Comparing the Effects of Changing Sampling Agencies and Laboratories for Six Nontidal Network Sites Pennsylvania - Maryland

Introduction

Beginning in October 2014 (WY 2015), the Maryland Department of Natural Resources (MDNR) will assume full responsibility for sampling six stations that are presently sampled by Pennsylvania Department of Environmental Protection (PADEP) South-central Regional Office staff and analyzed by the PADEP Bureau of Laboratories. MDNR will use the same procedures used at their (20) Maryland Nontidal stations, which means that there will be a change in field personnel, laboratories, constituent species and analytical methods. Although the methods are considered equivalent, it's important to measure and evaluate the effects of these changes on future calculations of loads and trends.

The intent of the proposed design is to estimate the overall, combined effect of changing agencies on future data uses. The relative contribution of field error vs. lab error will not be estimated, nor will specific biases due to differences in equipment, preservatives or filter types.

Logistics

The plan is to have an overlapping period of side-by-side sampling with both agencies during the months of August, September and October 2014 for both routine and storm sampling events. MDNR staff will meet PADEP field crews for the monthly (routine) sampling dates which are:

1st week: Town Creek, Antietam and Licking Creeks (no specific order)
2nd week: Conococheague, Tonoloway and Sidling Hill (no specific order)

Storm sampling will be coordinated on a case-by-case basis.

The exact locations of the sites are listed below. All are located in western Maryland.

STATION NAME	LOCATION	TOWN, COUNTY	LAT	LONG	USGS GAUGE	DRAIN AREA (SQ MI)
CONOCOCHEAGUE CRK	Along Md Sr494 Approx 3 Mi Dwnstr Fr Pa/Md Border	Fairview, Washington Co.	39.708100	-77.833300	01614500	494
LICKING CRK	Pectonville Road Bridge	Pectonville, Washington Co.	39.675965	-78.042486	01613525	193
TONOLOWAY CRK	300 yds upstrm of Timber Ridge Rd (SR 2005) Br	Thompson Twp, Fulton Co.	39.728333	-78.151944	01613095	113
ANTIETAM CRK	Upstrm Millers Church Rd Crossing @ Rocky Forge, Md	Rocky Forge, Washington Co.	39.716389	-77.607300	01619000	93
SIDELING HILL CRK	Zeigler Road Bridge; 4 Mi South Of Bellegrove, Md	Bellegrove, Washington Co.	39.649527	-78.344138	01610155	102
TOWN CRK	Pack Horse Rd Crossing; near Oldtown, Md	Cumberland, Allegheny Co.	39.553200	-78.555000	01609000	148

Sampling Design – Field Collection

1. Routine samples: Side-by-side routine sampling at each station for 3 months:
   6 sites (3 samples/site) = 18 routine samples

2. Storm samples: 1-2 storm samples per station: 6 sites (1-2 storms/site) ≈ 8 storms

3. Replicate Types:

   a. FS1/FS2: Each agency is to prepare **all** samples in duplicate to establish within-agency variance.

   b. FB: One field blank, prepared by rinsing de-ionized water through the sampling bottle and churn splitter, *using same source (DI) water.* Prepare a field blank every event to assess occurrence of contamination.

4. Sampling Procedure: EWI samples to be collected concurrently, e.g., each increment is to be sampled by both agencies, one right after the other, as they move across the cross-section. This will minimize the variability of the stream sampled.

5. Field staff to document any observed differences in techniques between MDNR and PADEP.

Sampling Design – Laboratory Analyses

Samples will be delivered to the respective agency's laboratory. PADEP samples will go to the PADEP Bureau of Laboratories and the MDNR samples will go to the Department of Health and Mental Hygiene using normal handling and shipping procedures.

Here are several special analytical and reporting procedures that will greatly improve the interpretation of data:

1. Analyze the sample replicates on different days to include the day-to-day lab variability. In other words, analyze FS1 samples on one day and the FS2 samples in a separate run on a different day.

2. The labs should analyze identical certified reference samples for each parameter, where feasible. Every run? Sources?

Constituent	Source	Concentration
TDN		
NO_{23}		
NO_2		
NH_4		
TDP		
PO_4		
TSS		
DOC		

3. Report low-level instrument readings, even if below reporting limits. DHMH does this routinely; PADEP does not.

Comments, table and graphs from Elgin Perry:

Here are my results based on computing minimum detectable differences as a function of the sample size (number of pairs of samples).

Table giving minimum detectable difference for select parameters for study design in increments of 6 pairs of samples. The standard deviations were obtained from prior methods comparison studies. If the sample size is 36, then the minimum detectable difference is typically in the neighborhood of the detection limit. For PO4 and N023 the minimum detectable difference is larger than the detection limit.

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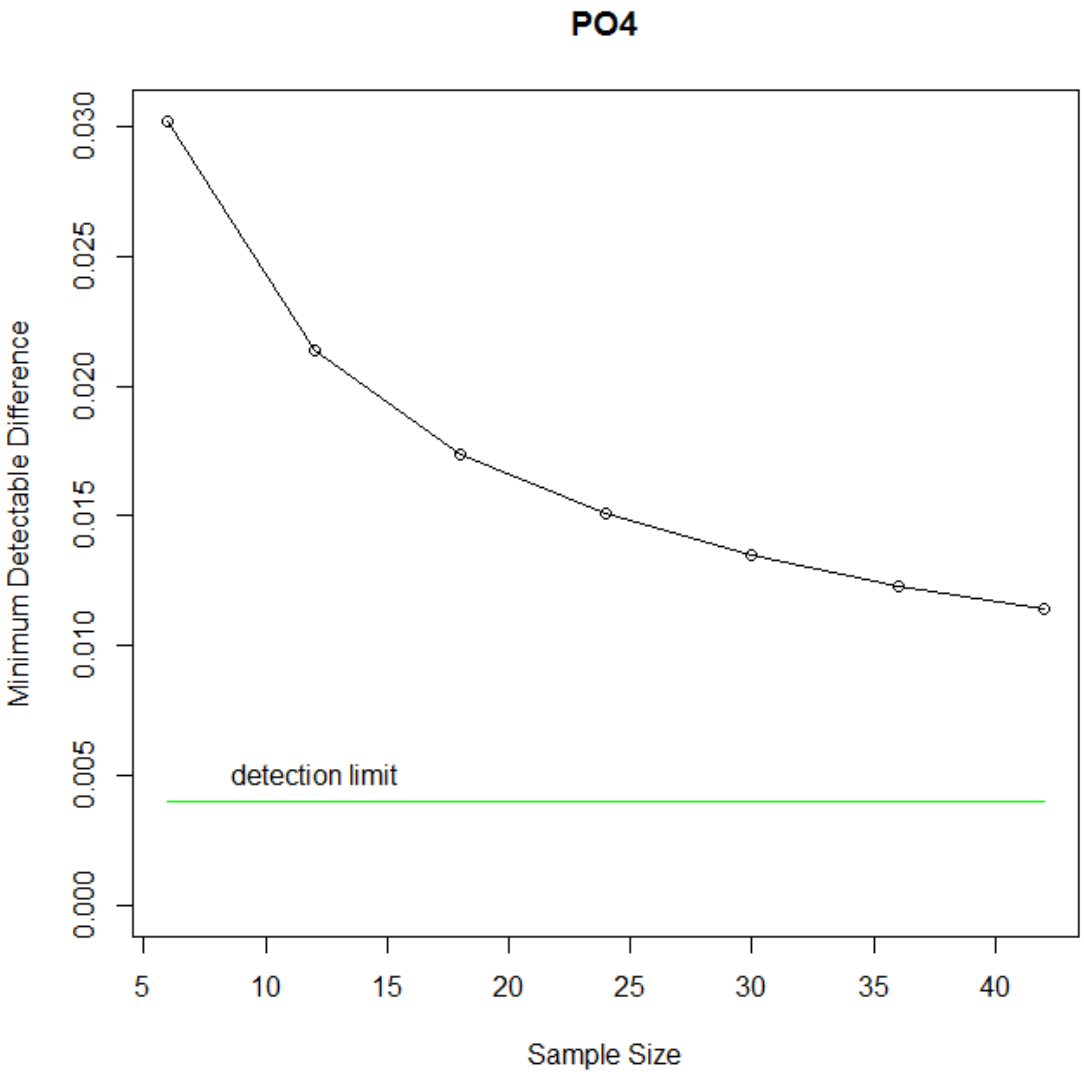
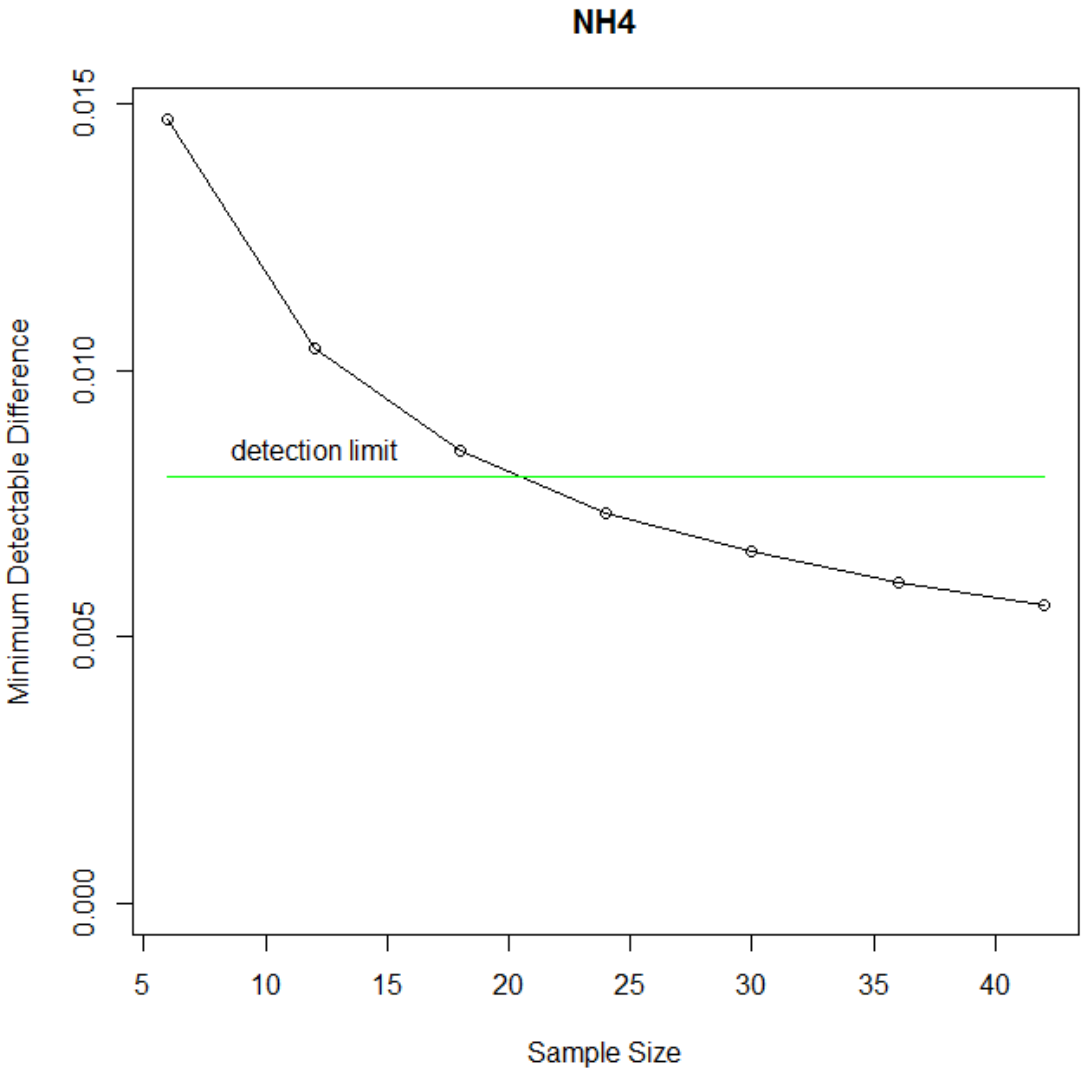
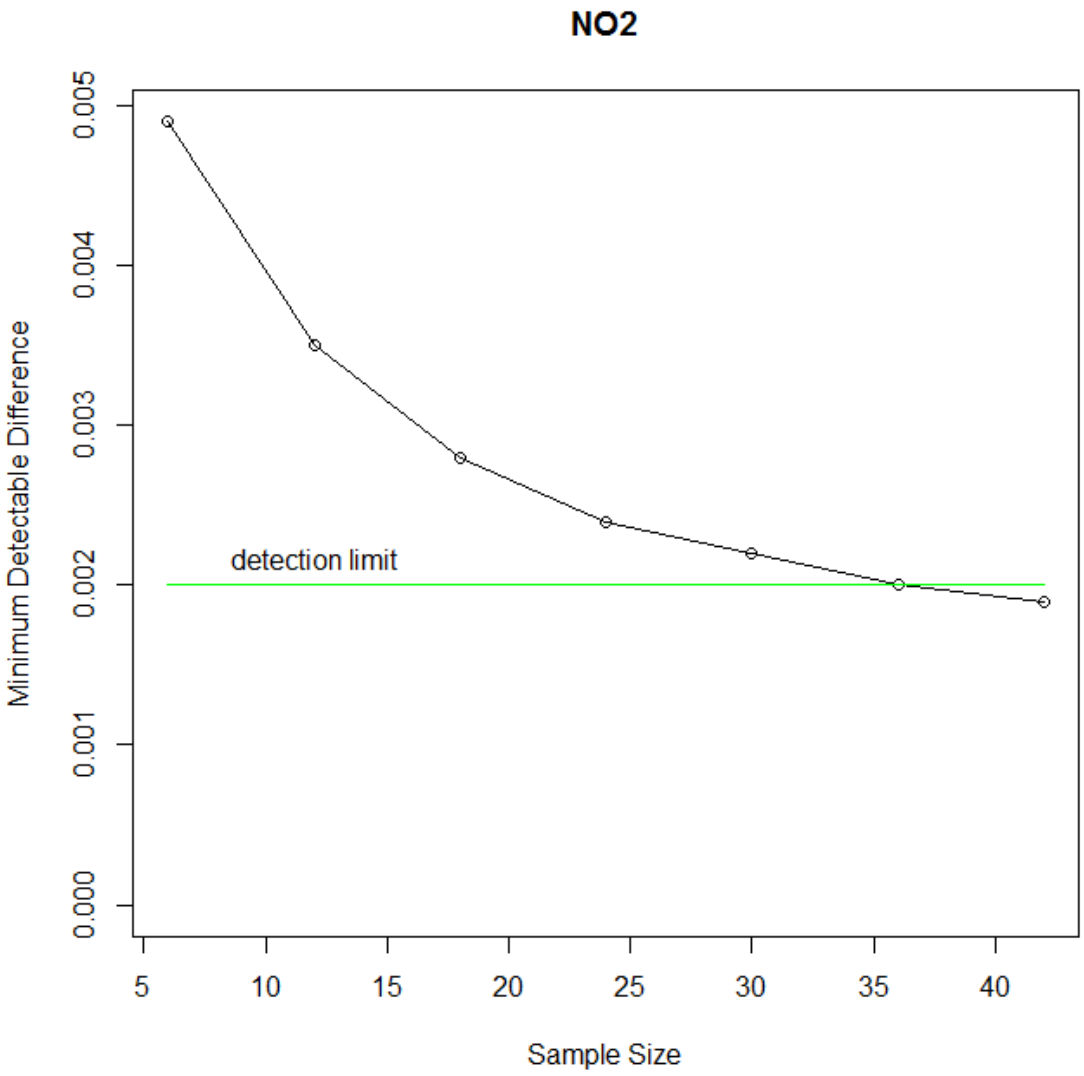
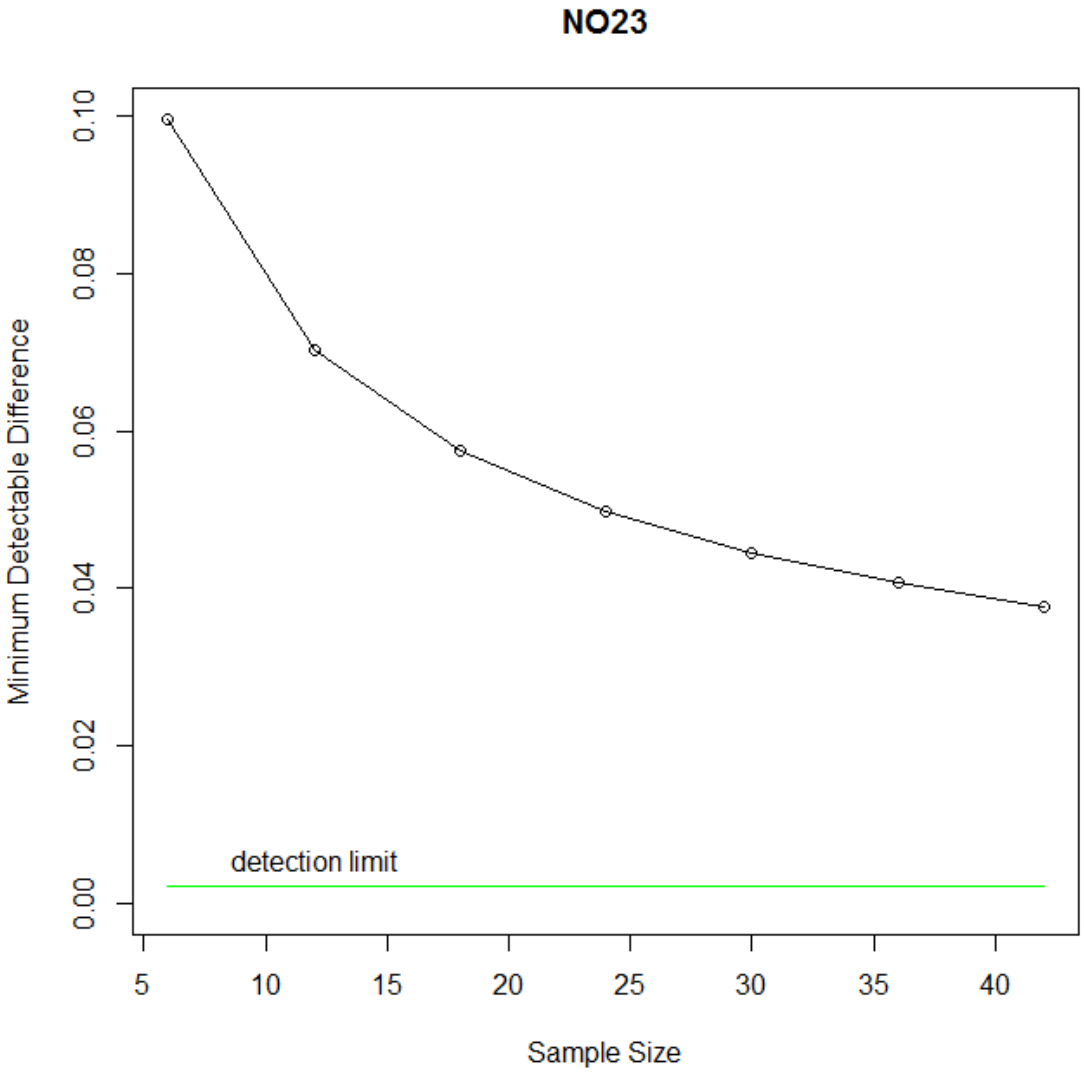
Minimum Detectable Difference for select parameters by sample size.

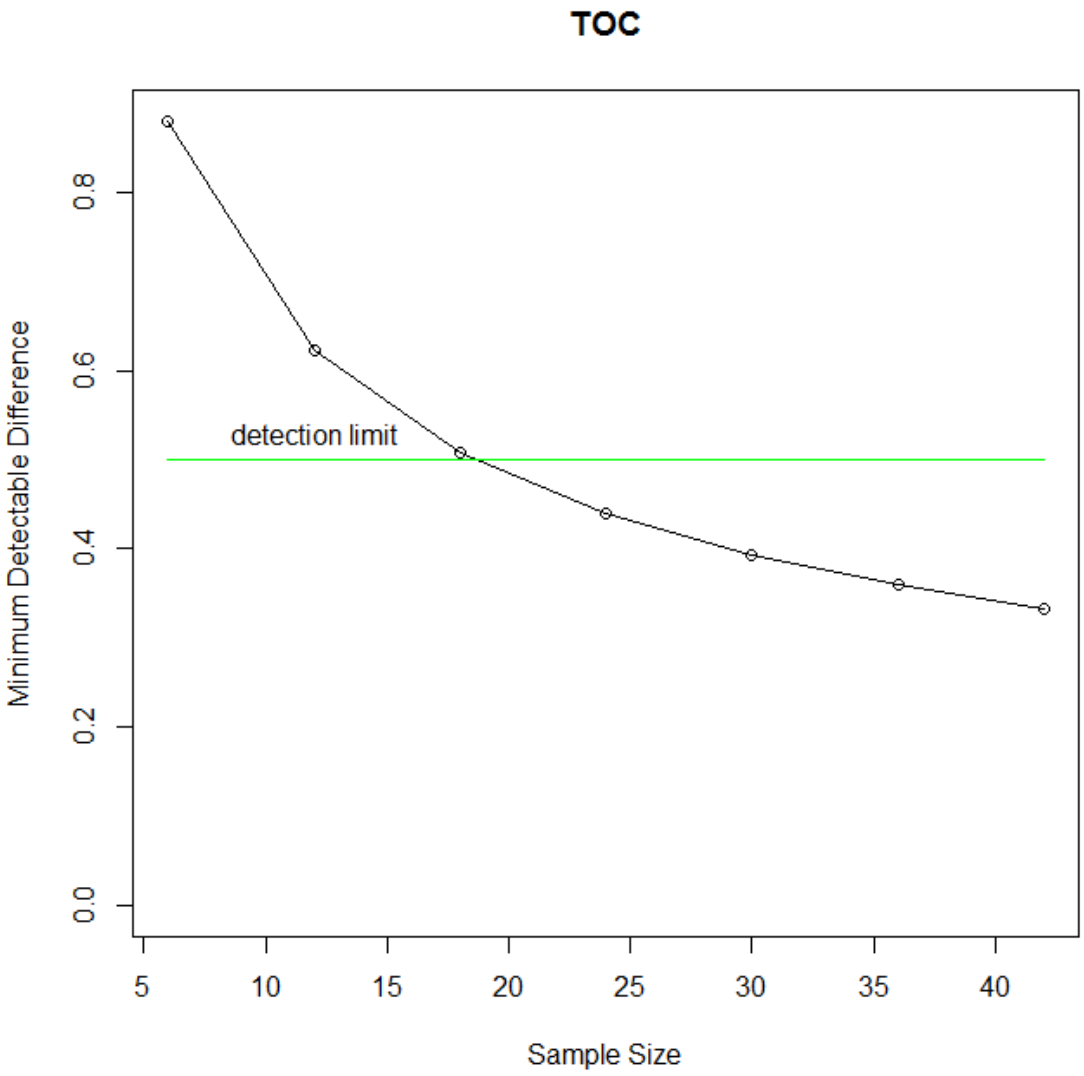
Parameter	std.dev	mdd6	mdd12	mdd18	mdd24	mdd30	mdd36	mdd42	dl
PO4	0.037	0.0302	0.0214	0.0174	0.0151	0.0135	0.0123	0.0114	0.004
NH4	0.018	0.0147	0.0104	0.0085	0.0073	0.0066	0.006	0.0056	0.008
NO2	0.006	0.0049	0.0035	0.0028	0.0024	0.0022	0.002	0.0019	0.002
NO23	0.122	0.0996	0.0704	0.0575	0.0498	0.0445	0.0407	0.0377	0.002
TOC	1.078	0.8802	0.6224	0.5082	0.4401	0.3936	0.3593	0.3327	0.5
TN	0.272	0.2221	0.157	0.1282	0.111	0.0993	0.0907	0.0839	NA
TP	0.03	0.0245	0.0173	0.0141	0.0122	0.011	0.01	0.0093	0.01
DIN	0.124	0.1012	0.0716	0.0585	0.0506	0.0453	0.0413	0.0383	NA

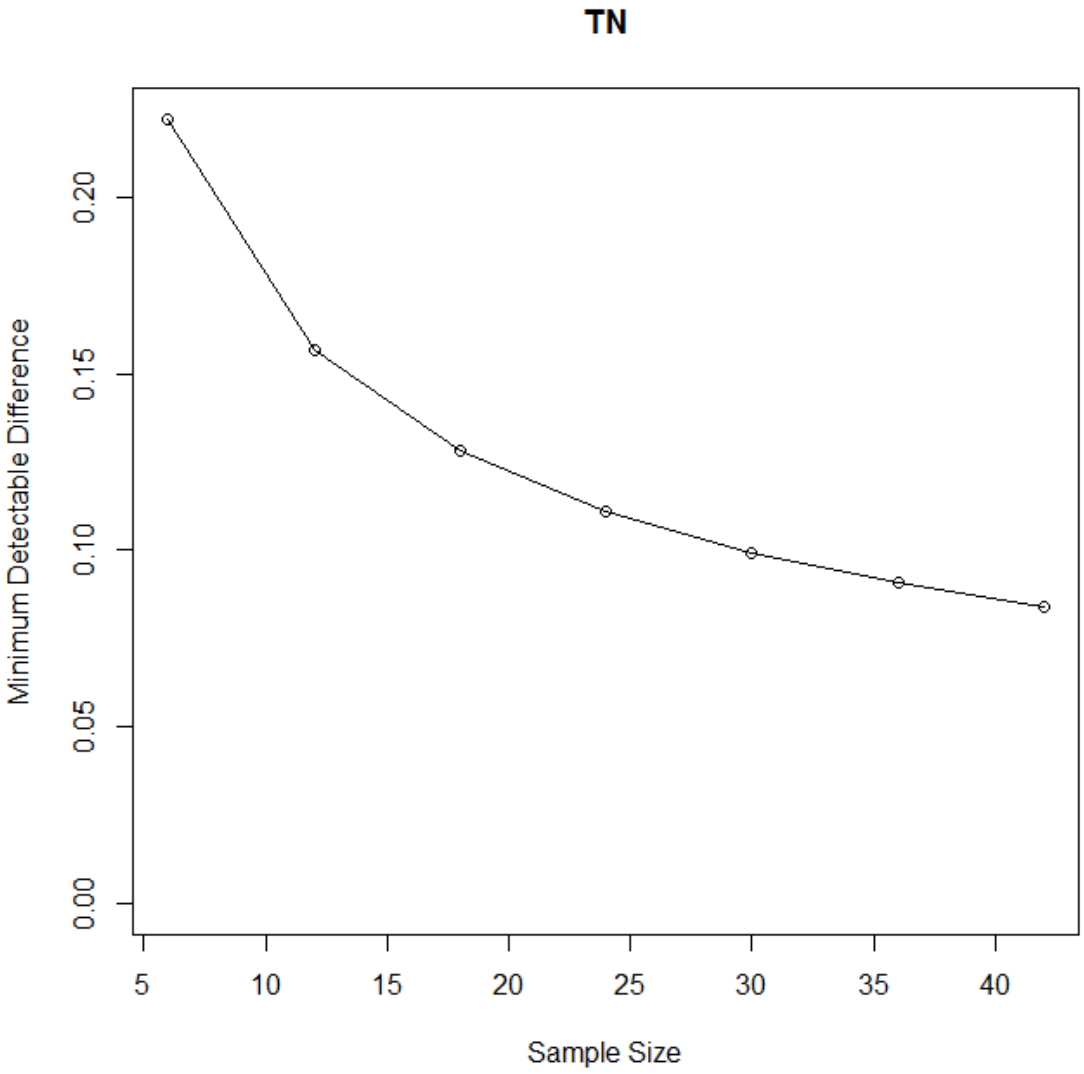

PO4
Minimum Detectable Difference
0.000
0.005
0.010
0.015
0.020
0.025
0.030
detection limit
5
10
15
20
25
30
35
40
Sample Size

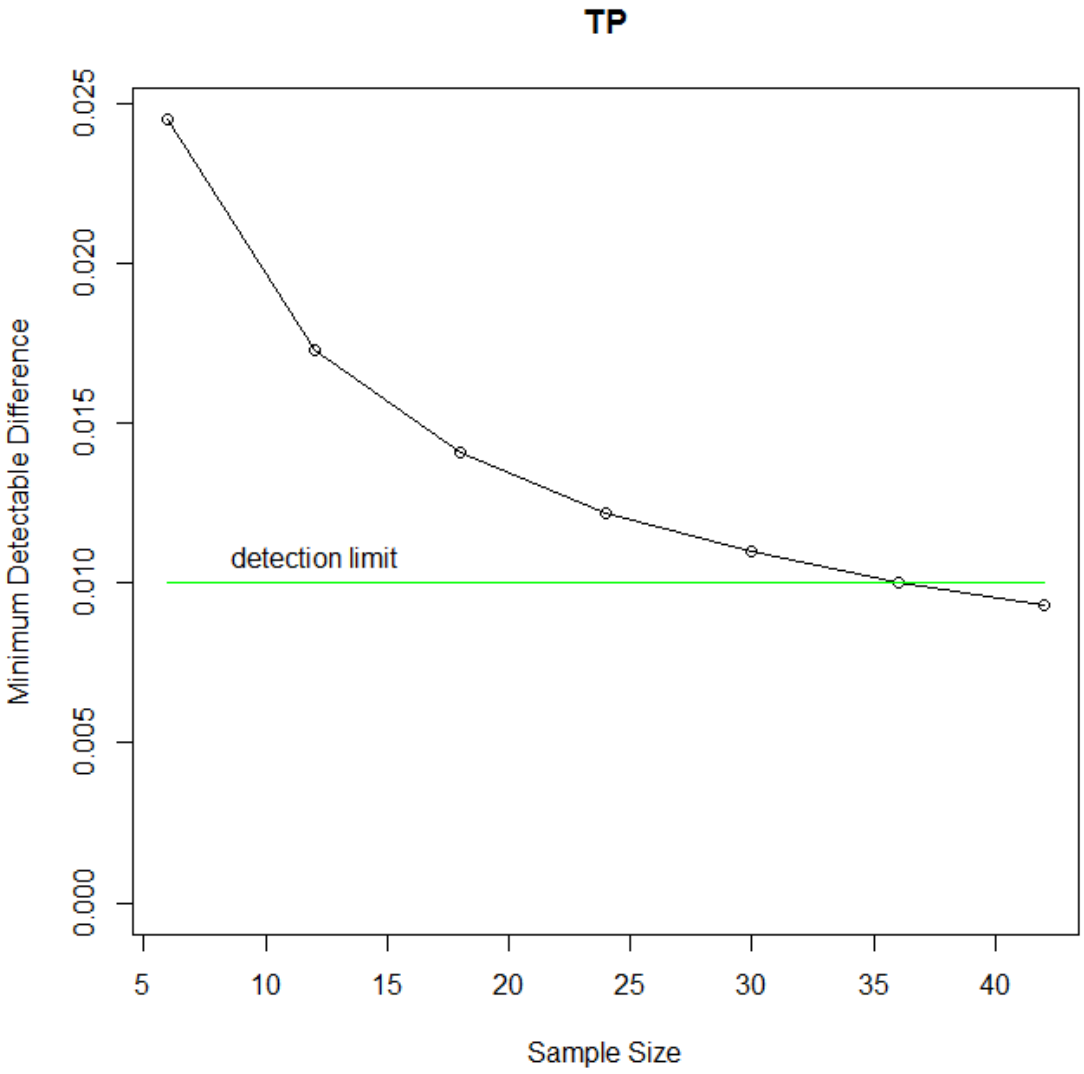

NH4
Minimum Detectable Difference
0.000
0.005
0.010
0.015
detection limit
5
10
15
20
25
30
35
40
Sample Size


NO2
Minimum Detectable Difference
0.000
0.001
0.002
0.003
0.004
0.005
detection limit
5
10
15
20
25
30
35
40
Sample Size


NO23
Minimum Detectable Difference
0.00
0.02
0.04
0.06
0.08
0.10
detection limit
5
10
15
20
25
30
35
40
Sample Size


TOC
Minimum Detectable Difference
0.0
0.2
0.4
0.6
0.8
detection limit
5
10
15
20
25
30
35
40
Sample Size


TN
Minimum Detectable Difference
0.00
0.05
0.10
0.15
0.20
5
10
15
20
25
30
35
40
Sample Size


TP
Minimum Detectable Difference
0.000
0.005
0.010
0.015
0.020
0.025
detection limit
5
10
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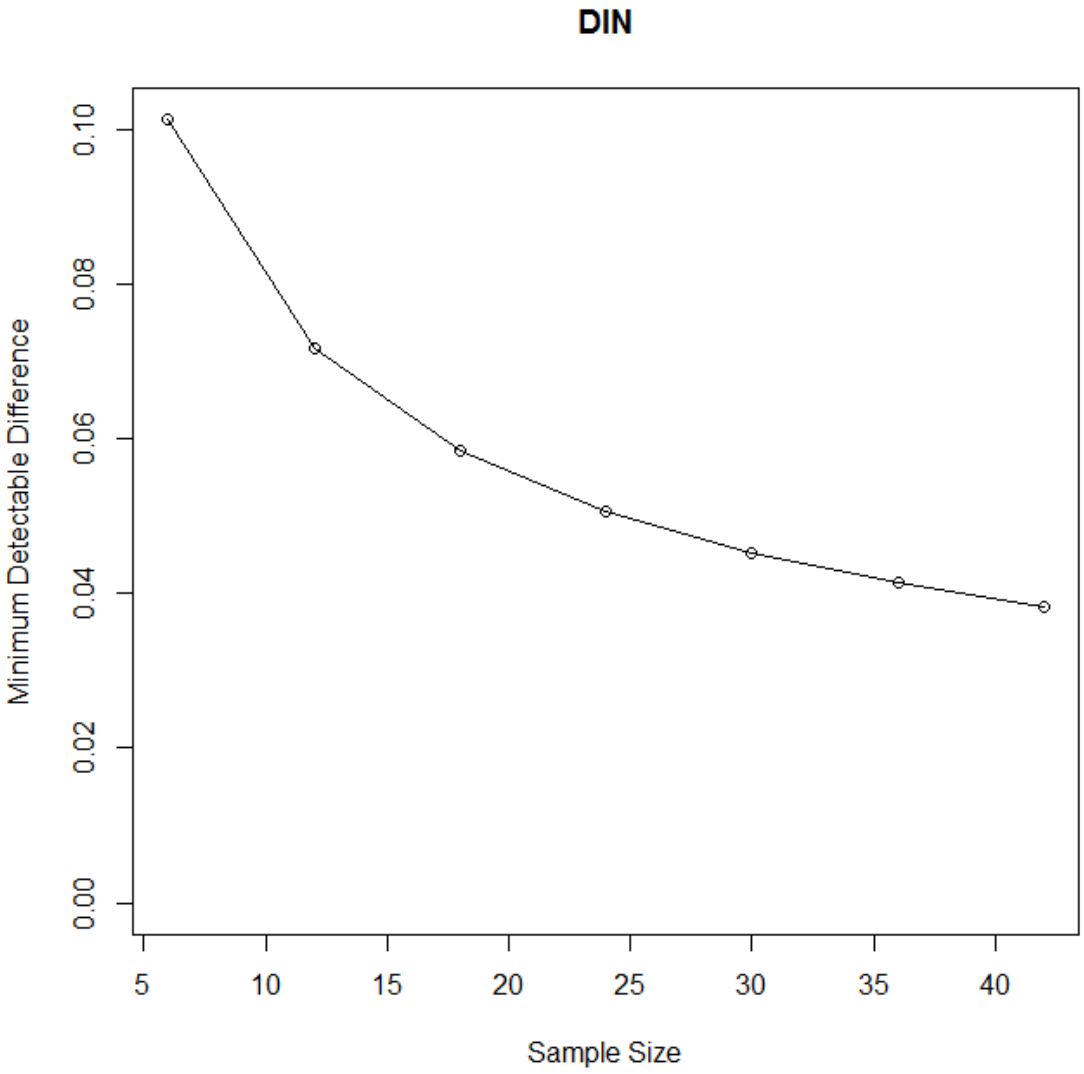
40
Sample Size


DIN
Minimum Detectable Difference
0.00
0.02
0.04
0.06
0.08
0.10
5
10
15
20
25
30
35
40
Sample Size