OLD DOMINION UNIVERSITY
WATER QUALITY LABORATORY

FINAL REPORT

A COMPARISON STUDY OF TWO INSTRUMENTS FOR THE DETERMINATION OF SILICATE CONCENTRATIONS IN ESTUARINE WATER SAMPLES

Report Prepared by:
Lori Ann Tew
Suzanne Doughten
Mike Lane

4211 COLLEY AVENUE
NORFOLK, VA 23508

DRAFT REPORT

A COMPARISON STUDY OF TWO INSTRUMENTS FOR THE DETERMINATION OF SILICATE CONCENTRATIONS IN ESTUARINE WATER SAMPLES

INTRODUCTION

Since the beginning of the Chesapeake Bay Mainstem Water Quality Monitoring Program (CBP), the Old Dominion University Water Quality Laboratory (WQL), formerly Applied Marine Research Laboratory (AMRL), has used an autoanalyzer system for the analysis of silicate. From June 1984 through December 1995, a Scientific Instruments Corporation® continuous flow autoanalyzer was used. The analysis was then switched to a Skalar® continuous flow autoanalyzer in January 1996. Although the sampler, integrator and software for the Skalar® system were updated in June 2004, the base chemistry unit and detectors were the originals bought in 1994. Increased maintenance requirements due to the age of the instrument led to the purchase of a Lachat Instruments® flow injection analyzer system in May 2012.

Although the continuous flow analyzer (CFA) and flow injection analyzer (FIA) methods are based on the same chemistry (EPA Method 366.0 – silicate combining with molybdate in acidic conditions, then reduced by ascorbic acid to form molybdenum blue), differences may exist in the analytical results that were obtained. This method comparison study was performed to determine the comparability of the data generated for the analysis of silicate on the different systems and to develop a conversion factor if needed.

STUDY METHODS AND DESIGN

The study was conducted using 100 frozen routine samples collected from March 2011 through December 2011. Samples included stations in the Chesapeake Bay Mainstem and Potomac River and were selected taking concentration, salinity and seasonal variability into account.

Fifty samples were analyzed the same day on both the Skalar CFA and Lachat FIA. The Skalar San^{plus} system is equipped with a Model SA 1074 autosampler, a Model SA 1521 Rinsing Valve, a Model SA 4001 Chemistry Unit and a Model SA 6250 Matrix Photometer. The sample absorbance is measured using an 810 nm filter, and background correction is measured with a 1010 nm filter. The Lachat QuikChem 8500 Series 2 FIA+ is equipped with a Model ASX-520 Sampler, a Model PDS-200 Auto Dilutor, a Model RP-150 Reagent Pump, a Model 31-114-27-2-A Reaction Manifold, a Heating Unit (Part A85132) and a colorimetric detector (Part 85080). The sample absorbance is measured using a 660 nm filter. This was then repeated with 50 additional samples on a separate analysis date. Two different analysts prepared the working standards on the separate dates. This is to account for variations which may occur with different analysts. The samples ranged from 0.005 to 3.6 mg Si/L with a mean of 0.7 mg/L. The salinity ranged from 0 to 31 parts per thousand (ppt), with a mean salinity of 16 ppt.

The samples were analyzed on the Skalar using artificial seawater (ASW) as the standard matrix and carrier solution. These standards for the regression curve were prepared manually. This is the procedure which has been used on this instrument for routine Chesapeake Bay Program samples. For the Lachat analyzer Type I reagent water was used for the carrier solution. The manually prepared ASW standards were analyzed to compare the results between the instruments with the same standards. Type I reagent water standards were prepared with the auto diluter on the Latchat. This is the procedure which will be used for the regression curve for routine Chesapeake Bay Program samples. A secondary standard made with a different silicate stock standard was prepared manually for both the ASW and Type I reagent water regression curve. These are analyzed to confirm the validity of the regression curve.

For quality control continuing calibration verification (CCV) standards, duplicate samples and spiked samples were analyzed a minimum of 10%. Zero check (blank) samples are analyzed a minimum of every 20 samples.

QUALITY CONTROL RESULTS

For the data report, Type I reagent water is simply referred to as DI.

Relative percent difference = RPD

The MDL for the Skalar was determined in Janaury 2012 to be 0.0007 mg Si/L. The MDL for the Lachat was determined in August 2012 to be 0.0014 mg Si/L. For purposes of this comparison study these MDLs were determined on one analysis date, because this is the procedure this laboratory has always utilized. AMQAW is now recommending that multiple dates be used to determine the MDL, so before reporting data from the Lachat an MDL study using multiple dates will be conducted.

Twelve replicate samples were analyzed. For the Skalar the RPD ranged from 0.35 to 12.28 with a mean of 2.82, and for the Lachat the range was 0.05 to 3.64 with a mean of 0.41. Twelve spiked samples were analyzed. For the Skalar the percent recovery ranged from 83% to 109% with a mean of 100%. For the Lachat ASW results the same spikes analyzed on the Skalar were used with a percent recovery ranged from 80% to 104% with a mean of 97%. For the Lachat DI results the spikes were made with the original DI standard used to make the regression curve. The percent recovery ranged from 93% to 108% with a mean of 100%.

A second source standard at a concentration of 0.4674 mg Si/L was analyzed on each instrument on both analysis days. The same second source standard was analyzed for the Skalar and Lachat ASW. For the Skalar the recovery was 104% and 100%. For the Lachat ASW the recovery was 101% and 99%. For the Lachat DI the recovery was 98% and 99%.

Continuing Calibration Verification standards (CCVs) were analyzed at three separate concentrations (0.2337, 0.7012 and 1.1686 mg Si/L). For the Skalar the CCVs had a percent recovery range of 98% to 105% and a mean of 102%. For the Lachat ASW the CCVs had a percent recovery range of 99% to 101% and a mean of 100%. For the Lachat DI the CCVs had a percent recovery range of 100% to 102% and a mean of 101%.

Ten blank samples were analyzed for the Skalar; the range of the blanks was -0.0085 to 0.0021 mg Si/L with a mean of -0.0031 mg Si/L. Ten blank samples were analyzed for the Lachat ASW; the range of the blanks was -0.0012 to 0.0006 mg Si/L with a mean of -0.0002 mg Si/L. Eight blank samples were analyzed for the Lachat DI; the range of the blanks was 0.0008 to 0.0027 mg Si/L with a mean of 0.0018 mg Si/L.

The actual mean for the 100 samples analyzed on the Skalar was 0.7438 mg Si/L and for the Lachat DI was 0.7252 mg Si/L. The difference of 0.0186 mg Si/L is less than the Practical Quantitation Limit (PQL, 0.0234 mg Si/L) for this analysis.

All of the QC samples were in control. The Lachat DI test gave equal or better QC sample results.

STATISTICAL RESULTS AND CONCLUSION

SIF values for the Skalar ranged from a minimum of 0.0084 mg/L to a maximum value of 3.6465 mg/L with a mean of 0.7438±0.5833(1Std.) mg/L. Values for the Lachat were nearly always lower than the Skalar ranging from a minimum of 0.0054 mg/L to a maximum value of 3.5126 mg/L with a mean of 0.7252±0.5945(1Std.) mg/L. Distributions of SIF values for both methods were negatively skewed, leptokurtotic (Table 1A;Figure 1A-B) and significantly different from normal (Table 1B). Historical SIF values collected at the range of sites typically sampled by ODU (lower Chesapeake Bay Mainstem) showed a lower mean and lower variability overall than the data presented in this study but was also negatively skewed, leptokurtotic, and non-normal (Table 1;Figure 2).

Mean difference between instruments (Lachat - Skalar) was -0.0186 mg/L and was typically negative (93% of all observations) ranging from -0.2375 mg/L to a maximum of 0.3034 mg/L. Most differences ranged from 0.00 to -0.04 mg/L (Figure 3) and differences between instruments failed tests for normality (W=0.56;P<0.01;D=0.29;P<0.01). The median difference between instruments was -0.0213 mg/L and was significantly different from 0 based on the results of a Wilcoxon's signed rank test (S=-1969;P<0.0001).

Table 1. Summary of A) Descriptive Statistics and B) Tests of Normality for SIF values for both instruments and for historical data collected at ODU sampling stations in the lower Chesapeake Bay Mainstem. All statistics presented were calculated using data collected during the months of March through December from 1996 through 2011 using the Skalar instrument.

A) Descriptive Statistics

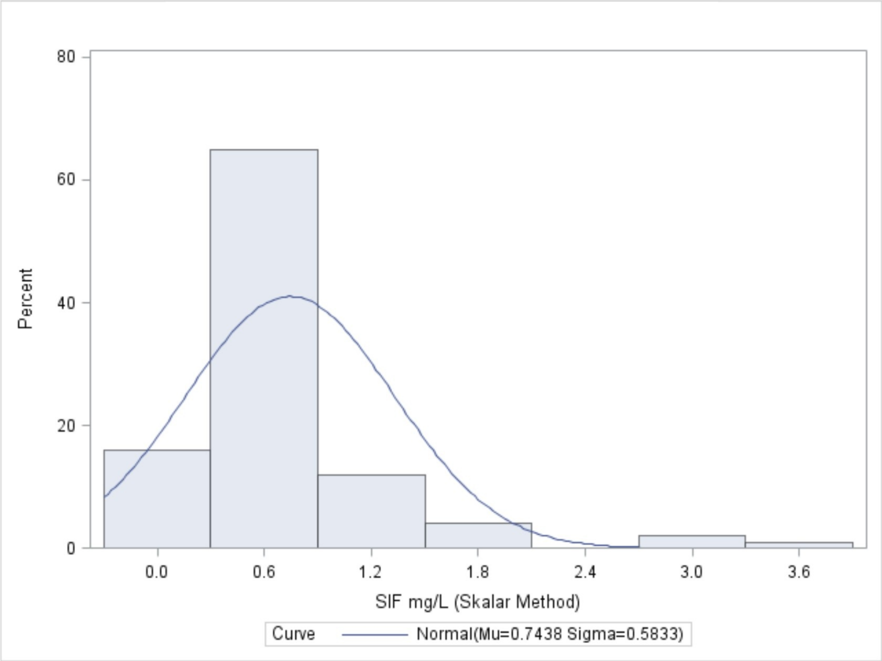
Instrument	N	Median	Mean	Std. Error of the Mean	Variance	Standard Deviation	CV	Skewness	Kurtosis
Skalar	100	0.6635	0.7438	0.0583	0.3402	0.5833	78.42	2.53	8.95
Lachat	100	0.6451	0.7252	0.0594	0.3534	0.5945	81.97	2.73	9.92
Mainstem	12987	0.3470	0.4065	0.0029	0.1086	0.3296	81.08	0.90	0.71

B) Tests of Normality

	Shapiro-Wilk's		Kolmogorov-Smirnov	
Instrument	W	P	D	P
Skalar	0.76	<0.0001	0.22	<0.01
Lachat	0.73	<0.0001	0.22	<0.01
Mainstem	N>2000		0.12	<0.01

A plot of Lachat SIF values against Skalar SIF values shows good agreement between methods with most values falling close to the equality line although at higher SIF concentrations the Lachat values appear, in general, to decrease relative to the Skalar values (Figure 4). Difference between instruments (Lachat - Skalar) decreases and increases in variability as the mean of both methods increases, overall, until concentrations reach 1.5 mg/L (Figures 5). Thereafter patterns in the difference are difficult to characterize due to a paucity of data but the plot does suggest that the difference between instruments may continue to decrease. Additional data are required to adequately characterize bias between instruments at higher concentrations. However, these results suggest that for concentrations within the ranges typically found in areas currently sampled by ODU specifically the lower Chesapeake Bay Mainstem (≈0.02 to 1.5 mg/L) the differences between instruments are relatively small. A total of 95% of data collected during the months of March through December from 1996 through 2011 at stations sampled by ODU were less than 1.0 mg/L and greater than 99% were less than 1.5 mg/L (Figure 6). A correction factor could be developed to compensate for differences between methods using these data but it should probably be limited to a concentration range that does not exceed 1.5 mg/L. Note that three observations exceeded the bounds typically used to identify outliers (Mean ± 2STD; see Figure 5) but an examination of sample collection and processing logs indicated no reason for eliminating these observations from any analyses.

A) Skalar



B) Lachat

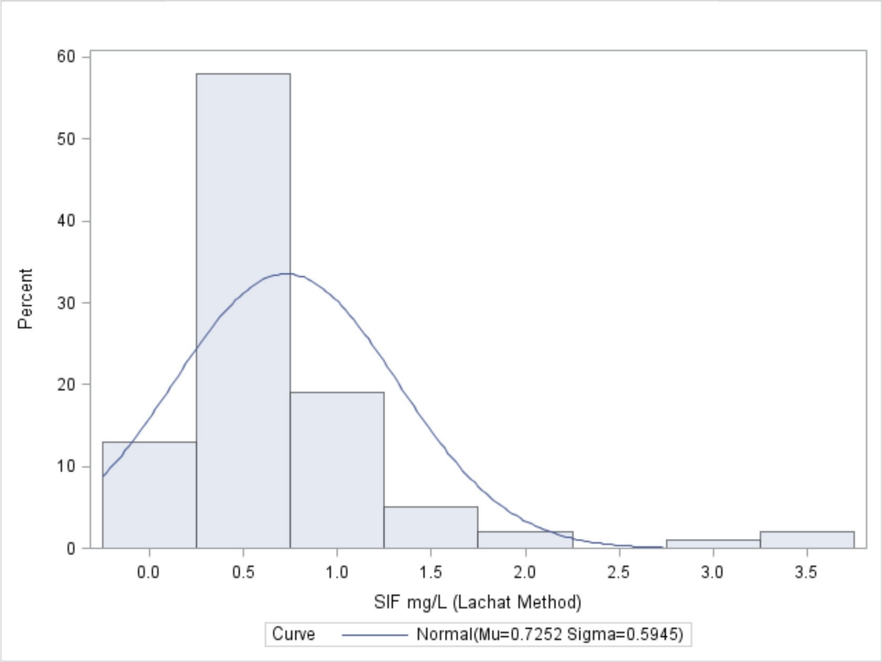


Figure 1. Frequency histograms of SIF values as determined using the A) Skalar and B) Lachat instruments for data collected in the Chesapeake Bay Mainstem and Potomac River for the period of March, 2011 through December, 2011. Also shown are fitted normal density curves for a population with the mean (Mu) and variance (Sigma) provided.

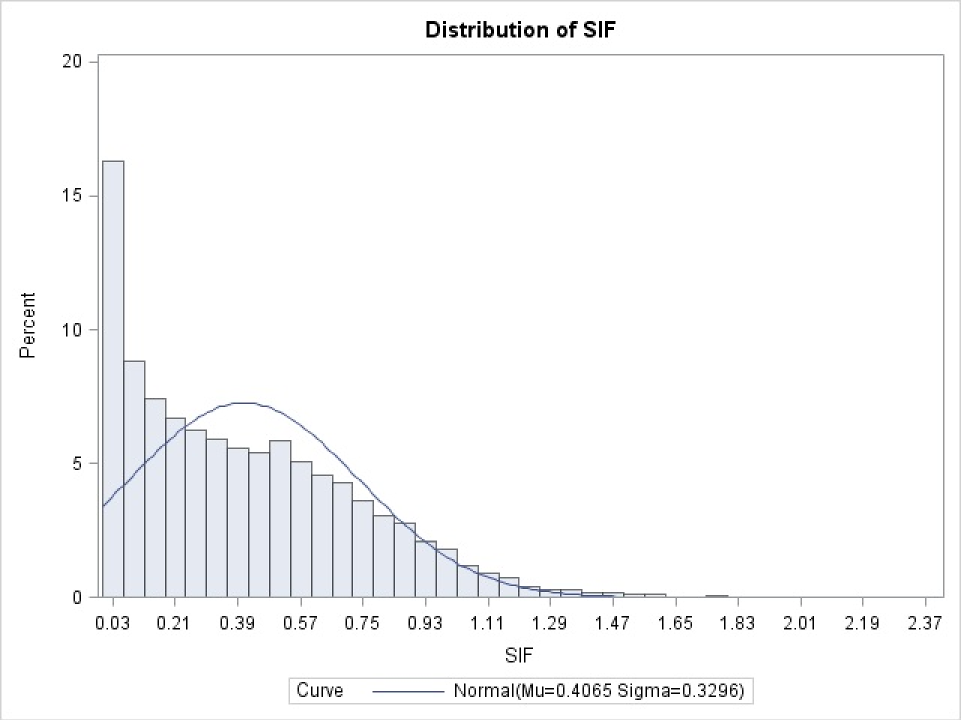


Figure 2. Frequency histogram of historical SIF values collected at stations regularly sampled by Old Dominion University in the lower Chesapeake Bay Mainstem for the months of March through December from 1996 through 2011. Also shown is the fitted normal density curves for a population with the mean (Mu) and variance (Sigma) provided. Note these data were measured using the Skalar method.

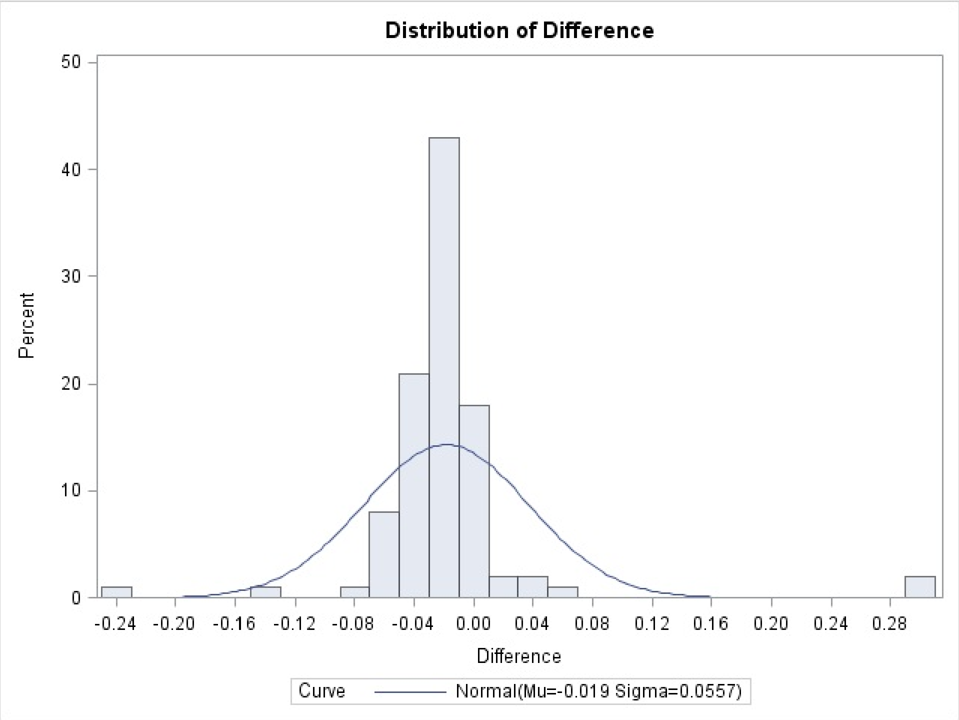


Figure 3. Frequency histogram of differences between instruments for the months of March through December, 2011. Also shown is the fitted normal density curves for a population with the mean (Mu) and variance (Sigma) provided. Note that these data were calculated by subtracting the Skalar values from the Lachat values.

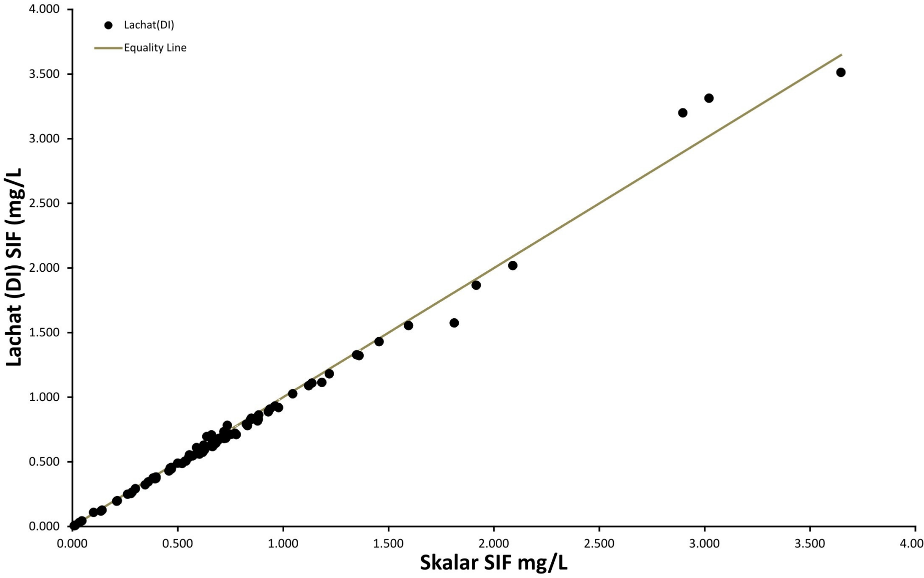


Figure 4. Scatter plot of SIF values as measured using the Lachat (DI) against those based on the Skalar.

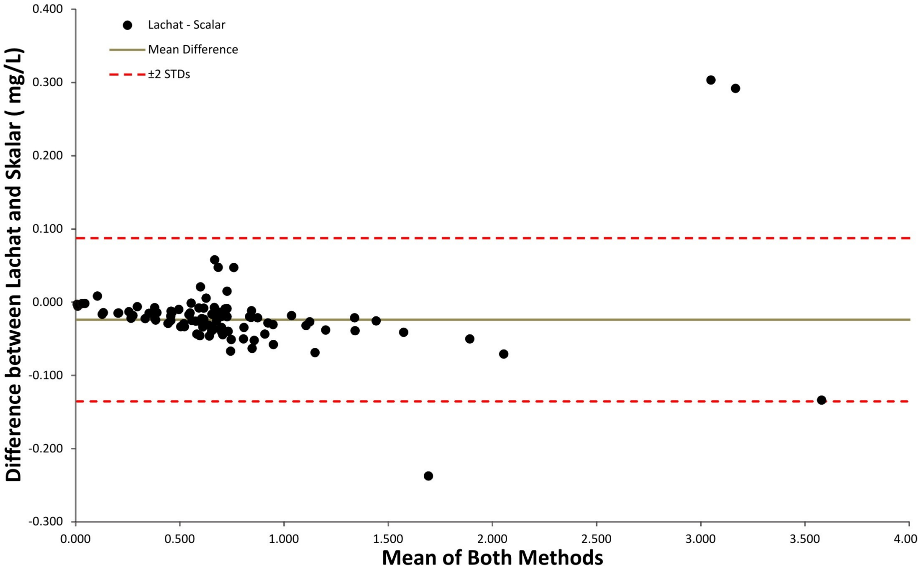


Figure 5. Plot of the difference in the Lachat and Skalar instruments against the mean for both instruments for SIF concentrations.

Overall the results indicate a relatively small negative bias between the Lachat and Skalar instruments that is proportional to concentration measured. Variability in this bias also increases with increased concentration. Within the concentration from 0.02 to 1.5 mg/L a change in instrumentation should not substantially affect status and trend analyses, however, a correction factor might be developed using these data for this concentration range, if necessary.

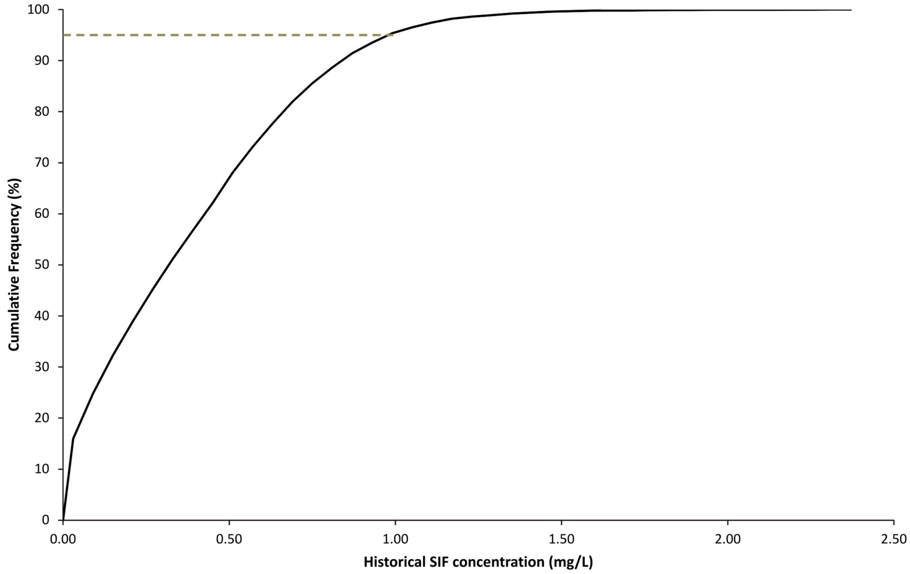


Figure 6. Cumulative frequency distribution of historical SIF concentrations for the months of March through December from 1996 through 2011 for stations sampled by Old Dominion University..