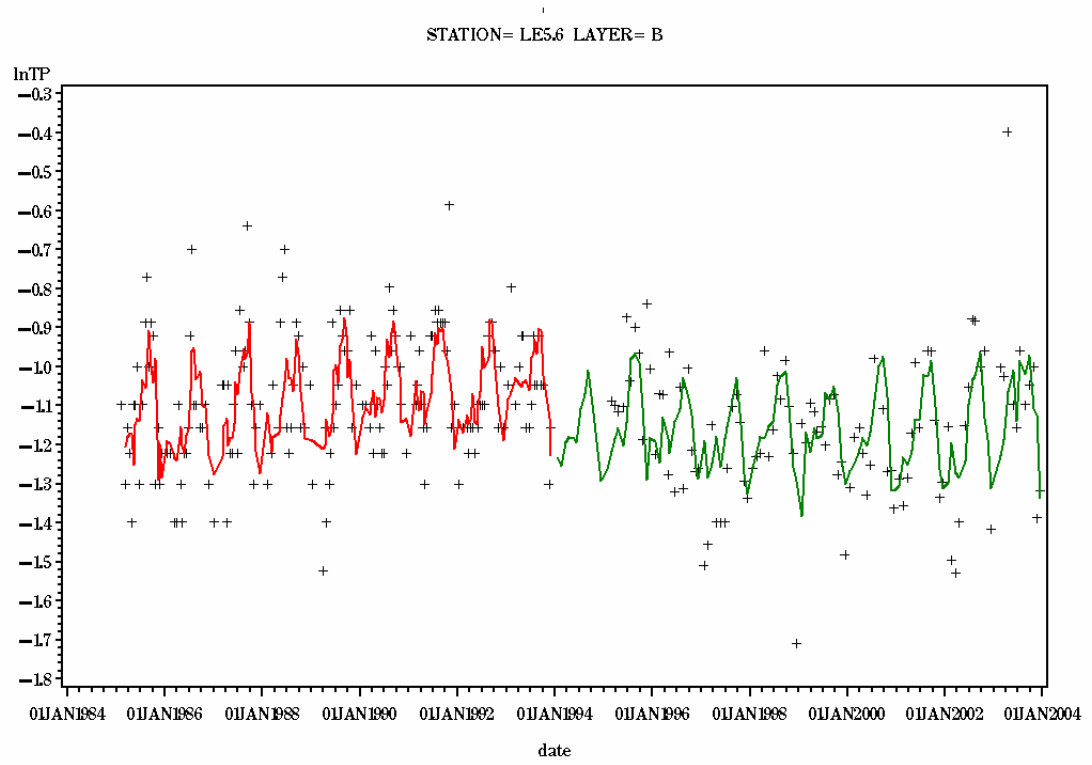
Root MSE = 0.1434 Total R-Square = 0.3163



Tributary	Station	Layer
James	LE5.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0663	0.0320	-33.36	<.0001
jan	-0.0835	0.0361	-2.31	0.0216
feb	-0.0453	0.0362	-1.25	0.2117
mar	0.0009	0.0301	0.03	0.9750
apr	-0.0351	0.0296	-1.19	0.2365
may	-0.0467	0.0287	-1.63	0.1047
jun	-0.0186	0.0290	-0.64	0.5217
jul	0.0659	0.0296	2.22	0.0271
aug	0.0968	0.0294	3.30	0.0011
sep	0.1312	0.0300	4.37	<.0001
oct	0.0493	0.0316	1.56	0.1194
nov	-0.0618	0.0321	-1.92	0.0556
dec	-0.0531	0.0344	-1.55	0.1234
rtemp	0.0053	0.0048	1.09	0.2766
cyear	0.0216	0.0057	3.81	0.0002
mc	-0.1899	0.0514	-3.70	0.0003
mc_cyear	-0.0206	0.0093	-2.22	0.0275
flow30	0.0631	0.0280	2.26	0.0250
AR1	-0.2339	0.0620	-3.77	0.0004

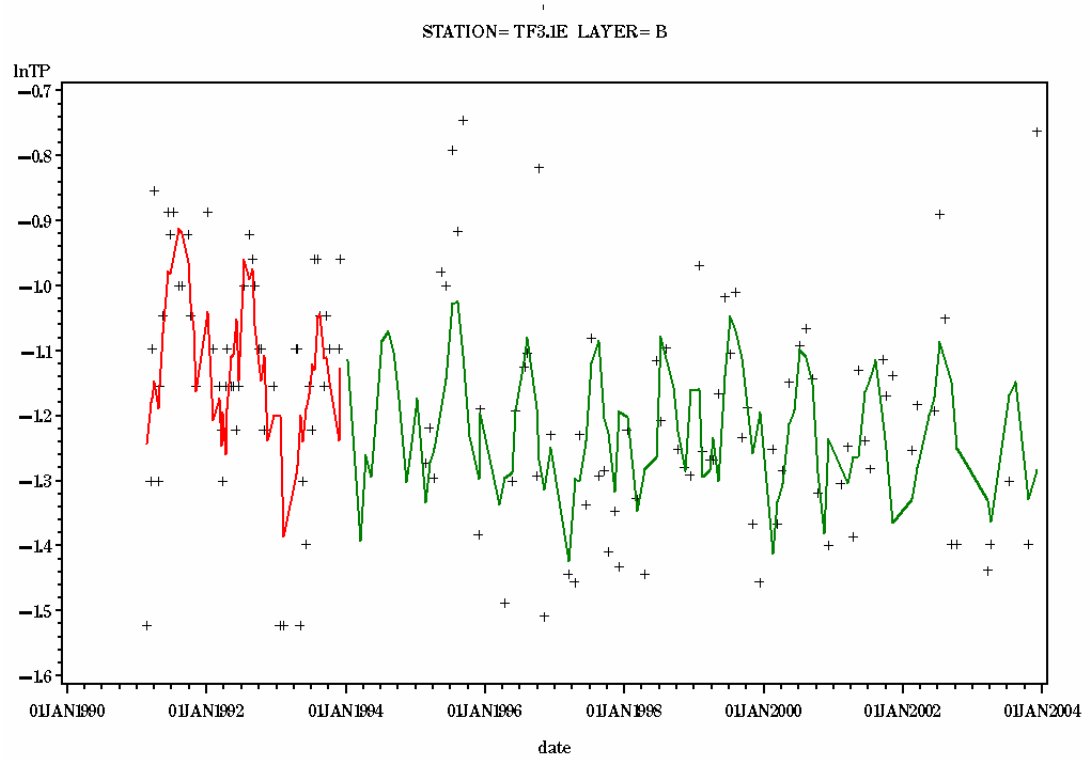
Root MSE = 0.1448 Total R-Square = 0.3349



Tributary	Station	Layer
James	LE5.6	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0346	0.0322	-32.13	<.0001
jan	-0.0961	0.0356	-2.70	0.0074
feb	-0.0533	0.0357	-1.49	0.1368
mar	-0.0525	0.0290	-1.81	0.0716
apr	-0.0233	0.0299	-0.78	0.4362
may	-0.0361	0.0284	-1.27	0.2049
jun	0.0021	0.0287	0.07	0.9424
jul	0.1112	0.0300	3.71	0.0003
aug	0.1311	0.0296	4.42	<.0001
sep	0.1609	0.0293	5.49	<.0001
oct	0.0622	0.0289	2.15	0.0323
nov	-0.0696	0.0317	-2.20	0.0289
dec	-0.1366	0.0336	-4.06	<.0001
rtemp	0.0074	0.0045	1.62	0.1065
cyear	0.0125	0.0057	2.19	0.0295
mc	-0.1413	0.0517	-2.74	0.0067
mc_cyear	-0.0097	0.0092	-1.05	0.2962
flow50	0.0675	0.0280	2.41	0.0168
AR1	-0.2493	0.0614	-4.06	0.0002

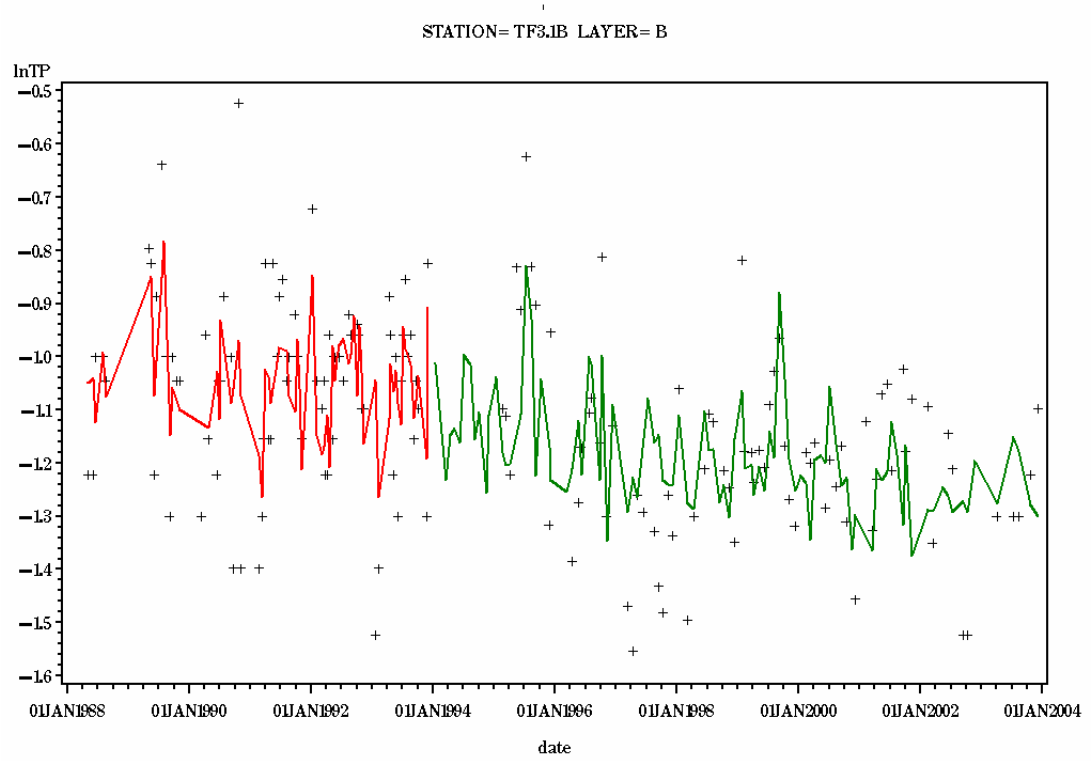
Root MSE = 0.1427 Total R-Square = 0.3880



Tributary	Station	Layer
Rappahannock	TF3.1E	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.2358	0.0649	-19.05	<.0001
jan	0.0378	0.0689	0.55	0.5840
feb	-0.1574	0.0531	-2.96	0.0037
mar	-0.1028	0.0411	-2.50	0.0139
apr	-0.0685	0.0387	-1.77	0.0794
may	-0.0277	0.0459	-0.60	0.5466
jun	0.0500	0.0411	1.22	0.2264
jul	0.1392	0.0423	3.29	0.0013
aug	0.1314	0.0427	3.08	0.0026
sep	0.0692	0.0433	1.60	0.1133
oct	-0.0061	0.0406	-0.15	0.8811
nov	-0.0759	0.0472	-1.61	0.1107
dec	0.0109	0.0469	0.23	0.8165
rtemp	0.0016	0.0059	0.28	0.7813
cyear	-0.0598	0.0308	-1.94	0.0549
mc	0.0351	0.0773	0.45	0.6508
mc_cyear	0.0531	0.0320	1.66	0.1000
flow150	-0.0899	0.0373	-2.41	0.0176
AR1	-0.1331	0.0945	-1.41	0.0847

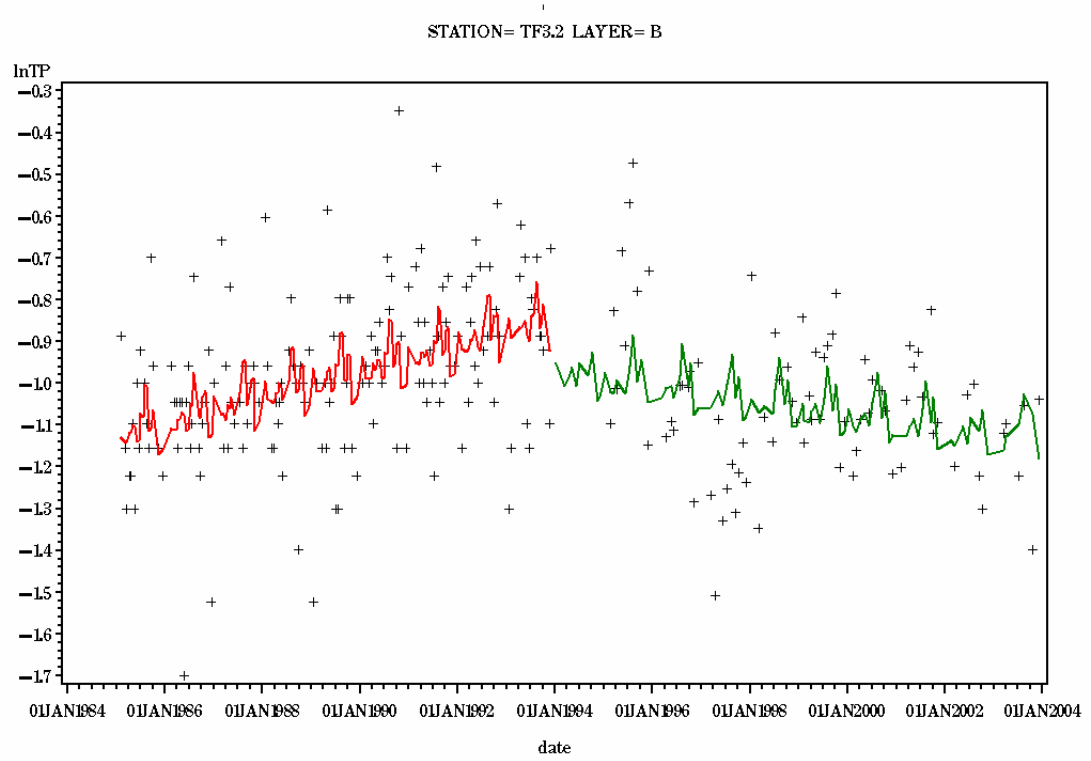
Root MSE = 0.1476 Total R-Square = 0.3818



Tributary	Station	Layer
Rappahannock	TF3.1B	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0563	0.0497	-21.24	<.0001
jan	0.0495	0.0736	0.67	0.5021
feb	-0.0485	0.0552	-0.88	0.3818
mar	-0.1015	0.0451	-2.25	0.0261
apr	-0.0368	0.0403	-0.91	0.3633
may	0.0304	0.0460	0.66	0.5105
jun	0.0158	0.0383	0.41	0.6810
jul	0.0989	0.0427	2.32	0.0221
aug	0.0449	0.0402	1.12	0.2659
sep	-0.0145	0.0411	-0.35	0.7242
oct	0.0299	0.0402	0.74	0.4588
nov	-0.0819	0.0444	-1.85	0.0673
dec	0.0138	0.0527	0.26	0.7939
rtemp	0.0029	0.0066	0.43	0.6659
cyear	-0.0026	0.0153	-0.17	0.8675
mc	-0.0502	0.0706	-0.71	0.4782
mc_cyear	-0.0154	0.0180	-0.85	0.3953
flow0	0.2184	0.0475	4.60	<.0001
flow20	-0.0901	0.0368	-2.45	0.0158
flow60	-0.0748	0.0377	-1.99	0.0490
AR1	-0.2399	0.0858	-2.80	0.0045

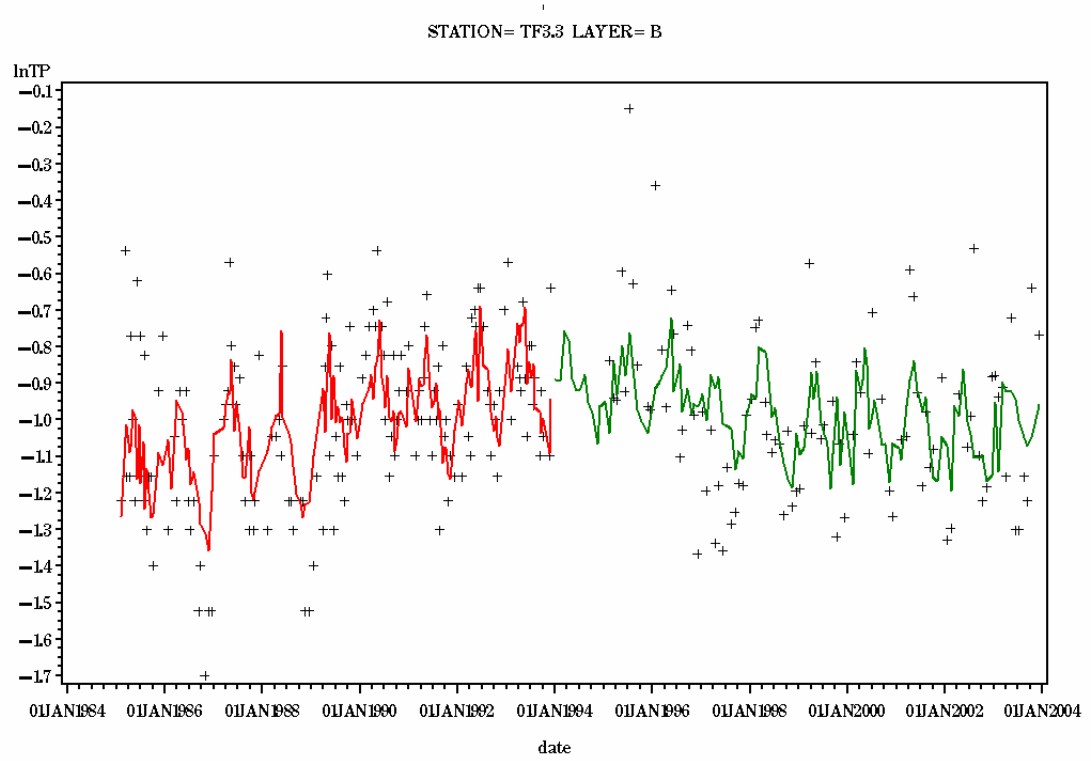
Root MSE = 0.1553 Total R-Square = 0.4205



Tributary	Station	Layer
Rappahannock	TF3.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8310	0.0320	-25.94	<.0001
jan	0.0157	0.0560	0.28	0.7788
feb	-0.0265	0.0507	-0.52	0.6019
mar	-0.0315	0.0364	-0.87	0.3879
apr	-0.0065	0.0338	-0.19	0.8482
may	0.0096	0.0387	0.25	0.8042
jun	-0.0291	0.0356	-0.82	0.4143
jul	0.0271	0.0370	0.73	0.4650
aug	0.1024	0.0371	2.76	0.0062
sep	-0.0032	0.0378	-0.08	0.9332
oct	0.0531	0.0351	1.51	0.1318
nov	-0.0607	0.0440	-1.38	0.1690
dec	-0.0504	0.0440	-1.15	0.2533
rtemp	-0.0018	0.0053	-0.34	0.7377
cyear	0.0310	0.0057	5.42	<.0001
mc	-0.1473	0.0557	-2.65	0.0087
mc_cyear	-0.0476	0.0105	-4.55	<.0001
AR1	-0.0104	0.0679	-0.15	0.4396

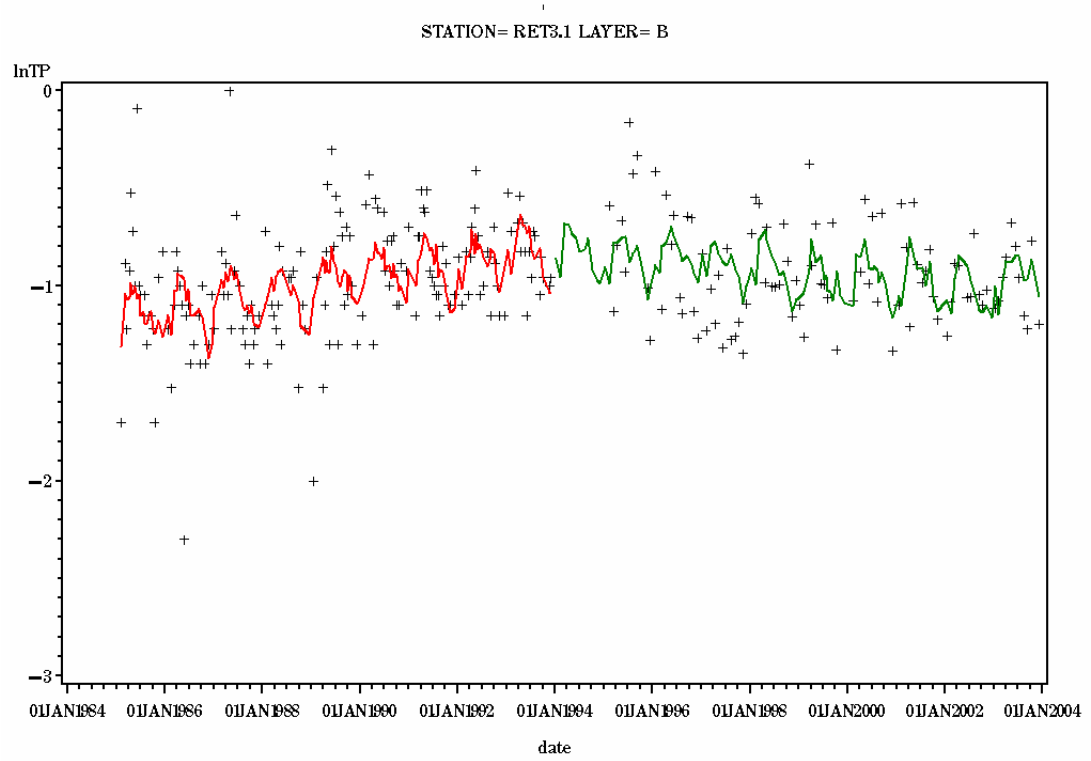
Root MSE = 0.1787 Total R-Square = 0.2121



Tributary	Station	Layer
Rappahannock	TF3.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8710	0.0402	-21.68	<.0001
jan	0.0300	0.0516	0.58	0.5617
feb	-0.0684	0.0518	-1.32	0.1880
mar	0.0891	0.0417	2.14	0.0338
apr	0.0818	0.0400	2.04	0.0422
may	0.1554	0.0428	3.63	0.0004
jun	0.0387	0.0393	0.98	0.3259
jul	0.0375	0.0409	0.92	0.3607
aug	-0.0296	0.0415	-0.71	0.4761
sep	-0.0809	0.0405	-2.00	0.0472
oct	-0.0988	0.0419	-2.35	0.0194
nov	-0.1186	0.0469	-2.53	0.0121
dec	-0.0361	0.0467	-0.77	0.4401
rtemp	0.0096	0.0060	1.59	0.1136
cyear	0.0295	0.0073	4.04	<.0001
mc	-0.0534	0.0653	-0.82	0.4146
mc_cyear	-0.0428	0.0118	-3.64	0.0003
flow10	0.1204	0.0322	3.74	0.0002
AR1	-0.1441	0.0658	-2.19	0.0182

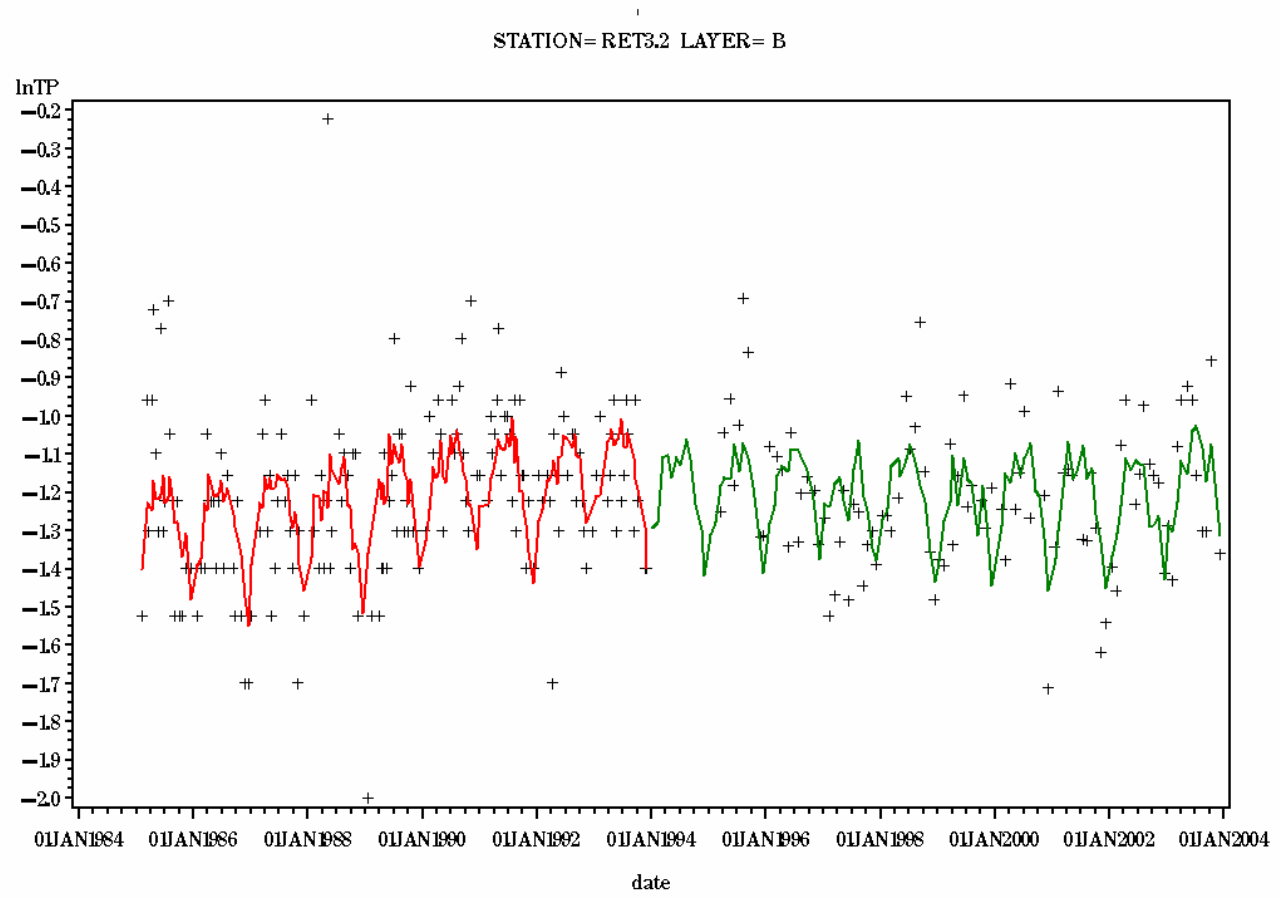
Root MSE = 0.1981 Total R-Square = 0.3065



Tributary	Station	Layer
Rappahannock	RET3.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8122	0.0475	-17.10	<.0001
jan	-0.0272	0.0649	-0.42	0.6760
feb	-0.1122	0.0672	-1.67	0.0962
mar	0.0825	0.0528	1.56	0.1193
apr	0.1339	0.0502	2.67	0.0081
may	0.1298	0.0547	2.37	0.0185
jun	0.1050	0.0517	2.03	0.0434
jul	0.0338	0.0536	0.63	0.5289
aug	-0.0058	0.0518	-0.11	0.9106
sep	0.0150	0.0510	0.29	0.7691
oct	-0.0639	0.0529	-1.21	0.2282
nov	-0.1468	0.0648	-2.26	0.0244
dec	-0.1441	0.0694	-2.08	0.0388
rtemp	0.0122	0.0083	1.47	0.1430
cyear	0.0368	0.0084	4.36	<.0001
mc	-0.0306	0.0771	-0.40	0.6919
mc_cyear	-0.0551	0.0138	-3.98	<.0001
flow20	0.1098	0.0425	2.59	0.0103
AR1	-0.0280	0.0652	-0.43	0.3356

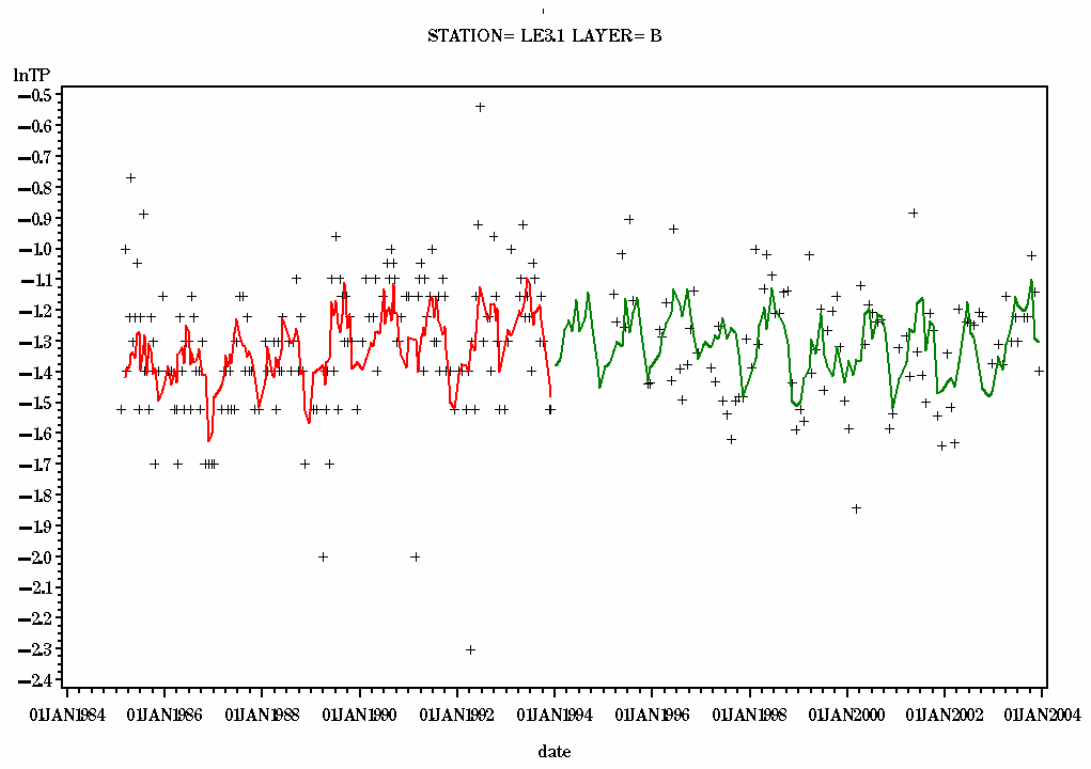
Root MSE = 0.2651 Total R-Square = 0.2265



Tributary	Station	Layer
Rappahannock	RET3.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1397	0.0364	-31.34	<.0001
jan	-0.0983	0.0459	-2.14	0.0334
feb	-0.0708	0.0475	-1.49	0.1374
mar	0.0359	0.0373	0.96	0.3363
apr	0.0779	0.0364	2.14	0.0334
may	0.0476	0.0397	1.20	0.2313
jun	0.1050	0.0389	2.70	0.0075
jul	0.0987	0.0386	2.56	0.0112
aug	0.1078	0.0374	2.88	0.0043
sep	0.0320	0.0378	0.85	0.3976
oct	-0.0243	0.0383	-0.64	0.5260
nov	-0.1027	0.0434	-2.37	0.0187
dec	-0.2088	0.0446	-4.69	<.0001
rtemp	0.0087	0.0054	1.62	0.1066
cyear	0.0163	0.0065	2.53	0.0120
mc	-0.0643	0.0598	-1.08	0.2832
mc_cyear	-0.0169	0.0106	-1.59	0.1125
flow20	0.0894	0.0320	2.79	0.0057
AR1	-0.1020	0.0645	-1.58	0.0621

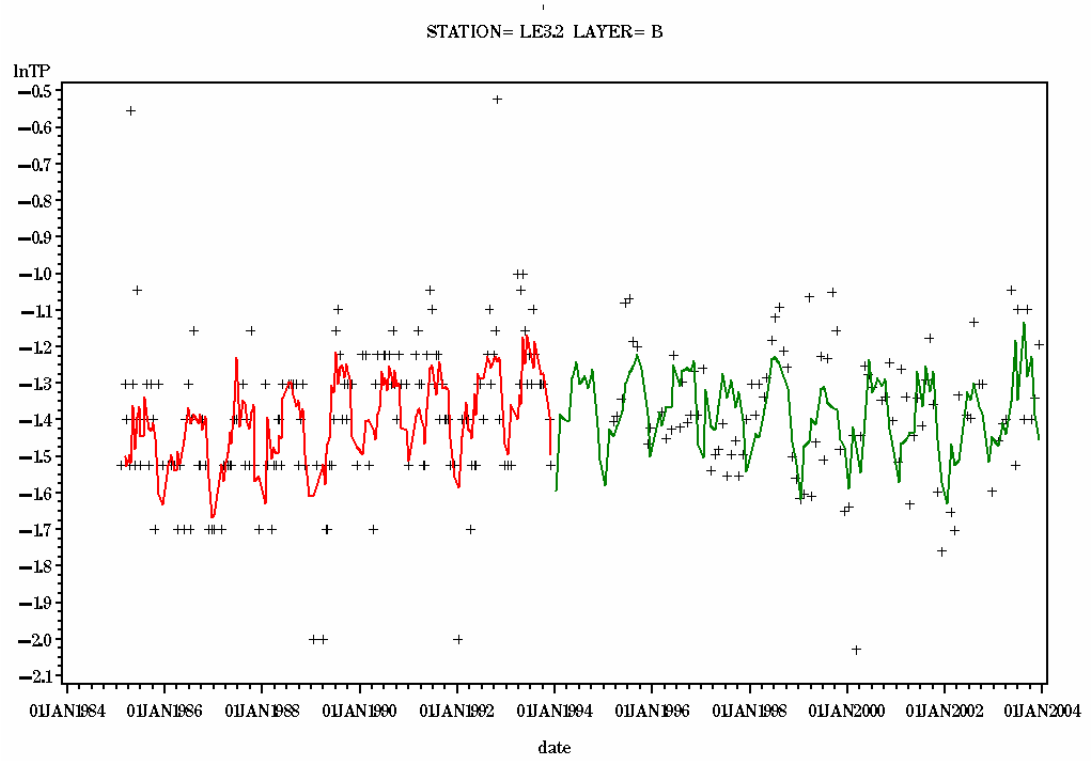
Root MSE = 0.1887 Total R-Square = 0.2537



Tributary	Station	Layer
Rappahannock	LE3.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.2648	0.0374	-33.80	<.0001
jan	-0.0605	0.0515	-1.18	0.2411
feb	-0.0545	0.0537	-1.02	0.3111
mar	-0.0374	0.0384	-0.97	0.3312
apr	0.0127	0.0368	0.34	0.7311
may	0.0240	0.0392	0.61	0.5416
jun	0.1331	0.0377	3.53	0.0005
jul	0.0735	0.0389	1.89	0.0599
aug	0.0589	0.0372	1.58	0.1144
sep	0.0840	0.0375	2.24	0.0261
oct	0.0187	0.0392	0.48	0.6344
nov	-0.1098	0.0437	-2.51	0.0127
dec	-0.1427	0.0450	-3.17	0.0017
rtemp	0.0071	0.0067	1.06	0.2915
cyear	0.0130	0.0067	1.96	0.0514
mc	-0.0375	0.0623	-0.60	0.5474
mc_cyear	-0.0140	0.0110	-1.27	0.2058
flow50	0.0797	0.0359	2.22	0.0273
flow20	0.0788	0.0344	2.29	0.0231
AR1	-0.1110	0.0650	-1.71	0.0490

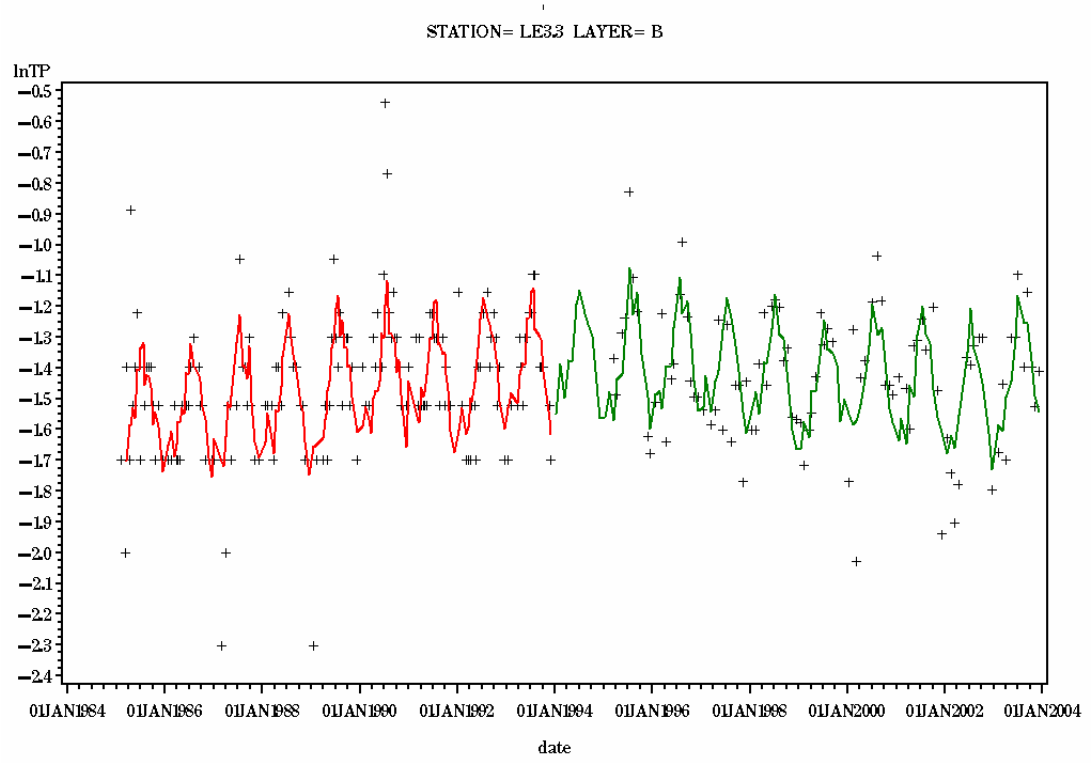
Root MSE = 0.1894 Total R-Square = 0.2335



Tributary	Station	Layer
Rappahannock	LE3.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.3161	0.0335	-39.23	<.0001
jan	-0.1670	0.0454	-3.68	0.0003
feb	-0.0377	0.0459	-0.82	0.4122
mar	-0.0582	0.0336	-1.73	0.0846
apr	-0.0451	0.0324	-1.39	0.1649
may	0.0111	0.0355	0.31	0.7538
jun	0.1055	0.0332	3.17	0.0017
jul	0.0681	0.0348	1.96	0.0514
aug	0.1154	0.0344	3.35	0.0009
sep	0.0810	0.0328	2.47	0.0142
oct	0.0869	0.0339	2.56	0.0110
nov	-0.0333	0.0387	-0.86	0.3905
dec	-0.1268	0.0388	-3.27	0.0012
rtemp	-0.0021	0.0061	-0.34	0.7365
cyear	0.0183	0.0060	3.04	0.0026
mc	-0.0622	0.0555	-1.12	0.2637
mc_cyear	-0.0190	0.0100	-1.90	0.0591
flow60	0.0940	0.0280	3.36	0.0009
AR1	-0.1352	0.0640	-2.11	0.0215

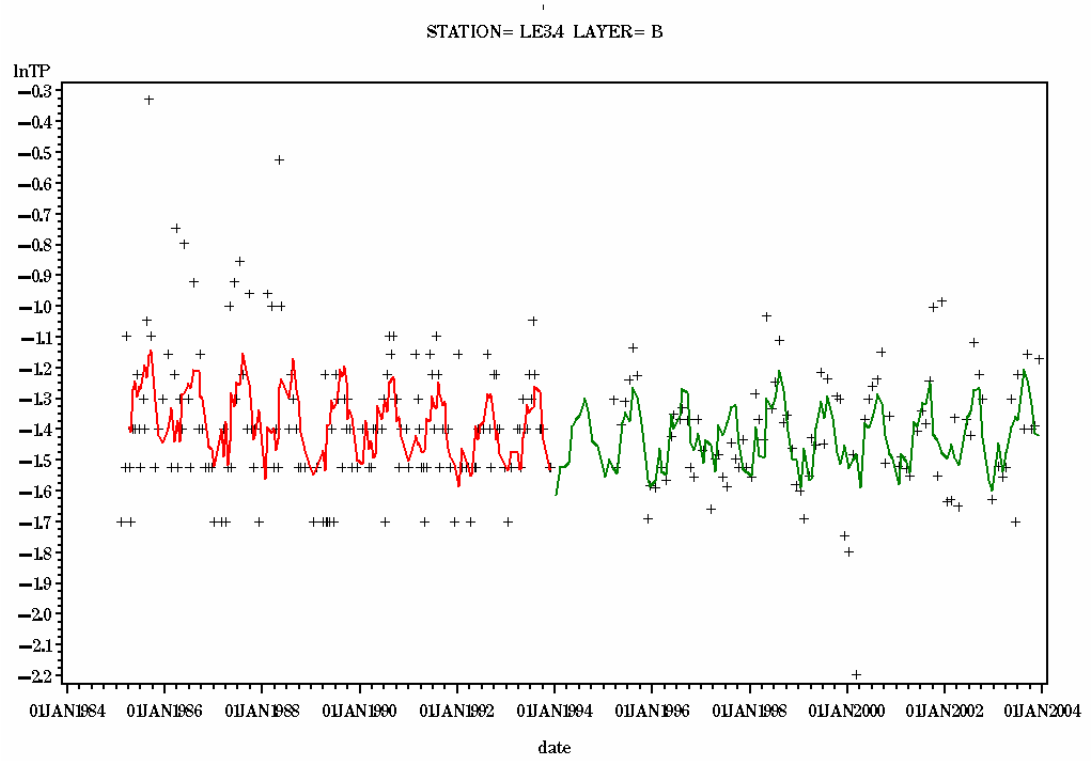
Root MSE = 0.1684 Total R-Square = 0.3001



Tributary	Station	Layer
Rappahannock	LE3.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.3985	0.0300	-46.59	<.0001
jan	-0.1321	0.0416	-3.17	0.0017
feb	-0.0961	0.0468	-2.05	0.0412
mar	-0.1485	0.0327	-4.54	<.0001
apr	-0.0361	0.0308	-1.17	0.2420
may	-0.0004	0.0334	-0.01	0.9909
jun	0.1376	0.0328	4.19	<.0001
jul	0.2582	0.0333	7.75	<.0001
aug	0.1461	0.0322	4.53	<.0001
sep	0.1286	0.0323	3.99	<.0001
oct	0.0260	0.0335	0.78	0.4378
nov	-0.1010	0.0391	-2.58	0.0104
dec	-0.1823	0.0402	-4.53	<.0001
rtemp	0.0041	0.0055	0.75	0.4541
cyear	0.0162	0.0054	2.99	0.0031
mc	0.0140	0.0493	0.28	0.7766
mc_cyear	-0.0257	0.0089	-2.89	0.0042
flow70	0.0610	0.0282	2.16	0.0315
flow10	0.0535	0.0264	2.02	0.0442
AR1	-0.0396	0.0656	-0.60	0.2753

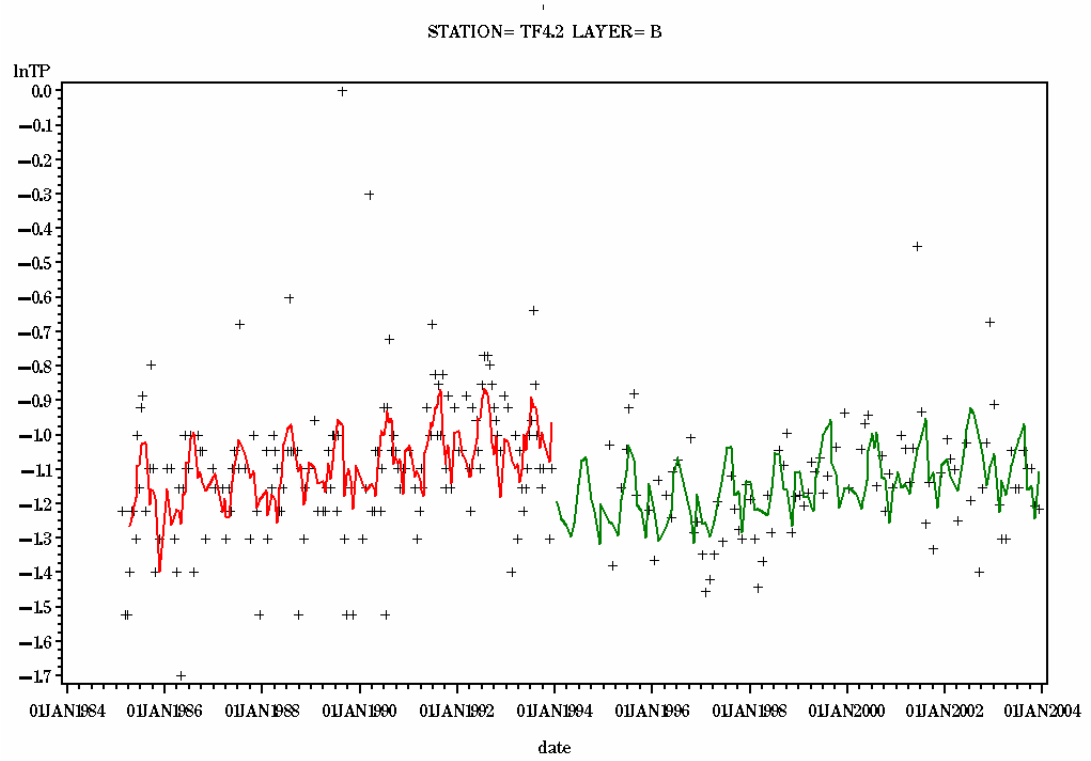
Root MSE = 0.1643 Total R-Square = 0.4696



Tributary	Station	Layer
Rappahannock	LE3.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.4653	0.0370	-39.65	<.0001
jan	-0.1295	0.0466	-2.78	0.0059
feb	-0.0269	0.0521	-0.52	0.6063
mar	-0.0683	0.0386	-1.77	0.0783
apr	-0.0915	0.0371	-2.47	0.0144
may	0.0481	0.0403	1.19	0.2338
jun	0.0571	0.0387	1.47	0.1416
jul	0.0820	0.0398	2.06	0.0407
aug	0.1445	0.0386	3.75	0.0002
sep	0.1266	0.0376	3.37	0.0009
oct	0.0048	0.0393	0.12	0.9039
nov	-0.0641	0.0440	-1.46	0.1465
dec	-0.0828	0.0452	-1.83	0.0681
rtemp	0.0104	0.0069	1.51	0.1322
cyear	-0.0165	0.0068	-2.44	0.0153
mc	0.0227	0.0606	0.37	0.7087
mc_cyear	0.0206	0.0109	1.89	0.0595
flow90	0.0670	0.0304	2.20	0.0286
AR1	-0.0986	0.0651	-1.52	0.0699

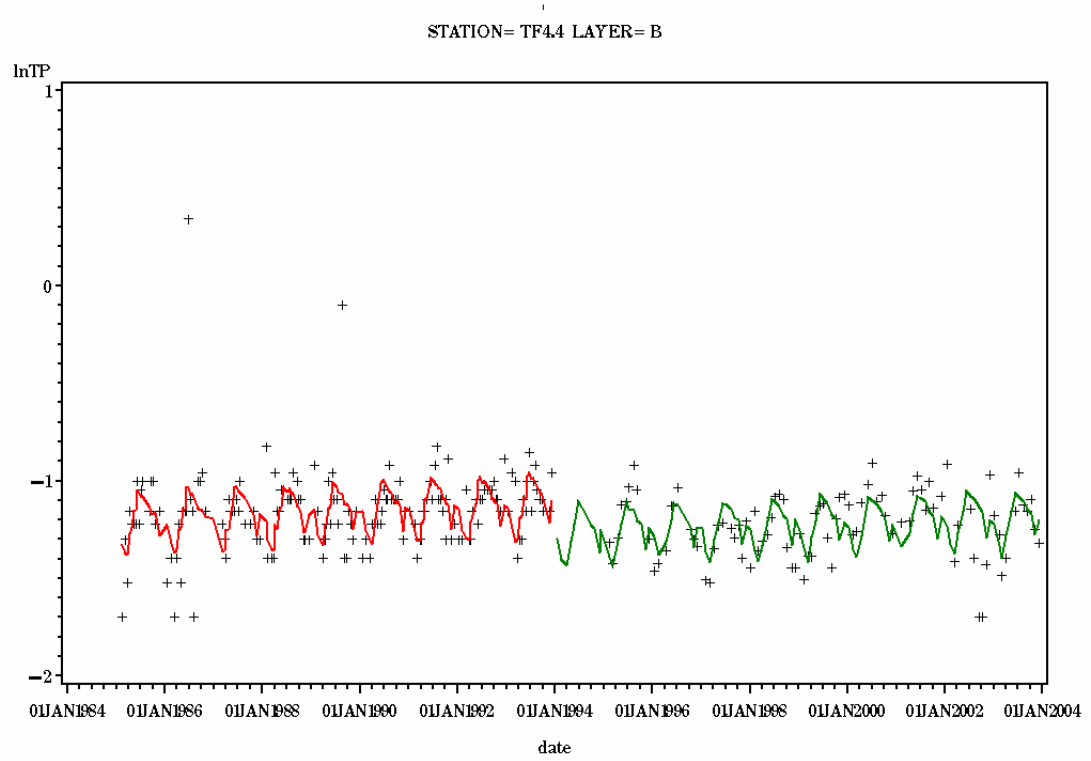
Root MSE = 0.1914 Total R-Square = 0.2407



Tributary	Station	Layer
York	TF4.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9909	0.0291	-34.05	<.0001
jan	-0.0059	0.0423	-0.14	0.8897
feb	-0.0708	0.0424	-1.67	0.0959
mar	-0.0622	0.0353	-1.76	0.0789
apr	-0.0787	0.0328	-2.40	0.0173
may	-0.0081	0.0354	-0.23	0.8197
jun	0.0629	0.0322	1.95	0.0522
jul	0.1295	0.0346	3.74	0.0002
aug	0.1327	0.0360	3.68	0.0003
sep	0.0023	0.0361	0.06	0.9502
oct	-0.0055	0.0339	-0.16	0.8723
nov	-0.1044	0.0422	-2.47	0.0141
dec	0.0082	0.0413	0.20	0.8425
rtemp	0.0003	0.0043	0.08	0.9388
cyear	0.0210	0.0054	3.91	0.0001
mc	-0.2142	0.0500	-4.28	<.0001
mc_cyear	-0.0095	0.0090	-1.06	0.2885
flow90	-0.0741	0.0277	-2.68	0.0079
AR1	0.0130	0.0661	0.20	0.4227

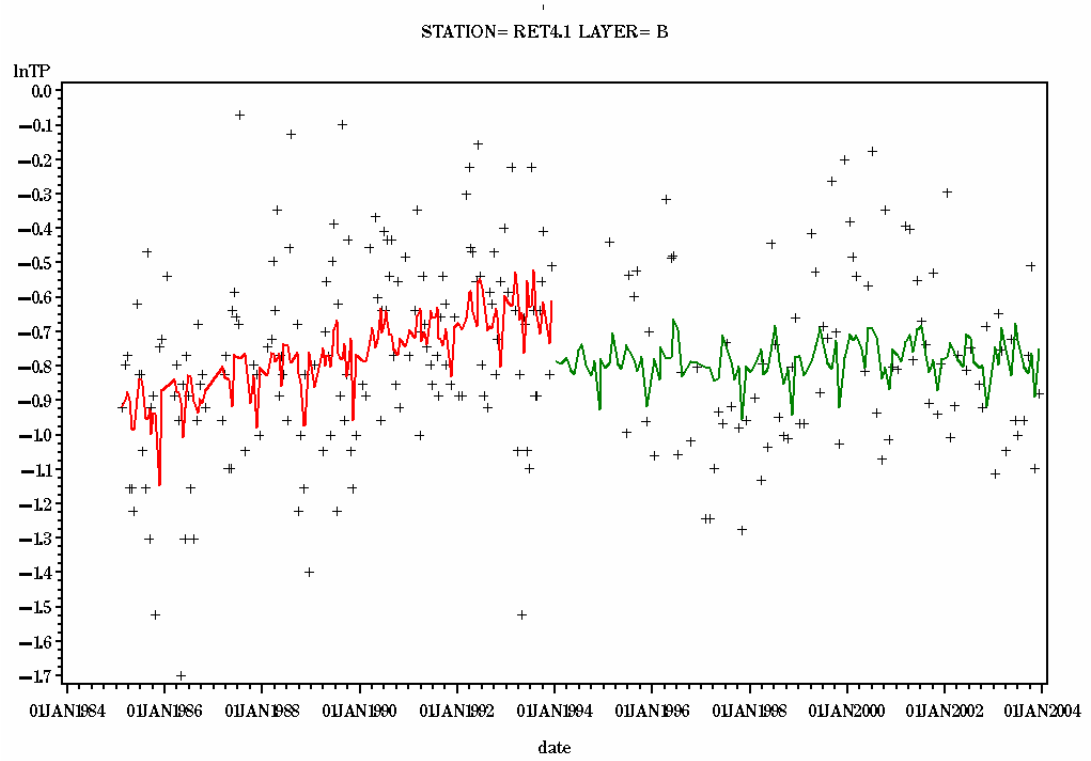
Root MSE = 0.1722 Total R-Square = 0.2576



Tributary	Station	Layer
York	TF4.4	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1108	0.0292	-38.01	<.0001
jan	-0.0198	0.0456	-0.43	0.6648
feb	-0.1253	0.0414	-3.03	0.0028
mar	-0.1766	0.0343	-5.15	<.0001
apr	-0.0673	0.0330	-2.04	0.0428
may	0.0341	0.0358	0.95	0.3413
jun	0.1440	0.0331	4.35	<.0001
jul	0.1223	0.0330	3.70	0.0003
aug	0.1002	0.0365	2.75	0.0064
sep	0.0478	0.0356	1.34	0.1810
oct	0.0265	0.0336	0.79	0.4321
nov	-0.0936	0.0425	-2.20	0.0286
dec	0.0077	0.0416	0.19	0.8534
rtemp	0.0037	0.0041	0.89	0.3748
cyear	0.0099	0.0054	1.84	0.0667
mc	-0.1540	0.0501	-3.07	0.0024
mc_cyear	-0.0025	0.0090	-0.28	0.7822
AR1	0.0101	0.0652	0.15	0.4390

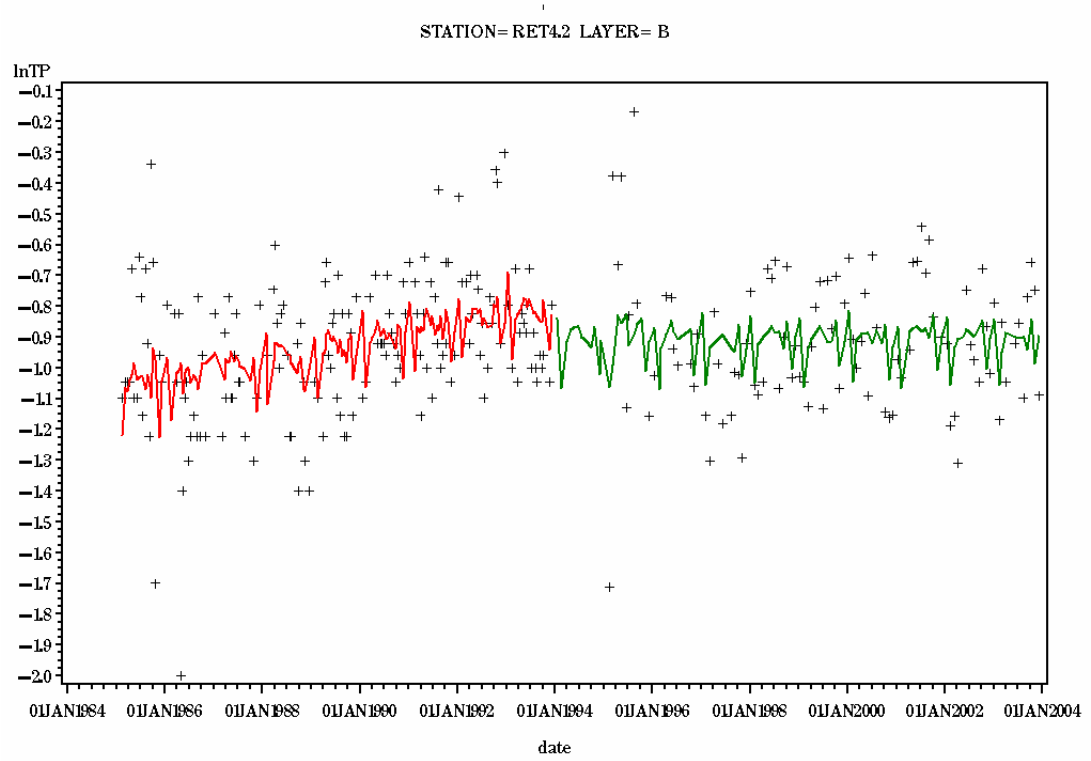
Root MSE = 0.1738 Total R-Square = 0.2950



Tributary	Station	Layer
York	RET4.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.5867	0.0504	-11.63	<.0001
jan	-0.0031	0.0713	-0.04	0.9656
feb	-0.0057	0.0686	-0.08	0.9340
mar	0.0381	0.0558	0.68	0.4962
apr	0.0072	0.0539	0.13	0.8932
may	-0.0243	0.0556	-0.44	0.6625
jun	0.0668	0.0511	1.31	0.1925
jul	0.0701	0.0526	1.33	0.1838
aug	0.0007	0.0536	0.01	0.9888
sep	-0.0362	0.0568	-0.64	0.5244
oct	-0.0024	0.0533	-0.04	0.9648
nov	-0.1350	0.0626	-2.16	0.0321
dec	0.0237	0.0639	0.37	0.7112
rtemp	-0.0052	0.0084	-0.62	0.5371
cyear	0.0383	0.0091	4.21	<.0001
mc	-0.2144	0.0893	-2.40	0.0172
mc_cyear	-0.0345	0.0155	-2.22	0.0273
AR1	-0.1178	0.0658	-1.79	0.0417

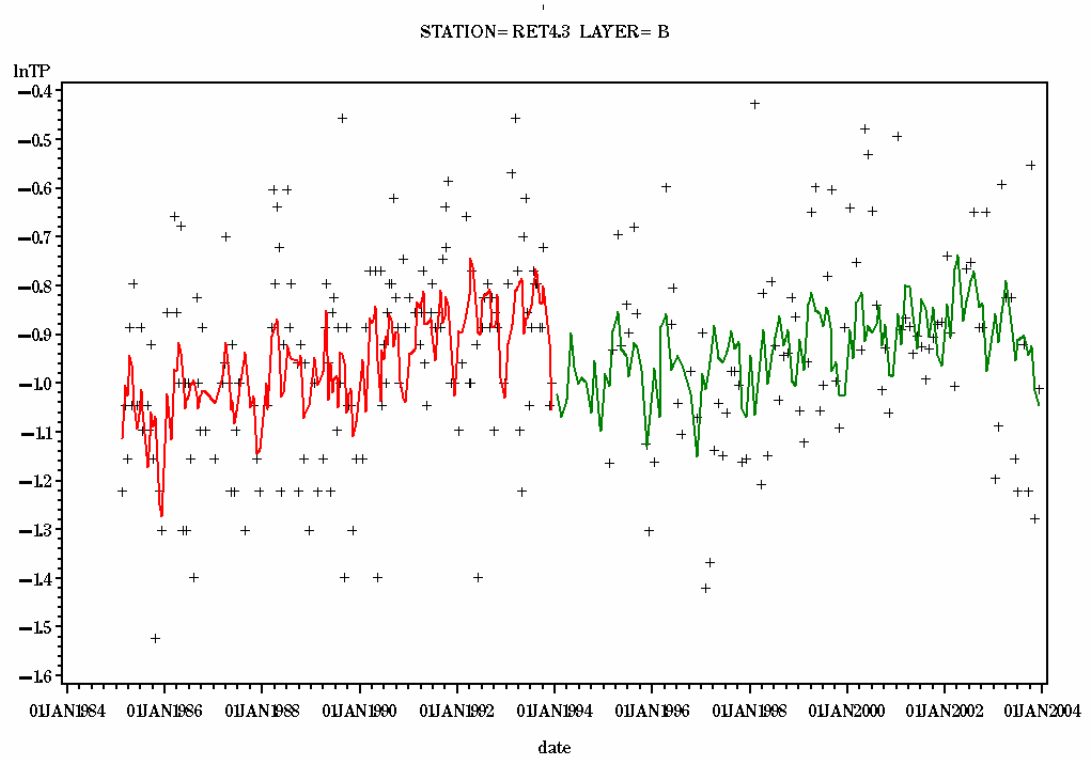
Root MSE = 0.2630 Total R-Square = 0.1319



Tributary	Station	Layer
York	RET4.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.7942	0.0408	-19.45	<.0001
jan	0.0771	0.0558	1.38	0.1682
feb	-0.1418	0.0541	-2.62	0.0093
mar	-0.0126	0.0463	-0.27	0.7854
apr	0.0286	0.0431	0.66	0.5076
may	0.0474	0.0488	0.97	0.3325
jun	0.0366	0.0425	0.86	0.3908
jul	0.0130	0.0440	0.29	0.7683
aug	0.0099	0.0447	0.22	0.8244
sep	-0.0128	0.0486	-0.26	0.7928
oct	0.0555	0.0439	1.26	0.2073
nov	-0.1006	0.0526	-1.91	0.0568
dec	-0.0003	0.0510	-0.01	0.9958
rtemp	0.0031	0.0071	0.44	0.6603
cyear	0.0303	0.0074	4.09	<.0001
mc	-0.1215	0.0705	-1.72	0.0864
mc_cyear	-0.0301	0.0125	-2.42	0.0163
AR1	-0.0910	0.0651	-1.40	0.0862

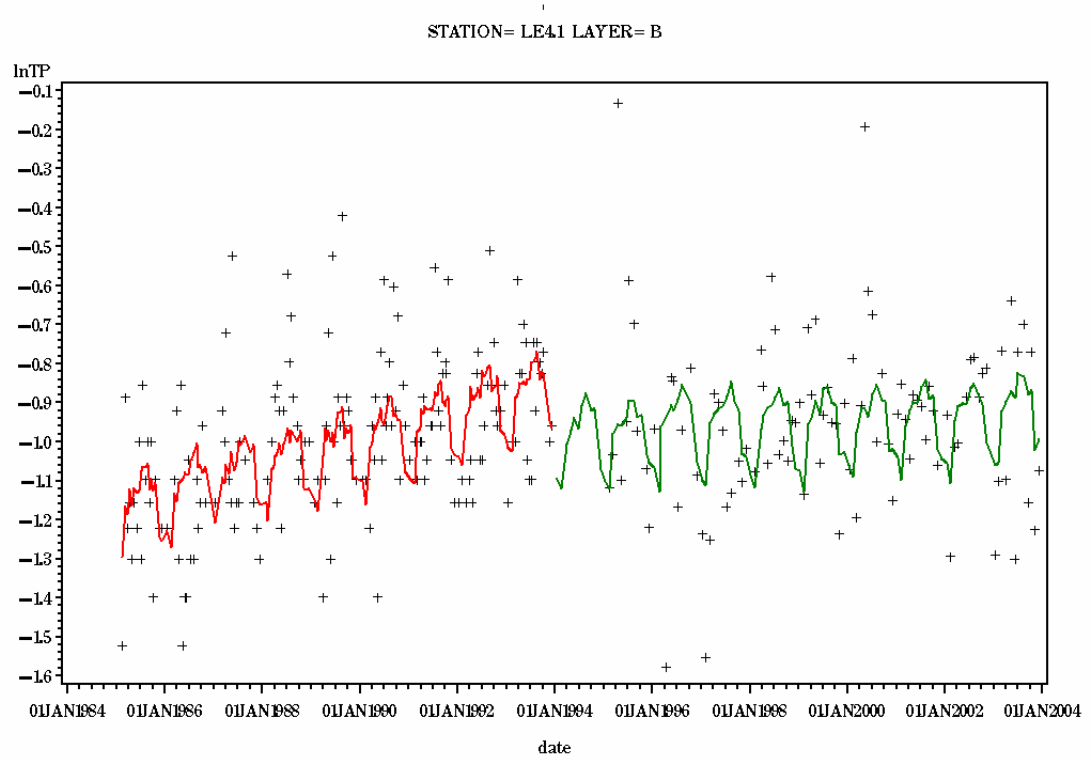
Root MSE = 0.2214 Total R-Square = 0.1383



Tributary	Station	Layer
York	RET4.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8233	0.0331	-24.89	<.0001
jan	-0.0027	0.0463	-0.06	0.9534
feb	-0.0569	0.0465	-1.22	0.2222
mar	0.0622	0.0367	1.70	0.0910
apr	0.1040	0.0361	2.88	0.0044
may	0.0140	0.0374	0.38	0.7078
jun	-0.0034	0.0355	-0.10	0.9236
jul	0.0279	0.0355	0.79	0.4326
aug	0.0527	0.0366	1.44	0.1517
sep	-0.0051	0.0383	-0.13	0.8936
oct	0.0209	0.0361	0.58	0.5620
nov	-0.0976	0.0436	-2.24	0.0262
dec	-0.1161	0.0448	-2.59	0.0102
rtemp	-0.0049	0.0057	-0.86	0.3918
cyear	0.0291	0.0060	4.85	<.0001
mc	-0.1670	0.0552	-3.02	0.0028
mc_cyear	-0.0178	0.0098	-1.81	0.0716
flow0	-0.0869	0.0280	-3.10	0.0022
AR1	-0.0540	0.0650	-0.83	0.2064

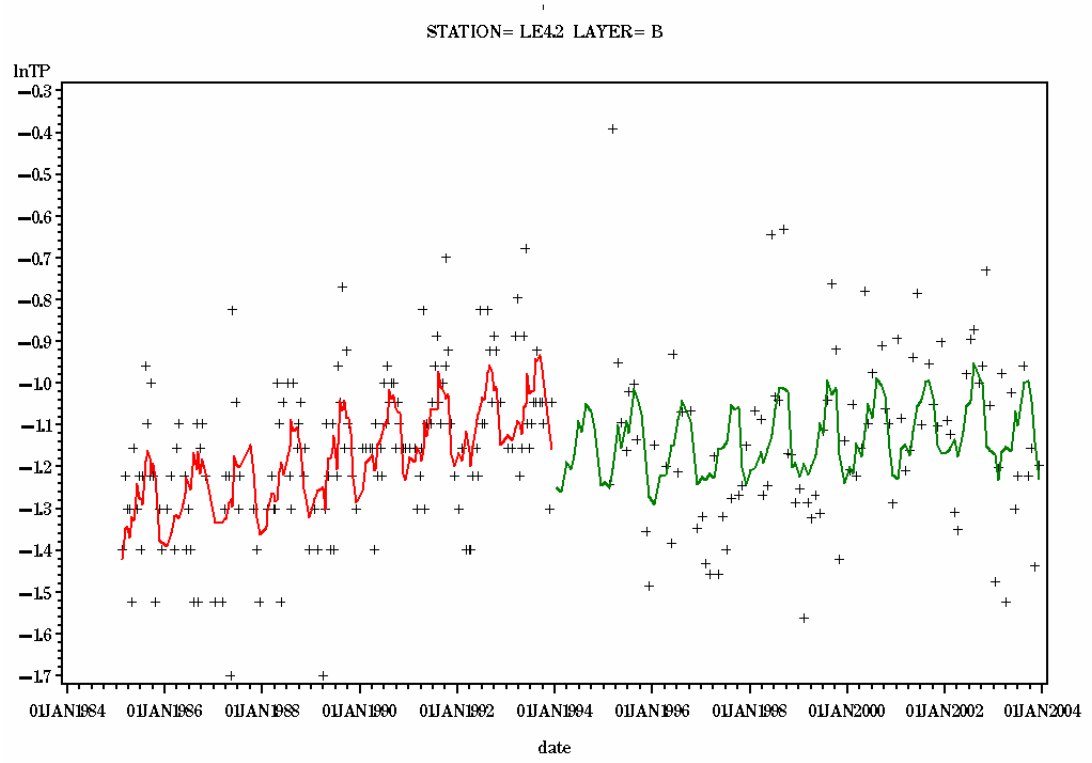
Root MSE = 0.1835 Total R-Square = 0.2154



Tributary	Station	Layer
York	LE4.1	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8467	0.0306	-27.63	<.0001
jan	-0.1157	0.0485	-2.38	0.0179
feb	-0.1481	0.0470	-3.15	0.0018
mar	-0.0087	0.0373	-0.23	0.8157
apr	0.0286	0.0353	0.81	0.4177
may	0.0439	0.0380	1.16	0.2492
jun	0.0396	0.0353	1.12	0.2624
jul	0.0829	0.0359	2.31	0.0216
aug	0.1036	0.0359	2.89	0.0042
sep	0.0576	0.0396	1.45	0.1472
oct	0.0584	0.0373	1.57	0.1182
nov	-0.0645	0.0441	-1.46	0.1454
dec	-0.0778	0.0471	-1.65	0.0998
rtemp	-0.0049	0.0059	-0.83	0.4054
cyear	0.0354	0.0056	6.35	<.0001
mc	-0.1381	0.0524	-2.64	0.0089
mc_cyear	-0.0298	0.0093	-3.22	0.0015
AR1	0.0474	0.0642	0.74	0.2330

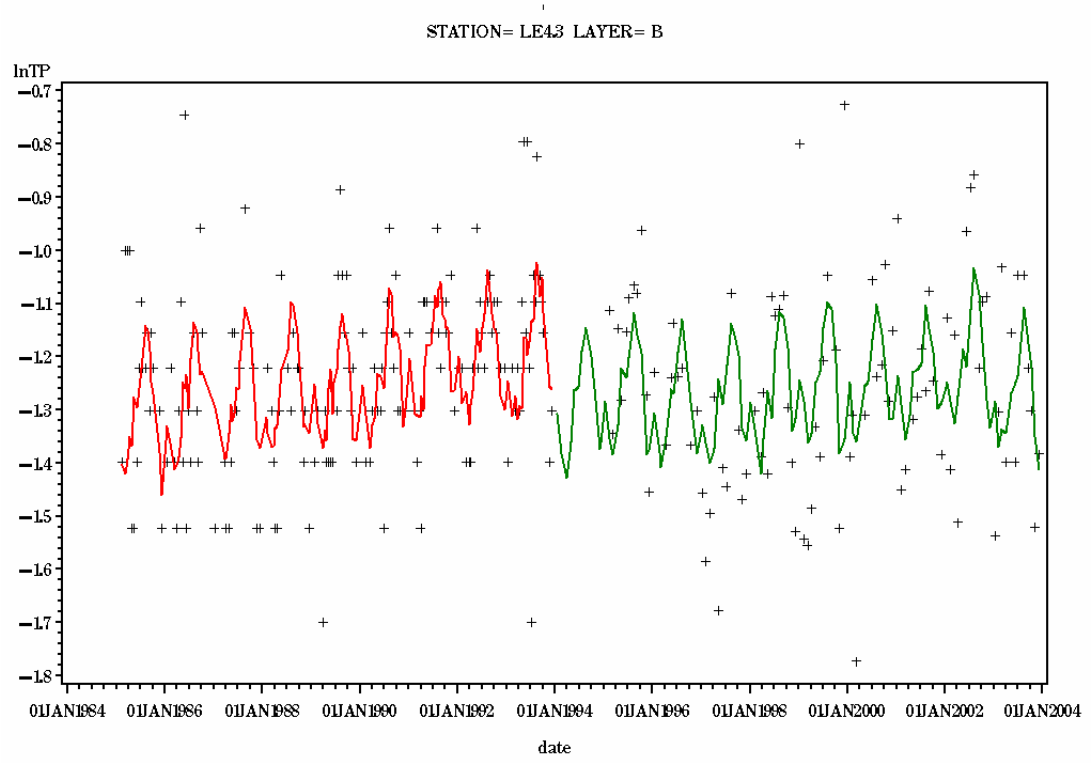
Root MSE = 0.1910 Total R-Square = 0.2346



Tributary	Station	Layer
York	LE4.2	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0276	0.0323	-31.82	<.0001
jan	-0.0879	0.0426	-2.06	0.0404
feb	-0.0791	0.0401	-1.97	0.0498
mar	-0.0430	0.0338	-1.27	0.2050
apr	-0.0529	0.0333	-1.59	0.1132
may	-0.0045	0.0356	-0.13	0.8987
jun	0.0449	0.0328	1.37	0.1726
jul	0.0422	0.0333	1.27	0.2064
aug	0.1241	0.0353	3.51	0.0005
sep	0.1109	0.0366	3.03	0.0027
oct	0.0780	0.0338	2.31	0.0217
nov	-0.0457	0.0392	-1.17	0.2449
dec	-0.0870	0.0402	-2.17	0.0312
rtemp	0.0072	0.0057	1.25	0.2117
cyear	0.0320	0.0059	5.46	<.0001
mc	-0.1384	0.0542	-2.55	0.0113
mc_cyear	-0.0248	0.0096	-2.59	0.0101
AR1	-0.1115	0.0640	-1.74	0.0459

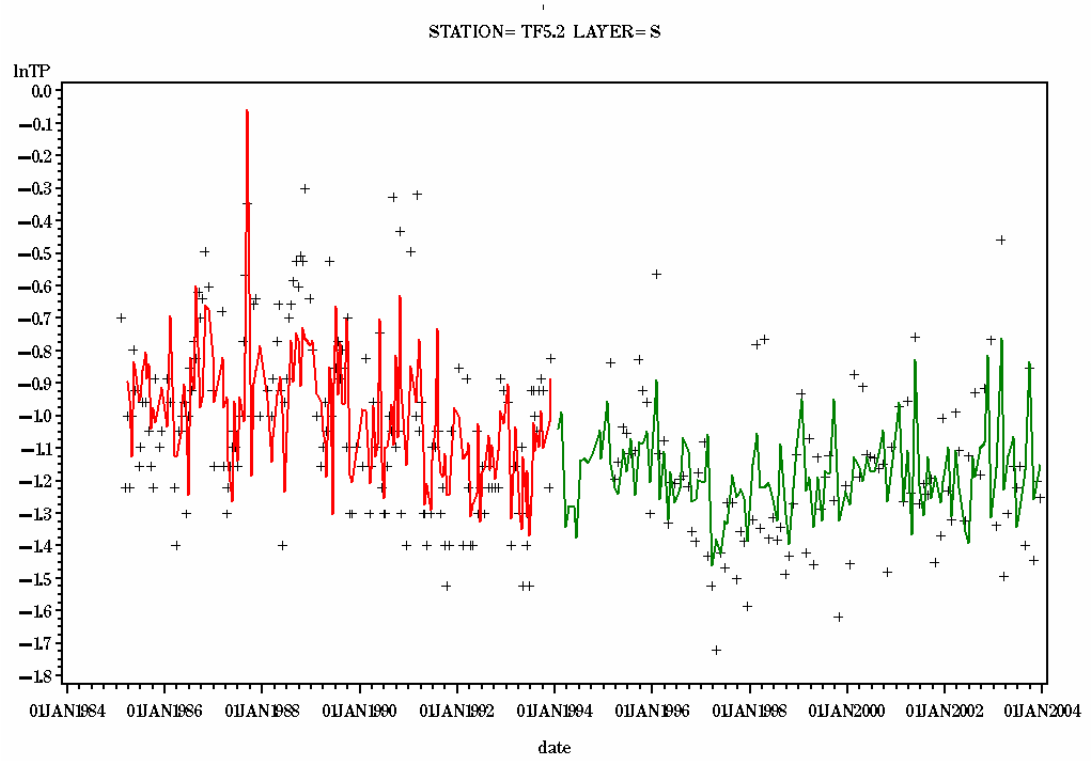
Root MSE = 0.1700 Total R-Square = 0.2769



Tributary	Station	Layer
York	LE4.3	B

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1723	0.0288	-40.65	<.0001
jan	-0.0155	0.0406	-0.38	0.7024
feb	-0.0768	0.0381	-2.01	0.0451
mar	-0.1044	0.0322	-3.25	0.0013
apr	-0.0746	0.0318	-2.34	0.0200
may	0.0234	0.0334	0.70	0.4840
jun	0.0157	0.0329	0.48	0.6327
jul	0.0832	0.0322	2.58	0.0104
aug	0.1520	0.0311	4.88	<.0001
sep	0.1094	0.0343	3.19	0.0016
oct	0.0493	0.0328	1.50	0.1347
nov	-0.0749	0.0382	-1.96	0.0511
dec	-0.0868	0.0381	-2.28	0.0237
rtemp	0.0026	0.0056	0.47	0.6413
cyear	0.0162	0.0053	3.04	0.0026
mc	-0.1132	0.0480	-2.36	0.0193
mc_cyear	-0.0123	0.0086	-1.43	0.1532
flow30	-0.0563	0.0253	-2.22	0.0272
AR1	-0.0552	0.0656	-0.84	0.2033

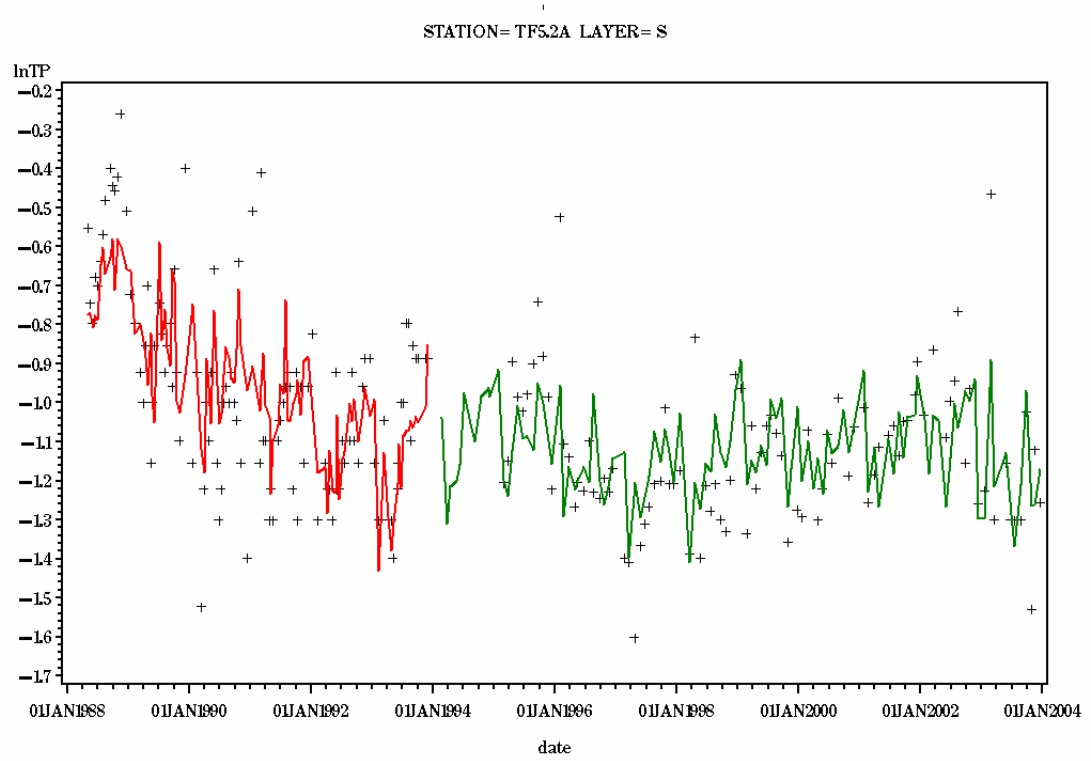
Root MSE = 0.1610 Total R-Square = 0.2700



Tributary	Station	Layer
James	TF5.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1586	0.0523	-22.17	<.0001
jan	0.0674	0.0474	1.42	0.1564
feb	0.0137	0.0464	0.30	0.7670
mar	-0.0531	0.0409	-1.30	0.1948
apr	-0.0652	0.0411	-1.59	0.1142
may	-0.0333	0.0412	-0.81	0.4199
jun	-0.0926	0.0403	-2.30	0.0225
jul	-0.0039	0.0419	-0.09	0.9268
aug	0.0452	0.0417	1.08	0.2796
sep	0.0510	0.0415	1.23	0.2197
oct	-0.0225	0.0405	-0.56	0.5786
nov	0.0795	0.0468	1.70	0.0907
dec	0.0137	0.0460	0.30	0.7657
rtemp	-0.0015	0.0043	-0.36	0.7215
cyear	-0.0358	0.0094	-3.79	0.0002
mc	0.0126	0.0831	0.15	0.8792
mc_cyear	0.0276	0.0151	1.84	0.0677
flow0	0.3712	0.0411	9.03	<.0001
flow30	-0.1807	0.0380	-4.76	<.0001
flow10	-0.1070	0.0438	-2.44	0.0153
flow70	-0.0433	0.0400	-1.08	0.2800
AR1	-0.3711	0.0594	-6.24	<.0001

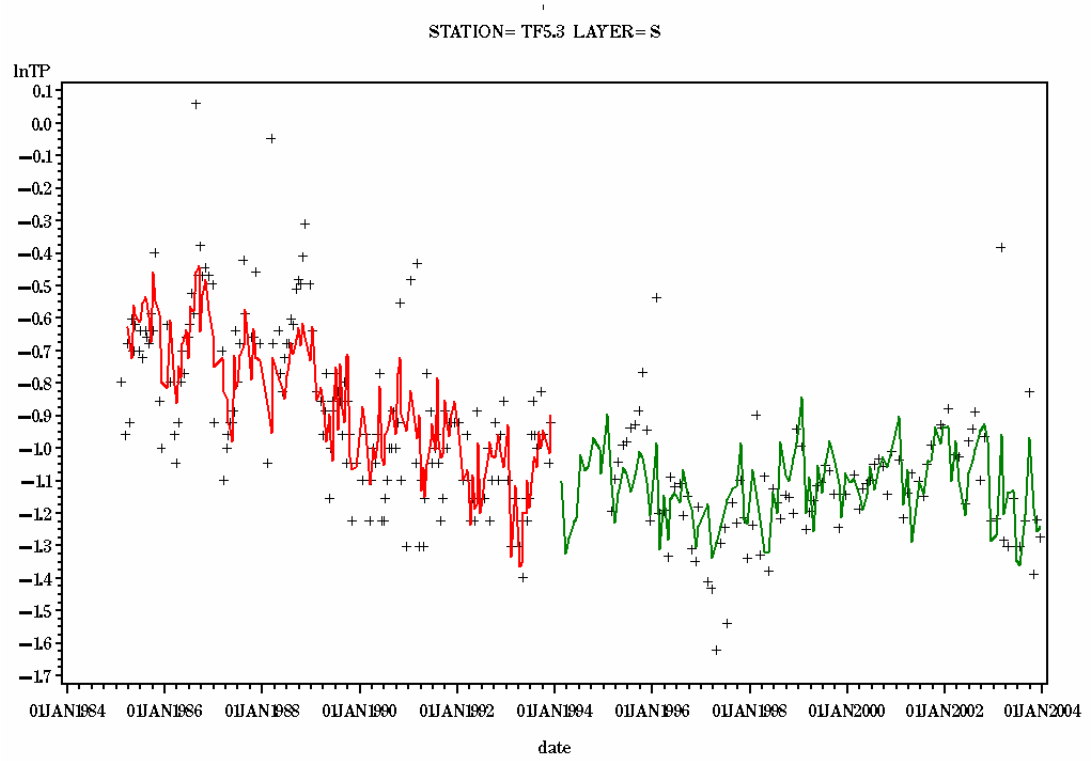
Root MSE = 0.1928 Total R-Square = 0.5100



Tributary	Station	Layer
James	TF5.2A	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.2339	0.0504	-24.50	<.0001
jan	0.0551	0.0483	1.14	0.2560
feb	-0.0616	0.0498	-1.24	0.2180
mar	-0.1005	0.0430	-2.34	0.0206
apr	-0.0259	0.0434	-0.60	0.5522
may	-0.0700	0.0403	-1.74	0.0843
jun	-0.0271	0.0400	-0.68	0.4993
jul	0.0243	0.0398	0.61	0.5421
aug	0.0495	0.0397	1.25	0.2139
sep	0.0470	0.0407	1.15	0.2497
oct	0.0142	0.0398	0.36	0.7218
nov	0.0679	0.0469	1.45	0.1496
dec	0.0272	0.0449	0.61	0.5457
rtemp	0.0038	0.0054	0.71	0.4813
cyear	-0.0838	0.0133	-6.31	<.0001
mc	0.1693	0.0704	2.40	0.0172
mc_cyear	0.0704	0.0161	4.37	<.0001
flow30	-0.1653	0.0427	-3.87	0.0001
flow0	0.2434	0.0478	5.09	<.0001
flow10	-0.1344	0.0482	-2.79	0.0058
flow40	-0.0803	0.0471	-1.70	0.0900
AR1	-0.2255	0.0724	-3.11	0.0020

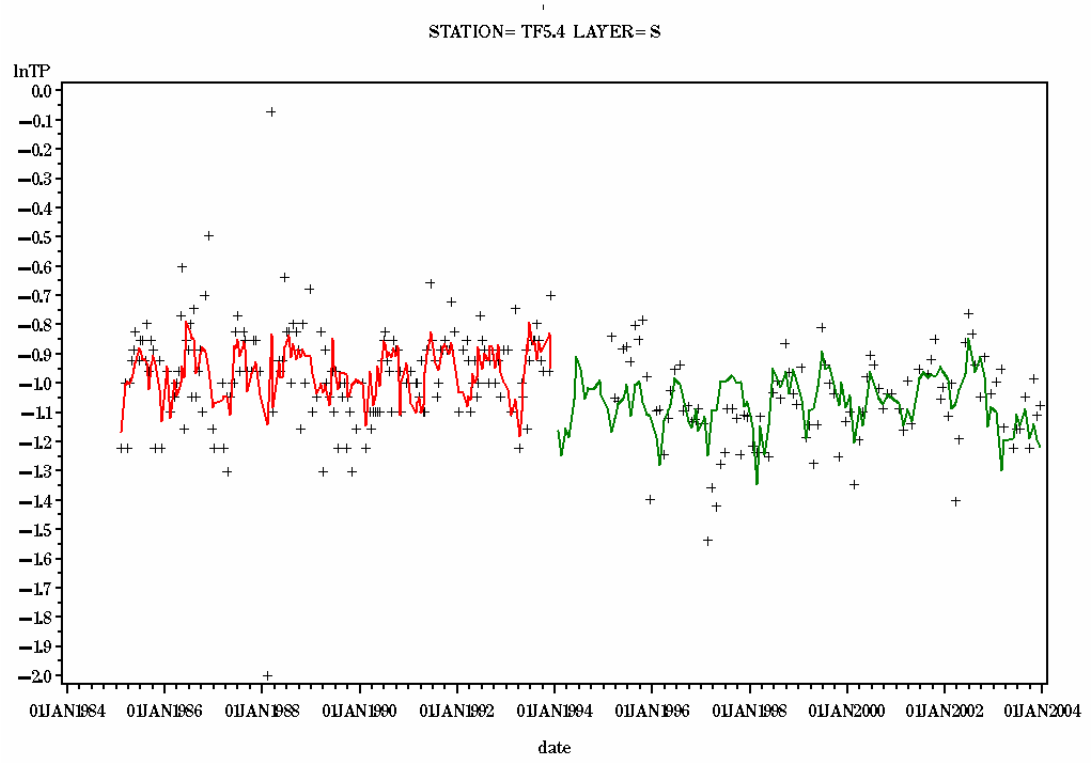
Root MSE = 0.1741 Total R-Square = 0.5406



Tributary	Station	Layer
James	TF5.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1573	0.0341	-33.91	<.0001
jan	0.0836	0.0426	1.96	0.0509
feb	-0.0513	0.0400	-1.28	0.2006
mar	-0.0749	0.0326	-2.30	0.0226
apr	-0.0954	0.0332	-2.87	0.0044
may	-0.0454	0.0327	-1.39	0.1660
jun	-0.0268	0.0323	-0.83	0.4081
jul	-0.0048	0.0328	-0.15	0.8845
aug	0.0601	0.0328	1.83	0.0680
sep	0.0603	0.0335	1.80	0.0728
oct	0.0669	0.0331	2.02	0.0440
nov	0.0447	0.0394	1.14	0.2574
dec	-0.0171	0.0375	-0.45	0.6497
rtemp	0.0069	0.0040	1.73	0.0843
cyear	-0.0631	0.0062	-10.19	<.0001
mc	0.0733	0.0548	1.34	0.1827
mc_cyear	0.0547	0.0100	5.49	<.0001
flow30	-0.1452	0.0324	-4.49	<.0001
flow10	-0.1576	0.0383	-4.11	<.0001
flow0	0.2046	0.0412	4.96	<.0001
flow70	-0.0835	0.0339	-2.46	0.0144
AR1	-0.1830	0.0631	-2.90	0.0034

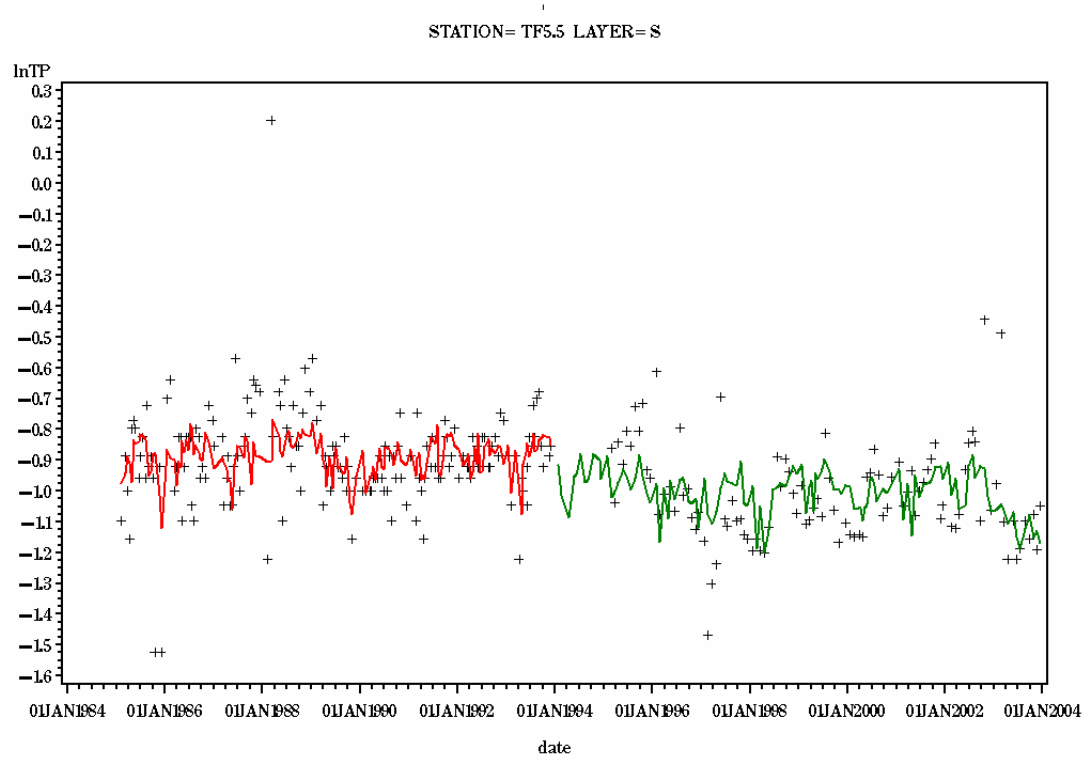
Root MSE = 0.1622 Total R-Square = 0.6506



Tributary	Station	Layer
James	TF5.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9501	0.0218	-43.66	<.0001
jan	-0.0211	0.0365	-0.58	0.5650
feb	-0.1435	0.0347	-4.13	<.0001
mar	-0.0453	0.0269	-1.69	0.0930
apr	-0.0814	0.0282	-2.89	0.0042
may	-0.0031	0.0266	-0.11	0.9086
jun	0.0984	0.0261	3.77	0.0002
jul	0.0661	0.0277	2.39	0.0177
aug	0.0443	0.0268	1.66	0.0992
sep	0.0428	0.0277	1.54	0.1240
oct	0.0270	0.0269	1.00	0.3171
nov	0.0343	0.0354	0.97	0.3330
dec	-0.0186	0.0345	-0.54	0.5912
rtemp	0.0039	0.0036	1.10	0.2741
cyear	0.0037	0.0039	0.93	0.3524
mc	-0.1083	0.0354	-3.06	0.0025
mc_cyear	-0.0065	0.0064	-1.02	0.3103
flow10	-0.0936	0.0307	-3.05	0.0026
flow0	-0.0841	0.0317	-2.65	0.0085
AR1	0.1489	0.0628	2.37	0.0122

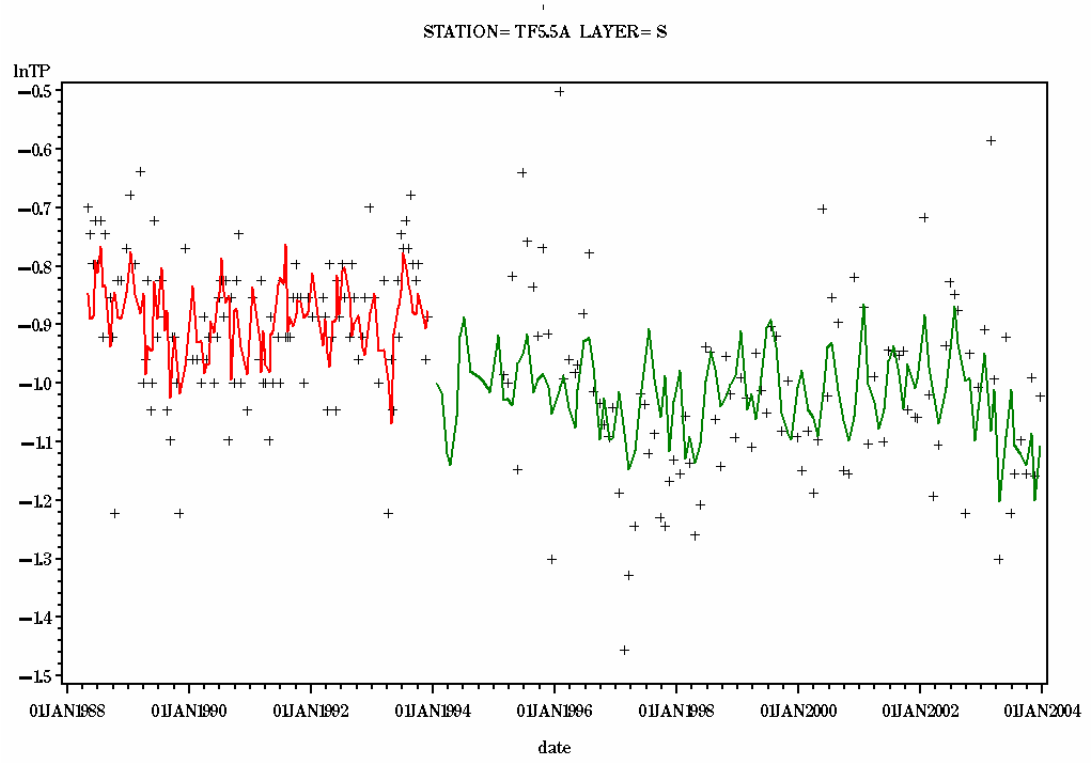
Root MSE = 0.1461 Total R-Square = 0.3426



Tributary	Station	Layer
James	TF5.5	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8682	0.0282	-30.75	<.0001
jan	0.0436	0.0387	1.13	0.2609
feb	-0.0619	0.0354	-1.75	0.0815
mar	-0.0166	0.0296	-0.56	0.5745
apr	-0.0565	0.0309	-1.83	0.0690
may	-0.0007	0.0297	-0.02	0.9819
jun	0.0168	0.0293	0.57	0.5669
jul	0.0379	0.0301	1.26	0.2098
aug	0.0037	0.0302	0.12	0.9025
sep	0.0075	0.0301	0.25	0.8040
oct	0.0243	0.0296	0.82	0.4127
nov	0.0192	0.0365	0.53	0.5998
dec	-0.0172	0.0353	-0.49	0.6262
rtemp	-0.0050	0.0042	-1.18	0.2375
cyear	0.0041	0.0050	0.82	0.4150
mc	-0.0840	0.0454	-1.85	0.0658
mc_cyear	-0.0162	0.0083	-1.96	0.0513
flow30	-0.1058	0.0300	-3.53	0.0005
flow10	-0.0811	0.0309	-2.63	0.0092
AR1	-0.0744	0.0632	-1.18	0.1242

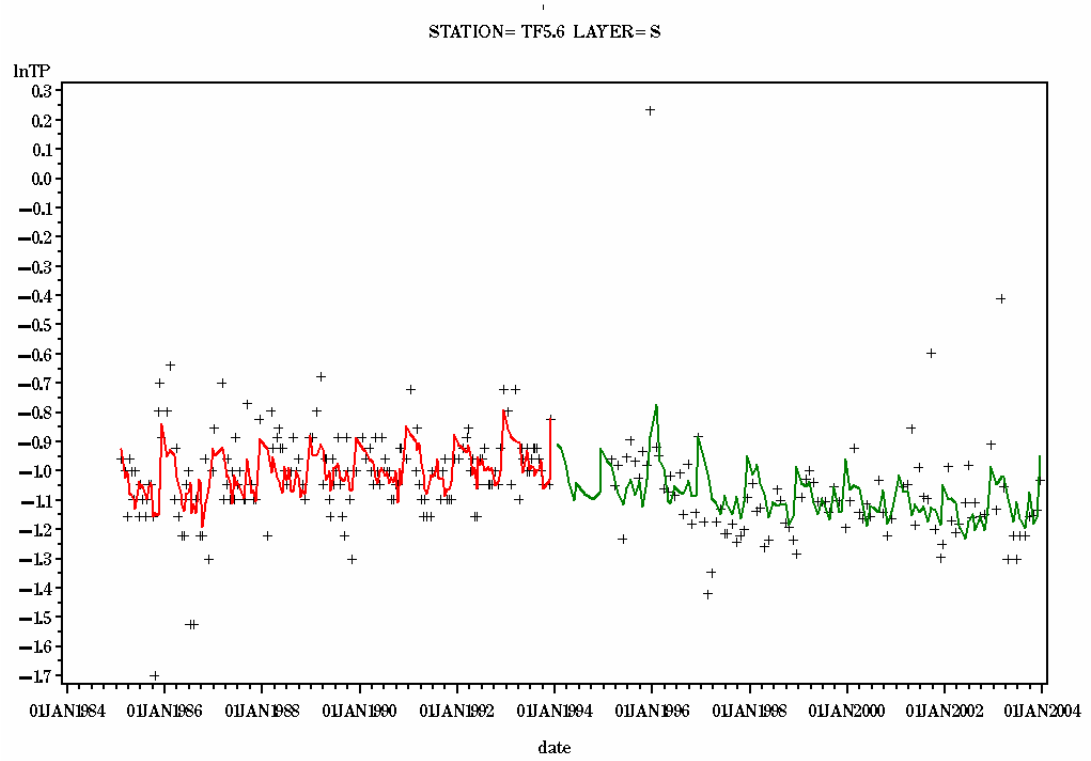
Root MSE = 0.1531 Total R-Square = 0.2662



Tributary	Station	Layer
James	TF5.5A	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8872	0.0321	-27.60	<.0001
jan	0.0731	0.0332	2.20	0.0291
feb	-0.0310	0.0322	-0.96	0.3374
mar	-0.0372	0.0293	-1.27	0.2051
apr	-0.0768	0.0296	-2.60	0.0101
may	-0.0121	0.0278	-0.44	0.6624
jun	0.0597	0.0278	2.15	0.0331
jul	0.0888	0.0281	3.16	0.0018
aug	0.0248	0.0281	0.88	0.3789
sep	-0.0302	0.0282	-1.07	0.2846
oct	0.0062	0.0281	0.22	0.8257
nov	-0.0445	0.0323	-1.38	0.1701
dec	-0.0206	0.0324	-0.64	0.5251
rtemp	-0.0011	0.0041	-0.26	0.7980
cyear	-0.0002	0.0085	-0.02	0.9817
mc	-0.1088	0.0447	-2.43	0.0159
mc_cyear	-0.0055	0.0102	-0.54	0.5870
flow50	-0.0771	0.0278	-2.77	0.0061
flow10	-0.0605	0.0281	-2.15	0.0327
AR1	-0.1230	0.0713	-1.73	0.0473

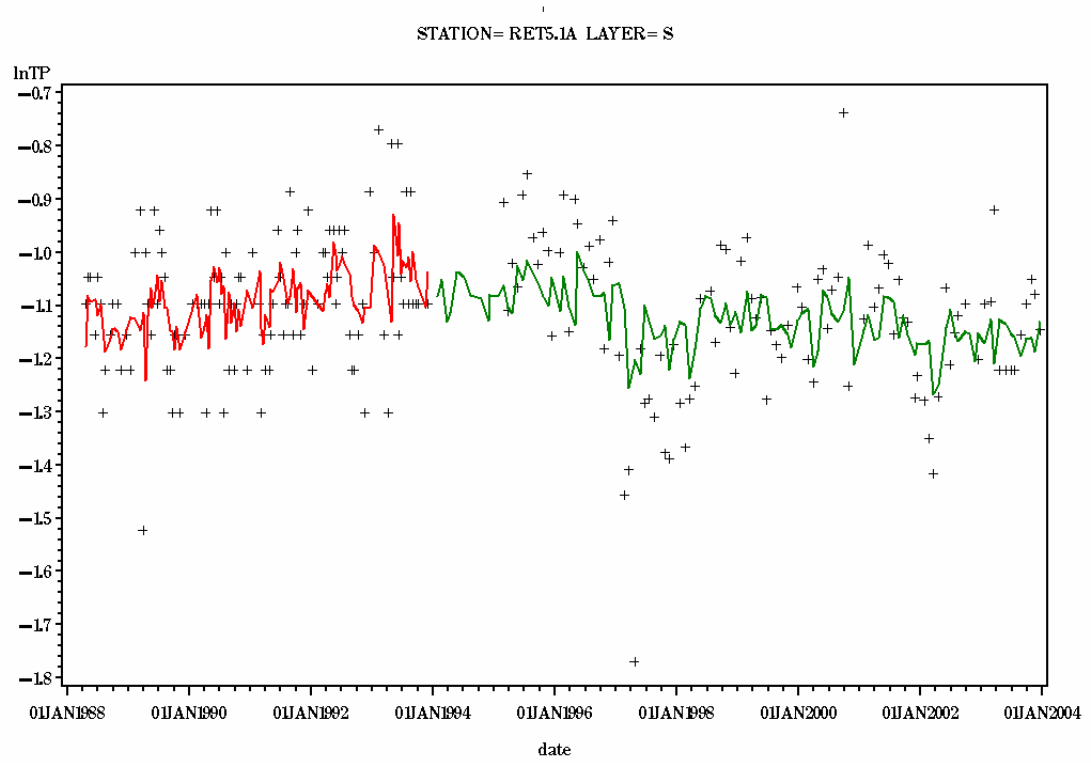
Root MSE = 0.1269 Total R-Square = 0.3639



Tributary	Station	Layer
James	TF5.6	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9411	0.0294	-31.98	<.0001
jan	0.0793	0.0376	2.11	0.0359
feb	0.0623	0.0344	1.81	0.0715
mar	0.0399	0.0294	1.36	0.1754
apr	-0.0111	0.0295	-0.38	0.7070
may	-0.0658	0.0291	-2.26	0.0246
jun	-0.0145	0.0293	-0.50	0.6206
jul	-0.0208	0.0305	-0.68	0.4952
aug	-0.0530	0.0299	-1.77	0.0778
sep	-0.0102	0.0303	-0.34	0.7370
oct	-0.0812	0.0298	-2.72	0.0070
nov	-0.0522	0.0339	-1.54	0.1249
dec	0.1274	0.0343	3.71	0.0003
rtemp	-0.0068	0.0045	-1.52	0.1305
cyear	0.0112	0.0053	2.14	0.0336
mc	-0.0817	0.0473	-1.73	0.0851
mc_cyear	-0.0235	0.0084	-2.79	0.0056
flow0	0.0480	0.0277	1.73	0.0846
AR1	-0.1361	0.0624	-2.18	0.0186

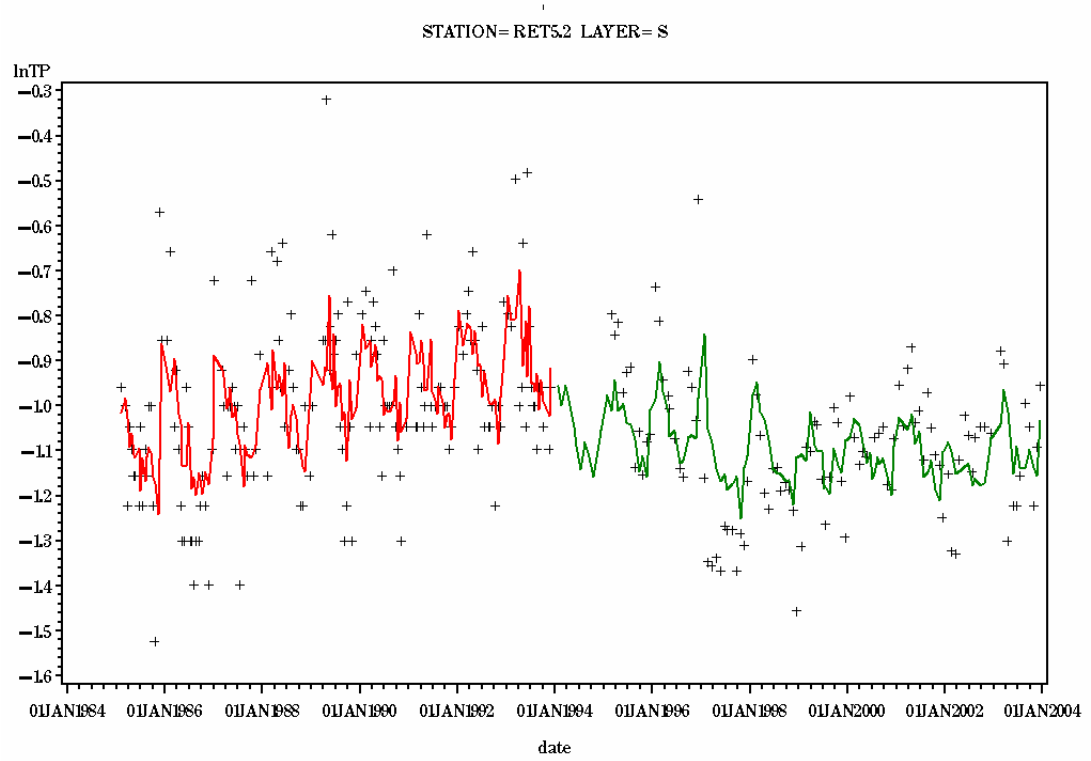
Root MSE = 0.1500 Total R-Square = 0.2445



Tributary	Station	Layer
James	RET5.1A	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0153	0.0384	-26.41	<.0001
jan	0.0074	0.0352	0.21	0.8349
feb	0.0263	0.0340	0.77	0.4402
mar	-0.0512	0.0306	-1.68	0.0954
apr	-0.0340	0.0294	-1.16	0.2489
may	0.0381	0.0295	1.29	0.1974
jun	0.0391	0.0294	1.33	0.1853
jul	0.0333	0.0295	1.13	0.2609
aug	-0.0020	0.0295	-0.07	0.9469
sep	0.0017	0.0295	0.06	0.9543
oct	-0.0102	0.0306	-0.33	0.7406
nov	-0.0502	0.0343	-1.46	0.1452
dec	0.0017	0.0328	0.05	0.9586
rtemp	-0.0010	0.0043	-0.22	0.8230
cyear	0.0218	0.0101	2.16	0.0319
mc	-0.0635	0.0532	-1.19	0.2340
mc_cyear	-0.0319	0.0120	-2.66	0.0084
AR1	-0.2521	0.0698	-3.61	0.0006

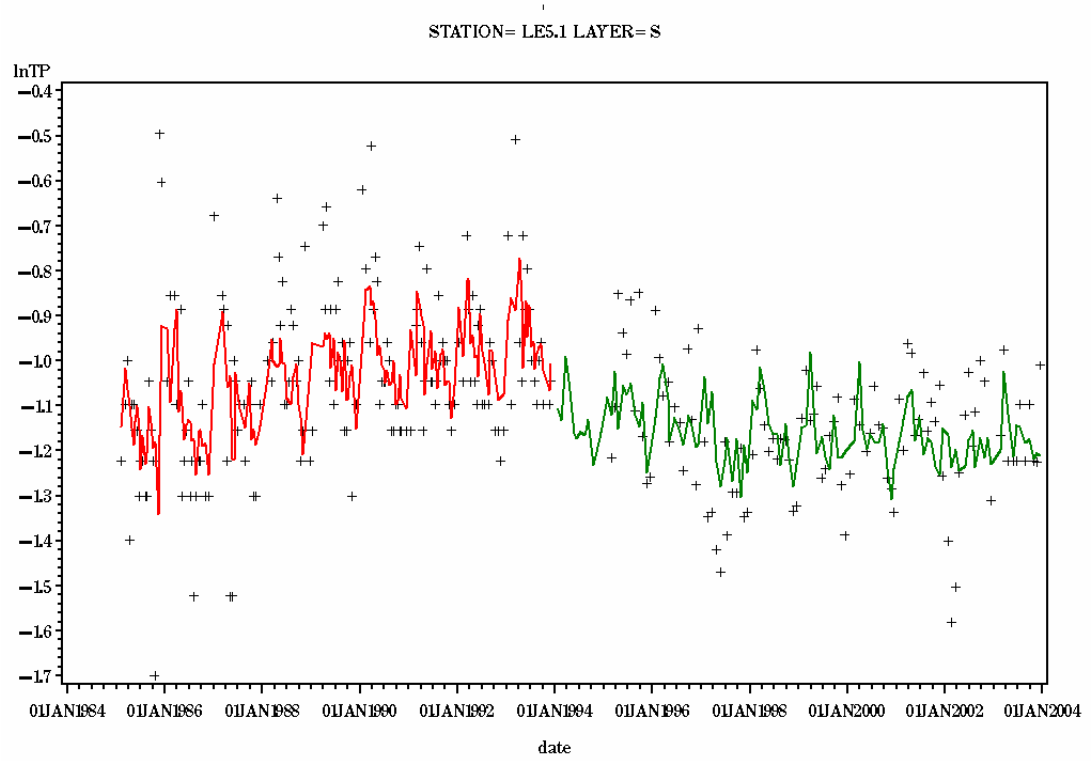
Root MSE = 0.1291 Total R-Square = 0.1822



Tributary	Station	Layer
James	RET5.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8640	0.0352	-24.52	<.0001
jan	0.0996	0.0393	2.53	0.0119
feb	0.0731	0.0359	2.04	0.0428
mar	0.0716	0.0312	2.29	0.0227
apr	0.0498	0.0311	1.60	0.1107
may	0.0062	0.0306	0.20	0.8392
jun	0.0012	0.0315	0.04	0.9700
jul	-0.0570	0.0315	-1.81	0.0719
aug	-0.0488	0.0313	-1.56	0.1200
sep	-0.0486	0.0314	-1.55	0.1232
oct	-0.0818	0.0314	-2.60	0.0098
nov	-0.0925	0.0347	-2.66	0.0083
dec	0.0272	0.0349	0.78	0.4376
rtemp	-0.0019	0.0046	-0.40	0.6863
cyear	0.0240	0.0063	3.83	0.0002
mc	-0.2035	0.0566	-3.60	0.0004
mc_cyear	-0.0285	0.0102	-2.80	0.0054
flow10	0.0726	0.0295	2.46	0.0146
AR1	-0.2707	0.0606	-4.46	<.0001

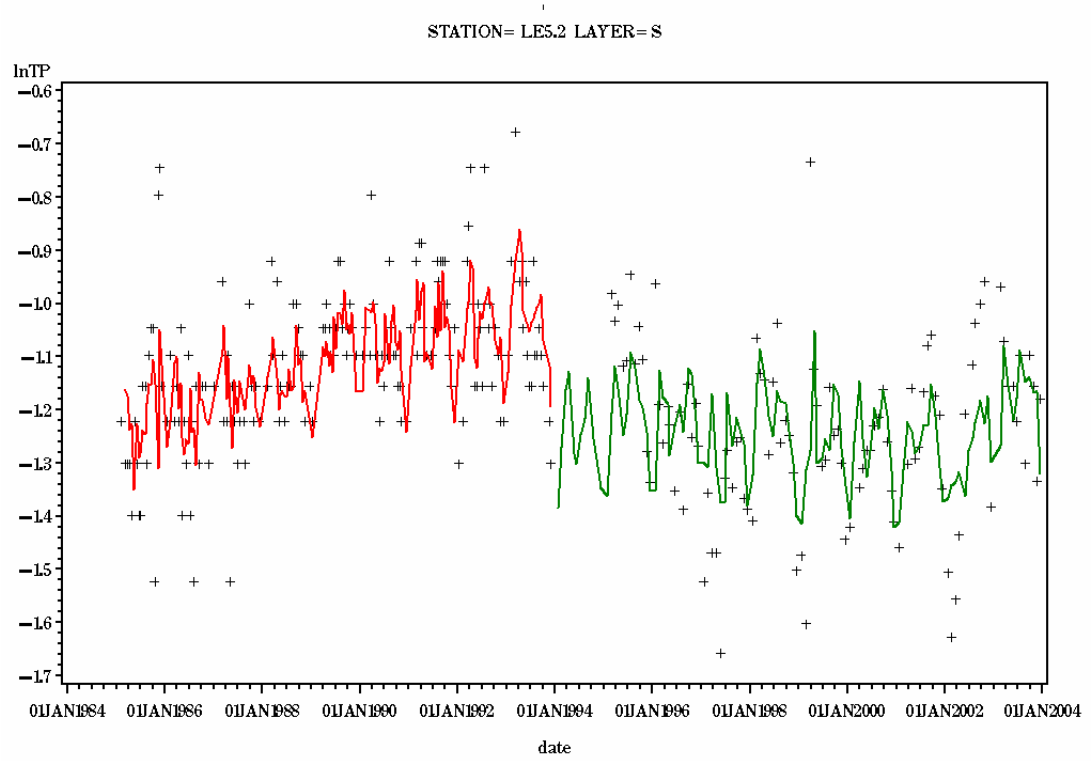
Root MSE = 0.1526 Total R-Square = 0.3553



Tributary	Station	Layer
James	LE5.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9207	0.0361	-25.50	<.0001
jan	0.0537	0.0374	1.44	0.1519
feb	0.0312	0.0354	0.88	0.3780
mar	0.1242	0.0310	4.01	<.0001
apr	0.0552	0.0315	1.75	0.0813
may	-0.0173	0.0304	-0.57	0.5691
jun	0.0028	0.0307	0.09	0.9265
jul	-0.0113	0.0313	-0.36	0.7177
aug	-0.0456	0.0311	-1.46	0.1442
sep	0.0018	0.0313	0.06	0.9548
oct	-0.0667	0.0309	-2.16	0.0317
nov	-0.0892	0.0341	-2.62	0.0094
dec	-0.0387	0.0354	-1.09	0.2757
rtemp	0.0073	0.0047	1.54	0.1239
cyear	0.0234	0.0064	3.66	0.0003
mc	-0.2223	0.0583	-3.81	0.0002
mc_cyear	-0.0271	0.0104	-2.60	0.0099
flow10	0.0682	0.0288	2.37	0.0186
AR1	-0.3057	0.0599	-5.11	<.0001

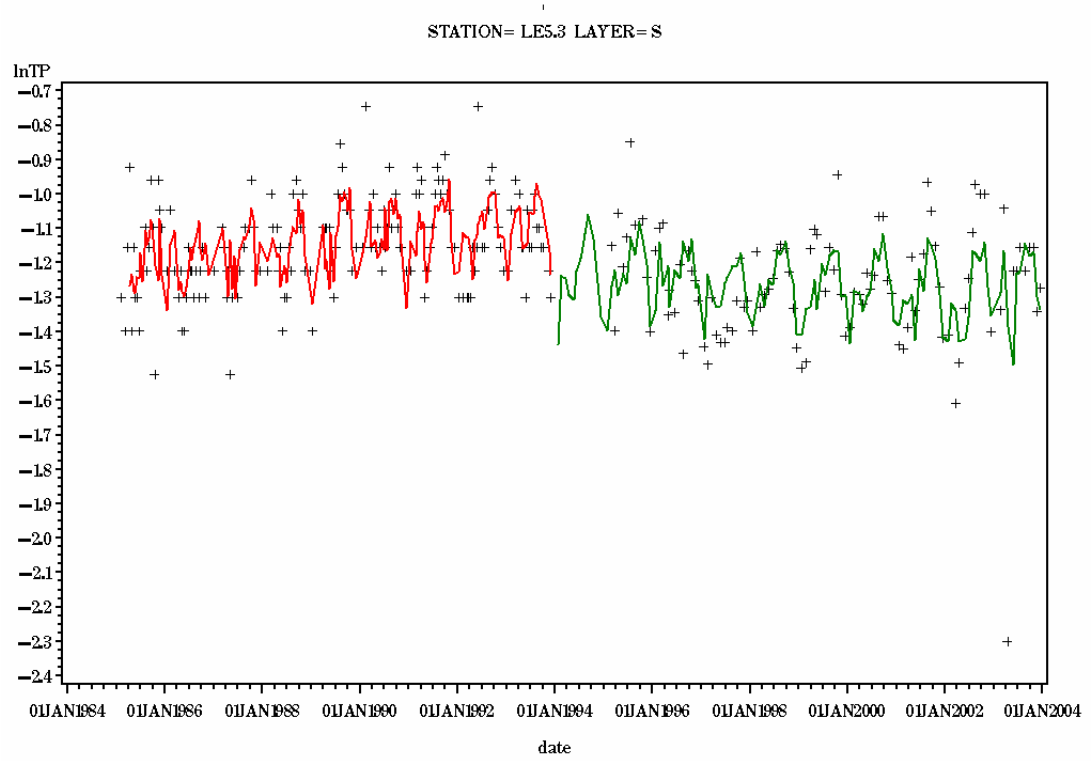
Root MSE = 0.1501 Total R-Square = 0.3766



Tributary	Station	Layer
James	LE5.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0026	0.0295	-33.99	<.0001
jan	-0.0989	0.0325	-3.04	0.0026
feb	-0.0052	0.0326	-0.16	0.8737
mar	0.0704	0.0258	2.73	0.0069
apr	0.0462	0.0258	1.79	0.0742
may	-0.0345	0.0253	-1.36	0.1748
jun	-0.0240	0.0258	-0.93	0.3527
jul	0.0414	0.0260	1.59	0.1136
aug	0.0203	0.0259	0.79	0.4326
sep	0.0710	0.0260	2.73	0.0068
oct	0.0261	0.0256	1.02	0.3097
nov	-0.0195	0.0282	-0.69	0.4899
dec	-0.0933	0.0295	-3.16	0.0018
rtemp	0.0040	0.0040	1.02	0.3107
cyear	0.0245	0.0053	4.66	<.0001
mc	-0.2528	0.0476	-5.31	<.0001
mc_cyear	-0.0213	0.0087	-2.46	0.0145
flow10	0.0613	0.0248	2.47	0.0141
flow40	0.0791	0.0271	2.92	0.0038
AR1	-0.2880	0.0606	-4.75	<.0001

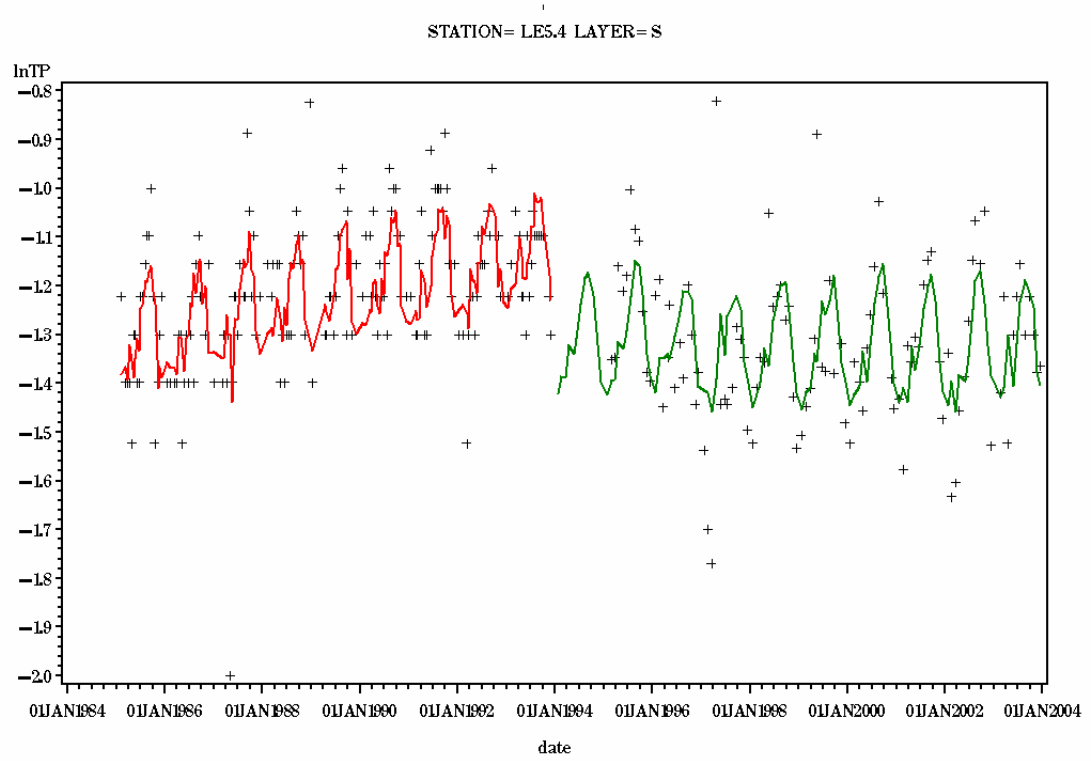
Root MSE = 0.1251 Total R-Square = 0.4618



Tributary	Station	Layer
James	LE5.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0735	0.0283	-37.95	<.0001
jan	-0.1157	0.0338	-3.42	0.0007
feb	-0.0033	0.0333	-0.10	0.9208
mar	0.0195	0.0270	0.72	0.4707
apr	-0.0544	0.0260	-2.09	0.0377
may	-0.0684	0.0255	-2.68	0.0079
jun	-0.0218	0.0266	-0.82	0.4132
jul	0.0459	0.0263	1.74	0.0824
aug	0.0798	0.0260	3.07	0.0024
sep	0.1155	0.0263	4.39	<.0001
oct	0.0880	0.0259	3.40	0.0008
nov	-0.0107	0.0286	-0.38	0.7074
dec	-0.0745	0.0311	-2.39	0.0175
rtemp	-0.0044	0.0043	-1.01	0.3119
cyear	0.0155	0.0051	3.04	0.0026
mc	-0.1650	0.0453	-3.65	0.0003
mc_cyear	-0.0209	0.0082	-2.55	0.0115
flow90	0.0811	0.0252	3.21	0.0015
flow20	0.0711	0.0282	2.52	0.0123
flow50	-0.0812	0.0257	-3.15	0.0018
AR1	-0.2268	0.0624	-3.64	0.0005

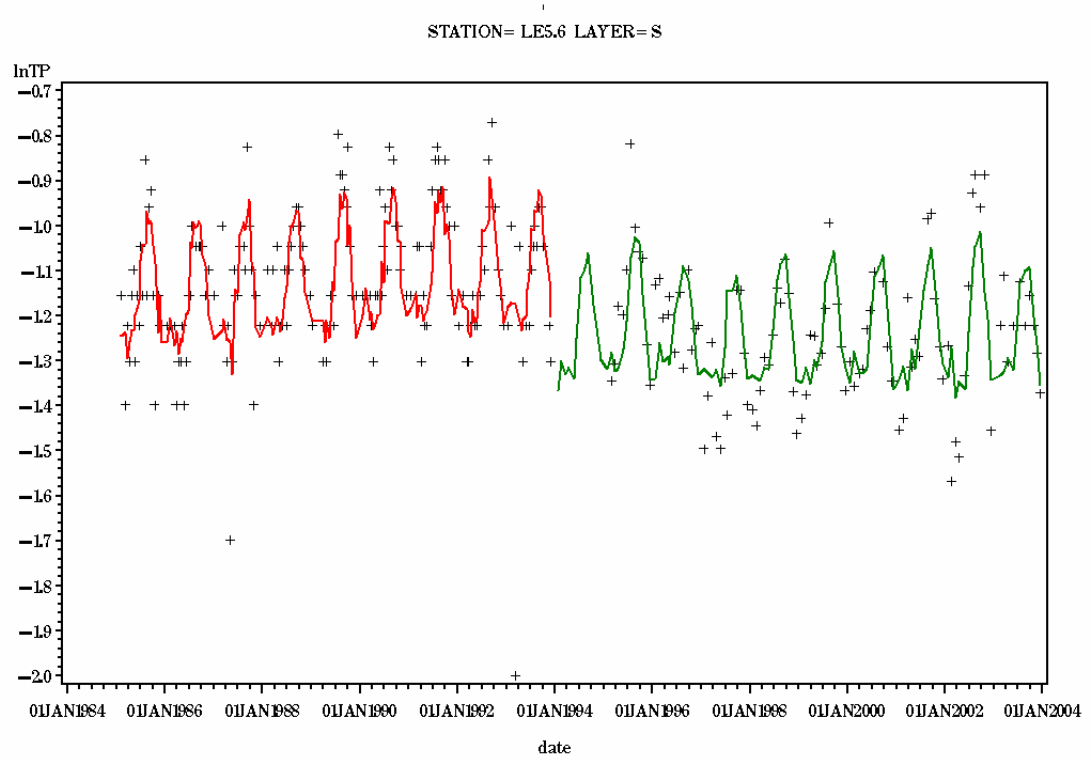
Root MSE = 0.1285 Total R-Square = 0.4283



Tributary	Station	Layer
James	LE5.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1134	0.0252	-44.17	<.0001
jan	-0.1029	0.0304	-3.38	0.0008
feb	-0.0770	0.0295	-2.61	0.0096
mar	-0.0780	0.0250	-3.12	0.0020
apr	-0.0092	0.0246	-0.37	0.7094
may	-0.0375	0.0238	-1.58	0.1155
jun	-0.0037	0.0241	-0.16	0.8767
jul	0.0732	0.0246	2.97	0.0033
aug	0.1197	0.0243	4.92	<.0001
sep	0.1340	0.0246	5.44	<.0001
oct	0.0860	0.0259	3.32	0.0010
nov	-0.0309	0.0269	-1.15	0.2528
dec	-0.0737	0.0287	-2.57	0.0109
rtemp	-0.0035	0.0043	-0.82	0.4113
cyear	0.0226	0.0044	5.10	<.0001
mc	-0.1988	0.0408	-4.88	<.0001
mc_cyear	-0.0250	0.0072	-3.45	0.0007
AR1	-0.1863	0.0621	-3.00	0.0027

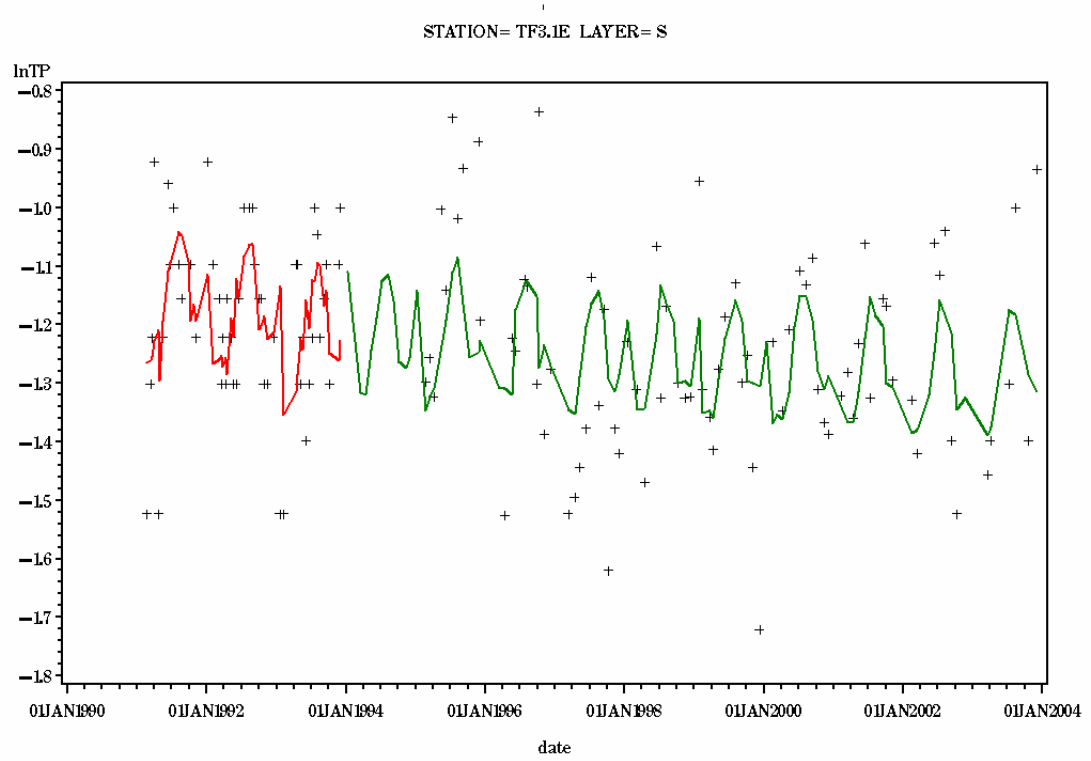
Root MSE = 0.1220 Total R-Square = 0.4576



Tributary	Station	Layer
James	LE5.6	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0979	0.0251	-43.75	<.0001
jan	-0.0917	0.0289	-3.17	0.0017
feb	-0.0547	0.0280	-1.95	0.0520
mar	-0.0932	0.0234	-3.98	<.0001
apr	-0.0880	0.0236	-3.73	0.0002
may	-0.0869	0.0228	-3.80	0.0002
jun	-0.0075	0.0231	-0.32	0.7456
jul	0.1174	0.0244	4.81	<.0001
aug	0.1521	0.0238	6.39	<.0001
sep	0.1813	0.0238	7.63	<.0001
oct	0.0796	0.0233	3.42	0.0007
nov	-0.0176	0.0257	-0.69	0.4924
dec	-0.0908	0.0273	-3.33	0.0010
rtemp	0.0068	0.0040	1.70	0.0896
cyear	0.0073	0.0044	1.66	0.0980
mc	-0.1358	0.0404	-3.36	0.0009
mc_cyear	-0.0087	0.0072	-1.21	0.2278
AR1	-0.2174	0.0616	-3.53	0.0007

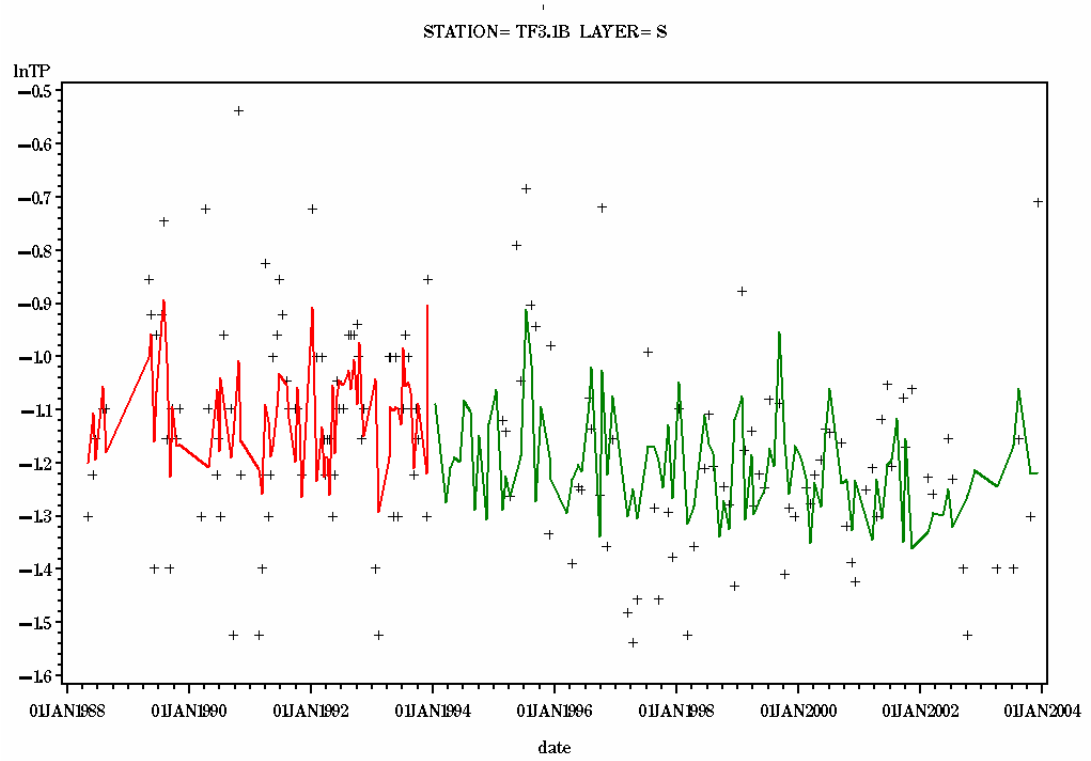
Root MSE = 0.1160 Total R-Square = 0.5465



Tributary	Station	Layer
Rappahannock	TF3.1E	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.2456	0.0642	-19.39	<.0001
jan	0.0813	0.0718	1.13	0.2603
feb	-0.1066	0.0546	-1.95	0.0534
mar	-0.0917	0.0441	-2.08	0.0397
apr	-0.0891	0.0398	-2.24	0.0272
may	-0.0349	0.0475	-0.73	0.4643
jun	0.0465	0.0422	1.10	0.2729
jul	0.1072	0.0452	2.37	0.0194
aug	0.1109	0.0422	2.63	0.0098
sep	0.0702	0.0449	1.56	0.1212
oct	-0.0303	0.0420	-0.72	0.4714
nov	-0.0366	0.0464	-0.79	0.4319
dec	-0.0268	0.0489	-0.55	0.5843
rtemp	-0.0040	0.0061	-0.66	0.5082
cyear	-0.0309	0.0308	-1.00	0.3188
mc	0.0161	0.0766	0.21	0.8341
mc_cyear	0.0247	0.0320	0.77	0.4418
AR1	-0.0986	0.0945	-1.04	0.1525

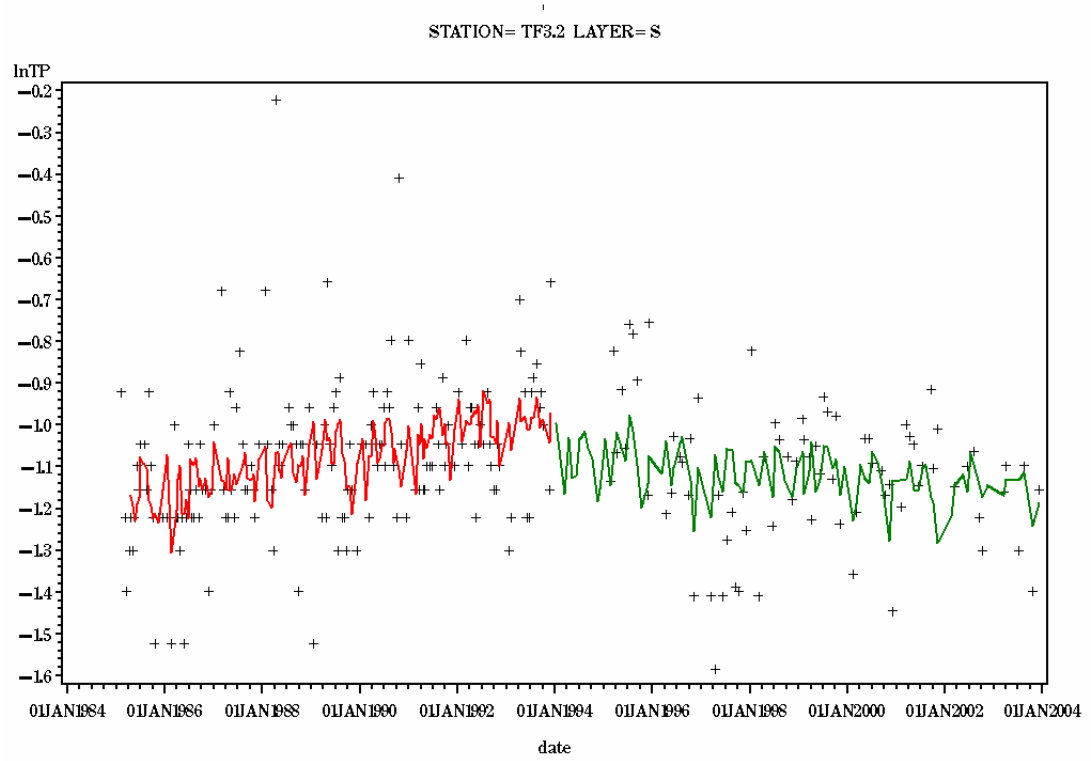
Root MSE = 0.1535 Total R-Square = 0.2695



Tributary	Station	Layer
Rappahannock	TF3.1B	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0987	0.0483	-22.76	<.0001
jan	0.0933	0.0777	1.20	0.2325
feb	-0.0860	0.0584	-1.47	0.1434
mar	-0.0761	0.0471	-1.62	0.1084
apr	-0.0419	0.0417	-1.00	0.3168
may	-0.0223	0.0457	-0.49	0.6264
jun	0.0221	0.0397	0.56	0.5787
jul	0.0712	0.0430	1.66	0.1002
aug	0.0514	0.0440	1.17	0.2452
sep	-0.0384	0.0428	-0.90	0.3717
oct	0.0283	0.0435	0.65	0.5164
nov	-0.0576	0.0450	-1.28	0.2026
dec	0.0560	0.0551	1.02	0.3112
rtemp	0.0014	0.0070	0.20	0.8397
cyear	0.0035	0.0149	0.23	0.8157
mc	-0.0748	0.0697	-1.07	0.2852
mc_cyear	-0.0092	0.0175	-0.53	0.5982
flow0	0.2208	0.0497	4.44	<.0001
flow20	-0.1281	0.0376	-3.41	0.0009
AR1	-0.1785	0.0863	-2.07	0.0237

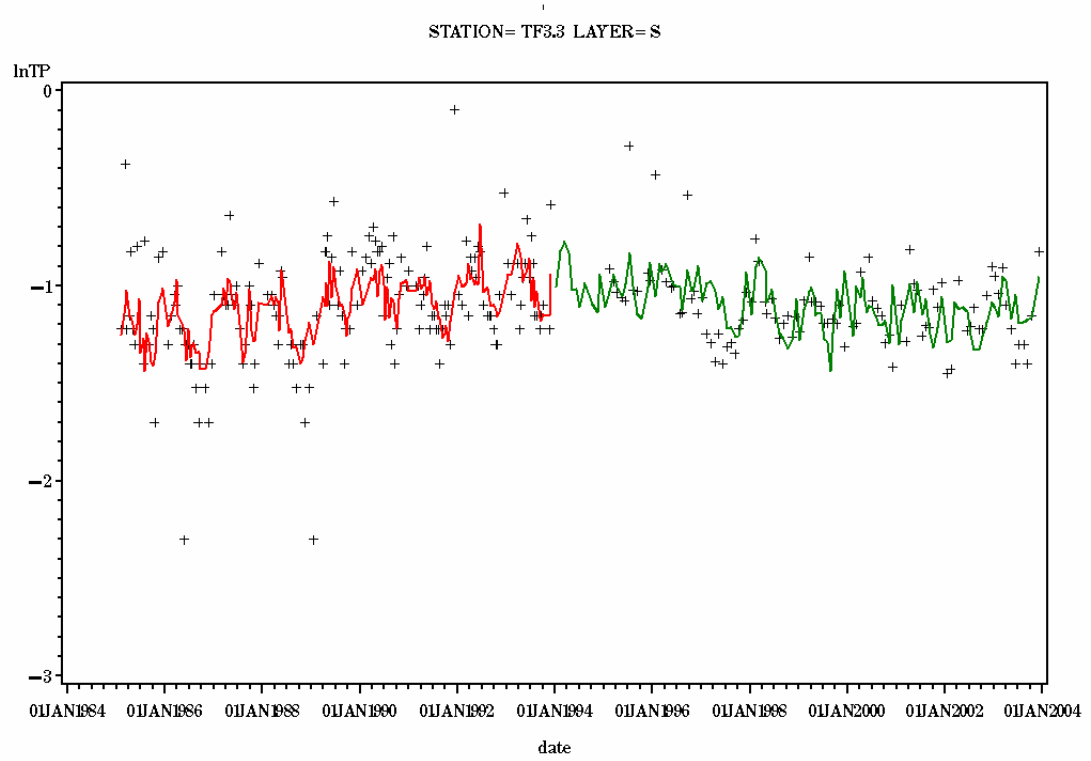
Root MSE = 0.1634 Total R-Square = 0.3300



Tributary	Station	Layer
Rappahannock	TF3.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9495	0.0298	-31.87	<.0001
jan	0.0442	0.0498	0.89	0.3757
feb	-0.0884	0.0498	-1.78	0.0771
mar	-0.0166	0.0352	-0.47	0.6378
apr	0.0428	0.0325	1.32	0.1897
may	-0.0096	0.0358	-0.27	0.7892
jun	-0.0031	0.0325	-0.09	0.9250
jul	0.0716	0.0354	2.02	0.0445
aug	0.0572	0.0337	1.70	0.0911
sep	-0.0051	0.0343	-0.15	0.8825
oct	-0.0250	0.0320	-0.78	0.4354
nov	-0.0710	0.0401	-1.77	0.0776
dec	0.0030	0.0426	0.07	0.9435
rtemp	-0.0051	0.0049	-1.04	0.2984
cyear	0.0273	0.0054	5.02	<.0001
mc	-0.1279	0.0511	-2.50	0.0130
mc_cyear	-0.0382	0.0098	-3.92	0.0001
flow150	-0.0803	0.0309	-2.60	0.0101
AR1	0.0155	0.0682	0.23	0.4109

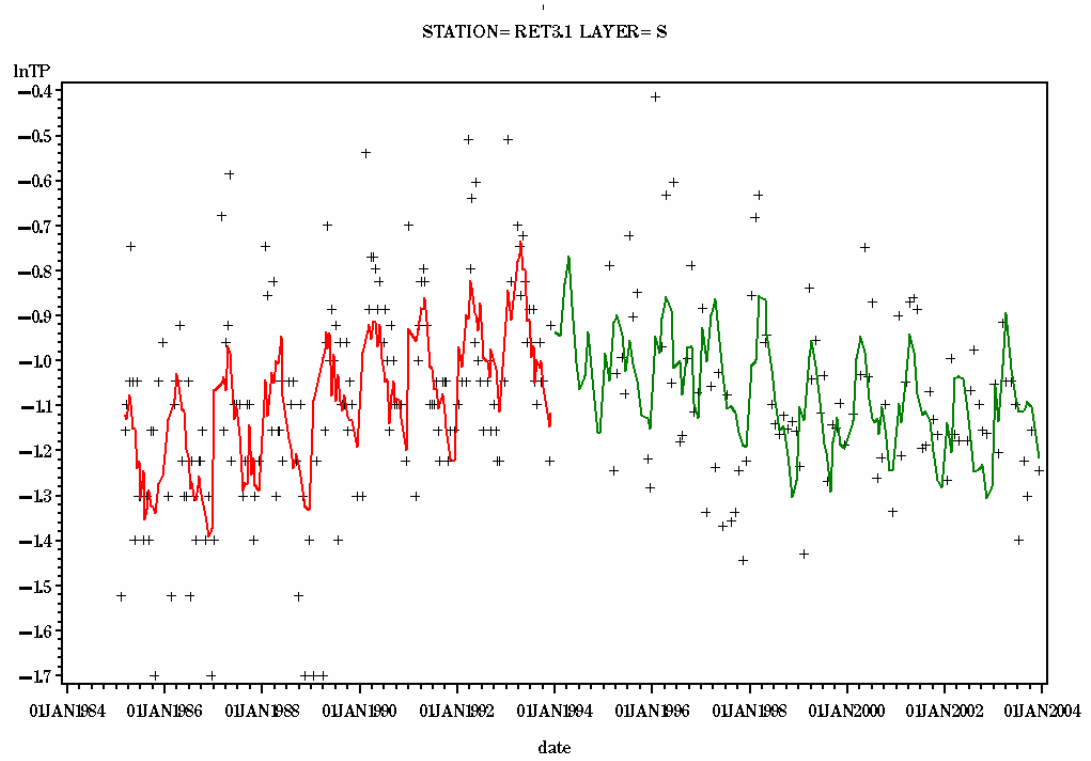
Root MSE = 0.1667 Total R-Square = 0.1815



Tributary	Station	Layer
Rappahannock	TF3.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9690	0.0450	-21.52	<.0001
jan	-0.0179	0.0562	-0.32	0.7502
feb	0.0197	0.0543	0.36	0.7172
mar	0.1104	0.0440	2.51	0.0127
apr	0.1043	0.0428	2.44	0.0155
may	0.0216	0.0458	0.47	0.6373
jun	0.0652	0.0433	1.51	0.1332
jul	-0.0261	0.0450	-0.58	0.5632
aug	-0.1005	0.0428	-2.35	0.0196
sep	-0.0987	0.0438	-2.26	0.0250
oct	-0.1241	0.0445	-2.79	0.0057
nov	-0.0676	0.0497	-1.36	0.1749
dec	0.1137	0.0495	2.30	0.0224
rtemp	0.0023	0.0065	0.35	0.7294
cyear	0.0277	0.0080	3.46	0.0006
mc	-0.0558	0.0733	-0.76	0.4476
mc_cyear	-0.0437	0.0131	-3.32	0.0010
flow10	0.1865	0.0350	5.33	<.0001
AR1	-0.1839	0.0631	-2.92	0.0033

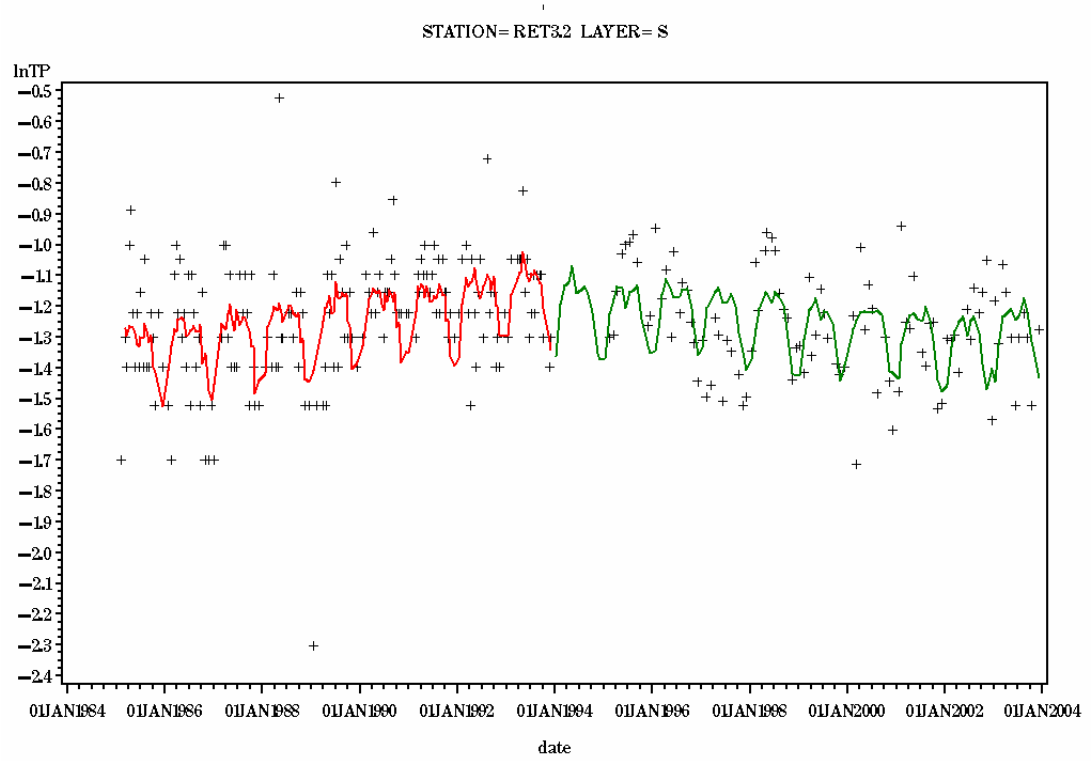
Root MSE = 0.2167 Total R-Square = 0.3144



Tributary	Station	Layer
Rappahannock	RET3.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9219	0.0299	-30.80	<.0001
jan	0.0703	0.0426	1.65	0.1003
feb	0.0051	0.0477	0.11	0.9157
mar	0.1177	0.0336	3.50	0.0006
apr	0.1582	0.0325	4.87	<.0001
may	0.1089	0.0349	3.12	0.0020
jun	0.0265	0.0335	0.79	0.4297
jul	-0.0207	0.0342	-0.60	0.5460
aug	-0.0700	0.0325	-2.15	0.0323
sep	-0.0423	0.0324	-1.30	0.1938
oct	-0.0798	0.0337	-2.37	0.0185
nov	-0.1330	0.0415	-3.21	0.0015
dec	-0.1410	0.0426	-3.31	0.0011
rtemp	0.0024	0.0052	0.46	0.6464
cyear	0.0340	0.0054	6.31	<.0001
mc	-0.0858	0.0485	-1.77	0.0780
mc_cyear	-0.0482	0.0089	-5.42	<.0001
flow10	0.0692	0.0284	2.44	0.0155
flow40	0.0563	0.0277	2.03	0.0434
AR1	0.0052	0.0643	0.08	0.4679

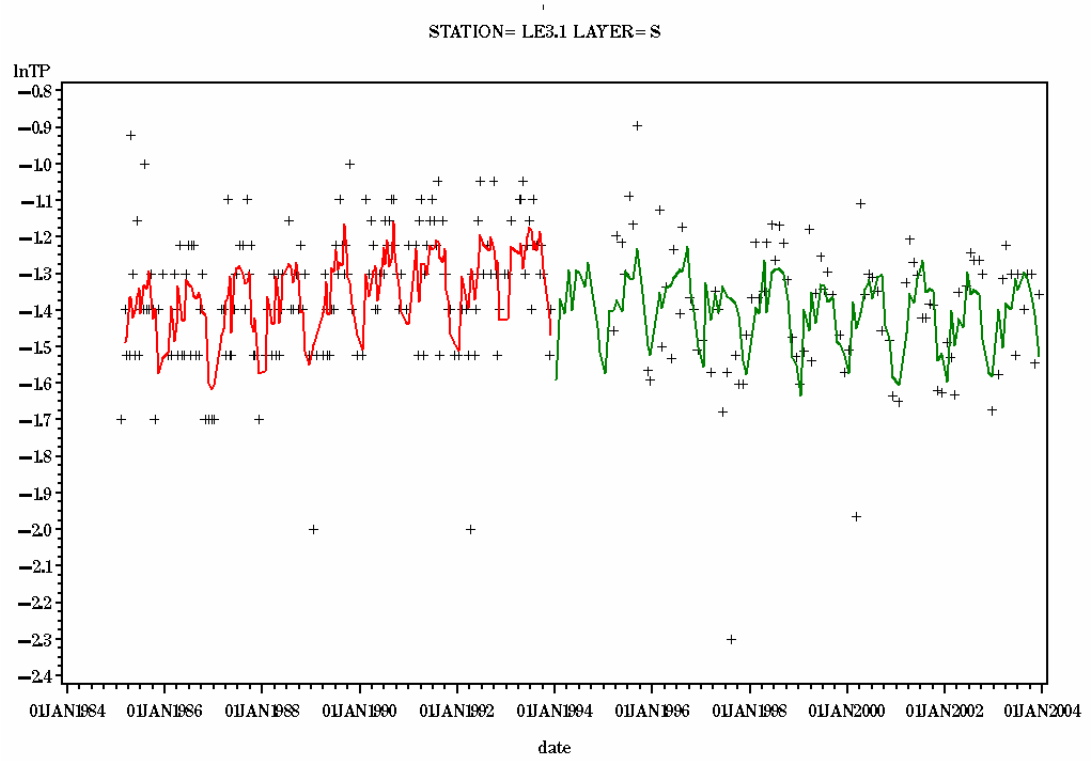
Root MSE = 0.1734 Total R-Square = 0.3855



Tributary	Station	Layer
Rappahannock	RET3.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1475	0.0294	-39.09	<.0001
jan	-0.1326	0.0413	-3.21	0.0015
feb	-0.0068	0.0444	-0.15	0.8784
mar	0.0518	0.0322	1.61	0.1091
apr	0.0781	0.0317	2.47	0.0143
may	0.0896	0.0334	2.68	0.0078
jun	0.0371	0.0334	1.11	0.2676
jul	0.0580	0.0334	1.74	0.0837
aug	0.0786	0.0316	2.49	0.0136
sep	0.0563	0.0335	1.68	0.0939
oct	-0.0262	0.0328	-0.80	0.4259
nov	-0.1335	0.0402	-3.32	0.0010
dec	-0.1504	0.0391	-3.85	0.0002
rtemp	-0.0037	0.0052	-0.72	0.4722
cyear	0.0222	0.0053	4.21	<.0001
mc	-0.0629	0.0478	-1.32	0.1895
mc_cyear	-0.0331	0.0088	-3.76	0.0002
flow60	0.0518	0.0258	2.01	0.0454
AR1	-0.0037	0.0640	-0.06	0.4771

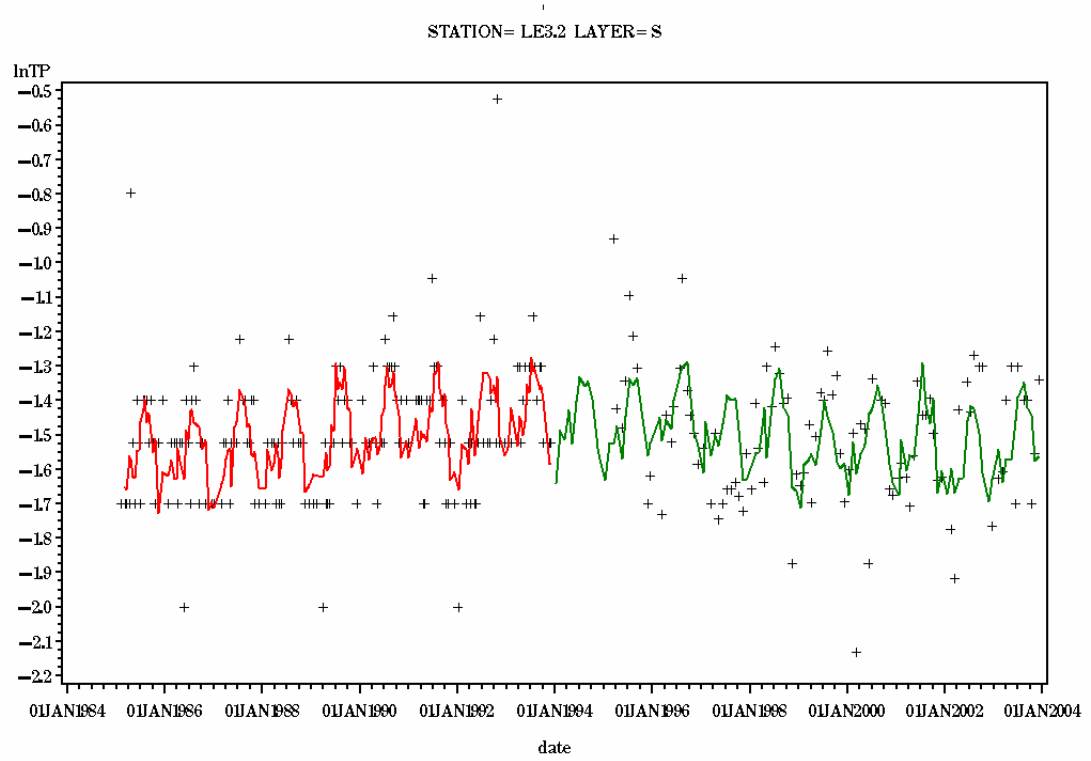
Root MSE = 0.1690 Total R-Square = 0.2695



Tributary	Station	Layer
Rappahannock	LE3.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.2840	0.0306	-41.89	<.0001
jan	-0.1656	0.0413	-4.01	<.0001
feb	0.0259	0.0449	0.58	0.5651
mar	-0.0368	0.0316	-1.16	0.2455
apr	0.0532	0.0306	1.74	0.0838
may	-0.0107	0.0322	-0.33	0.7411
jun	0.0894	0.0315	2.84	0.0049
jul	0.0917	0.0320	2.86	0.0045
aug	0.0776	0.0307	2.53	0.0120
sep	0.1019	0.0312	3.26	0.0013
oct	0.0078	0.0330	0.24	0.8139
nov	-0.0878	0.0366	-2.40	0.0171
dec	-0.1466	0.0366	-4.00	<.0001
rtemp	0.0078	0.0053	1.48	0.1389
cyear	0.0158	0.0055	2.90	0.0041
mc	-0.1040	0.0508	-2.05	0.0418
mc_cyear	-0.0196	0.0091	-2.16	0.0317
flow50	0.0739	0.0280	2.64	0.0088
AR1	-0.1037	0.0641	-1.62	0.0580

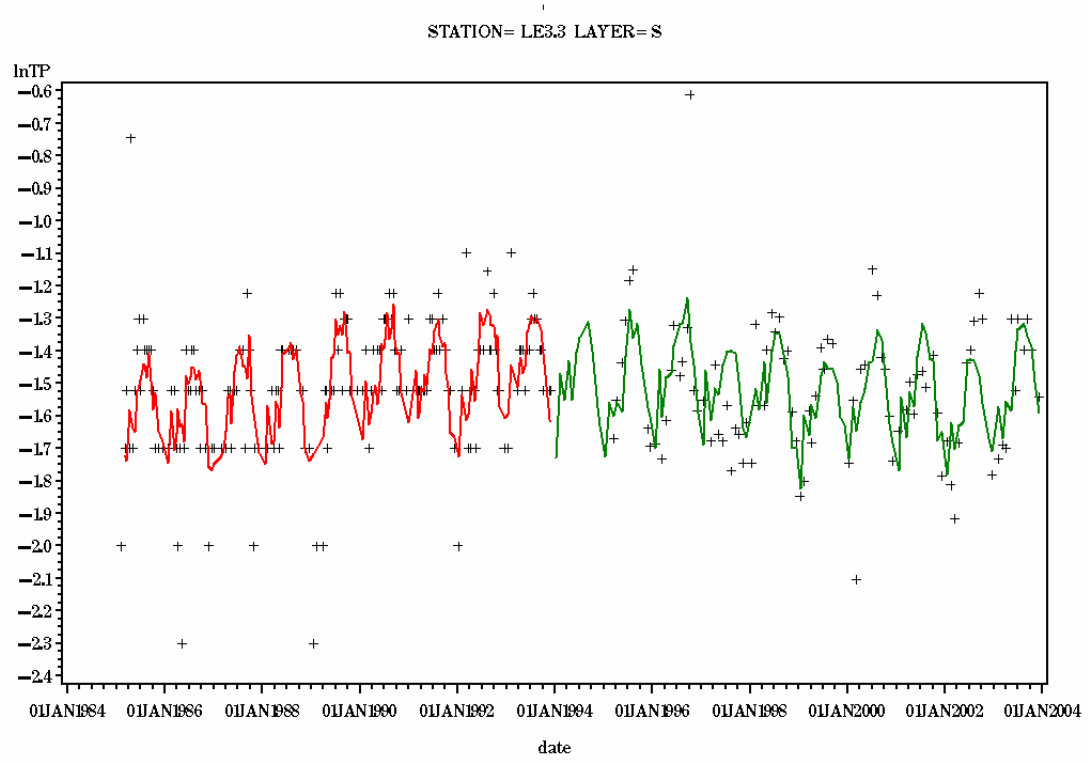
Root MSE = 0.1589 Total R-Square = 0.3020



Tributary	Station	Layer
Rappahannock	LE3.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.4381	0.0289	-49.68	<.0001
jan	-0.1329	0.0435	-3.06	0.0025
feb	-0.0192	0.0439	-0.44	0.6618
mar	-0.0690	0.0310	-2.22	0.0271
apr	-0.0097	0.0302	-0.32	0.7493
may	-0.0640	0.0323	-1.99	0.0482
jun	0.0536	0.0310	1.73	0.0856
jul	0.1503	0.0321	4.69	<.0001
aug	0.1380	0.0312	4.43	<.0001
sep	0.1002	0.0306	3.27	0.0012
oct	0.0456	0.0317	1.44	0.1511
nov	-0.0937	0.0371	-2.53	0.0121
dec	-0.0992	0.0362	-2.74	0.0066
rtemp	0.0018	0.0055	0.32	0.7491
cyear	0.0140	0.0052	2.71	0.0072
mc	-0.0346	0.0489	-0.71	0.4805
mc_cyear	-0.0219	0.0088	-2.50	0.0131
flow50	0.0967	0.0271	3.56	0.0004
AR1	-0.0565	0.0635	-0.89	0.1906

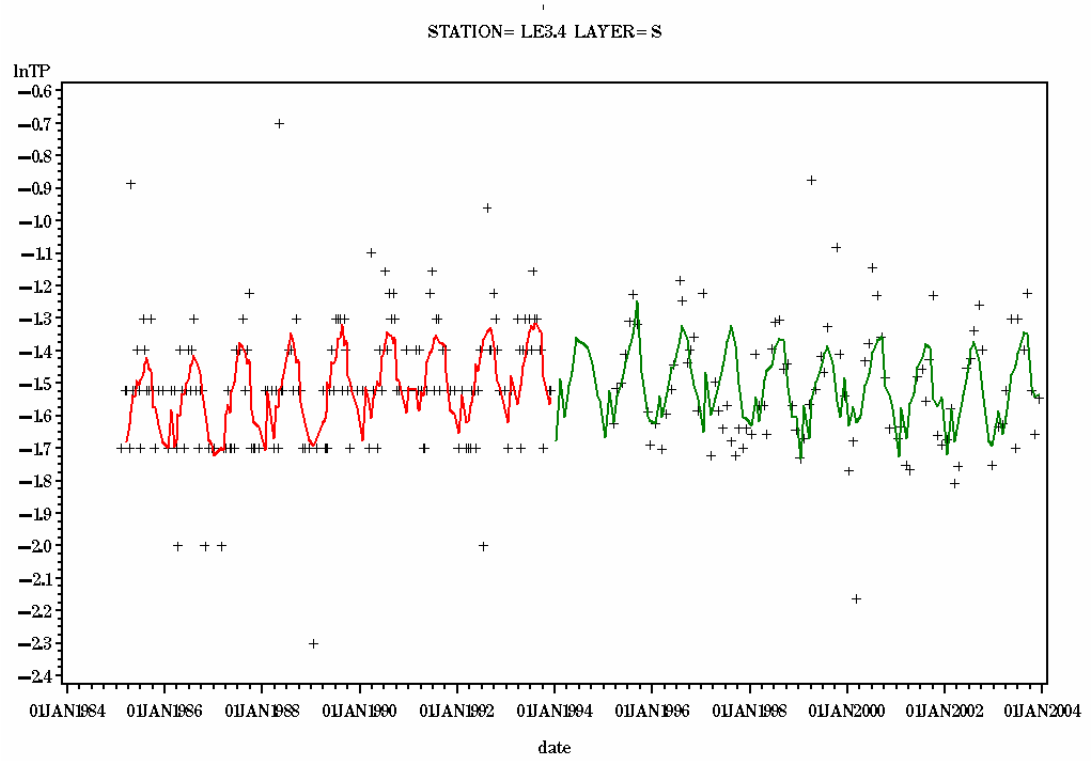
Root MSE = 0.1609 Total R-Square = 0.3072



Tributary	Station	Layer
Rappahannock	LE3.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.4398	0.0286	-50.32	<.0001
jan	-0.1925	0.0401	-4.80	<.0001
feb	-0.0237	0.0451	-0.53	0.5998
mar	-0.1135	0.0307	-3.70	0.0003
apr	-0.0083	0.0298	-0.28	0.7799
may	-0.0467	0.0319	-1.46	0.1445
jun	0.0997	0.0313	3.19	0.0016
jul	0.1579	0.0317	4.98	<.0001
aug	0.1492	0.0303	4.92	<.0001
sep	0.1452	0.0319	4.55	<.0001
oct	0.0570	0.0319	1.79	0.0750
nov	-0.0889	0.0389	-2.28	0.0233
dec	-0.1354	0.0367	-3.69	0.0003
rtemp	0.0059	0.0052	1.14	0.2546
cyear	0.0168	0.0051	3.27	0.0012
mc	-0.0583	0.0487	-1.20	0.2330
mc_cyear	-0.0222	0.0088	-2.53	0.0122
flow50	0.0747	0.0291	2.57	0.0109
flow10	0.0560	0.0258	2.17	0.0308
AR1	-0.0557	0.0644	-0.86	0.1970

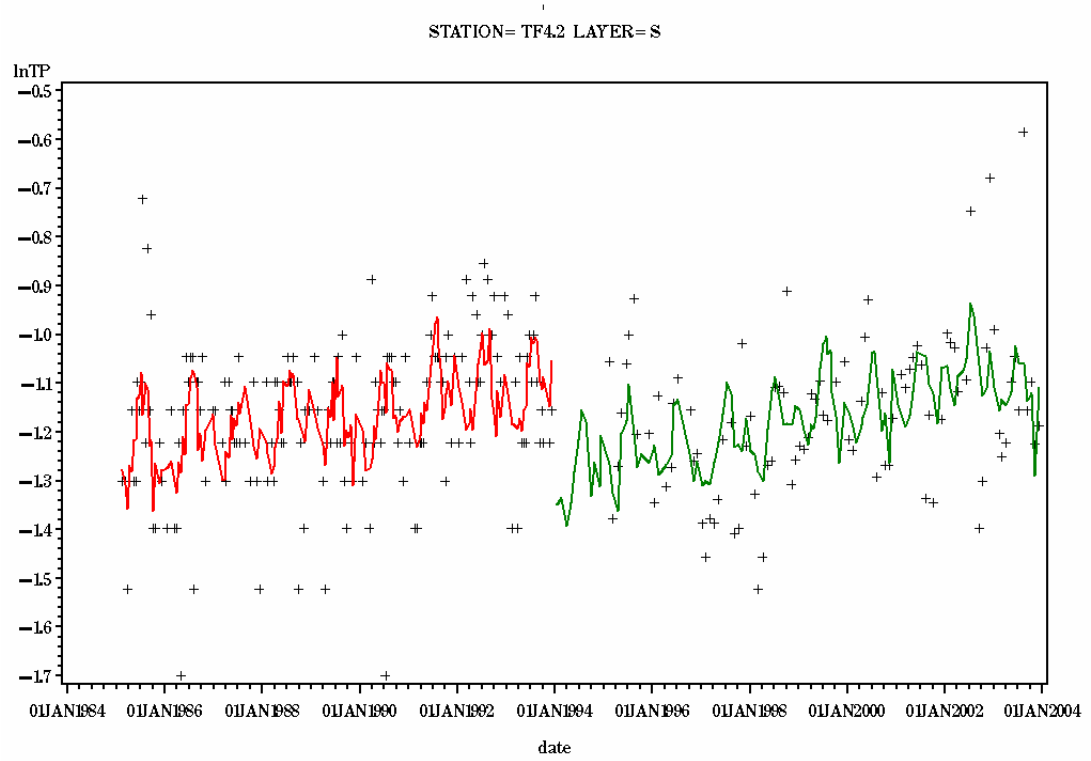
Root MSE = 0.1588 Total R-Square = 0.4213



Tributary	Station	Layer
Rappahannock	LE3.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.4611	0.0297	-49.12	<.0001
jan	-0.1561	0.0415	-3.77	0.0002
feb	-0.0347	0.0465	-0.75	0.4562
mar	-0.1151	0.0330	-3.49	0.0006
apr	-0.0431	0.0320	-1.35	0.1796
may	0.0196	0.0351	0.56	0.5770
jun	0.0715	0.0325	2.20	0.0286
jul	0.1228	0.0336	3.65	0.0003
aug	0.1481	0.0320	4.63	<.0001
sep	0.1276	0.0325	3.92	0.0001
oct	0.0009	0.0331	0.03	0.9777
nov	-0.0574	0.0392	-1.46	0.1447
dec	-0.0841	0.0391	-2.15	0.0325
rtemp	0.0080	0.0059	1.37	0.1721
cyear	0.0119	0.0054	2.22	0.0273
mc	-0.0280	0.0496	-0.56	0.5735
mc_cyear	-0.0168	0.0089	-1.88	0.0615
flow70	0.0626	0.0265	2.36	0.0189
AR1	-0.0214	0.0639	-0.33	0.3702

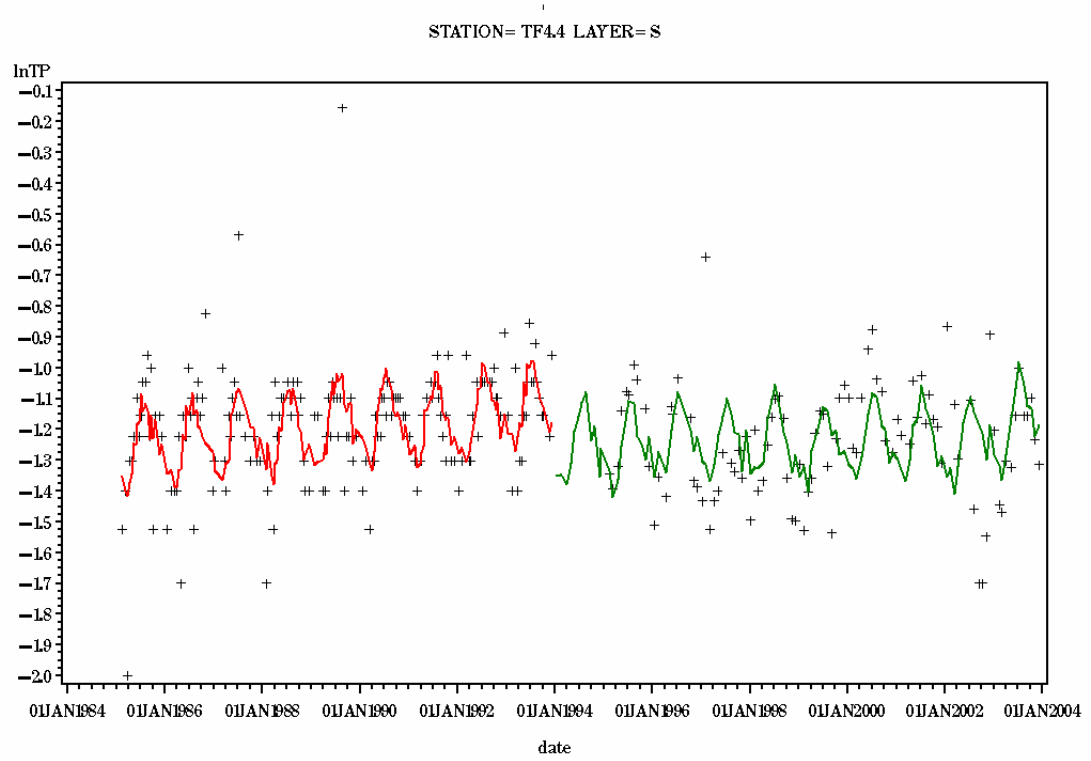
Root MSE = 0.1698 Total R-Square = 0.2925



Tributary	Station	Layer
York	TF4.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0909	0.0237	-46.11	<.0001
jan	-0.0244	0.0337	-0.73	0.4691
feb	-0.0565	0.0319	-1.77	0.0777
mar	-0.0845	0.0273	-3.10	0.0022
apr	-0.0531	0.0259	-2.05	0.0410
may	0.0020	0.0284	0.07	0.9442
jun	0.0668	0.0259	2.58	0.0104
jul	0.1106	0.0269	4.11	<.0001
aug	0.0845	0.0278	3.03	0.0027
sep	-0.0123	0.0290	-0.43	0.6711
oct	-0.0203	0.0277	-0.73	0.4642
nov	-0.0543	0.0336	-1.61	0.1077
dec	0.0416	0.0311	1.34	0.1830
rtemp	-0.0029	0.0034	-0.86	0.3918
cyear	0.0161	0.0042	3.82	0.0002
mc	-0.1731	0.0403	-4.30	<.0001
mc_cyear	0.0025	0.0071	0.35	0.7283
flow40	-0.0785	0.0211	-3.72	0.0002
AR1	-0.0170	0.0647	-0.26	0.3975

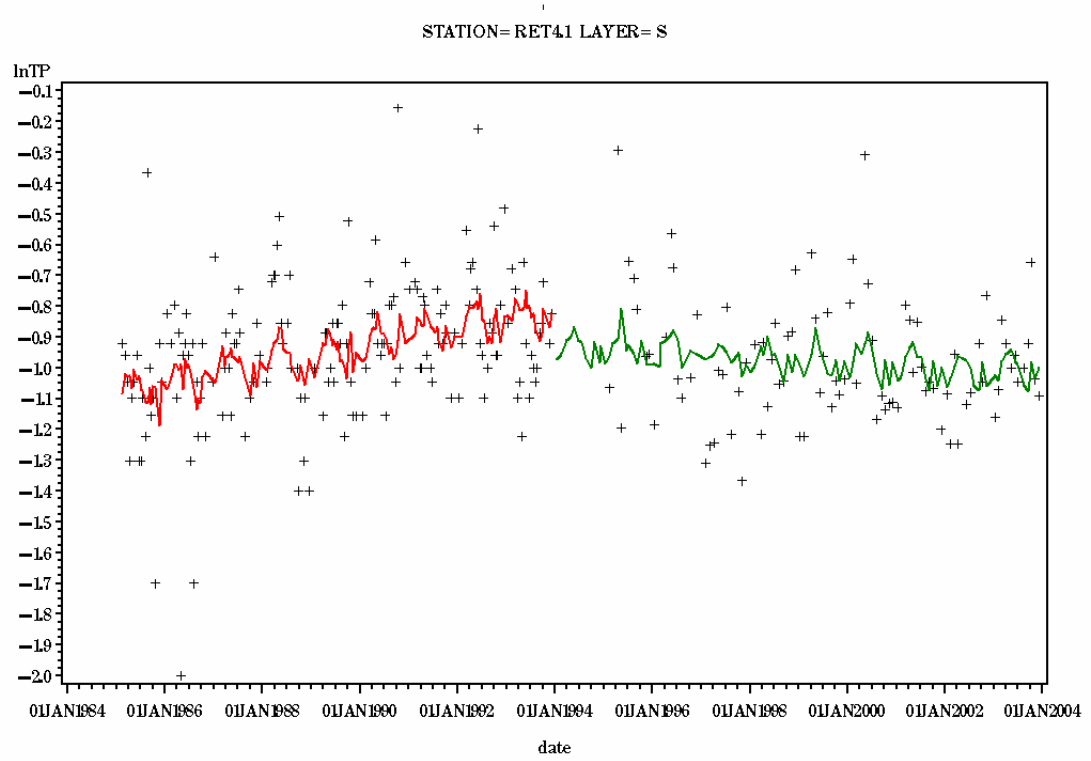
Root MSE = 0.1377 Total R-Square = 0.2772



Tributary	Station	Layer
York	TF4.4	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.1160	0.0269	-41.51	<.0001
jan	-0.0975	0.0379	-2.57	0.0107
feb	-0.0845	0.0379	-2.23	0.0266
mar	-0.1409	0.0314	-4.48	<.0001
apr	-0.0797	0.0303	-2.63	0.0091
may	0.0319	0.0321	0.99	0.3217
jun	0.1012	0.0309	3.27	0.0012
jul	0.1524	0.0303	5.02	<.0001
aug	0.1197	0.0315	3.80	0.0002
sep	0.0459	0.0327	1.41	0.1611
oct	0.0371	0.0310	1.20	0.2325
nov	-0.0639	0.0368	-1.74	0.0836
dec	-0.0217	0.0360	-0.60	0.5468
rtemp	0.0014	0.0038	0.38	0.7022
cyear	0.0158	0.0048	3.31	0.0011
mc	-0.1534	0.0457	-3.36	0.0009
mc_cyear	-0.0083	0.0081	-1.03	0.3058
flow20	0.0695	0.0267	2.60	0.0098
AR1	-0.0030	0.0640	-0.05	0.4814

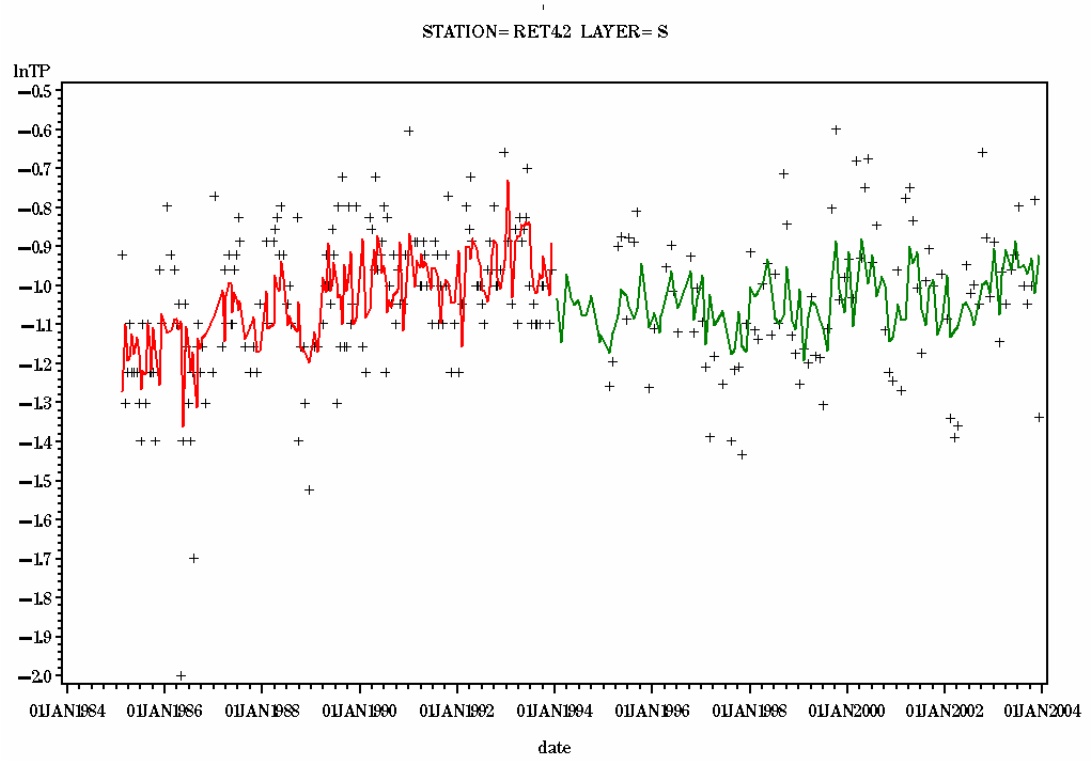
Root MSE = 0.1595 Total R-Square = 0.3142



Tributary	Station	Layer
York	RET4.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.7959	0.0405	-19.64	<.0001
jan	-0.0386	0.0539	-0.72	0.4743
feb	-0.0218	0.0539	-0.40	0.6864
mar	0.0315	0.0444	0.71	0.4788
apr	0.0408	0.0421	0.97	0.3335
may	0.0676	0.0441	1.53	0.1271
jun	0.0346	0.0428	0.81	0.4194
jul	0.0198	0.0419	0.47	0.6381
aug	-0.0365	0.0434	-0.84	0.4012
sep	-0.0675	0.0450	-1.50	0.1355
oct	0.0139	0.0432	0.32	0.7472
nov	-0.0511	0.0525	-0.97	0.3318
dec	0.0072	0.0521	0.14	0.8907
rtemp	-0.0017	0.0068	-0.24	0.8074
cyear	0.0304	0.0072	4.20	<.0001
mc	-0.1400	0.0707	-1.98	0.0489
mc_cyear	-0.0391	0.0123	-3.18	0.0017
AR1	-0.1010	0.0650	-1.55	0.0655

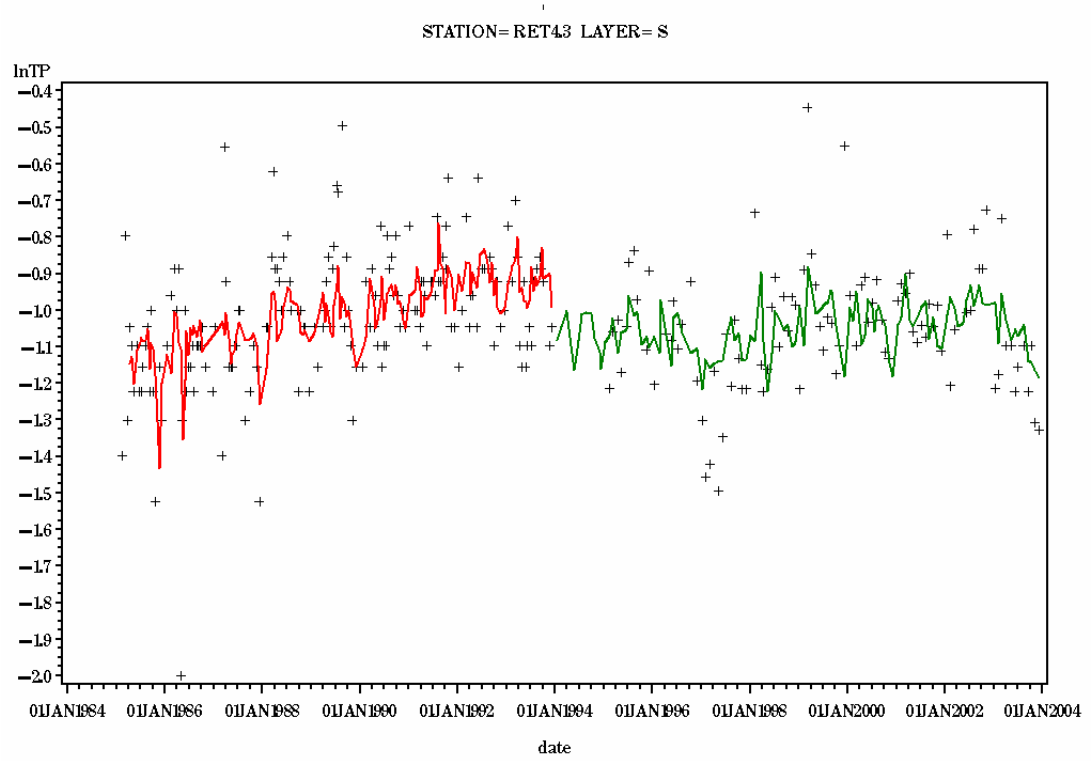
Root MSE = 0.2144 Total R-Square = 0.1321



Tributary	Station	Layer
York	RET4.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8867	0.0363	-24.42	<.0001
jan	0.0466	0.0386	1.21	0.2293
feb	-0.0704	0.0387	-1.82	0.0704
mar	0.0064	0.0341	0.19	0.8514
apr	0.0448	0.0329	1.36	0.1745
may	0.0468	0.0365	1.28	0.2009
jun	0.0408	0.0329	1.24	0.2158
jul	-0.0118	0.0337	-0.35	0.7267
aug	-0.0498	0.0343	-1.45	0.1482
sep	-0.0029	0.0365	-0.08	0.9374
oct	0.0346	0.0338	1.02	0.3073
nov	-0.0554	0.0391	-1.42	0.1577
dec	-0.0298	0.0377	-0.79	0.4308
rtemp	0.0051	0.0051	1.00	0.3190
cyear	0.0316	0.0065	4.83	<.0001
mc	-0.2002	0.0617	-3.25	0.0013
mc_cyear	-0.0201	0.0108	-1.86	0.0648
flow0	0.0865	0.0269	3.22	0.0015
AR1	-0.2534	0.0622	-4.08	0.0002

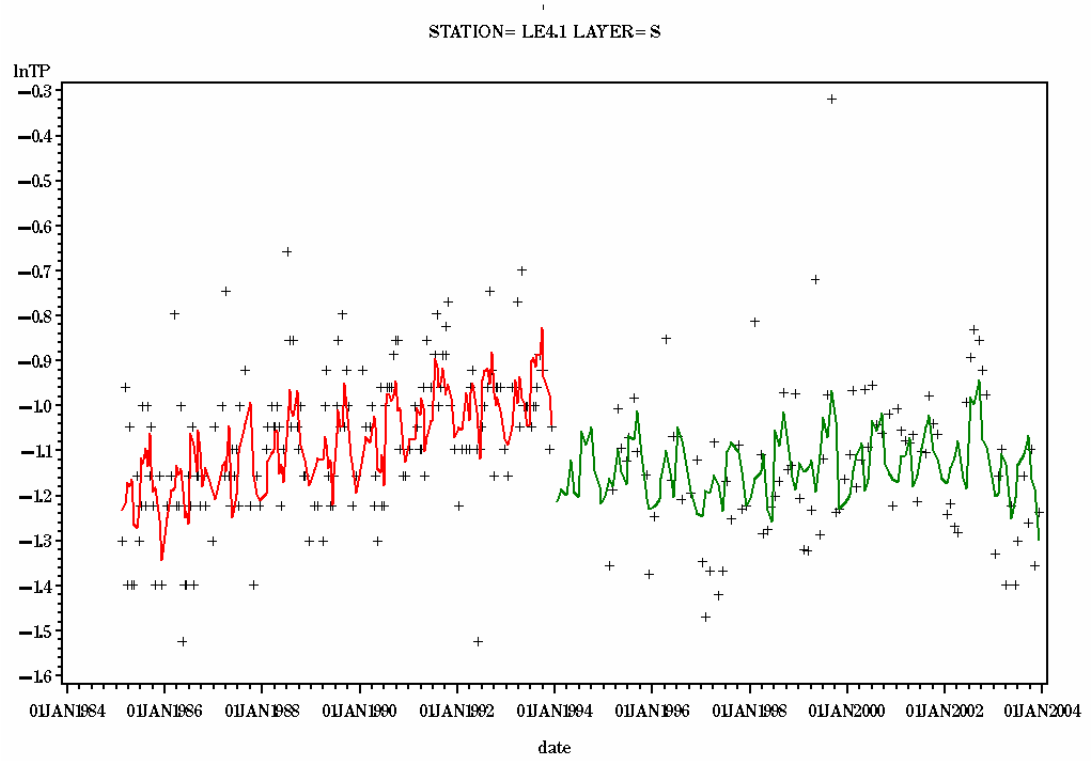
Root MSE = 0.1636 Total R-Square = 0.2835



Tributary	Station	Layer
York	RET4.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.8692	0.0338	-25.68	<.0001
jan	-0.0181	0.0382	-0.47	0.6354
feb	-0.0284	0.0396	-0.72	0.4746
mar	0.0718	0.0333	2.15	0.0322
apr	-0.0016	0.0322	-0.05	0.9603
may	-0.0381	0.0333	-1.14	0.2541
jun	0.0057	0.0319	0.18	0.8572
jul	0.0612	0.0315	1.94	0.0532
aug	0.0512	0.0326	1.57	0.1172
sep	0.0320	0.0332	0.96	0.3360
oct	-0.0061	0.0322	-0.19	0.8498
nov	-0.0432	0.0365	-1.19	0.2369
dec	-0.0864	0.0384	-2.25	0.0255
rtemp	-0.0035	0.0039	-0.89	0.3745
cyear	0.0306	0.0062	4.94	<.0001
mc	-0.1966	0.0564	-3.49	0.0006
mc_cyear	-0.0300	0.0101	-2.96	0.0034
flow90	-0.0964	0.0276	-3.49	0.0006
AR1	-0.2185	0.0630	-3.47	0.0008

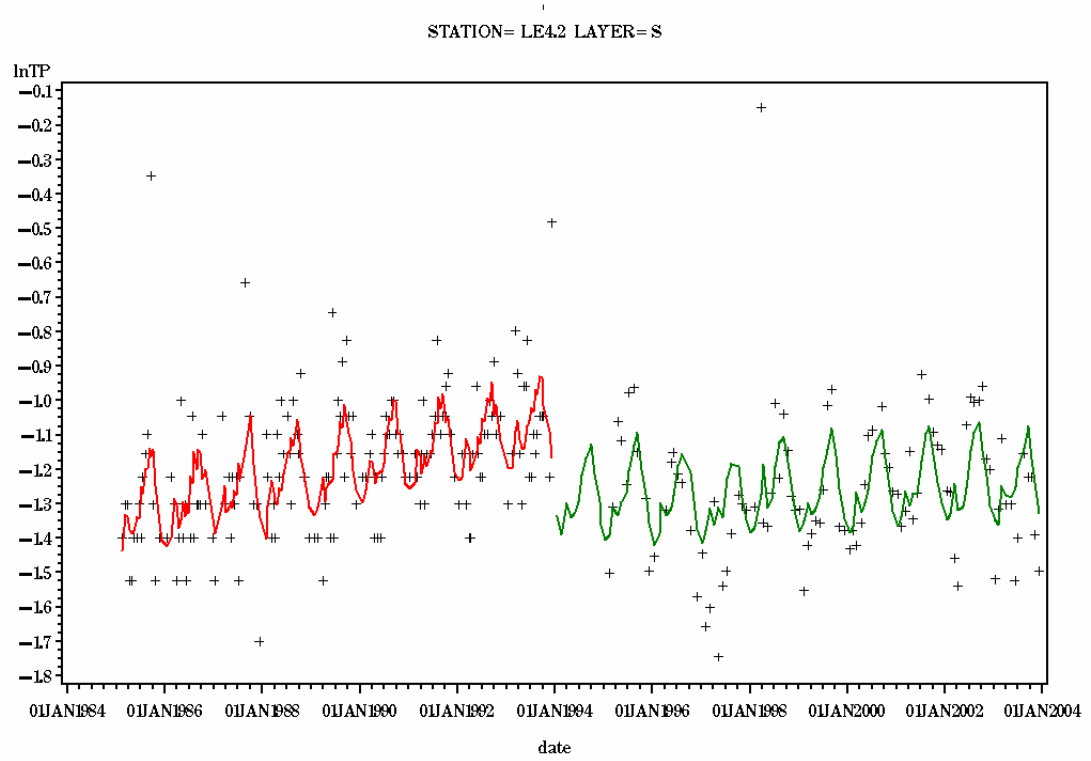
Root MSE = 0.1576 Total R-Square = 0.2725



Tributary	Station	Layer
York	LE4.1	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-0.9350	0.0272	-34.40	<.0001
jan	-0.0651	0.0343	-1.90	0.0588
feb	-0.0292	0.0334	-0.88	0.3822
mar	-0.0041	0.0282	-0.14	0.8860
apr	0.0311	0.0274	1.13	0.2579
may	-0.0471	0.0293	-1.61	0.1088
jun	-0.0609	0.0275	-2.22	0.0275
jul	0.0809	0.0275	2.94	0.0036
aug	0.0695	0.0278	2.50	0.0130
sep	0.1123	0.0299	3.76	0.0002
oct	0.0168	0.0295	0.57	0.5691
nov	-0.0242	0.0326	-0.74	0.4584
dec	-0.0800	0.0344	-2.33	0.0207
rtemp	-0.0004	0.0042	-0.10	0.9173
cyear	0.0300	0.0049	6.14	<.0001
mc	-0.2098	0.0459	-4.57	<.0001
mc_cyear	-0.0288	0.0081	-3.55	0.0005
flow30	-0.0586	0.0224	-2.62	0.0095
AR1	-0.1316	0.0633	-2.08	0.0232

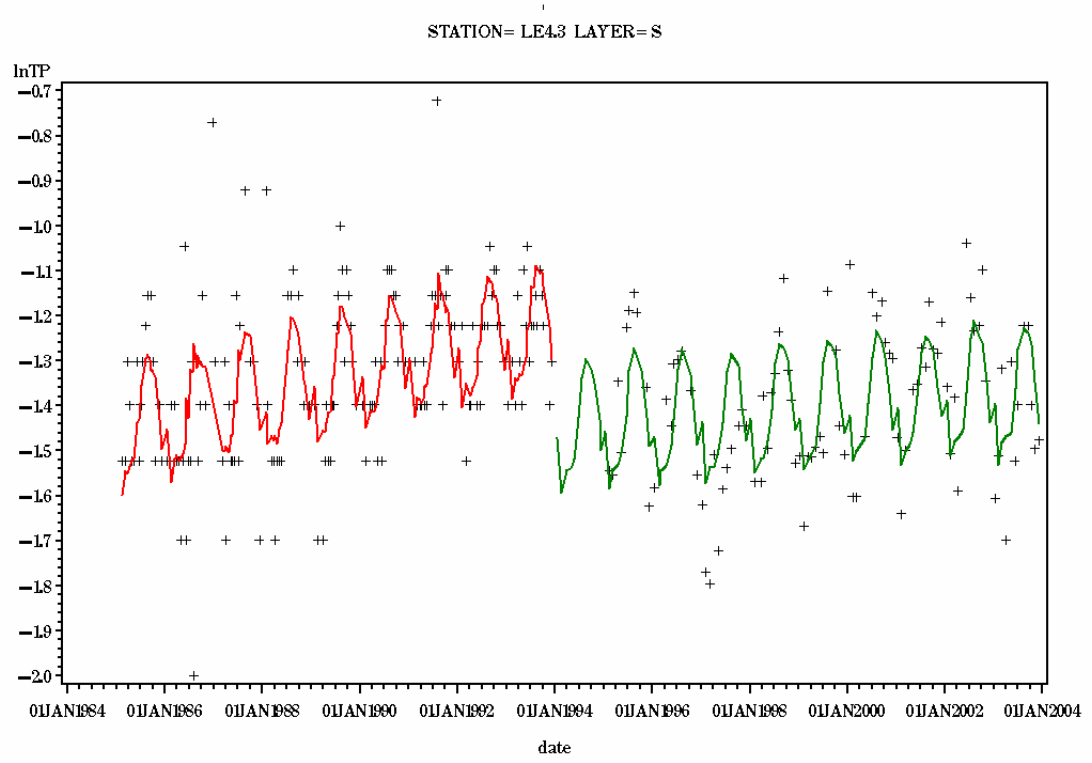
Root MSE = 0.1415 Total R-Square = 0.3237



Tributary	Station	Layer
York	LE4.2	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.0492	0.0332	-31.61	<.0001
jan	-0.1246	0.0423	-2.95	0.0035
feb	-0.1063	0.0411	-2.59	0.0103
mar	-0.0157	0.0347	-0.45	0.6505
apr	-0.0542	0.0336	-1.61	0.1087
may	-0.0425	0.0359	-1.19	0.2370
jun	-0.0135	0.0337	-0.40	0.6898
jul	0.0696	0.0337	2.07	0.0397
aug	0.1197	0.0355	3.37	0.0009
sep	0.1632	0.0367	4.45	<.0001
oct	0.0803	0.0354	2.27	0.0241
nov	-0.0029	0.0402	-0.07	0.9431
dec	-0.0731	0.0412	-1.78	0.0768
rtemp	0.0015	0.0056	0.27	0.7900
cyear	0.0304	0.0059	5.12	<.0001
mc	-0.2395	0.0559	-4.29	<.0001
mc_cyear	-0.0244	0.0098	-2.49	0.0135
AR1	-0.1169	0.0633	-1.85	0.0374

Root MSE = 0.1743 Total R-Square = 0.3047



Tributary	Station	Layer
York	LE4.3	S

Variable	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	-1.2086	0.0244	-49.63	<.0001
jan	-0.0248	0.0333	-0.74	0.4571
feb	-0.1431	0.0324	-4.42	<.0001
mar	-0.1061	0.0268	-3.95	0.0001
apr	-0.1018	0.0270	-3.77	0.0002
may	-0.0753	0.0278	-2.71	0.0073
jun	0.0030	0.0270	0.11	0.9129
jul	0.1011	0.0268	3.77	0.0002
aug	0.1502	0.0264	5.69	<.0001
sep	0.1312	0.0291	4.51	<.0001
oct	0.1028	0.0274	3.76	0.0002
nov	0.0197	0.0315	0.62	0.5334
dec	-0.0567	0.0323	-1.75	0.0809
rtemp	0.0029	0.0046	0.64	0.5239
cyear	0.0262	0.0044	5.95	<.0001
mc	-0.2357	0.0413	-5.70	<.0001
mc_cyear	-0.0178	0.0073	-2.44	0.0153
AR1	-0.0598	0.0643	-0.93	0.1797

Root MSE = 0.1368 Total R-Square = 0.4507

Appendix C – 07/08/05 Presentation to the TMAW

Method Adjustment Analyses for VA DEQ Nutrient Determinations

Introduction

- **1984 until 1994**
  - **TN calculated as TKNW + $NO_{23}F$(NO_2F + NO_3F)**
  - **TP measured directly (analyzed by DCLS).**

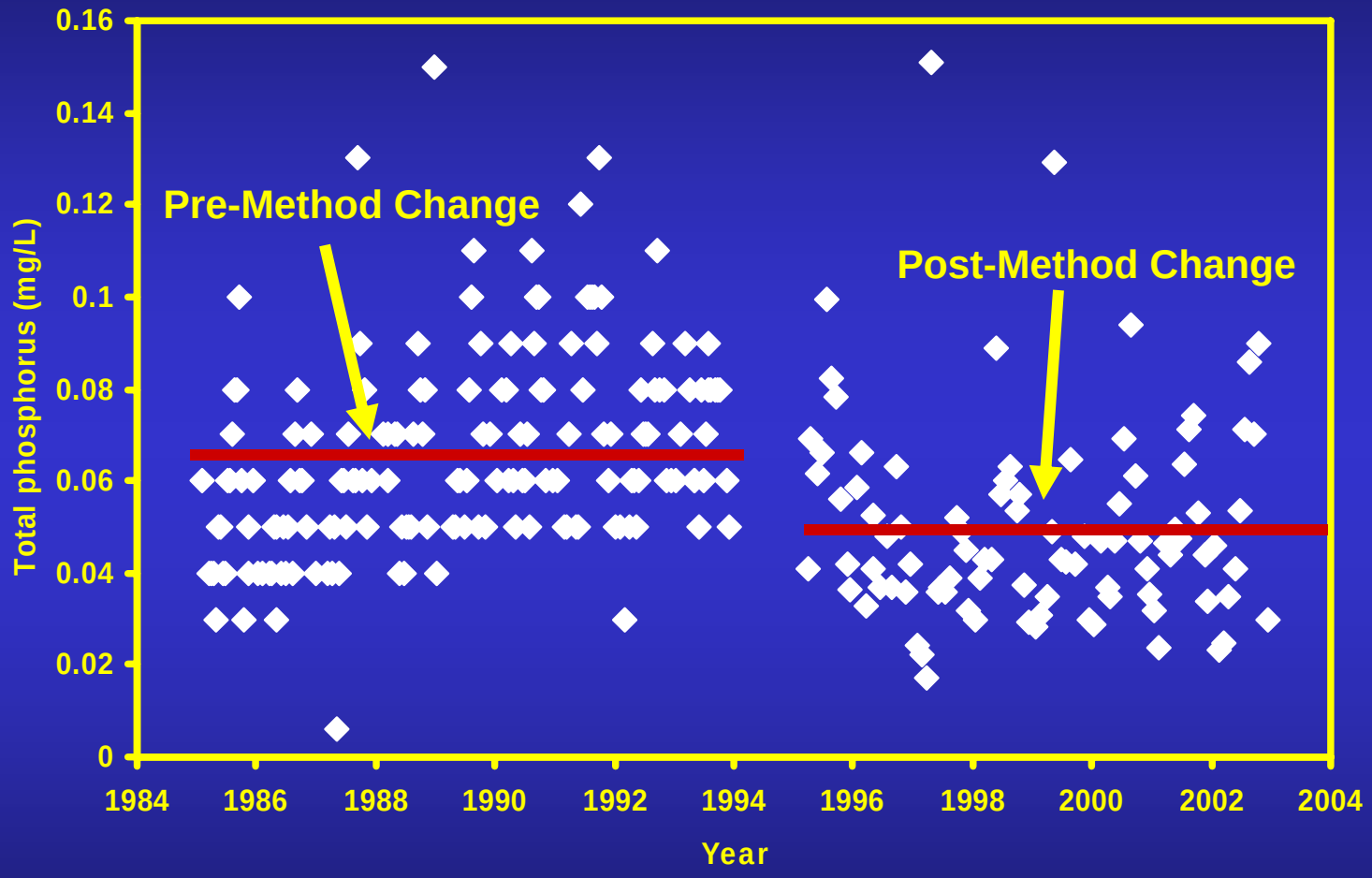
- **January 1994**
  - **TN calculated as TDN + PN (analyzed by VIMS).**
  - **TP calculated as TDP + PP (analyzed by VIMS).**

- **February 1995 to the present**
  - **DCLS adopts VIMS methods for PC, PN, PP, and TDN**
  - **DCLS uses EPA method 365.2 for TDP.**

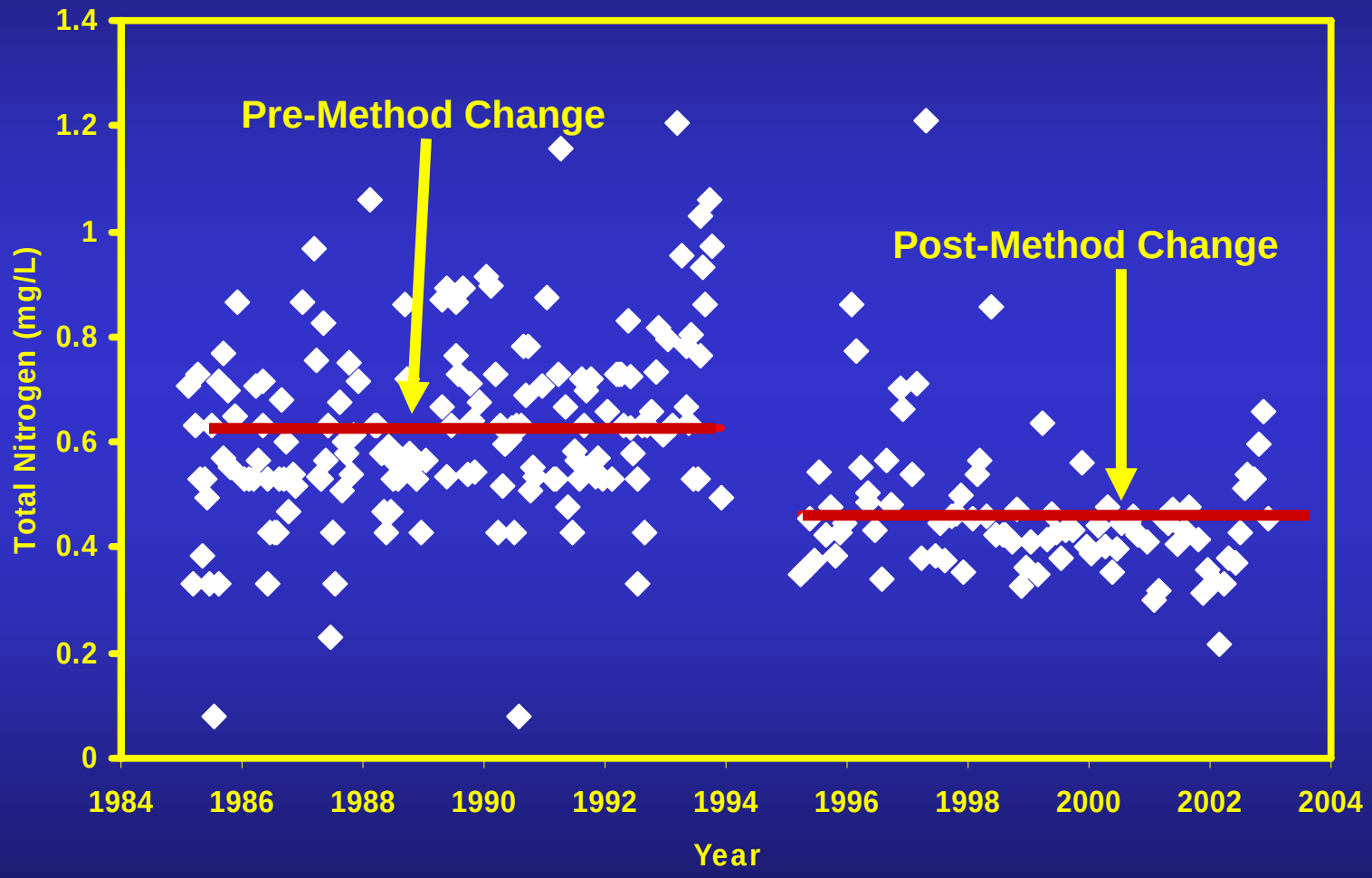
- **Changes resulted in step trends in both parameters.**

- **Adversely affects statistical analyses.**

Example – TP at Station LE5.4



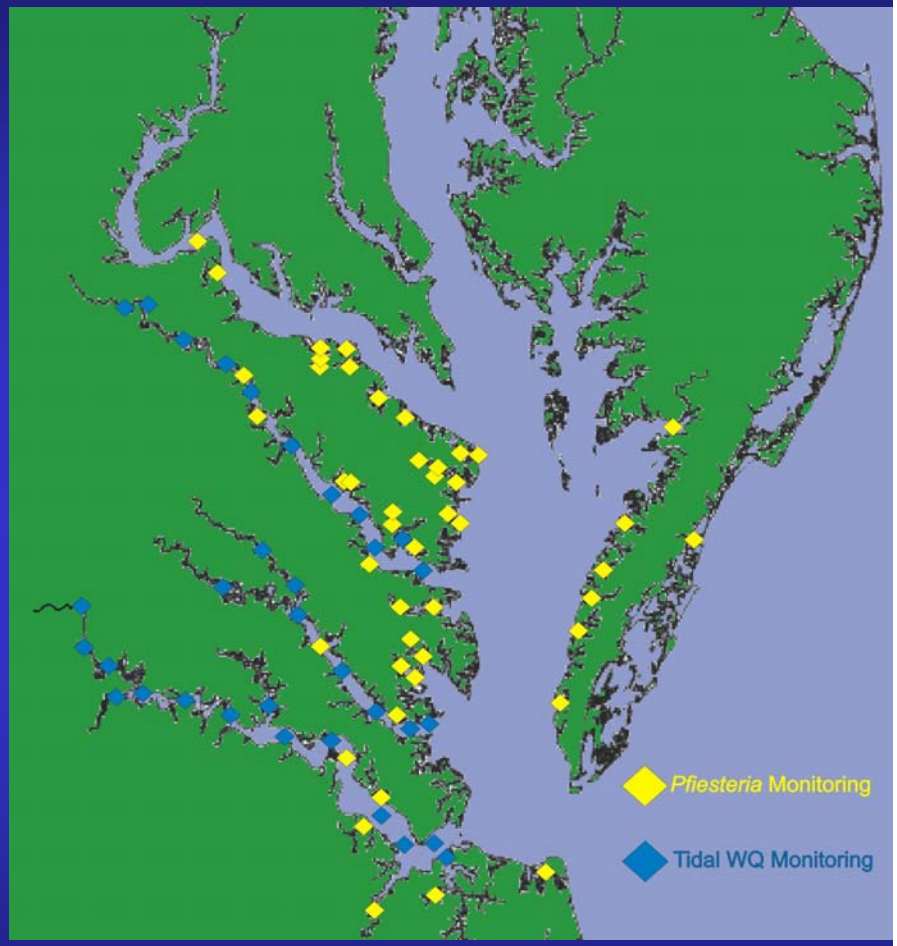
Example – TN at Station LE5.4



Methods

- 33 Tidal Monitoring Stations (1998-2003).
- 46 *Pfiesteria* Monitoring stations (1998-2002).
- Focus on Tidal Monitoring data only but *Pfiesteria* Monitoring data also analyzed.
- For CBP TP, there was an average of 33 with a min. of 11 and max. of 42 samples per station.
- For CBP TN, there was an average of 28 samples per station with a min. of 10 and max. of 75 samples per station.
- Sample collection and processing reflect historical methods used except:

  change in instrumentation.



Total Phosphorus

Definition of Bias

- **New Method – Old Method = Difference Between Methods.**
- **A negative value indicates Old Method is biased high relative to the New Method i.e. consistent with historical bias.**
- **A positive value indicates Old Method is biased low relative to the New Method in contrast with the historical bias.**

TP - Paired Comparisons (CBP Only)

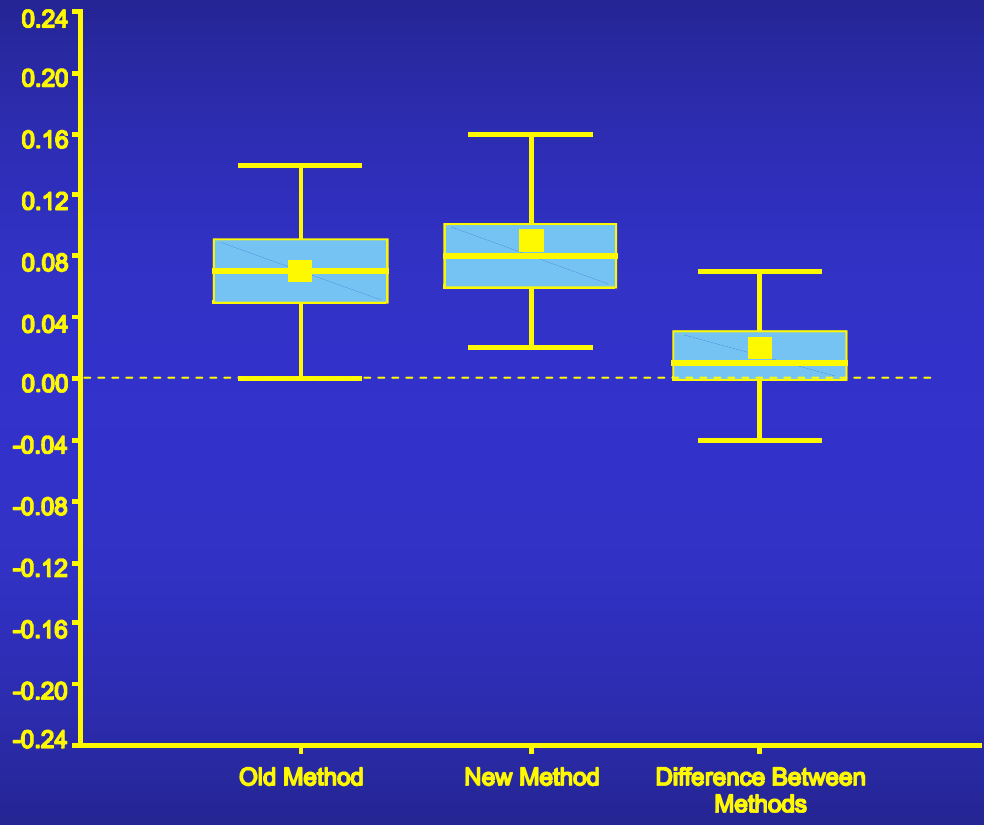
- Mean difference between methods significantly different from zero:

  Student's t:
  t value =8.00; Prob. >| t | <0.0001

  Wilcoxon Signed Rank:
  S value =219432; Prob. >|S| <0.0001

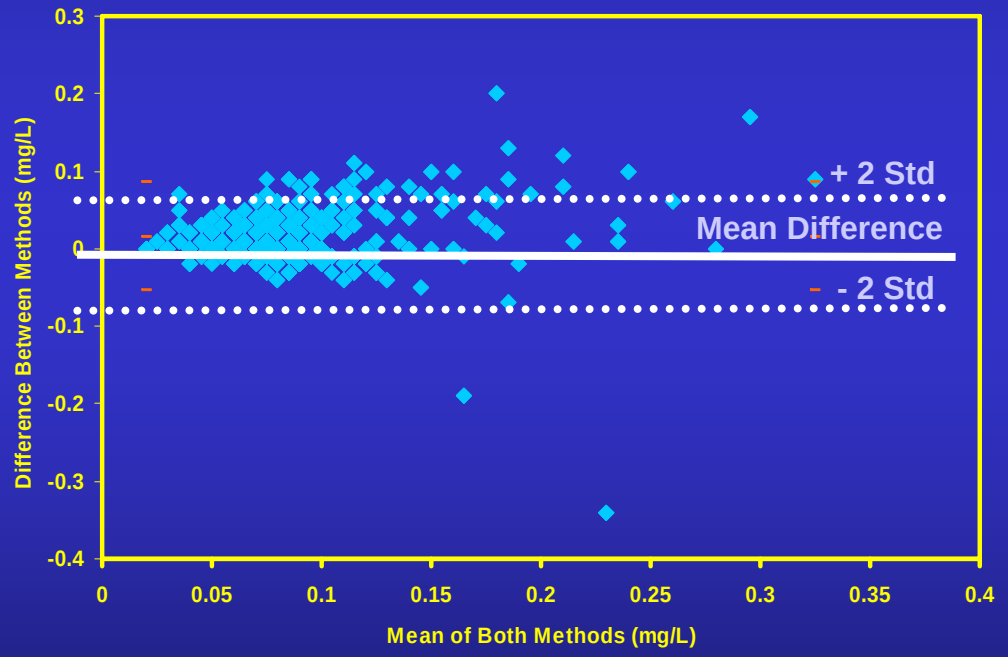
- Mean difference between methods = 0.02±0.035 mg/L.

- 75% of all differences at or above 0.00.



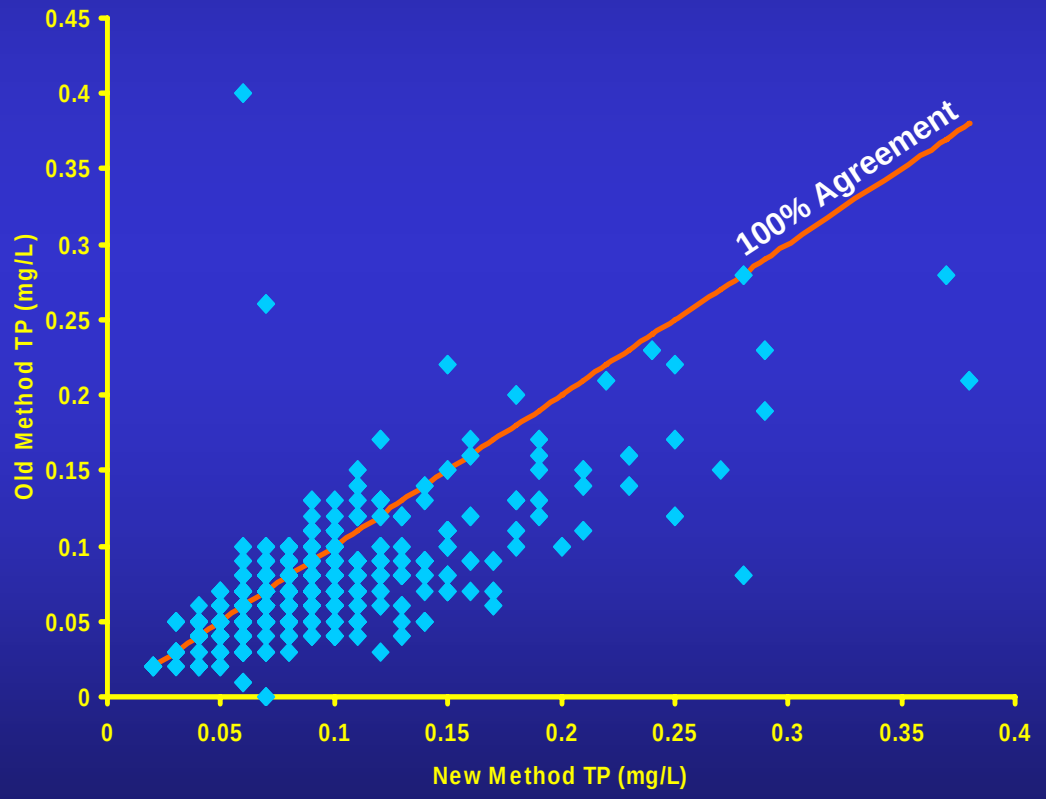
TP - Screening Analyses (CBP Only)

- Mean difference between methods: 0.02±0.035 mg/L.
- Old TP Method biased low relative to New TP Method up to mg/L.
- Variability of difference increases with increasing concentration.
- This conflicts with earlier observations in the historical data.



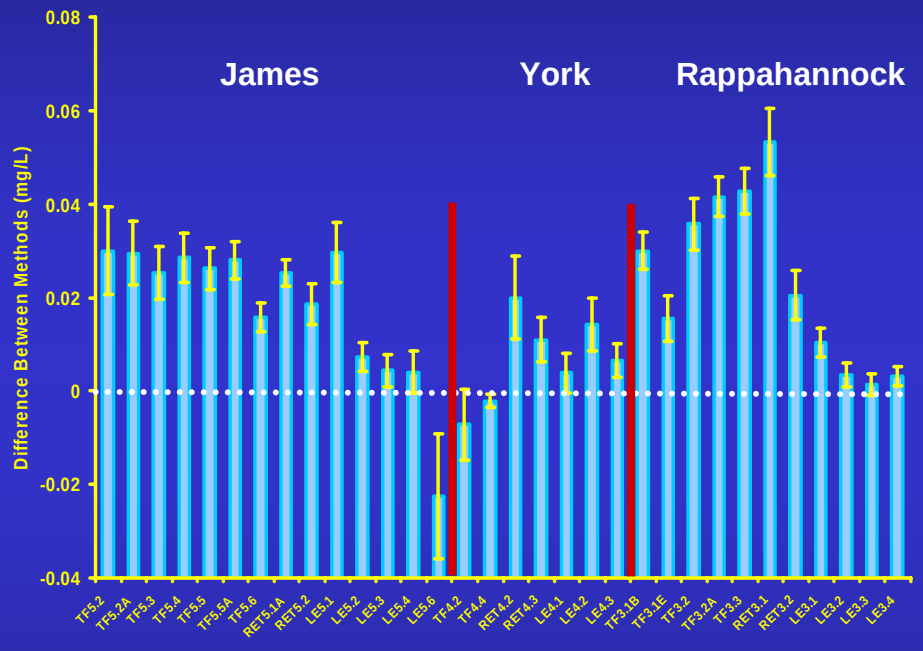
TP – Screening Analyses (CBP Only)

- Old Method biased low.
- Variability increasing with increasing concentration.
- More outliers at the higher concentrations.



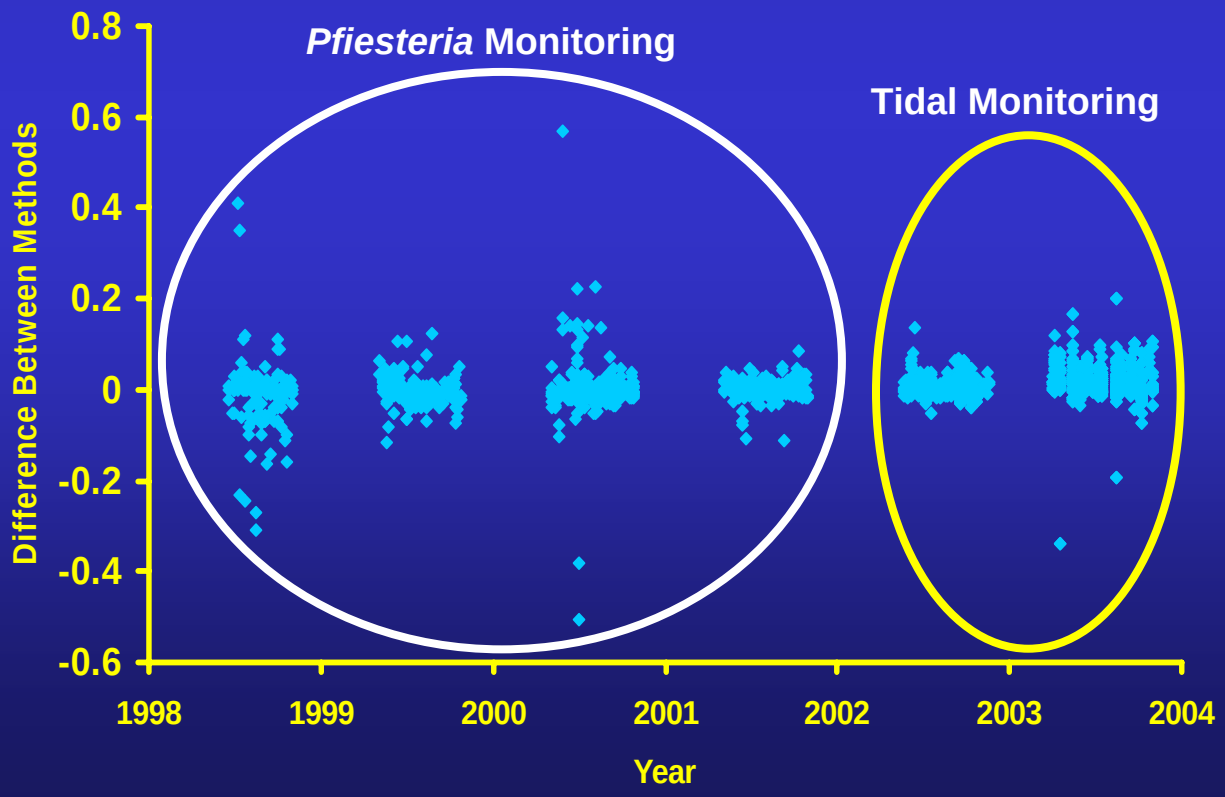
TP – Spatial Effects on Bias (CBP Only)

- Bias at most stations was positive.
- Only three stations had a mean bias < 0.00.
- In the James, bias decreased moving downstream.
- In the York, bias fluctuated but in general increased moving downstream.
- In the Rappahannock, bias increased to RET3.1 and then decreased downstream.
- Spatial patterns do not explain the difference between the current bias and bias observed in the historical data.



TP – Temporal Effects on Bias (All Data)

- Only *Pfiesteria* Monitoring data was available prior to 2002.
- Slight increasing trend in the bias from 98-03 (|R|=0.21;p>0.01).
- For *Pfiesteria* data alone and with 2002 CBP data – no significant difference between methods.



TP – Environmental Effects (CBP Only)

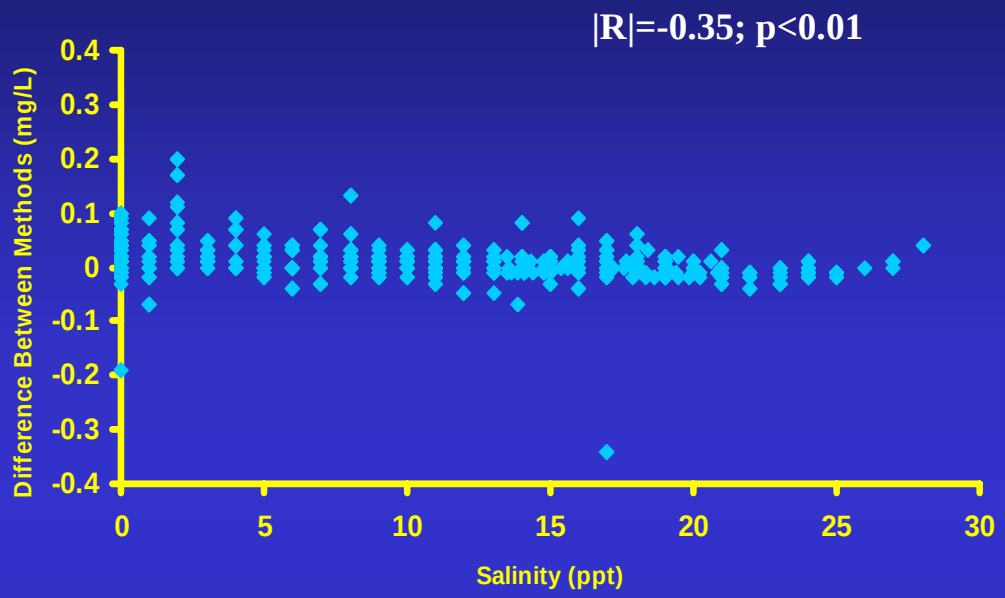
	Date	Month	Salinity	Salinity^2	Temperature
Difference	0.16;<0.01	-0.12;<0.01	-0.35;<0.01	-0.33;<0.01	-0.02;0.61
	Depth	pH	CHL a	TSS	PC
Difference	-0.05;0.14	-0.02;0.45	0.37;<0.01	0.47;<0.01	0.17;<0.01

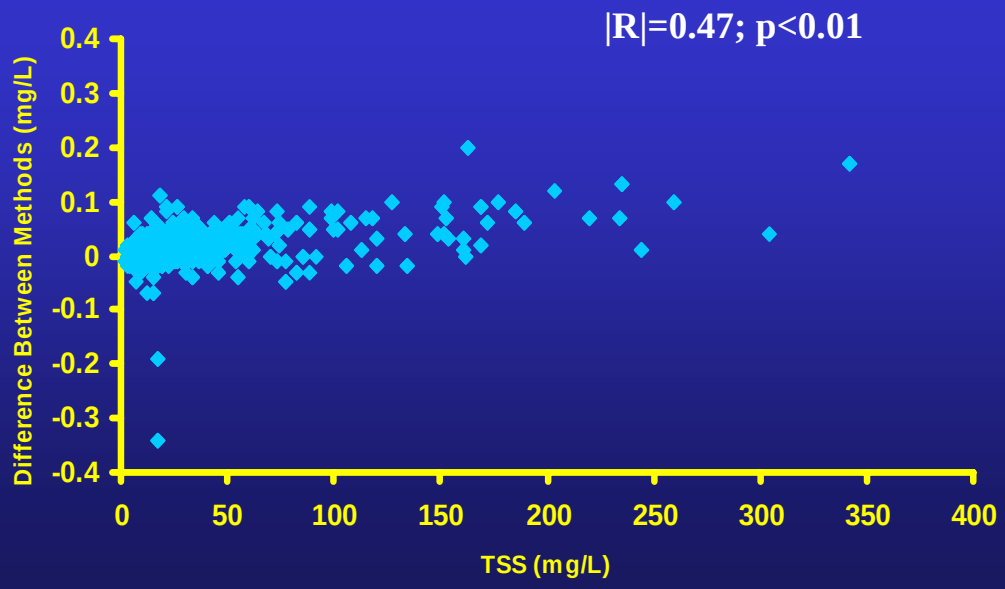
Shown are Pearson's |R| and associated p values. All correlations based on > 850 observations except CHL a (483)

- Bias correlated with salinity, TSS and Chl a.
- May explain difference source of the current bias.
- Same pattern with the *Pfiesteria* data but generally smaller correlations.

TP – Environmental Effects (CBP Only)

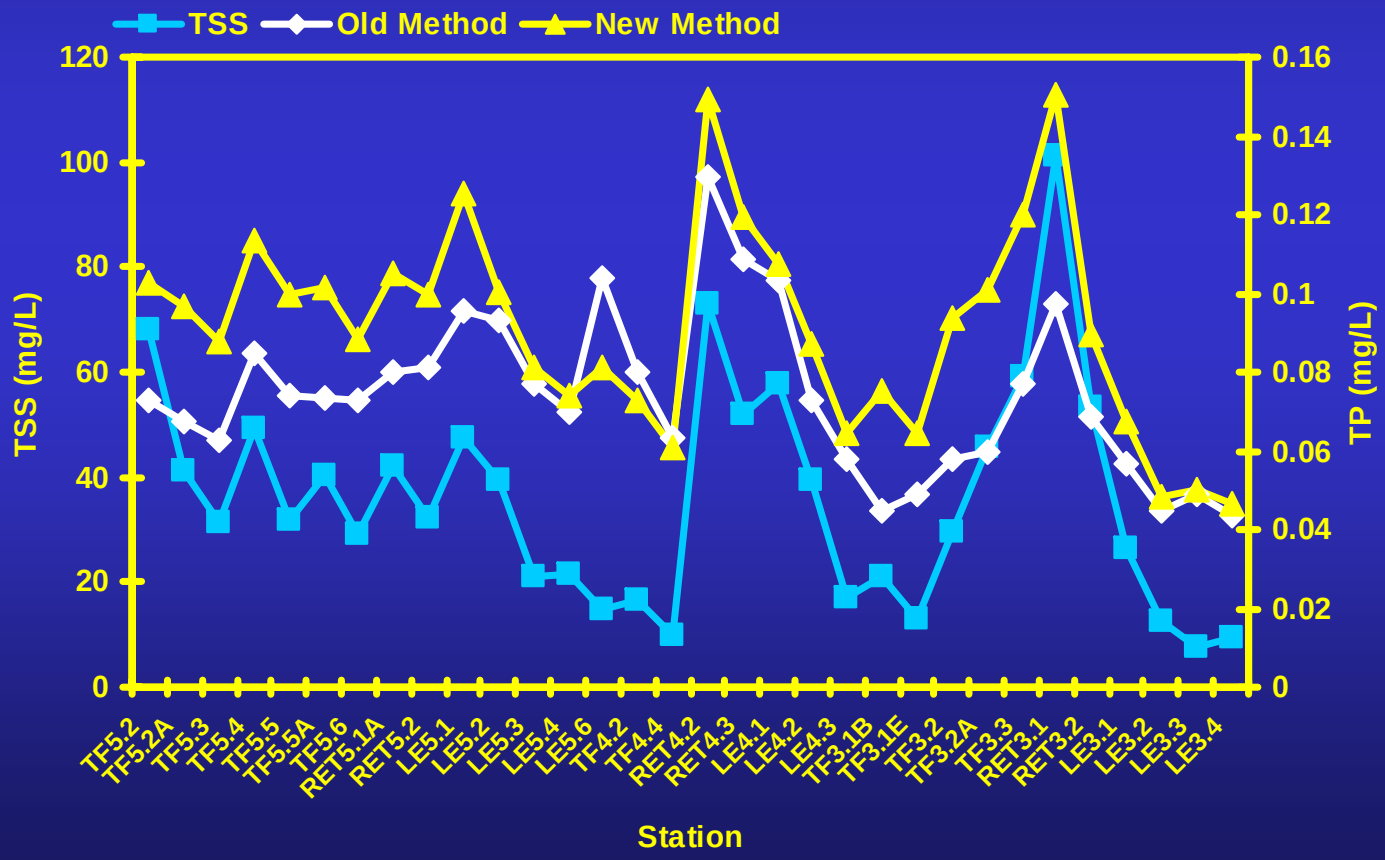
- Bias negatively correlated with salinity.
- Bias positively correlated with TSS.
- Relationship appears to be stronger for TSS than salinity.
- Environmental effects do not SEEM to explain the difference between the current and historical bias.





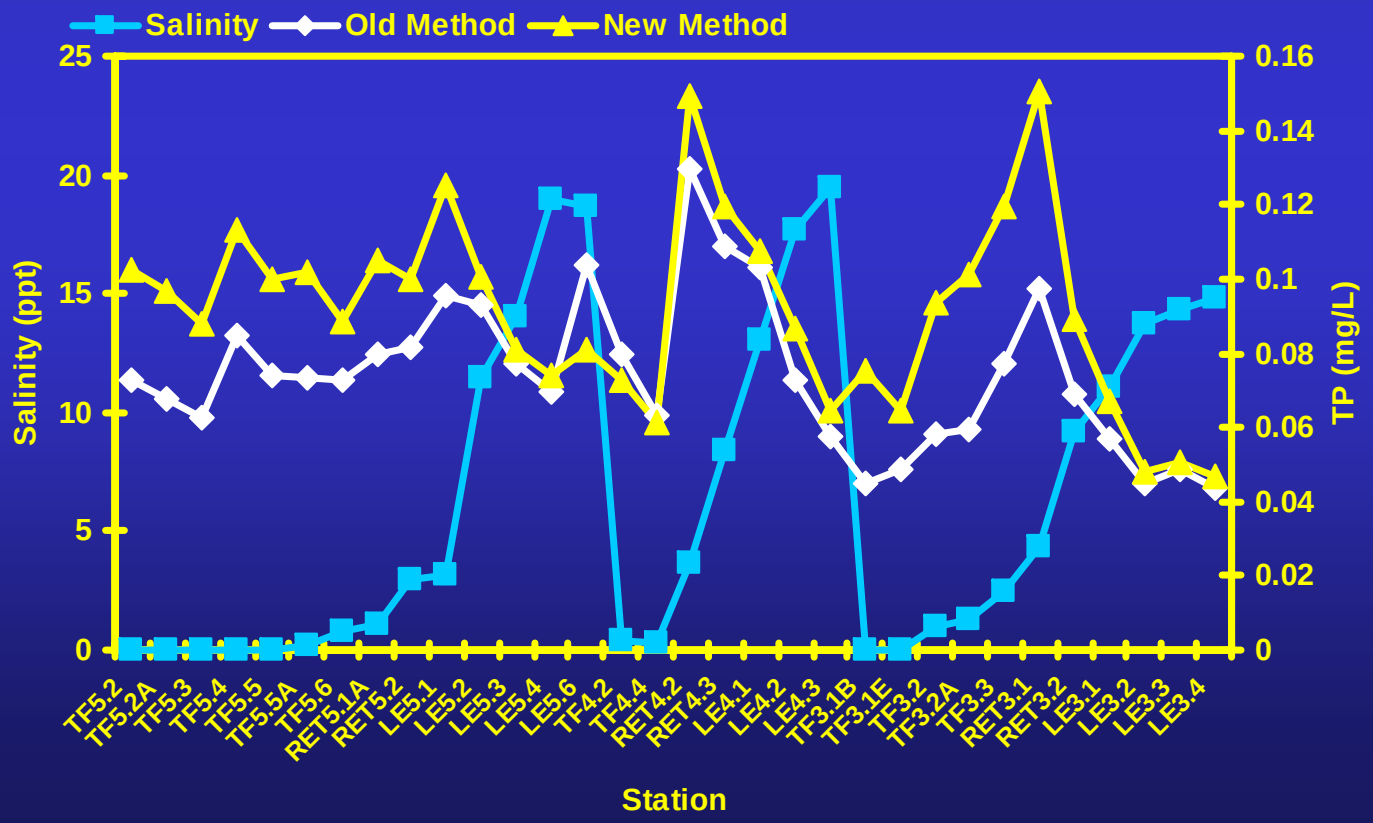
TP – Environmental Effects (CBP Only)

- New Method correlated to TSS with |R|=0.83;p<0.0001
- Old Method correlated to TSS with |R|=0.56;p<0.0001.
- New Method seems to respond more closely to changes in TSS than Old Method.

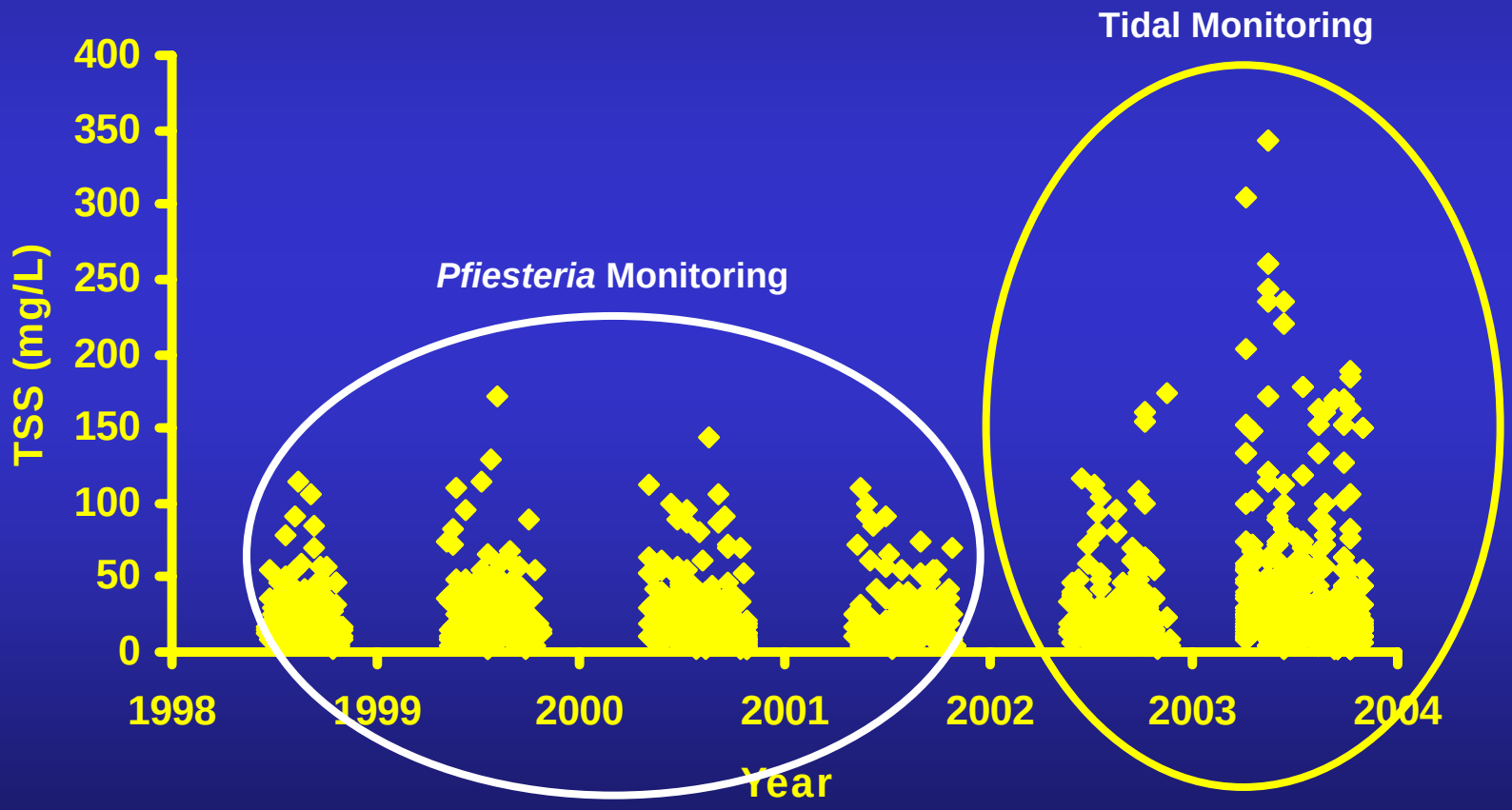


TP – Environmental Effects (CBP Only)

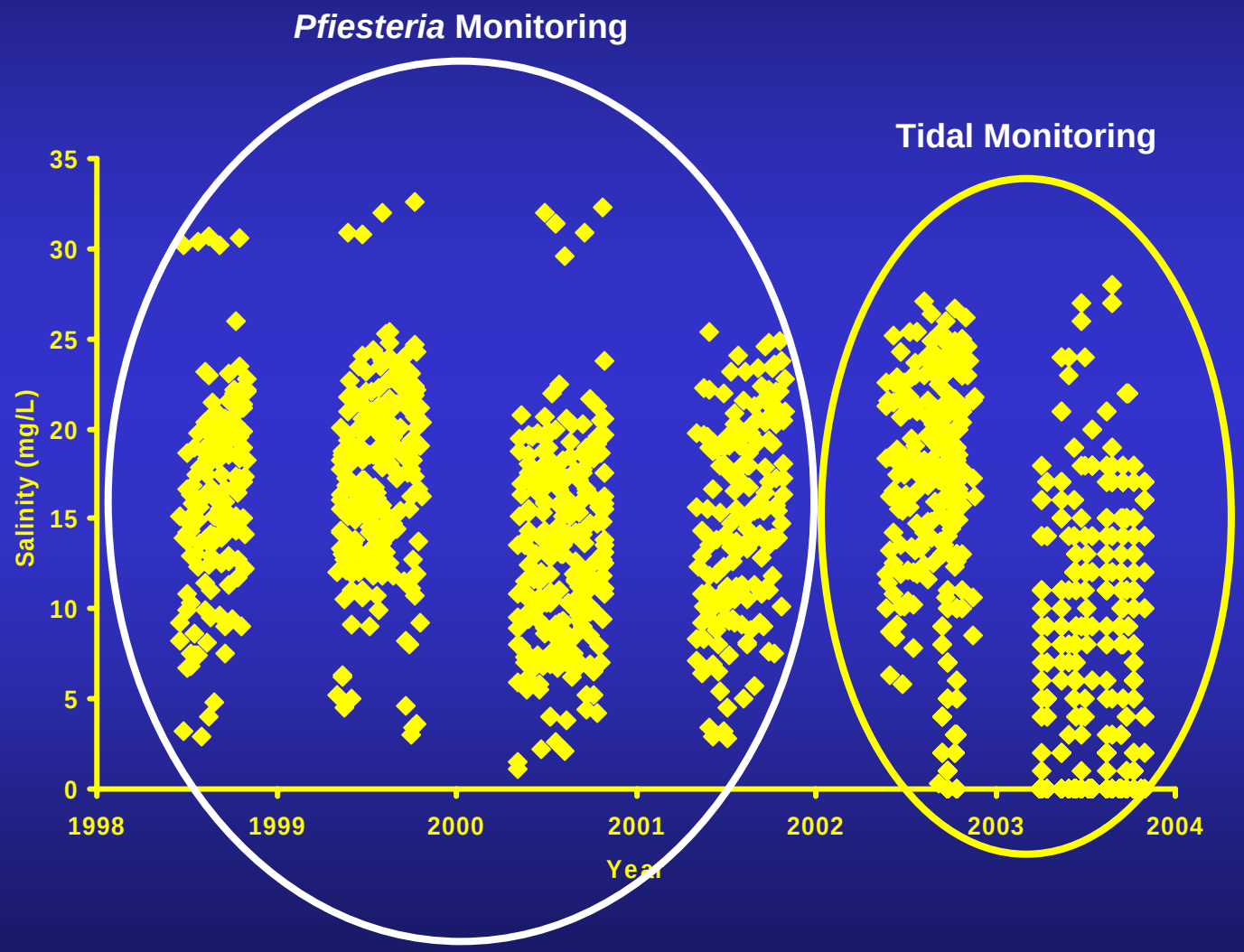
- New Method correlated to Salinity with |R|=-0.20;p<0.0001.
- Old Method correlated to Salinity with |R|=0.07;p=0.03.
- Neither method responds readily to salinity.



TP – Environmental Effects (All Data)



TP – Temporal Patterns in Bias



TP - Conclusions

- Significant difference between methods.
- Old Method biased low relative to the New Method.
- Opposite of pattern in historical data.
- Bias showed no consistent spatial pattern.
- Slight increase in bias during 2003.
- Increase due to high values in TSS.

TP – Conclusions

- **Spatial, temporal or environmental effect do not explain the difference between current and historical bias.**
- **Difference may be due to a change in instrumentation and/or other procedures.**
- **Current bias due to difference in accuracy between methods at high levels of TSS.**

TP – Recommendations

- Data are not conducive to method adjustment.
- Blocked Seasonal Kendall for TP until additional studies are available.
- Another paired study?
  - Use old instrumentation or more trouble than it is worth?
  - Do we control for season or not?
  - Do we control sampling locations for TSS, salinity or not?
  - Are there other effects?

Appendix D - Assessment of 1994 Methods Change for Total Phosphorus using Split Sample Data

Assessment of 1994 Methods Change for Total Phosphorus using Split Sample Data.

submitted to

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June, 2005

Introduction

This report addresses the apparent change of estimated total Phosphorus (TP) concentration that occurs coincident with a change in the methods for assaying TP in three Virginia Tributaries to the Chesapeake Bay. The results presented here are present and analysis of split sample data and additional analysis of the intervention analysis results. For the split sample data analysis, two data sets were combined. One data set, 9495_Method_Comparison_Data4.xls, contains data from the Pfiesteria program, River Input Monitoring program, and Tributary Monitoring Program between 1998 and 2003. The second data set, CBP_VNTP_DATA.XLS contains data from the CB nontidal stations. Numerous methods of developing an adjustment factor using these split sample data were attempted and proved unsuccessful. Thus addition analyses of the intervention analysis results were undertaken and a successful adjustment factor was developed.

Background

In 1994, the Virginia Department of Environmental Quality which oversees the tidal monitoring of nutrients in these Virginia tributaries implemented the new TP (TDPLF + PPWLF) to replace the old acid persulfate assay of TP. This was simultaneous with a change in method for TN. No split sample data to quantify the effects of this change were collected for either parameter at the time of the methods change. Subsequently, it was noted that a time series of TN data for the lower James appeared to exhibit a step down change at the time of the methods change. On inspection, there appeared to be a similar step down effect in TP. A follow up split sample study was implemented to assess whether these abrupt changes might be explained by the methods change. Note that in between the date of the methods change and the follow-up split sample study, additional changes to the TP measurement process were implemented such as the change of laboratory equipment. Therefore the split sample methods comparison does not measure all of the differences between the pre-1994 data and the post-1994 data.

This report offers an adjustment procedure based on additional modeling of the step estimates obtained from the intervention analysis. An analysis of the split sample data is presented and it is concluded that the split sample data do not yield information that quantifies an adjustment factor that removes the step trends that have been observed in the time series of TP data. An alternative adjustment factor is derived from analysis of the step estimates from the intervention analysis. Validation results are presented to show that this adjustment factor performs well. These two analyses are presented in the report in two parts.

Part 1. Analysis of the Split Sample Data

The fundamental null hypothesis in the analysis of the split sample study is that there is no difference between the TP measured by these two methods. A number of alternatives to this null hypothesis are considered. The simplest alternative hypothesis is that the methods differ, but that this difference remains constant for all sampling conditions. More complex alternatives are also considered. It is possible that the difference between methods is influenced by many factors including: other water quality constituents, spatial patterns, the program office processing the

samples, or date or season of collection. Results of statistical analyses to examine these alternative hypotheses are reported here.

Part 1. Methods

The data were pre-screened by DEQ to remove observations with detection limit or other problems. Using these pre-screened data, variables for the old method and the new method were created as TPOLD and TPNEW. The difference was computed as TPDIFF = TPNEW-TPOLD. It follows that a positive difference would indicate a step up between the old and new methods while a negative difference would indicate a step down.

```
tpdiff = tpnew - tpold;
lntpnew = log(tpnew);
lntpold = log(tpold);
lntpdiff = lntpnew - lntpold;
```

Because water quality parameters typically follow a log-normal distribution, these variables were also transformed by logarithms and the difference was computed as LNTPDIFF = log(TPNEW) - log(TPOLD). This difference variable is better suited to statistical methods that assume normality. Note that this mathematical expression equates to the logarithm of the ratio of TPNEW to TPOLD. That is LNTPDIFF = log(TPNEW) - log(TPOLD) = log(TPNEW/ TPOLD).

To check if the log difference between the methods might be affected by other water quality constituents, correlation analysis and graphical assessment of association was done for the following variables: mean of log TP, specific conductance, water temperature, pH, dissolved oxygen, log total suspended solids, program office, DEQ_program, distance from the Chesapeake Bay, and date of collection.

There are associations of the LNTNIFF with 7of the water quality variables as well as spatial and temporal trends. There are positive associations with pH, LNTSS, DATE, and BKM. There are negative associations with LNTNMEAN, Specific Conductance, salinity, and water temperature. Greater detail about these associations can be discerned in the corresponding scatter plots.

In reviewing the plots, it becomes clear by observing the loess regression line of central tendency that the trend of LNTPDIFF is not monotone with respect to pH, DO, or lnTSS. The trend is monotone with respect to salinity, specific conductance, and distance from the bay. Because salinity and specific conductance are known to have a longitudinal gradient in the tributaries to the bay, it is probably best to think of this correlation of LNTPDIFF with salinity and with specific conductance as a consequence of all of these variables having a longitudinal trend and not infer that there is some cause and effect between them. The correlation indicates that there is an increasing trend with date. However, if we plot salinity versus date, we discover that there is a tendency to have more freshwater samples toward the end of the period of record. Thus what appears to be an association with time is in fact another aspect of the longitudinal spatial trend. Thus while there appear to be many pairwise association between variables, the underlying cause

for these associations is that most variables have a spatial trend. One exception to this generality is the variable LNTSS. This variable has a significant correlation with the LNTPDIFF, but it does not have a monotone upstream-downstream gradient. The variable LNTSS appears to have an association with LNTPDIFF that is independent of a longitudinal gradient.

Table 1. Spearman Correlation coefficients between the LNTNIFF variable and selected water quality variables:

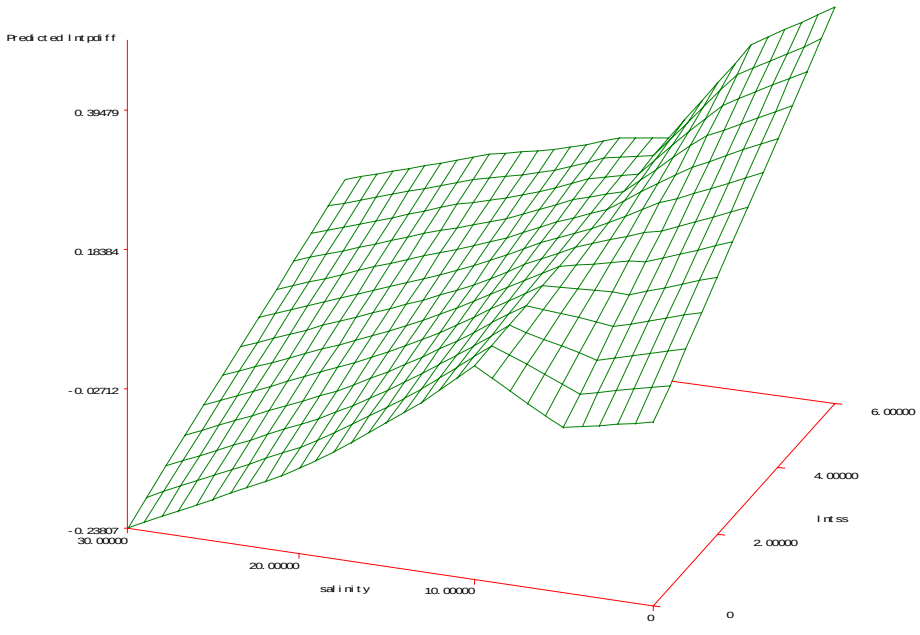
Water Quality Variable	Statistic	Pearson correlation/ p-value	Spearman Correlation/ p-value
lntnmean	correlation	-0.38393	-0.45976
	p-value	<.0001	<.0001
SpCond	correlation	-0.17993	-0.16555
	p-value	<.0001	<.0001
Salinity	correlation	-0.22589	-0.22318
	p-value	<.0001	<.0001
WTemp	correlation	0.08478	0.15009
	p-value	0.0018	<.0001
PH	correlation	-0.17581	-0.18186
	p-value	<.0001	<.0001
DO	correlation	0.01893	0.01436
	p-value	0.4860	0.5974
lntss	correlation	0.18189	0.19134
	p-value	<.0001	<.0001
Date	correlation	0.34513	0.29029
	p-value	<.0001	<.0001
BKM	correlation	0.13717	0.18527
	p-value	<.0001	<.0001

These observations are reinforced by StepWise regression analysis. In stepwise regression, the SALINITY and LNTSS are chosen as the most important predictors. Other variables are chosen by the stepwise procedure (table 2) but the p-values indicate that they are of much less importance. Even though salinity and tss appear highly significant in the statistical sense, together they explain only a small proportion of the total variation in the difference between the methods (r-square = 0.0836).

Table 2. Summary of Stepwise Selection regression results where the dependent variable is LNTPDIFF and the potential independent variables include: specific conductance, water temperature, pH, dissolved oxygen, logarithm of total suspended solids, date, distance to bay, and salinity.

Step	Variable Entered	Partial R-Square	Model R-Square	F Value	Pr > F
1	Salinity	0.0655	0.0655	108.12	<.0001
2	lntss	0.0181	0.0836	30.47	<.0001
3	WTemp	0.0036	0.0872	6.01	0.0143
4	PH	0.0028	0.0900	4.79	0.0287
5	BKM	0.0022	0.0922	3.72	0.0541
6	Date	0.0027	0.0949	4.63	0.0315

Having selected SALINITY and LNTSS as important predictors, these variables were used in a LOESS procedure to examine nonlinearity the relation of the method difference to these variables. A plot of the resulting surface (fig. 1) shows that when both salinity and lntss are near zero, the two methods show little difference. However, as salinity increases, the difference between the new method and the old method decreases so that at an extreme salinity of 30, the new method is on average about 78% of the old. On the other hand, as lntss increases, the difference increases and at an extreme lntss of 6.0, the new method is 148 % of the old method. Note that in this plots (fig 1) the surface deviates from a plane only slightly. Thus is appears reasonable to use a multiple linear regression to estimate adjustment factors for every level of LNTSS and SALINITY.



V

Based on these findings, it would be reasonable to adjust the data collected by the old method as follows: Use the multiple linear regression equation shown above to estimate the difference of the logarithms of the new and old methods. The antilog of this difference is an estimate of the geometric mean of the ratio of the new method TP to the old method TP. Multiply all old method observations by this ratio to adjust the data to be more comparable to the new method for data analyses that involve a comparison of data from both methods (e.g. trend assessment). The regression equation derived by these methods is:

lnaf = 0.05213 + 0.05299 (lntss) - 0.01054 (Salinity) Eqn. 1.0

where: lnaf = the logarithm of the adjustment factor,
lntss = the logarithm of TSS for measured for the sample, and
Salinity = the salinity measured for the sample.

However, a validation test of this adjustment procedure based on split sample data shows that it is not effective at removing the step trends that were observed in the time series of monitoring data. The validation test involved adjusting the monitoring data collected by the old method as described and rerunning the intervention analysis. In many cases, the size of the step became larger rather than smaller when this procedure was implemented. In general there were 38 significant steps after the adjustment (table 2) as compared to 37 before (table 1). The distribution of steps remains heavily weighted toward steps down at 54 while steps up are only 9. This adjustment was calculated on an observation by observation basis using the salinity and tss that were concurrently observed. Because the adjustment estimate is a least squares fit through many observations, it is possible that a better adjustment might be obtained by computing the adjustment on a station by station basis using the mean salinity and mean tss for that station. This approach based on means was implemented and it performed no better than the approach based on individual observations.

Table 1. Summary by direction and statistical significance (p<=0.05) of step trends found by the intervention analysis before adjusting the pre methods change data for methods change effects.

Direction		Not Significant	Significant	Total
Step down	count	19	35	54
	percent	35.19	64.81	100.0
Step up	count	7	2	9
	percent	77.78	22.22	100.0
Total	count	26	37	63
	percent	41.3	58.7	100.0

Table 2. Summary by direction and statistical significance (p<=0.05) of step trends found by the intervention analysis after adjusting the pre-methods change data for methods change effects using adjustment factors derived from the split sample data.

Direction		Not S Significant	Significant	Total
Step down	count	16	38	54
	percent	29.63	70.37	100.0
Step up	count	9	0	9
	percent	100.00	0.00	100.0
Total	count	25	38	63
	percent	39.68	60.32	100.0

Part 2 - Comparison of Split Sample results to Intervention Analysis results.

Additional analyses have been conducted to assess the failure of the adjustment procedure based on the split sample data. The goal is to understand why the adjustment derived from the split sample data is not effective for removal of the step trends that have been observed and if possible develop a procedure that is effective at this task. This section focuses on a comparison of trends in the split sample data to trends in the step estimates obtained from the intervention analysis. For this analysis, the step estimates from the intervention analysis are considered estimates of the methods change effect. Keep in mind that the intervention analysis is conducted on data collected insitu and may be influenced by changing factors in the environment other than the methods change.

Because the adjustment based on modeling these trends in the split sample data failed to remove the step trends observed in the monitoring data, it is natural to compare trends in the split sample methods effect estimate to trends in the intervention analysis methods effect estimate. The step trends for the intervention analysis of the monitoring data are observed only once for each station/layer combination, thus the station/layer must be the basic unit for comparison. For each station/layer, the estimate of the step trend from the intervention analysis is paired with the mean difference of the new and old methods from the split sample data. Figure 2 shows a comparison of the two. There is some association here, but it is not strong. The failure of these two differences to correlate more strongly suggests that the two are measurements of different phenomena.

As noted in the work above, the log difference of new and old methods has trends that associate with salinity and TSS. This is evident in the response surface (fig 1) and for simplicity we show these trends in scatter plots in figures 3 and 4. In figures 5 and 6 we examine trends against these same variables for the Step Estimates of method difference.

Next we assess the step estimates from the intervention analysis to see if these show similar associations with salinity and TSS. The results are shown in figures 5 and 6.

In comparing figures 3 and 5, it is clear that both the mean methods difference from the split sample study and the step estimates from the intervention analysis have some similarity in trend. Both the TPDIFF and the StepEstimate tend to decrease as salinity increases. However, there is also a marked difference. In the split sample study (figure 3) we see that the methods difference is positive in fresh water and tend toward zero as salinity increases. The step trend estimates from the monitoring data are near zero for fresh water and tend to become negative as salinity increases.

Figure 2. Scatter plot of the mean difference of the new and old methods from the split sample data versus the estimate of the step trend from the intervention analysis for each Station/layer.

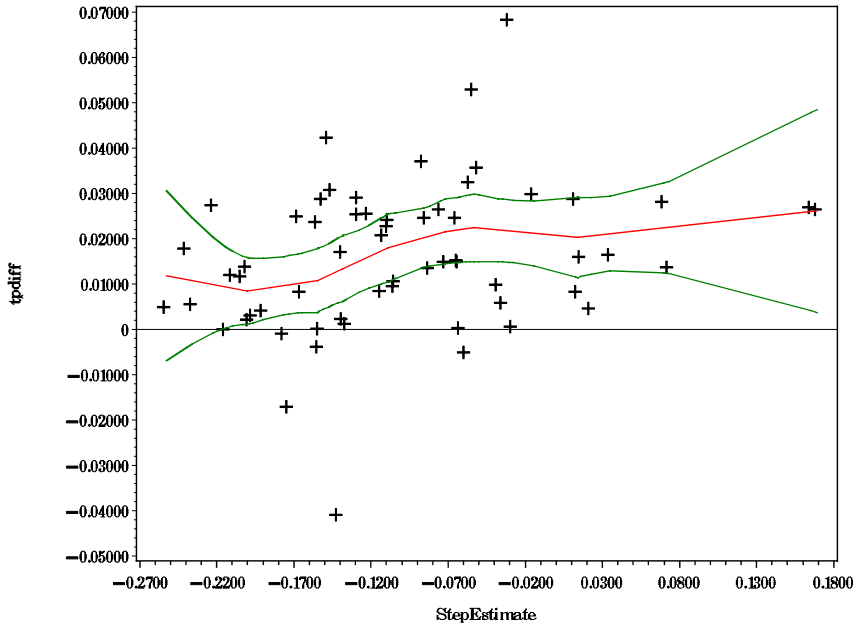


Figure 3. The mean difference of logarithms of old and new method measurements of TP for each station shown as a scatter plot against the mean salinity for each station collected by the split sample program.

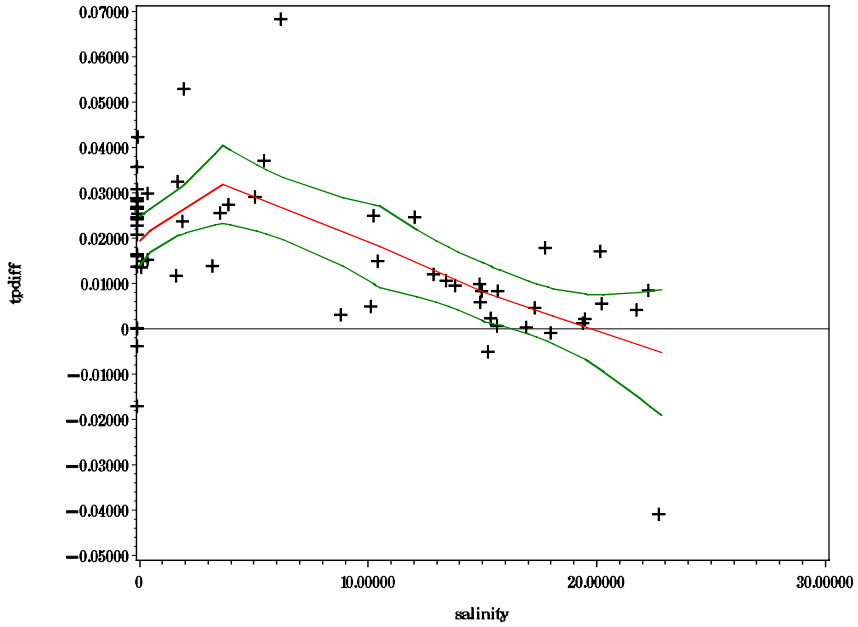


Figure 4. The mean difference of logarithms of old and new method measurements of TP for each station shown as a scatter plot against the mean logarithm of TSS for each station collected by the split sample program.

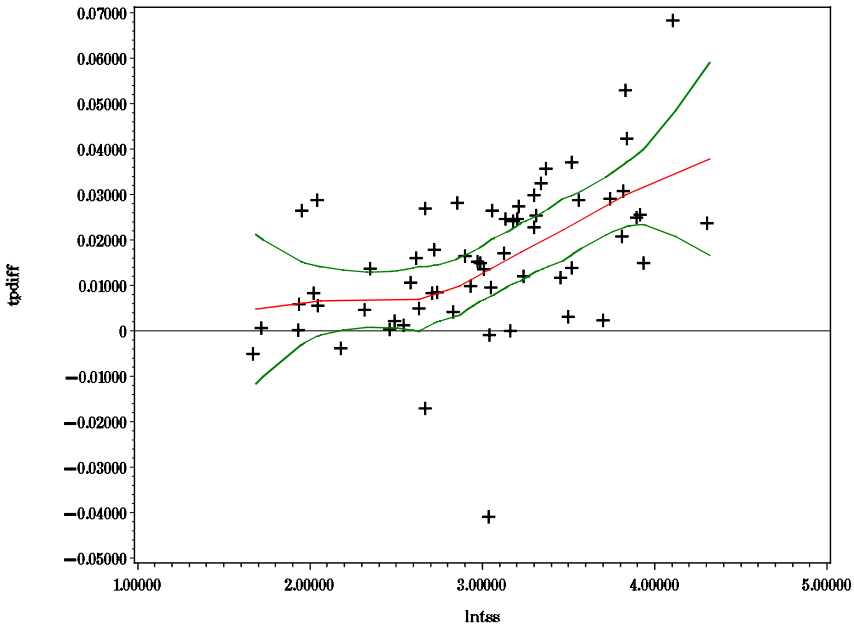


Figure 5. Step trend estimates from the intervention analysis for each station shown as a scatter plot against the mean pre-methods change salinity for each station.

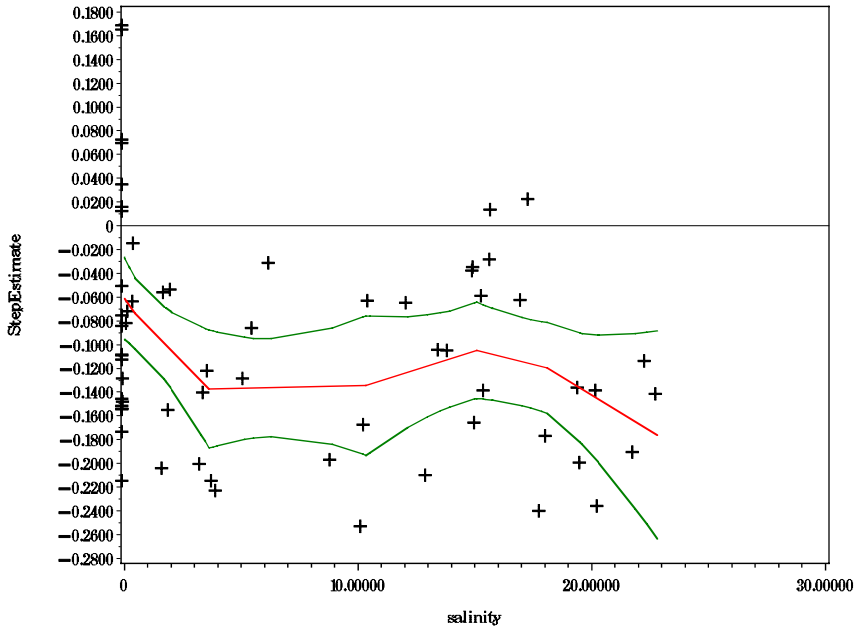
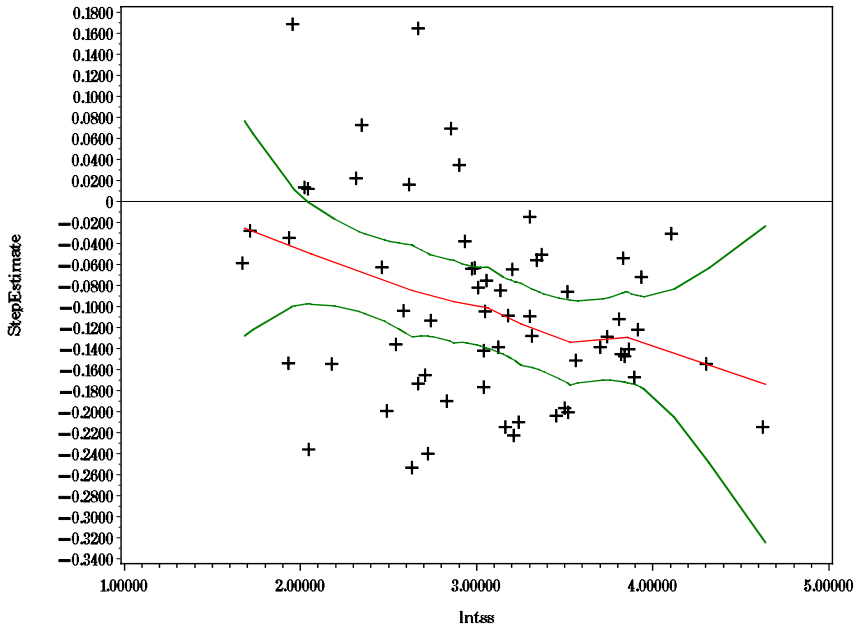


Figure 6. Step trend estimates from the intervention analysis for each station shown as a scatter plot against the mean pre-methods change logarithm of TSS for each station.



In comparing figures 4 and 6, we also see some similarity and some differences. In the both the split sample study (figure 4) and the step trend estimates (figure 6) the method difference appears to be near zero when the logarithm of TSS is low. However, as the logarithm of TSS increases,

the split sample study shows that the difference between methods tends to become positive while the intervention analysis shows that the difference becomes negative.

Given these marked and statistically significant differences it seems reasonable to conclude that the method difference measured by the two studies is for some reason not the same. Because the split sample data did not yield a successful adjustment factor, the split sample data is abandoned as a basis for developing the adjustment factor. Instead, an adjustment factor based on a model of the Step Estimates as a function of logarithm of TSS and Salinity is explored. The coefficients of this model have been estimated using multiple linear regression analysis where the Step trend estimate for each station is the dependent variable and the mean logarithm of TSS and mean Salinity of the pre-methods change period of record are the independent variables. The resulting equation is:

lnaf = 0.12605 - 0.14471(mn_lntss) - 0.00471(mn_Sal) **Eqn. 2.0**

where: lnaf = the logarithm of the adjustment factor,
mn_lntss = the mean of logarithms of TSS for the pre-methods change period, and
mn_Sal = the mean of salinity for the pre-methods change period

The adjustment may be applied in the logarithm of TP metric as:

lntp_aj = lntp + lnaf;

where: lntp = the logarithm of TP, and
lntp_aj = the logarithm of adjusted TP.

Or may be applied in the native TP metric as

TP_aj = TP * 10**ln_aj.

All logarithms are logarithms in base 10. This adjustment is applied to the old method data to make it comparable to the new method data.

The statistics for the estimates of the coefficients in this regression relationship are:

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	0.12605	0.05534	2.28	0.0263
lntss	1	-0.14471	0.03782	-3.83	0.0003
salinity	1	-0.00471	0.00138	-3.41	0.0012

As one would surmise from figures 5 and 6, both lntss and salinity are significant predictors of the methods change effect.

The adjustment based on equation **2.0** resolves most of the step trends that were observed in the time series data at CBP stations (table 3). The distribution of steps down vs. steps up are now much more nearly equal at 30 and 33 respectively. Only 11 of the post adjustment steps appear statistically significant as compared to 37 before adjustment. Whereas all but 2 of the significant unadjusted steps were steps down, after adjustment, the significant steps are split with 4 down and 7 up. The significant four down-step station/layers are: LE3.4/B, TF5.2A/B, TF5.2A/S, and TF5.3/B. The significant seven up-step station/layers are: LE4.3/S, LE5.1/S, LE5.2/S, TF4.2/B, TF4.2/S, TF4.4/B, and TF4.4/S. Note that these remaining step trends are frequently close spatially.

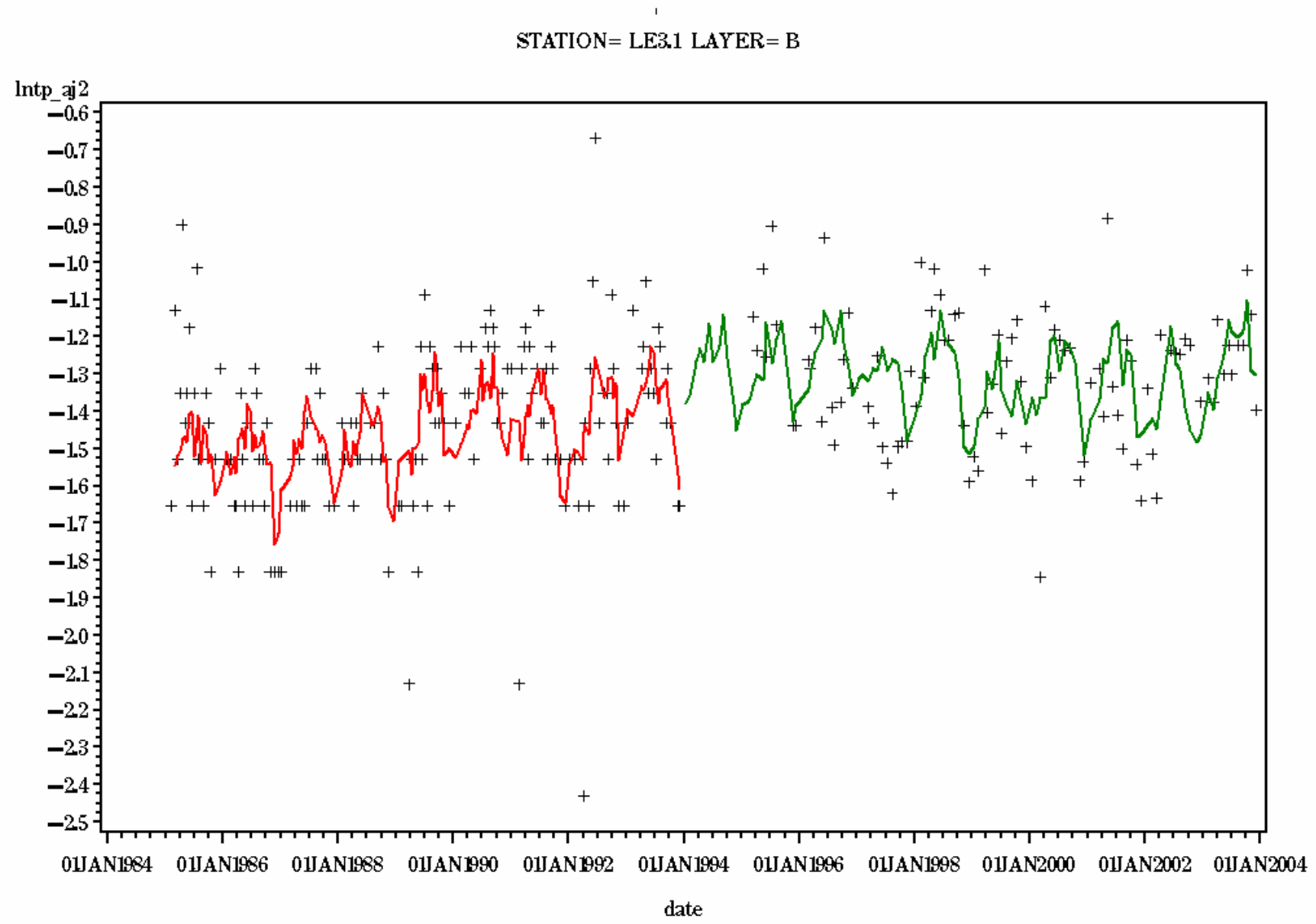
Table 3. Summary by direction and statistical significance (p<=0.05) of step trends found by the intervention analysis after adjusting the pre-methods change data for methods change effects using adjustment factors derived from the intervention estimates data.

Direction		Not Significant	Significant	Total
Step down	count	23	7	30
	percent	76.67	23.33	100.0
Step up	count	29	4	33
	percent	87.88	12.12	100.0
Total	count	52	11	63
	percent	82.54	17.46	100.0

Graphical analysis of the time series of the adjusted pre-1994 data as compared to the post-1994 data with trend lines and a step at 1994 can be viewed in the graphical appendix of this report. The graphs cover the 63 station/layer cases that were analyzed to reach the conclusions cited above.

The adjustment factor based on **Eqn. 2.0** removes most of the step trends that were observed in the TP data time series data. Thus it seems reasonable to apply this adjustment if data analysis or a comparison of data involves data measured under both the new and old methods. If data analysis does not entail a comparison of data from the two methods, it is better to leave the data unadjusted. Therefore it is recommended that the original data remain in the data base and the adjustment be implemented as needed.

Graphical Appendix to Analysis of Assessment of 1994 Methods Change for Total Phosphorus using Split Sample Data.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−1.4
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−1.6
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−1.9
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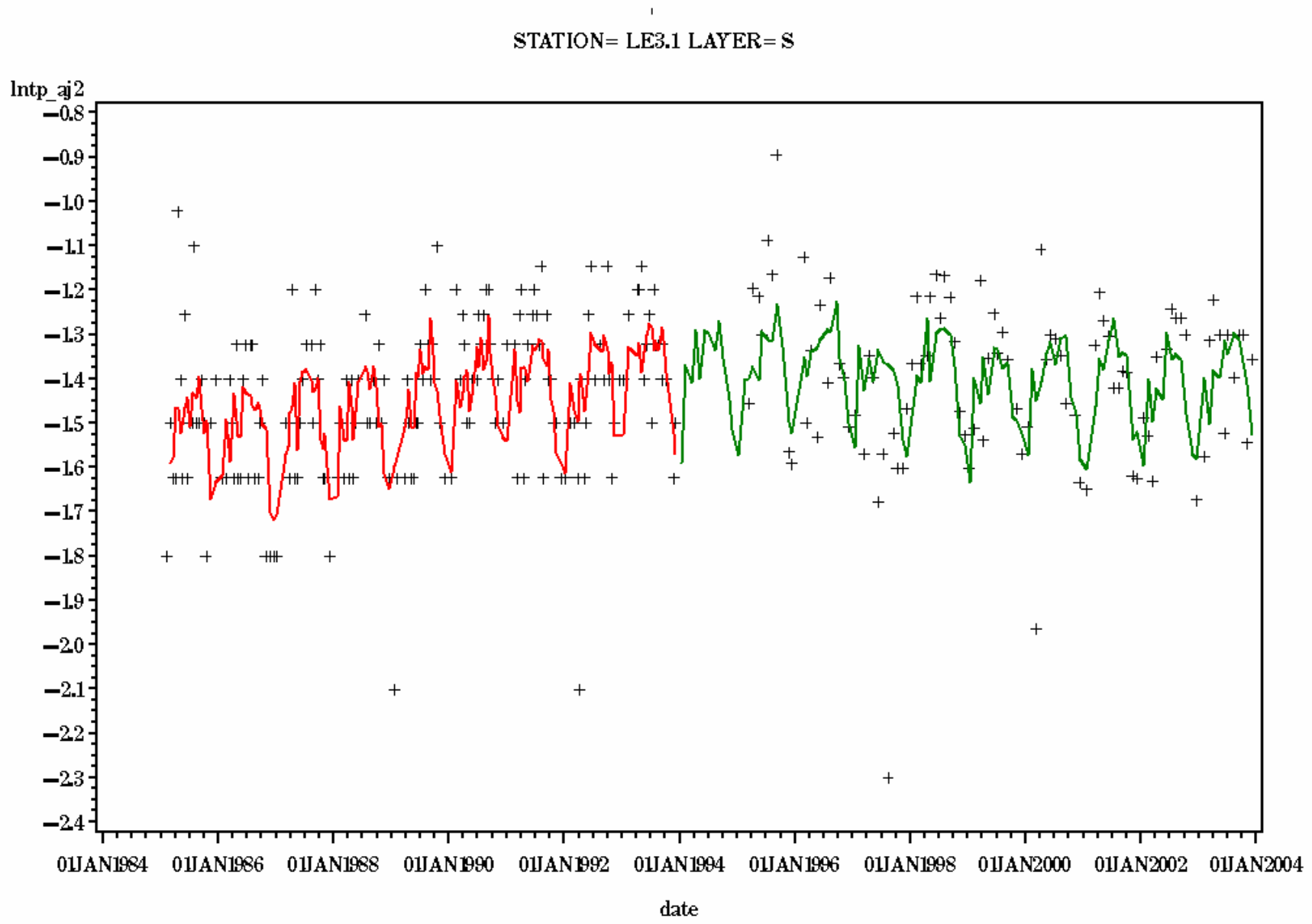
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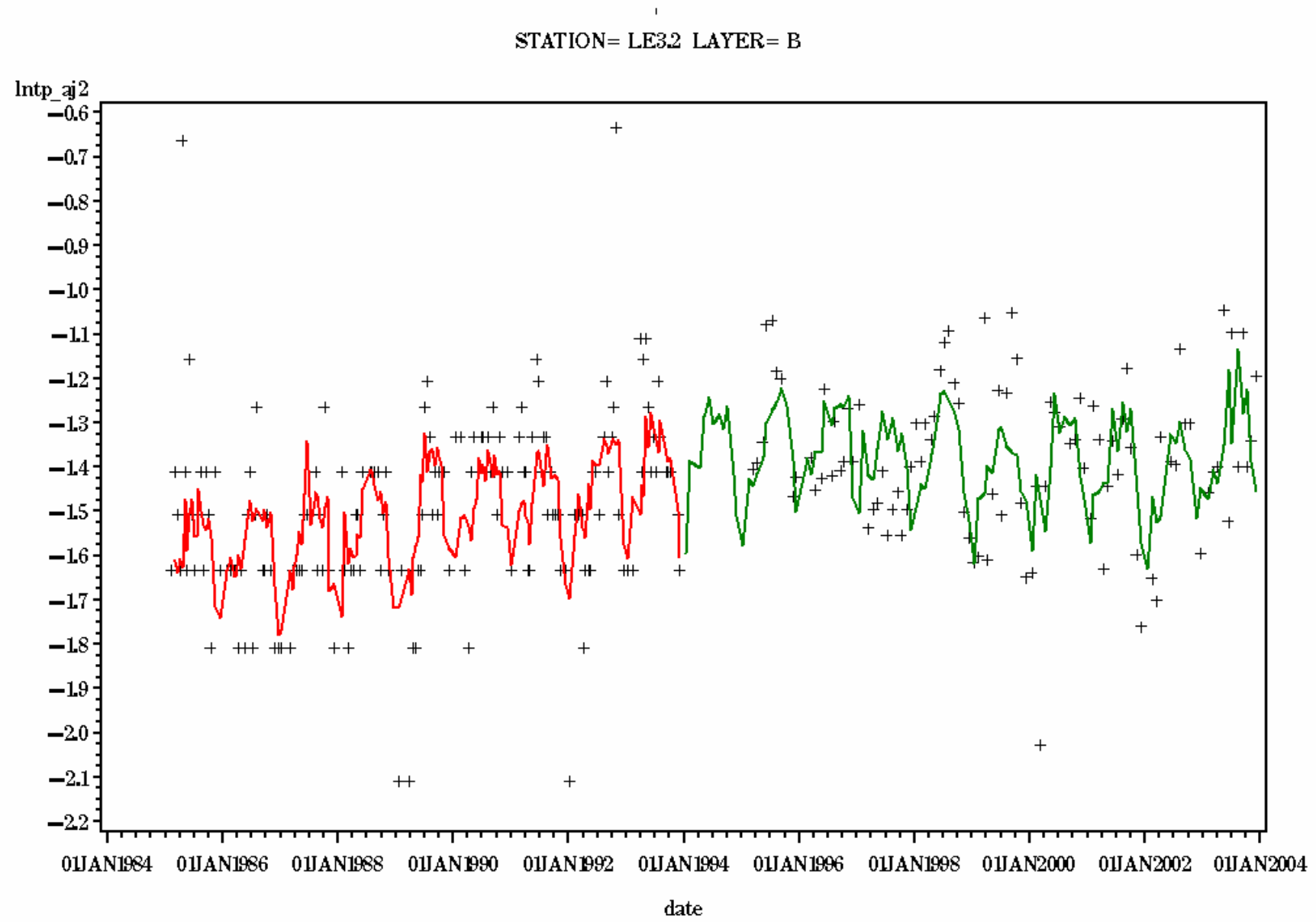
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−1.3
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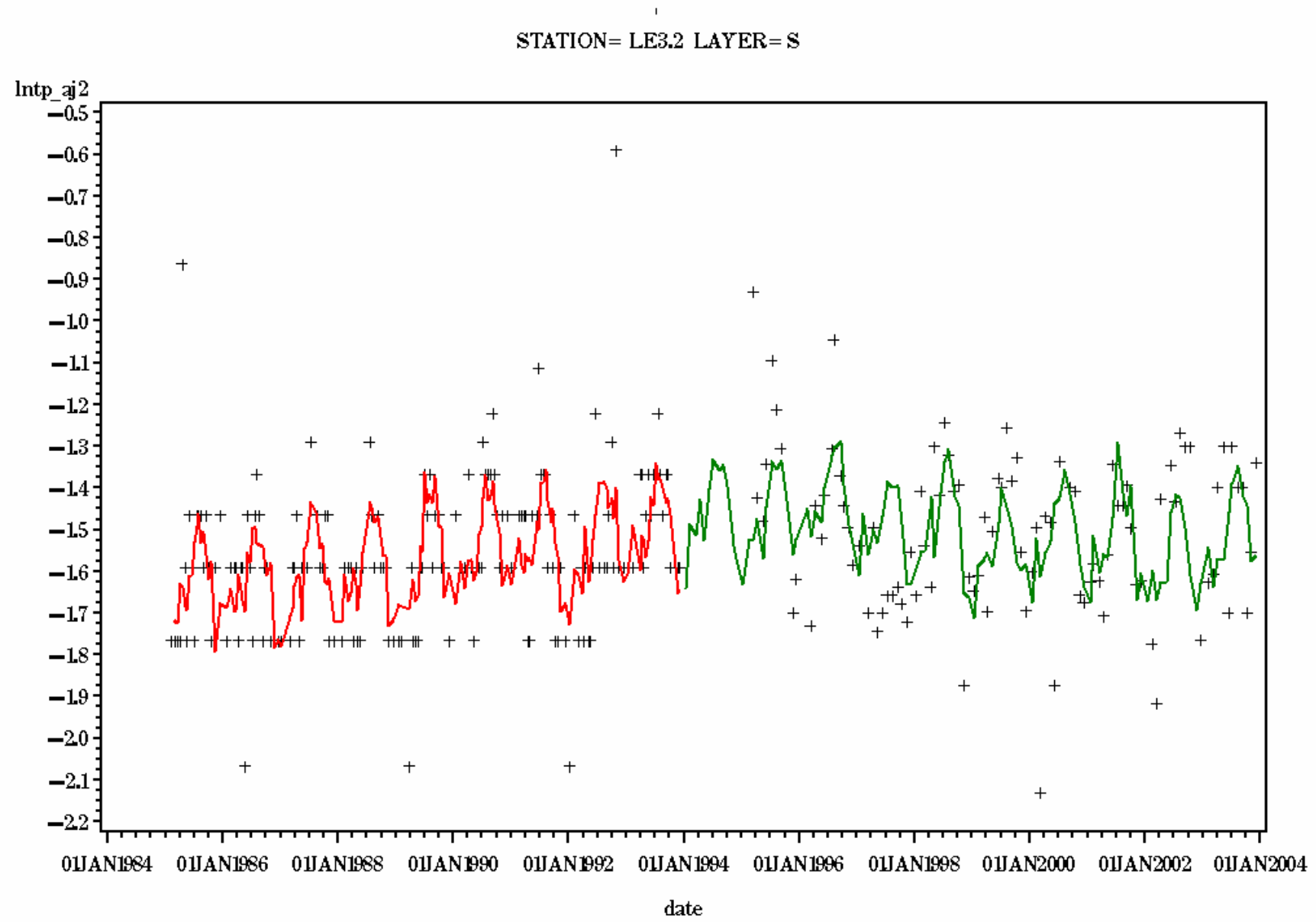
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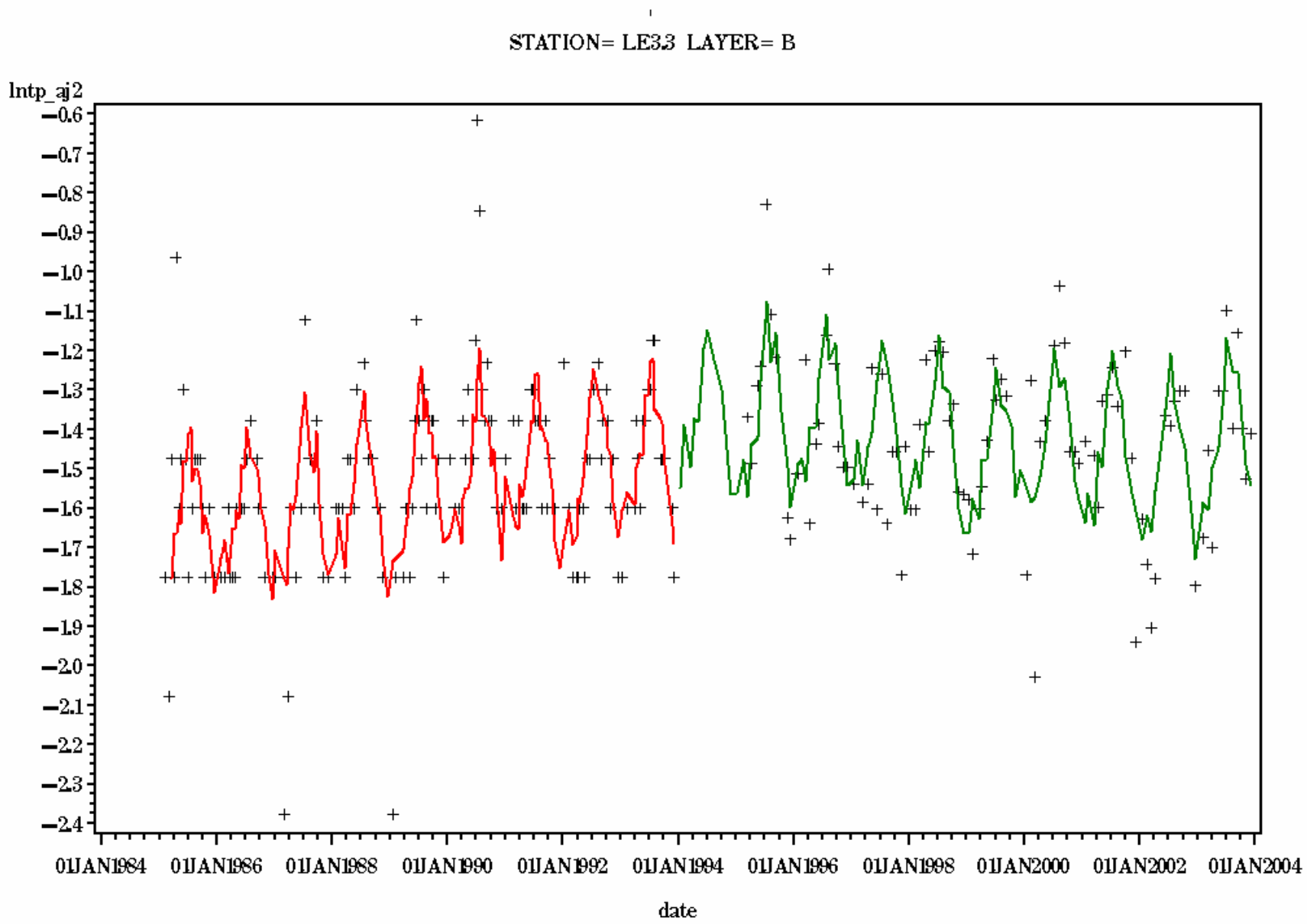
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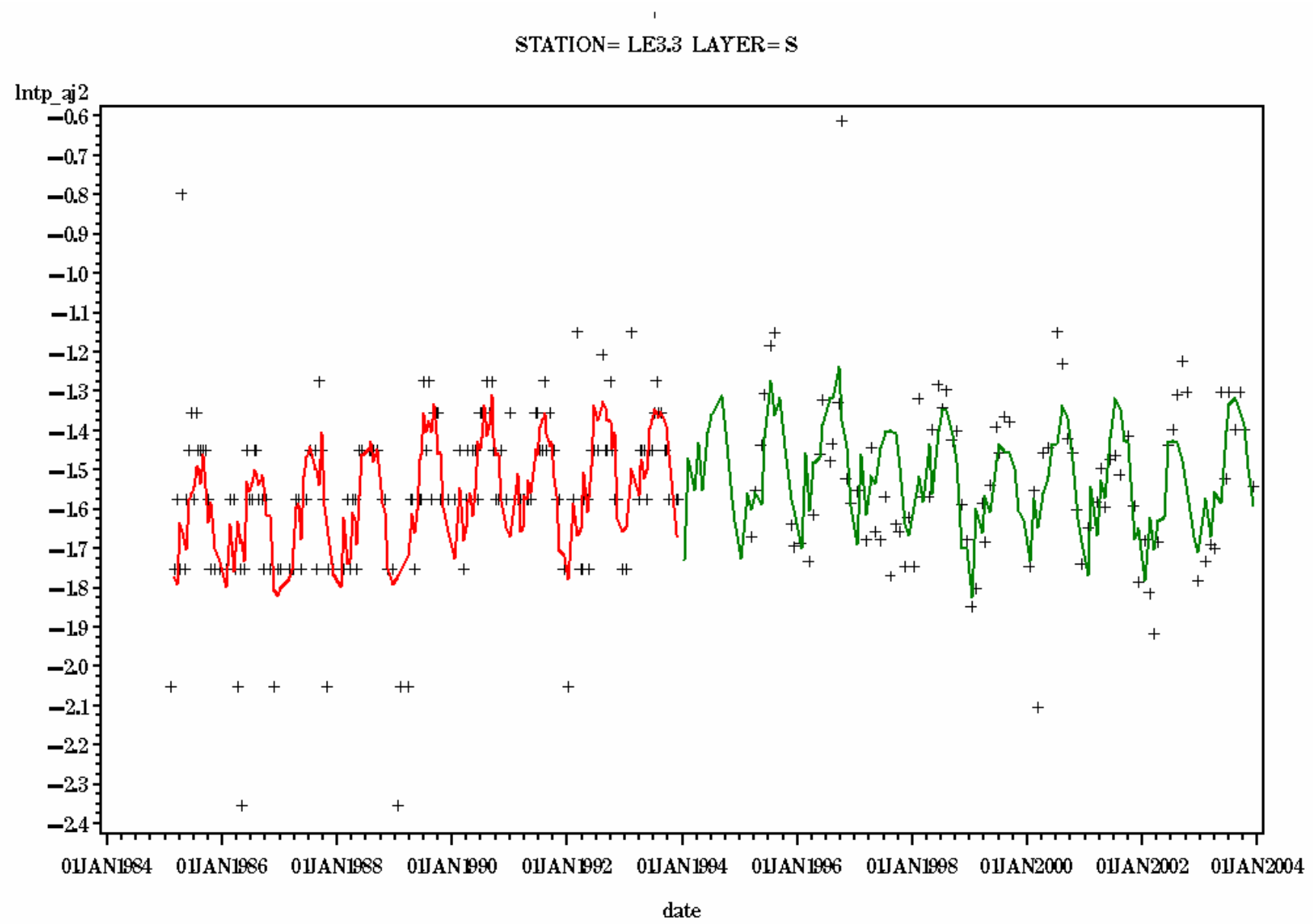
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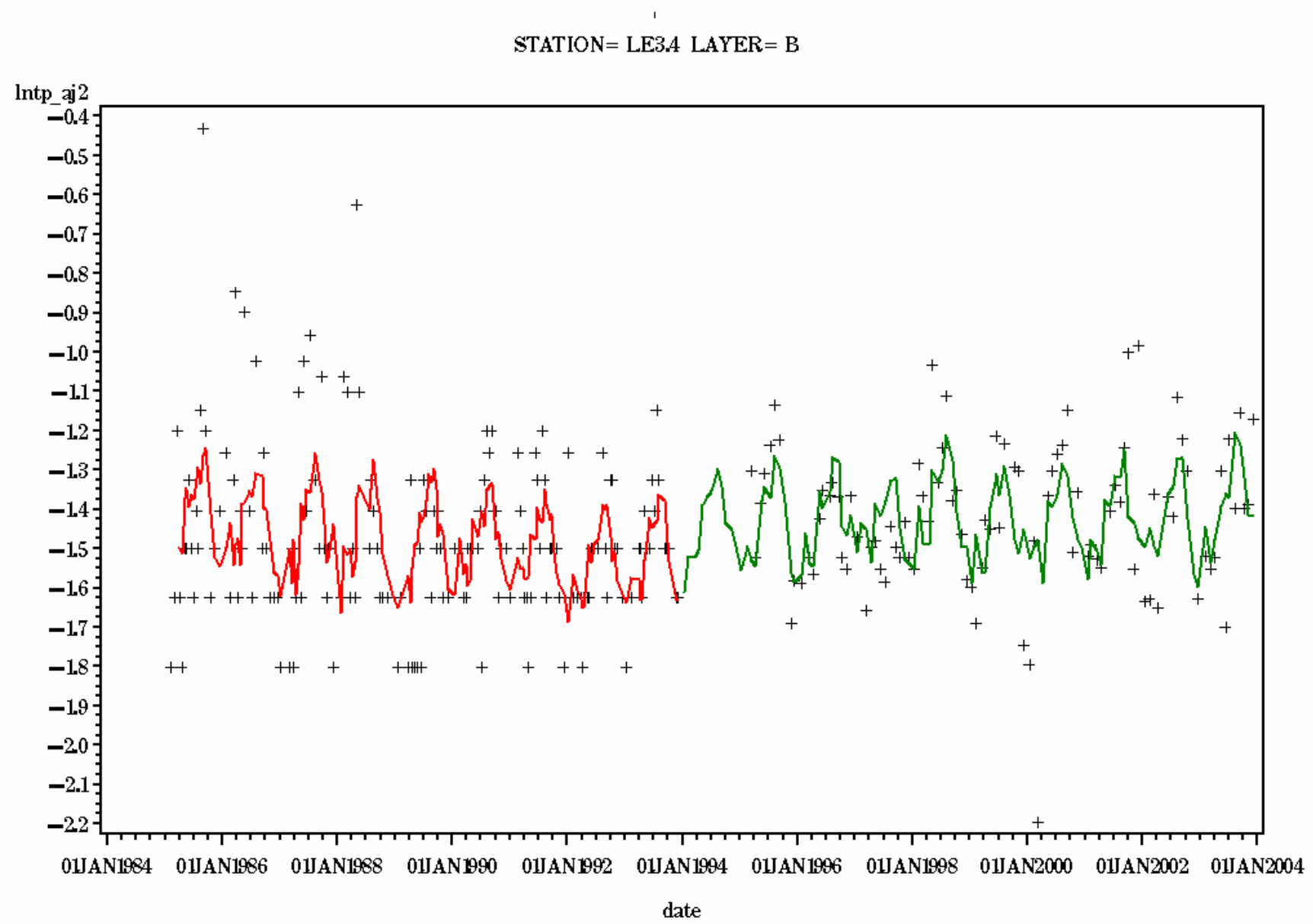
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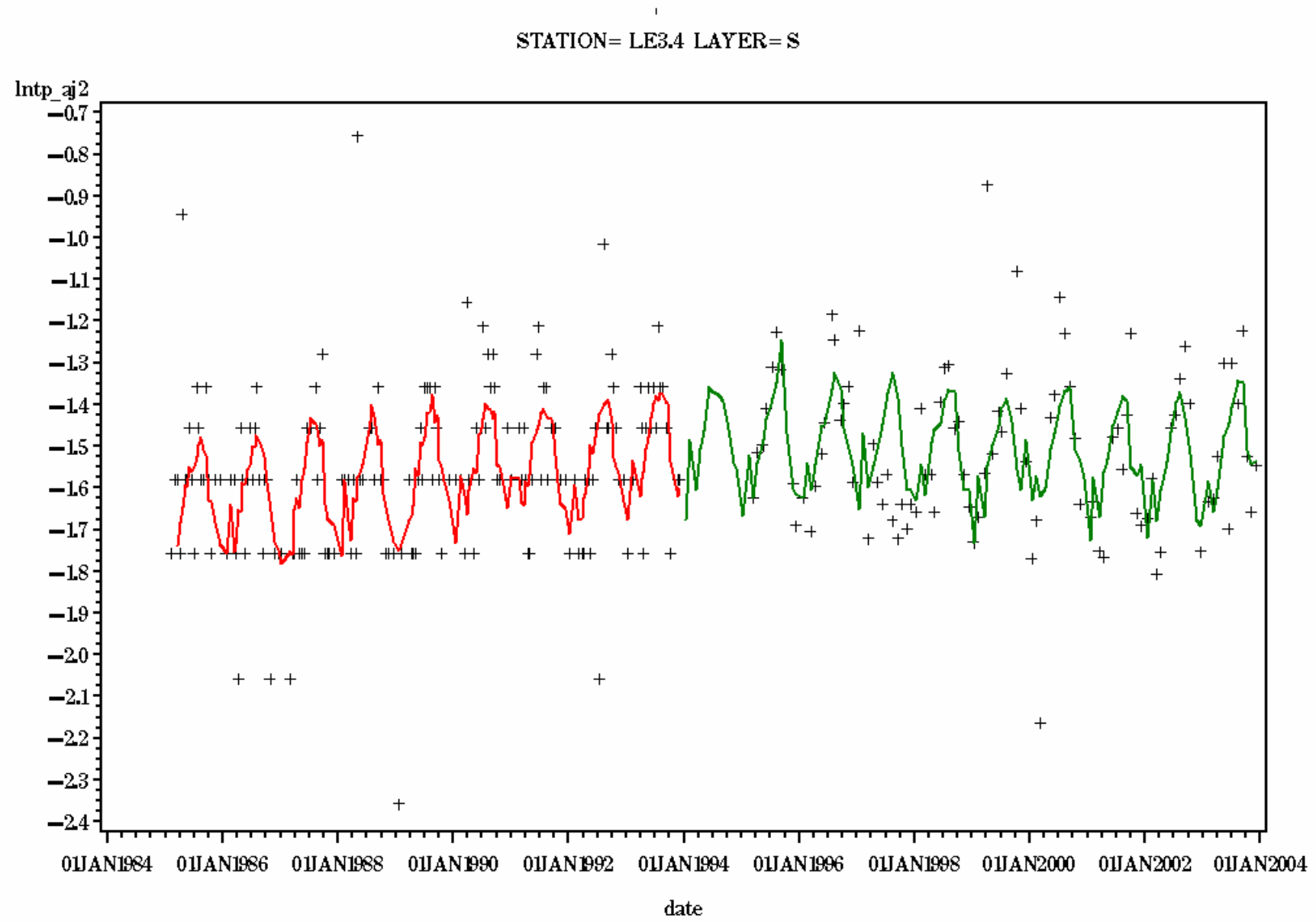
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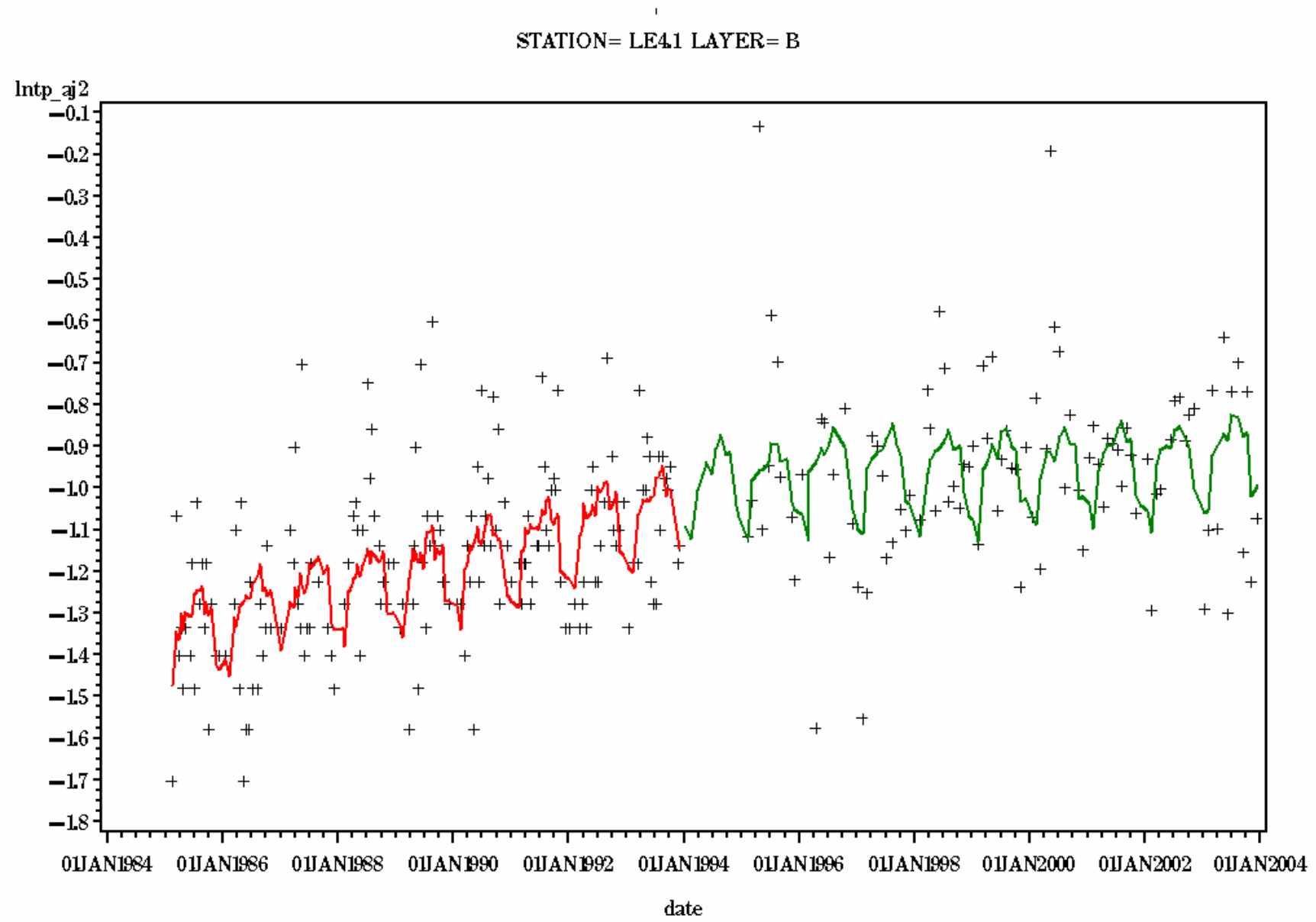
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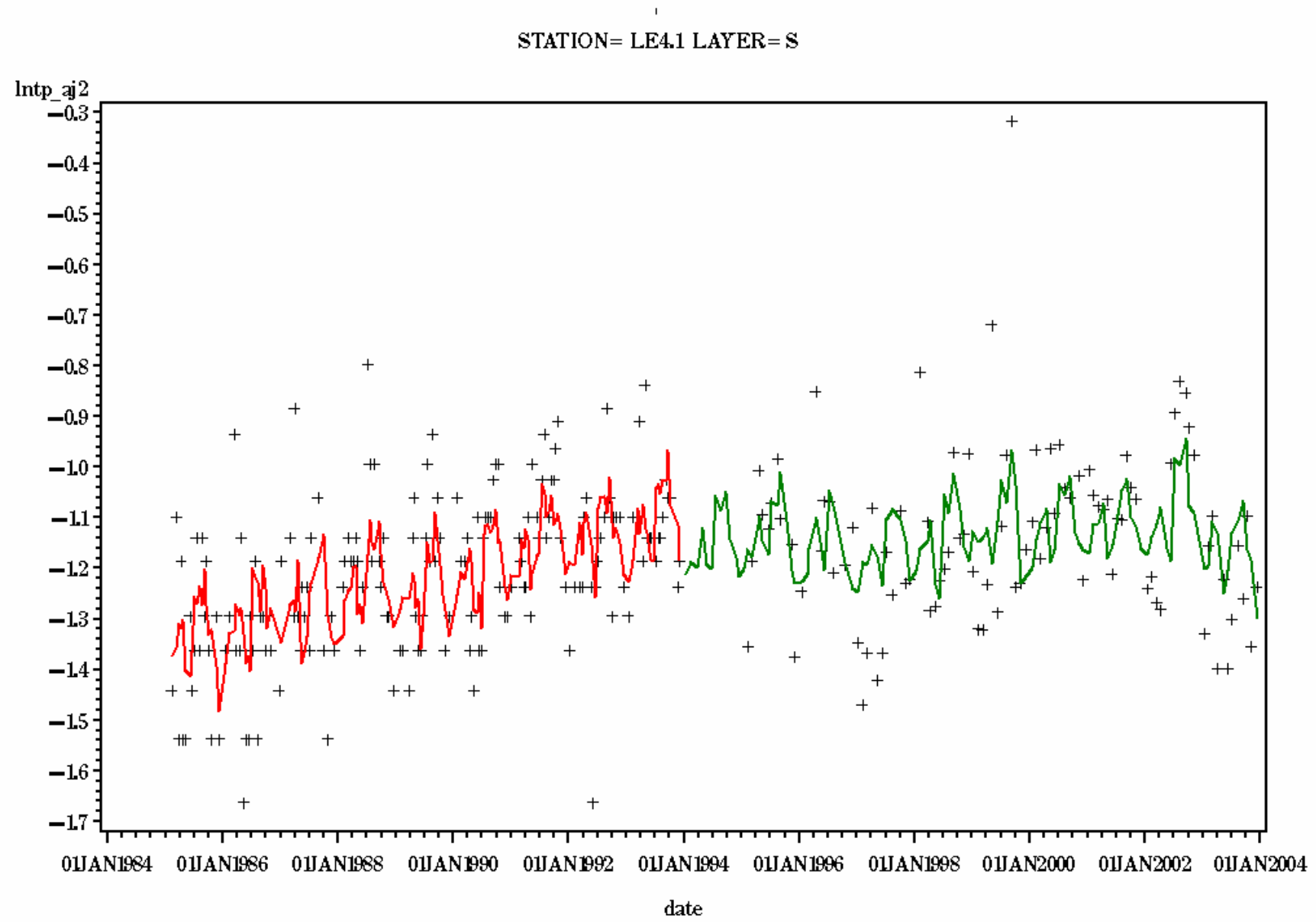
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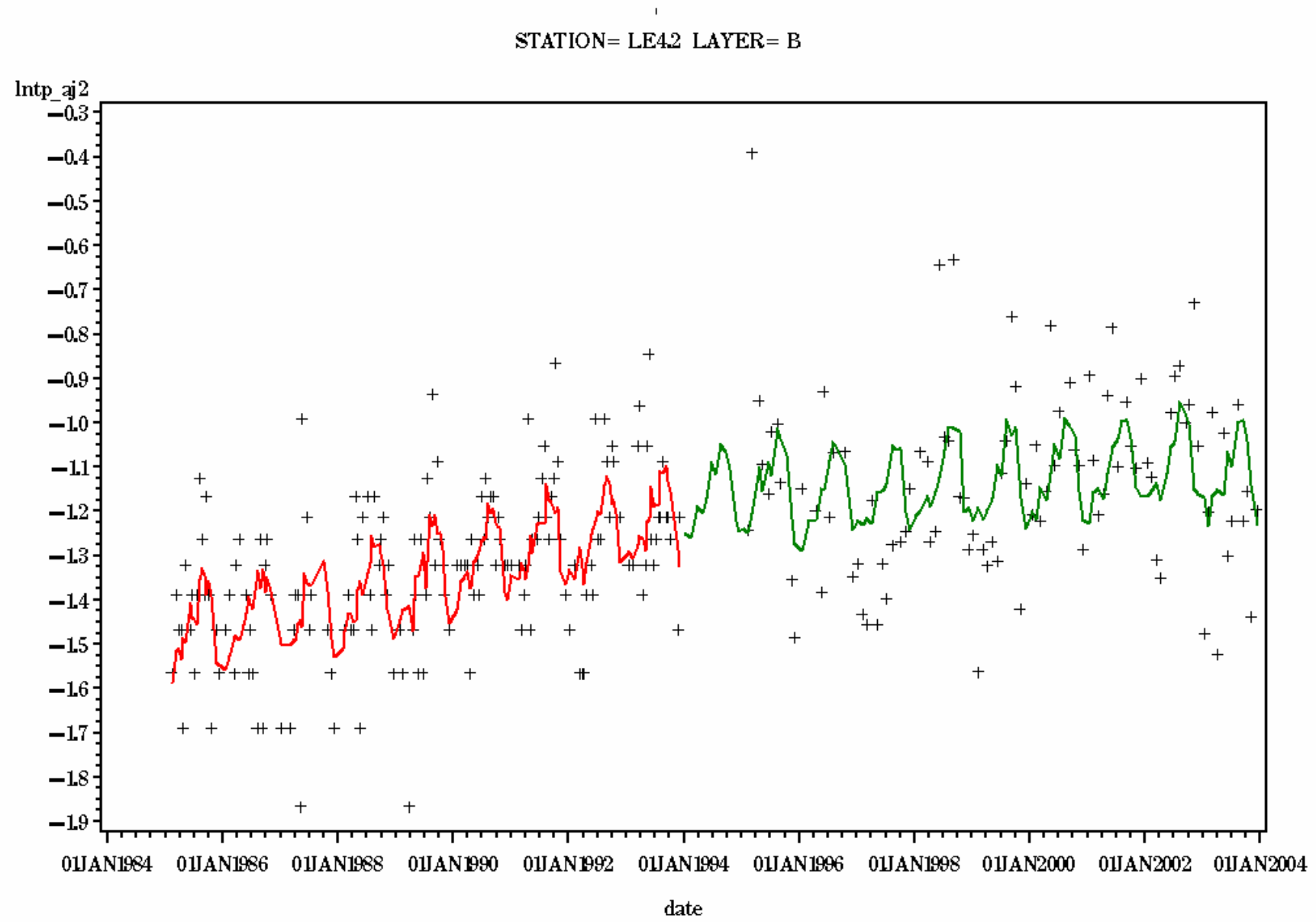
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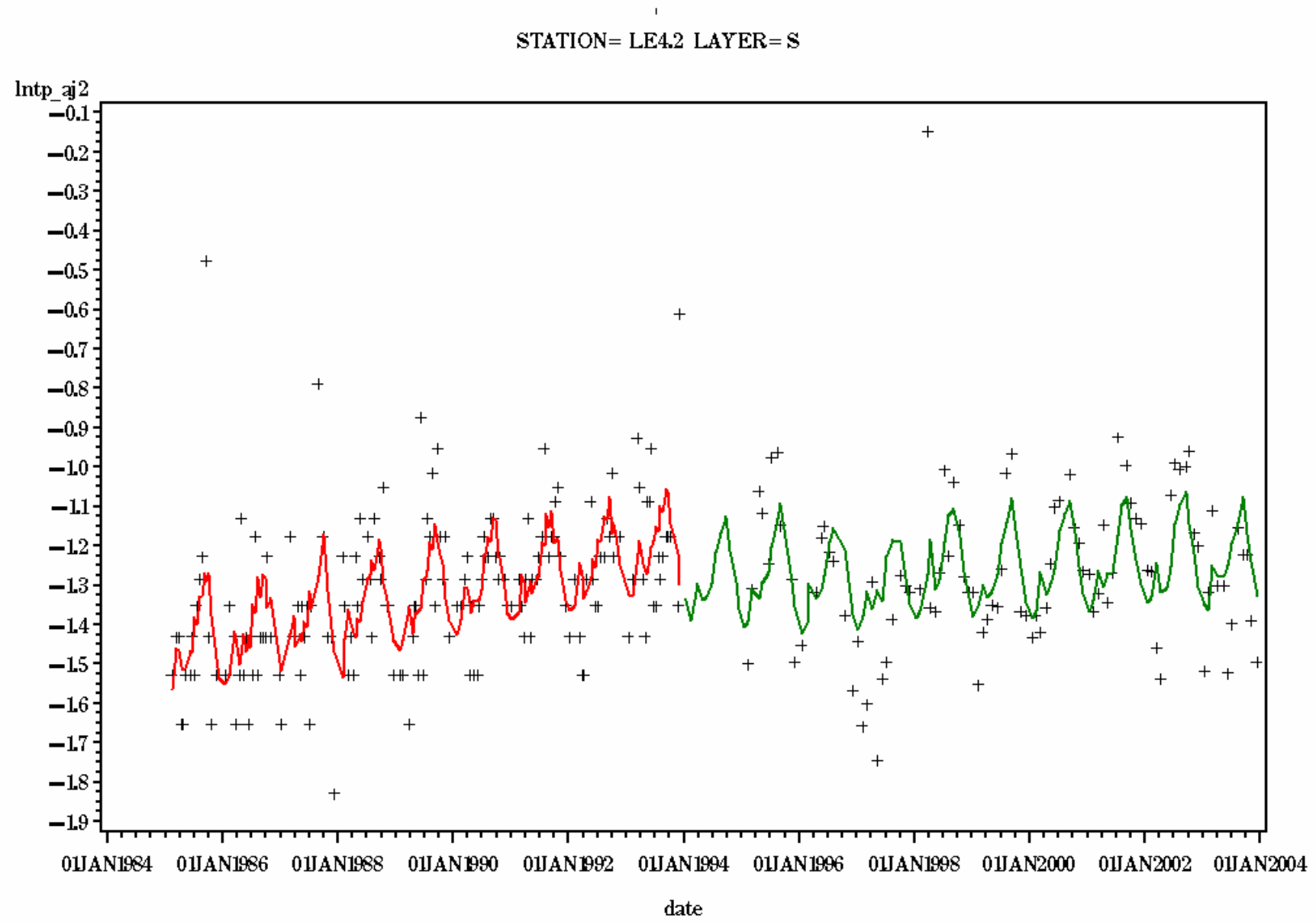
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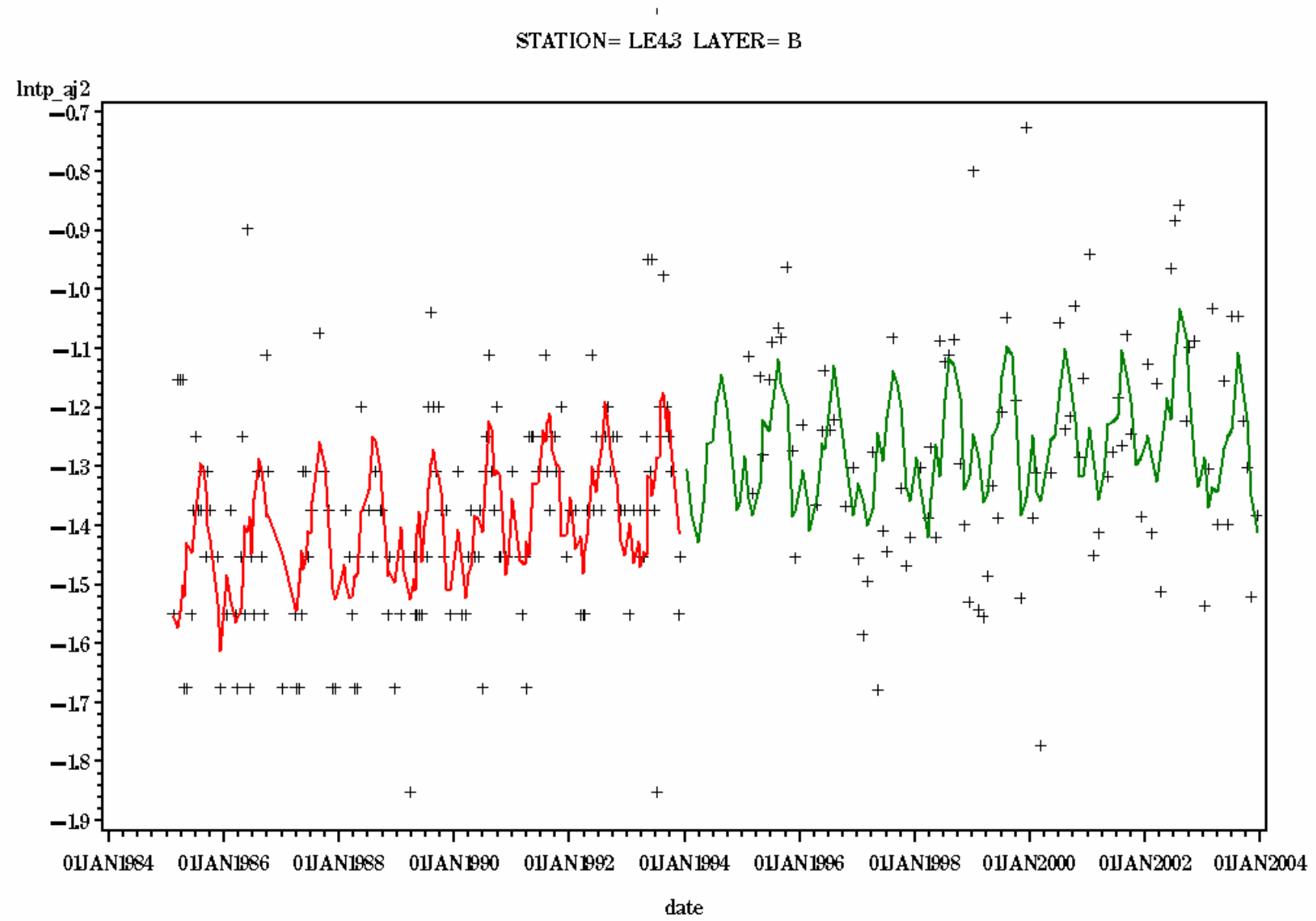
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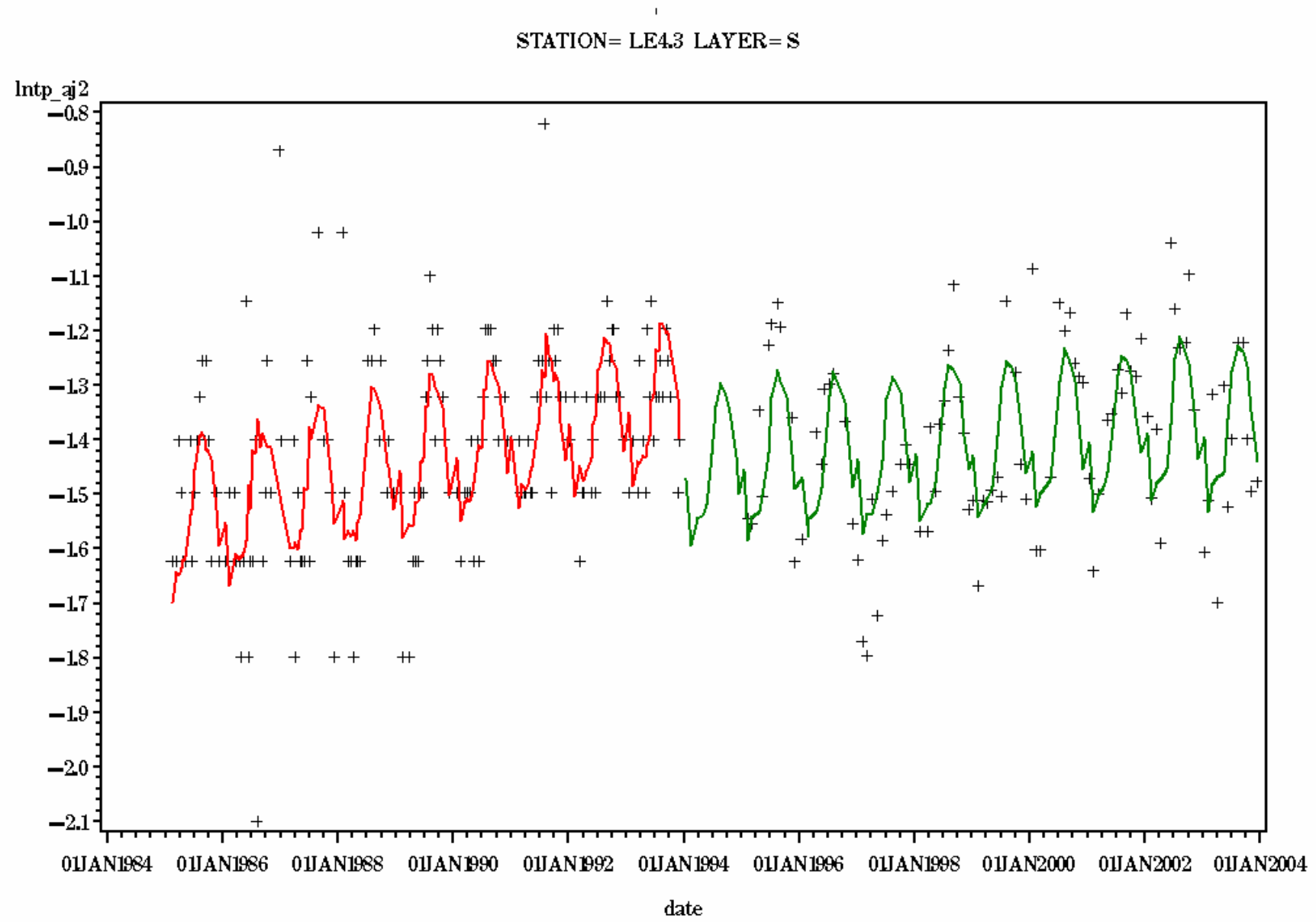
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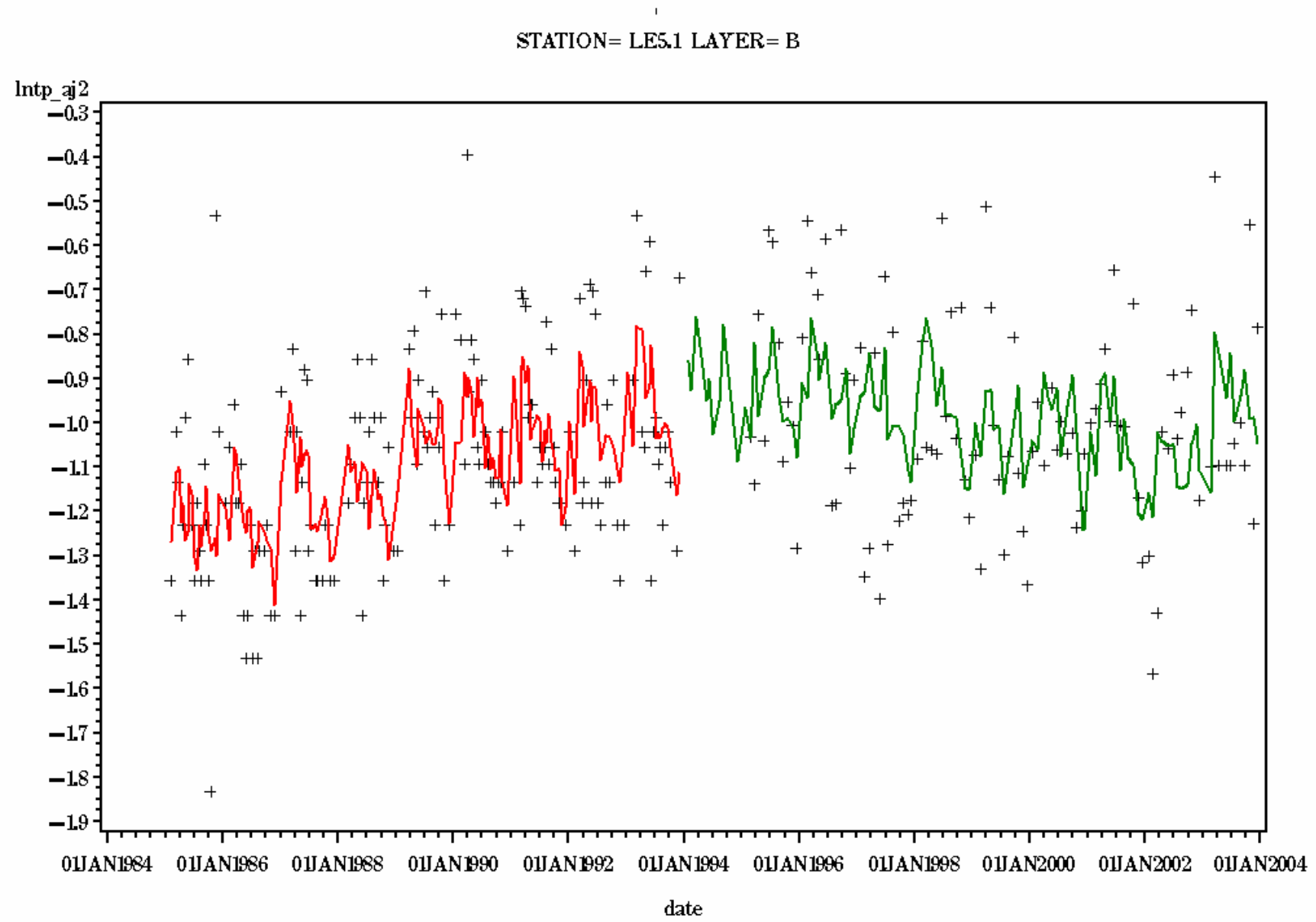
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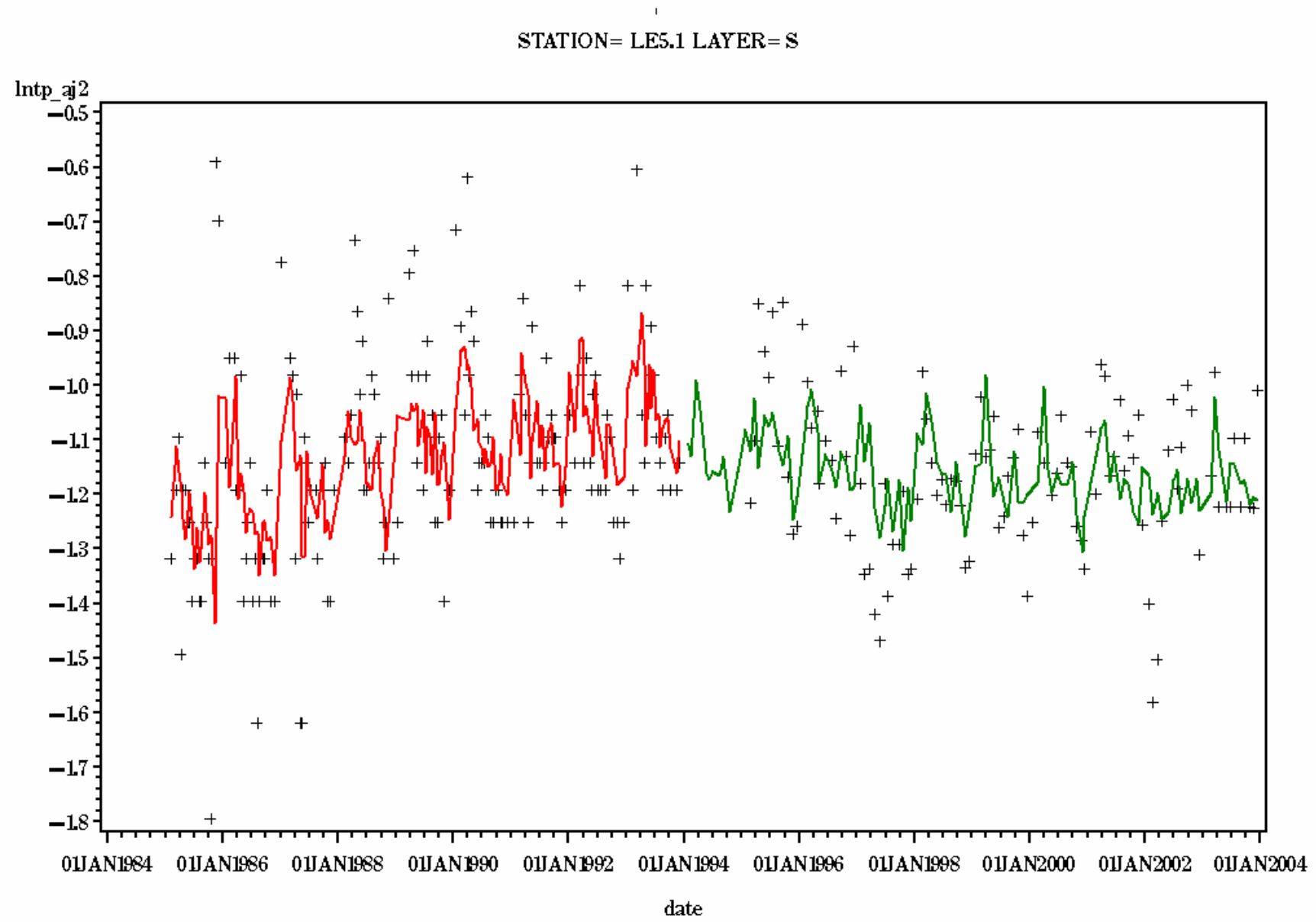
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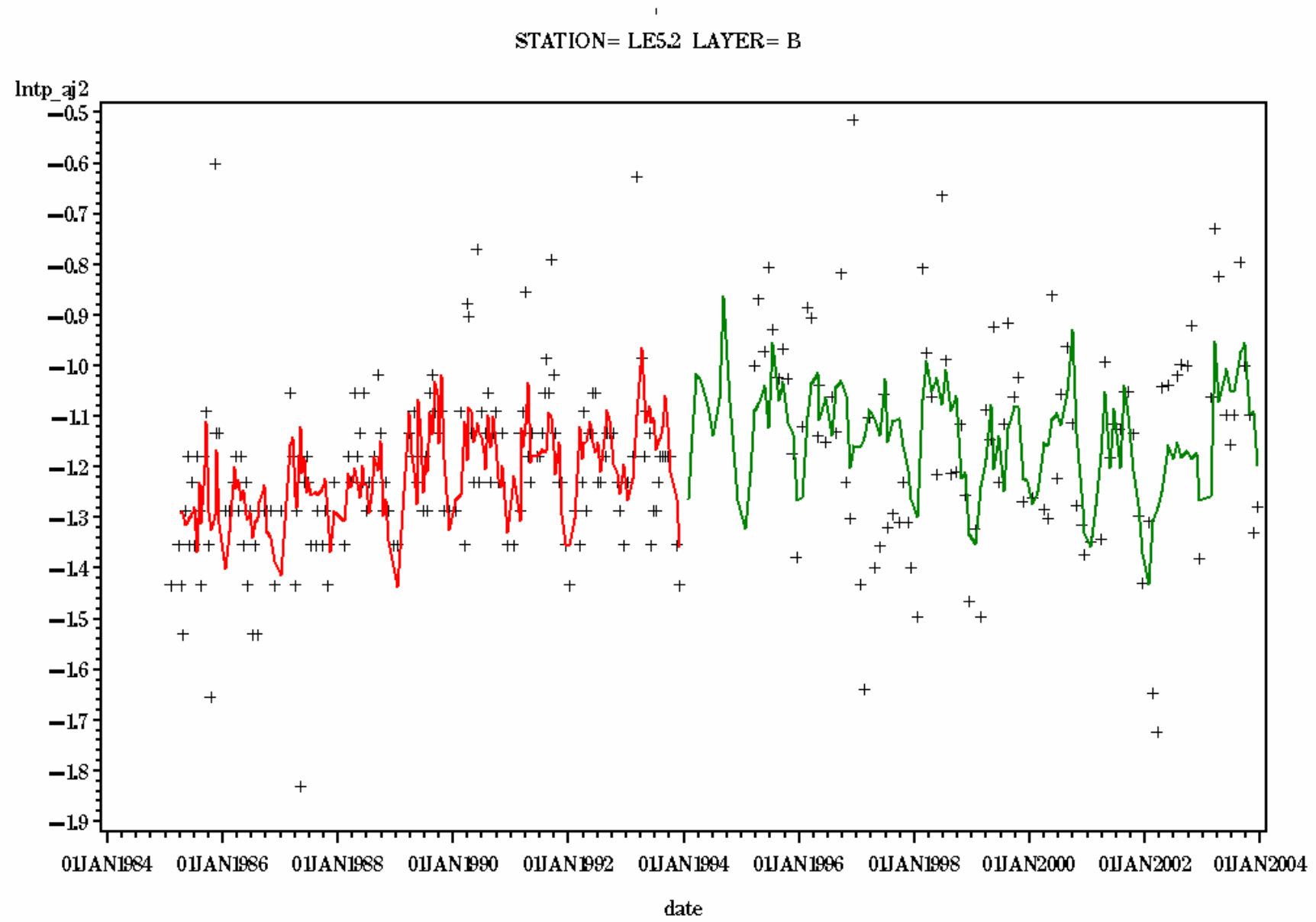
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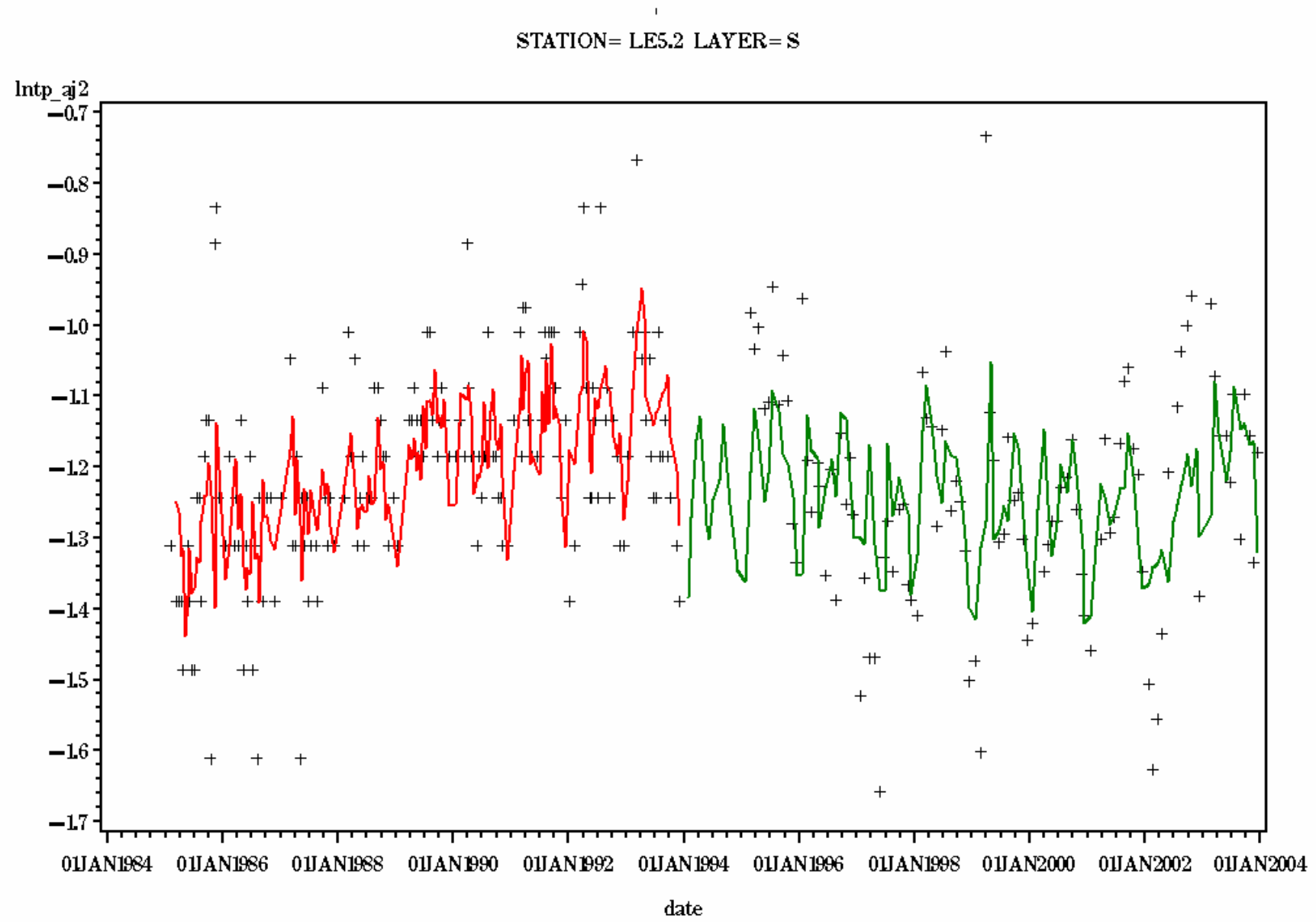
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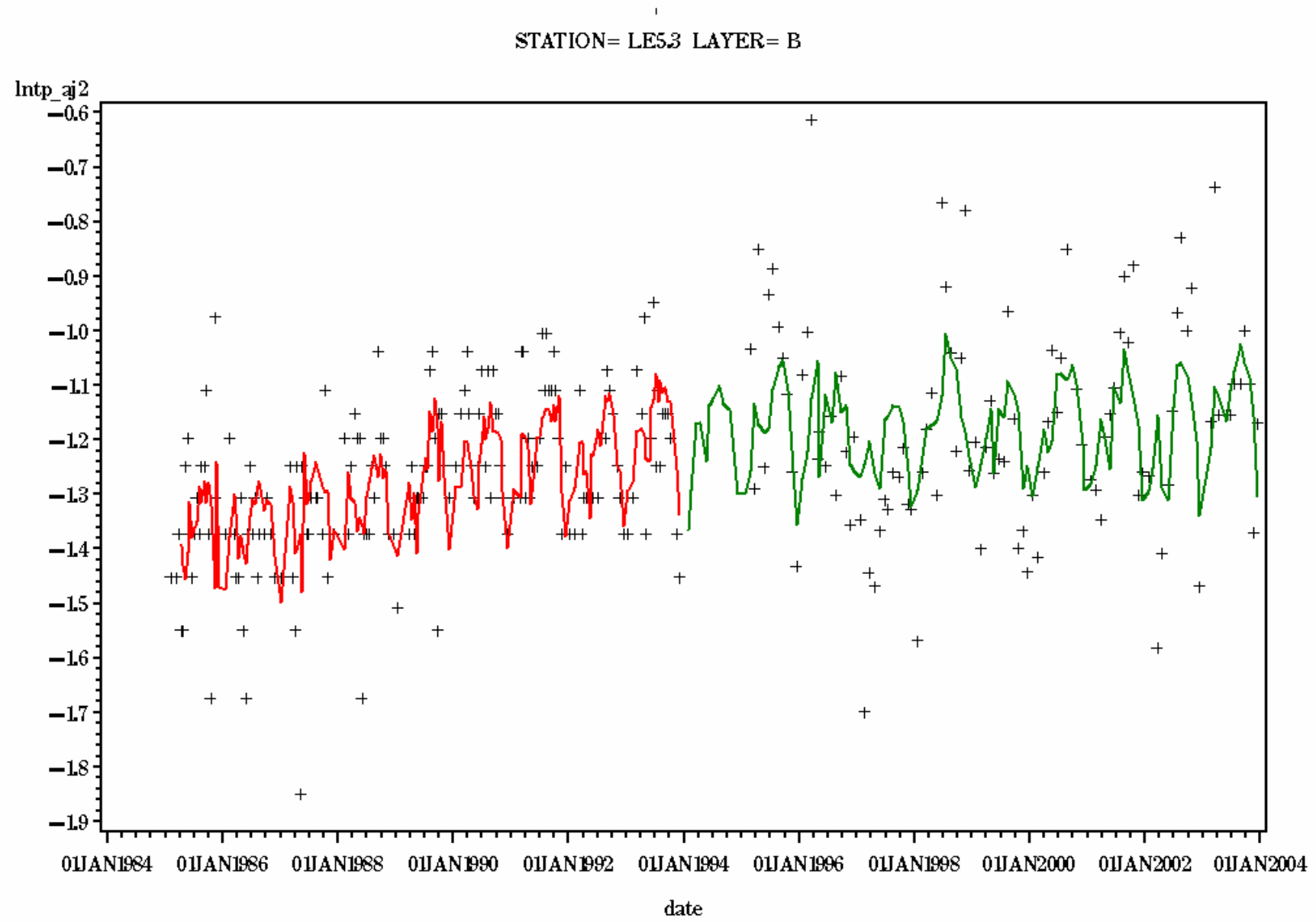
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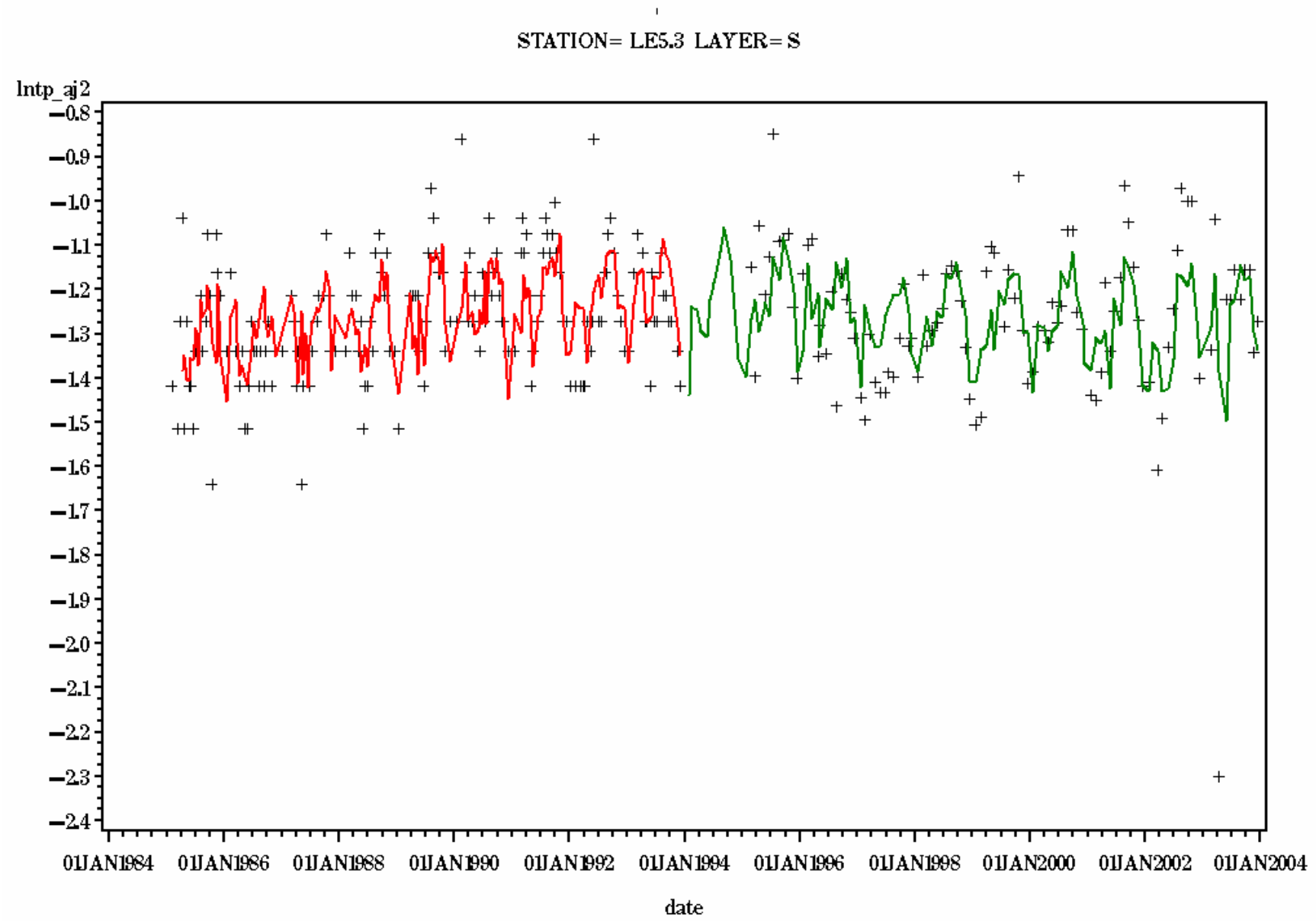
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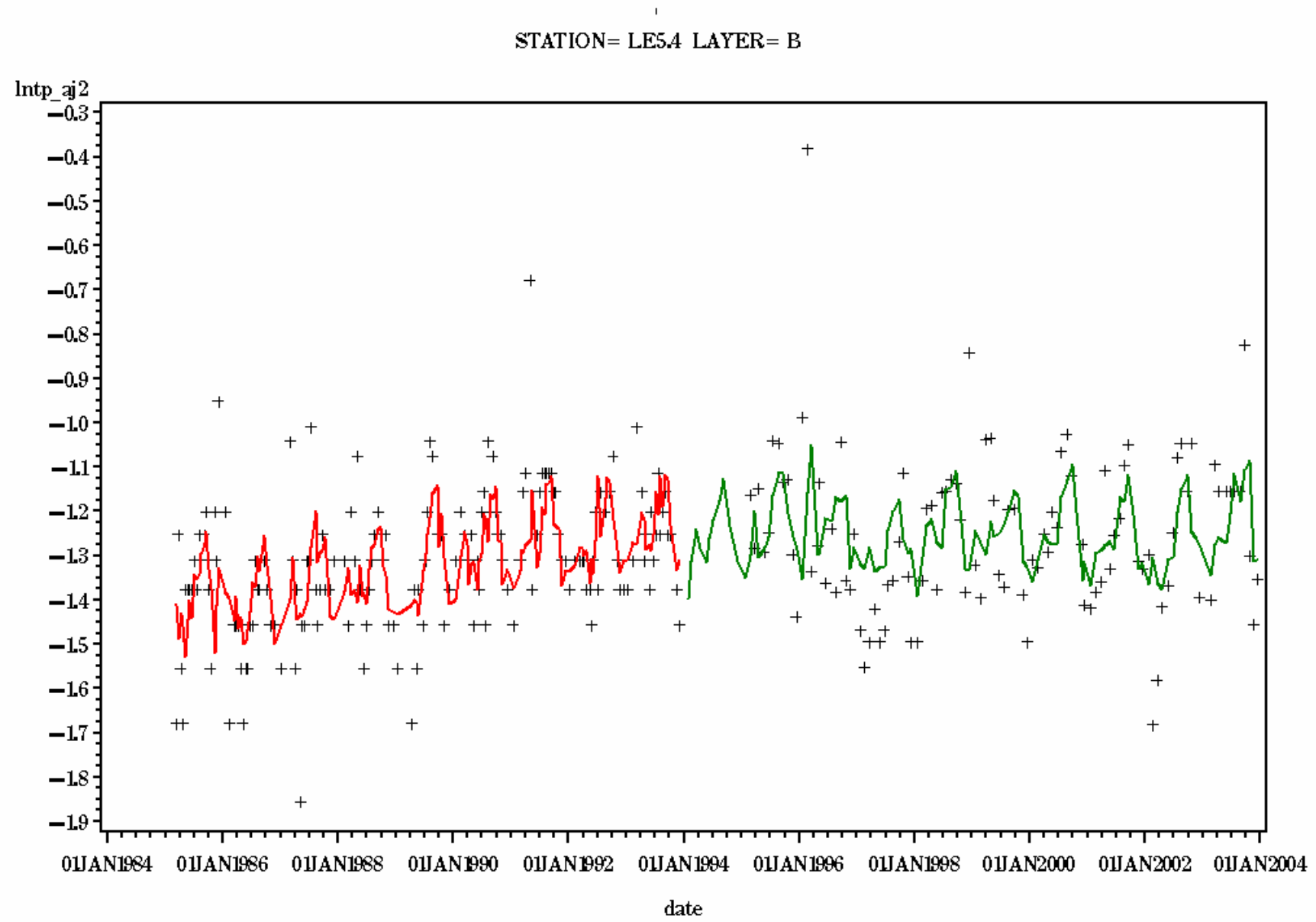
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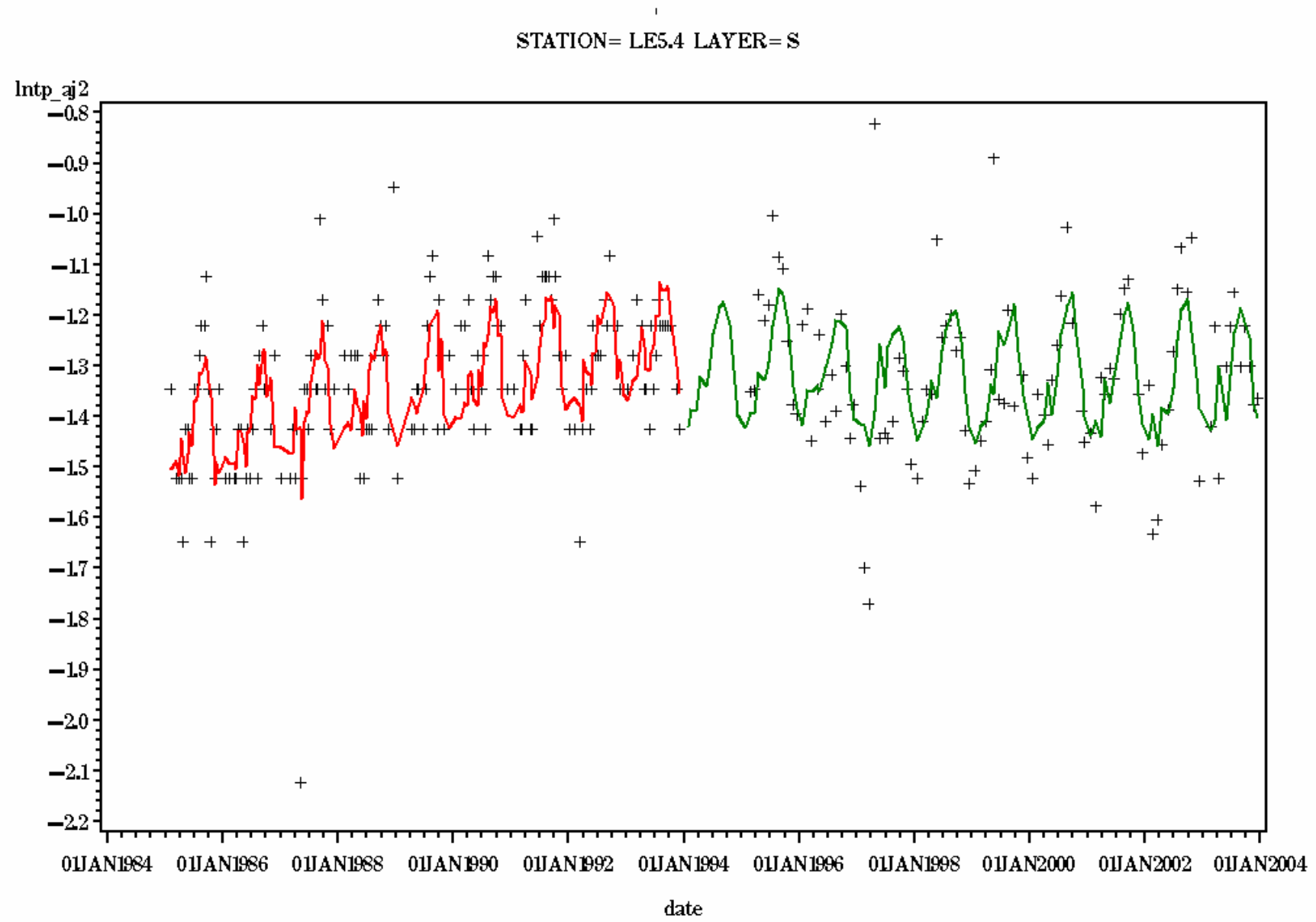
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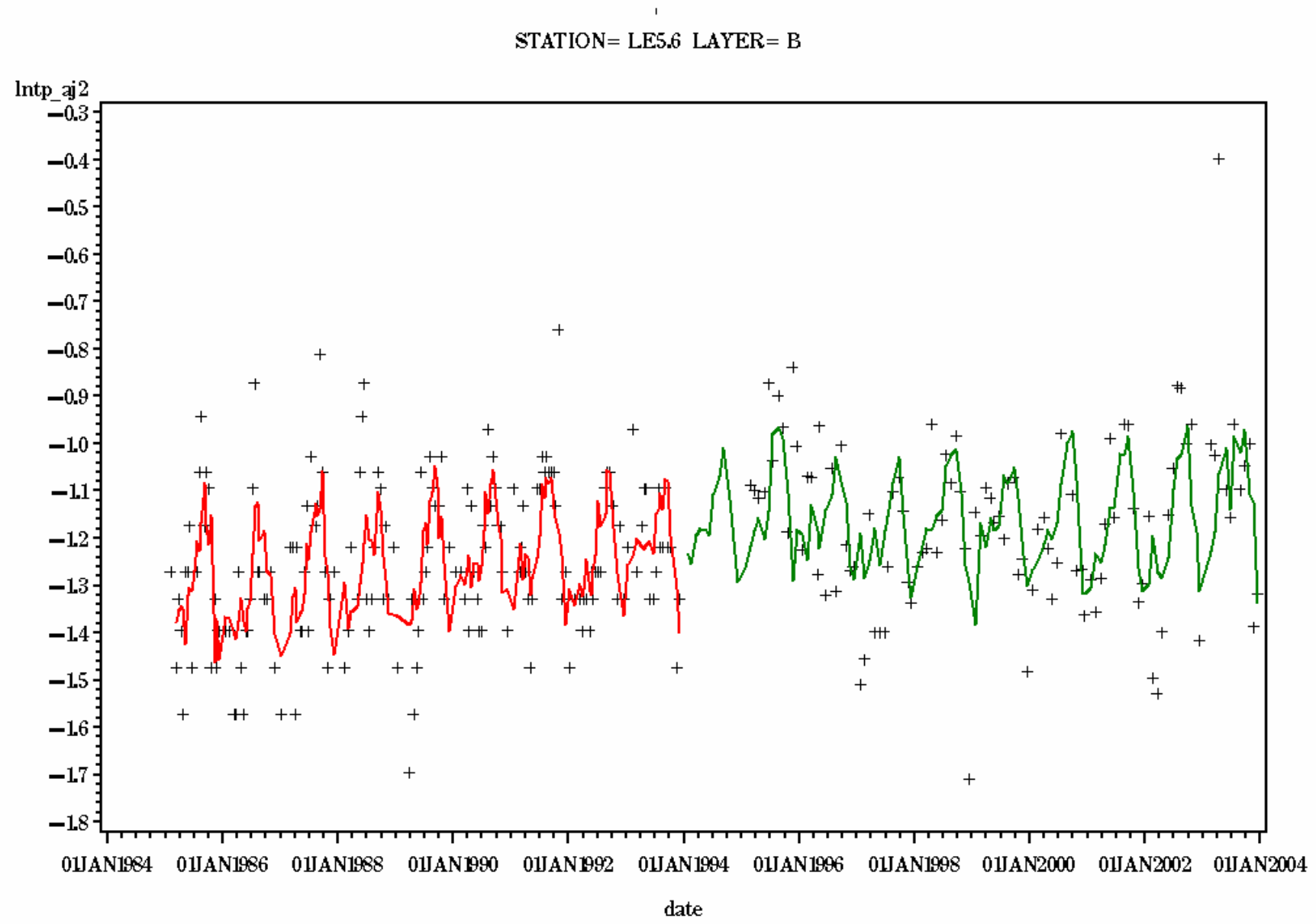
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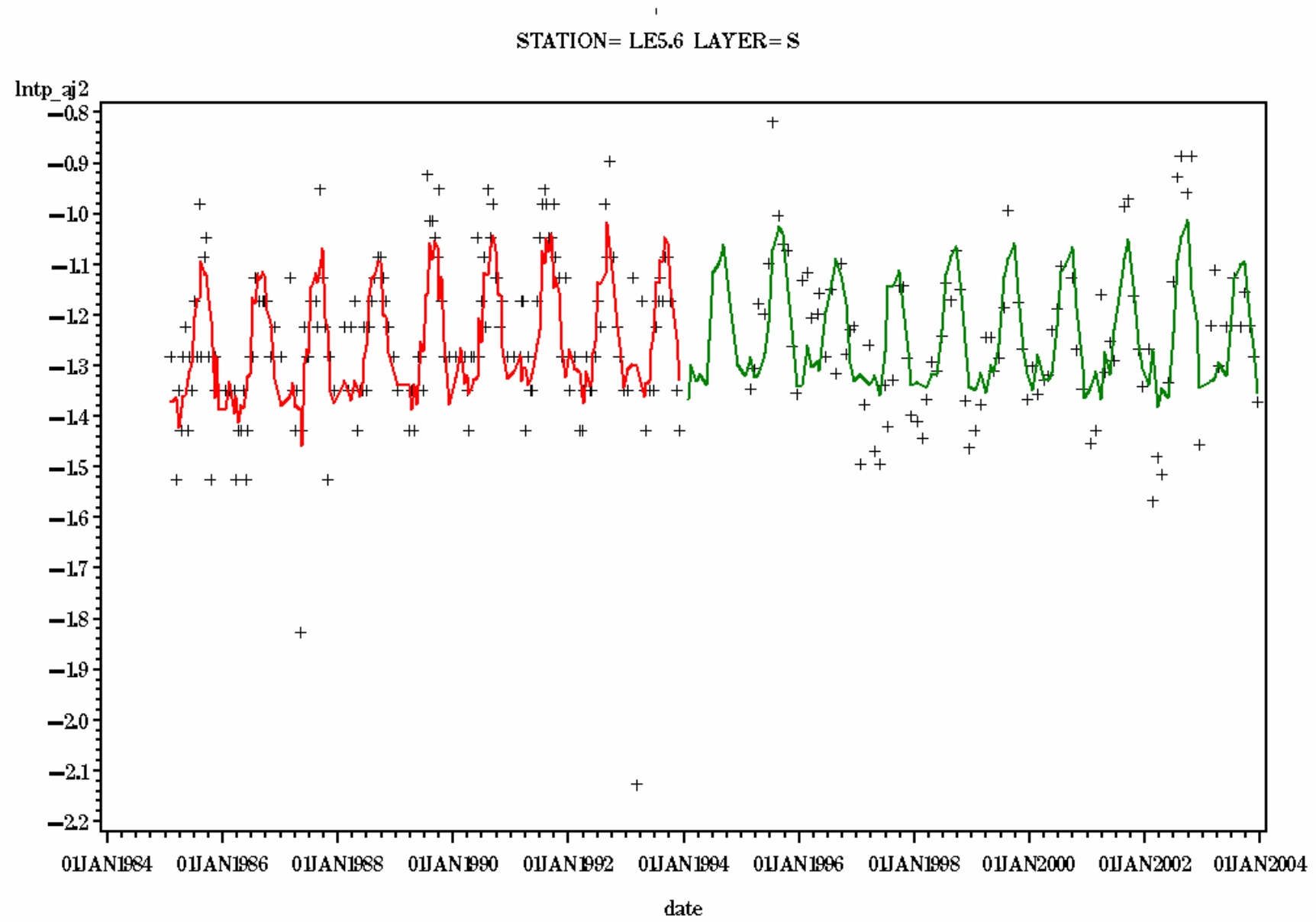
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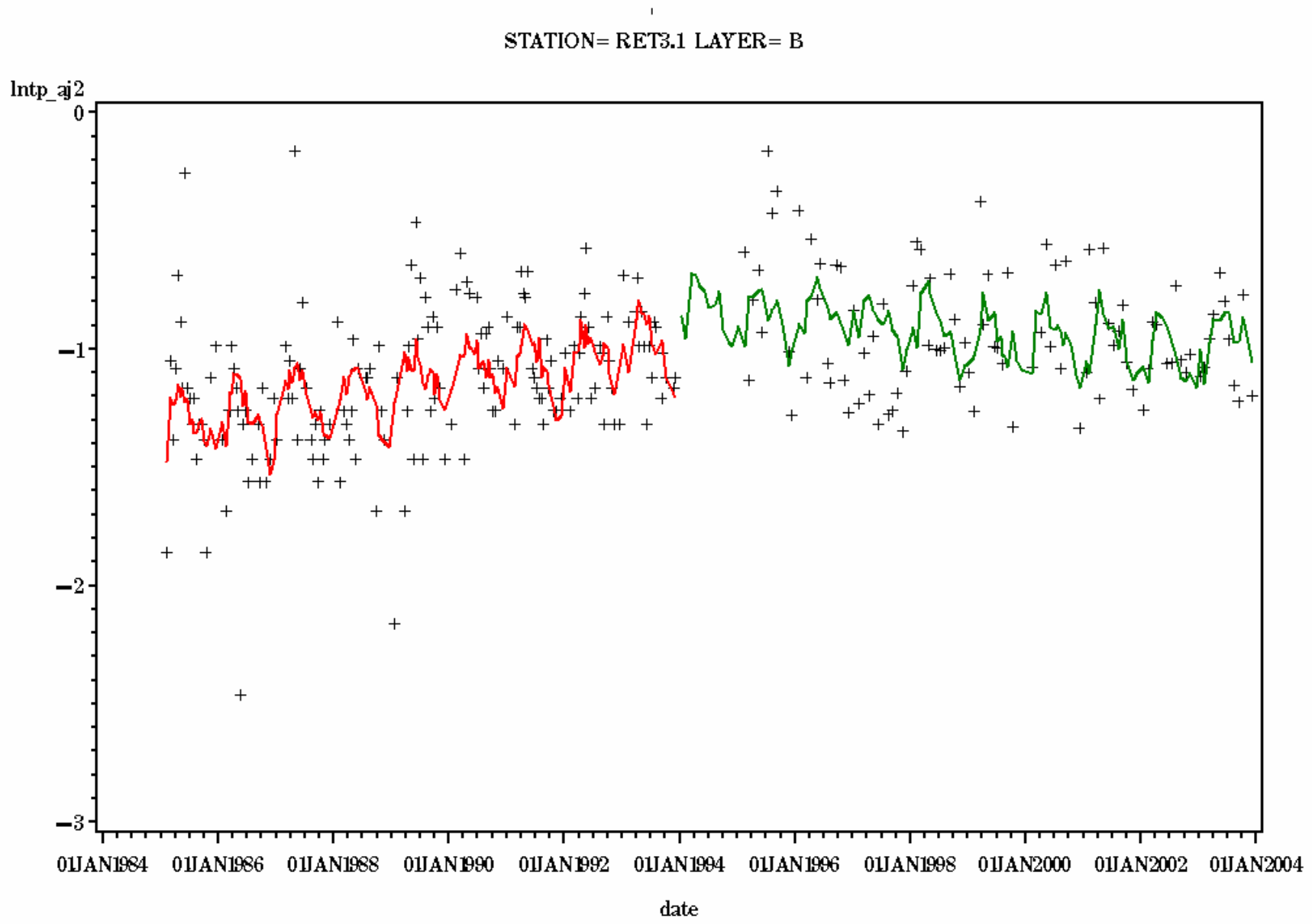
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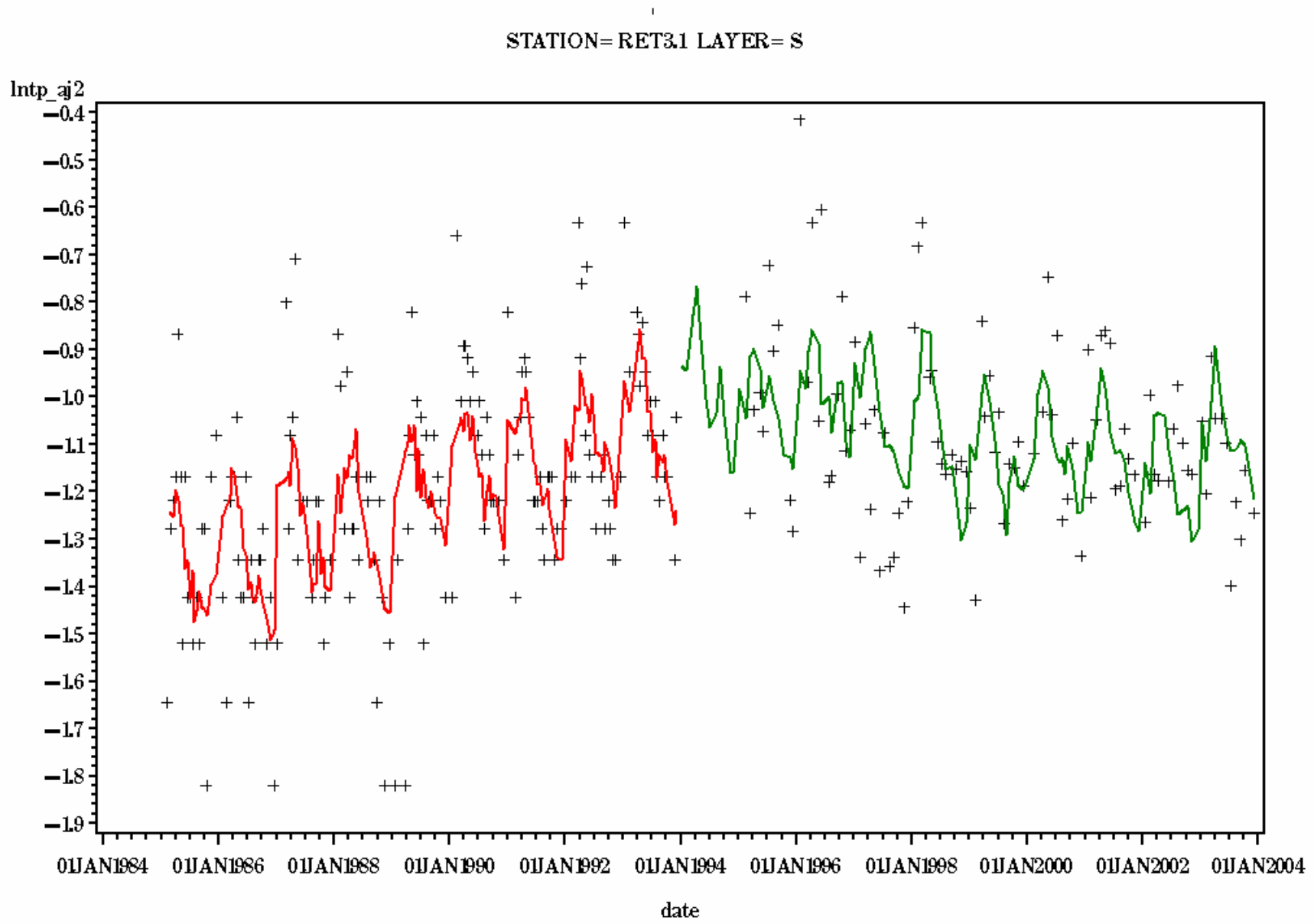
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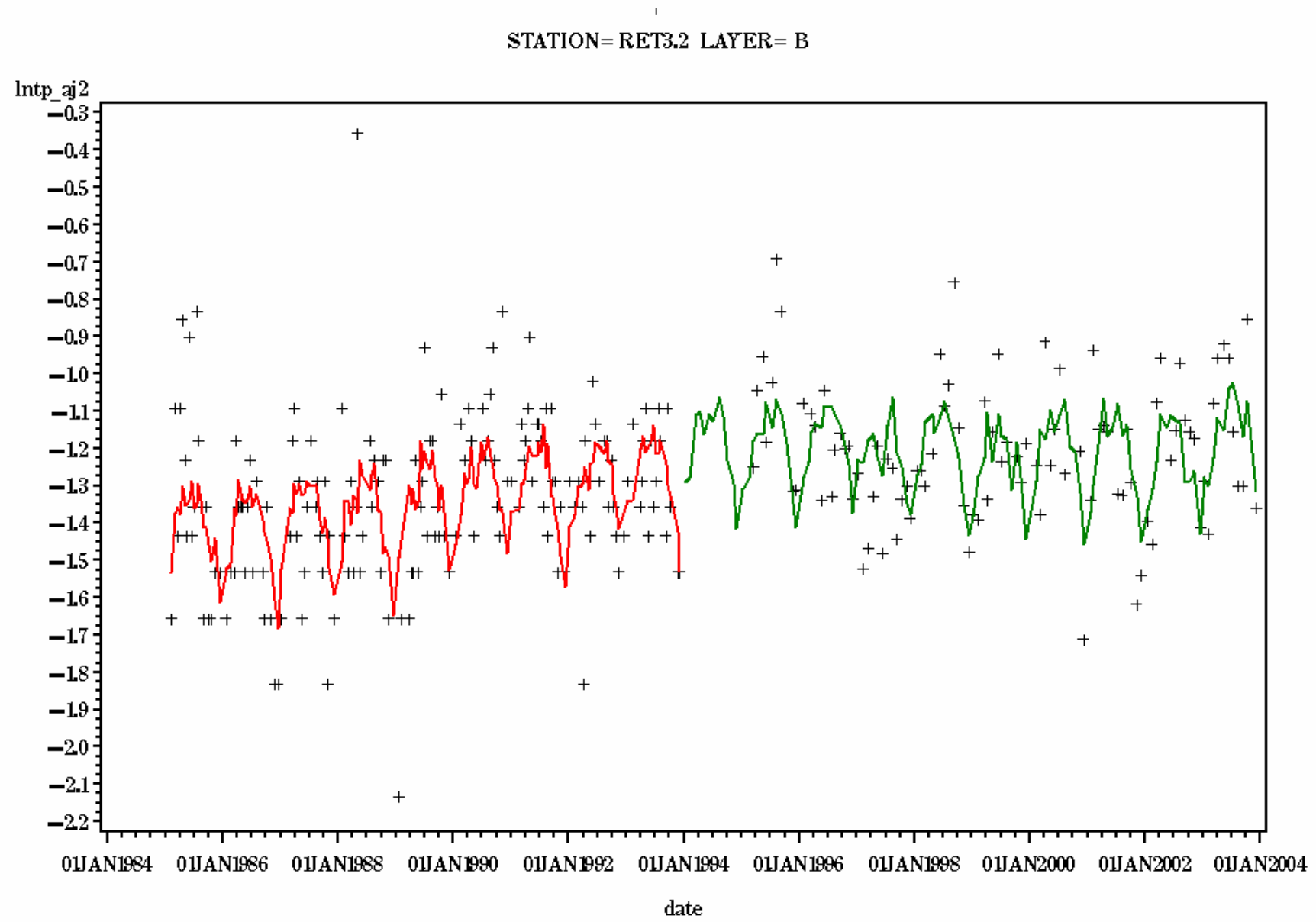
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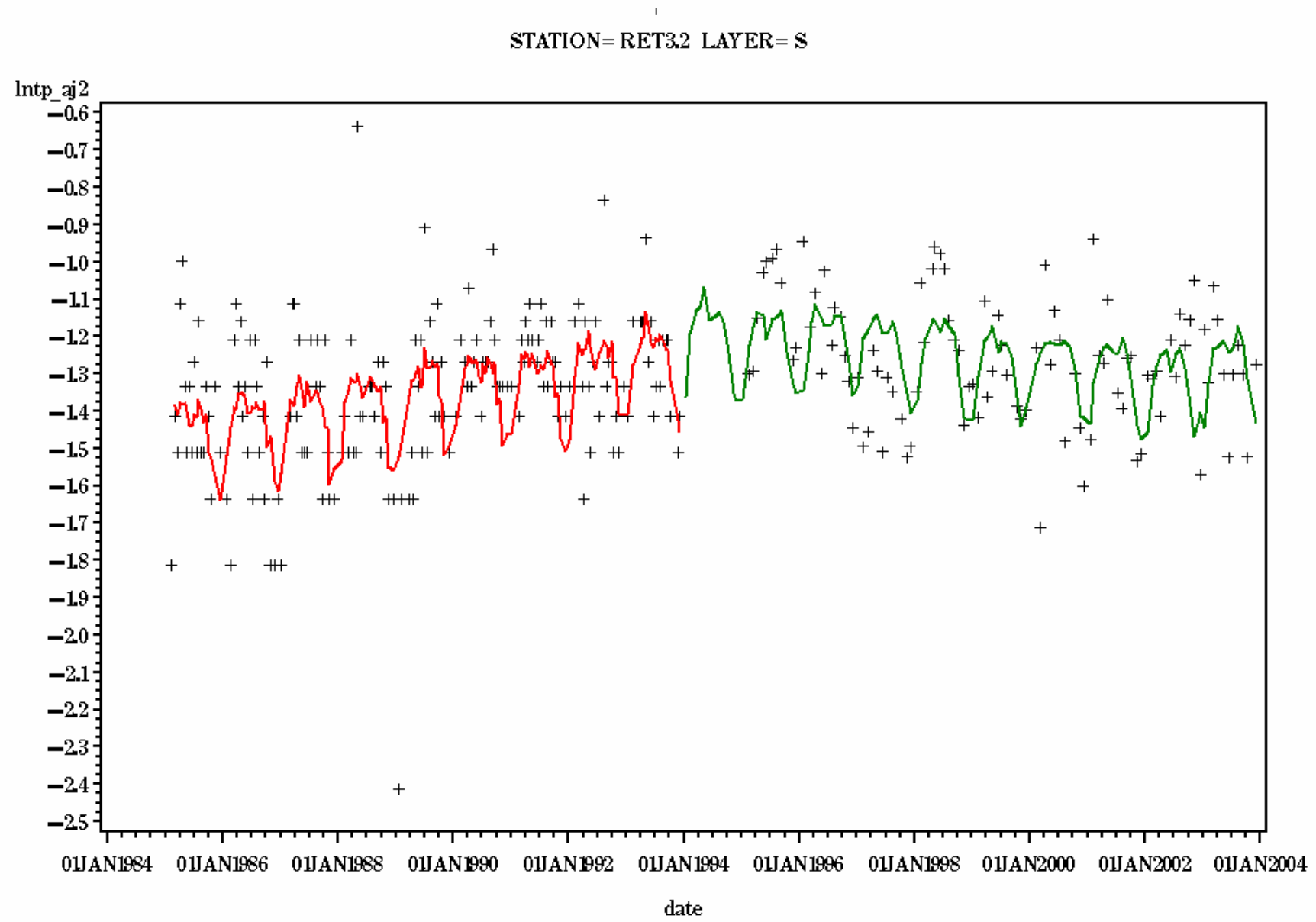
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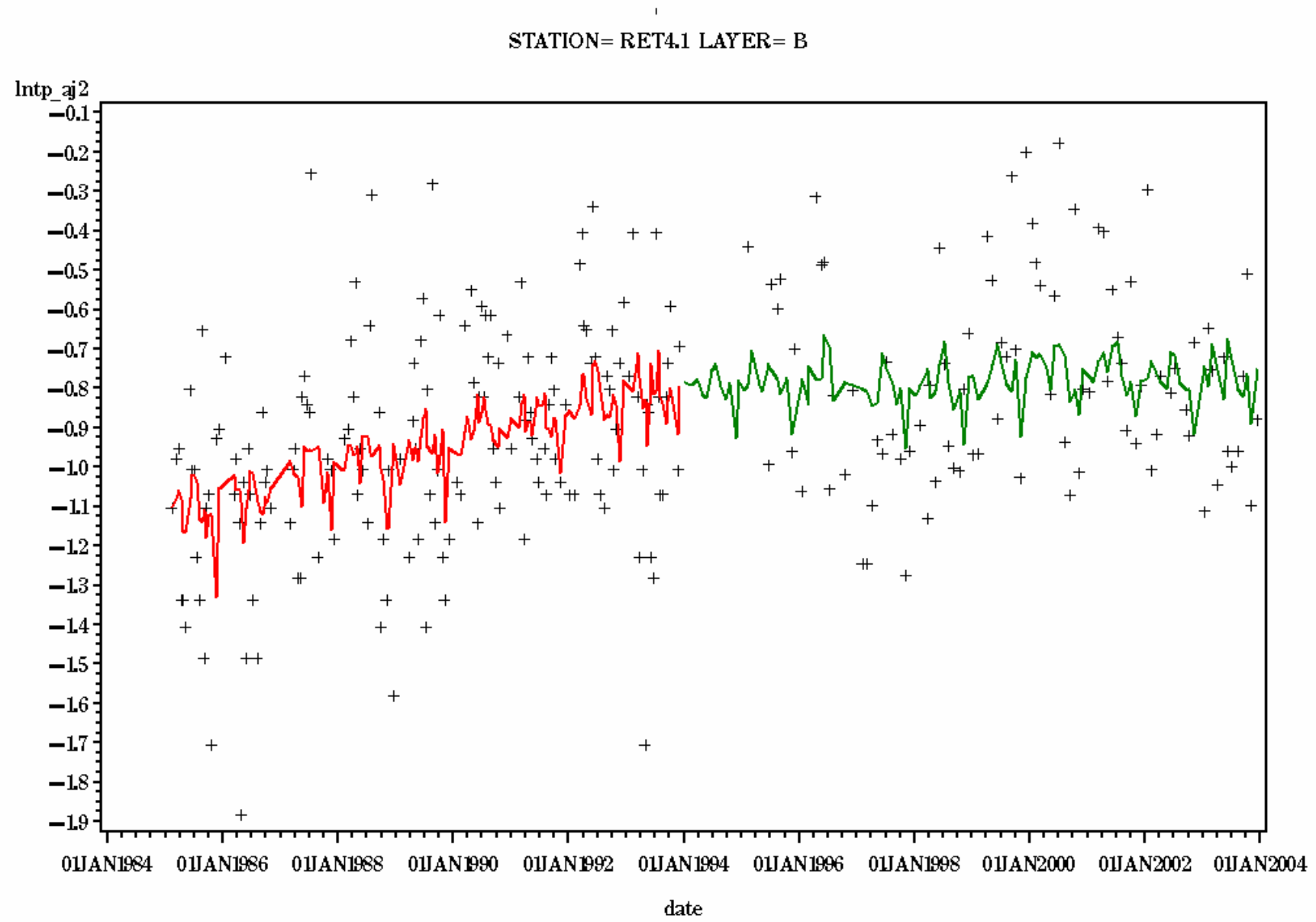
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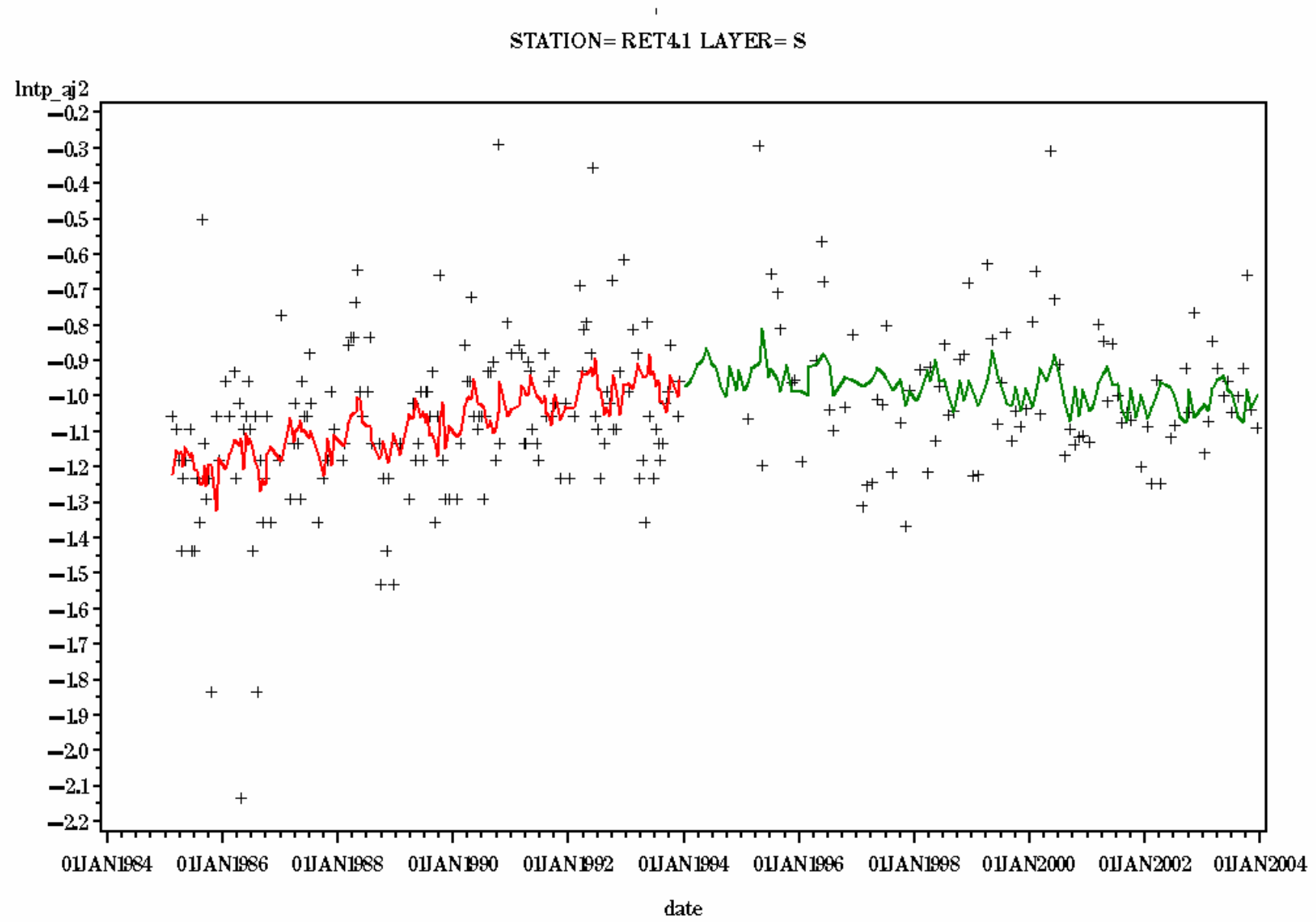
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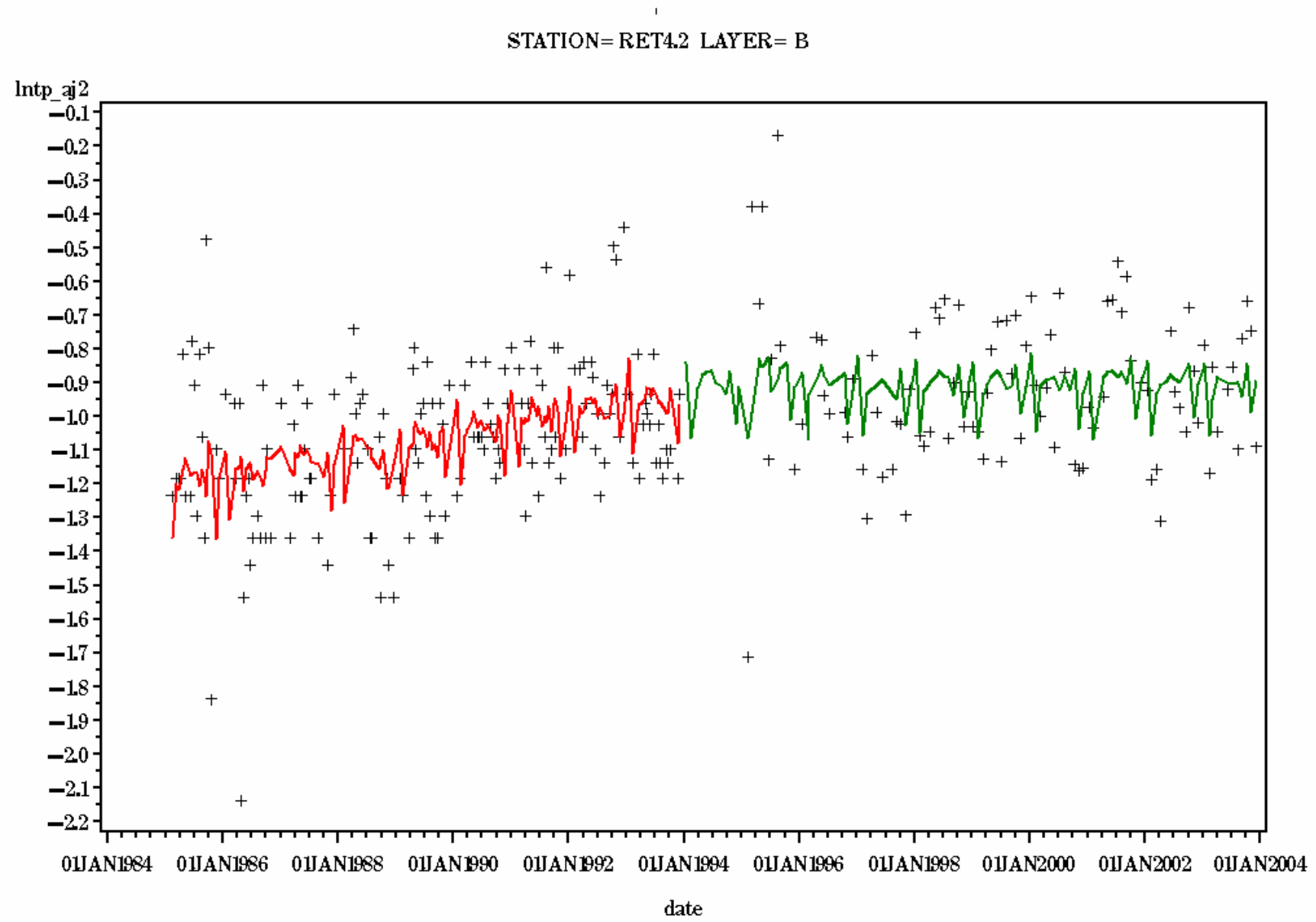
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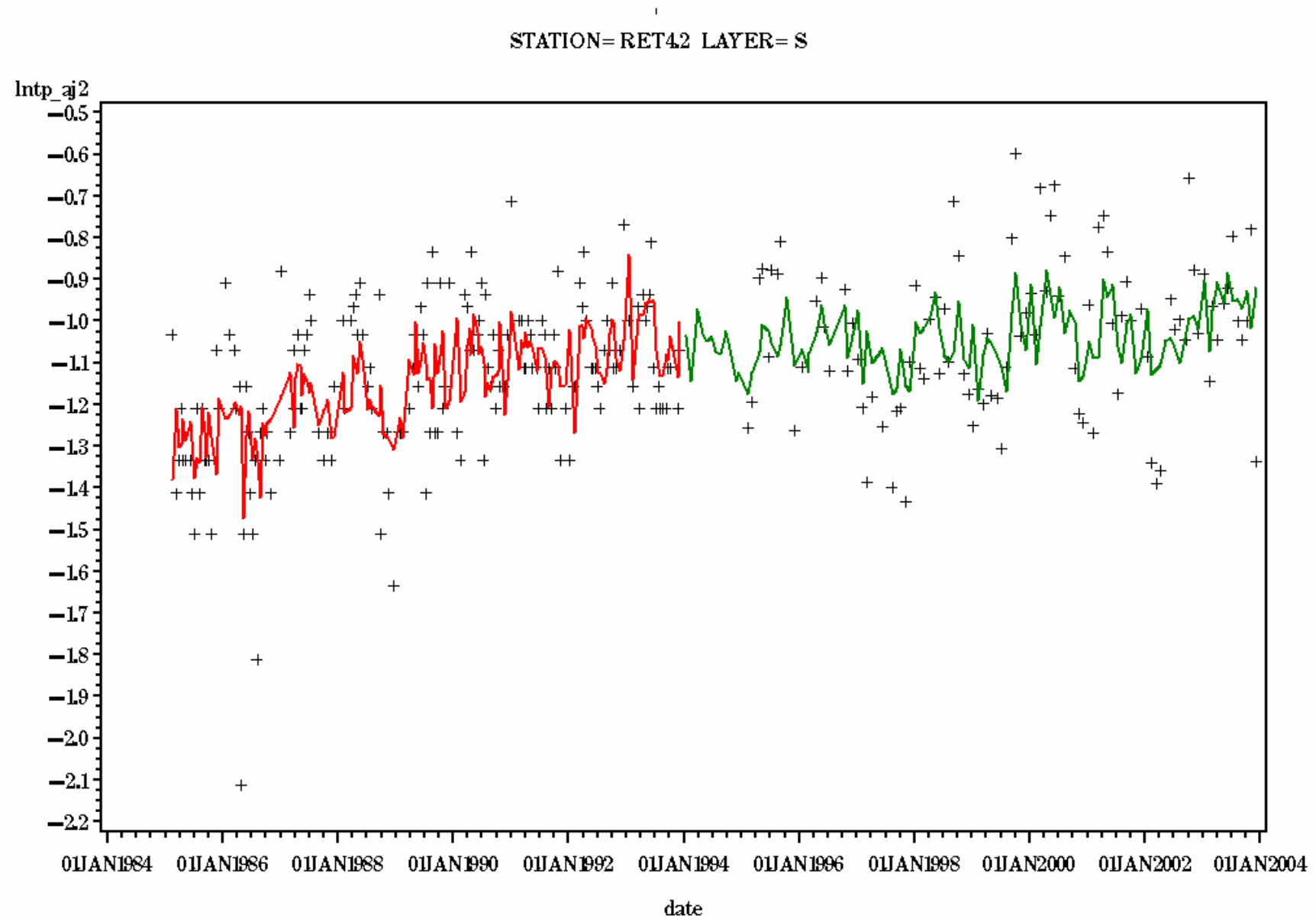
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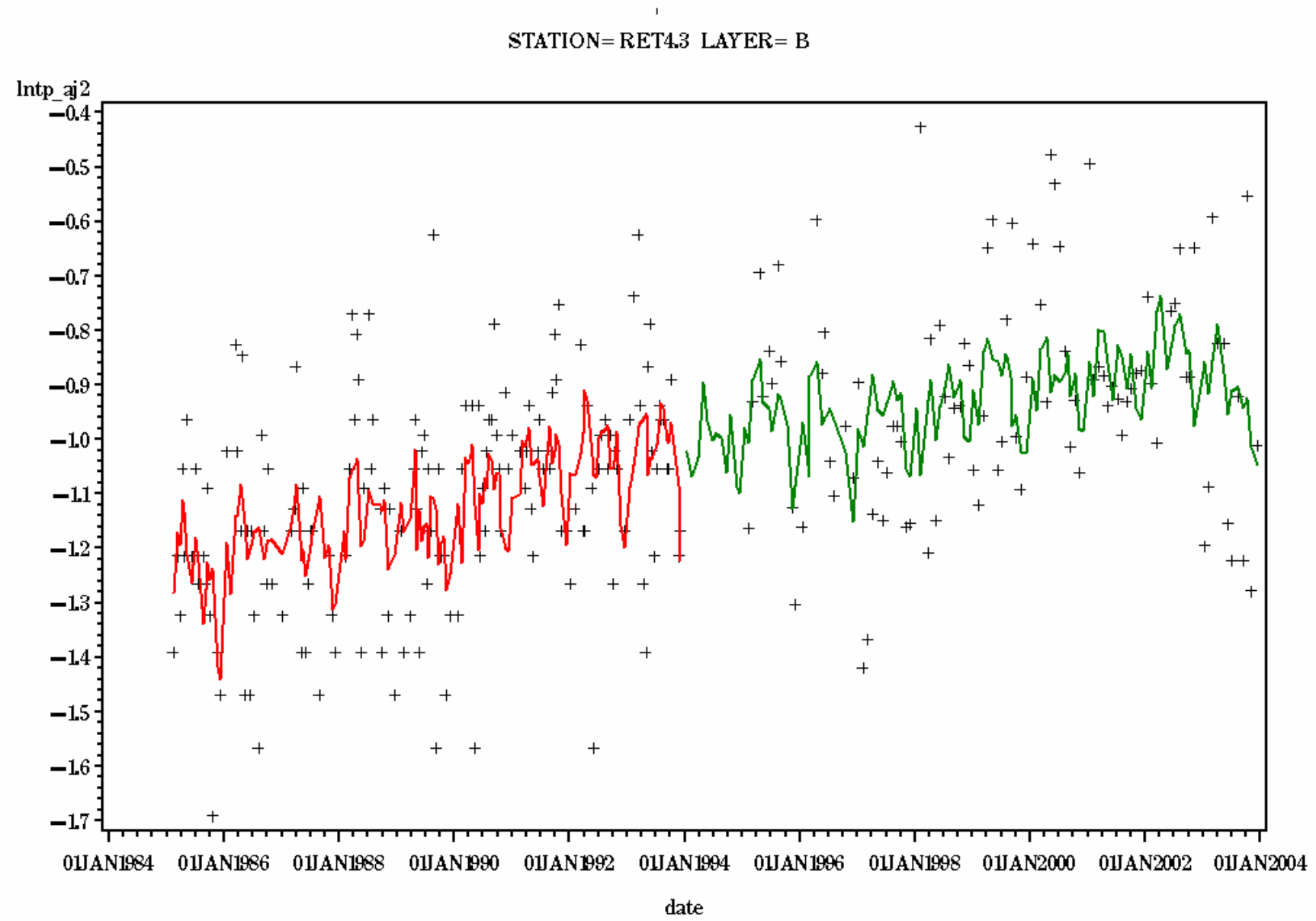
STATION= RET4.3 LAYER= B
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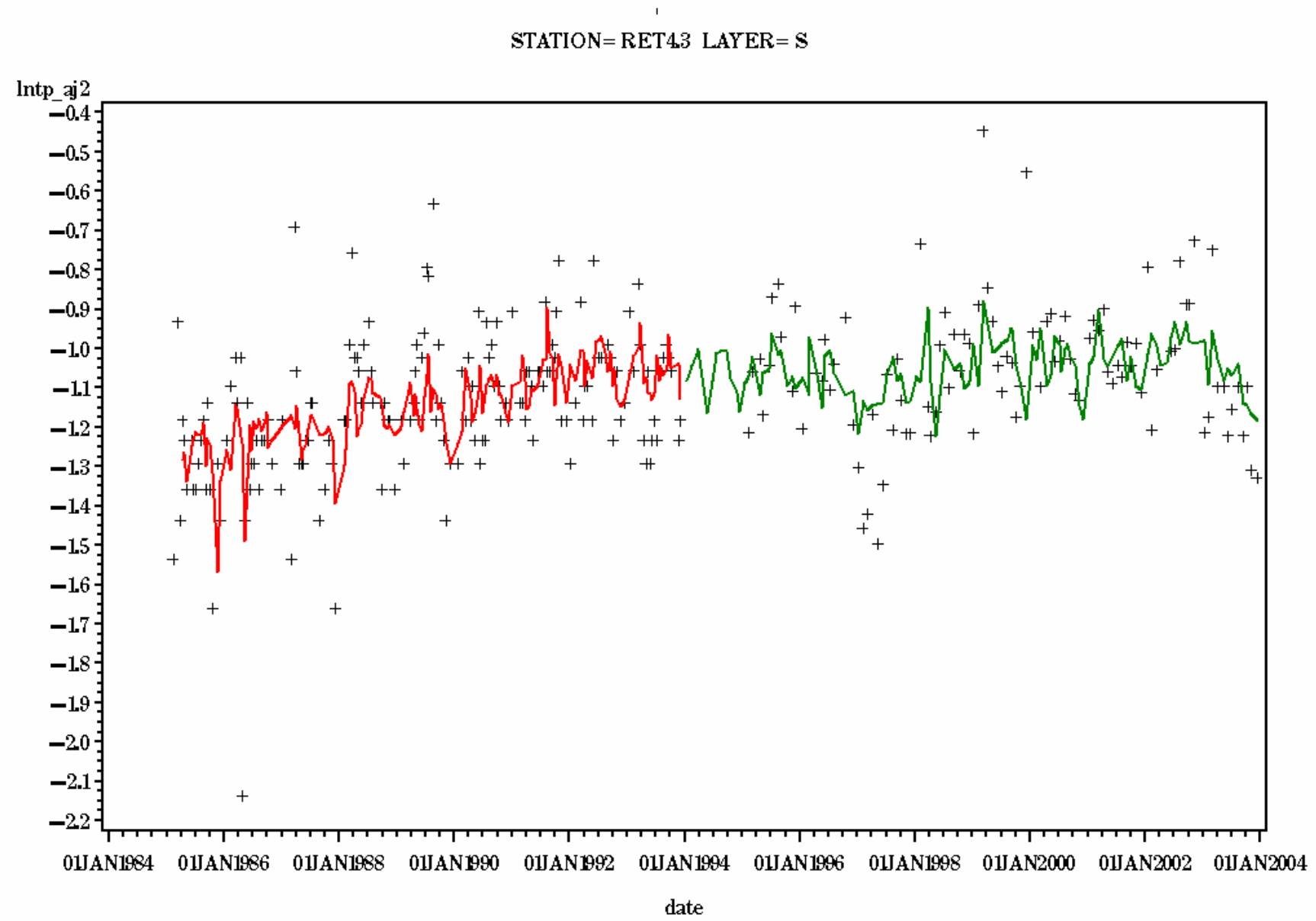
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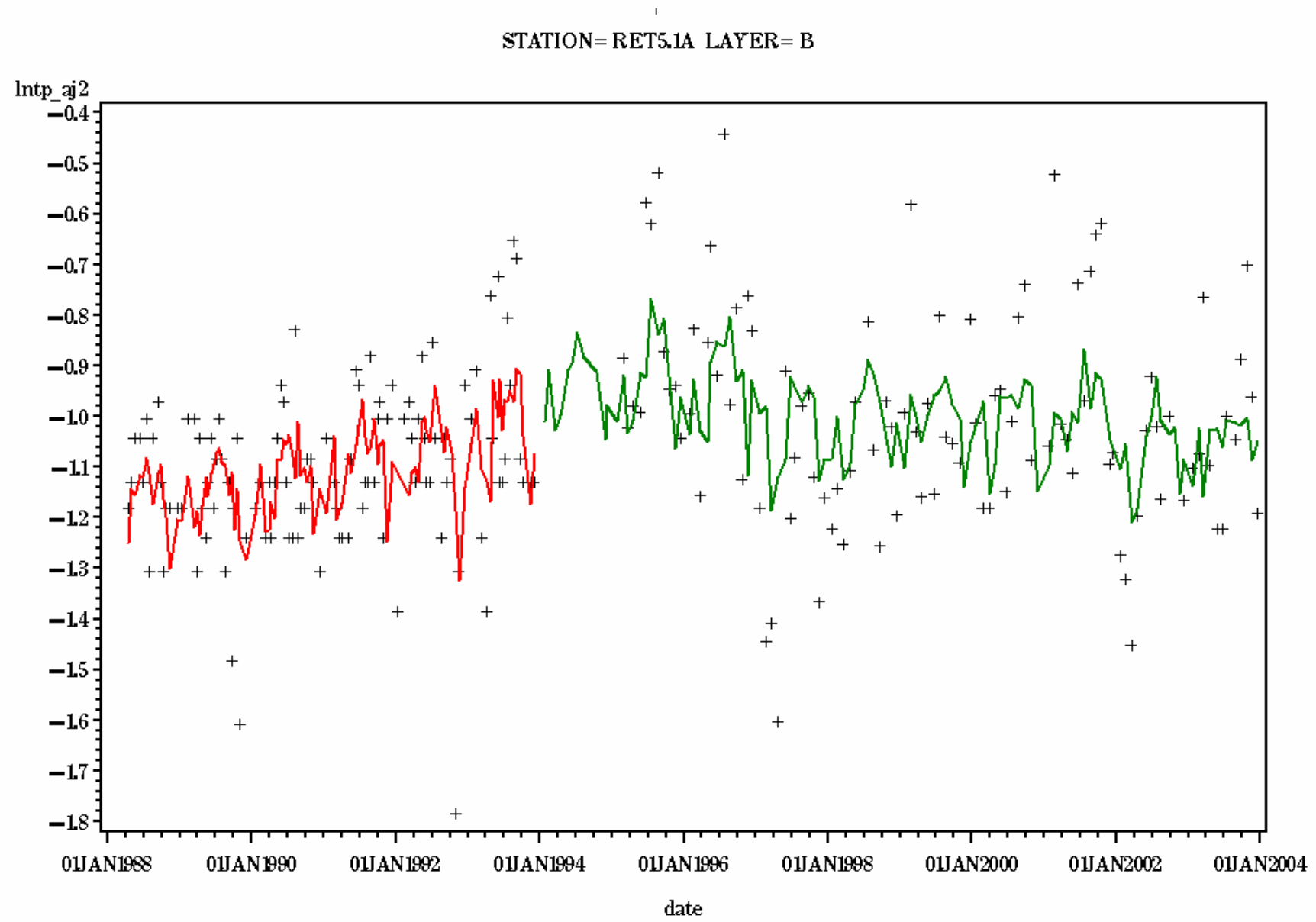
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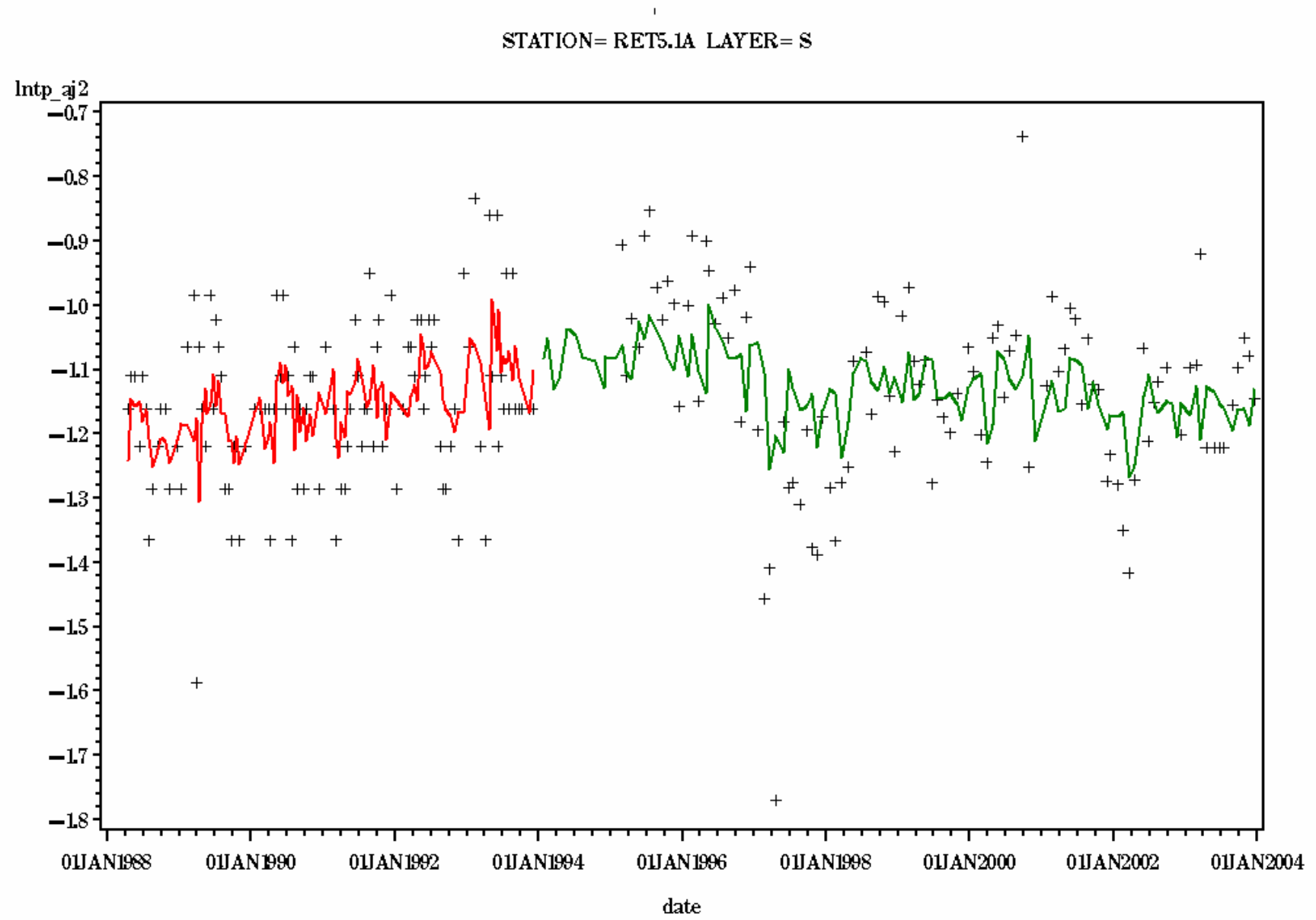
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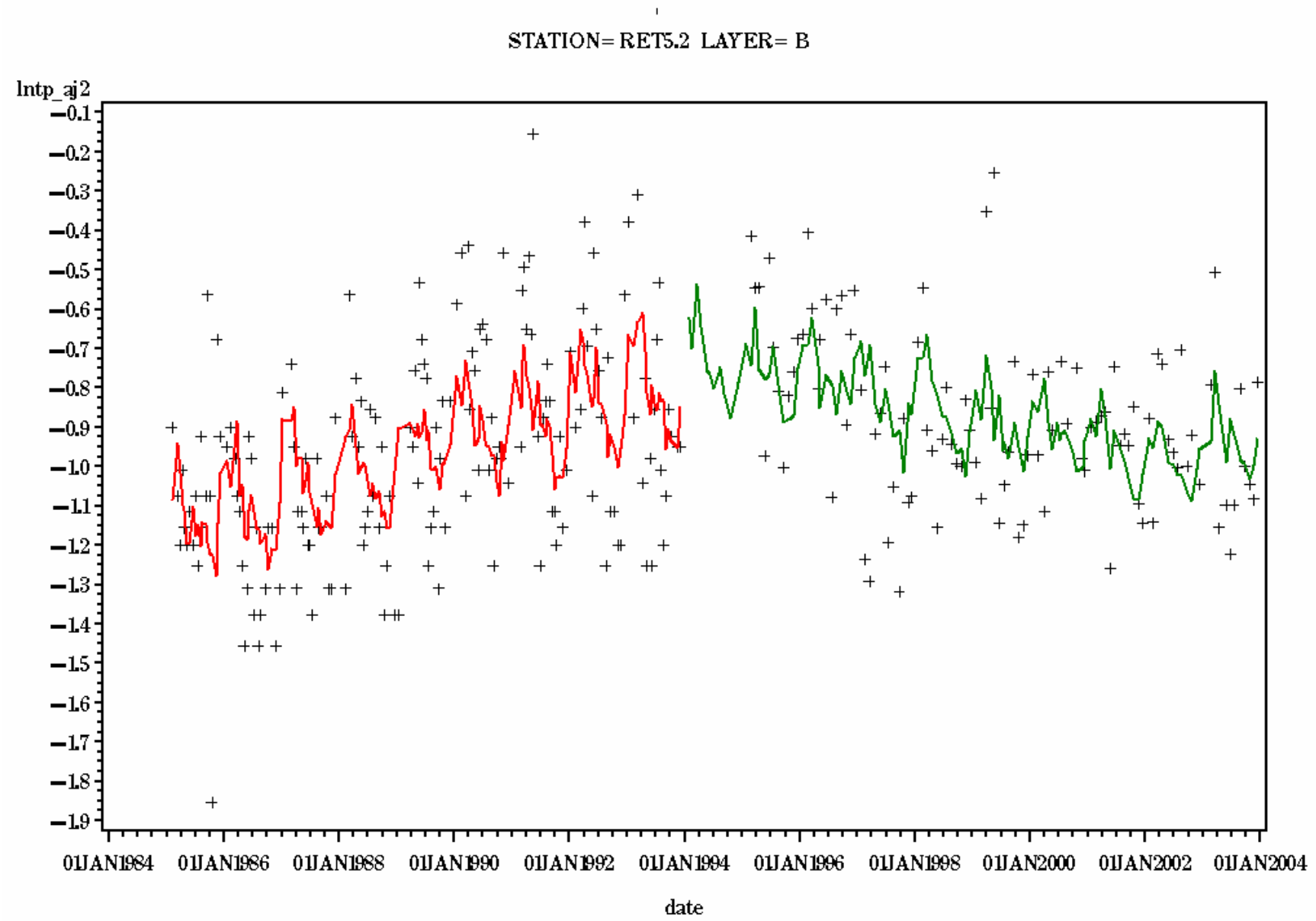
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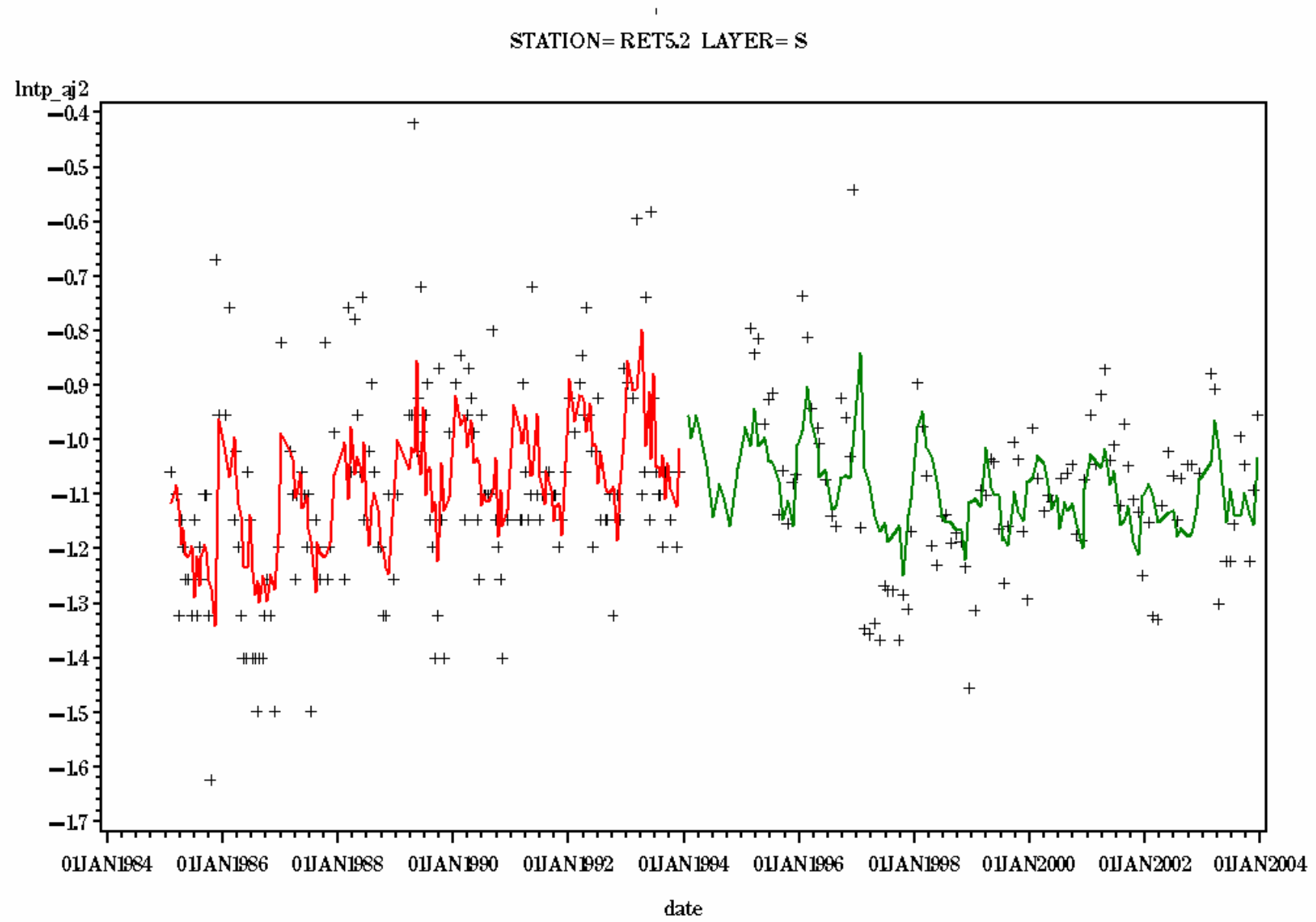
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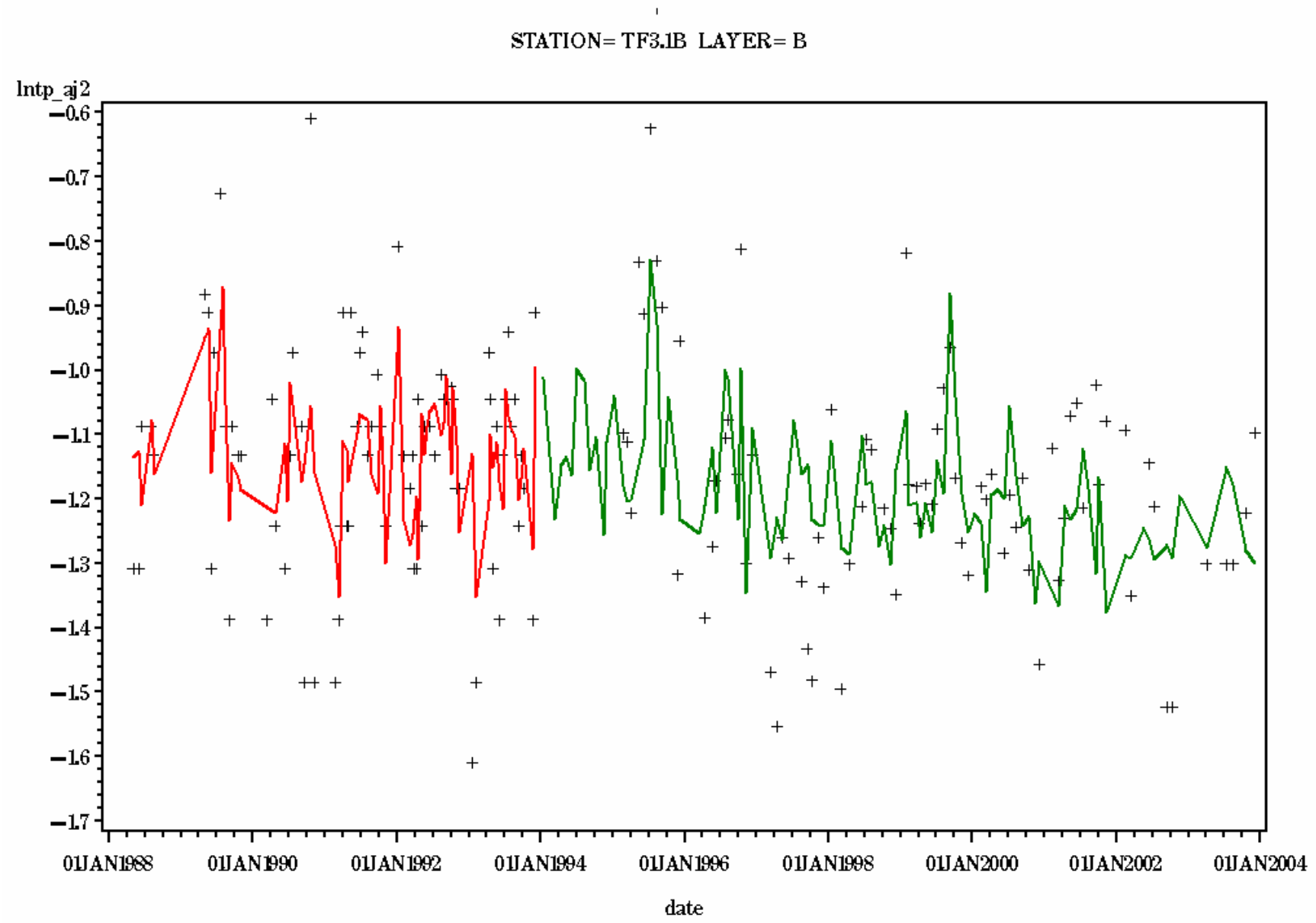
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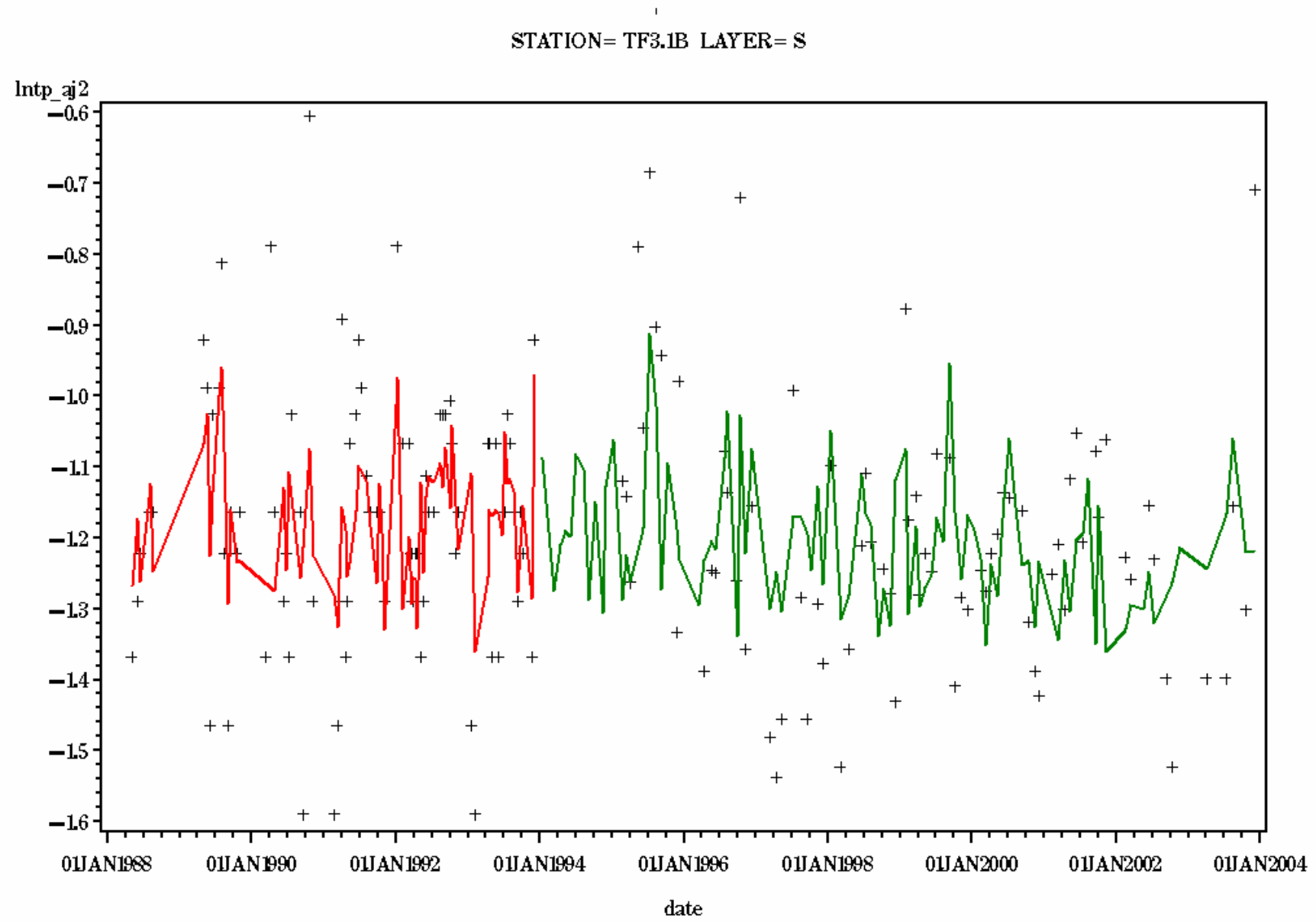
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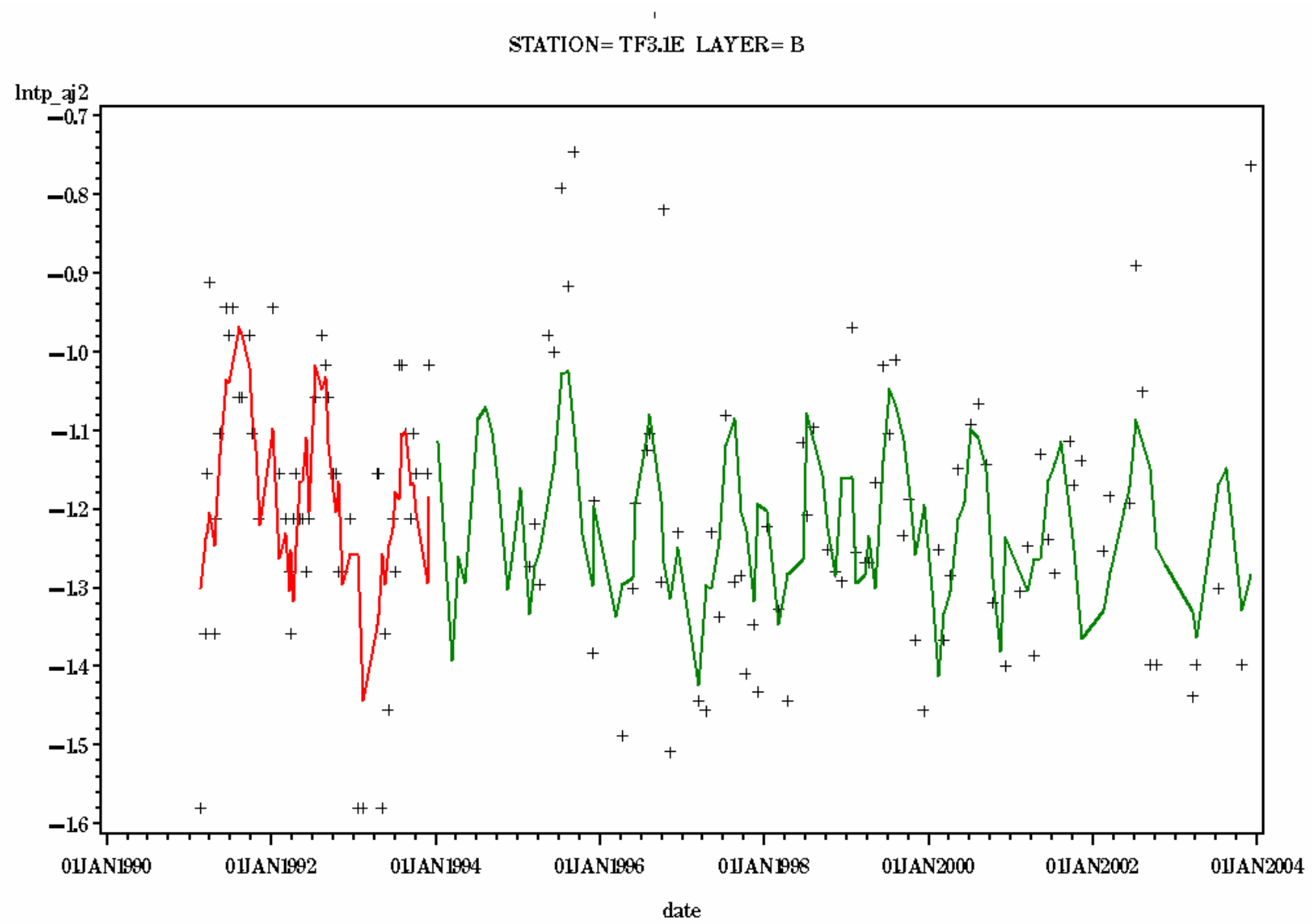
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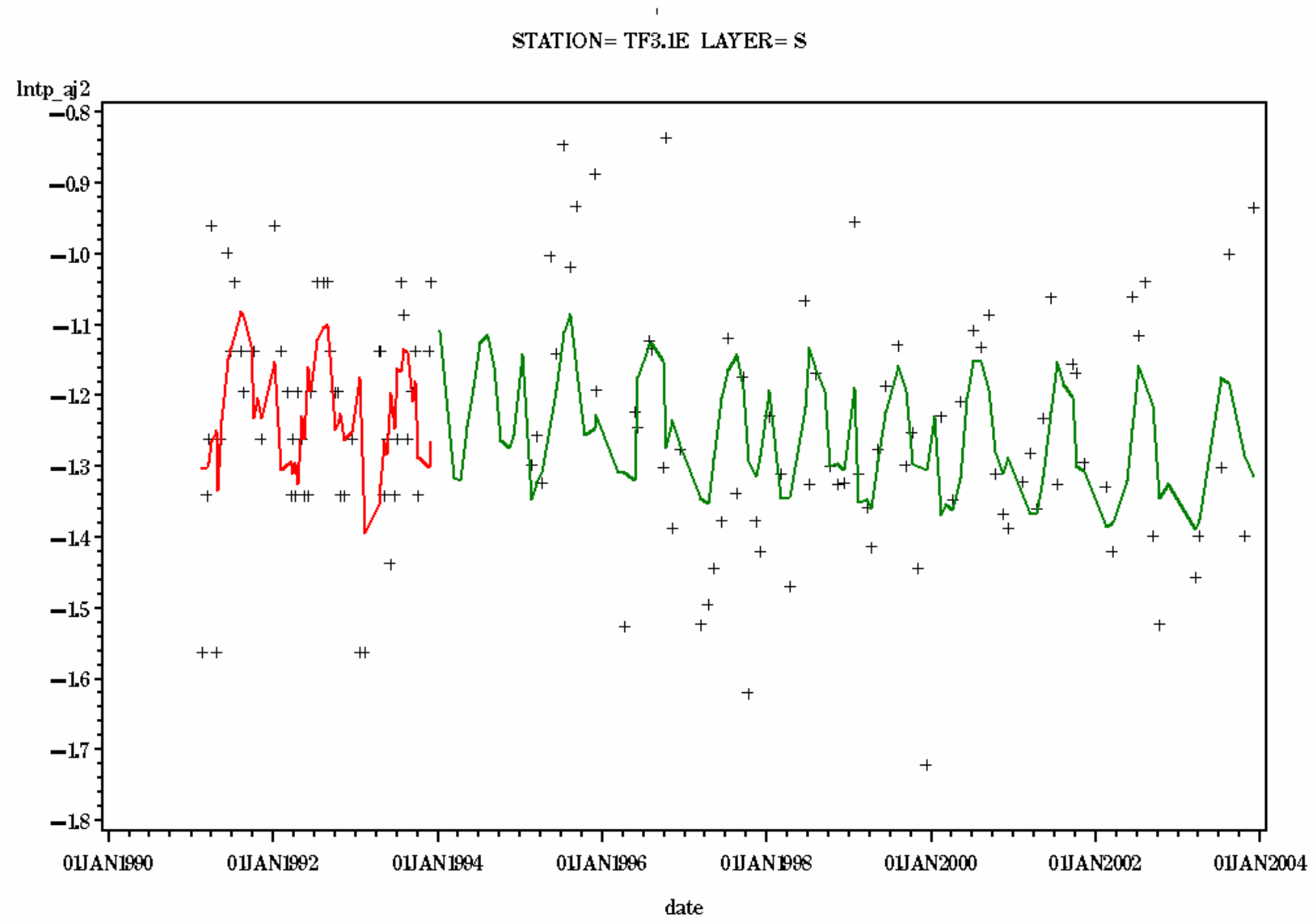
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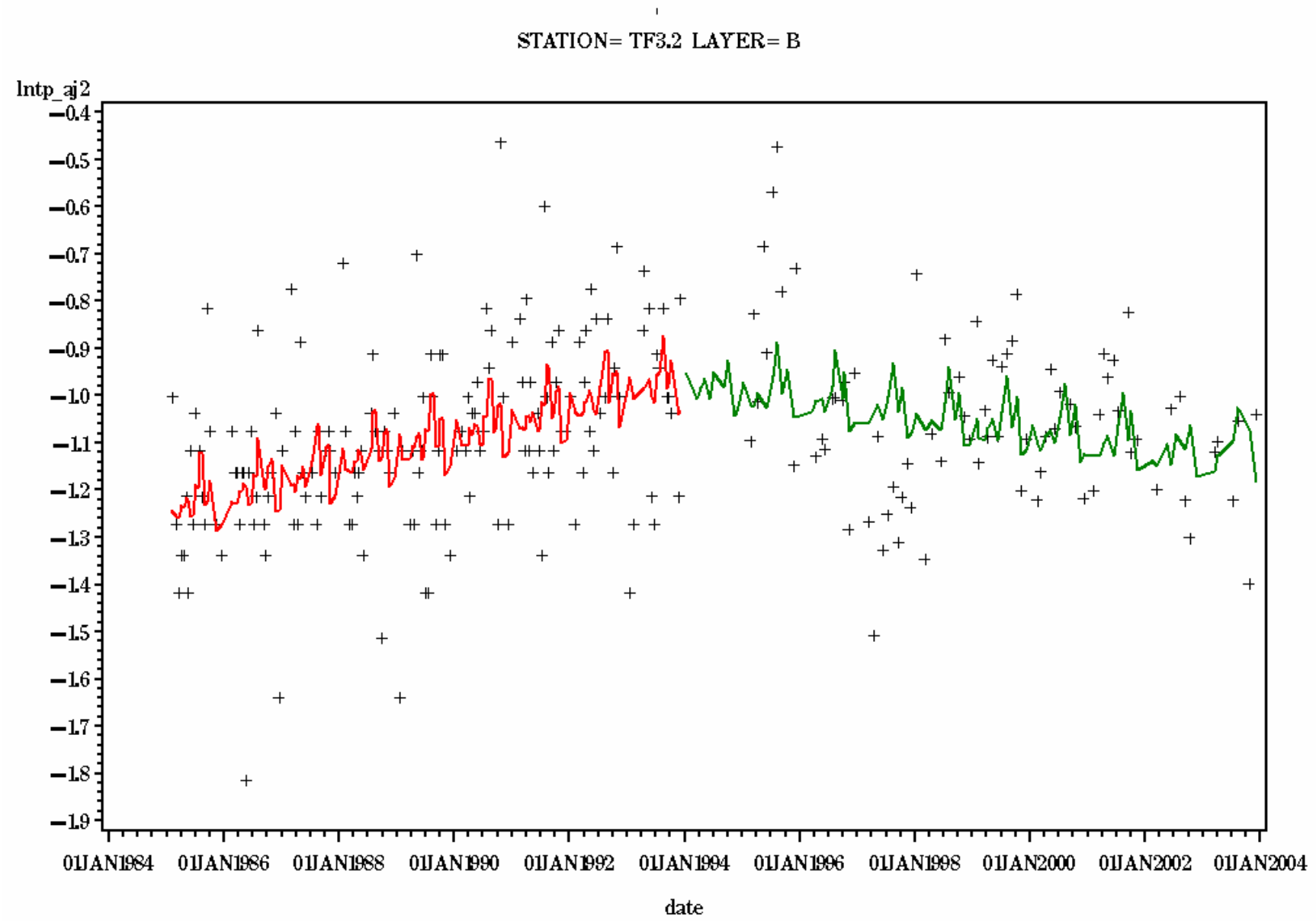
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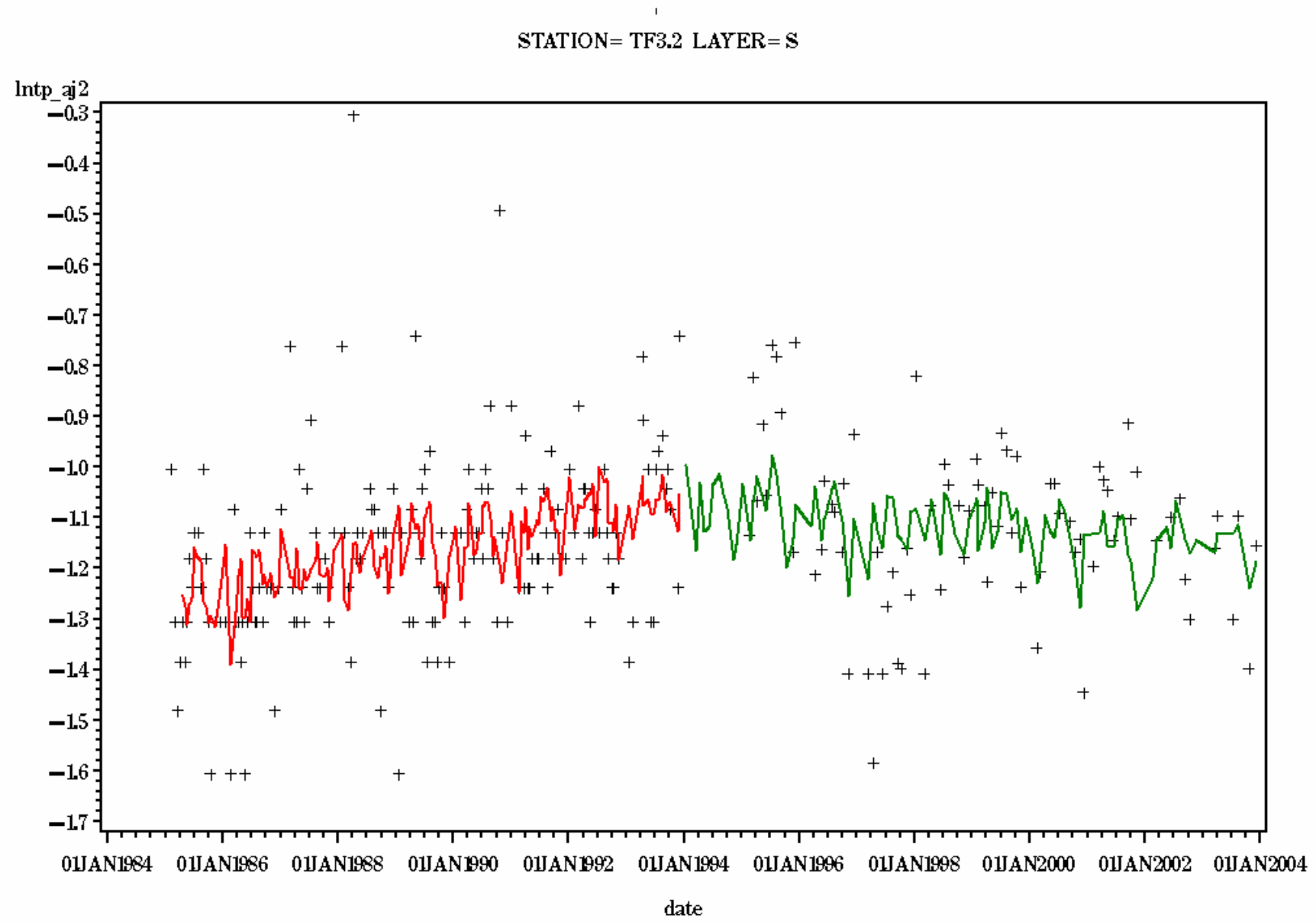
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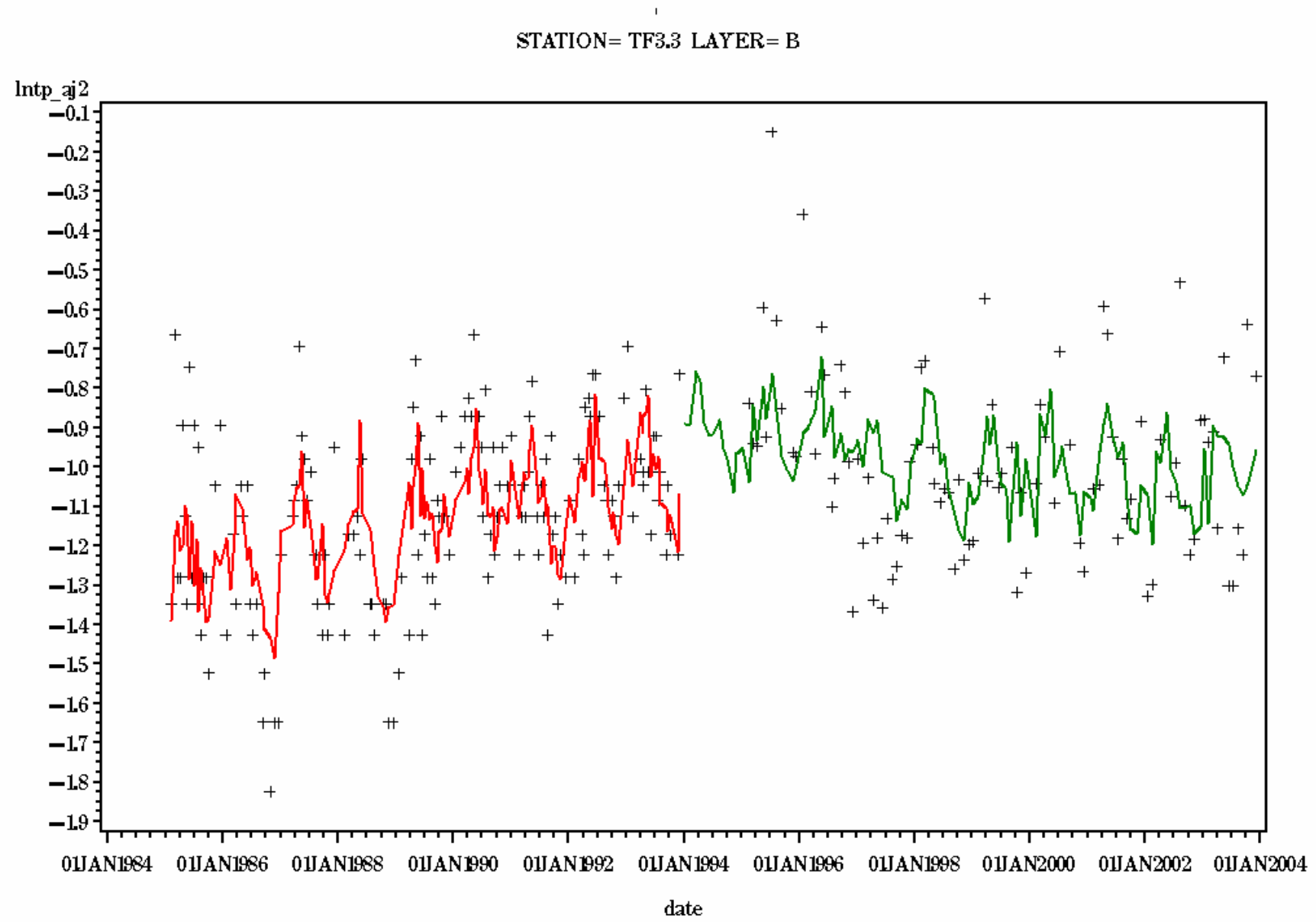
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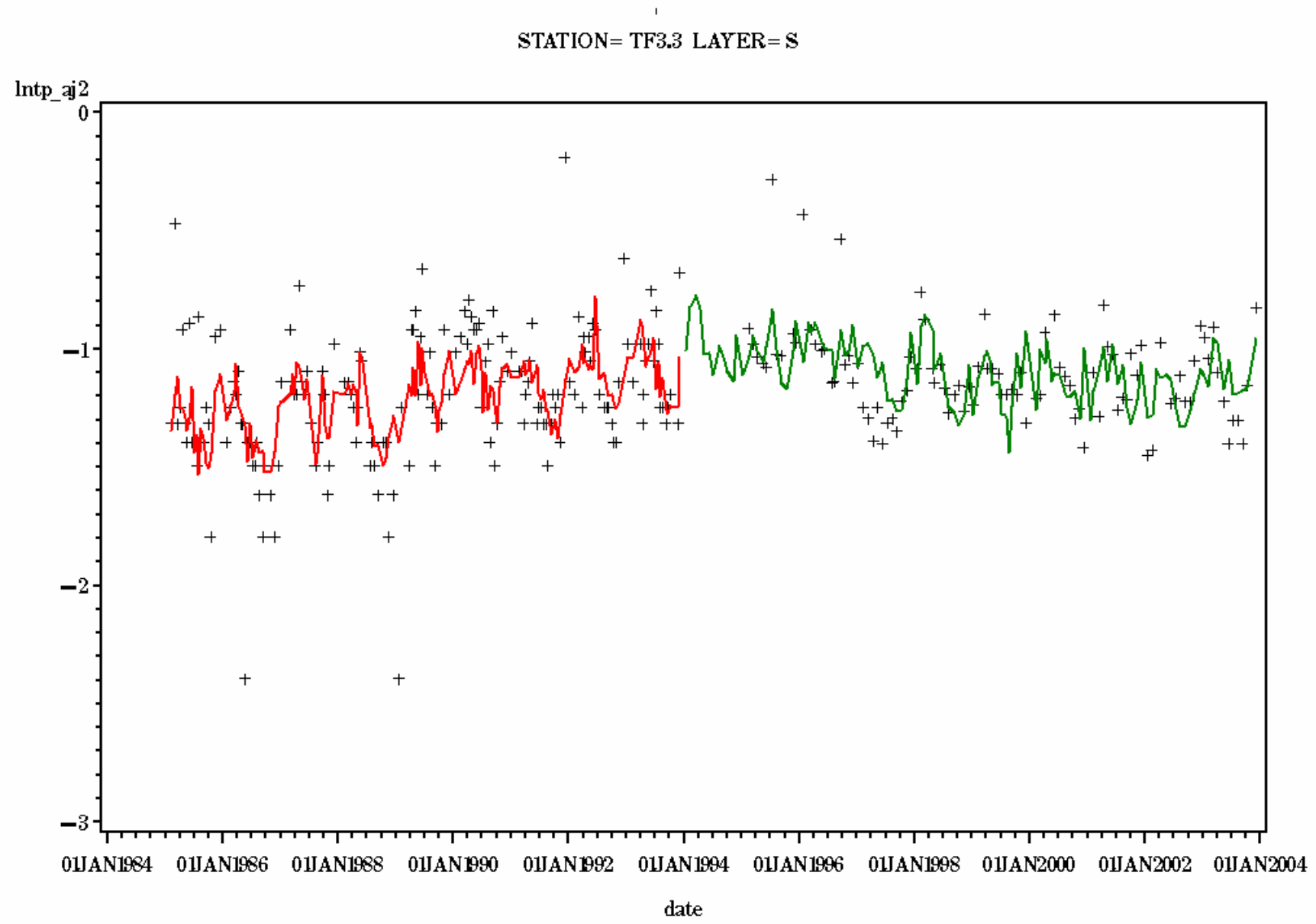
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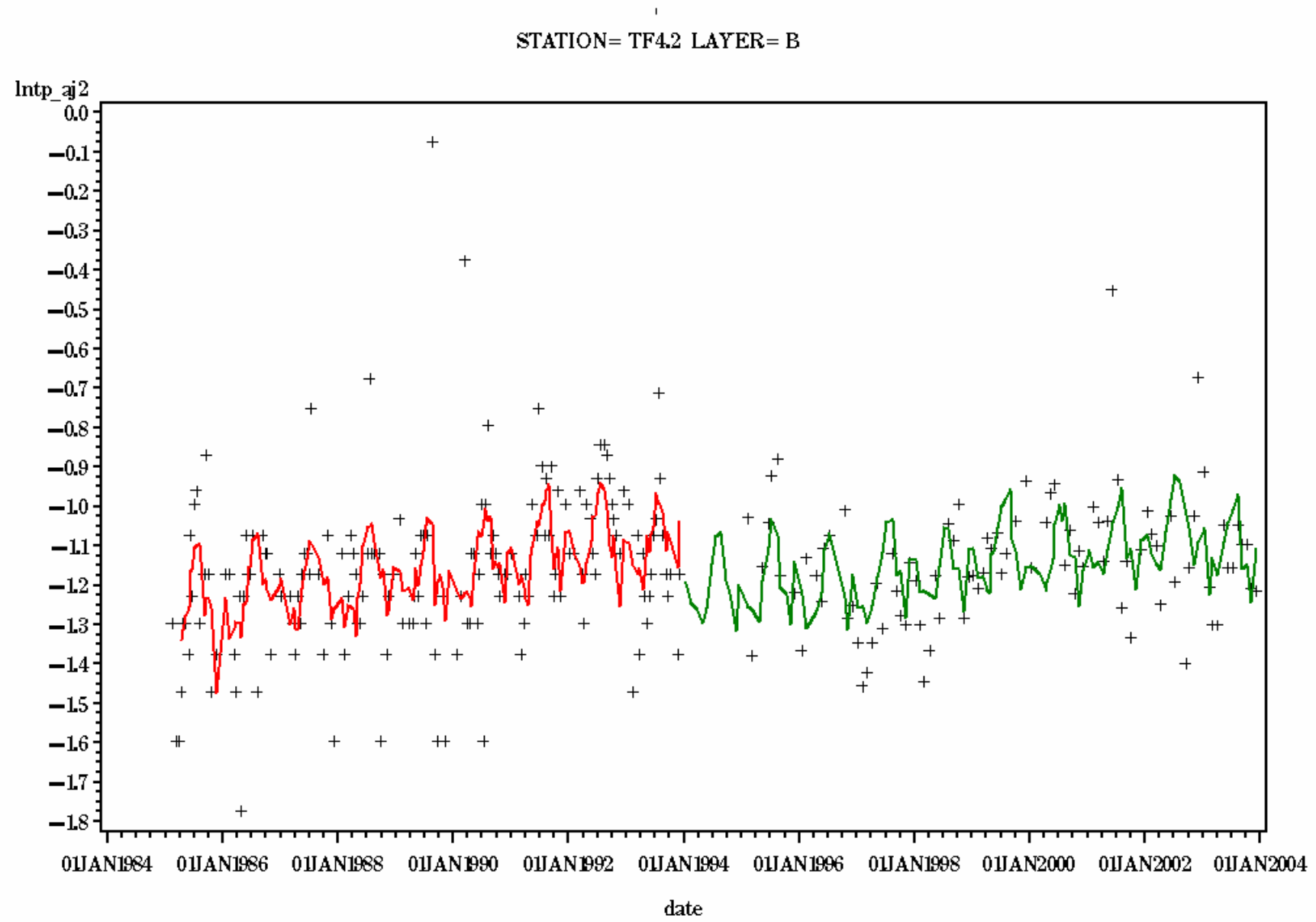
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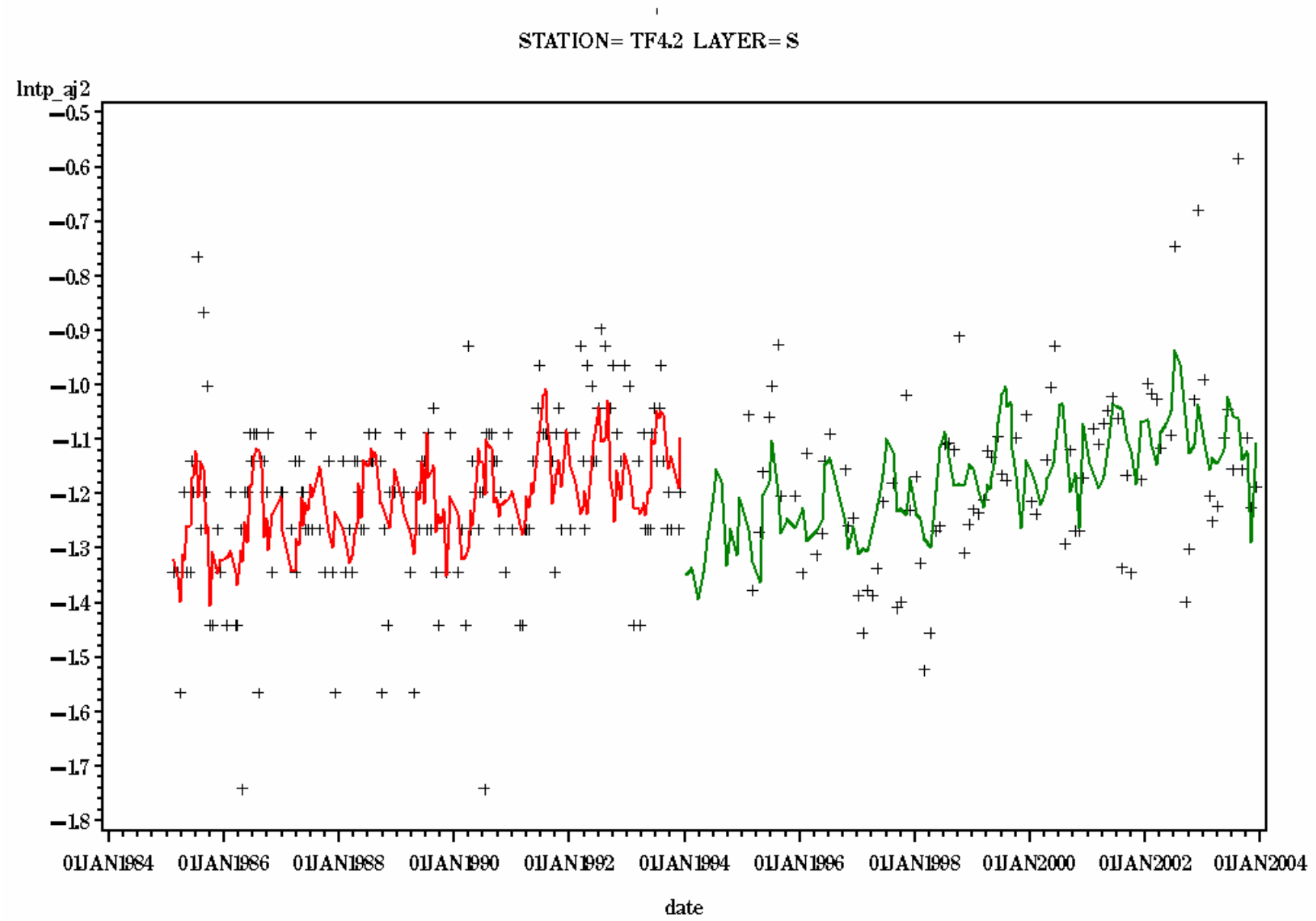
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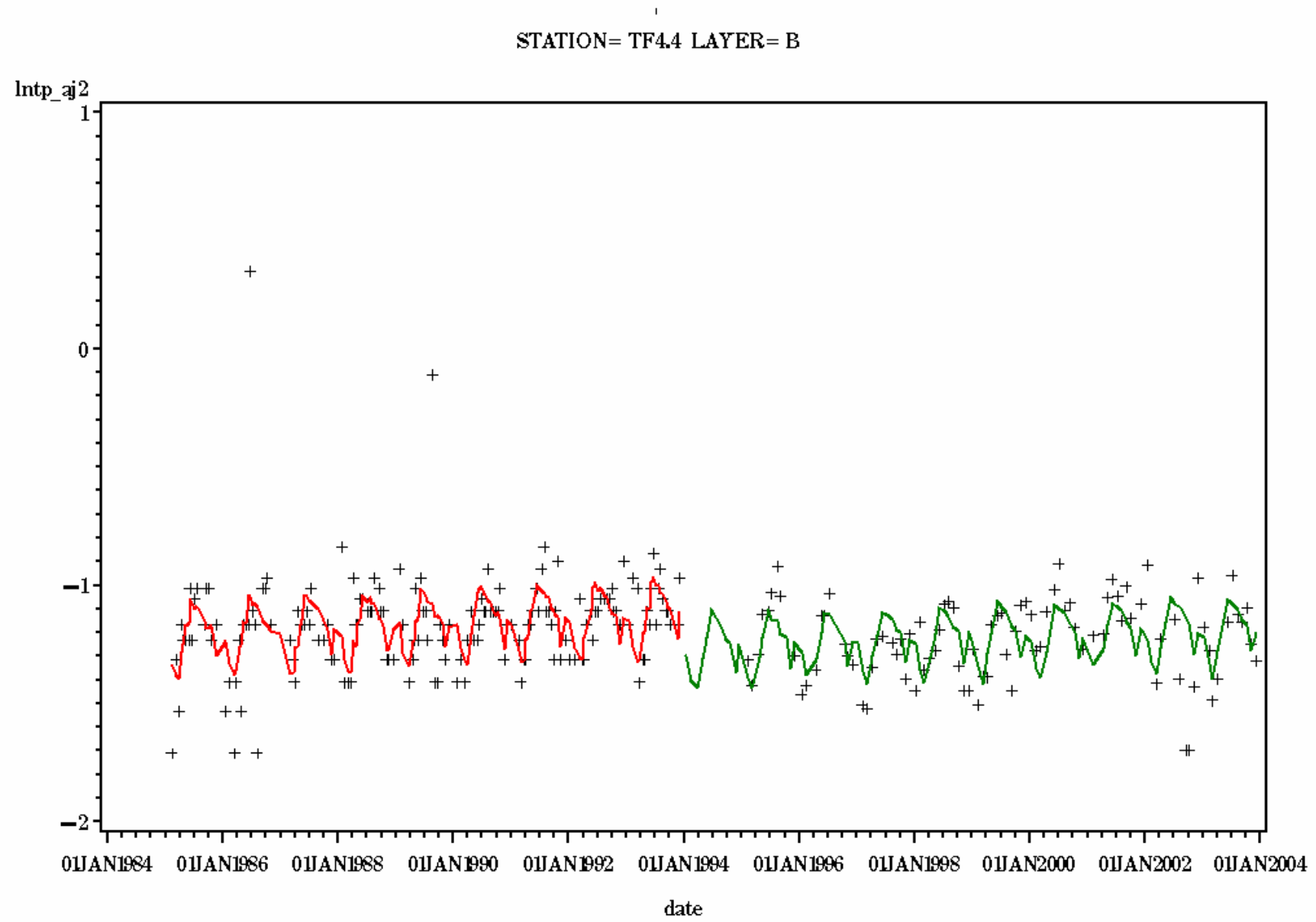
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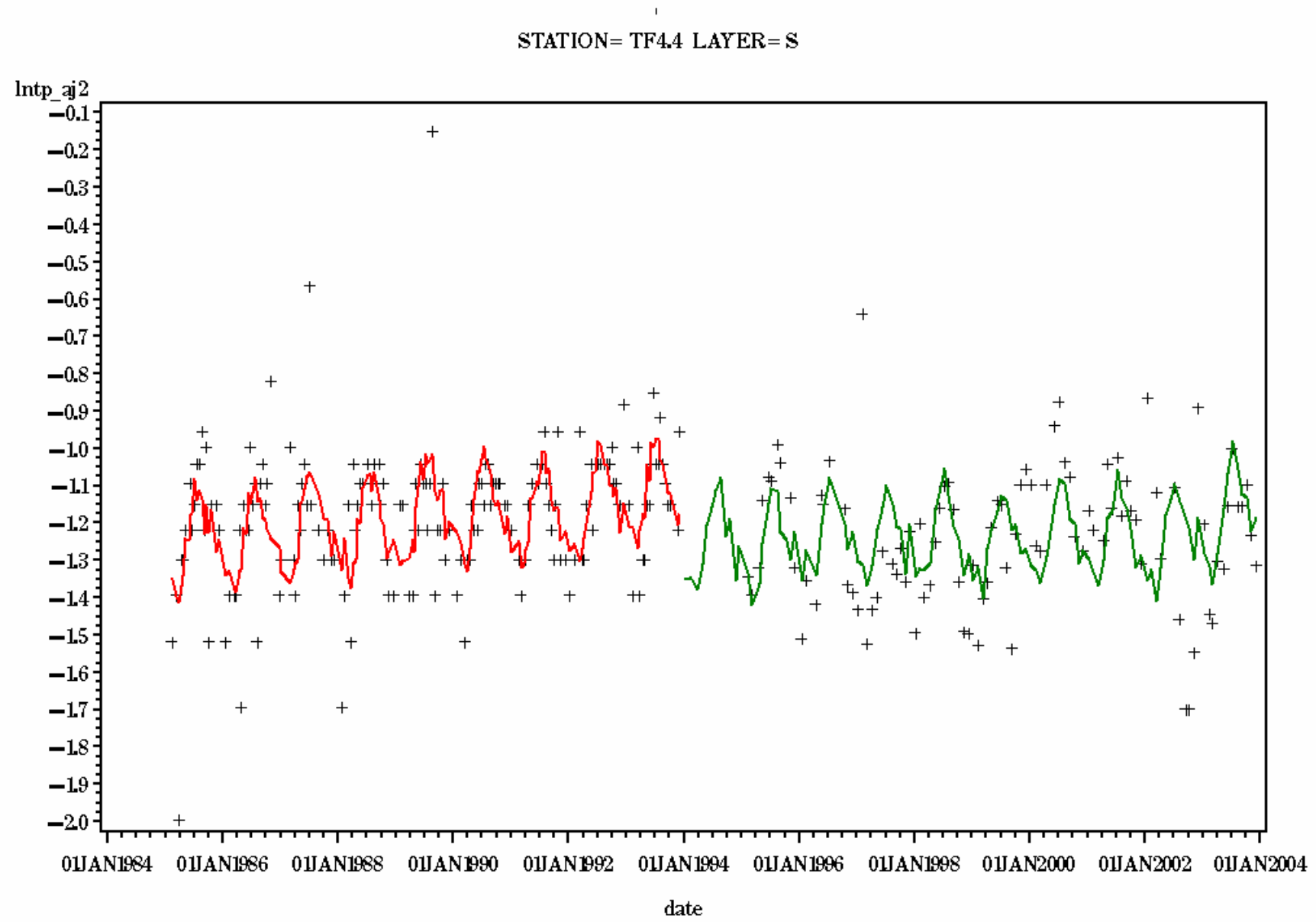
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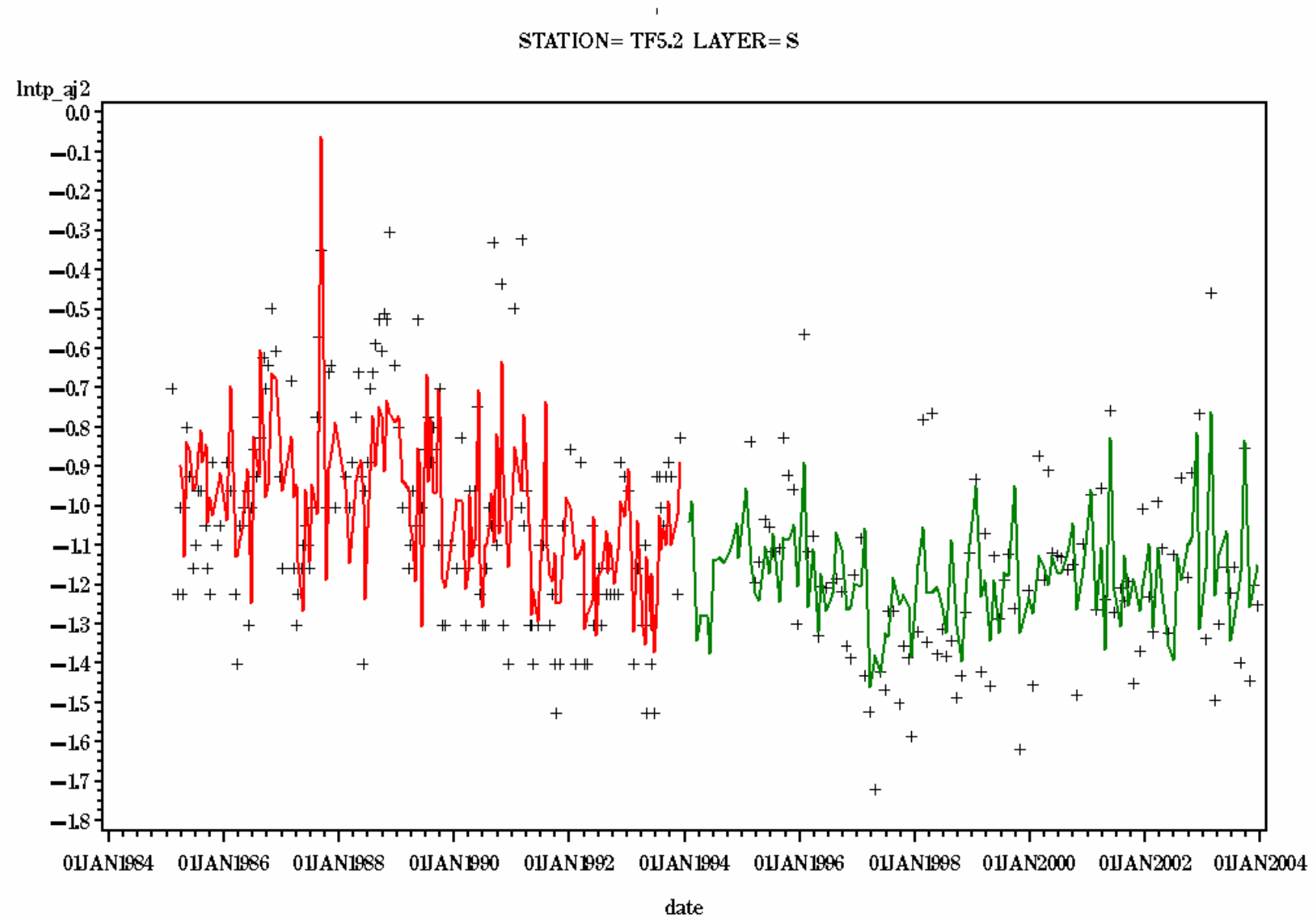
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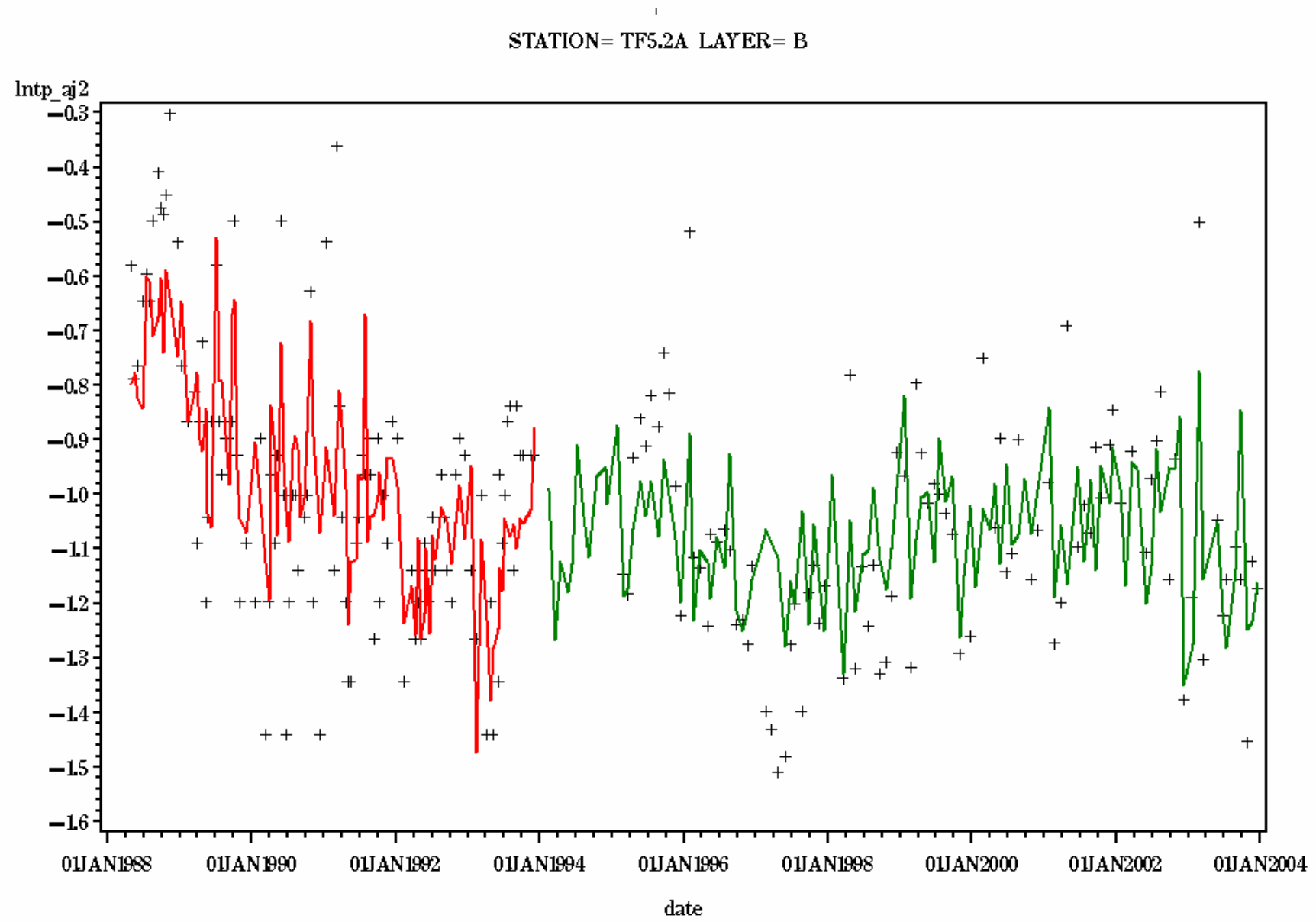
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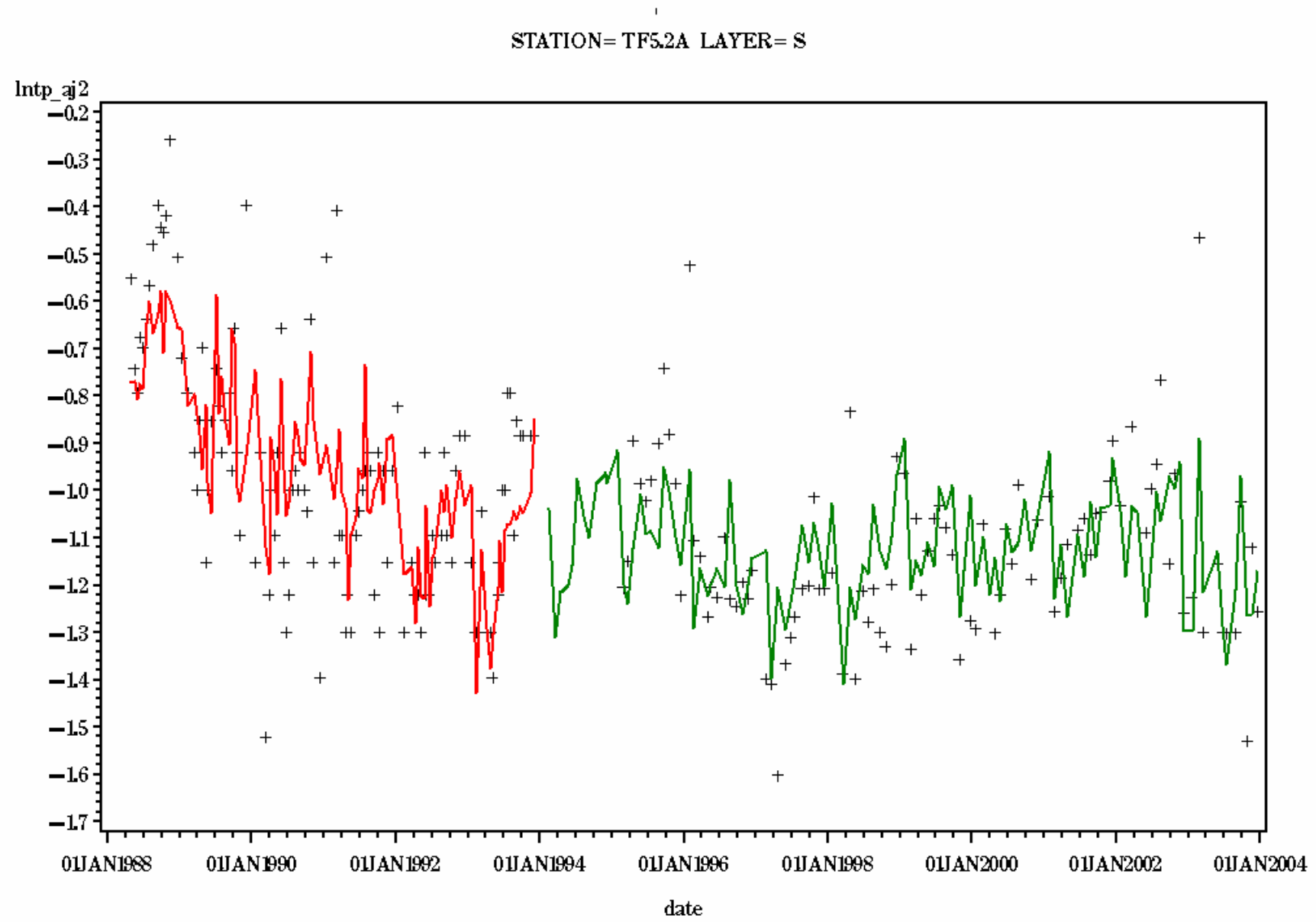
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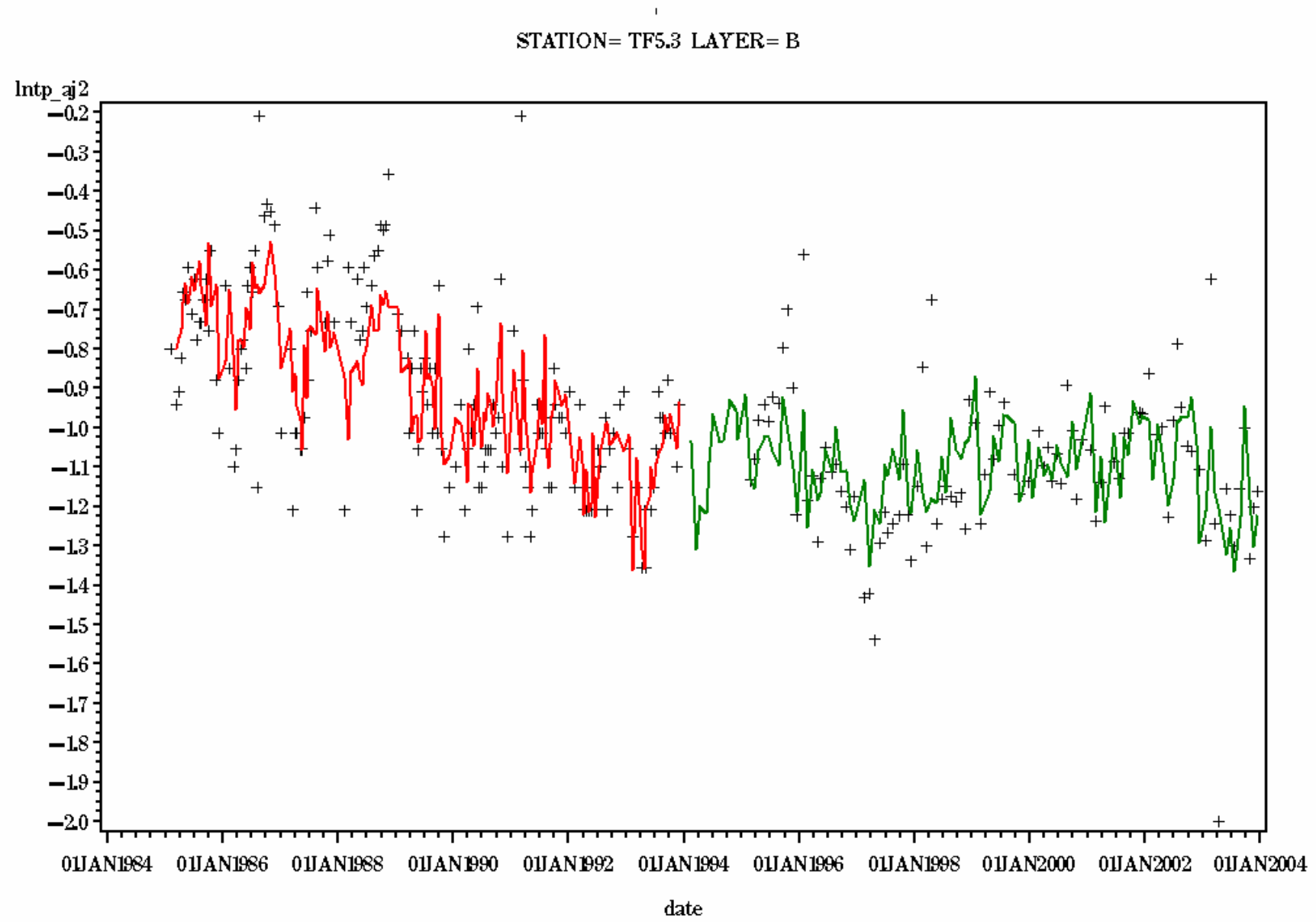
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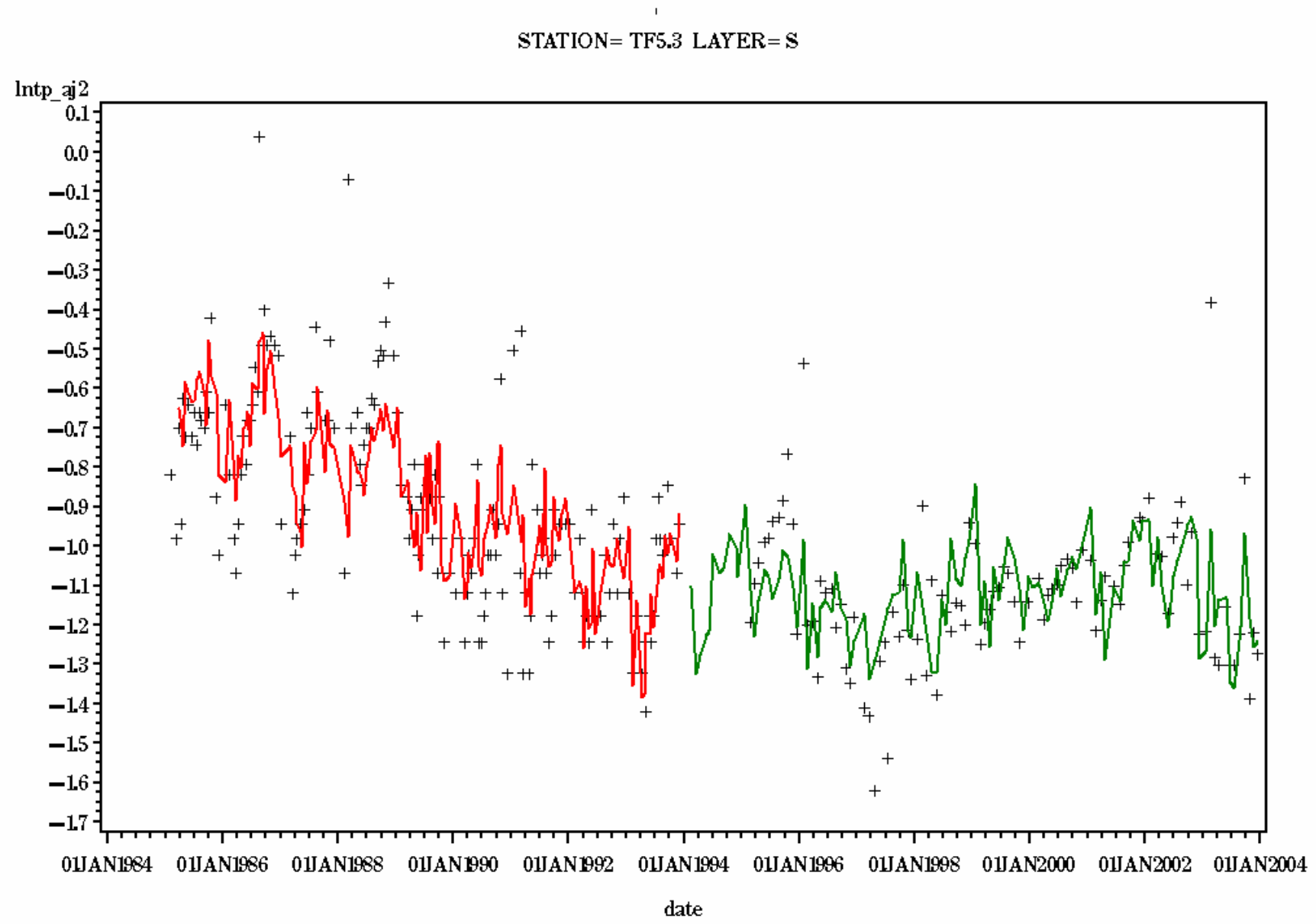
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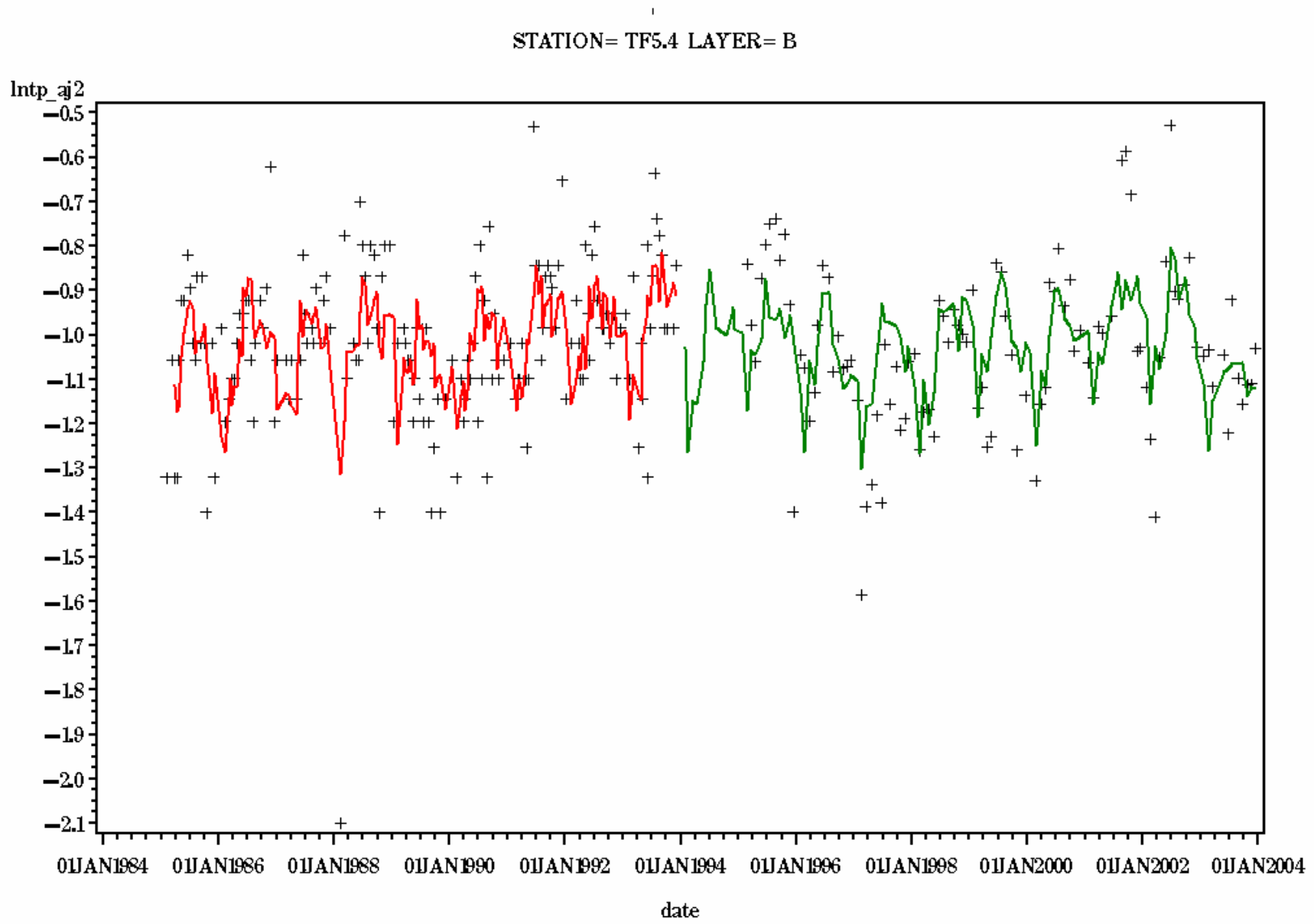
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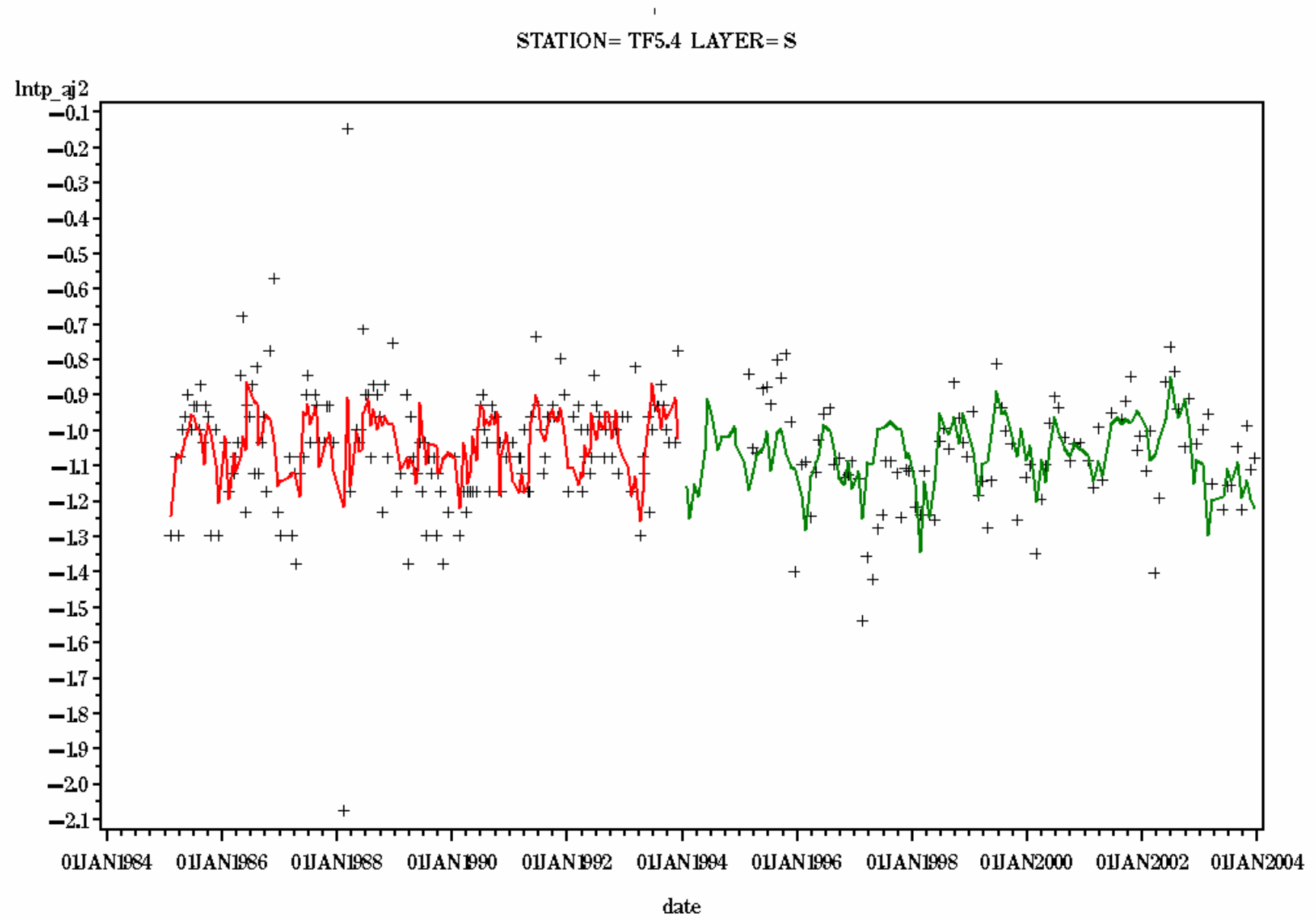
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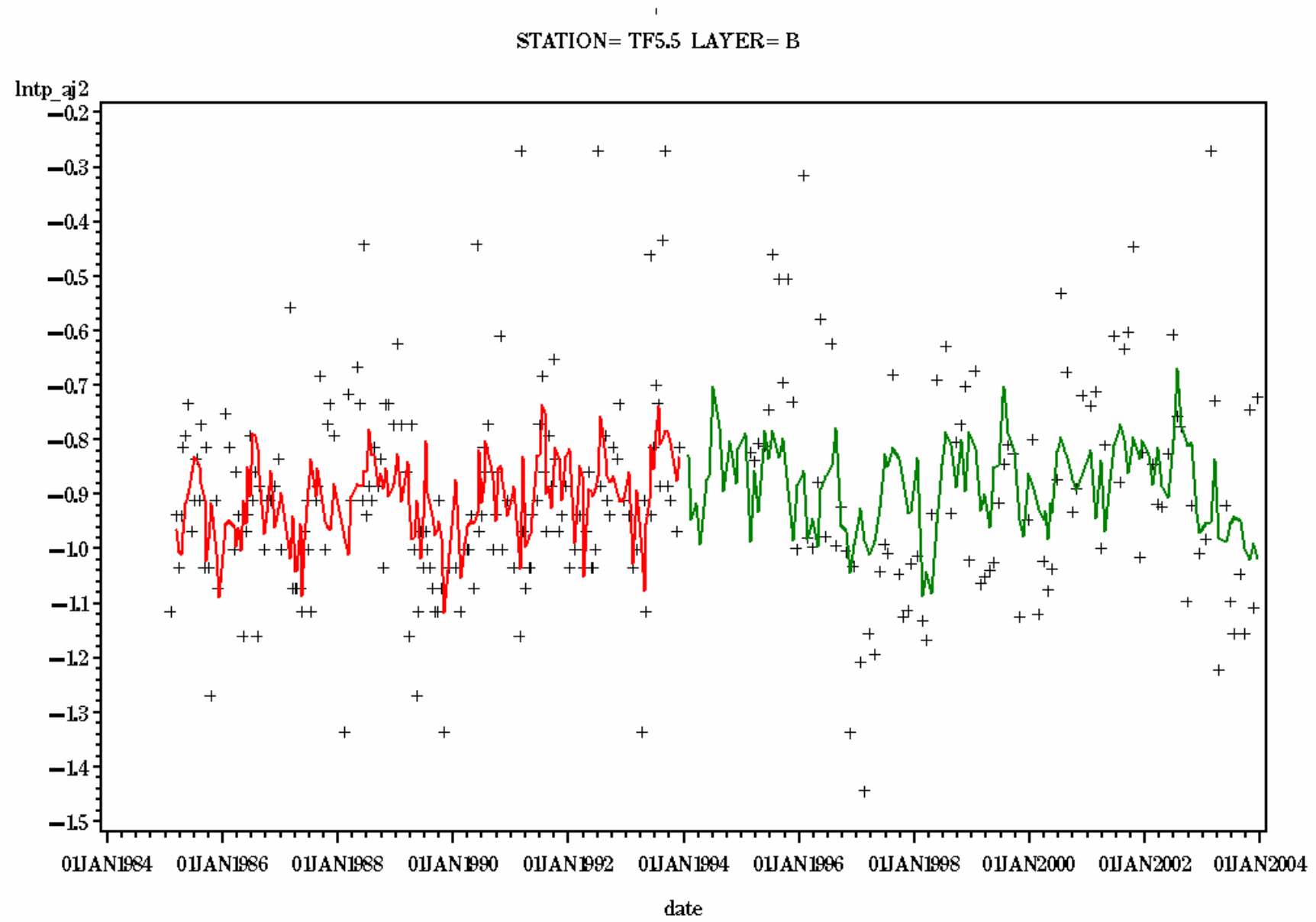
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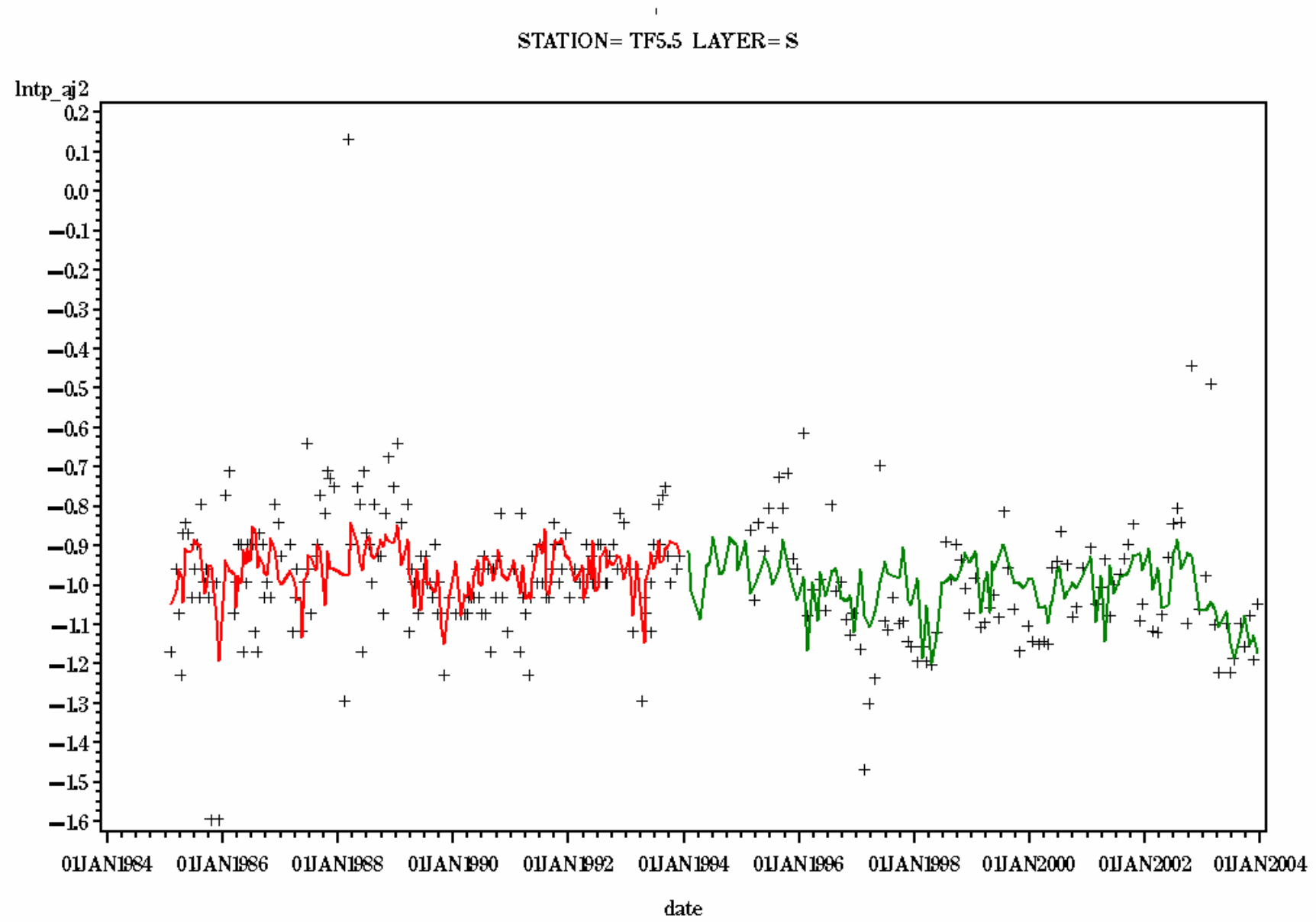
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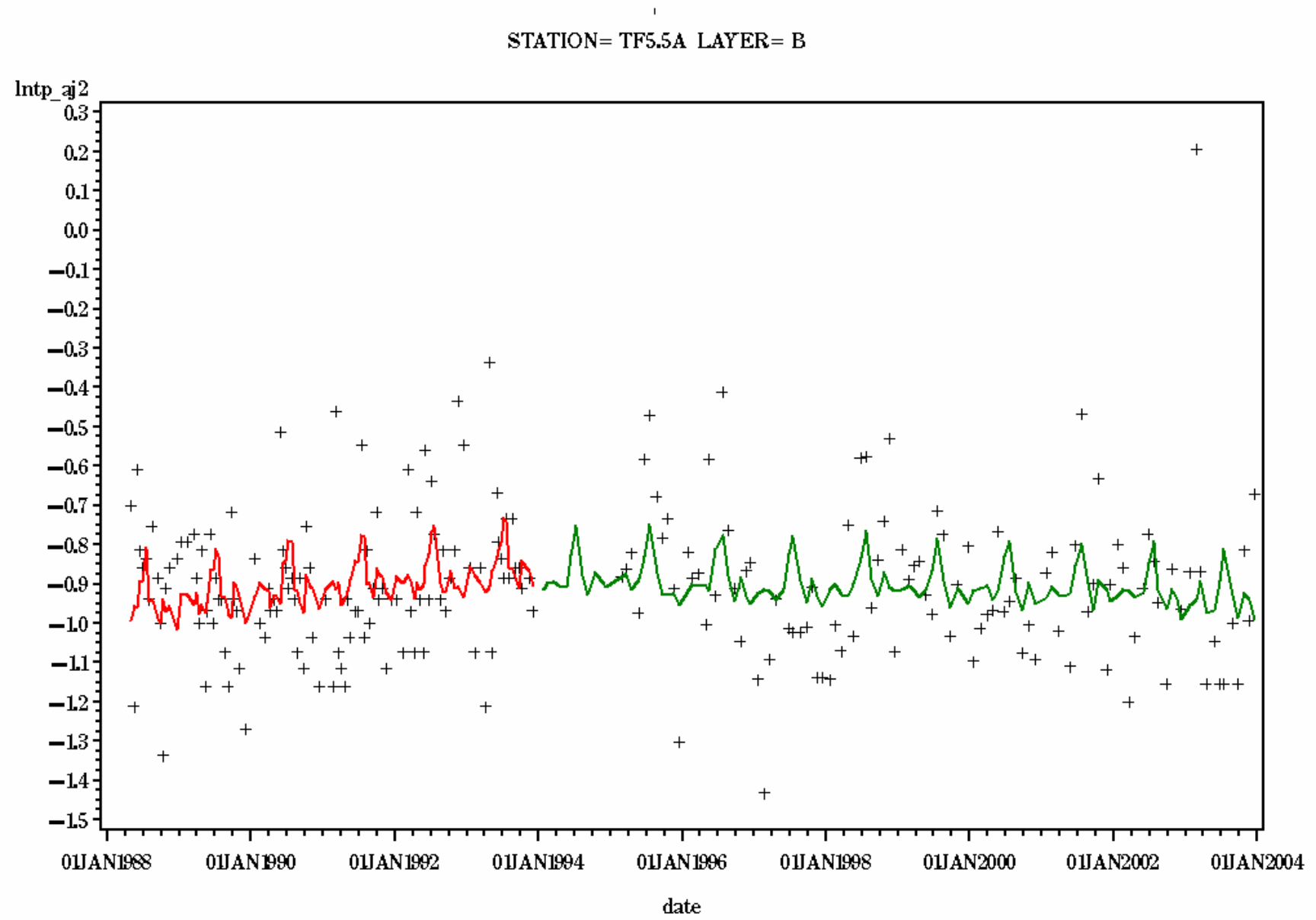
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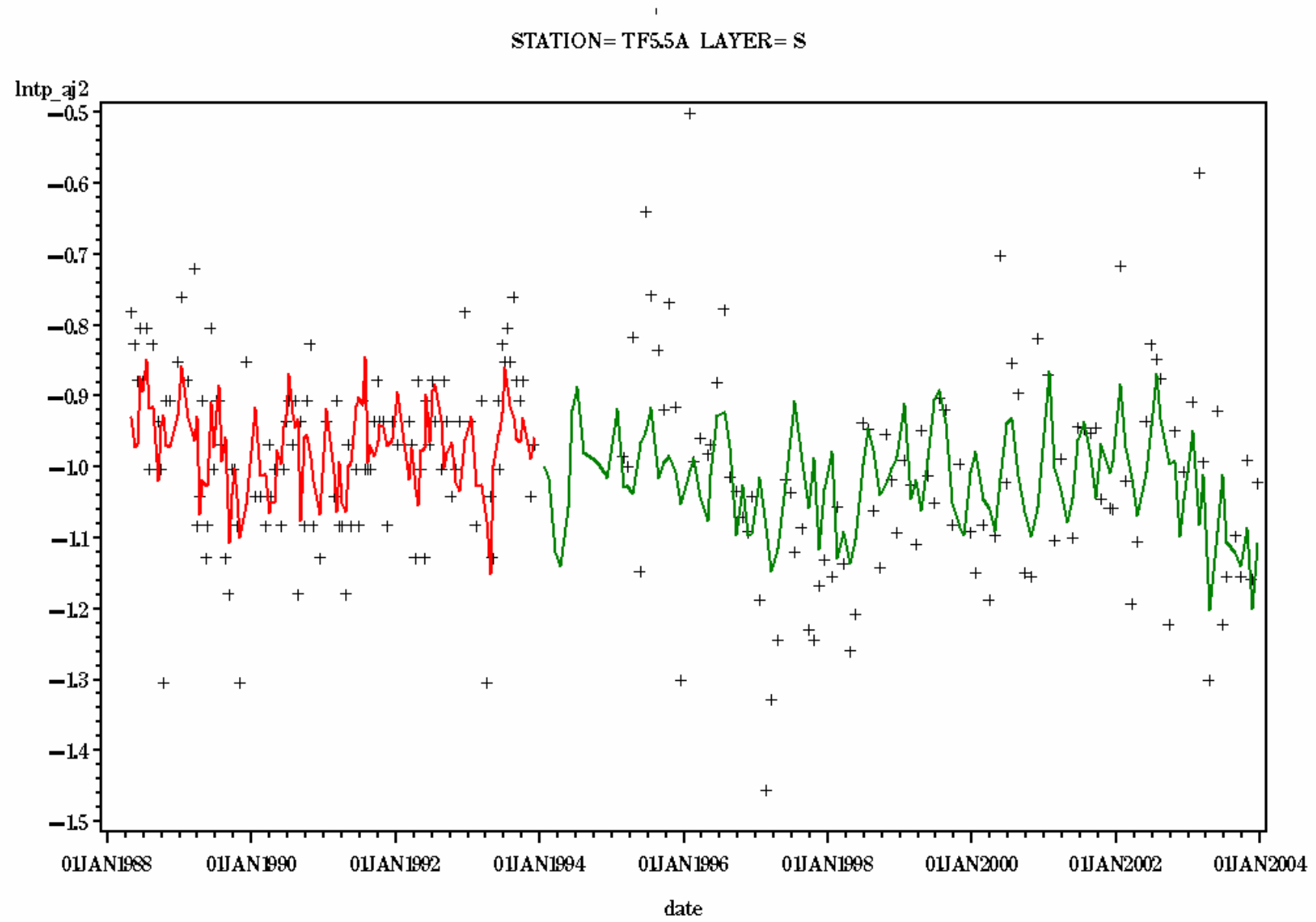
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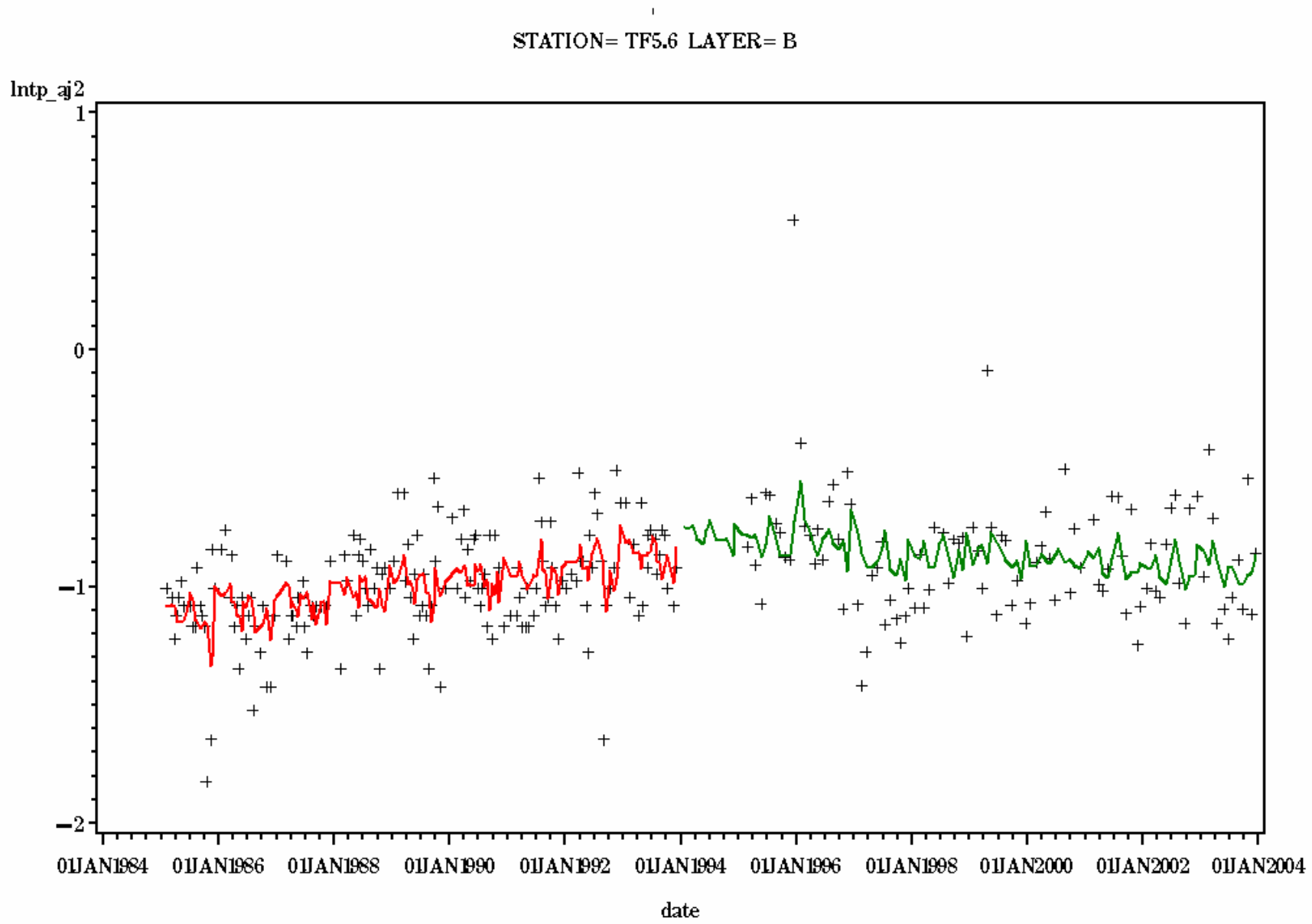
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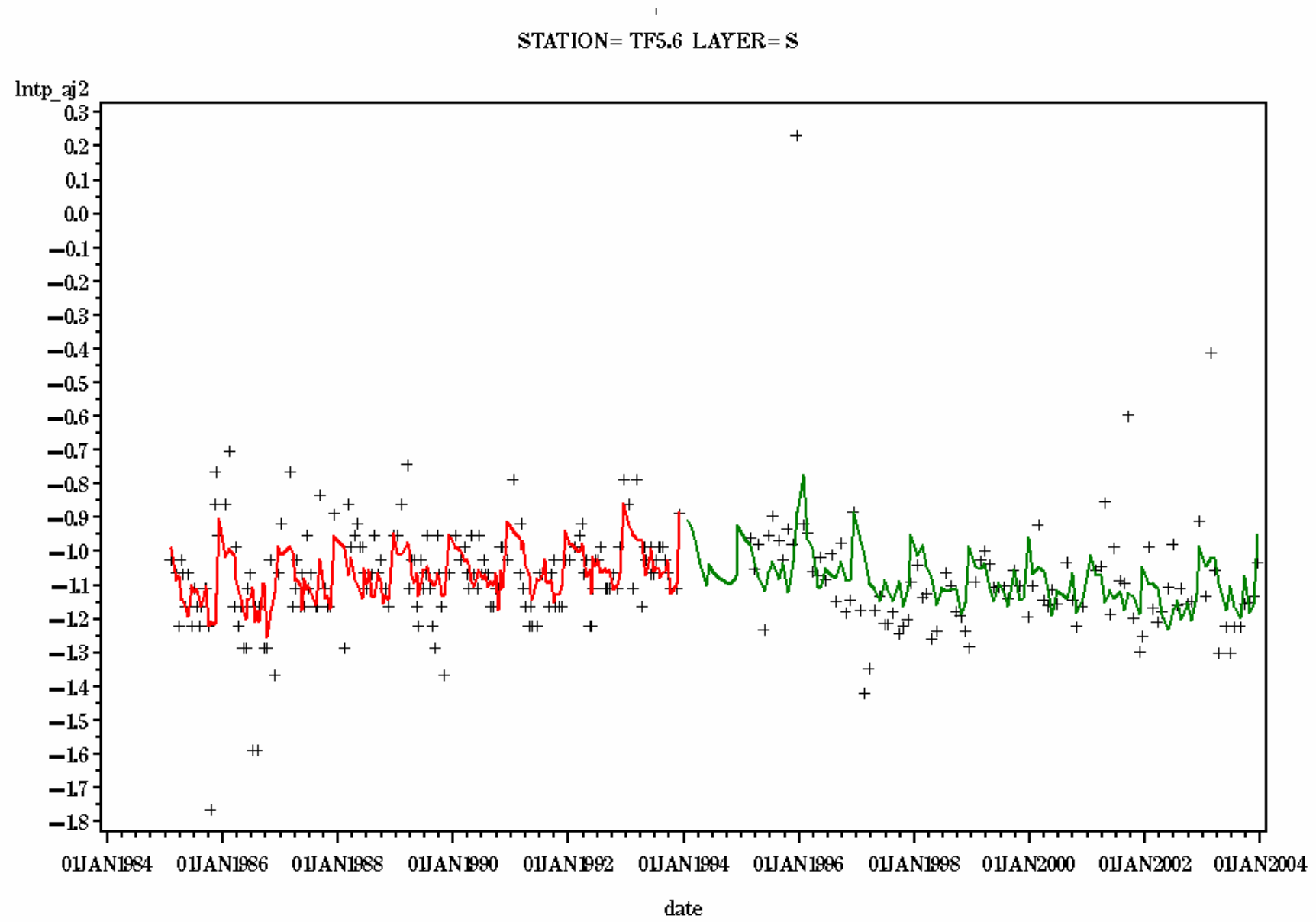
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CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 043

CATEGORY CODE: Analytical Methods (AM)

ISSUE TITLE: Comparability of parameter estimates from whole water and filtered samples for MD Department of Health and Mental Hygiene data

DATE OF INTRODUCTION OF THIS TO THE SYSTEM: June 2006, revised April 2009

STATEMENT OF ISSUE:
The Maryland Department of Health and Mental Hygiene (DHMH) has analyzed water quality samples collected at 54 non-tidal fresh water stations under the CORE/Trend monitoring program from the program's inception in 1974 to the present time. From 1974 through June 2005, DHMH performed whole water analyses (i.e., samples collected by the monitoring staff were not filtered in the field prior to processing at the DHMH lab). In June 2005, DHMH upgraded their old laboratory equipment, thus enabling them to process field-filtered samples. Although this change resulted in DHMH achieving analytical consistency with other labs processing samples in the Chesapeake Bay Program and obtaining more accurate results, the procedural change may result in step trends in the data, which may be due solely to the methods change.

PROPOSED SOLUTION:
Compare split samples from DHMH that were collected from the 54 non-tidal stations and determine which variables, if any, might be affected by the methods change. In the Maryland data base, whole and filtered parameters are coded as different types using a "type" variable (*variablename*_T) that is associated with each parameter (e.g., NH4_T = W for whole NH4 and NH4_T = F for filtered NH4). In the CIMS data base, filtered versus whole water samples are implied in the variable name (e.g., NH4f versus NH4w) or are identified as such in the analytical method code description. As a result, there is no need to post-process data if a methods effect is detected. Any potential adjustment to the data would only be needed for the purpose of conducting analyses that span the entire data record, where the different variables and/or different method codes would be mixed.

DISCUSSION:
Introduction
Water quality samples were collected as part of a special study at 54 non-tidal fresh water stations in October and November 2004 and July 2005 and analyzed at the State of Maryland's DHMH lab. The list of stations is provided in Appendix A of this report.

Whole water parameters analyzed by DHMH included orthophosphate (PO4w), ammonium (NH4w), nitrite (NO2w), nitrite plus nitrate (NO23w), total organic carbon (TOC), total Kjeldahl nitrogen (TKNw), and total phosphorus (TP). Filtered water parameters analyzed by DHMH included orthophosphate (PO4f), ammonium (NH4f), nitrite (NO2f), nitrite plus nitrate (NO23f), particulate carbon (PC), dissolved organic carbon

(DOC), particulate nitrogen (PN), total dissolved nitrogen (TDN), particulate phosphorus (PP), and total dissolved phosphorus (TDP).

Comparisons were made between PO4w and PO4f, NH4w and NH4f, NO2w and NO2f, TOC measured directly and calculated from PC plus DOC, total nitrogen (TN) calculated from TKNw plus NO23 and calculated from PN plus TDN, total phosphorus (TP) measured directly and calculated from PP plus TDP, and dissolved inorganic nitrogen (DIN) calculated as NO23w plus NH4w and calculated as NO23f plus NH4f.

Before any parameters were calculated or comparisons made, the data set was screened for values that were reported at concentrations below the reliable method detection limit. These concentrations were then set to the method detection limit and divided in half. Concentrations were divided in half because the "true" concentration is unknown, and it seems reasonable to assume that the "true" concentration is halfway between zero and the detection limit. Setting data to half of the detection limit is also unbiased for the mean, if the analytical method cannot result in negative measurements and the distribution of all measurements between zero and the detection limit is uniform. A list of parameters that needed to be censored and the detection limits is presented in Appendix B. Finally, in those cases where duplicate records were present, the mean of duplicates was calculated and used in these analyses.

Graphical analysis

Whole and filtered data were first compared graphically by plotting the difference (whole minus filtered) against station using a zero reference line for all three months of data. Symbols falling above the line indicate that whole water concentrations exceed filtered. Conversely, symbols falling below the line indicate that filtered exceeds whole. Symbols falling on the line indicate no difference between whole and filtered. All figures follow at the end of this report.

Statistical analysis

Whole and filtered data were also compared statistically using the Wilcoxon Signed Rank test on the log ratio of whole to filtered concentrations. Taking the logarithm of each parameter and then subtracting the filtered parameter from its corresponding whole water parameter calculates this ratio. The log ratio is based on the principle of logarithms that states: $\log_b x - \log_b y = \log_b(x/y)$. Working with log-transformed data (base 10 was used in these analyses) also helps meet the distributional assumptions of the Wilcoxon Signed Rank test. Probability values (p-values) for the Wilcoxon Signed Rank test of ≤ 0.05 are assumed to indicate a statistically significant difference between whole and filtered concentrations.

The log ratios can also be used to adjust the data for the change in laboratory methods. In this case, it would be logical to adjust the whole water samples to filtered concentrations because: 1) whole water samples are no longer being collected, so the adjustment would only have to be done once; and 2) the new filtered laboratory analysis methods are more reliable than the old methods, so there would be little sense in adjusting the better data.

Mean log ratios were calculated for each parameter in need of adjustment (means were calculated across all stations and months) and are presented in Table 3. The adjustment can be made using the equation presented below.

ADJUSTED(WHOLE) = WHOLE * ANTILOG(-MEAN(LOGDIFF))

Where:

LOGDIFF = $\log_{10}$(WHOLE) – $\log_{10}$(FILTERED)
ADJUSTED(WHOLE) = The whole water sample adjusted to match the filtered water sample.

Note that adjustment factors calculated from the mean log ratios are provided in column four of Table 3. These adjustment factors can be directly multiplied by the respective whole water parameter to calculate the adjusted whole water parameter. The mean log ratios were calculated after first censoring the data to the detection limit in place when the sample was analyzed. Censored data were then divided in half as described in the introduction. This procedure should be followed by anyone wishing to adjust the whole water samples.

Orthophosphate

The orthophosphate plot (Figure 1) shows a consistent positive bias where PO4w exceeds PO4f (positive differences). Only two data points are below the zero reference line for all stations and all three months. The remaining data are either on the line (no difference between whole and filtered) or above the line. The results of quantitative measures of the differences are shown in Tables 1 and 2, which follow at the end of this report. The mean difference (whole minus filtered) is 0.017 mg/L. Although the difference in mean concentrations is not large, it is four times larger than the detection limit of 0.004 mg/L. In addition, the result of the Wilcoxon Signed Rank test indicates the difference is statistically significant ($p<0.0001$) and the mean difference, calculated as a percent of filtered concentration, is 73%. **Based on these results, it is recommended that an adjustment factor be applied to the whole water PO4w concentrations before any analyses are conducted on the entire data record.**

Ammonium

The comparison of NH4w to NH4f shown in Figure 2 also indicates that generally whole water concentrations exceed filtered. This is particularly true of the samples collected in July 2005, where 43 out of 52 differences are positive, indicating a possible seasonal effect. Differences calculated using the October and November 2004 data tend to be more random above and below the zero reference line. Note that a pair of observations collected at station NBP0689 in October 2004 were deleted from this analysis because of a two order of magnitude difference between the whole (0.004 mg/L) and filtered (0.42 mg/L) concentrations. The observations were deleted at the discretion of the data analyst. A later check on the results by the lab did not find any mistakes in the analysis of the samples (Asoka Katamulua, personal communication). The mean difference between whole and filtered NH4 is 0.003 mg/L, which is less than the detection limit of 0.008 mg/L (Table 1). The mean difference as a percent of the mean filtered concentration of 6% is not statistically significant ($p=0.06$) (Table

2). **Based on these results, an adjustment factor for NH4w does not appear warranted.**

Nitrite

As shown in Figure 3, nitrite data also have a consistent positive bias, where whole water concentrations exceed filtered. The figure indicates that only three differences are negative (filtered exceeds whole) for all three months of data. The mean difference of 0.003 mg/L only slightly exceeds the detection limit of 0.002 mg/L; however, the mean difference as a percent of the mean filtered concentration is 29%. Also, the difference between the two methods is statistically significant ($p<0.0001$). As a result, **it would be advisable to adjust the NO2w data before any analyses are performed that span the entire data record.**

Nitrite plus nitrate

The results for NO23 are presented in Figure 4. Many of the differences are on or close to the zero reference line; however, that may be due to how the plot was scaled to accommodate larger differences. Most of the differences not on the reference line are positive, indicating that whole water results exceed filtered. Although the mean difference as a percent of the filtered concentration is only 4%, the absolute difference of 0.056 mg/L greatly exceeds the detection limit of 0.002 mg/L. The difference between whole and filtered is statistically significant ($p<0.0001$), so **an adjustment to NO23w should be made before the entire data record is used.**

Total organic carbon

The difference plot of TOC measured directly compared to TOC calculated from filtered parameters (PC plus DOC) has a much different pattern than the other data (Figure 5). For TOC, the majority of differences are negative, indicating that whole water sample results are less than filtered. One explanation for having higher filtered concentrations compared to whole water is that the laboratory analysis method for filtered samples breaks down more carbon in the sample. The mean difference between whole and filtered TOC is –0.809 mg/L, which exceeds the detection limit of 0.5 mg/L. The mean difference as a percent of the filtered concentration is –21%. The difference between whole and filtered concentrations is statistically significant ($p<0.0001$, so **an adjustment to TOC measured directly should be made before the entire data record is used.**

Total nitrogen

Total nitrogen calculated from whole parameters (TKNw plus NO23w) and filtered parameters (PN plus TDN) appears to be fairly evenly distributed above and below the zero reference line (Figure 6). There does appear to be a seasonal pattern to the data, where 40 differences are positive for July and six are negative. Differences for October and November are more evenly distributed about the reference line. TN is not measured directly, so there is no detection limit. The mean difference between concentrations measured by both methods is –0.006 mg/L, and the mean difference a percent of the filtered concentration is only –0.3%. The Wilcoxon Signed Rank test failed to detect a statistically significant difference between the two methods ($p=0.6$). Based on these results, it appears that **no adjustment is needed for TN** analyses that span the entire data record.

Total phosphorus

There appears to be little difference between TP measured directly and TP calculated from PP plus TDP (Figure 7), although two of the larger differences may be compressing the smaller differences about the zero reference line. Unlike some of the other data, there does not appear to be a seasonal effect. The mean difference between whole and filtered TP is 0.001 mg/L, which is an order of magnitude less than the detection limit of 0.01 mg/L for TP measured directly. The mean difference as a percent of the mean filtered concentration is –2%, which is not statistically significant (p=0.7). It **does not appear necessary to adjust whole water TP concentrations for analyses that span the entire data record.**

Dissolved inorganic nitrogen

The plot of DIN calculated from whole (NO23w plus NH_4w) and filtered parameters (NO23f plus NH_4f) (Figure 8) has almost exclusively positive differences, indicating a strong bias that whole exceeds filtered concentrations. The mean difference between whole and filtered DIN is 0.059 mg/L; however, DIN is calculated, so there is no detection limit to which it can be compared. The mean difference as a percent of the mean filtered concentration is only 4%; however due to the strong bias the difference is statistically significant ($p<0.0001$). Given these results, it is **recommended that NO23w be adjusted before the data are combined with filtered data to calculate DIN.**

SENSE OF THE RESOURCES NEEDED TO RESPOND:
Members of the Analytical Methods and Quality Assurance Workgroup (AMQWA) and data analysts are requested to review this document and provide comments by 30 December 2005.

PRIORITY RANKING:
Four (high). A decision regarding the need to adjust the historic (whole water) samples is needed so that procedures can be developed in time to conduct trend analyses in the spring of 2006.

SUBMITTER/RESPONSIBLE PARTY:
Name: William D. Romano
Natural Resources Biologist

Organization: Maryland Department of Natural Resources
580 Taylor Avenue, D-2
Annapolis, MD 21401
(410) 260-8655

ACTIONS TO DATE:
Informed AMQWA of potential problems in a PowerPoint presentation that was made at their meeting at the Chesapeake Biological Laboratory in Solomons, MD on 21 July 2005. Prepared a draft report on 6 October 2005. Analyses performed in WholevsFiltered.SAS program.

OVERALL RESOLUTIONS SUMMARY OF ACTIONS:

RECOMMENDED ACTIONS:
As stated above, the data analysis issue described in this report resulted from a change in methods from whole water analyses to filtered water analyses, not from a flaw in the older data or in the laboratory analyses of data collected prior to the methods change in July 2005. Data collected prior to the methods change are just as valid as the data collected after the methods change, but the data should not be combined over the entire period of record without performing the adjustments described under the statistical analysis section. Failure to adjust the older data could result in a step trend in time series analyses that is due to a change in laboratory analysis methods as opposed to the implementation of best management practices.

ACTIONS NUMBER:
1. Designated Respondent:
2. Action:
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary:

Table 1. Mean difference, standard deviation, range of differences (whole minus filtered), and detection limit.

Parameter	Mean difference (mg/L)	Standard deviation	Range	Detection limit (mg/L)
PO4	0.017	0.037	0.378	0.004
NH4	0.003	0.018	0.217	0.008
NO2	0.003	0.006	0.045	0.002
NO23	0.056	0.122	0.982	0.002
TOC	-0.809	1.078	7.229	0.5
TN	-0.006	0.272	2.705	NA
TP	-0.001	0.030	0.297	0.01
DIN	0.059	0.124	0.992	NA

NA – Calculated, not measured directly.

Table 2. Mean difference, mean concentration (filtered), percent difference, and significance value.

Parameter	Mean difference (mg/L)	Mean filtered concentration (mg/L)	Percent difference	Wilcoxon signed rank test p-value
PO4	0.017	0.024	73	<0.0001
NH4	0.003	0.050	6	0.06
NO2	0.003	0.011	29	<0.0001
NO23	0.056	1.529	4	<0.0001
TOC	-0.809	3.890	-21	<0.0001
TN	-0.006	2.025	-0.3	0.6
TP	-0.001	0.058	-2	0.7
DIN	0.059	1.582	4	<0.0001

Table 3. Mean log difference (calculated as whole minus filtered), sample size, and whole to filtered adjustment factor.

Parameter	Mean log difference	Sample size	Adjustment factor
PO4	0.2546775	156	0.55632
NH4	-0.0259742	155	1.06163
NO2	0.1043403	156	0.78643
NO23	0.0151074	156	0.96581
TOC	-0.0925479	156	1.23751
TN	0.0022400	156	0.99486
TP	-0.0316263	156	1.07554
DIN	0.0134365	155	0.96954

Figure 1. Paired DHMH whole vs. filtered samples for PO4

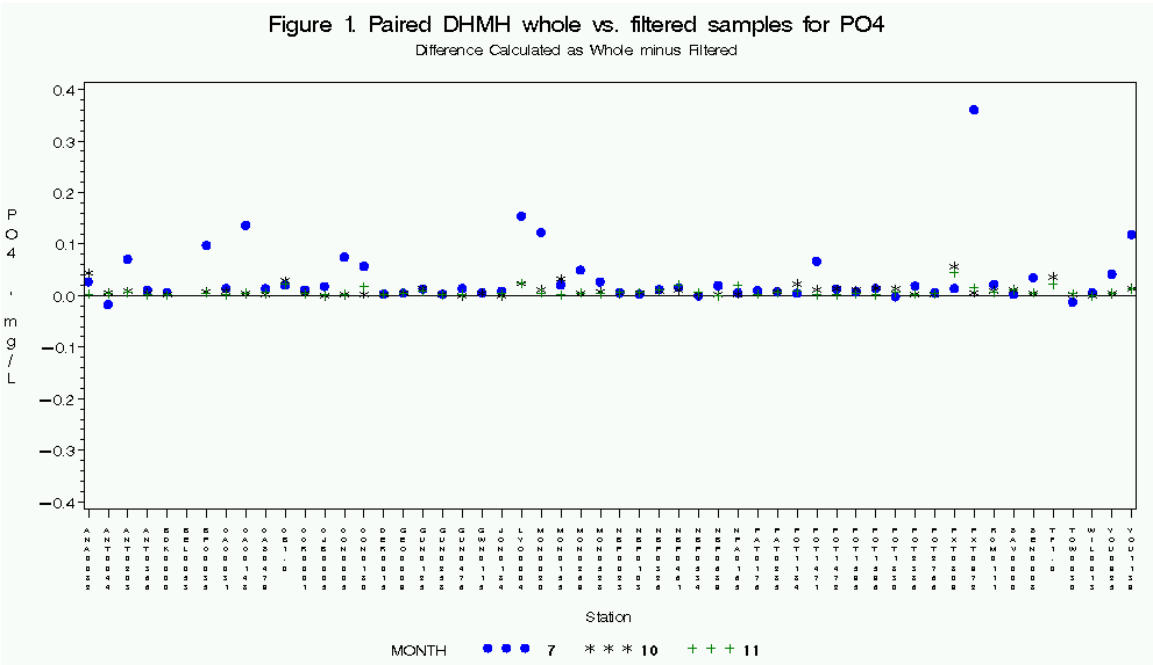


Figure 2. Paired DHMH whole vs. filtered samples for NH4

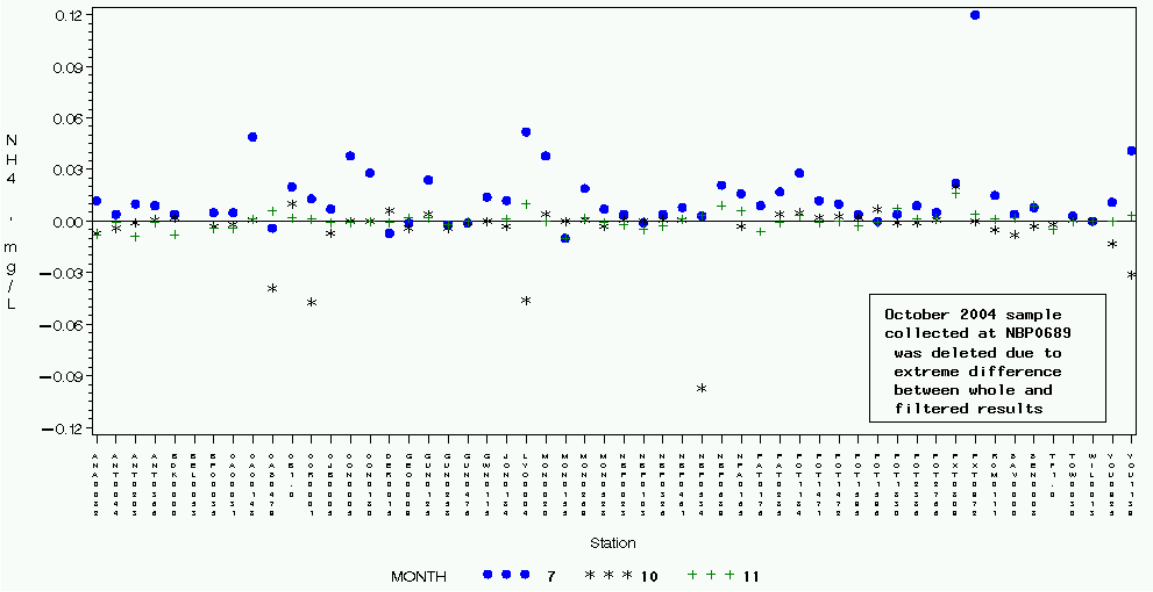


Figure 3. Paired DHMH whole vs. filtered samples for NO2

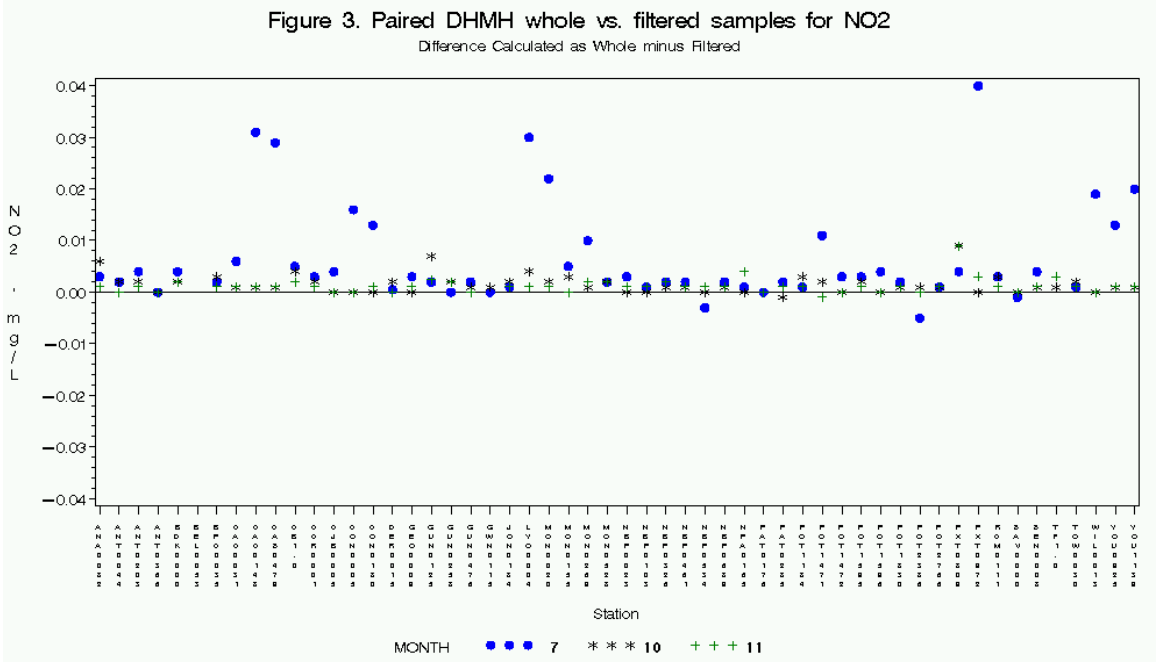


Figure 4. Paired DHMH whole vs. filtered samples for NO23

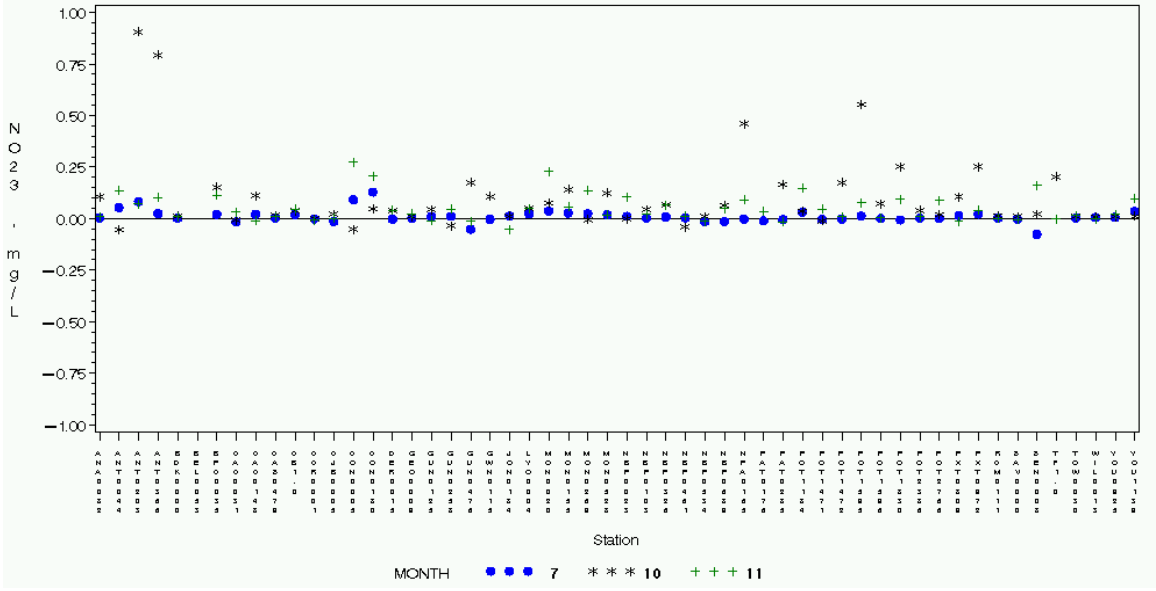


Figure 5. Paired DHMH whole vs. filtered samples for TOC

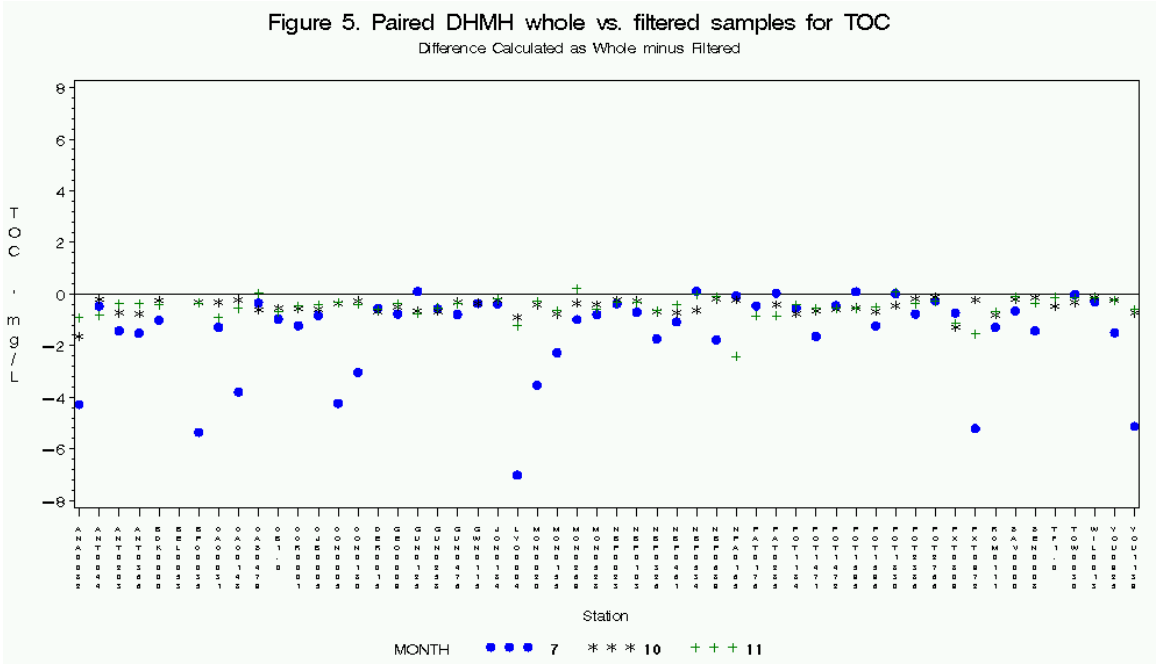


Figure 6. Paired DHMH whole vs. filtered samples for TN

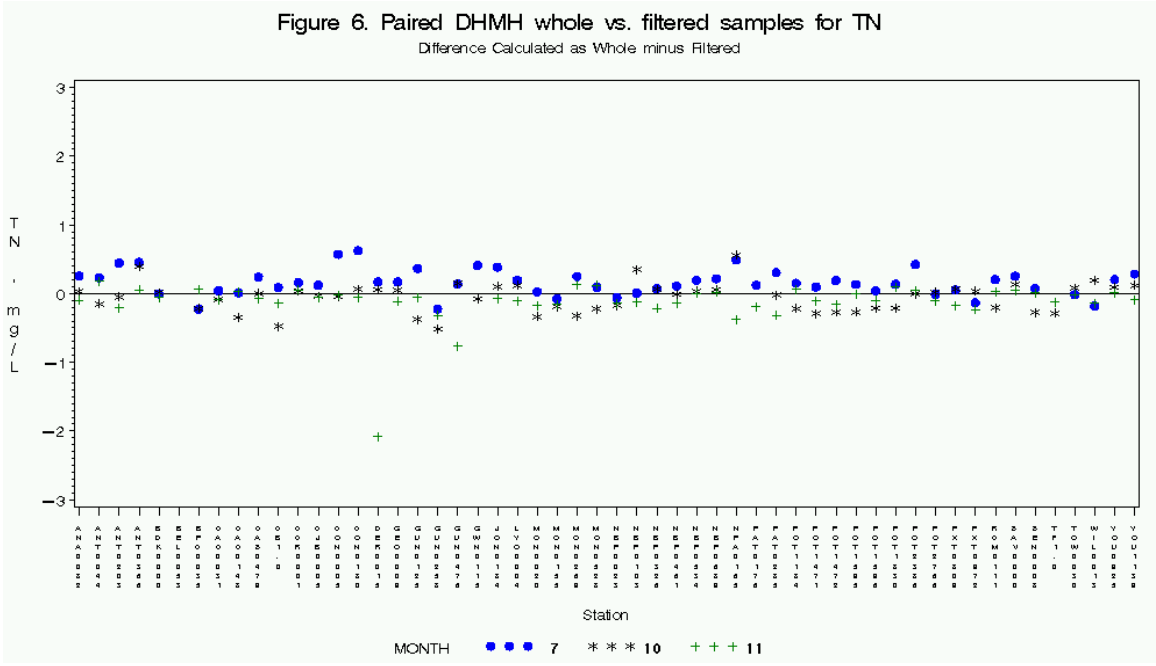


Figure 7. Paired DHMH whole vs. filtered samples for TP

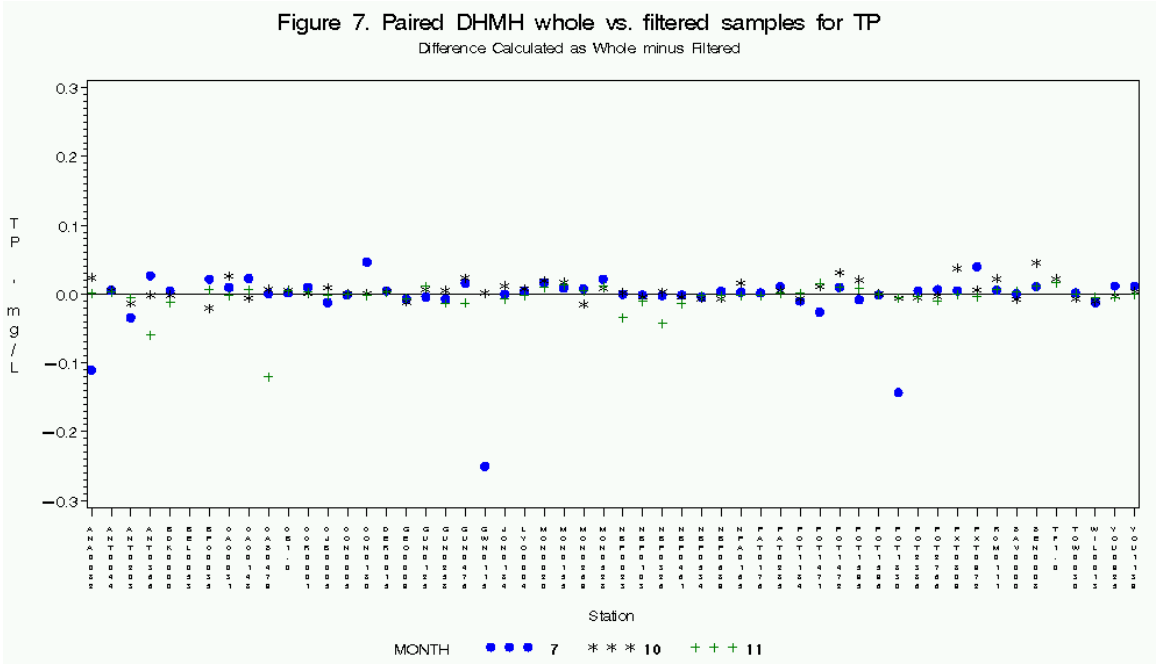
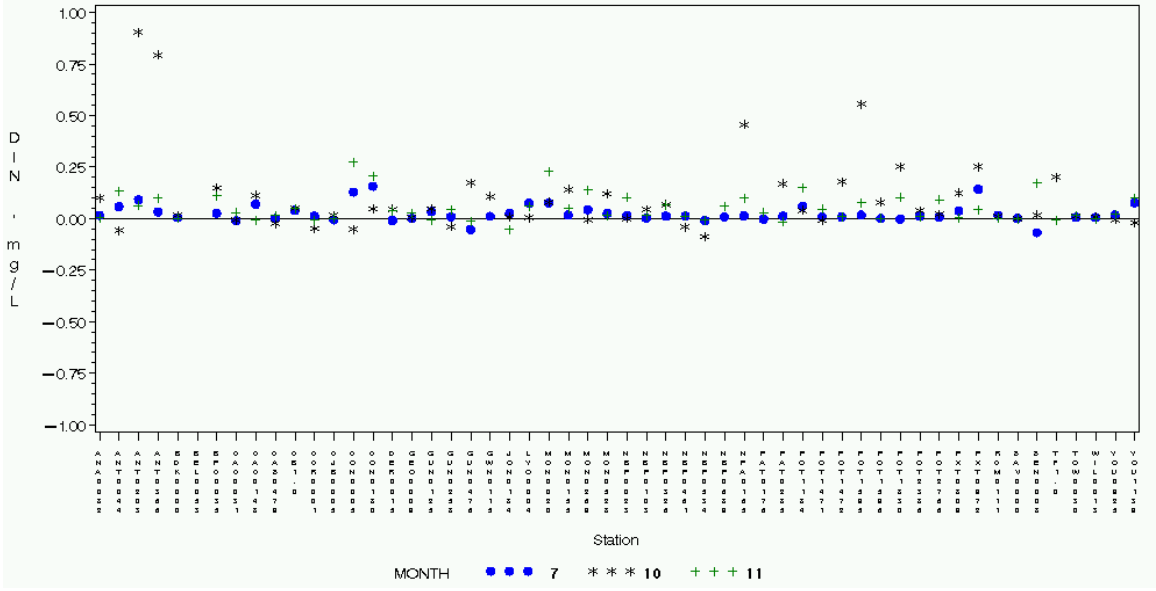


Figure 8. Paired DHMH whole vs. filtered samples for DIN



Appendix A

1) ANA0082
2) ANT0044
3) ANT0203
4) ANT0366
5) BDK0000
6) BEL0053
7) BPC0035
8) CAC0031
9) CAC0148
10) CAS0479
11) CB1.0
12) CCR0001
13) CJB0005
14) CON0005
15) CON0180
16) DER0015
17) GEO0009
18) GUN0125
19) GUN0258
20) GUN0478
21) GWN0115
22) JON0184
23) LYO0004
24) MON0020
25) MON0155
26) MON0269
27) MON0528
28) NBP0023
29) NBP0103
30) NBP0326
31) NBP0461
32) NBP0534
33) NBP0689
34) NPA0165
35) PAT0176
36) PAT0285
37) POT1184
38) POT1471
39) POT1472
40) POT1595
41) POT1596
42) POT11830
43) POT2386
44) POT2766
45) PXT0809
46) PXT0972
47) RCM0111
48) SAV0000
49) SEN0008
50) TF1.0 (sampling discontinued in the CORE/Trend program)
51) TOW0030
52) WIL0013
53) YOU0925
54) YOU1139

Appendix B

Table B-1. List of censored parameters and detection limits.

Parameter	Detection limit (mg/L)
PO4f	0.004
TDP	0.006
PP	0.003
TKNw	0.1
NO2f	0.002
NH4f	0.008
TP	0.01

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 044

CATEGORY CODE: DM, FM

ISSUE TITLE: Secchi Hits Bottom and still visible

DATE OF INTRODUCTION OF THIS ISSUE TO THE SYSTEM: 16-Apr-08

STATEMENT OF ISSUE: What do we do with field readings for secchi when the secchi does not dissapear (still clear to bottom)?

PROPOSED SOLUTION: Presenting to TMAW to determine best solution. See discussion for suggested options.

DISCUSSION:
Right now there are a few options. The first is what is suggested in the CBP User's Guide:

1. **Put the depth (bottom) in the reported_value field, add the ">" in the Qualifier field, adding also a problem code to signify "Secchi reading was not available, water was clear to bottom".**

    i. **PROS: There would be an actual value (instead of a null) in the record. There would be clear-cut flags showing something is different about the record. The value should reflect the total depth at the site, and therefore would not require anyone to go to another field (total depth) to hunt down that data, if so desired in the data analysis.**
    Comments from Peter Bergstrom as well:
    - **a.** If the Secchi disk is visible on bottom, this will not affect the median if that is calculated, as long as less than half of the values used for the median are affected.
    - **b.** If, instead of the median, the user calculates the percentage of Secchi values above a target, as is done for some "report cards," having the Secchi disk visible on bottom will not affect this percentage as long as the bottom depth is greater than the target. The targets

used vary by salinity regime and between report cards; for example, in mesohaline segments, some report cards use 0.97 m, while others use 1.63 m as the target.

ii. **CONS: There would be a number value which some users might assume is the actual secchi depth (without attention paid to the qualifier or problem fields).**

2. **Use a false, impossible value (for instance, -99) for the reported value, but then also add a ">" in the qualifier column and a problem code to signify water was clear to bottom.**
   i. **PROS: The negative secchi value will be an automatic flag for a user.**
   ii. **CONS: The user, if they wanted to use the bottom value as the secchi depth, would need to then transplant the total depth value to the secchi value field in their analysis, which could add an element of human error. For programs that search for a certain range of readings (always more than zero for secchi), these values (-99) would be skipped over, regardless of whether their total depth reading was within the targeted range.**

3. **Enter a null value for the secchi, and have a problem code associated signifying the secchi went to the bottom.**
   i. **PROS: Analysts would not use any problematic secchi values. Technically, this correctly reflects the definition of secchi readings.**
   ii. **CONS: Data that are null could be deleted or excluded from analyses where they may be relevant. If nulls are kept, the user could want to transplant the total depth value to the secchi value field in their analysis, which could add an element of human error. For programs that search for a certain range of readings, these values (null) would be skipped over, regardless of whether the total depth reading was within the targeted range.**

SENSE OF THE RESOURCES REQUIRED TO RESPOND:

PRIORITY RANKING:

SUBMITTER/RESPONSIBLE PARTY:

Name: Tami Huber or Mary Ellen Ley

Organization:CBPO

ACTIONS TO DATE: submitted to CBPO monitoring staff and Marcia Olson

OVERALL RESOLUTION SUMMARY OF ALL ACTIONS AND DATE COMPLETED:
Marcia suggested it is best to keep the old method (#1 above), and let some analyst groups (TMAW, especially) know of the need to always look at all fields associated with data records (problem code, comments,etc). – April 18, 2008
RECOMMENDED ACTIONS: (Copy next section for as many actions as needed)
Add problem code for Secchi –**"Secchi reading was not available, water was clear to bottom"**

ACTION NUMBER:

1. Designated Respondent:
   (Name/Organization and/or specific Workgroup)

2. Action:

3. Resources Needed:

4. Due Date:

5. Action Item Resolution Summary:

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 045

CATEGORY CODE: HI

ISSUE TITLE: Investigation of TSS Step Trend at Virginia mainstem stations

DATE OF INTRODUCTION OF THIS TO THE SYSTEM: June 2008

STATEMENT OF ISSUE:

The Virginia Department of Environmental Quality (VA DEQ) has long-term water quality data at 27 monitoring stations in the Chesapeake mainstem. From 1985 to 1995, VA DEQ contracted with the Virginia Institute of Marine Sciences (VIMS) to collect and analyze samples at 19 of these stations, while Old Dominion University (ODU) was responsible for monitoring the remaining stations. Starting in 1996, the VA Mainstem Bay monitoring program was consolidated at one organization and ODU took over all mainstem stations. An examination of the total suspended sediment (TSS) time-series indicates the presence of a negative step trend that is only apparent at stations initially sampled by VIMS. At these stations, the overall magnitude of TSS appears to abruptly drop starting in early 1999. Additional, the time-series after 1998 appears to have less temporal variation than previous to 1998. Although the downward step did not begin until three years after the lab change, the fact that the pattern seems to only be found at stations sampled by the two data sources suggests the existence of methodological confounding.

PROPOSED SOLUTION:

On May 1, 2008, the Tidal Monitoring and Assessment Workgroup (TMAW) recommended flagging all TSS data collected at stations monitored by both VIMS and ODU (hereafter referred to as "switchover" stations) to alert users to the TSS step trend, even though cause was not determined. A "flag" would consist of a statement inserted into the TSS metadata that summarizes the step trend and references this document.

DISCUSSION:

TSS time-series were analyzed for all Bay mainstem stations, including those in Maryland waters. A Wilcoxon rank-sum test was used to determine if the median TSS was significantly higher for the interval 1985-1995 (1995 being the last year VIMS sampled in the mainstem) relative to the interval 1/1/1996-12/31/2007. The year 1996 was chosen as a break point rather than 1999 because known method changes can be traced only to 1996. Dates were randomly excluded so as to standardize sampling frequency between the two time-frames.

The time-series at all the switchover stations exhibit a significant negative step trend (Figure 1). Four stations in the MD mainstem show a significant step trend, but the cause of this pattern (inadequate rinsing of filters) has been determined. A significant step trend was

not detected at any mainstem station sampled exclusively by ODU. At stations where step trends were found in the surface layer, a similar pattern is found in the other layers, though not significantly in the below pycnocline layer.

A number of steps were taken to determine if there are any methodological or sampling factors that can be tied to the TSS step trend.

Comparison of Standard Operating Procedures

A methods matrix was compiled by Cindy Johnson to rule out differences in VIMS and ODU standard operating procedures (SOPs). Although minor discrepancies were found (for instance, VIMS stored filters in a 60°C oven, while ODU stored them in a dissector), none of the methodological differences could be related to the step trend.

Field audit notes were also examined to determine if auditors observed deviations from SOPs during sampling. In the 1990 Laboratory and Field Evaluation Report, the auditor for VIMS noted that there "appeared to be insufficient shaking of sample once captured from hose to bottle prior to nutrient filtration". This note refers to "nutrient" filtration, and it is not known if this also affected TSS filtration, if VIMS treated all samples in this way consistently, or whether they later rectified this behavior. **However, TMAW considered this a possible explanation for the high concentration and variability of TSS at switchover stations prior to 1996.**

Analysis of QA/QC Samples

Variability between field duplicates, lab replicates, and split-sample and co-located sample results were also examined. Tami Huber assisted in pulling out field duplicate data collected from 1988 to 1992 for VIMS, ODU, and Chesapeake Bay Laboratories (CBL). The relative percent difference (RPD) between duplicate pairs was compared for all three laboratories (Figure 2). From 1988 to 1990 and 1993 to 1995, the average RPD for VIMS duplicates was not significantly greater than values for either ODU or CBL. But in 1991 and 1992, the RPD for VIMS duplicates was significantly greater. The mean standard deviation for field duplicates mirrors this pattern (Figure 2). Lab replicate data collected through 1986 to 1991 (summarized in ***Guide to Using CBP Water Quality Monitoring Data***, 1991) did not reveal significant differences between laboratories. Split-sample results collected from 1987 to 1993 show individual incidents of VIMS scoring significantly higher TSS values than the other laboratories (particularly in 1991), but it did not do so consistently nor more often than other labs.

From 1985 to 1990, VIMS and MDDNR sampled at CB5.3 (sometimes referred to as the "overlap" station). Over this five year period, VIMS tended to record significantly higher levels of TSS than MDDNR—in some cases almost by a factor of 10 (see Figure 3). Differences in other water quality parameters, such as chlorophyll and total phosphorus, were also observed. Bruce Nielsen attributed the differences to non-random time and within-layer depth differences in sampling, and recommended against using the co-located data as a QA/QC tool (Memorandum "RE:Statement on Colocated Samples", 1990). VIMS discontinued sampling at the overlap station in 1990 due in part to this recommendation.

There does not appear to be systematic bias in QA/QC samples indicating consistent problems with either VIMS or ODU data. Comparison of co-located samples shows a pattern of VIMS data being biased high in comparison to CBL but is inconclusive.

Analysis of Weather Events

Event tables were examined to determine if VIMS sampled under different weather conditions than ODU and MDDNR, possibly owing to differences in boat capability or other factors. If VIMS sampled on rougher water than ODU did at the same stations then one might expect to find increased variability in their samples and possibly higher TSS values. Two-hundred dates (half pre-1996, half post-1996) were randomly selected from the sampling record of each mainstem station and then aggregated by data source. Dates were then classified into low and high wave height and wind speed categories based on what was recorded in event tables. Then the number of dates falling into each category was totaled for each data source, pre-1996 and post-1996. At the switchover stations, VIMS sampled on significantly more days with high wave heights and high wind speeds than ODU did (χ^2=53.1,p<0.0001). However, at the stations only sampled by ODU, more dates with high wave heights were sampled ***after*** 1996 than before 1996 (χ^2=20.0, p<0.0001). Because TSS is not elevated after 1996 at these stations, the case cannot be made that the step trend observed at the switchover stations is related to weather. Moreover, ODU sampled on 90% of the same "rough weather" days sampled by VIMS but did not record unusually high wave heights or wind speeds, suggesting that these parameters are too subjective for accurate comparisons to be made.

Differences in weather during sampled conditions before and after 1996 do not appear to be the cause of the TSS step trend.

Examination of Covariate Time-series

The time-series for covariates (i.e., TP, PP, TN, PN, PC, and secchi depth) of TSS were analyzed at the switchover stations to determine if they contain a post-1996 step trend. Four of the 19 switchover stations exhibited a significant negative step for TP, but no stations exhibited a significant step trend for particulate phosphorus. Negative step trends were detected for all TN time-series but were attributed to trends in TDN rather than PN. Secchi depth at all the switchover stations exhibited a significant downward trend, but this pattern goes counter to what one would expect from the trend in TSS.

Presence of a true environmental TSS step trend is not corroborated by other water quality parameters.

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Graphical analysis

All figures follow at the end of this report.

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SUBMITTER/RESPONSIBLE PARTY:

Name: Tish Robertson
Data Analyst

Organization: VA Department of Environmental Quality
629 East Main St.
Richmond, VA 23219
(804) 698-4309

ACTIONS TO DATE:

Presented the above findings to AMQAW on March 31, 2008 and TMQAW on May 1, 2008.

OVERALL RESOLUTIONS SUMMARY OF ACTIONS:

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Figure 1a. Surface TSS time-series (1985 to 2007) at the switchover stations. Vertical line marks 1/1/1996, when VIMS was replaced by ODU as the data collection organization.

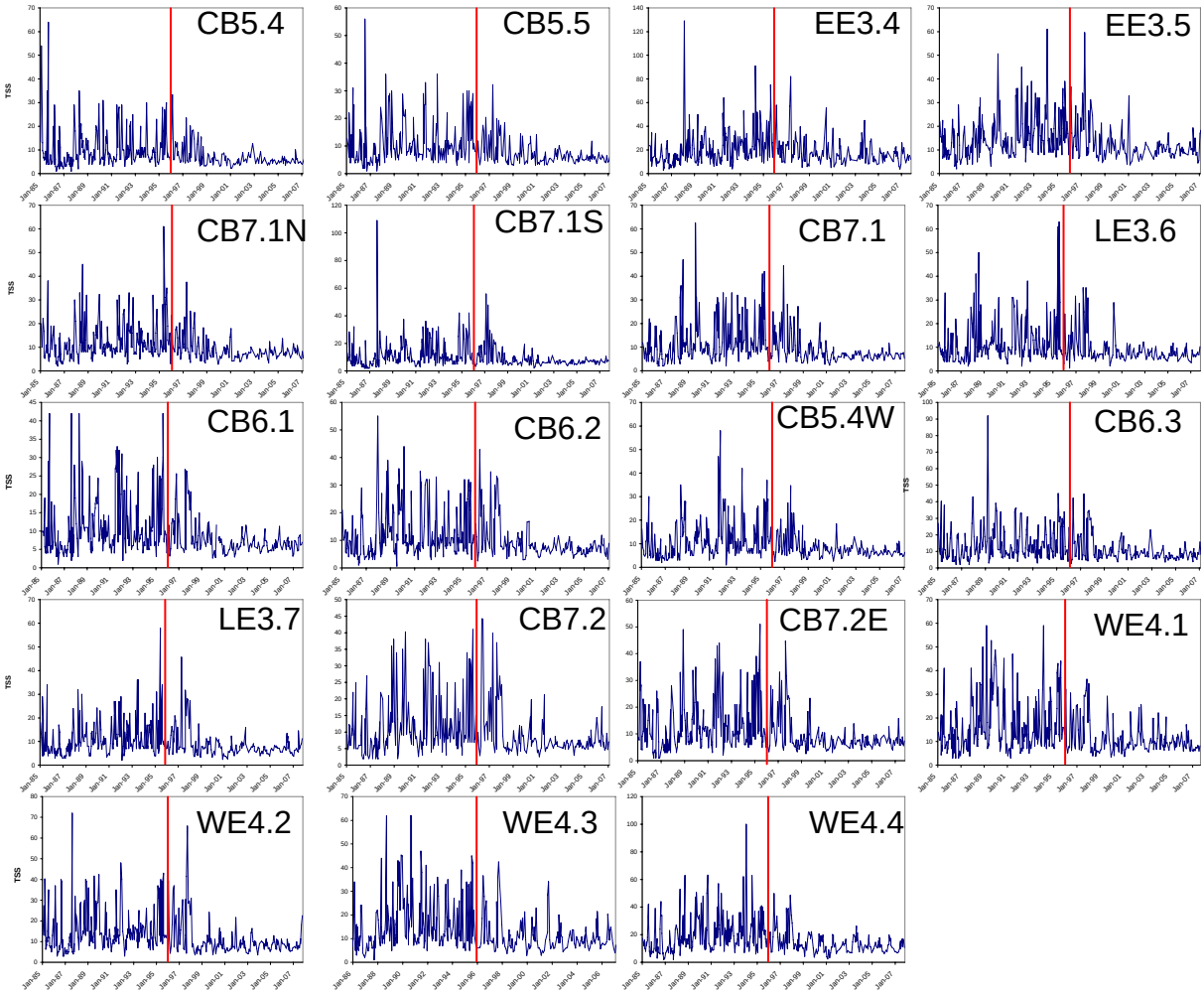


Figure 1b. Surface TSS time-series (1985 to 2007) at MD mainstem stations. Vertical line marks 1/1/1996. Station IDs that are underlined indicate stations with a significant negative step trend post-1996.

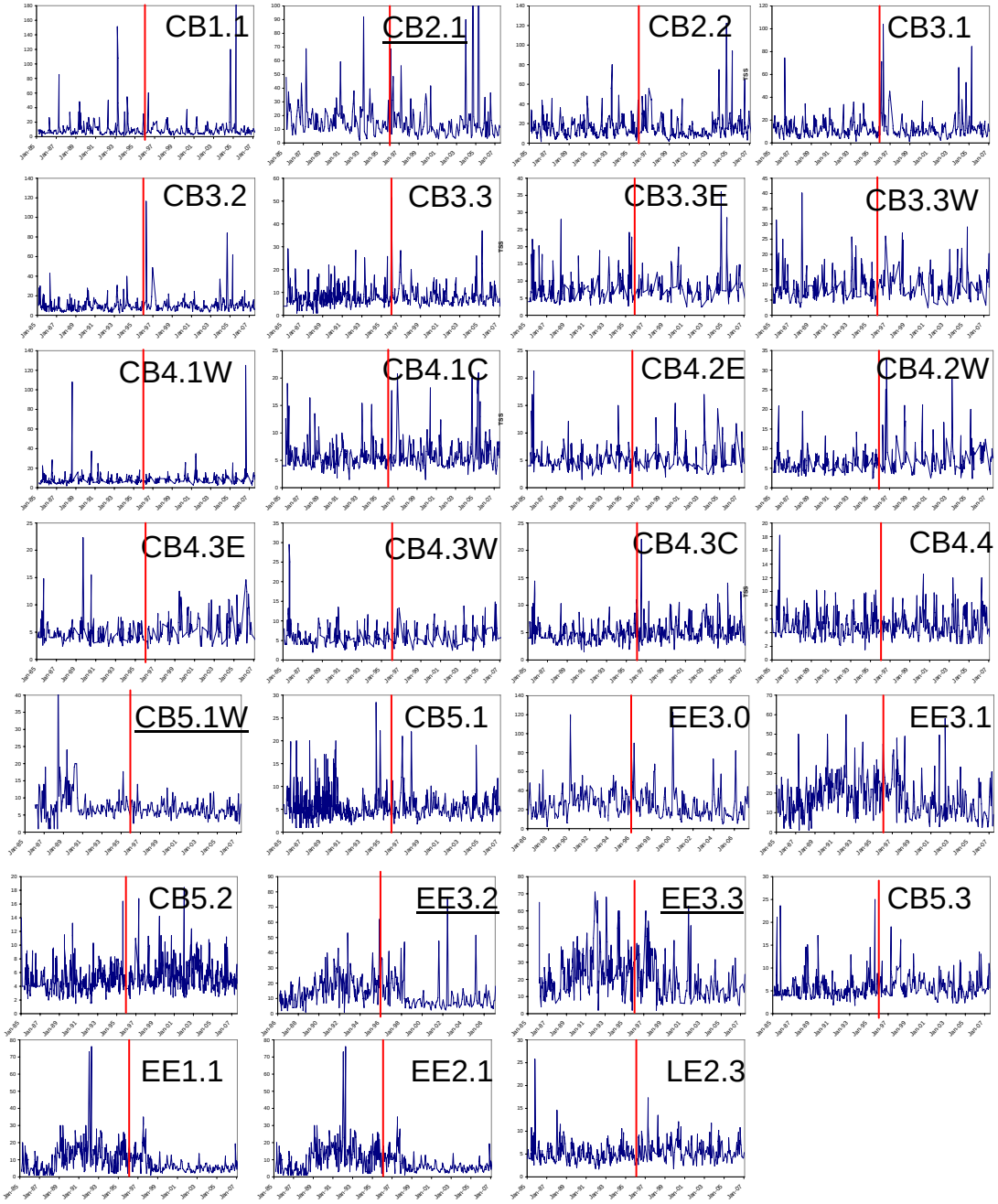


Figure 1c. Surface TSS time-series (1985 to 2007) at ODU-only mainstem stations. Vertical line marks 1/1/1996.

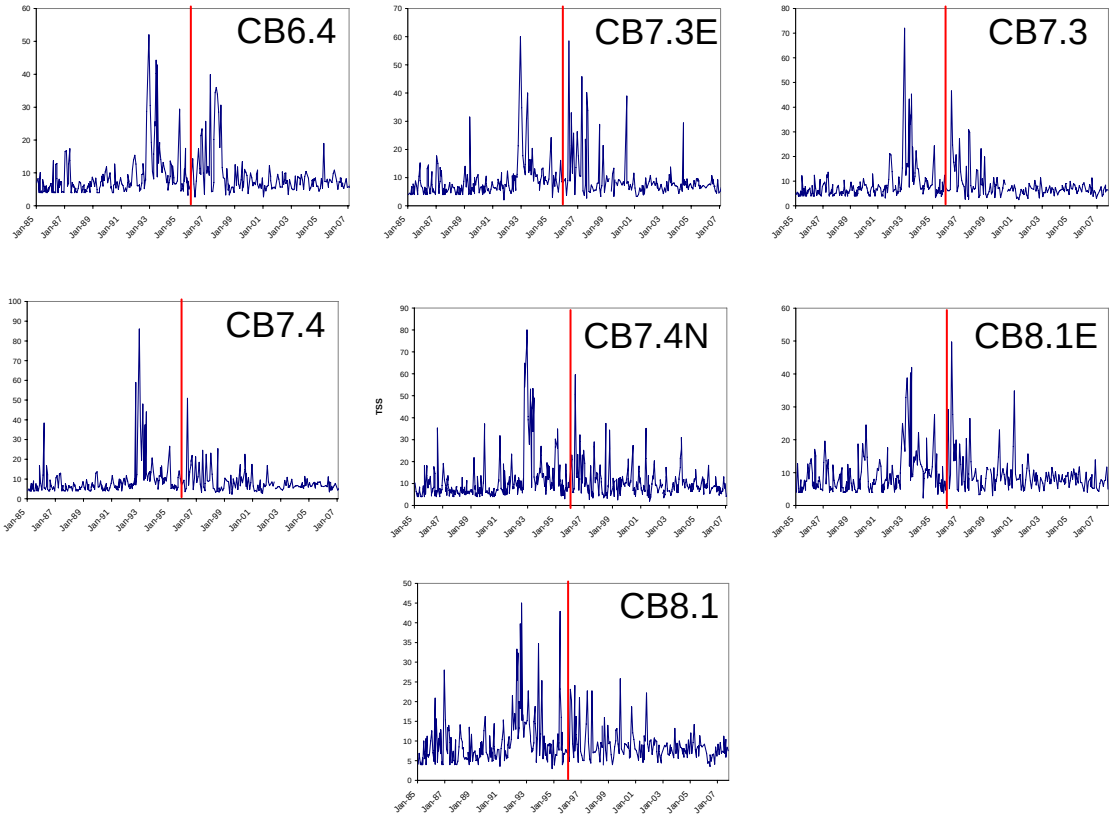


Figure 1d. Map of mainstem stations. Triangles represent MD stations. Squares represent VIMS-ODU stations, and circles represent "ODU-only" stations. Only stations that were continuously sampled from 1985 to 2007 are shown.

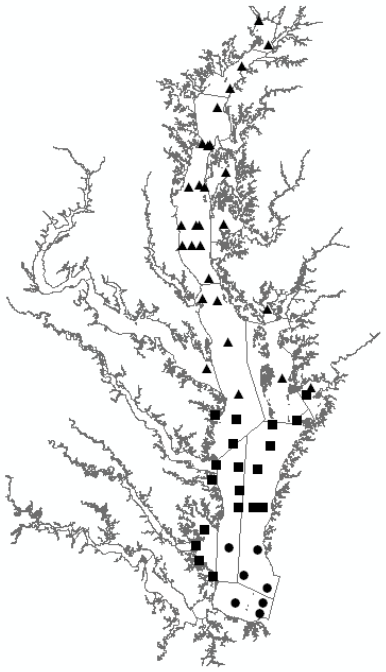


Figure 2. Average relative percent difference and standard deviation for field duplicates. Bars represent standard error of the mean.

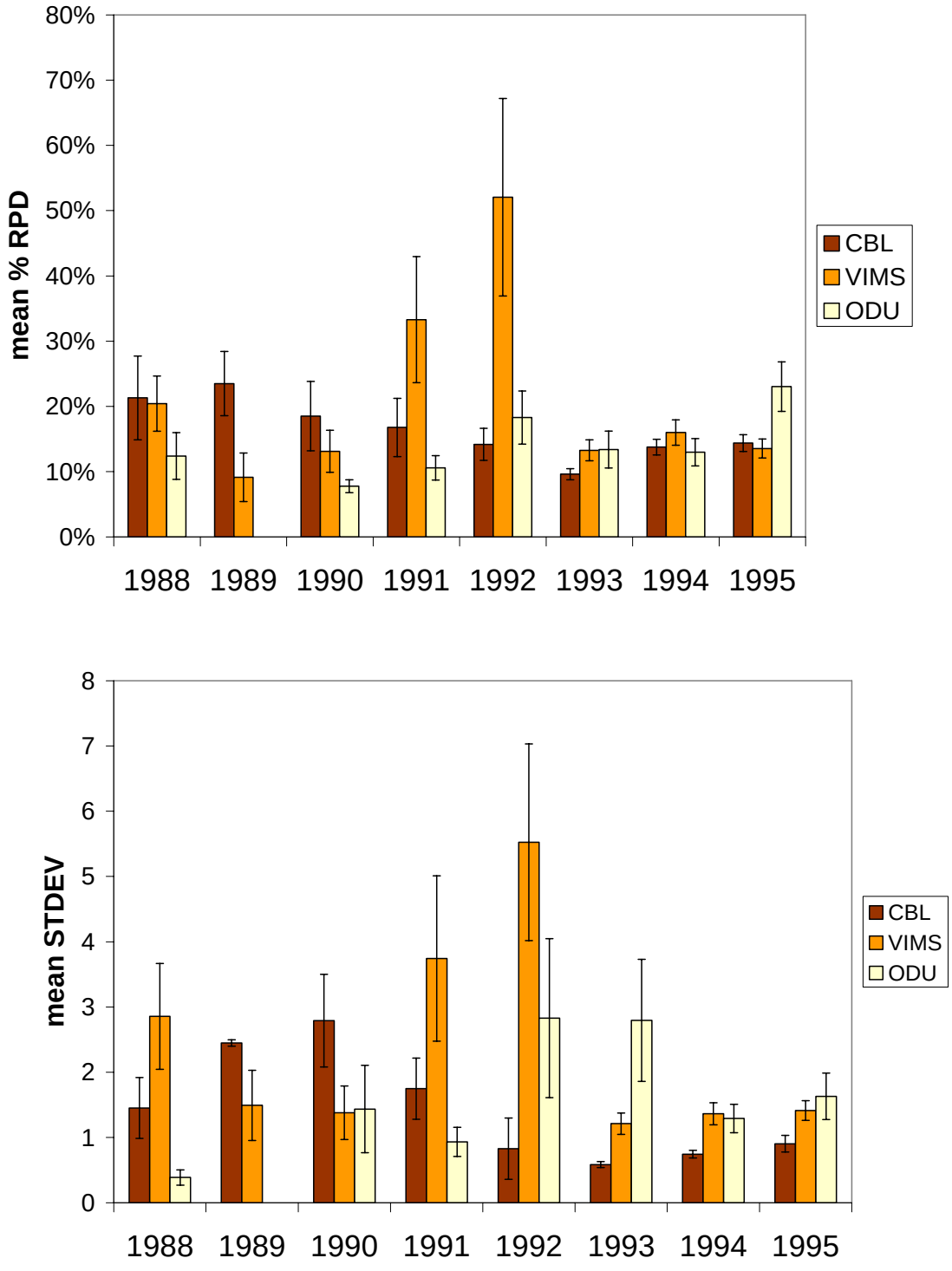


Figure 3. Surface TSS concentrations at CB5.3 (overlap station).
Source: Dave Jasinski

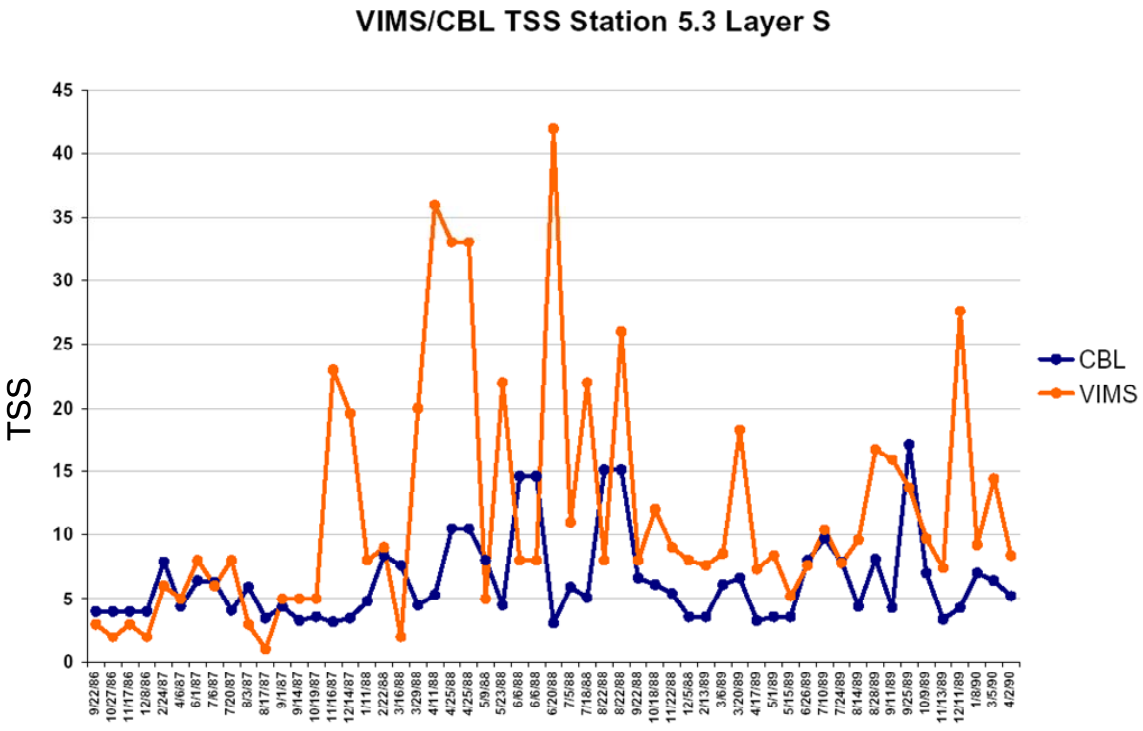


Table 1. Spearman's correlation coefficients for TSS & TP and TSS & secchi depth by station. "Complete" refers to non-averaged time-series; "yearly" refers to year-averaged time-series. Only significant correlations ($p<0.05$) are shown.

station	TSS vs. TP				TSS vs. secchi depth			
	pre-1996		post-1996		pre-1996		post-1996	
	complete	yearly	complete	yearly	complete	yearly	complete	yearly
CB1.1[CBL]	0.67		0.72	0.76	-0.79		-0.84	-0.45
CB2.1[CBL]	0.67		0.74	0.87	-0.77	-0.65	-0.80	-0.65
CB3.1[CBL]	0.43		0.47	0.78	-0.86	-0.88	-0.85	-0.79
CB2.2[CBL]	0.60	0.80	0.62	0.69	-0.82	-0.77	-0.86	-0.75
CB3.2[CBL]	0.47		0.41	0.76	-0.81	-0.85	-0.76	-0.65
CB3.3C[CBL]	0.33		0.55	0.84	-0.53		-0.69	-0.70
CB3.3E[CBL]	0.59		0.44	0.87	-0.67		-0.67	-0.75
CB3.3W[CBL]	0.38		0.53	0.86	-0.66		-0.64	-0.81
CB4.1C[CBL]	0.27		0.40	0.65	-0.47	-0.44	-0.58	
CB4.1E[CBL]		0.69	0.42		-0.44	-0.72	-0.65	
CB4.1W[CBL]	0.47		0.67	0.63	-0.70	-0.75	-0.70	
CB4.2C[CBL]	0.22		0.36		-0.37		-0.54	
CB4.2E[CBL]	0.26		0.40	0.69	-0.55		-0.61	-0.68
CB4.2W[CBL]	0.43		0.63	0.90	-0.64	-0.74	-0.74	
CB4.3C[CBL]			0.20		-0.34		-0.35	
CB4.3E[CBL]	0.21		0.23		-0.43		-0.46	
CB4.3W[CBL]	0.48	0.83	0.56	0.70	-0.57		-0.73	
CB4.4[CBL]	0.32	0.74	0.45		-0.54	-0.62	-0.58	
CB5.1[CBL]	0.23	0.70	0.40		-0.38		-0.62	
CB5.1W[CBL]	0.17		0.20		-0.21		-0.48	
CB5.2[CBL]	0.19		0.26		-0.53		-0.35	
CB5.3[CBL]			0.37		-0.47	-0.73	-0.49	
EE3.0[CBL]	0.25		0.38		-0.68	-0.71	-0.59	
EE3.1[CBL]								
EE3.2[CBL]			0.41	0.63			-0.46	
EE3.3[CBL]	0.26		0.53		-0.44		-0.58	
CB5.4[VIMS/ODU]	0.21		0.52	0.64	-0.35		-0.31	
CB5.4W[VIMS/ODU]	0.43		0.53	0.73	-0.35	-0.41	-0.53	
CB5.5[VIMS/ODU]	0.31	0.71	0.45	0.64	-0.25		-0.42	
CB6.1[VIMS/ODU]	0.35	0.63	0.57	0.67	-0.31		-0.51	
CB6.2[VIMS/ODU]	0.35	0.57	0.63	0.89			-0.55	
CB6.3[VIMS/ODU]	0.41		0.50	0.83	-0.46		-0.45	
CB7.1[VIMS/ODU]	0.25		0.52	0.82			-0.54	
CB7.1N[VIMS/ODU]			0.44	0.78	-0.25		-0.47	
CB7.1S[VIMS/ODU]	0.30	0.62	0.44	0.73	-0.28		-0.39	
CB7.2[VIMS/ODU]	0.34	0.70	0.49	0.53	-0.32		-0.41	
CB7.2E[VIMS/ODU]	0.33		0.44	0.69	-0.34		-0.44	
EE3.4[VIMS/ODU]	0.38	0.61	0.59	0.60	-0.47		-0.57	
EE3.5[VIMS/ODU]	0.30	0.61	0.49		-0.36		-0.57	
LE3.6[VIMS/ODU]	0.35		0.45	0.69	-0.36			
LE3.7[VIMS/ODU]	0.29		0.57	0.76	-0.32		-0.54	
WE4.1[VIMS/ODU]	0.34		0.58	0.74	-0.29		-0.59	
WE4.2[VIMS/ODU]	0.27		0.48	0.63			-0.51	
WE4.3[VIMS/ODU]	0.23		0.67		-0.36		-0.69	
WE4.4[VIMS/ODU]	0.41		0.69	0.83	-0.37	-0.72	-0.65	
CB6.4[ODU]	0.23		0.51		-0.65	-0.62	-0.43	
CB7.3[ODU]			0.38	0.69	-0.63	-0.71	-0.34	
CB 7.3E[ODU]			0.49	0.89	-0.52	-0.79	-0.49	
CB7.4[ODU]			0.32	0.86	-0.51		-0.39	
CB7.4N[ODU]			0.56	0.63	-0.57	-0.72	-0.33	
CB8.1[ODU]			0.38	0.69	-0.65	-0.88	-0.32	
CB8.1E[ODU]			0.37	0.81	-0.71		-0.44	

Figure 4. Box plot of TSS-TP correlation coefficients by data source. Non-significant correlations were excluded from samples. Only one ODU station had a significant correlation pre-1996.

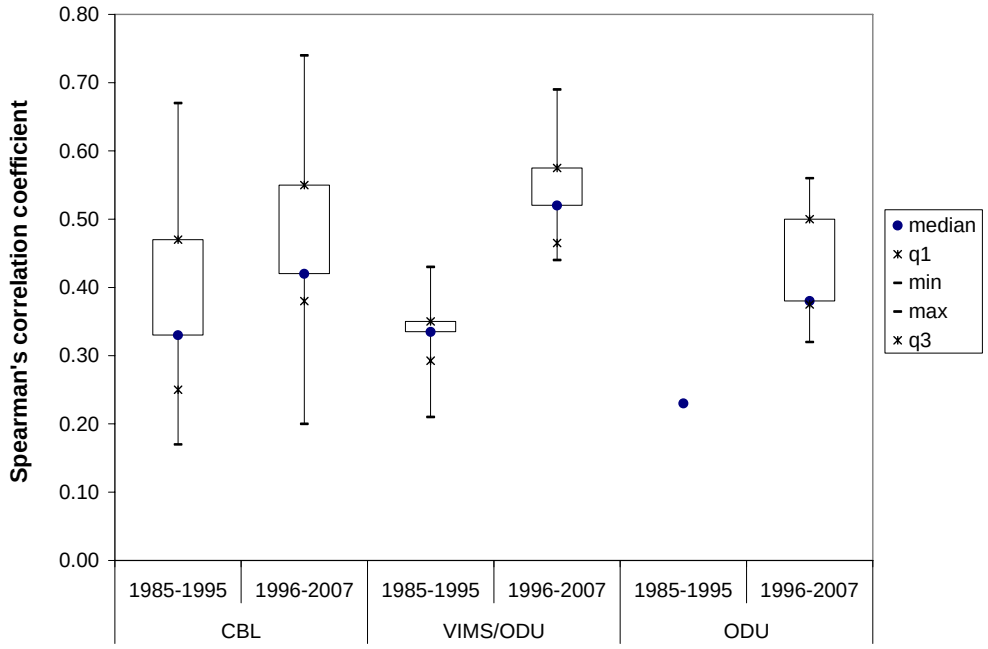
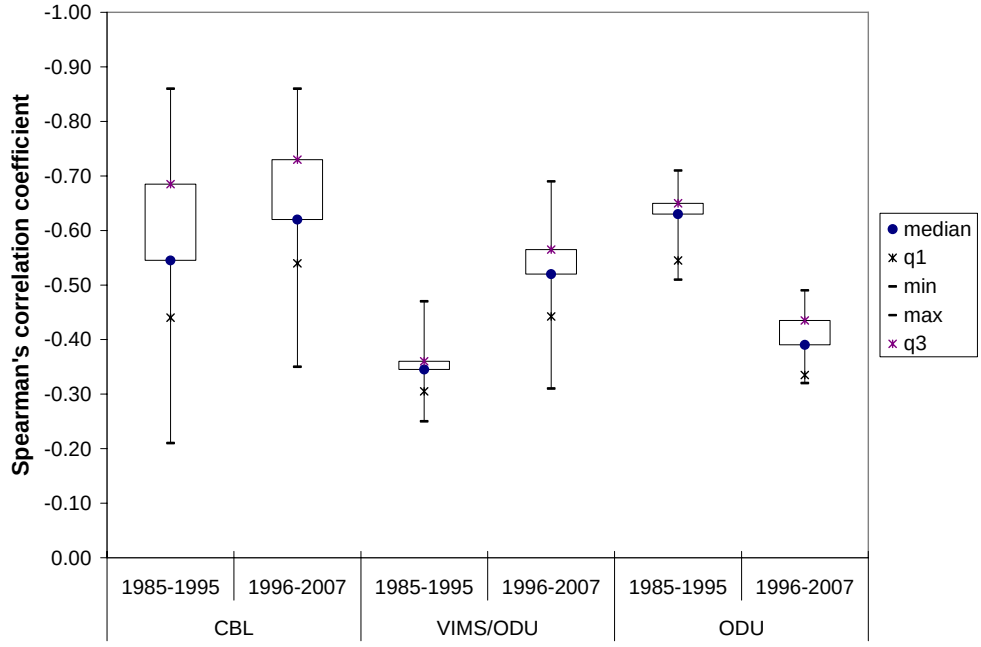


Figure 5. Box plot of TSS-secchi depth correlation coefficients by data source. Non-significant correlations were excluded.



CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 045

CATEGORY CODE: HI

ISSUE TITLE: Investigation of TSS Step Trend at Virginia mainstem stations

DATE OF INTRODUCTION OF THIS TO THE SYSTEM: June 2008

STATEMENT OF ISSUE:

The Virginia Department of Environmental Quality (VA DEQ) has long-term water quality data at 27 monitoring stations in the Chesapeake mainstem. From 1985 to 1995, VA DEQ contracted with the Virginia Institute of Marine Sciences (VIMS) to collect and analyze samples at 19 of these stations, while Old Dominion University (ODU) was responsible for monitoring the remaining stations. Starting in 1996, the VA Mainstem Bay monitoring program was consolidated at one organization and ODU took over all mainstem stations. An examination of the total suspended sediment (TSS) time-series indicates the presence of a negative step trend that is only apparent at stations initially sampled by VIMS. At these stations, the overall magnitude of TSS appears to abruptly drop starting in early 1999. Additional, the time-series after 1998 appears to have less temporal variation than previous to 1998. Although the downward step did not begin until three years after the lab change, the fact that the pattern seems to only be found at stations sampled by the two data sources suggests the existence of methodological confounding.

PROPOSED SOLUTION:

On May 1, 2008, the Tidal Monitoring and Assessment Workgroup (TMAW) recommended flagging all TSS data collected at stations monitored by both VIMS and ODU (hereafter referred to as "switchover" stations) to alert users to the TSS step trend, even though cause was not determined. A "flag" would consist of a statement inserted into the TSS metadata that summarizes the step trend and references this document.

DISCUSSION:

TSS time-series were analyzed for all Bay mainstem stations, including those in Maryland waters. A Wilcoxon rank-sum test was used to determine if the median TSS was significantly higher for the interval 1985-1995 (1995 being the last year VIMS sampled in the mainstem) relative to the interval 1/1/1996-12/31/2007. The year 1996 was chosen as a break point rather than 1999 because known method changes can be traced only to 1996. Dates were randomly excluded so as to standardize sampling frequency between the two time-frames.

The time-series at all the switchover stations exhibit a significant negative step trend (Figure 1). Four stations in the MD mainstem show a significant step trend, but the cause of this pattern (inadequate rinsing of filters) has been determined. A significant step trend was

not detected at any mainstem station sampled exclusively by ODU. At stations where step trends were found in the surface layer, a similar pattern is found in the other layers, though not significantly in the below pycnocline layer.

A number of steps were taken to determine if there are any methodological or sampling factors that can be tied to the TSS step trend.

Comparison of Standard Operating Procedures

A methods matrix was compiled by Cindy Johnson to rule out differences in VIMS and ODU standard operating procedures (SOPs). Although minor discrepancies were found (for instance, VIMS stored filters in a 60°C oven, while ODU stored them in a dissector), none of the methodological differences could be related to the step trend.

Field audit notes were also examined to determine if auditors observed deviations from SOPs during sampling. In the 1990 Laboratory and Field Evaluation Report, the auditor for VIMS noted that there "appeared to be insufficient shaking of sample once captured from hose to bottle prior to nutrient filtration". This note refers to "nutrient" filtration, and it is not known if this also affected TSS filtration, if VIMS treated all samples in this way consistently, or whether they later rectified this behavior. **However, TMAW considered this a possible explanation for the high concentration and variability of TSS at switchover stations prior to 1996.**

Analysis of QA/QC Samples

Variability between field duplicates, lab replicates, and split-sample and co-located sample results were also examined. Tami Huber assisted in pulling out field duplicate data collected from 1988 to 1992 for VIMS, ODU, and Chesapeake Bay Laboratories (CBL). The relative percent difference (RPD) between duplicate pairs was compared for all three laboratories (Figure 2). From 1988 to 1990 and 1993 to 1995, the average RPD for VIMS duplicates was not significantly greater than values for either ODU or CBL. But in 1991 and 1992, the RPD for VIMS duplicates was significantly greater. The mean standard deviation for field duplicates mirrors this pattern (Figure 2). Lab replicate data collected through 1986 to 1991 (summarized in ***Guide to Using CBP Water Quality Monitoring Data***, 1991) did not reveal significant differences between laboratories. Split-sample results collected from 1987 to 1993 show individual incidents of VIMS scoring significantly higher TSS values than the other laboratories (particularly in 1991), but it did not do so consistently nor more often than other labs.

From 1985 to 1990, VIMS and MDDNR sampled at CB5.3 (sometimes referred to as the "overlap" station). Over this five year period, VIMS tended to record significantly higher levels of TSS than MDDNR—in some cases almost by a factor of 10 (see Figure 3). Differences in other water quality parameters, such as chlorophyll and total phosphorus, were also observed. Bruce Nielsen attributed the differences to non-random time and within-layer depth differences in sampling, and recommended against using the co-located data as a QA/QC tool (Memorandum "RE:Statement on Colocated Samples", 1990). VIMS discontinued sampling at the overlap station in 1990 due in part to this recommendation.

There does not appear to be systematic bias in QA/QC samples indicating consistent problems with either VIMS or ODU data. Comparison of co-located samples shows a pattern of VIMS data being biased high in comparison to CBL but is inconclusive.

Analysis of Weather Events

Event tables were examined to determine if VIMS sampled under different weather conditions than ODU and MDDNR, possibly owing to differences in boat capability or other factors. If VIMS sampled on rougher water than ODU did at the same stations then one might expect to find increased variability in their samples and possibly higher TSS values. Two-hundred dates (half pre-1996, half post-1996) were randomly selected from the sampling record of each mainstem station and then aggregated by data source. Dates were then classified into low and high wave height and wind speed categories based on what was recorded in event tables. Then the number of dates falling into each category was totaled for each data source, pre-1996 and post-1996. At the switchover stations, VIMS sampled on significantly more days with high wave heights and high wind speeds than ODU did (χ^2=53.1,p<0.0001). However, at the stations only sampled by ODU, more dates with high wave heights were sampled ***after*** 1996 than before 1996 (χ^2=20.0, p<0.0001). Because TSS is not elevated after 1996 at these stations, the case cannot be made that the step trend observed at the switchover stations is related to weather. Moreover, ODU sampled on 90% of the same "rough weather" days sampled by VIMS but did not record unusually high wave heights or wind speeds, suggesting that these parameters are too subjective for accurate comparisons to be made.

Differences in weather during sampled conditions before and after 1996 do not appear to be the cause of the TSS step trend.

Examination of Covariate Time-series

The time-series for covariates (i.e., TP, PP, TN, PN, PC, and secchi depth) of TSS were analyzed at the switchover stations to determine if they contain a post-1996 step trend. Four of the 19 switchover stations exhibited a significant negative step for TP, but no stations exhibited a significant step trend for particulate phosphorus. Negative step trends were detected for all TN time-series but were attributed to trends in TDN rather than PN. Secchi depth at all the switchover stations exhibited a significant downward trend, but this pattern goes counter to what one would expect from the trend in TSS.

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At the May 1, 2008 TMAW meeting, it was suggested at the TMAW meeting that by smoothing the time-series out by year and rerunning the correlation tests, the coefficients for the switchover stations (pre-1996) would be smaller, on average, than the coefficients at the other stations. In addition, Michael Williams presented averaged Pearson's test p-values that indicated correlations at the switchover stations tended to be non-significant. Follow-up non-parametric analysis did not support either supposition. While it is true that pre-1996 TSS-secchi depth correlations tended to be lower at the switchover stations compared to elsewhere (in fact, most were non-significant), the post-1996 correlations at these stations are no better. Furthermore, the relationship between these parameters after 1996 at the ODU-only stations was virtually nonexistent, despite being moderately correlated, on average, when the time-series were not averaged by year. When yearly-aggregated time-series are analyzed, few of any of the correlations, including those in MD, were found to be significant. Most were significant when complete time-series were used (see Table 1). These results strongly suggest that smoothing time-series by year may not capture the temporal variation needed to assess data source consistency in covariates. **At any rate, this approach did not reveal any major QA/QC problems regarding the VIMS TSS data.**

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Graphical analysis

All figures follow at the end of this report.

SENSE OF THE RESOURCES NEEDED TO RESPOND:

Members of the Analytical Methods and Quality Assurance Workgroup (AMQWA) and interested data analysts are requested to review this document and provide comments by 9/1/2008.

PRIORITY RANKING:

Three (medium). The decision to flag all ODU and VIMS TSS data needs to be approved by AMQAW.

SUBMITTER/RESPONSIBLE PARTY:

Name: Tish Robertson
Data Analyst

Organization: VA Department of Environmental Quality
629 East Main St.
Richmond, VA 23219
(804) 698-4309

ACTIONS TO DATE:

Presented the above findings to AMQAW on March 31, 2008 and TMQAW on May 1, 2008.

OVERALL RESOLUTIONS SUMMARY OF ACTIONS:

RECOMMENDED ACTIONS:

ACTIONS NUMBER:
1. Designated Respondent:
2. Action:
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4. Due Date:
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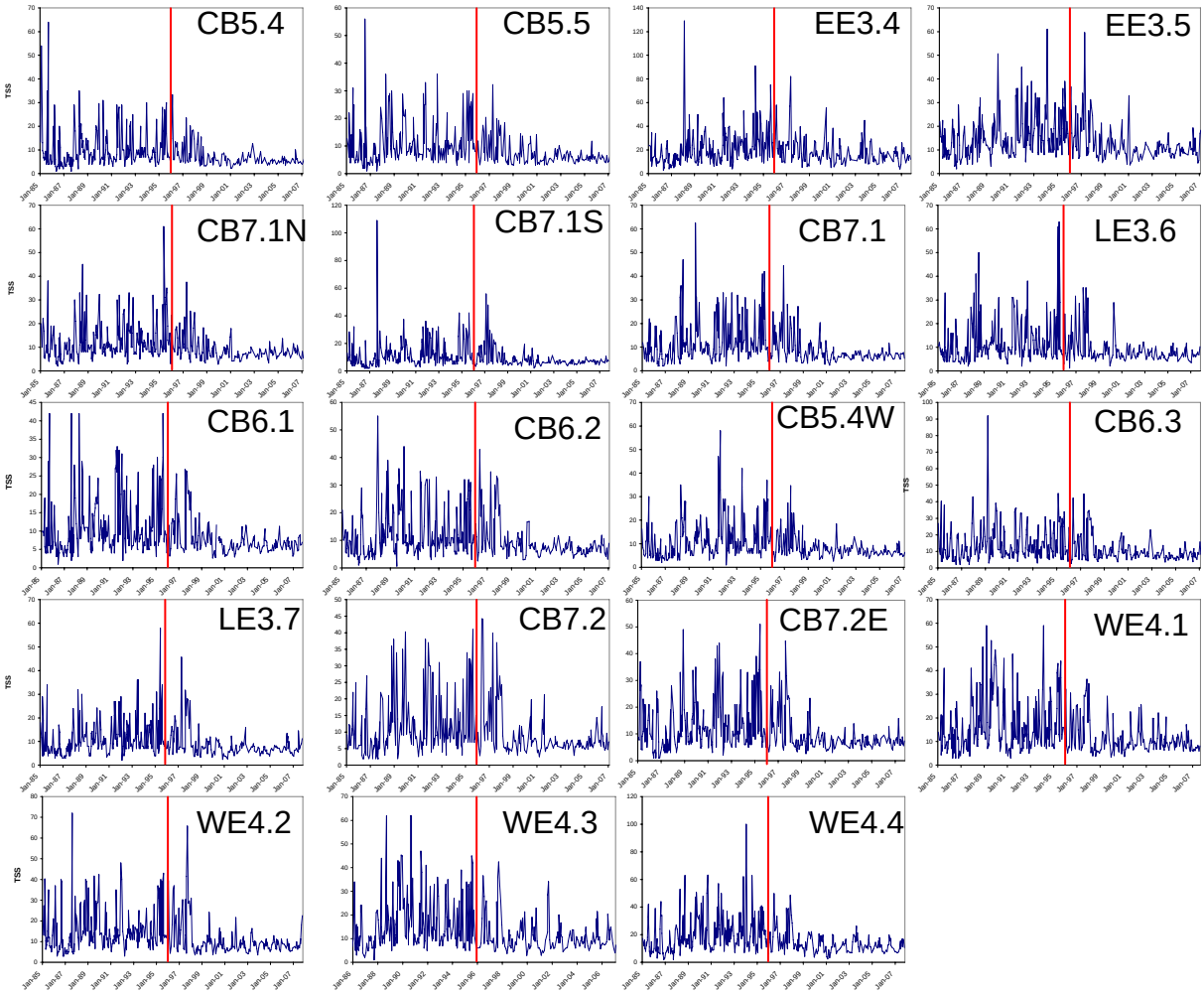


Figure 1b. Surface TSS time-series (1985 to 2007) at MD mainstem stations. Vertical line marks 1/1/1996. Station IDs that are underlined indicate stations with a significant negative step trend post-1996.

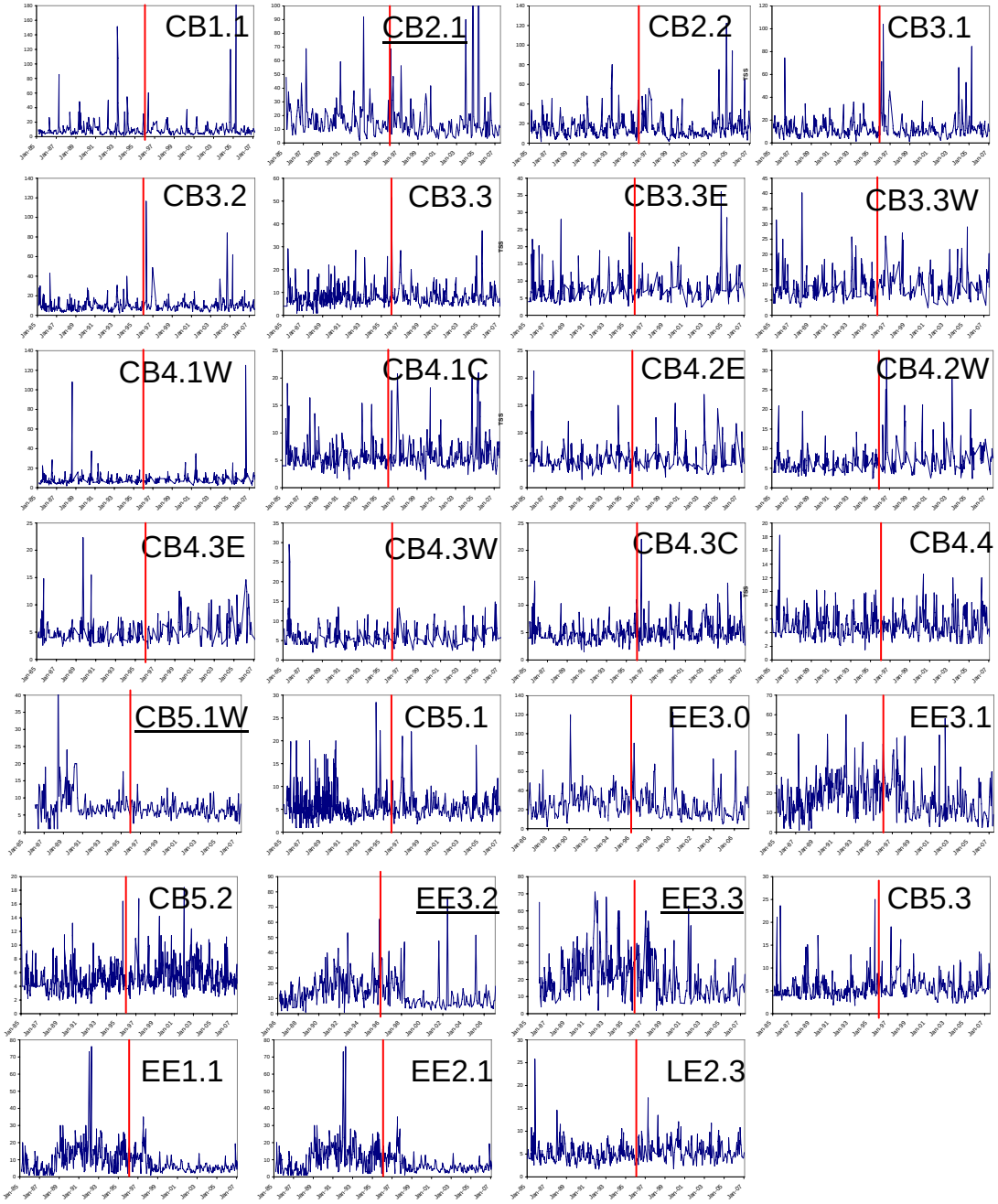


Figure 1c. Surface TSS time-series (1985 to 2007) at ODU-only mainstem stations. Vertical line marks 1/1/1996.

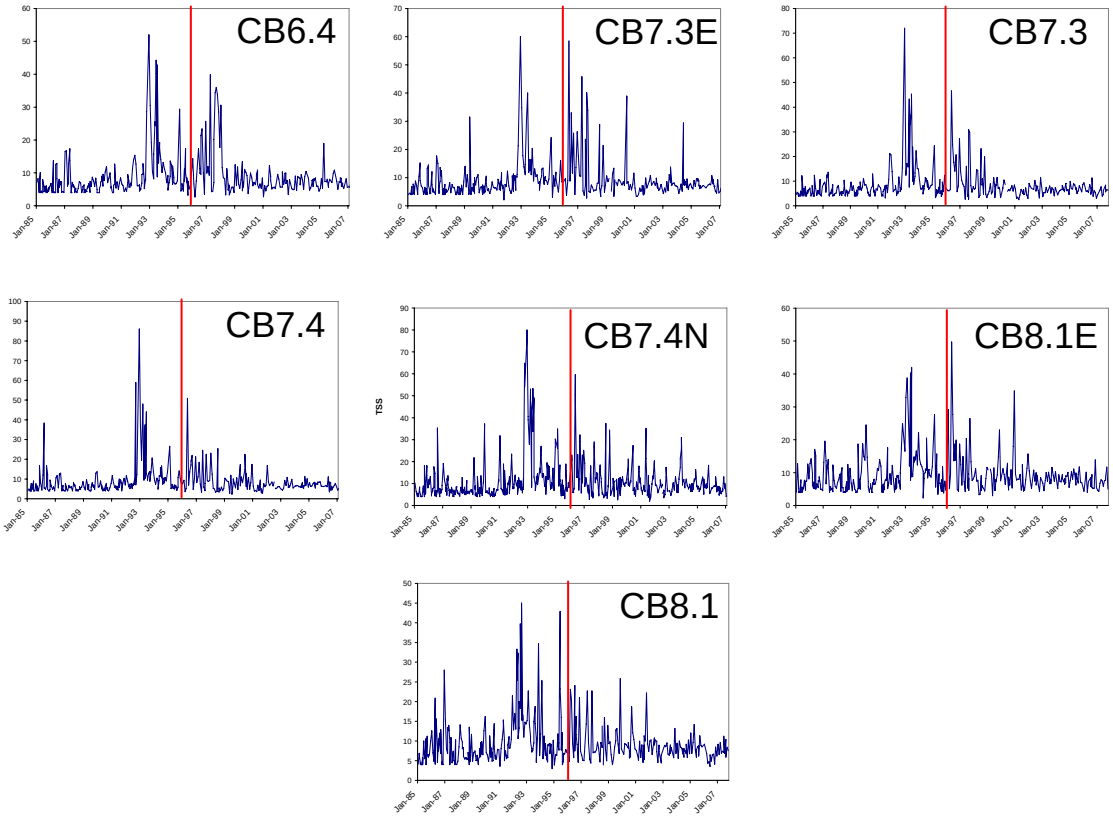


Figure 1d. Map of mainstem stations. Triangles represent MD stations. Squares represent VIMS-ODU stations, and circles represent "ODU-only" stations. Only stations that were continuously sampled from 1985 to 2007 are shown.

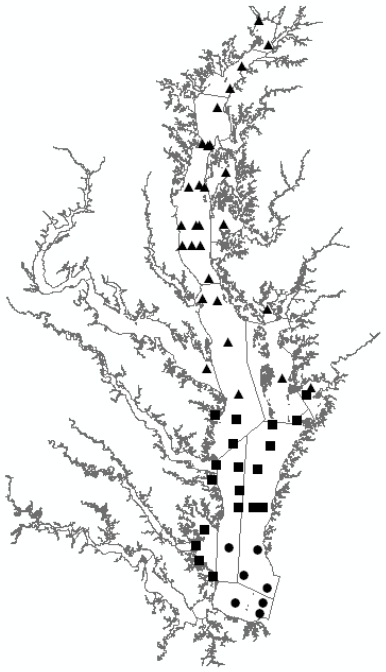


Figure 2. Average relative percent difference and standard deviation for field duplicates. Bars represent standard error of the mean.

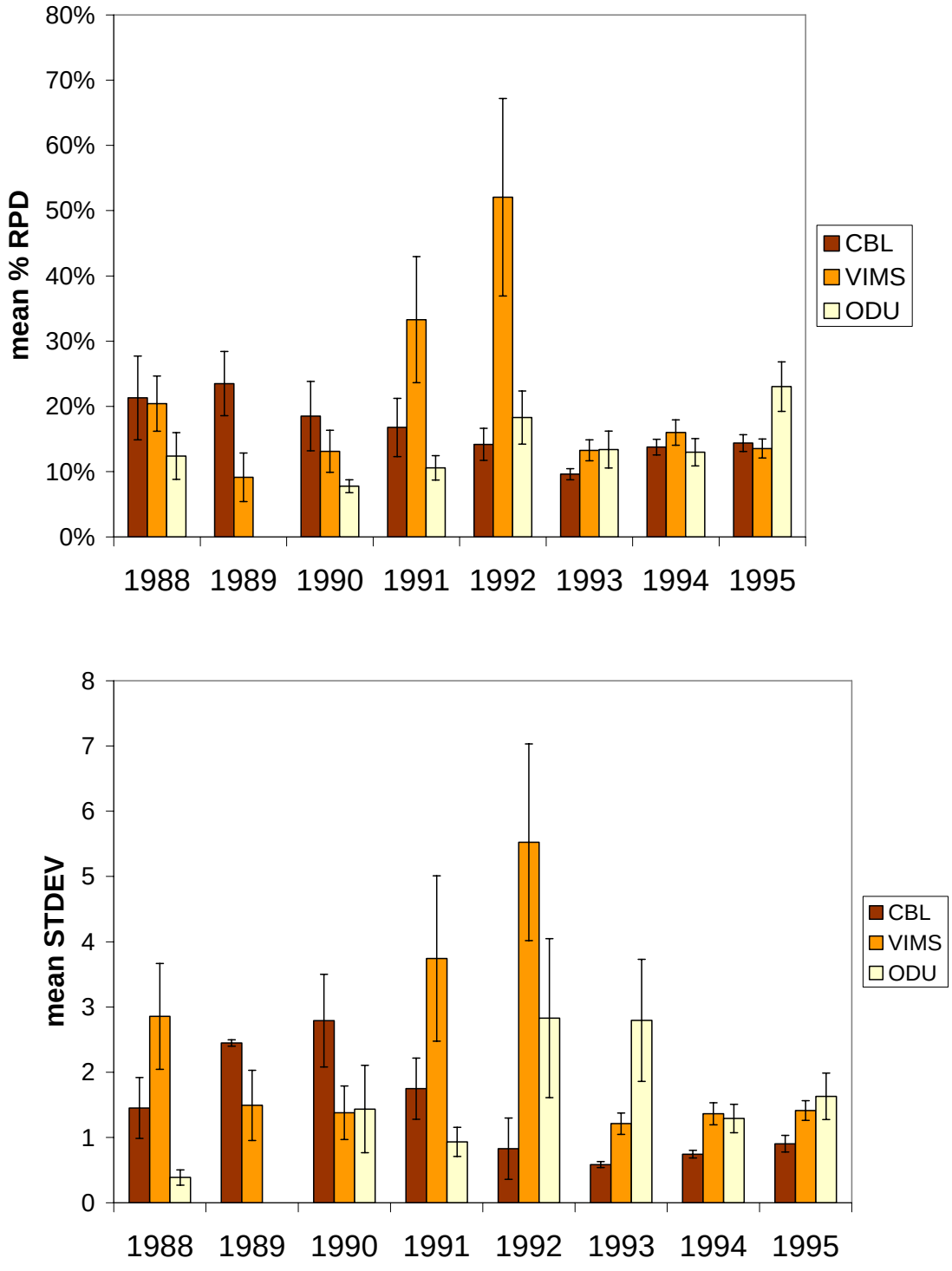


Figure 3. Surface TSS concentrations at CB5.3 (overlap station).
Source: Dave Jasinski

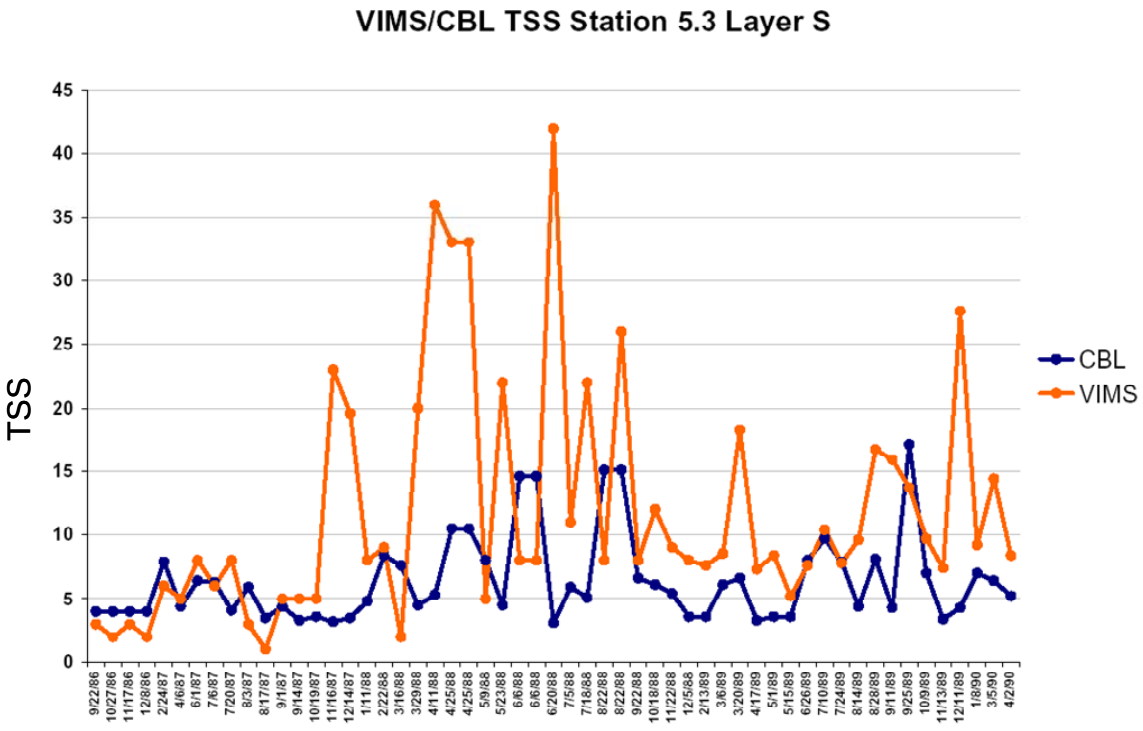


Table 1. Spearman's correlation coefficients for TSS & TP and TSS & secchi depth by station. "Complete" refers to non-averaged time-series; "yearly" refers to year-averaged time-series. Only significant correlations ($p<0.05$) are shown.

station	TSS vs. TP				TSS vs. secchi depth			
	pre-1996		post-1996		pre-1996		post-1996	
	complete	yearly	complete	yearly	complete	yearly	complete	yearly
CB1.1[CBL]	0.67		0.72	0.76	-0.79		-0.84	-0.45
CB2.1[CBL]	0.67		0.74	0.87	-0.77	-0.65	-0.80	-0.65
CB3.1[CBL]	0.43		0.47	0.78	-0.86	-0.88	-0.85	-0.79
CB2.2[CBL]	0.60	0.80	0.62	0.69	-0.82	-0.77	-0.86	-0.75
CB3.2[CBL]	0.47		0.41	0.76	-0.81	-0.85	-0.76	-0.65
CB3.3C[CBL]	0.33		0.55	0.84	-0.53		-0.69	-0.70
CB3.3E[CBL]	0.59		0.44	0.87	-0.67		-0.67	-0.75
CB3.3W[CBL]	0.38		0.53	0.86	-0.66		-0.64	-0.81
CB4.1C[CBL]	0.27		0.40	0.65	-0.47	-0.44	-0.58	
CB4.1E[CBL]		0.69	0.42		-0.44	-0.72	-0.65	
CB4.1W[CBL]	0.47		0.67	0.63	-0.70	-0.75	-0.70	
CB4.2C[CBL]	0.22		0.36		-0.37		-0.54	
CB4.2E[CBL]	0.26		0.40	0.69	-0.55		-0.61	-0.68
CB4.2W[CBL]	0.43		0.63	0.90	-0.64	-0.74	-0.74	
CB4.3C[CBL]			0.20		-0.34		-0.35	
CB4.3E[CBL]	0.21		0.23		-0.43		-0.46	
CB4.3W[CBL]	0.48	0.83	0.56	0.70	-0.57		-0.73	
CB4.4[CBL]	0.32	0.74	0.45		-0.54	-0.62	-0.58	
CB5.1[CBL]	0.23	0.70	0.40		-0.38		-0.62	
CB5.1W[CBL]	0.17		0.20		-0.21		-0.48	
CB5.2[CBL]	0.19		0.26		-0.53		-0.35	
CB5.3[CBL]			0.37		-0.47	-0.73	-0.49	
EE3.0[CBL]	0.25		0.38		-0.68	-0.71	-0.59	
EE3.1[CBL]								
EE3.2[CBL]			0.41	0.63			-0.46	
EE3.3[CBL]	0.26		0.53		-0.44		-0.58	
CB5.4[VIMS/ODU]	0.21		0.52	0.64	-0.35		-0.31	
CB5.4W[VIMS/ODU]	0.43		0.53	0.73	-0.35	-0.41	-0.53	
CB5.5[VIMS/ODU]	0.31	0.71	0.45	0.64	-0.25		-0.42	
CB6.1[VIMS/ODU]	0.35	0.63	0.57	0.67	-0.31		-0.51	
CB6.2[VIMS/ODU]	0.35	0.57	0.63	0.89			-0.55	
CB6.3[VIMS/ODU]	0.41		0.50	0.83	-0.46		-0.45	
CB7.1[VIMS/ODU]	0.25		0.52	0.82			-0.54	
CB7.1N[VIMS/ODU]			0.44	0.78	-0.25		-0.47	
CB7.1S[VIMS/ODU]	0.30	0.62	0.44	0.73	-0.28		-0.39	
CB7.2[VIMS/ODU]	0.34	0.70	0.49	0.53	-0.32		-0.41	
CB7.2E[VIMS/ODU]	0.33		0.44	0.69	-0.34		-0.44	
EE3.4[VIMS/ODU]	0.38	0.61	0.59	0.60	-0.47		-0.57	
EE3.5[VIMS/ODU]	0.30	0.61	0.49		-0.36		-0.57	
LE3.6[VIMS/ODU]	0.35		0.45	0.69	-0.36			
LE3.7[VIMS/ODU]	0.29		0.57	0.76	-0.32		-0.54	
WE4.1[VIMS/ODU]	0.34		0.58	0.74	-0.29		-0.59	
WE4.2[VIMS/ODU]	0.27		0.48	0.63			-0.51	
WE4.3[VIMS/ODU]	0.23		0.67		-0.36		-0.69	
WE4.4[VIMS/ODU]	0.41		0.69	0.83	-0.37	-0.72	-0.65	
CB6.4[ODU]	0.23		0.51		-0.65	-0.62	-0.43	
CB7.3[ODU]			0.38	0.69	-0.63	-0.71	-0.34	
CB 7.3E[ODU]			0.49	0.89	-0.52	-0.79	-0.49	
CB7.4[ODU]			0.32	0.86	-0.51		-0.39	
CB7.4N[ODU]			0.56	0.63	-0.57	-0.72	-0.33	
CB8.1[ODU]			0.38	0.69	-0.65	-0.88	-0.32	
CB8.1E[ODU]			0.37	0.81	-0.71		-0.44	

Figure 4. Box plot of TSS-TP correlation coefficients by data source. Non-significant correlations were excluded from samples. Only one ODU station had a significant correlation pre-1996.

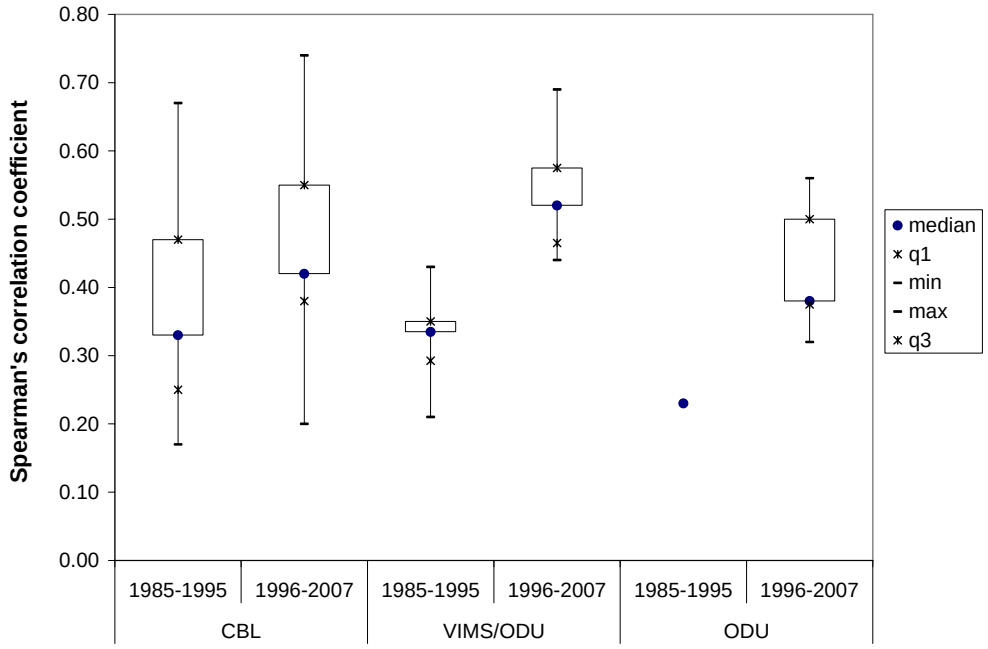
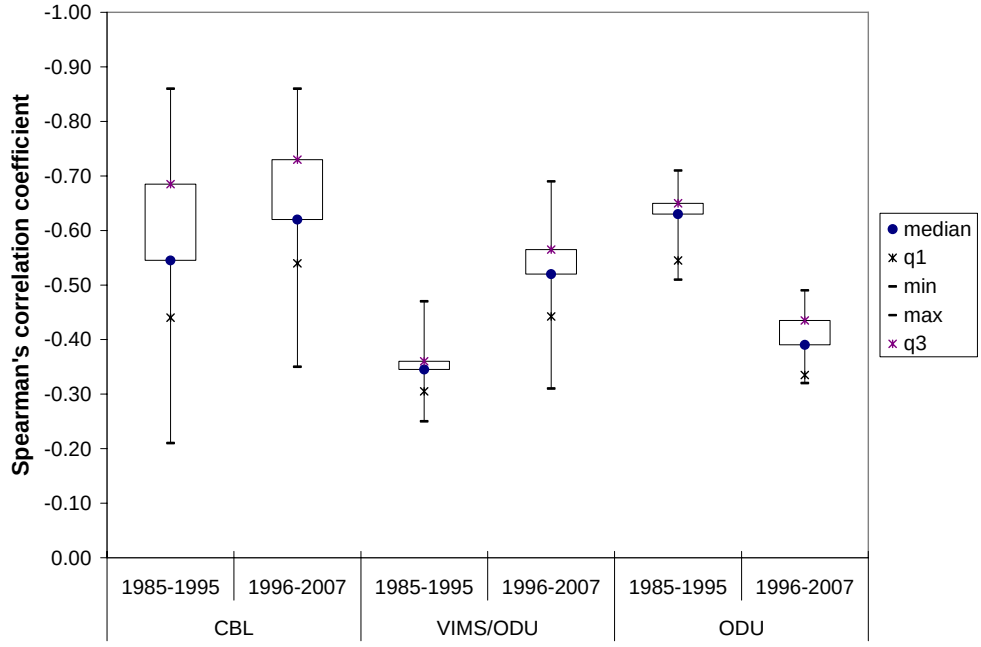


Figure 5. Box plot of TSS-secchi depth correlation coefficients by data source. Non-significant correlations were excluded.



CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 046

CATEGORY CODE: Analytical Methods (AM)

ISSUE TITLE: Comparison of chlorophyll and pheophytin analyzed at DHMH and CBL

DATE OF INTRODUCTION OF THIS TO THE SYSTEM: May 2009

STATEMENT OF ISSUE:
The Maryland Department of Health and Mental Hygiene (DHMH) analyzed water quality samples for chlorophyll and pheophytin that were collected by the Maryland Department of Natural Resources (DNR) at main Bay, tidal, and some non-tidal stations from the 1980s through December 2008. In December 2008 DHMH ceased analyzing chlorophyll and pheophytin samples for DNR and the Nutrient Analytical Services Laboratory at the Chesapeake Biological Laboratory (CBL) in Solomons, MD began analyzing the samples in January 2009 (DHMH continues to analyze a limited number of chlorophyll and pheophytin samples for the U.S. Geological Survey as part of the River Input Monitoring Program for Maryland's four river input sites, as well as a limited number of samples for special projects.) As a result, DHMH's chlorophyll and pheophytin data are the data that appear in the publicly available data base (Chesapeake Information Management System – CIMS) through December 2008 and CBL's data are the data that appear in CIMS beginning January 2009.

DHMH used Shimadzu 240 spectrophotometers to analyze chlorophyll and pheophytin during the time they analyzed chlorophyll and pheophytin samples for DNR. Although the same two spectrophotometers used by DHMH have been shipped to CBL for their use, there is still some concern that a step trend in the data record could occur following the transfer of samples from DHMH to CBL as a result of differences in sample handling and preparation between the two laboratories. Subtle differences in how samples are handled and analyzed have resulted in step trends for other parameters. CBL staff is experienced at analyzing water quality samples for chlorophyll and pheophytin; however, CBL normally uses a fluorometer.

PROPOSED SOLUTION:
In an attempt to assess any potential step trend in the data resulting from the transition from DHMH to CBL, one machine was retained by DHMH and the other was shipped to CBL in November 2008. The CBL machine was set up by a Shimadzu representative who also trained CBL staff in how to operate the machine and interpret the output.

During November and December 2008, crews from DNR's Annapolis Field Office collected split samples from a subset of 13 main Bay and six tidal tributary stations. The stations included from CB1.1 (tidal fresh zone) to CB5.3 (mesohaline zone) in the main Bay, plus three embayment stations and three other tidal stations. The 140 samples that were collected over the two months represent the full range of salinity zones in Maryland's tidal waters and a wide range in

chlorophyll concentrations. These data are presented in Appendix A. A map showing the station locations is presented in Figure 1.

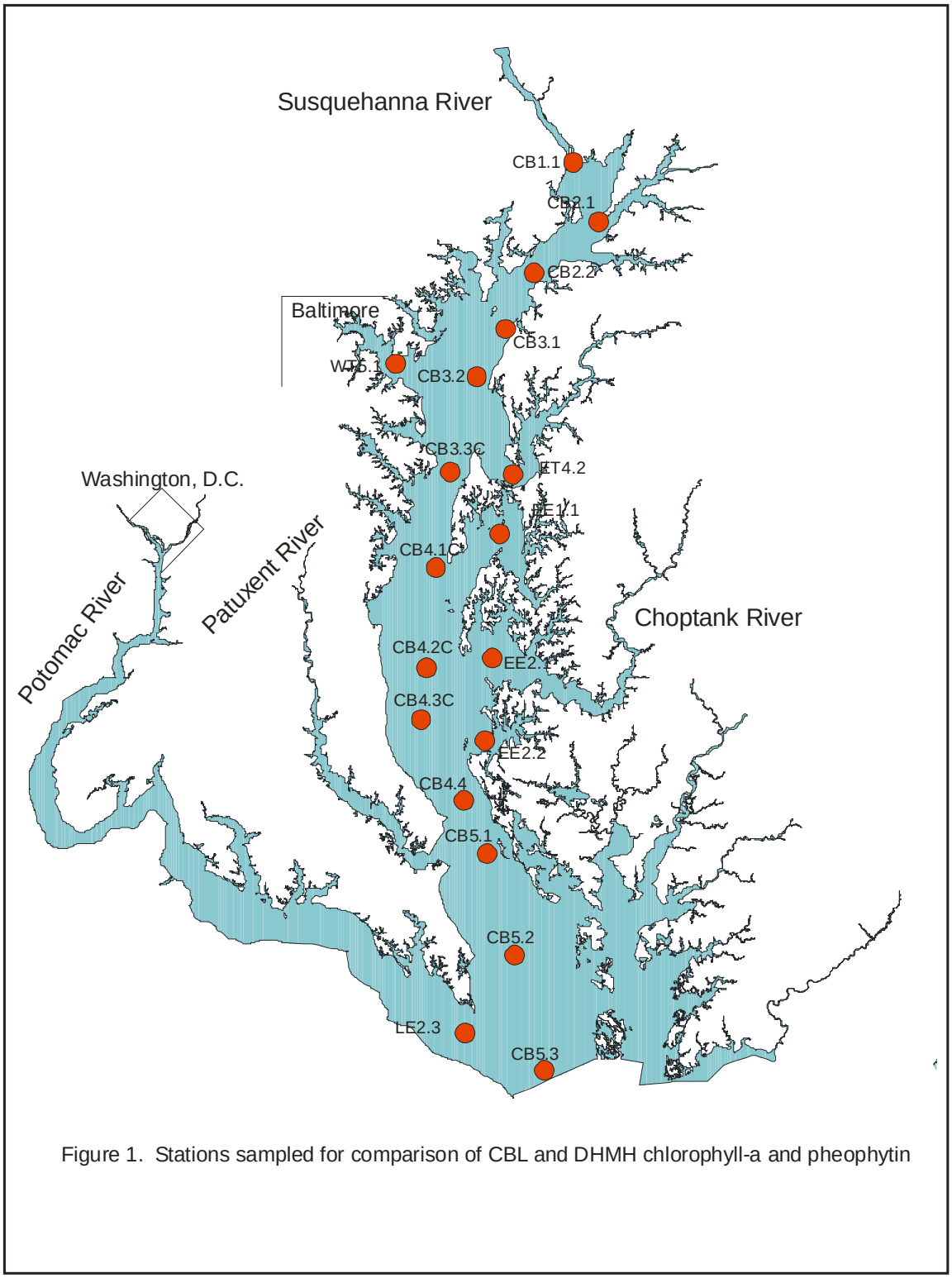


Figure 1. Stations sampled for comparison of CBL and DHMH chlorophyll-a and pheophytin

DISCUSSION:

Laboratory notes

The CBL method detection limits for active chlorophyll-***a*** and pheophytin are 0.62 µg/L and 0.74 µg/L, respectively. The method detection limits were calculated as described in Title 40 CFR, Appendix C. DHMH uses the concentration for the lowest quality control standard, which for chlorophyll is 0.1 µg/L.

Both laboratories used the same protocols (***Standard Methods for the Examination of Water and Wastewater***, American Public Health Association, American Water Works Association, and Water Environment Federation) for the determination of active chlorophyll-***a*** and pheophytin, corrected for turbidity and the same equations:

$$Chla = 26.7\ [(OD664b - OD750b) - (OD665a - OD750a)] * K$$
$$Pheo = 26.7\ [1.7\ (OD665a - OD750a) - (OD664b - OD750b)] * K,$$

where K = (extract volume/sample volume * light path).

Although DHMH and CBL follow the same methods, there are minor differences in how the samples are prepared. CBL reported using the same concentration of acid as DHMH for extracting the pigments; however, CBL uses a 5 centimeter micro cell cuvette, which holds 3 milliliters of sample, whereas DHMH used a 5 centimeter semi-micro cuvette, which holds 7 milliliters of sample. Though different, the volume of cuvettes used by DHMH and CBL does not matter, because the path length of both cuvettes is the same.

CBL reported initially having some difficulty achieving the recommended 0.007 nanometers wavelength for their extracted material at the 750 optical density wavelength, which is used to correct for turbidity. To extract the phytopigments and obtain a clear sample CBL first grinds the sample for 15 minutes. After grinding, the sample is transferred to another tube by filtering the sample through a 0.45 micron polytetrafluoroethylene (Teflon®) filter or a nylon syringe filter and centrifuged for 30 minutes at 3,000 revolutions per minute to separate the ground-up filter and other particulate matter from the supernatant. CBL reported that for very turbid samples, even filtering and the centrifugation may not get the optical density absorbance down to 0.007 nanometers. It is not clear what DHMH did when they received highly turbid samples.

Finally, CBL uses a 10 milliliter extract volume, whereas DHMH used 14 milliliters to extract the sample. As long as the extract volume is accounted for in the calculation of chlorophyll and pheophytin, the extract volume does not matter.

Basic statistics

Basic statistics for the data set were calculated using Statistical Analysis System (SAS®) software and are presented in Table 1. As shown in Table 1 the means for active chlorophyll-***a*** (total chlorophyll minus pheophytin), for both labs are virtually identical and the ranges and standard deviations are quite close. The results for pheophytin are not as good. The mean concentration of pheophytin and the range of concentrations recovered by CBL are considerably higher than DHMH (The

CBL arithmetic mean pheophytin concentration is approximately 60% larger than the DHMH mean concentration.)

Table 1. Basic statistics for the comparison of active chlorophyll-*a* and pheophytin at DHMH and CBL.

Variable	N	Mean	Std. Dev.	Minimum	Maximum
CBL Chla	140	8.32	5.3	1.15	26.70
DHMH Chla	140	8.22	4.4	1.99	22.73
CBL Pheo	140	4.64	4.1	-0.96	20.74
DHMH Pheo	140	2.91	3.4	-4.49	15.97

Graphical comparisons

These data are also compared graphically using notched box and whisker plots in Figure 2 for chlorophyll and Figure 3 for pheophytin.

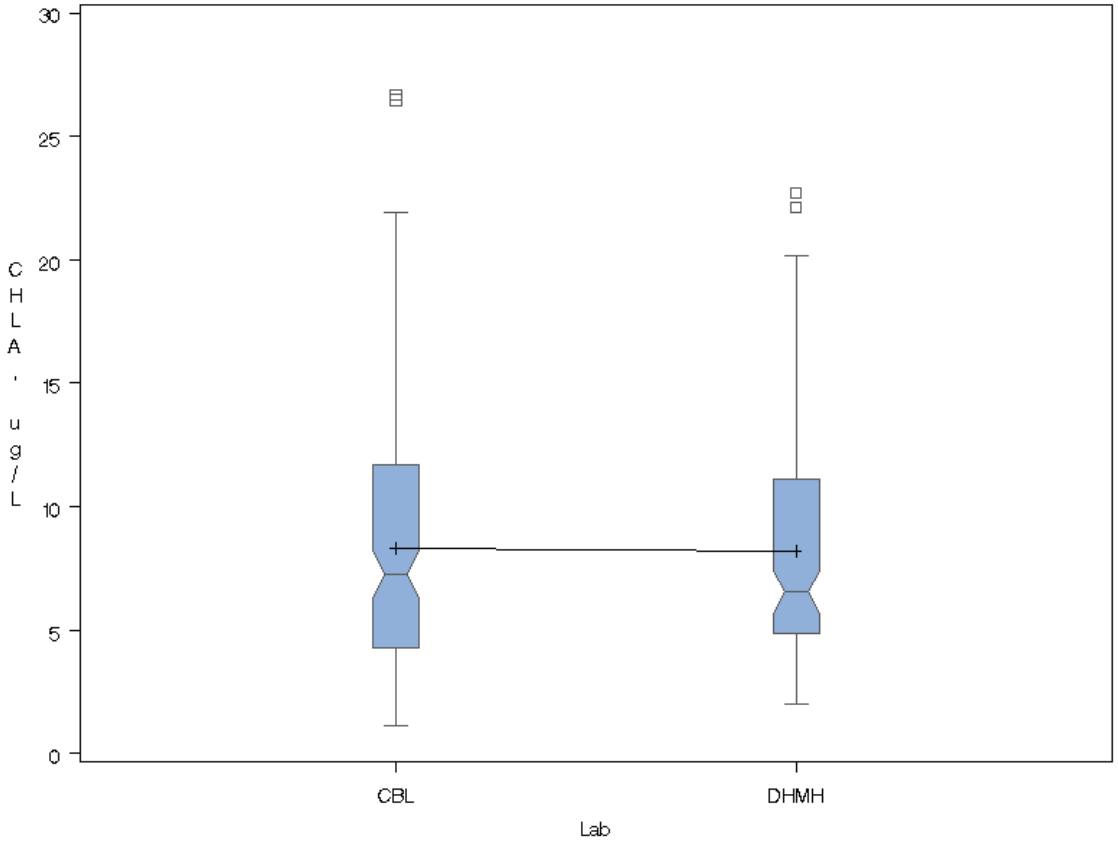


Figure 2. Comparison of November and December of active chlorophyll-*a* (total chlorophyll minus pheophytin) split samples for DHMH and CBL.

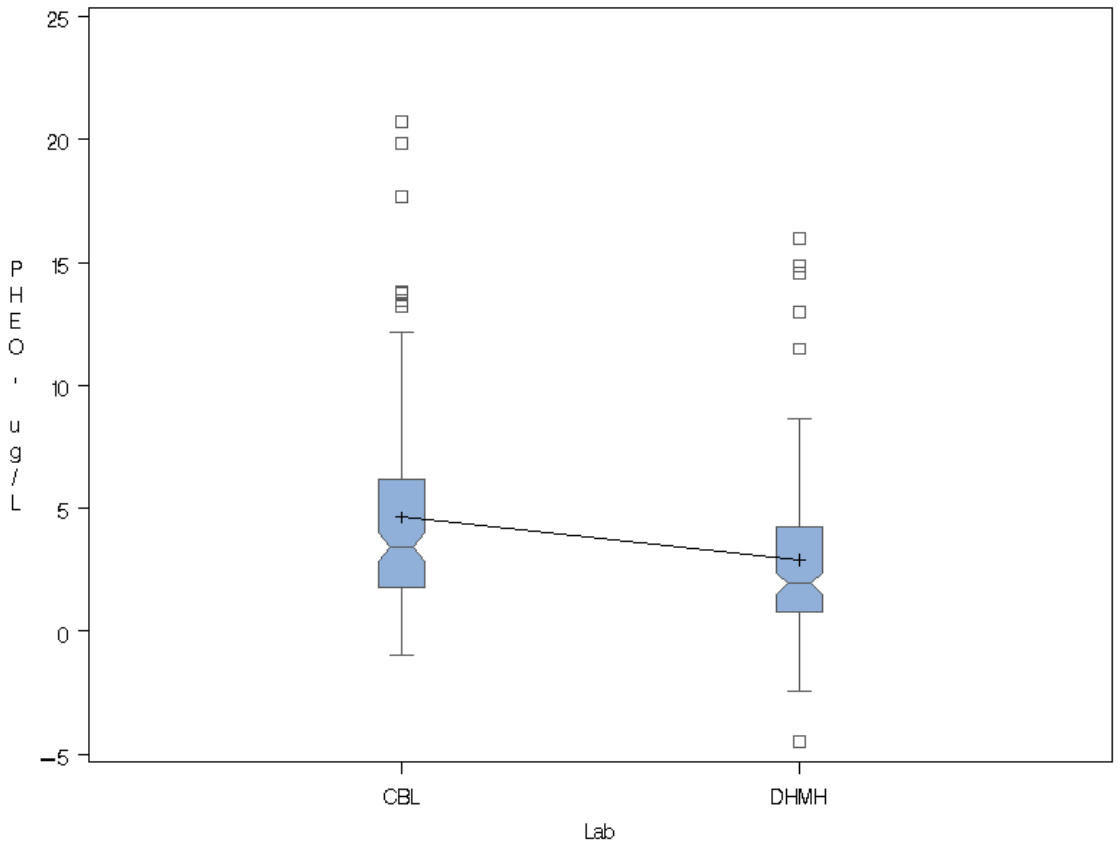


Figure 3. Comparison of November and December pheophytin split samples for DHMH and CBL.

Notched box and whisker plots show the range in concentrations, the inter-quartile range, the median, and the mean (+ sign) of the distribution. The endpoint of the notches show the median plus and minus 1.58*(inter-quartile range/√n). The medians of two notched box-and-whisker plots are significantly different at the 0.05 level if the notches do not overlap.

The notches in Figure 2 do overlap, so the median chlorophyll values for samples analyzed at DHMH and CBL are not significantly different at the 0.05 level. The notches around the median pheophytin values shown in Figure 3 do not overlap, so the median concentrations of pheophytin analyzed at DHMH and CBL are significantly different at the 0.05 level, with CBL concentrations significantly higher than DHMH.

Statistical comparisons

Chlorophyll and pheophytin for both laboratories were also compared statistically using the Wilcoxon Signed Rank test on the log ratio of CBL to DHMH samples (i.e., log (CBL/DHMH). Taking the logarithm of each parameter and then subtracting the DHMH value from its corresponding CBL value calculates this ratio. The log ratio is based on the principle of logarithms that states: $\log_b x - \log_b y = \log_b (x/y)$. Working with log-transformed data (base 10 was used in these analyses) also helps meet the symmetry assumption of the Wilcoxon Signed Rank test. Probability values (p-values) for the Wilcoxon Signed Rank test

of $\leq$0.05 are assumed to indicate a statistically significant difference between samples analyzed at DHMH and at CBL.

The p-value for the chlorophyll log ratio was 0.8799, which is not significant; however, the p-value for pheophytin (<0.0001) indicates that there is a significant difference between the concentrations analyzed at the two laboratories, with CBL higher than DHMH.

The significant difference between the laboratories for pheophytin was further explored using SAS® PROC GLM, a General Linear Model, because the magnitude of the arithmetic mean differences (calculated as CBL pheophytin minus DHMH pheophytin) were not consistent when calculated by month and layer (Table 2). The surface and above pycnocline mean differences for November were small relative to the mean differences for bottom and above pycnocline in December. Smaller mean differences indicate better agreement between the labs.

Table 2. Arithmetic mean difference between pheophytin measured by CBL and DHMH (CBL – DHMH) by month and layer.

Month/Layer	Surface (ug/L)	Above pycnocline (ug/L)	Below pycnocline (ug/L)	Bottom (ug/L)
November	0.92	0.74	1.43	1.55
December	1.70	2.18	1.70	3.30

The pheophytin log ratio ($\log_{10}$(CBL) – $\log_{10}$(DHMH)) was used to test for month and layer effects, i.e., if there were significant differences between both months and among all layers. The p-values for month and layer were 0.8152 and 0.9994, respectively which indicates that differences between months and among layers were not significant. Therefore, we cannot infer that the difference between the labs can be attributed to one month of data or the other. Graphs showing the differences between the labs for both chlorophyll and pheophytin by month and layer are presented in Appendix B.

The variability in the pheophytin concentrations for the DHMH and CBL November and December 2008 splits was compared to the variability in pheophytin for the laboratories that participate in the coordinated split sample program. In order to achieve a balanced design, the data from the coordinated split sample program were screened to find a subset of data where the laboratories, stations, dates, and layers were equally represented. This balanced design approach precluded any station, date, or layer from having undue influence on the results of this analysis and helped satisfy the balanced design assumption of SAS® PROC GLM. This screening resulted in a data set composed of four laboratories (DHMH, CBL, ODU, and DCLS), one layer (surface), and 12 dates.

Replicate data (RepNo=2) and bottom data were only available for a limited number of cruise dates, so they were deleted from the final data set. Data for only one station (MCB4.4) were used because data for PMS10 were not available for all four laboratories on all dates. This pre-screening made controlling for station and layer un-necessary, resulting in the following model statement:

```
PROC GLM DATA=SplitSampDB;
   CLASS Lab CruiseDate;
    MODEL log10PHEO = Lab CruiseDate;
      RANDOM Lab;
       LSMEANS Lab / PDIFF STDERR;
```

Data were available for 19 stations, 6 dates, and 4 layers in the November and December 2008 DHMH and CBL pheophytin split, thus variability attributable to these variables was controlled using the following model statement:

```
PROC GLM DATA=GetBoxes;
   CLASS Station Date Layer Lab;
    MODEL log10PHEO = Date*Station*Layer Lab;
      RANDOM Lab;

      LSMEANS LAB / PDIFF;
```

There were negative values in both data sets, so a constant (5.5) was added to all pheophytin values prior to applying a log10 transformation to the data, which helped meet the distributional assumptions of the general linear model.

The standard deviation for the labs for the coordinated split sample data and the DHMH and CBL November and December 2008 splits were ~0.07 and ~0.06, respectively. These standard deviations were calculated using the expected mean square error and the Type III sums of squares mean square error for the Lab term. These results indicate that the variability in the results for the DHMH and CBL splits is comparable to the variability between the four labs whose data were analyzed in the coordinated split sample program.

SENSE OF THE RESOURCES NEEDED TO RESPOND:
Members of the Analytical Methods and Quality Assurance Workgroup (AMQWA) and data analysts are requested to review this document and provide comments by 1 June 2009.

PRIORITY RANKING:
Two (low). The difference between CBL and DHMH for active chlorophyll-*a* is not statistically significant. Although the difference between the laboratories for pheophytin is statistically significant, no one is currently performing trend analyses on that parameter, so a potential step in the data has little practical importance for trend assessment.

SUBMITTER/RESPONSIBLE PARTY:
Name: William D. Romano
Natural Resources Biologist

Organization: Maryland Department of Natural Resources
580 Taylor Avenue, D-2
Annapolis, MD 21401
(410) 260-8655

ACTIONS TO DATE:
Informed AMQWA of potential problems in a PowerPoint presentation that was made at their meeting at the VA Department of Environmental Quality

Piedmont Regional Office in Glen Allen, VA on 27 February 2009. Prepared this report. Analyses performed in CHLACompare.SAS program.

OVERALL RESOLUTIONS SUMMARY OF ACTIONS:

RECOMMENDED ACTIONS:
The data analysis issue described in this report resulted from a change in the laboratories from DHMH to CBL for the analysis of chlorophyll and pheophytin samples. The comparisons described above were made using the same two spectrophotometers (one in each laboratory) that had been used by DHMH. Although DHMH did not conduct side-by-side comparisons of the two machines while they were both used at DHMH, there is no reason to believe that the different machines produced different results. In addition, this would not explain why chlorophyll-*a* results from different machines at different laboratories would be the same and pheophytin results would be different.

CBL started analyzing chlorophyll and pheophytin samples collected under the tidal, non-tidal, and shallow water monitoring programs in January 2009 when the second machine was transferred to CBL. Thus, chlorophyll and pheophytin analyses performed by CBL on behalf of DNR will be done using same two machines previously used by DHMH. Data analysts who use the pheophytin data should be aware of a possible step change in the data following the laboratory change in January 2009. It would be prudent to test the pheophytin and chlorophyll data for step tends resulting from the laboratory change after two or so years of post-change data have been collected. Pheophytin may be important in multiple regression analyses to post-calibrate continuous monitoring and data-flow fluorescence data, which measure total chlorophyll. Data analysts should be aware of this potential problem for other analysis tasks as well.

ACTIONS NUMBER:
1. Designated Respondent:
2. Action:
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary:

Appendix A
Data used in these analyses

Station	Date	Depth	Rep	Layer	DHMH Pheo	DHMH ChlA	CBL_Pheo	CBL_ChlA
CB1.1	11/19/2008	0.5	1	S	2.77	5.61	6.97	4.81
CB1.1	11/19/2008	4	1	B	7.13	6.48	10.25	5.70
CB1.1	12/18/2008	0.5	1	S	1.08	3.36	2.51	5.34
CB1.1	12/18/2008	4	1	B	1.94	4.86	2.43	5.61
CB2.1	11/19/2008	0.5	1	S	-0.78	2.62	1.68	1.87
CB2.1	11/19/2008	5	1	B	-1.16	2.99	0.96	2.40
CB2.1	12/18/2008	0.5	1	S	-0.15	3.99	2.28	3.20
CB2.1	12/18/2008	5	1	B	0.9	3.99	1.32	3.92
CB2.2	11/19/2008	0.5	1	S	-2.44	3.49	-0.96	3.20
CB2.2	11/19/2008	0.5	2	S	-1.25	2.99	-0.71	3.20
CB2.2	11/19/2008	3	1	AP	-1.25	2.99	-0.96	3.20
CB2.2	11/19/2008	7	1	BP	1.84	1.99	2.71	1.78
CB2.2	11/19/2008	11	1	B	2.79	3.49	4.95	1.78
CB2.2	12/18/2008	0.5	1	S	1.84	5.48	3.10	4.63
CB2.2	12/18/2008	0.5	2	S	1.99	4.98	2.39	5.34
CB2.2	12/18/2008	5	1	AP	0.1	5.48	3.20	4.27
CB2.2	12/18/2008	8	1	BP	2.32	4.49	2.51	5.34
CB2.2	12/18/2008	12	1	B	14.88	14.95	19.86	12.28
CB3.1	11/19/2008	0.5	1	S	-1.59	2.99	0.57	1.42
CB3.1	11/19/2008	7	1	AP	-1.1	2.49	-0.14	2.14
CB3.1	11/19/2008	12	1	BP	1.45	4.49	3.52	3.20
CB3.1	11/19/2008	13	1	B	2.54	5.48	5.52	3.20
CB3.1	12/18/2008	0.5	1	S	0.7	3.49	1.78	3.20
CB3.1	12/18/2008	1	1	AP	-0.15	3.99	0.82	3.92
CB3.1	12/18/2008	5	1	BP	1.2	6.48	2.03	8.19
CB3.1	12/18/2008	13	1	B	7.48	13.46	11.61	12.82
CB3.2	11/19/2008	0.5	1	S	-0.03	3.59	0.79	3.84
CB3.2	11/19/2008	8	1	AP	0.66	4.78	2.39	4.49
CB3.2	11/19/2008	11	1	B	3.81	5.61	5.10	4.81
CB3.2	11/19/2008	11	1	BP	4.56	4.86	5.47	4.81
CB3.2	12/17/2008	0.5	1	AP	0.42	8.37	0.43	10.04
CB3.2	12/17/2008	0.5	1	S	0.39	7.78	0.43	10.04
CB3.2	12/17/2008	6	1	BP	3.07	11.59	6.68	12.02
CB3.2	12/17/2008	11	1	B	-4.49	20.19	9.48	13.88
CB3.3C	11/19/2008	0.5	1	S	0.63	6.28	1.47	5.55
CB3.3C	11/19/2008	7	1	AP	1.88	4.19	1.09	5.34
CB3.3C	11/19/2008	15	1	BP	1.41	5.08	3.65	4.27
CB3.3C	11/19/2008	23	1	B	3.63	4.49	5.07	4.27
CB3.3C	11/19/2008	23	2	B	3.89	4.49	4.81	4.54
CB3.3C	12/17/2008	0.5	1	S	4.87	11.66	3.14	14.95
CB3.3C	12/17/2008	2	1	AP	2.03	11.36	3.70	12.60
CB3.3C	12/17/2008	8	1	BP	3.65	14.35	5.72	14.31
CB3.3C	12/17/2008	24	1	B	7.27	13.46	8.01	16.66
CB3.3C	12/17/2008	24	2	B	5.77	14.95	10.36	15.81

CB4.1C	12/17/2008	0.5	1	S	4.71	13.08	6.89	14.42
CB4.1C	12/17/2008	11	1	AP	6.24	12.34	6.78	14.15
CB4.1C	12/17/2008	21	1	BP	7.03	12.34	9.37	15.49
CB4.1C	12/17/2008	32	1	B	14.88	17.57	17.70	21.36
CB4.2C	12/17/2008	0.5	1	S	5.44	10.47	5.66	11.53
CB4.2C	12/17/2008	9	1	AP	4.43	8.97	4.91	10.04
CB4.2C	12/17/2008	17	1	BP	7.15	11.06	7.13	12.60
CB4.2C	12/17/2008	26	1	B	12.98	14.65	13.76	16.45
CB4.3C	11/17/2008	0.5	1	S	1.89	7.66	1.52	8.94
CB4.3C	11/17/2008	9	1	AP	0.56	4.67	1.66	4.14
CB4.3C	11/17/2008	17	1	BP	1.87	4.67	2.82	4.01
CB4.3C	11/17/2008	26	1	B	4.58	6.54	6.01	5.21
CB4.3C	12/17/2008	0.5	1	S	4.16	7.78	4.78	10.47
CB4.3C	12/17/2008	9	1	AP	5.14	6.58	4.06	9.40
CB4.3C	12/17/2008	19	1	BP	14.59	15.55	13.78	16.87
CB4.3C	12/17/2008	27	1	B	15.97	17.94	20.74	20.08
CB4.4	11/17/2008	0.5	1	S	1.12	8.04	1.59	8.41
CB4.4	11/17/2008	11	1	AP	1.27	5.79	1.72	5.47
CB4.4	11/17/2008	21	1	BP	1.55	4.86	2.47	4.54
CB4.4	11/17/2008	31	1	B	3.23	5.98	3.95	5.77
CB4.4	12/16/2008	0.5	1	S	2.62	6.54	3.00	7.74
CB4.4	12/16/2008	11	1	AP	3.16	6.92	4.57	9.08
CB4.4	12/16/2008	21	1	BP	6.34	10.28	7.94	13.08
CB4.4	12/16/2008	31	1	B	7.36	16.45	10.84	18.69
CB5.1	11/17/2008	0.5	1	S	1.51	8.04	1.47	8.81
CB5.1	11/17/2008	11	1	AP	0.3	5.98	1.47	6.01
CB5.1	11/17/2008	23	1	BP	1.61	4.67	2.50	4.14
CB5.1	11/17/2008	34	1	B	3.23	5.79	3.78	5.47
CB5.1	12/16/2008	0.5	1	S	3.03	5.61	3.87	7.34
CB5.1	12/16/2008	11	1	AP	5.06	8.41	5.97	10.01
CB5.1	12/16/2008	23	1	BP	8.67	11.21	8.36	12.95
CB5.1	12/16/2008	34	1	B	11.51	18.32	13.80	21.89
CB5.2	11/17/2008	0.5	1	S	1.01	9.72	1.36	10.41
CB5.2	11/17/2008	0.5	2	S	1.51	9.34	1.27	10.41
CB5.2	11/17/2008	9	1	AP	0.43	8.6	1.24	8.94
CB5.2	11/17/2008	19	1	BP	0.56	7.29	2.10	6.41
CB5.2	11/17/2008	30	1	B	1.89	5.05	2.80	4.67
CB5.2	12/16/2008	0.5	1	S	2.84	5.79	3.28	6.81
CB5.2	12/16/2008	0.5	2	S	2.21	6.17	2.40	6.94
CB5.2	12/16/2008	9	1	AP	3.48	5.42	3.74	6.54
CB5.2	12/16/2008	19	1	BP	3.31	5.98	2.66	7.34
CB5.2	12/16/2008	30	1	B	5.61	12.71	6.22	14.15
CB5.3	11/17/2008	0.5	1	S	0.47	6.73	0.43	7.61
CB5.3	11/17/2008	9	1	AP	0.34	6.73	1.12	7.48
CB5.3	11/17/2008	17	1	BP	0.37	4.86	1.66	5.07
CB5.3	11/17/2008	25	1	B	0.57	5.08	1.58	4.70
CB5.3	12/16/2008	0.5	1	S	2.37	5.61	2.35	6.81
CB5.3	12/16/2008	9	1	AP	1.48	5.98	2.39	6.68

CB5.3	12/16/2008	17	1	BP	2.56	6.73	3.55	7.48
CB5.3	12/16/2008	26	1	B	6.73	11.59	7.32	13.62
EE1.1	11/25/2008	0.5	1	S	1.2	13.46	2.03	13.48
EE1.1	11/25/2008	5	1	AP	0.39	14.39	2.39	13.22
EE1.1	11/25/2008	9	1	BP	1.08	15.14	2.72	14.28
EE1.1	11/25/2008	12	1	B	0.97	15.51	2.64	14.55
EE1.1	12/17/2008	0.5	1	S	1.5	4.78	6.19	1.58
EE1.1	12/17/2008	3	1	AP	1.29	4.78	6.84	1.54
EE1.1	12/17/2008	7	1	BP	2.12	4.78	6.62	1.15
EE1.1	12/17/2008	12	1	B	2.51	6.28	7.48	2.84
EE2.1	11/25/2008	0.5	1	S	0.78	9.16	1.46	10.41
EE2.1	11/25/2008	3	1	AP	1.93	8.41	1.91	10.15
EE2.1	11/25/2008	5	1	BP	0.22	9.72	1.92	10.41
EE2.1	11/25/2008	7	1	B	0.41	9.53	2.20	10.41
EE2.1	12/17/2008	0.5	1	S	2.75	4.78	4.91	3.31
EE2.1	12/17/2008	2	1	AP	3.56	4.19	4.91	3.31
EE2.1	12/17/2008	5	1	BP	3.68	4.49	5.77	3.05
EE2.1	12/17/2008	7	1	B	3.47	4.49	5.98	3.44
EE2.2	11/25/2008	0.5	1	S	0.75	8.41	0.92	9.08
EE2.2	11/25/2008	0.5	2	S	1.12	8.04	1.38	8.81
EE2.2	11/25/2008	10	1	B	0.58	8.97	1.44	9.21
EE2.2	12/17/2008	0.5	1	S	1.98	2.99	4.00	1.42
EE2.2	12/17/2008	0.5	2	S	1.79	3.18	3.60	2.00
EE2.2	12/17/2008	11	1	B	2.67	4.49	5.16	2.94
ET4.2	11/25/2008	0.5	1	S	0.37	12.71	2.06	13.08
ET4.2	11/25/2008	5	1	AP	0.37	12.71	1.86	12.82
ET4.2	11/25/2008	9	1	BP	1.55	11.4	1.94	13.48
ET4.2	11/25/2008	13	1	B	2.54	10.28	3.96	10.15
ET4.2	12/17/2008	0.5	1	S	6.28	10.47	12.18	7.26
ET4.2	12/17/2008	5	1	AP	6.46	9.87	12.18	9.21
ET4.2	12/17/2008	9	1	BP	7.6	9.57	13.24	9.18
ET4.2	12/17/2008	13	1	B	7.6	9.57	13.46	11.06
LE2.3	11/17/2008	0.5	1	S	1.57	7.85	1.47	7.88
LE2.3	11/17/2008	7	1	AP	1.7	6.54	0.64	7.21
LE2.3	11/17/2008	13	1	BP	-0	6.28	2.07	5.55
LE2.3	11/17/2008	19	1	B	2.06	5.68	3.14	5.98
LE2.3	12/16/2008	0.5	1	S	1.12	5.42	1.09	6.01
LE2.3	12/16/2008	7	1	AP	1.48	5.98	1.83	6.68
LE2.3	12/16/2008	13	1	BP	4.35	11.21	5.69	11.88
LE2.3	12/16/2008	19	1	B	4.58	10.47	6.54	11.21
WT5.1	11/25/2008	0.5	1	S	6.34	22.13	8.65	26.49
WT5.1	11/25/2008	5	1	AP	5.95	22.73	7.39	26.70
WT5.1	11/25/2008	11	1	BP	2.42	19.14	4.91	20.51
WT5.1	11/25/2008	16	1	B	5.92	15.85	8.39	16.87
WT5.1	12/16/2008	0.5	1	S	0.84	12.56	11.96	2.24
WT5.1	12/16/2008	2	1	AP	-0.84	12.56	11.96	2.24
WT5.1	12/16/2008	13	1	BP	1.41	5.08	5.13	2.35
WT5.1	12/16/2008	14.7	1	B	0.93	5.98	4.49	2.99

Appendix B
Plots of pheophytin and chlorophyll data by month and layer

Figure B-1. November surface pheophytin data.

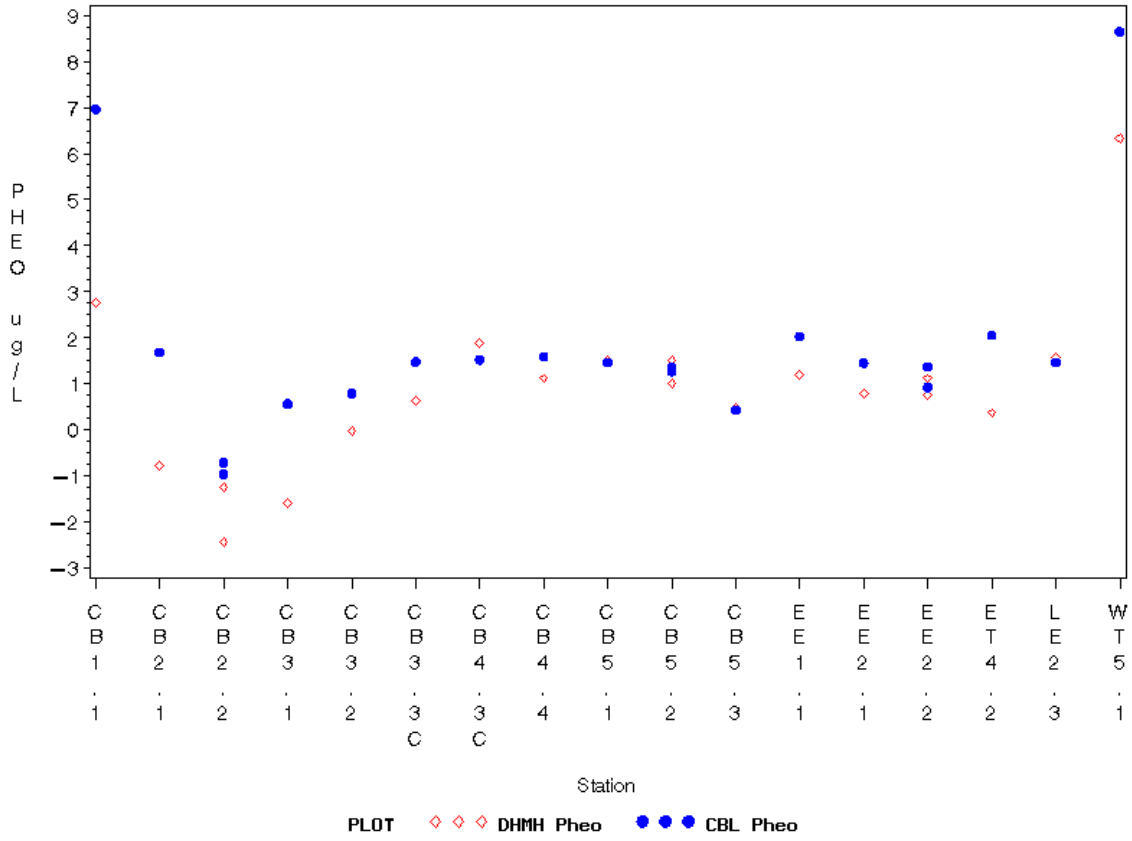


Figure B-2. November above pycnocline pheophytin data.

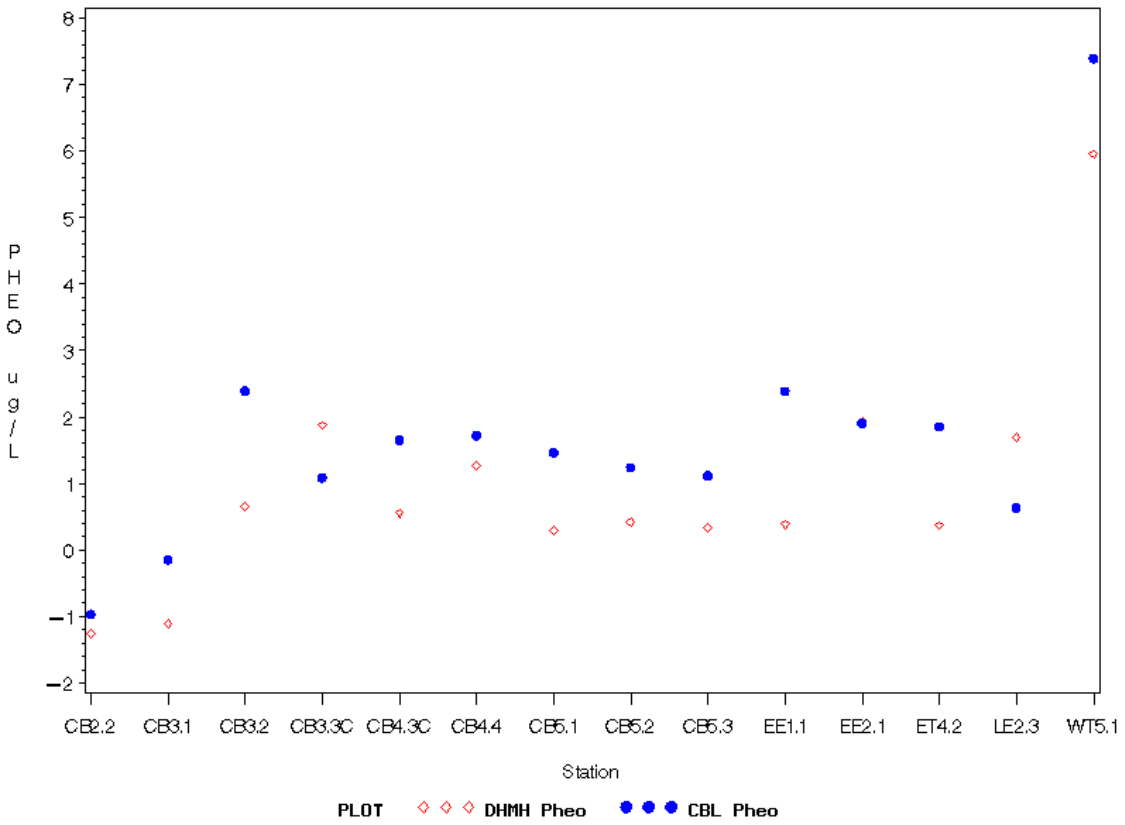


Figure B-3. November below pycnocline pheophytin data.

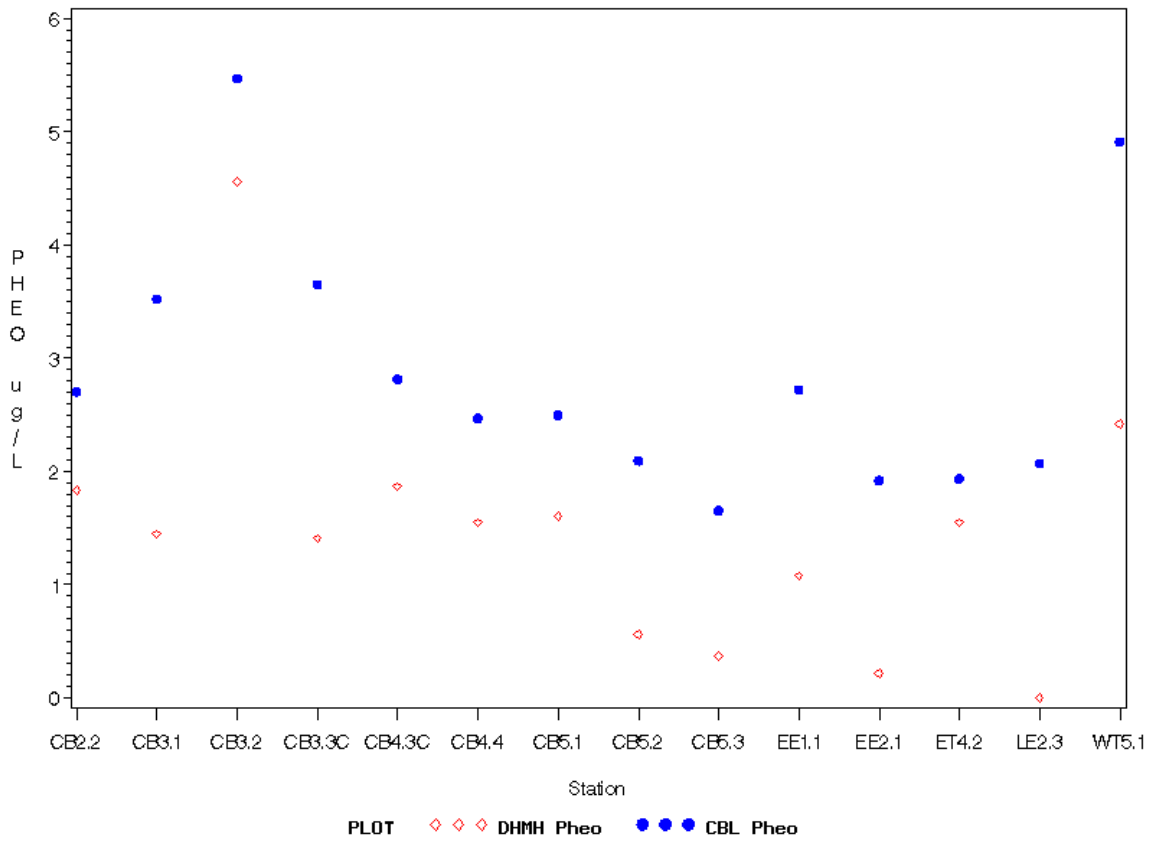


Figure B-4. November bottom pheophytin data.

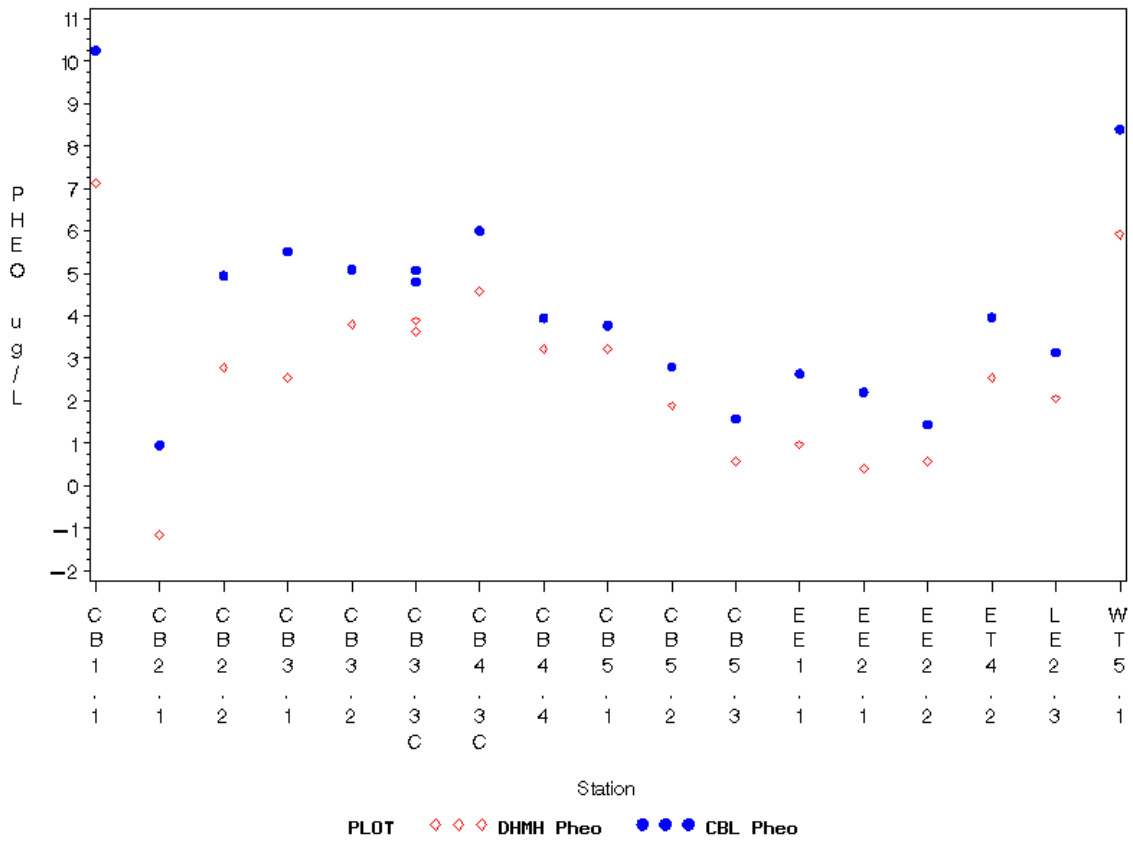


Figure B-5. December surface pheophytin data.

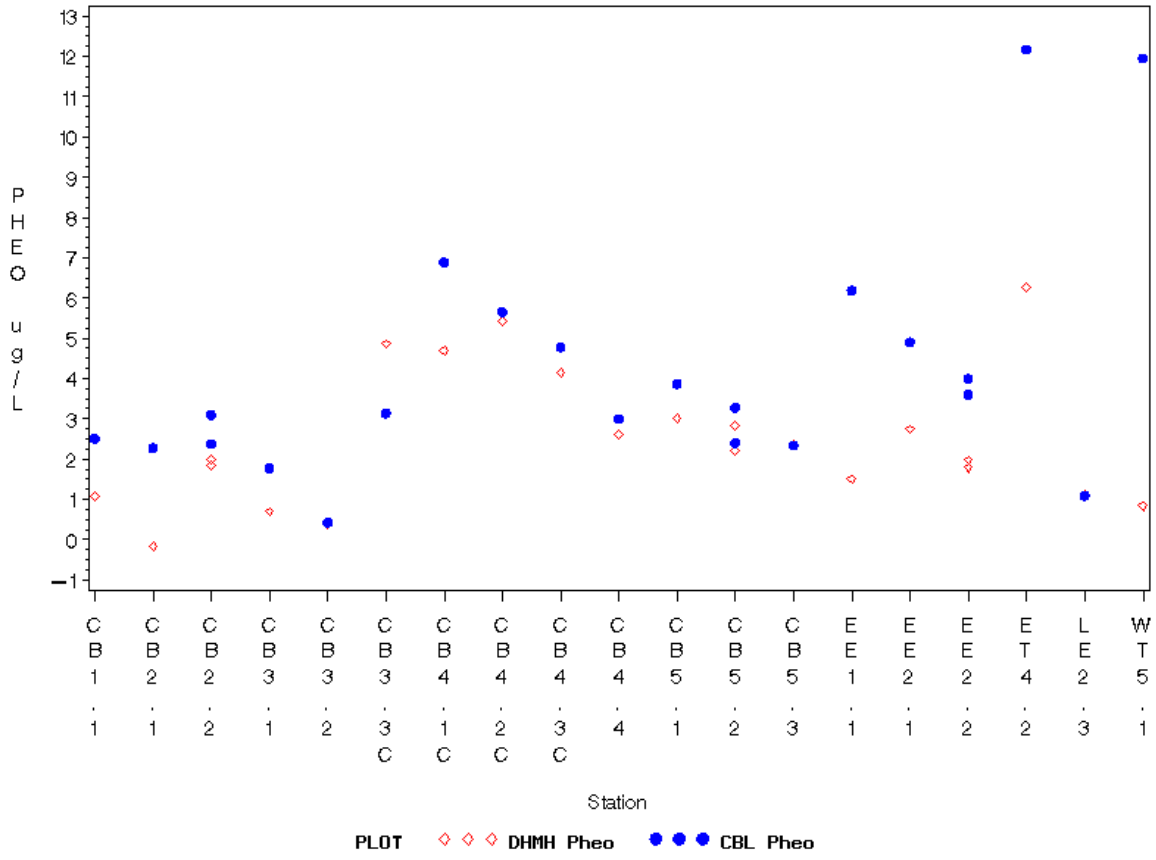


Figure B-6. December above pycnocline pheophytin data.

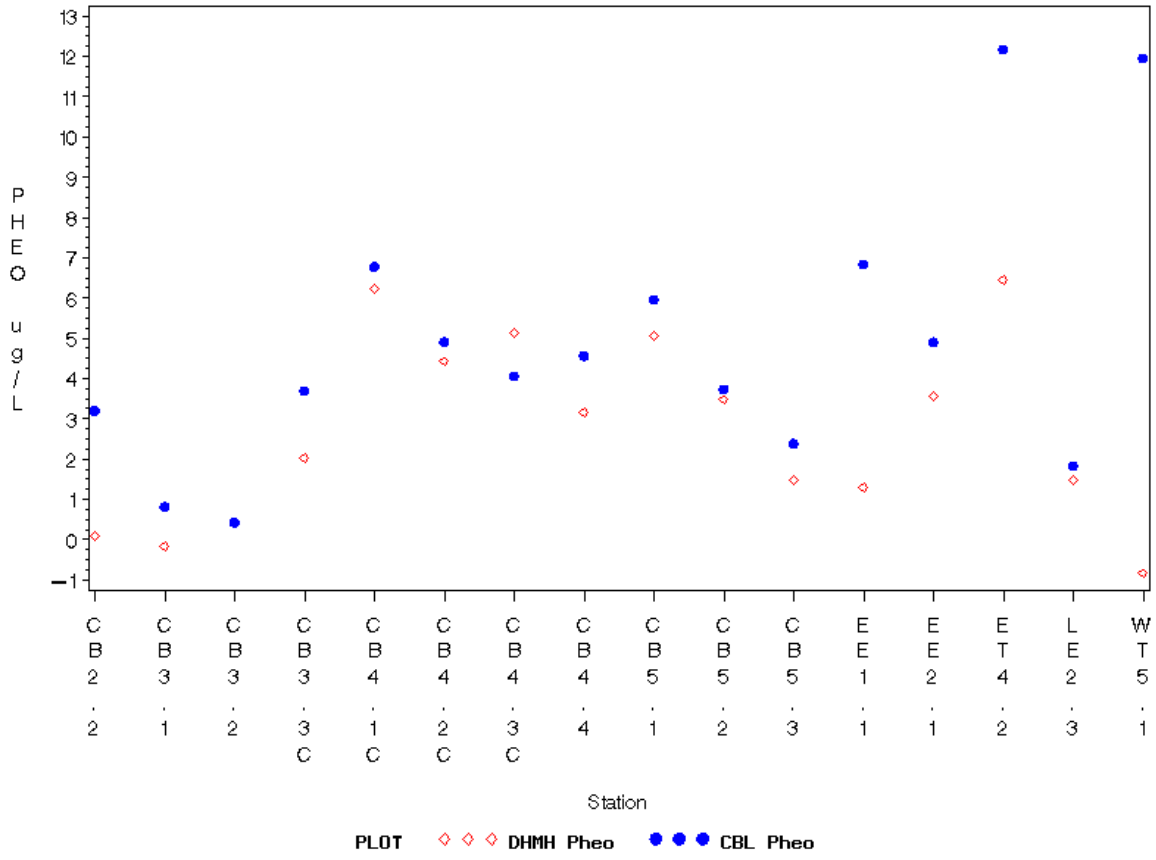


Figure B-7. December below pycnocline pheophytin data.

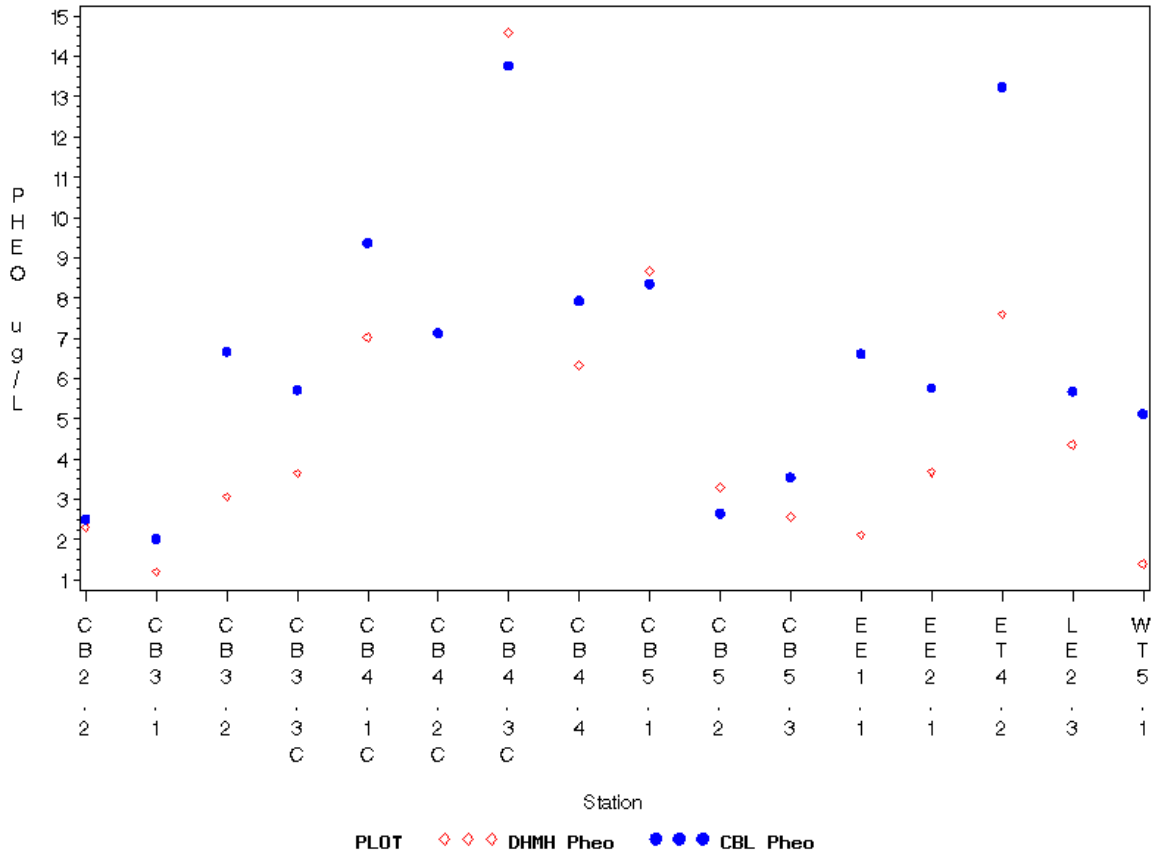


Figure B-8. December bottom pheophytin data.

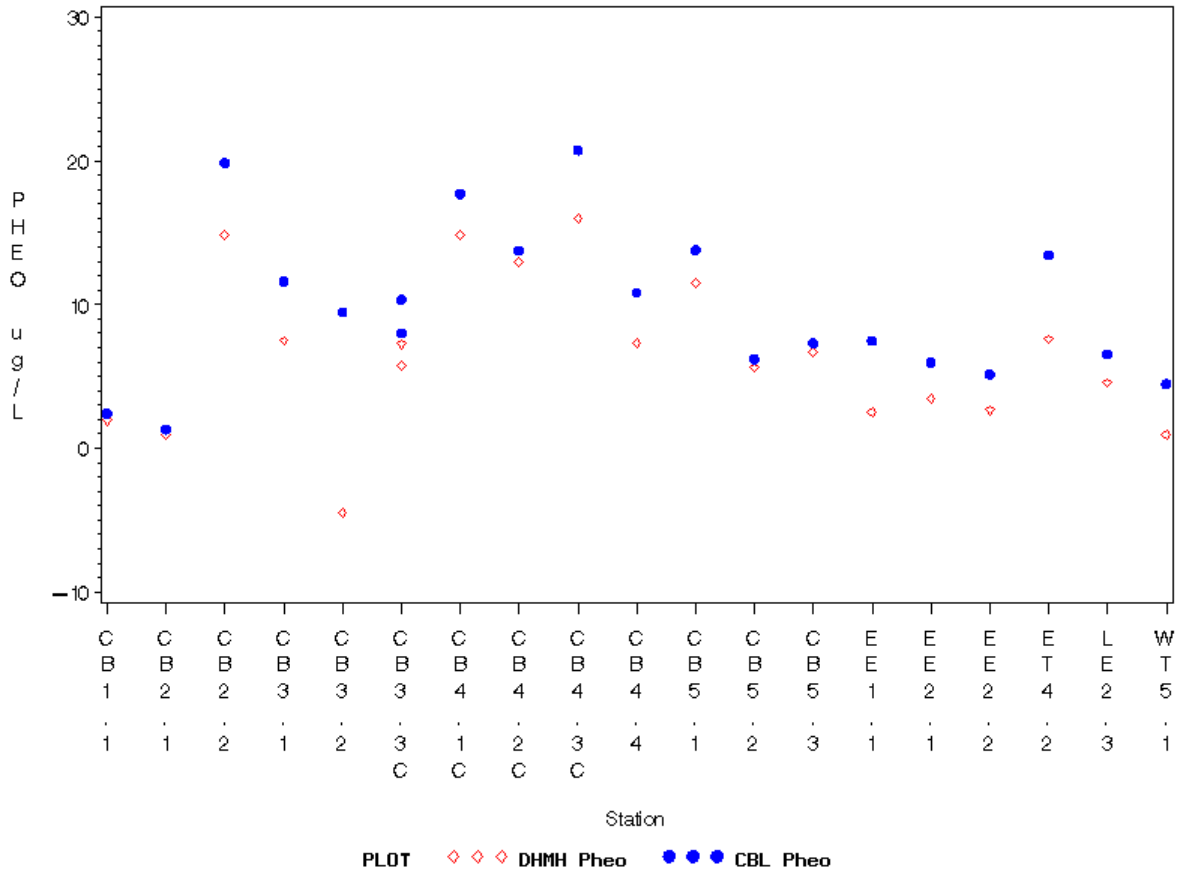


Figure B-9. November surface chlorophyll data.

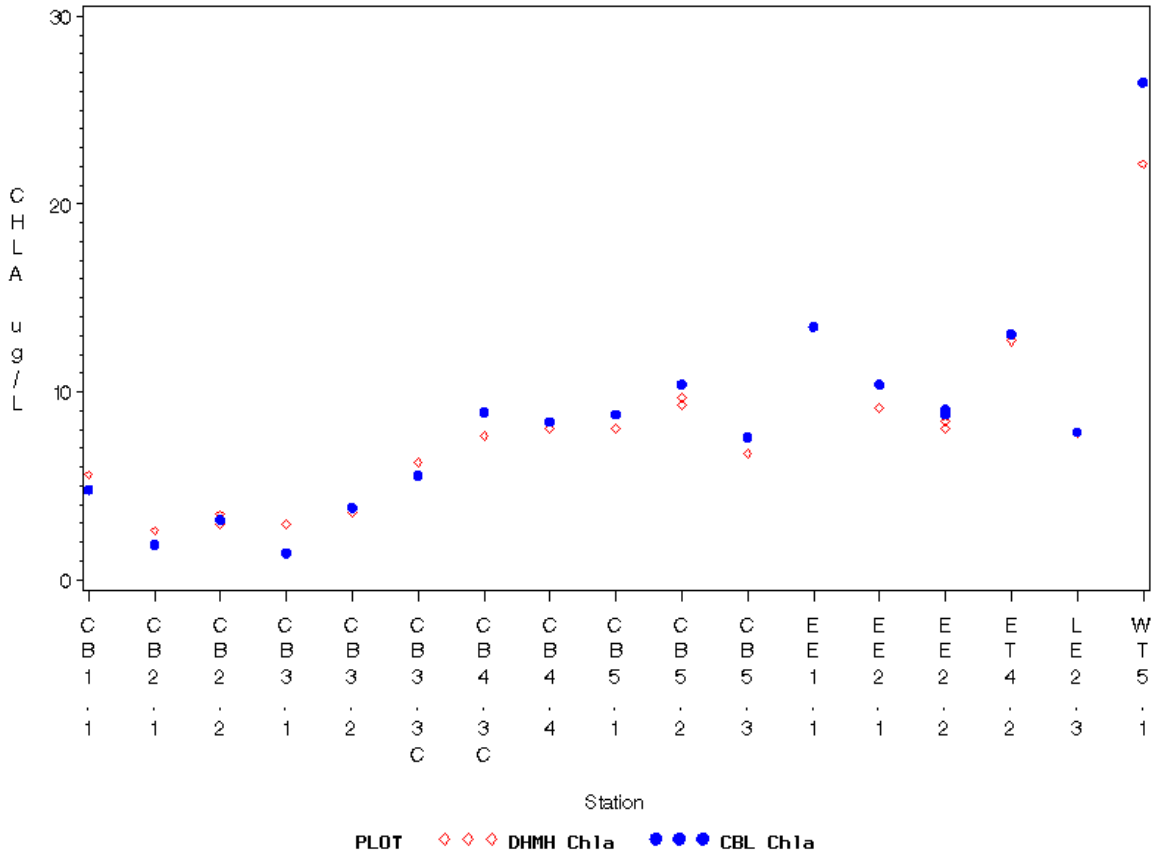


Figure B-10. November above pycnocline chlorophyll data.

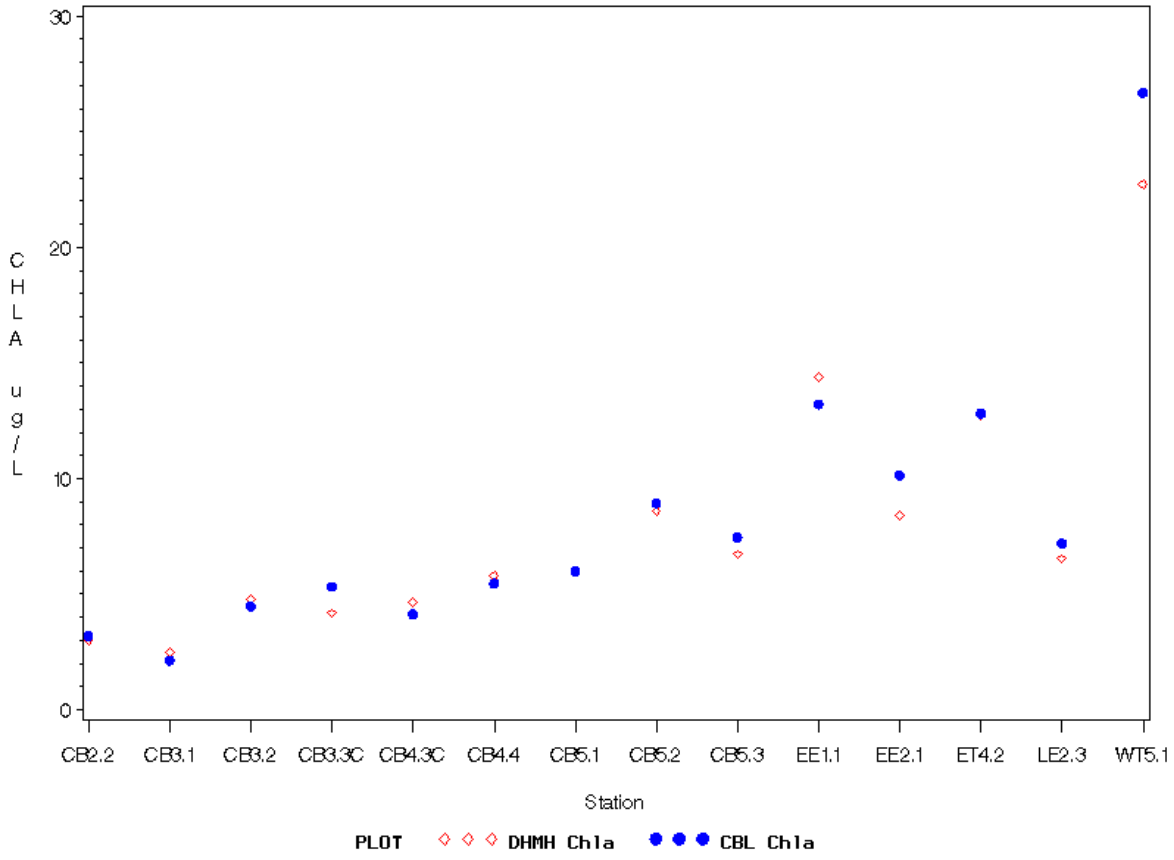


Figure B-11. November below pycnocline chlorophyll data.

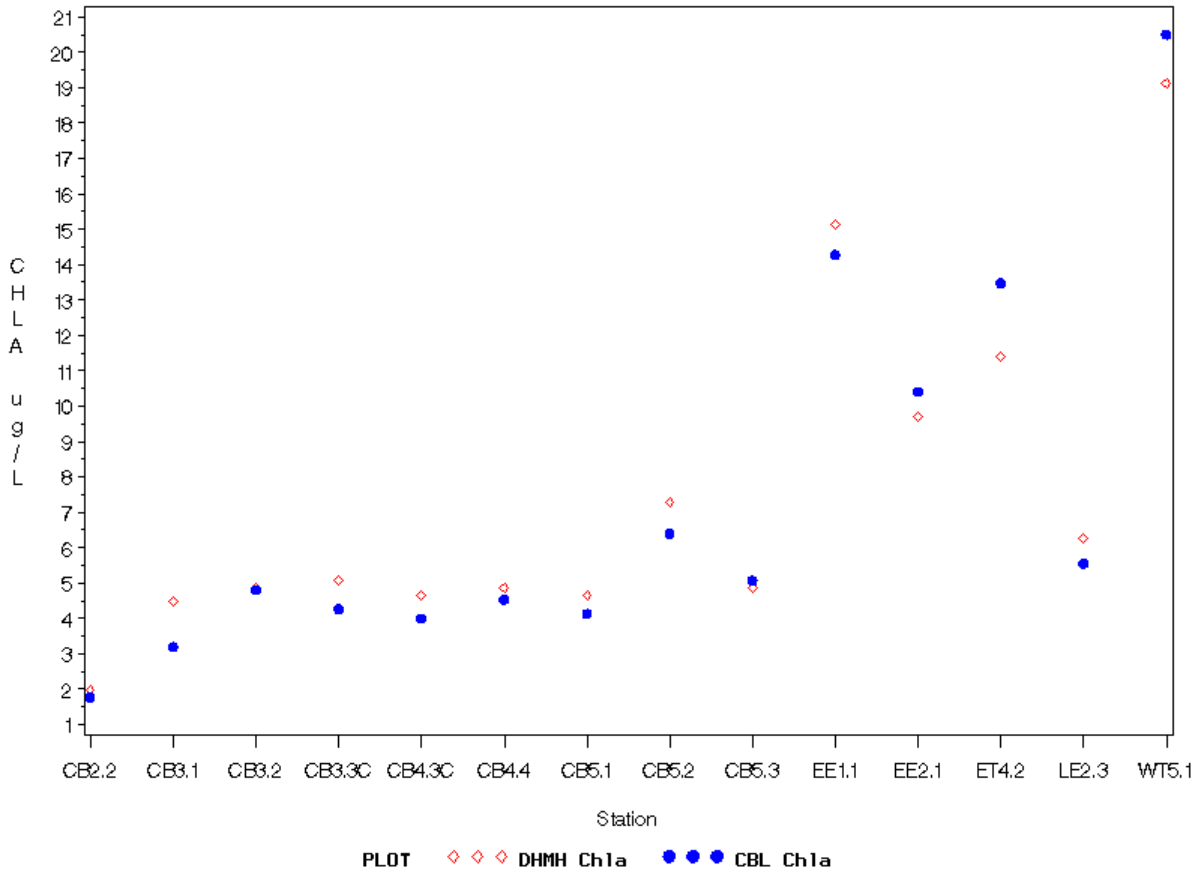


Figure B-12. November bottom chlorophyll data.

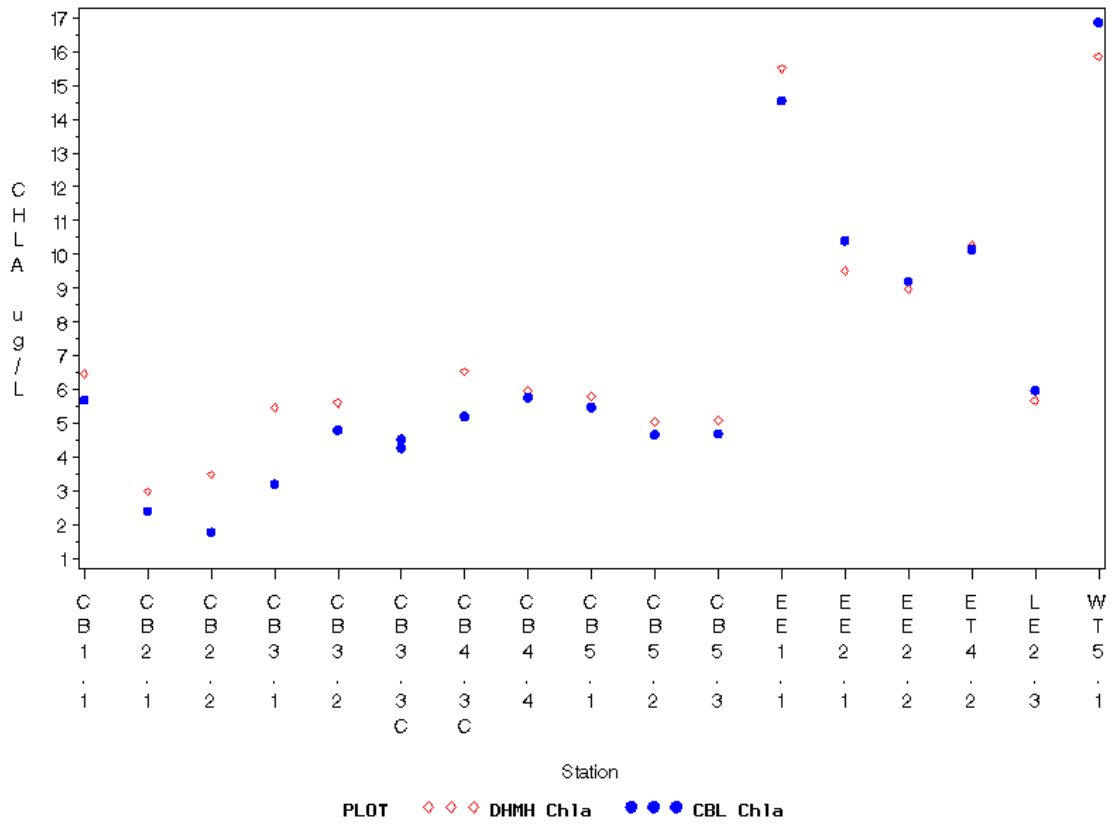


Figure B-13. December surface chlorophyll data.

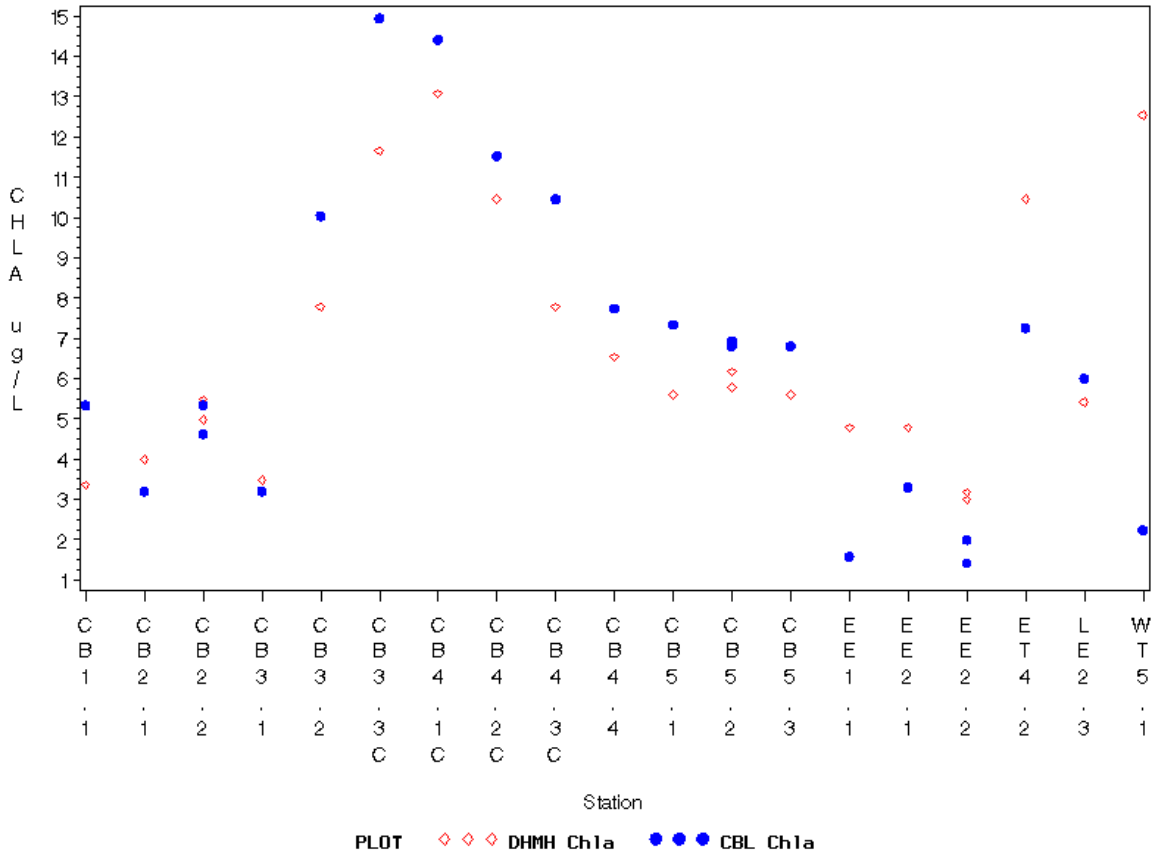


Figure B-14. December above pycnocline chlorophyll data.

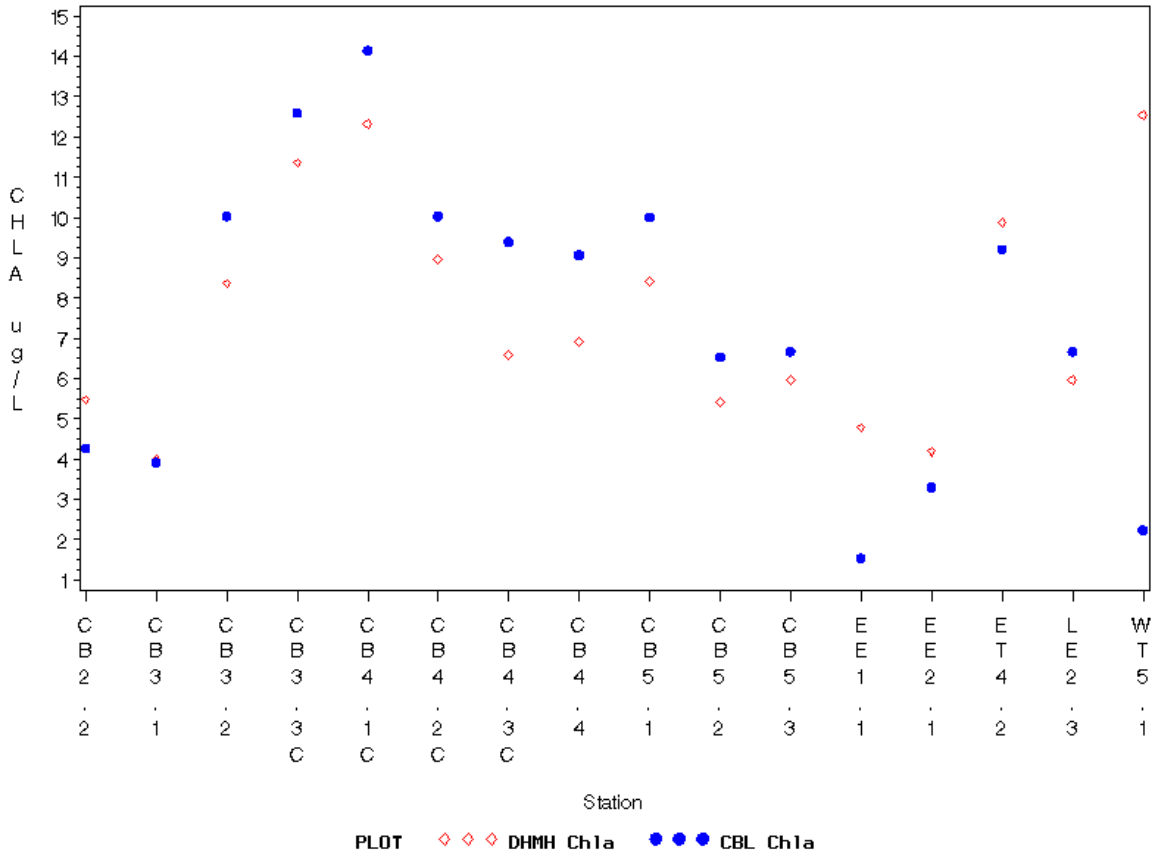


Figure B-15. December below pycnocline chlorophyll data.

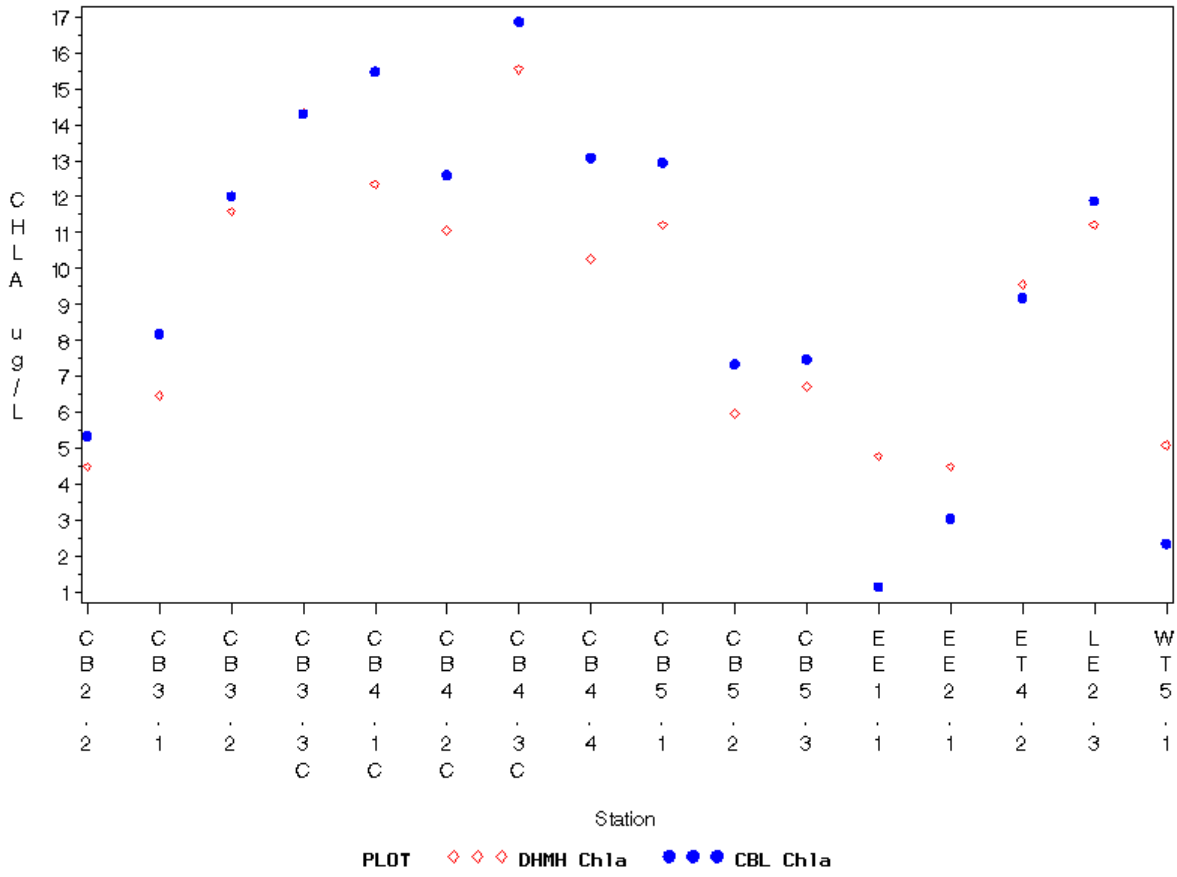
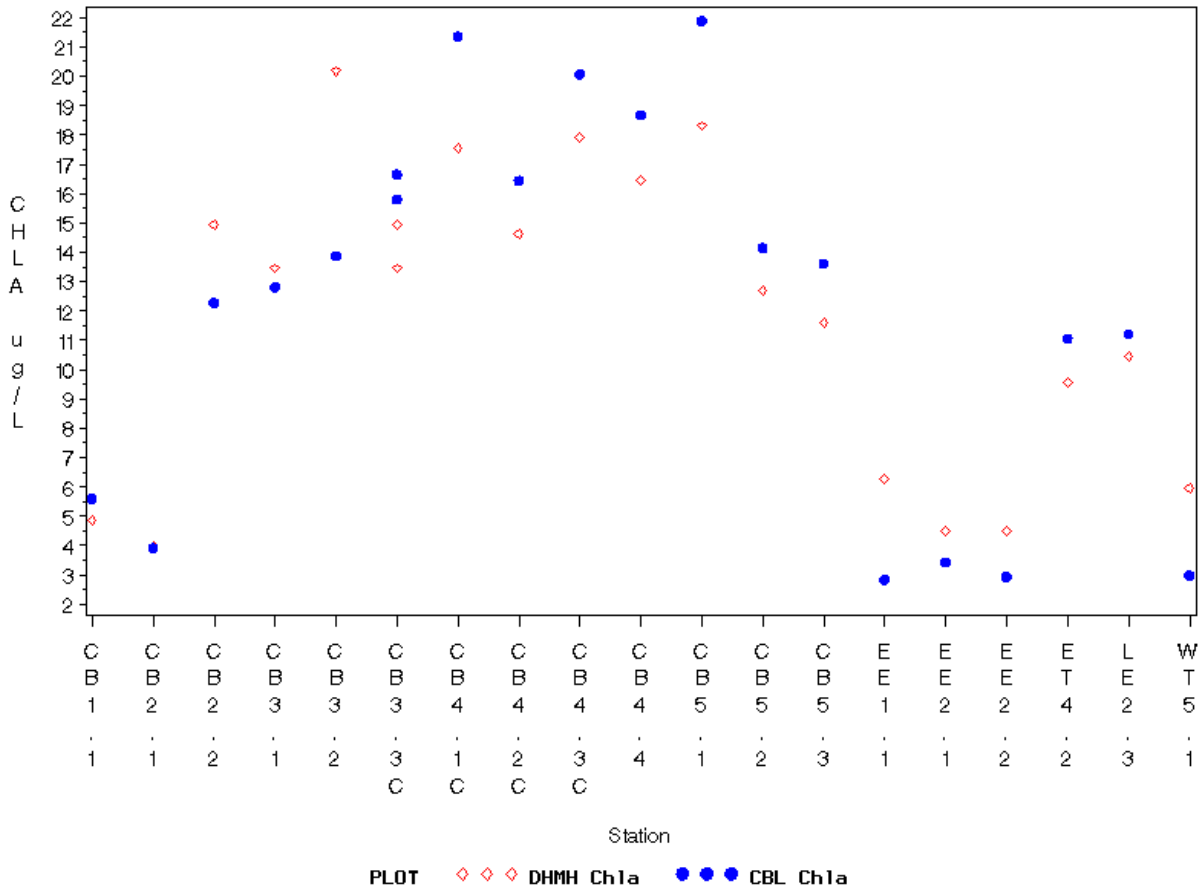


Figure B-16. December bottom chlorophyll data.



CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 048

CATEGORY CODE: Analytical Methods (AM)

ISSUE TITLE: Comparison of total suspended solids samples analyzed using Whatman and Environmental Express filter pads

DATE OF INTRODUCTION OF THIS TO THE SYSTEM: January 2010

STATEMENT OF ISSUE:
The Maryland Department of Health and Mental Hygiene (DHMH) analyzed water samples collected under the CORE/Trend monitoring program from the mid-1970s to the present. The CORE/Trend monitoring program currently consists of a network of 54 stations located in non-tidal areas. A list of the non-tidal CORE/Trend stations appears in Appendix A. DHMH also analyzes samples collected under the non-tidal network monitoring program, which started in July 2005 and continues to the present time. The non-tidal network is a network of 13 stations located in non-tidal areas where enhanced monitoring allows for the calculation of nutrient and sediment loads. A list of the non-tidal network stations appears in Appendix B.

Samples collected for the analysis of total suspended solids (TSS) in the CORE/Trend and non-tidal network monitoring programs were historically filtered using Whatman 24 mm diameter, 1.5 micro meter pore size filter pads from the start of the CORE/Trend and non-tidal network monitoring programs to June 2009. In July 2009, DHMH switched pad manufacturers for TSS from Whatman to Environmental Express, which produces 47 mm diameter, 1.5 micro meter pore size pads. In an attempt to assess any potential impacts on monitoring results (i.e., step trends) that could result from the change in filter pad types, samples were collected at 35 of the 54 CORE/Trend stations. Thirty-four samples were collected in April and 32 samples were collected in May 2009 by the Maryland Department of Natural Resources (DNR) field office as part of routine sampling under the CORE/Trend monitoring program. Samples were also collected at five unknown stations by the Maryland Department of the Environment in March as part of the total maximum daily load program. CORE/Trend stations GUN0125, POT1472, and PXT0809 were only sampled in April and CON0180 and GWN0115 were only sampled in May. The remaining 30 stations were sampled in both April and May. No samples were collected under the non-tidal network monitoring program; however, because the methods and stream properties as similar, there is no reason to believe there would be a different response. The full data set used in these analyses is provided in Appendix C. The stations listed in Appendix A and B are the only stations potentially affected by this change in filter pads.

Note that data for CORE/Trend station TF1.0 (formerly PXT0603) will not be affected by the July 2009 filter pad change at DHMH, because the Chesapeake Biological Laboratory (CBL) started analyzing water quality samples for this station starting in July 2005. Although CBL uses the same pad manufacturer (Whatman) previously used by DHMH, CBL uses a smaller filter pad pore size (0.7 micro meter) to analyze their TSS

samples. Other studies comparing the effect of changing from a 1.5 micro meter pore size pad to a 0.7 micro meter pore size pad have indicated that a positive step increase is likely to occur resulting from the smaller pore size pad filtering more suspended material. Therefore, analysts who work with TSS data for TF1.0 should be advised of the possibility of a positive step increase in the data that may have resulted from the change in laboratories and filter pad pore sizes that occurred in July 2005.

PROPOSED SOLUTION:

An experiment was conducted to assess the potential for step trends in the data that could result from the change from Whatman to Environmental Express filter pads where the 71 samples were sub-sampled and analyzed using both pad types. For each sample, the sub-sample for the Whatman pad was extracted before the sub-sample for the Environmental express pad. Based on the analyses described below, it does not appear that the change of filter pads results in methods induced change in the TSS data.

DISCUSSION:

Graphical comparisons

A plot of the 71 data pairs indicates that with the exception of sample number 49 (Figure 1), which has a difference of 220 mg/L, the two filter pad types produce similar results. Sample number 49 (DHMH laboratory sequence number 1775) was collected at Potomac River CORE/Trend station POT2386 on 4 May 2009. Comments on the field sheet (field sequence number 0905C18) indicate that the sample was collected under high flow conditions. Field office staff stated that the "Maryland side of [the] River [is] muddy; debris and mud [are coming] from [an] upstream tributary." Similar high flow and muddy conditions were also reported for other stations sampled on that date. In addition, some stations could not even be sampled due to flooding. Sample 49 is clearly an outlier that should not dictate the results of the remaining 70 pairs of observations, so based on professional judgment sample 49 was deleted from further analyses.

A graph of the differences (calculated as Environmental Express minus Whatman) is presented in Figure 2. Most of the differences (43) are positive and range from 0.3 to 33 mg/L. Twenty three differences are negative and range from -66.4 to -0.2 mg/L. Four differences are zero. The number of positive differences in this comparison indicates that the Environmental Express pads are biased high relative to the Whatman filter pads.

One possible explanation for the positive bias in the Environmental Express pads is that DHMH staff poured the Whatman sample aliquots into a graduated cylinder first, since that was the routine filter used at the time; aliquots for the Environmental Express pads were poured second. If the samples were not well mixed it is possible that the Environmental Express aliquot could have had more suspended material as a result of settling. An unbiased procedure would have been to systematically alternate the samples to pour first and then record the order with the data. With this information, the data analysts could assess if there was an order effect or a filter pad diameter effect.

Statistical comparisons

Basic statistics were calculated using Statistical Analysis System (SAS®) software and are presented in Table 1. The summary statistics presented in Table 1 show that the TSS concentrations obtained using the two different filter pad types are remarkably close. There is only a difference of 0.82 mg/L between the two means, which is below the DHMH method detection limit of 1.88 mg/L.

Table 1. Basic statistics for the pad types (sample number 49 deleted).

Pad type	N	Mean	Std. Dev.	Minimum	Maximum
Whatman	70	34.42	62.6	1.5	408
Environmental Express	70	35.24	63.0	1.5	421

The filter pad concentrations were also compared statistically using the Wilcoxon Signed Rank test on the log ratio of the Environmental Express samples to the Whatman samples [i.e., log (Environmental Express\Whatman)]. Taking the logarithm of each datum and then subtracting the Whatman value from its corresponding Environmental Express value calculates this log ratio. The log ratio is based on the principle of logarithms that states: $\log_b x - \log_b y = \log_b(x/y)$. Working with log-transformed data (base 10 was used in these analyses) also helps meet the symmetry assumption of the Wilcoxon Signed Rank test. A probability value (p-value) for the Wilcoxon Signed Rank test of ≤ 0.05 is assumed to indicate a statistically significant difference between the filter pad types.

The p-value for the log ratio was 0.013, which based on the above criterion is a statistically significant difference; however, the p-value for a paired t-test indicates the two filter pads do not produce significantly different results (p=0.1098). Based on the output of SAS PROC UNIVARIATE with the NORMAL PLOT options, the variable log10Diff appears to be symmetrical, but the results of the Shapiro-Wilk test of normality indicate that the data are not from a normal distribution (p<0.0001). Therefore, the t-test results are not used in this assessment.

Although the difference between the filter pad types is statistically significant (p=0.013), as shown in Table 1, the difference is small relative to measurement error (i.e. detection limit) and very small relative to environmental variability (Figure 2). Therefore it is reasonable to infer that while the difference is statistically significant, it is not important. In addition, it is not clear if the minor difference is the result of the filter pad diameter or the order in which the samples were sub-sampled (All of the Whatman samples were obtained first.) Because the difference is small and it is likely that it is an artifact of laboratory procedure, it is recommended that no data adjustment is needed as a result of this filter change.

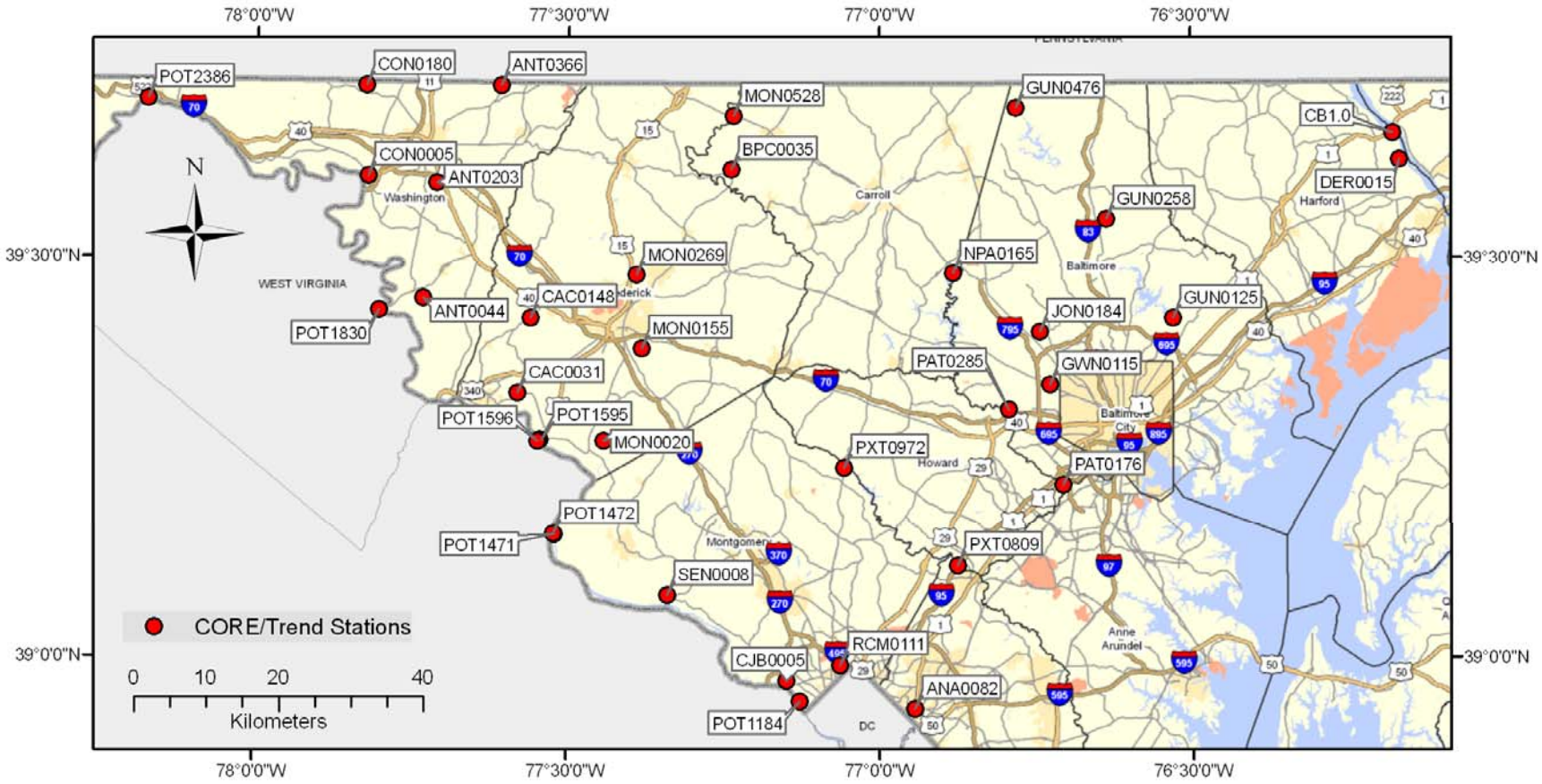


Figure 1. CORE/Trend stations that were sampled as part of this comparison.

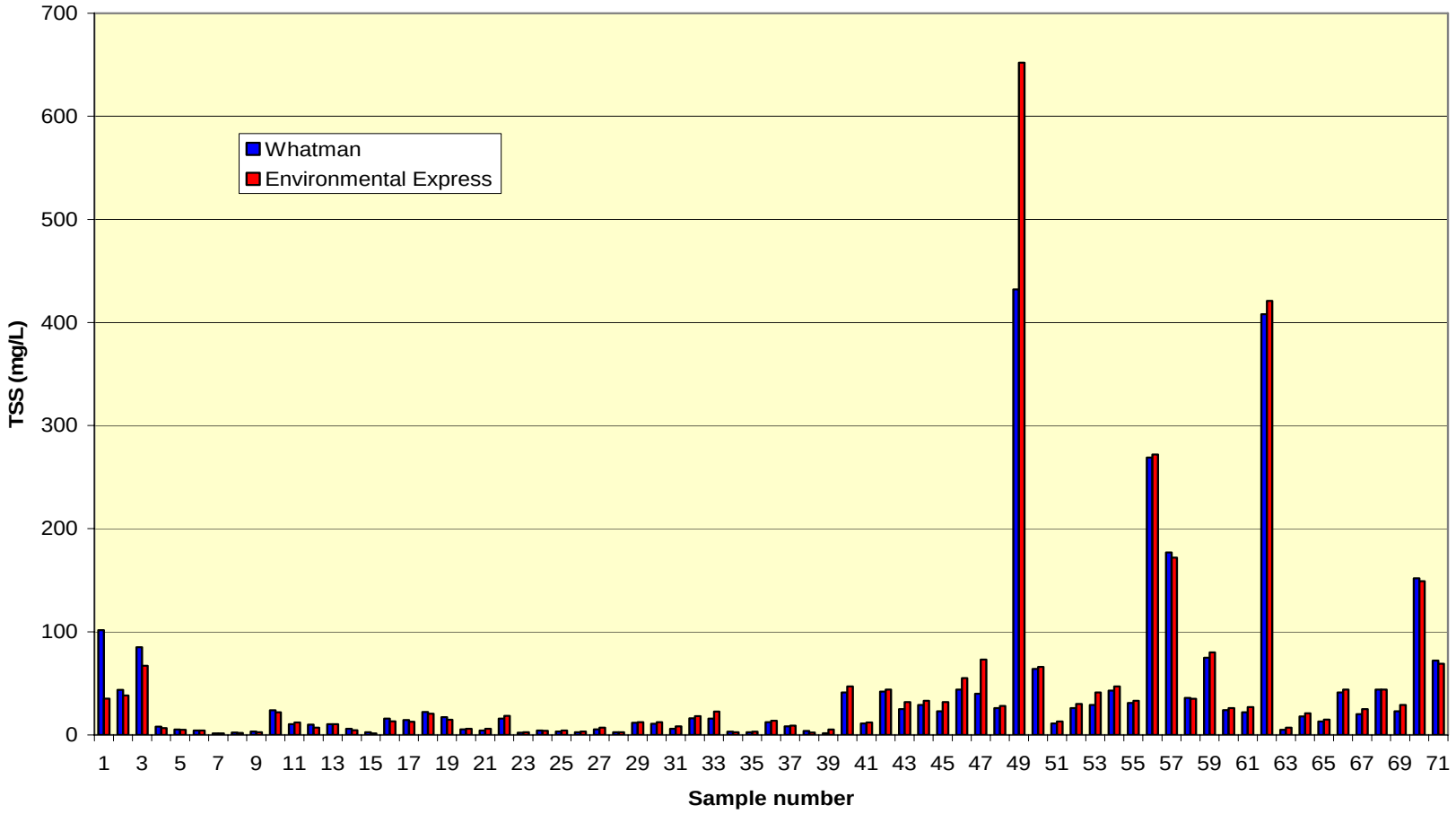


Figure 2. Comparison of Whatman and Environmental Express filter pads.

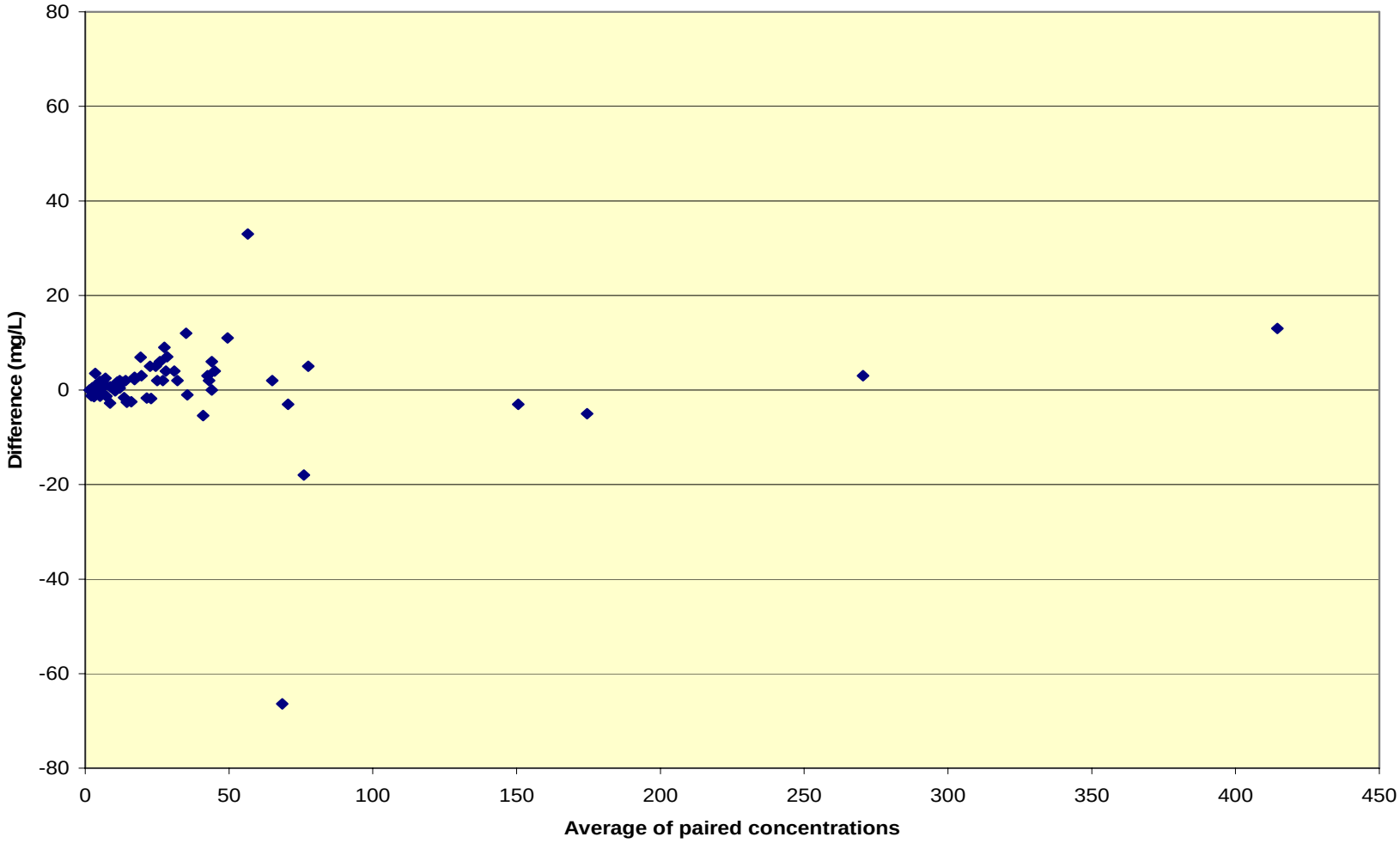


Figure 3. Difference between Environmental Express and Whatman filter pads plotted against the average of the two pads.

SENSE OF THE RESOURCES NEEDED TO RESPOND:
Members of the Analytical Methods and Quality Assurance Workgroup (AMQWA) and data analysts are requested to review this document and provide comments by 31 January 2010.

PRIORITY RANKING:
Two (low). The difference between Whatman and Environmental Express filter pads is statistically significant (p=0.013); however, the difference between the arithmetic means of the two pads is not meaningful (Table 1) and may be a result of the order in which the samples were filtered.

SUBMITTER/RESPONSIBLE PARTY:
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Natural Resources Biologist

Organization: Maryland Department of Natural Resources
580 Taylor Avenue, D-2
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ACTIONS TO DATE:
1) A graphical comparison of the data was presented to the Analytical Methods and Quality Assurance Workgroup by staff of DHMH during the quarterly meeting on 2 June 2009. 2) Prepared this report. Statistical analyses were performed in WhatmanvsEEpadsforTSS.SAS program.

OVERALL RESOLUTIONS SUMMARY OF ACTIONS:

RECOMMENDED ACTIONS:
It is recommended that DHMH routinely analyze a standard reference material (SRM) for TSS at a frequency of one per day or one per 25 samples. The percent recovery of the SRM must be calculated and tracked to evaluate bias or trends in the TSS methods over time.

Finally, although no step trend is expected to result in the data following the change in filter pads it would be prudent to re-visit this issue after a few years of post-change data become available.

ACTIONS NUMBER:
1. Designated Respondent:
2. Action:
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary:

Appendix A

Stations in the CORE/Trend monitoring network

1) ANA0082
2) ANT0044
3) ANT0203
4) ANT0366
5) BDK0000
6) BEL0053
7) BPC0035
8) CAC0031
9) CAC0148
10) CAS0479
11) CB1.0
12) CCR0001
13) CJB0005
14) CON0005
15) CON0180
16) DER0015
17) GEO0009
18) GUN0125
19) GUN0258
20) GUN0478
21) GWN0115
22) JON0184
23) LYO0004
24) MON0020
25) MON0155
26) MON0269
27) MON0528
28) NBP0023
29) NBP0103
30) NBP0326
31) NBP0461
32) NBP0534
33) NBP0689
34) NPA0165
35) PAT0176
36) PAT0285
37) POT1184
38) POT1471
39) POT1472
40) POT1595
41) POT1596
42) POT11830
43) POT2386
44) POT2766
45) PXT0809
46) PXT0972
47) RCM0111
48) SAV0000
49) SEN0008
50) TF1.0 (analyzed at Chesapeake Biological Lab starting July 2005)
51) TOW0030
52) WIL0013
53) YOU0925
54) YOU1139

Appendix B

Stations in the non-tidal network

1) ANT0047
2) BEL0053
3) GWN0115
4) DER0015
5) NPA0165
6) TF1.2
7) MON0546
8) TUK0181
9) WIL0013
10) GEO0009
11) GUN0258
12) PXT0972
13) CAC0148

Appendix C

Data used in this report

Date	SampleID	Sample Volume	Whatman Pad	Environmental Express Pad	Station Name
3/30/2009	2530001	58	101.7	35.3	MDE
3/30/2009	2530002	80	43.7	38.3	MDE
3/30/2009	2562001	150	85	67	MDE
3/30/2009	2562002	150	8	6.7	MDE
3/30/2009	2562003	150	5.3	5	MDE
4/7/2009	1546	300	4.2	4.2	PAT0176
4/7/2009	1547	300	1.5	1.5	PAT0285
4/7/2009	1549	300	2.3	2	NPA0165
4/7/2009	1550	300	3.3	2.5	JON0184
4/7/2009	1551	300	23.8	22	GUN0125
4/7/2009	1552	300	10.3	12	DER0015
4/7/2009	1553	300	10	7.2	CB1.0
4/7/2009	1554	300	10.5	10.3	CB1.0
4/7/2009	1555	300	5.8	4.5	GUN0476
4/7/2009	1556	300	2.7	1.5	GUN0258
4/7/2009	1557	300	15.8	13.2	ANT0366
4/7/2009	1559	300	14.3	12.7	ANT0203
4/7/2009	1560	300	22.2	20.5	CON0005
4/7/2009	1561	300	17.2	14.7	POT2386
4/10/2009	1572	300	5.5	5.8	PXT0809
4/10/2009	1573	300	4.2	6	PXT0972
4/10/2009	1574	300	15.8	18.5	POT1184
4/10/2009	1575	300	2.2	2.7	CJB0005
4/10/2009	1576	300	4.2	4	RCM0111
4/10/2009	1577	300	3.2	4.2	ANA0082
4/10/2009	1578	300	2.7	3.2	SEN0008
4/10/2009	1579	300	5.5	7	MON0155
4/10/2009	1580	300	2.7	2.7	CAC0031
4/10/2009	1581	300	11.8	12.2	POT1596
4/10/2009	1582	300	10.8	12.2	POT1595
4/10/2009	1583	300	5.8	8.3	MON0020
4/10/2009	1584	300	16	18.2	POT1471
4/10/2009	1585	300	15.8	22.7	POT1472
4/10/2009	1586	300	3	2.7	MON0528
4/10/2009	1587	300	2.7	3	BPC0035
4/10/2009	1588	300	12.2	13.8	POT1830
4/10/2009	1589	300	8.3	9	ANT0044
4/10/2009	1590	300	3.7	2.3	CAC0148
4/10/2009	1591	300	1.7	5.2	MON0269
5/13/2009	1762	300	41	47	PAT0176
5/13/2009	1763	300	11	12	PAT0285
5/13/2009	1764	300	42	44	GWN0115
5/13/2009	1765	300	25	32	NPA0165
5/13/2009	1768	300	29	33	JON0184
5/13/2009	1771	300	23	32	ANT0203
5/13/2009	1772	300	44	55	ANT0366

Comparison of total suspended solids samples analyzed using Whatman and Environmental Express filter pads

Date	SampleID	Sample Volume	Whatman Pad	Environmental Express Pad	Station Name
5/13/2009	1773	300	40	73	CON0180
5/13/2009	1774	300	26	28	CON0005
5/13/2009	1775	300	432	652	POT2386
5/13/2009	1776	300	64	66	DER0015
5/13/2009	1778	300	11	13	CB1.0
5/13/2009	1780	300	26	30	GUN0476
5/13/2009	1781	300	29	41	GUN0258
5/13/2009	1801	300	43	47	MON0155
5/13/2009	1802	300	31	33	CAC0031
5/13/2009	1803	300	269	272	POT1596
5/13/2009	1804	300	177	172	POT1595
5/13/2009	1805	300	36	35	MON0020
5/13/2009	1806	300	75	80	POT1471
5/13/2009	1807	300	24	26	SEN0008
5/13/2009	1809	300	22	27	PXT0972
5/13/2009	1810	300	408	421	POT1184
5/13/2009	1811	300	5	7	CJB0005
5/13/2009	1812	300	18	21	RCM0111
5/13/2009	1813	300	13	15	ANA0082
5/13/2009	1815	300	41	44	BPC0035
5/13/2009	1816	300	20	25	MON0528
5/13/2009	1817	300	44	44	MON0269
5/13/2009	1818	300	23	29	CAC0148
5/13/2009	1819	300	152	149	POT1830
5/13/2009	1820	300	72	69	ANT0044

CHESAPEAKE BAY PROGRAM DATA ANALYSIS ISSUES TRACKING SYSTEM

ISSUE TRACKING NUMBER: 049

CATEGORY CODE: Analytical Methods (AM)

ISSUE TITLE: Comparison of alkaline phenol and salicylate NH4 analysis methods at the Maryland Department of Health and Mental Hygiene

DATE OF INTRODUCTION OF THIS TO THE SYSTEM: September 2010

STATEMENT OF ISSUE:
The Maryland Department of Health and Mental Hygiene (DHMH) analyzed water quality samples for NH4 using the alkaline phenol (phenate) method from the 1980s through 24 March 2010. On 25 March 2010 DHMH changed to the salicylate method (Lachat Method 10-107-06-2-O) to eliminate staff exposure to hazardous phenol vapors, reduce hazardous waste removal costs, and achieve better precision in their results.

Any change in methods has the potential to affect long term trend results. This change could potentially affect all of the monitoring stations that have samples analyzed at DHMH. Stations where an impact is most likely to be observed include those with a long historical record and that will be sampled long into the future. Long term monitoring programs that may be affected include the CORE/Trend, non-tidal network, and coordinated split sample programs. Stations sampled as part of the Deep Creek Lake monitoring program are less likely to be affected, since that program has a much shorter sampling record and may not be continued long into the future.

Monitoring stations in the CORE/Trend network that may be affected by this change in methods are listed in Appendix A, stations in the non-tidal network are listed in Appendix B, and the station in the coordinated split sample program is PMS10 on the Potomac River.

The monitoring results generated by DHMH are submitted by the Maryland Department of Natural Resources (DNR) to the U.S. Environmental Protection Agency Chesapeake Bay Program for inclusion in the publicly available Chesapeake Information Management System (CIMS) data base.

PROPOSED SOLUTION:
DHMH split and analyzed NH4 samples that were collected in December 2009 and January 2010 as part of the routine CORE/Trend monitoring program, the non-tidal network program, the coordinated split sample program, stations sampled by the Maryland Department of the Environment (MDE) for the Total Maximum Daily Load program, and seven de-ionized water blanks. Data from the monitoring programs and the blanks were combined to assess the potential for step trends that may result from changing from the phenate to the salicylate method. These data are presented in Appendix C.

BACKGROUND:
Laboratory notes
The phenate method involves a reaction between ammonia, phenol, and hypochlorite in an alkaline solution, which results in an intense blue

product (indophenol). The blue color is proportional to the ammonia concentration, which is assessed using a colorimeter. The salicylate method is a variation of the phenate method that does not require the use and disposal of the toxic compound phenol. The salicylate method involves a series of reactions that form 5-aminosalicylate, which is oxidized to form a blue-green colored dye that is proportional to the amount of ammonia present in the sample.

Basic statistics

Basic statistics for the data set were calculated using Statistical Analysis System (SAS®) software and are presented in Table 1. As shown in Table 1 the means and standard deviations for NH4 measured by the two methods are virtually identical and the minimums and maximums are quite close. The mean difference between the methods (calculated as salicylate minus phenate) of approximately 0.0028 mg/L is 1.75 times larger than the proposed 2010 NH4 method detection limit of 0.0016 mg/L. Although the mean absolute difference between the methods is quite small, the relative percent difference, calculated as salicylate method minus phenate method divided by the mean of both, ranges from -600 percent to 1,000 percent. The range in the relative percent differences is quite large.

Table 1. Basic statistics for the comparison of the salicylate and phenate methods.

Method	N	Mean	Std. Dev.	Minimum	Maximum
Salicylate	148	0.043	0.150	-0.005	1.611
Phenate	148	0.040	0.151	-0.008	1.648

Graphical comparisons

In addition to the statistical comparison, these data are compared graphically below. Notched box and whisker plots show the range in concentrations, the inter-quartile range, the median, and the mean of the distribution. The endpoint of the notches show the median plus and minus 1.58*(inter-quartile range/√n). The box plots presented in Figure 1 are difficult to interpret because the wide range in outlying concentrations compresses the central part of the plot.

The methods were also compared using a one-to-one line plot, which shows one method plotted against the other with the plot axes set to the same length. The one-to-one line plot in Figure 2 shows how similar the results are and shows the positive bias associated with the salicylate method, since most of the data fall just above the one-to-one line.

Differences between methods are sometimes a function of the concentration, with the differences often increasing as the concentrations increase. The differences between the salicylate and phenate methods (calculated as salicylate minus phenate) were plotted against the mean of both methods to determine if the differences change as a function of the concentration (Figure 3). Although there is quite a range in the concentrations, most are clustered at the low end of the distribution. The plot does illustrate the positive bias associated with the salicylate method. Of the 148 data pairs, 28 have negative differences (below the zero reference line), 14 have zero differences (on the zero reference line), and 106 have positive differences (above the zero reference line. The median difference (blue line in Figure 3) is 0.002 mg/L.

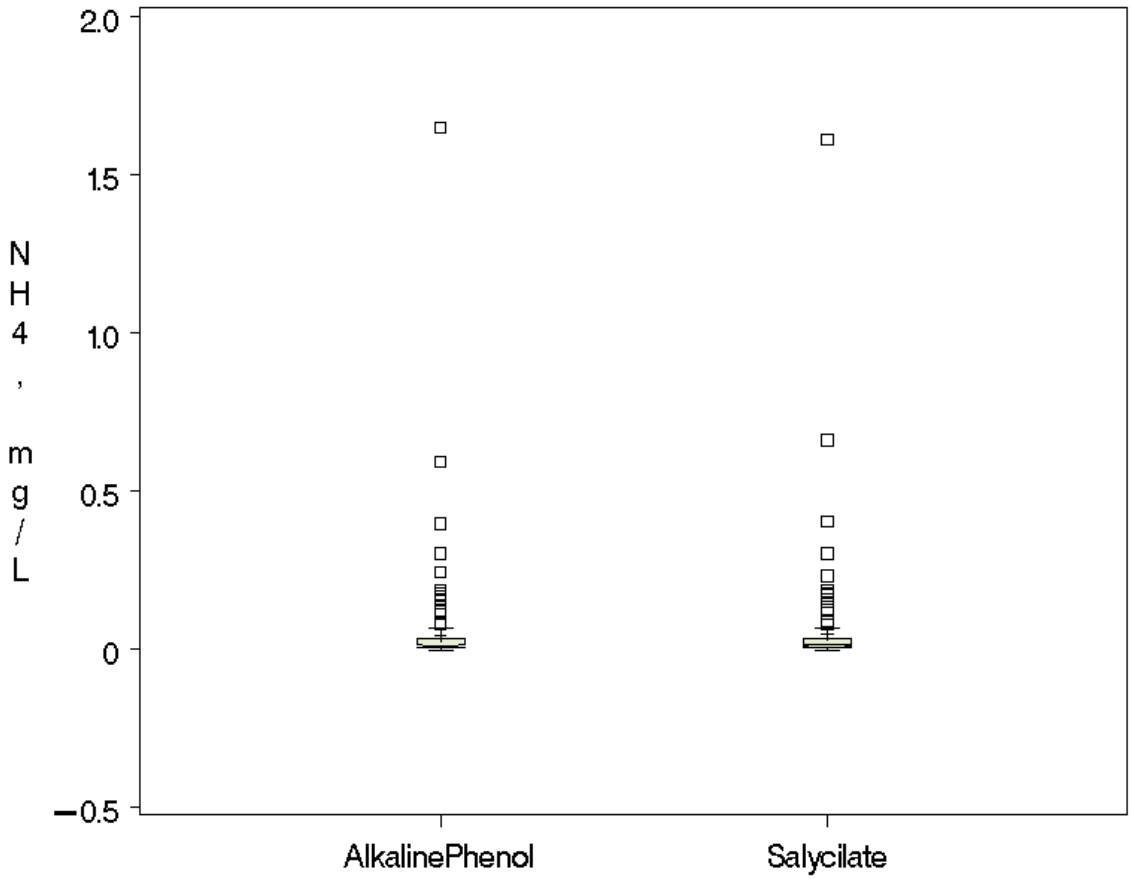

Figure 1. Box plots comparing laboratory methods for the analysis of ammonia.

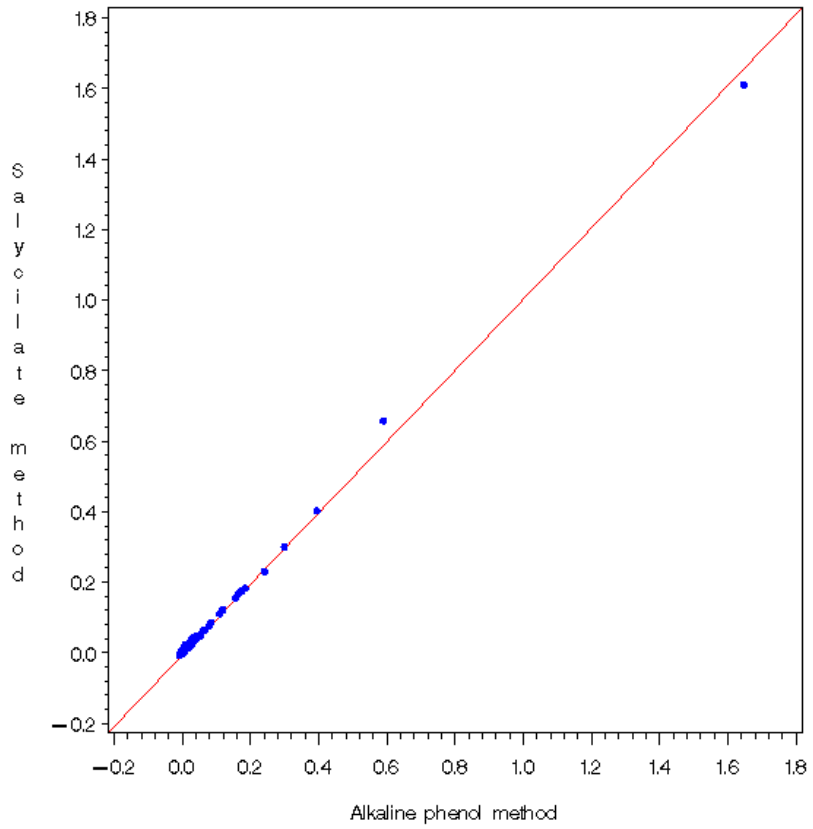

Figure 2. One-to-one line plot comparing the salicylate and phenate methods for analyzing ammonia samples.

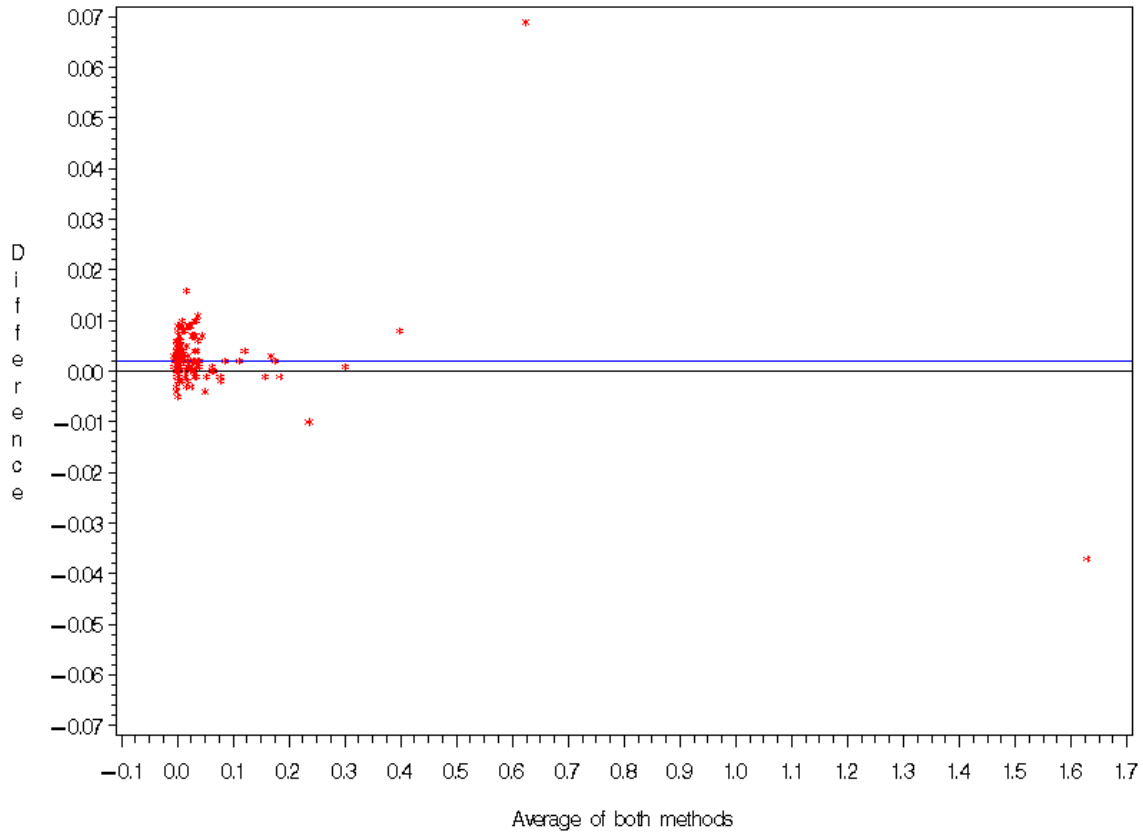

Figure 3. Difference between salicylate and phenate methods, calculated as salicylate minus alkaline phenol, plotted against the mean of both. The blue line shows the median difference.

Regression analysis was used to test whether the difference between the methods (log10 salicylate minus log10 phenate) changes as a function of the mean of the logs of both (data were log transformed to better comply with the distributional assumptions of linear regression). A constant (0.009) was added to the concentration data so all of the data could be log transformed, including negative numbers. This logarithm transformation was used for the regression analysis and the log ratio test. The regression results plotted in Figure 4 show the differences (green circles), predicted differences (black line), and the upper and lower 95 percent confidence limits of the mean of the predicted values (red lines).

Figure 4 shows that the variance of the data is not constant over the range in concentrations, with higher variance associated with lower concentrations. There also appears to be higher bias (a larger difference between the methods) associated with lower concentrations that decreases as the concentrations increase.

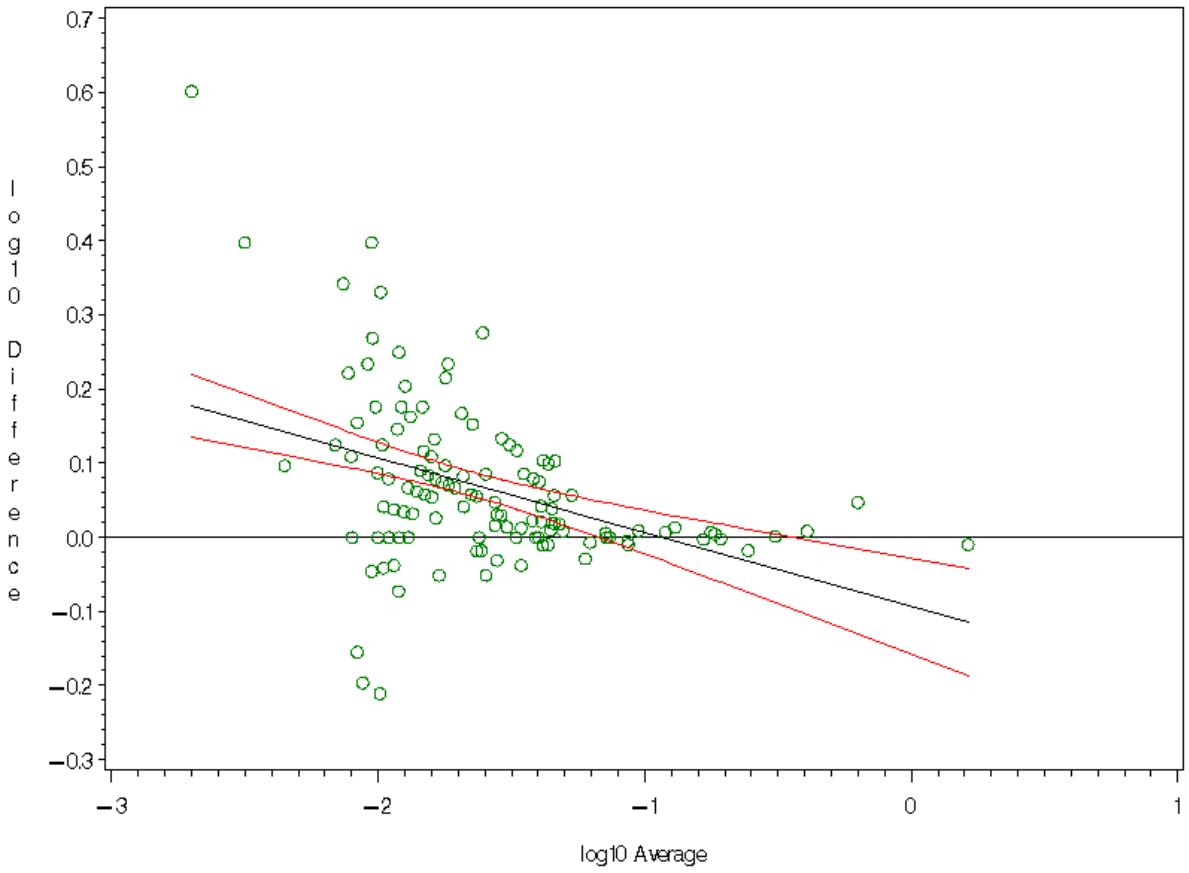

Figure 4. Regression plot showing log10(salicylate method + constant) minus log10(phenate method + constant) (green circles), predicted values (black line), and upper and lower 95% confidence limits of the mean (red lines) plotted against mean of logs of both methods.

Statistical comparisons

The differences between the two methods were also compared statistically using the Wilcoxon Signed Rank test on the log of the ratio of salicylate to alkaline phenol samples (i.e., log (salicylate/phenate) and using the Student's t-test for paired data. Taking the logarithm of each concentration and then subtracting the log-phenate value from its corresponding log-salicylate value calculates the log ratio. The log ratio is based on the principle of logarithms that states: $\log_b x - \log_b y = \log_b(x/y)$. Working with log-transformed data (base 10 was used in these analyses) also helps meet the symmetry assumption of the Wilcoxon Signed Rank test. Probability values (p-values) for the Wilcoxon Signed Rank test of ≤ 0.05 are assumed to indicate a statistically significant difference between samples analyzed using the two methods.

The p-values on the method differences for the Wilcoxon signed-rank test and the Student's t-test were <0.0001. Although the difference

between the two methods is statistically significant and the bias is pronounced, those issues do not necessarily mean that an adjustment factor needs to be developed for the purpose of performing trend analyses because of the small magnitude of the difference.

The possible need to develop an adjustment factor was tested by creating two ten year test data sets consisting of trend censored NH4 data (censored to the highest historical detection limit) for the 1999 through 2008 time period. Both data sets were tested for trends by using a seasonally adjusted linear regression model with a centered date term and a centered date squared term to assess the effects of the methods change on linear and non-linear trends.

The first data set contained NH4 data that were measured by the phenol method and were censored to the highest detection limit, but otherwise un-modified. Trends were assessed for the 54 CORE/Trend monitoring stations to establish a "baseline" for the number and direction of statistically significant linear and non-linear trends ($p \leq 0.01$). The second data set had the mean difference between the methods added to the last five years of data to simulate a step trend in the data due to a phenol to salicylate methods change. Trends were re-run on the test data set and the differences in trends and direction of trends were compared between the un-modified and the "step trend" data sets.

Changes in the direction and magnitude of linear and non-linear trends were detected between the un-modified and step trend data sets; however, on the whole these changes were fairly minor. The changes were of three types, negative significant to negative non-significant (eight); negative non-significant to positive non-significant (14); and positive non-significant to positive significant (two). Although effects of the methods change were observed, changes of direction that would be considered important e.g., negative significant to positive significant, and may have warranted an adjustment to the data, were not observed.

Over time, adding a constant, such as the mean difference between the methods, would result in a step trend in the data. Another test was conducted where random error was added along with the mean difference to account for the fact that we do not have a perfect estimate of the method difference. Adding random error to the data reduced the number of differences that were detected.

SENSE OF THE RESOURCES NEEDED TO RESPOND:
Members of the Analytical Methods and Quality Assurance Workgroup (AMQWA) and data analysts are requested to review this document and provide comments by 1 October 2010.

PRIORITY RANKING:
Two (low). Although statistically significant the difference between the phenate and salicylate methods is not likely to have an impact on the ability to detect trends in NH4.

SUBMITTER/RESPONSIBLE PARTY:
Name: William D. Romano
Natural Resources Biologist

Organization: Maryland Department of Natural Resources

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(410) 260-8655

ACTIONS TO DATE:
Prepared this report. Analyses performed in DHMHNH4Methods.epg SAS program.

OVERALL RESOLUTIONS SUMMARY OF ACTIONS:

RECOMMENDED ACTIONS:
The data analysis issue described in this report resulted from a change in the methods DHMH uses to analyze NH4. The comparisons described above indicate that a statistically significant difference exists between the two methods with the new method likely to result in higher NH4 concentrations than the old method. While the differences are not likely to cause dramatic changes in NH4 trends, these analyses were performed on a seasonally limited period of data (December and January). Mean concentrations of NH4 vary seasonally with the highest concentrations typically observed in January. Concentrations decrease through April, rise through July, then decrease to their lowest point in October and then begin to rise again. Having data for different seasons would help determine if the observed change has a seasonal component.

ACTIONS NUMBER:
1. Designated Respondent:
2. Action:
3. Resources Needed:
4. Due Date:
5. Action Item Resolution Summary:

Appendix A

Stations in the CORE/Trend monitoring network

1) ANA0082
2) ANT0044
3) ANT0203
4) ANT0366
5) BDK0000
6) BPC0035
7) CAC0031
8) CAC0148
9) CAS0479
10) CB1.0
11) CCR0001
12) CJB0005
13) CON0005
14) CON0180
15) DER0015
16) ET5.0
17) GEO0009
18) GUN0125
19) GUN0258
20) GUN0476
21) GWN0115
22) JON0184
23) LYO0004
24) MON0020
25) MON0155
26) MON0269
27) MON0528
28) NBP0023
29) NBP0103
30) NBP0326
31) NBP0461
32) NBP0534
33) NBP0689
34) NPA0165
35) PAT0176
36) PAT0285
37) POT1184
38) POT1471
39) POT1472
40) POT1595
41) POT1596
42) POT1830
43) POT2386
44) POT2766
45) PXT0809
46) PXT0972
47) RCM0111
48) SAV0000
49) SEN0008
50) TF1.0 (analyzed at Chesapeake Biological Lab starting July 2005)
51) TOW0030
52) WIL0013
53) YOU0925
54) YOU1139

Appendix B

Stations in the non-tidal network

1) ANT0047
2) BEL0053
3) GWN0115
4) DER0015
5) NPA0165
6) TF1.2
7) MON0546
8) TUK0181
9) WIL0013
10) GEO0009
11) GUN0258
12) PXT0972
13) CAC0148

Appendix C

Data used in these analyses

LABSEQNUM	SalycilateMethod	AlkalinePhenolMethod	REPNUMBER	STATIONNAME	SAMPLEDATE
1205	0.001	-0.002		MDE	
1224	0.011	0.008	1	PAT0176	12/1/2009
1225	0.018	0.010	1	PAT0285	12/1/2009
1226	0.003	0.001	1	GWN0115	12/1/2009
1227	0.011	0.007	1	NPA0165	12/1/2009
1228	0.087	0.085	1	JON0184	12/1/2009
1229	0.004	-0.002	1	GUN0125	12/1/2009
1230	0.005	0.001	1	DER0015	12/1/2009
1231	0.038	0.028	1	CB1.0	12/1/2009
1232	0.040	0.030	1	CB1.0	12/1/2009
1232	0.043	0.032	1	CB1.0	12/1/2009
1233	0.003	0.000	1	GUN0476	12/1/2009
1234	0.009	0.003	1	GUN0258	12/1/2009
1235	0.025	0.016	1	ANT0203	12/1/2009
1236	0.030	0.023	1	ANT0366	12/1/2009
1237	0.001	-0.002	1	CON0180	12/1/2009
1238	0.006	-0.003	1	CON0005	12/1/2009
1239	0.004	-0.002	1	POT2386	12/1/2009
1240	0.004	-0.002	1	NBP0103	12/1/2009
1241	0.003	-0.002	1	NBP0023	12/1/2009
1243	-0.001	-0.003	1	POT2766	12/1/2009
1244	0.002	-0.004	1	WIL0013	12/1/2009
1245	0.019	0.014	1	BDK0000	12/1/2009
1246	0.029	0.020	1	NBP0461	12/1/2009
1247	0.035	0.028	1	NBP0326	12/1/2009
1248	0.008	0.005	1	CAS0479	12/2/2009
1249	0.006	-0.002	1	YOU0925	12/2/2009
1250	0.031	0.031	1	CCR0001	12/2/2009
1251	0.034	0.030	2	CCR0001	12/2/2009
1252	0.038	0.034	1	YOU1139	12/2/2009
1252	0.037	0.035	1	YOU1139	12/2/2009
1253	0.301	0.300	1	LYO0004	12/2/2009
1254	1.611	1.648	1	NBP0689	12/2/2009
1255	0.170	0.167	1	NBP0534	12/2/2009
1256	0.112	0.110	1	SAV0000	12/2/2009
1257	0.006	0.001	1	GEO0009	12/9/2009
1258	0.048	0.041	1	PXT0809	12/2/2009
1259	0.003	-0.001	1	PXT0972	12/2/2009
1260	0.033	0.026	1	RCM0111	12/2/2009
1261	0.001	-0.002	1	CJB0005	12/2/2009
1262	0.007	0.000	1	POT1184	12/2/2009
1263	0.033	0.031	1	ANA0082	12/2/2009
1264	0.014	0.010	1	MON0155	12/2/2009
1265	0.003	0.000	1	CAC0031	12/2/2009
1266	0.002	0.000	1	POT1596	12/2/2009
1267	0.000	-0.002	1	POT1595	12/2/2009
1268	0.007	0.001	1	MON0020	12/2/2009

LABSEQNUM	SalycilateMethod	AlkalinePhenolMethod	REPNUMBER	STATIONNAME	SAMPLEDATE
1269	0.001	-0.003	1	POT1472	12/2/2009
1270	0.010	0.007	1	POT1471	12/2/2009
1271	0.001	-0.002	1	SEN0008	12/2/2009
1272	0.007	0.002	1	BPC0035	12/2/2009
1273	0.006	0.004	1	MON0528	12/2/2009
1274	0.006	0.001	1	MON0269	12/2/2009
1275	0.015	0.015	1	CAC0148	12/2/2009
1276	0.006	0.001	1	POT1830	12/2/2009
1277	0.001	-0.002	1	ANT0044	12/2/2009
1278	-0.004	-0.005		MDE	
1279	-0.005	-0.008		MDE	
1280	0.002	0.000		MDE	
1281	-0.004	-0.007		MDE	
1282	0.001	-0.002		MDE	
1304	0.077	0.079	1	BEL0053	12/3/2009
1305	0.036	0.035	1	DER0015	12/3/2009
1306	0.014	0.015	1	GWN0115	12/3/2009
1307	0.001	0.002	1	DI BLANK	12/3/2009
1308	0.019	0.014	1	ANT0043	12/4/2009
1309	-0.002	0.002	1	DI BLANK	12/4/2009
1310	0.015	0.016	1	PMS10	12/7/2009
1311	0.015	0.018	1	PMS10	12/7/2009
1312	0.019	0.018	1	PMS10	12/7/2009
1347	0.008	0.004		MDE	
1348	0.008	0.006		MDE	
1349	0.010	0.007		MDE	
1350	0.003	0.003		MDE	
1351	0.009	0.005		MDE	
1352	0.002	0.004		MDE	
1353	0.016	0.008		MDE	
1354	0.002	0.003		MDE	
1355	0.001	0.001		MDE	
1356	0.005	0.004		MDE	
1357	0.032	0.033		MDE	
1358	0.003	0.002		MDE	
1359	0.009	0.005		MDE	
1360	0.014	0.005		MDE	
1383	0.053	0.054	1	ET5.0	12/14/2009
1384	-0.002	0.001	1	DI BLANK	12/14/2009
1385	0.231	0.241	1	BEL0053	12/14/2009
1386	0.063	0.062	1	DER0015	12/14/2009
1387	0.065	0.065	1	TUK0181	12/14/2009
1388	-0.001	0.004	1	DI BLANK	12/14/2009
1389	0.020	0.018	1	ANT0047	12/14/2009
1390	0.021	0.019	1	CAC0148	12/14/2009
1391	0.063	0.063	1	MON0546	12/14/2009
1393	0.049	0.053	1	DI BLANK	12/15/2009
1393	0.049	0.053	1	DI BLANK	12/15/2009
1394	0.040	0.038	1	GUN0258	12/15/2009

LABSEQNUM	SalycilateMethod	AlkalinePhenolMethod	REPNUMBER	STATIONNAME	SAMPLEDATE
1395	0.008	0.006	1	GWN0115	12/15/2009
1396	0.013	0.011	1	NPA0165	12/15/2009
1397	0.002	0.003		MDE	
1398	0.020	0.017		MDE	
1399	0.002	0.001		MDE	
1400	0.003	0.001		MDE	
1401	0.009	0.006		MDE	
1402	0.002	0.002		MDE	
1403	0.659	0.590		MDE	
1404	0.027	0.018		MDE	
1405	0.025	0.009		MDE	
1406	0.015	0.005		MDE	
1407	0.022	0.021		MDE	
1408	0.010	0.005		MDE	
1411	0.015	0.005		MDE	
1412	-0.001	-0.001	1	DI BLANK	12/15/2009
1413	0.034	0.035	1	GEO0009	12/15/2009
1414	0.005	0.003	1	PLD0001	12/15/2009
1414	0.004	0.003	1	PLD0001	12/15/2009
1415	0.015	0.012	1	CCR0001	12/15/2009
1424	0.016	0.013		MDE	
1426	0.002	0.003		MDE	
1427	0.007	0.004		MDE	
1428	0.001	0.001		MDE	
1429	0.001	0.002		MDE	
1430	0.001	0.001		MDE	
1431	0.002	0.000		MDE	
1432	0.000	0.001		MDE	
1433	0.000	0.001		MDE	
1434	0.001	0.001		MDE	
1435	0.030	0.030	1	POT2386	1/4/2010
1436	0.040	0.034	1	ANT0203	1/4/2010
1437	0.007	0.000	1	CON0005	1/4/2010
1438	0.007	0.005	1	CON0180	1/4/2010
1439	0.123	0.119	1	ANT0366	1/4/2010
1440	0.038	0.036	1	PAT0176	1/5/2010
1441	0.041	0.040	1	PAT0285	1/5/2010
1442	0.012	0.009	1	GWN0115	1/5/2010
1443	0.007	0.009	1	NPA0165	1/5/2010
1444	0.004	0.004	1	JON0184	1/5/2010
1445	0.030	0.028	1	GUN0125	1/5/2010
1447	0.024	0.027	1	CB1.0	1/5/2010
1448	0.026	0.025	2	CB1.0	1/5/2010
1449	0.008	0.007	1	GUN0476	1/5/2010
1450	0.018	0.020	1	GUN0258	1/5/2010
1451	0.024	0.024	1	CAS0479	1/5/2010
1452	0.040	0.038	1	YOU0925	1/5/2010
1453	0.176	0.174	1	YOU1139	1/5/2010
1454	0.403	0.395	1	LYO0004	1/5/2010

LABSEQNUM	SalycilateMethod	AlkalinePhenolMethod	REPNUMBER	STATIONNAME	SAMPLEDATE
1455	0.184	0.185	1	NBP0689	1/5/2010
1457	0.077	0.078	1	SAV0000	1/5/2010
1458	0.157	0.158	1	GEO0009	1/5/2010