

Accurate Measurement of Particulate Nitrogen and Phosphorus in Environmental Water Samples

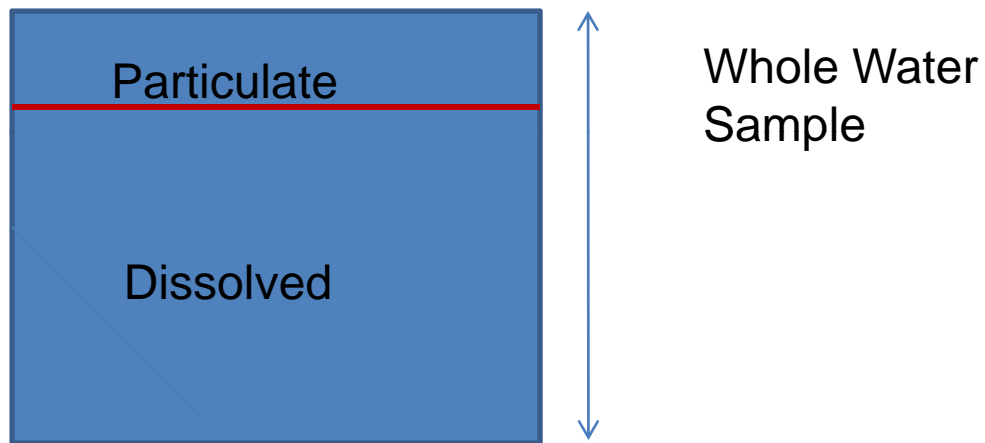
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UMCES, Chesapeake Biological
Laboratory

Outline

- Total Versus Particulate and Dissolved
- Methods Used
- Examples of Data Using Direct Measurements
 - Chesapeake Bay
 - Near Coastal
 - Fresh Water Ponds
- **SRM, Chesapeake Bay Split Sample Program**
- **Chesapeake Bay Blind Audit Program**

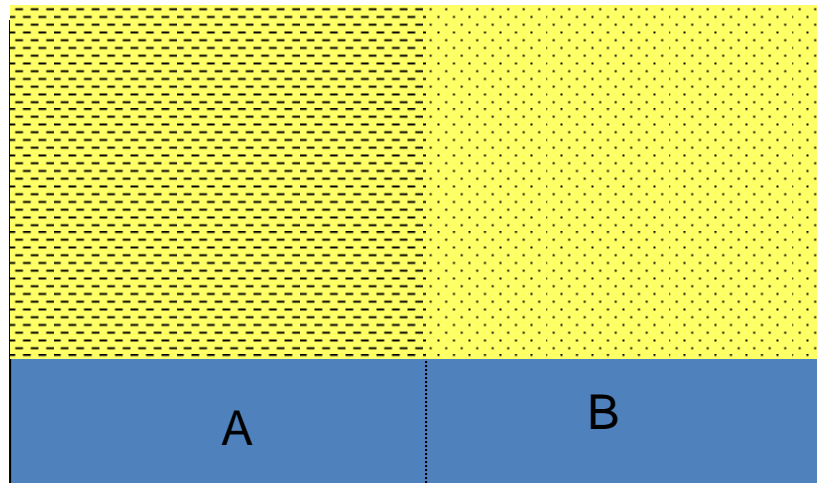
Components Of A Whole Water Sample



Advantages of Direct Particulate Analysis

1. A representative sample can always be obtained.
2. Additional Information is Obtained
 1. Contribution of biological community
 2. How the various fractions may shift spatially and temporally

“By-Difference” vs Direct Analysis of Particulates



“By Difference”..... $\text{Total} - \text{Dissolved} = \text{Particulate}$

Consequences: Opportunity for negative particulate values.

Direct Measurement: Can always obtain a representative sample

Methods

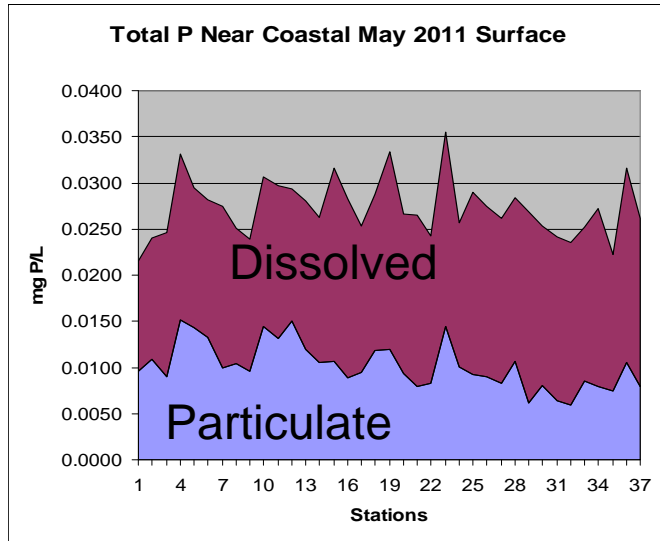
- Particulate Nitrogen: EPA Method 440.0...
(high temperature combustion, using thermal conductivity detection). Exeter Analytical CE440 Elemental Analyzer.
- Particulate Phosphorus: Aspila, et al. 1976
(high temperature ashing/acid extraction)

Examples of Particulate and Dissolved Distributions

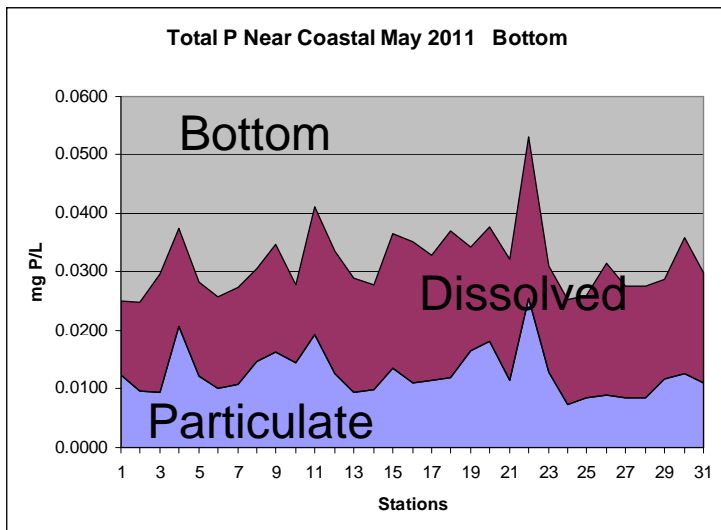
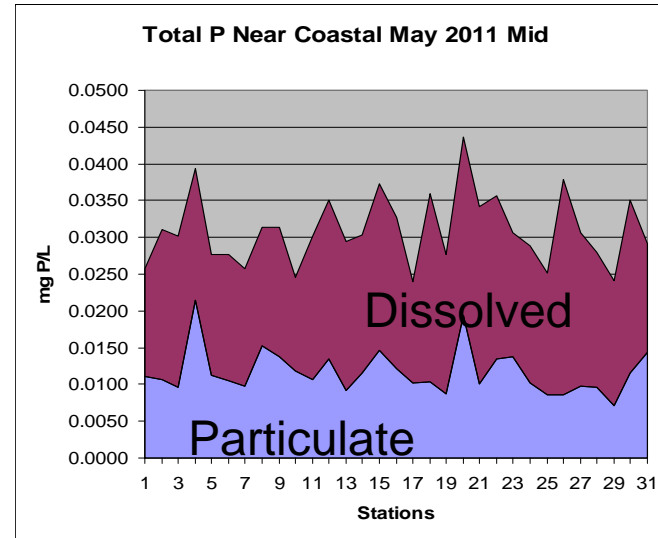
- Coastal DNR Coastal Survey May 2011
- Estuarine... Chesapeake Bay 2001-2003
- Agricultural Ponds... Calvert County, MD

Total P Near Coastal May 2011

Surface



Mid



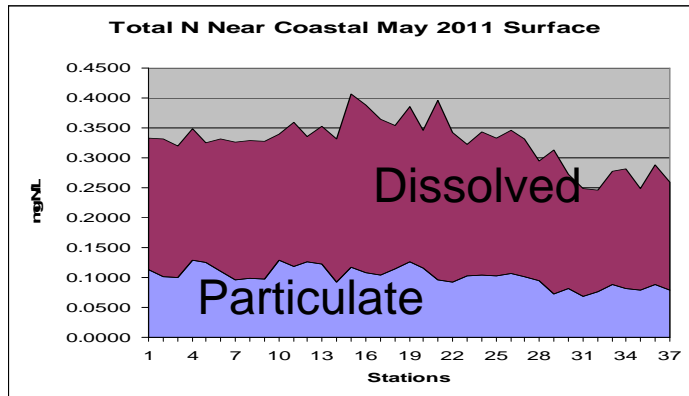
Surface: Particulate: 39%

Mid: Particulate 37.8%

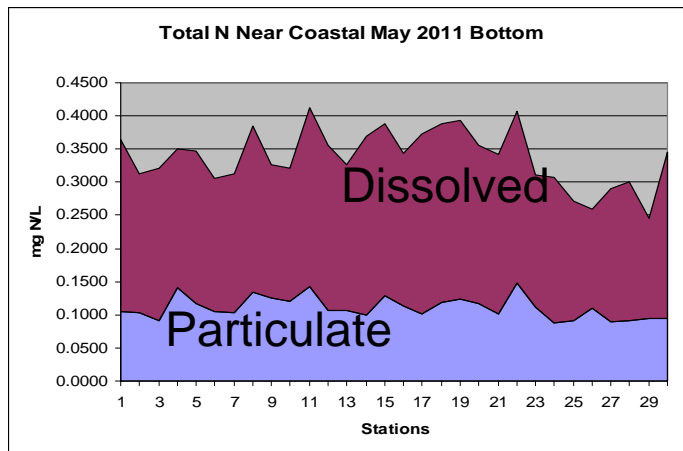
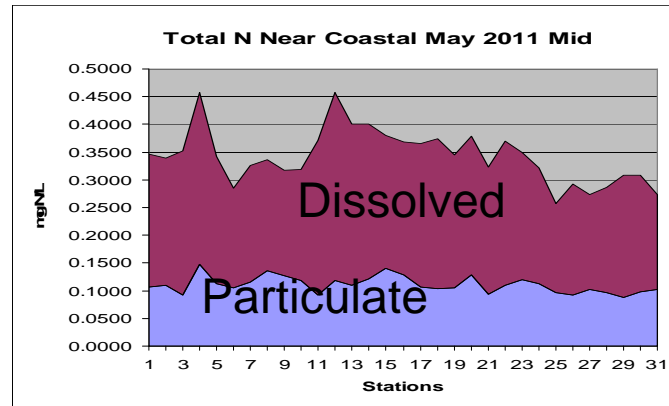
Bottom (10 m): 37%

Total N Near Coastal May 2011

Surface



Mid



Bottom

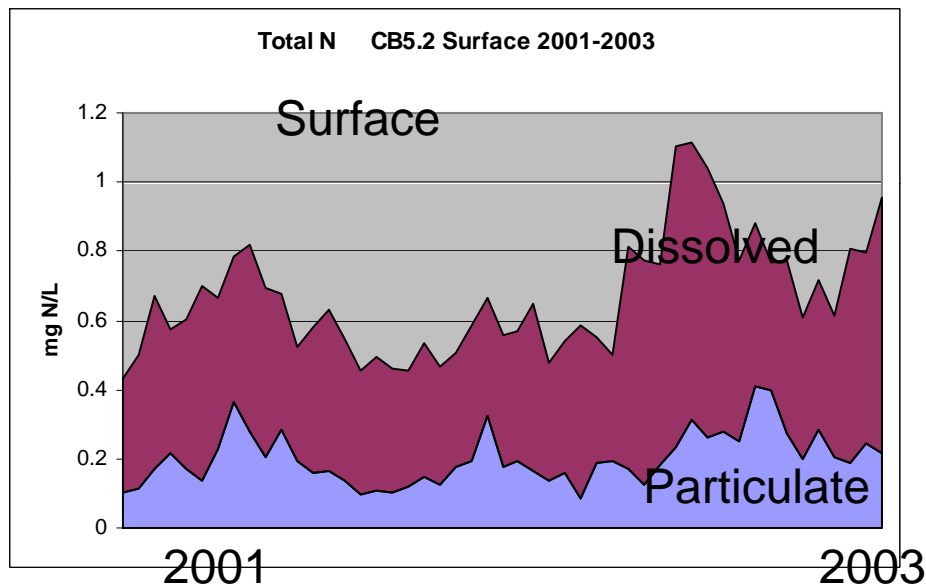
Surface Particulate: 32.9%

Mid Particulate: 32.6%

Bottom (10 m): 31.1%

Chesapeake Bay 2001-2003

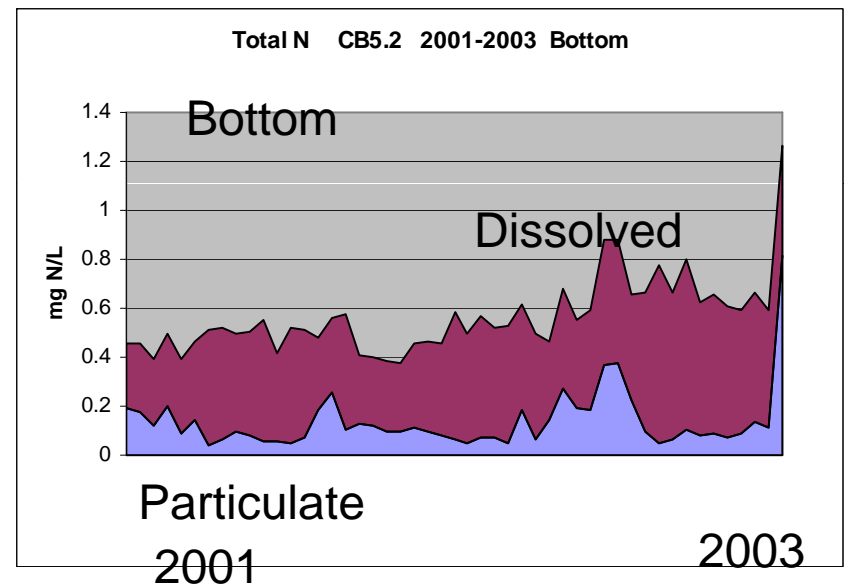
Upper Bay Total N



Particulate Fraction

Mean: 30.1%

Range: 15-50%



Particulate Fraction

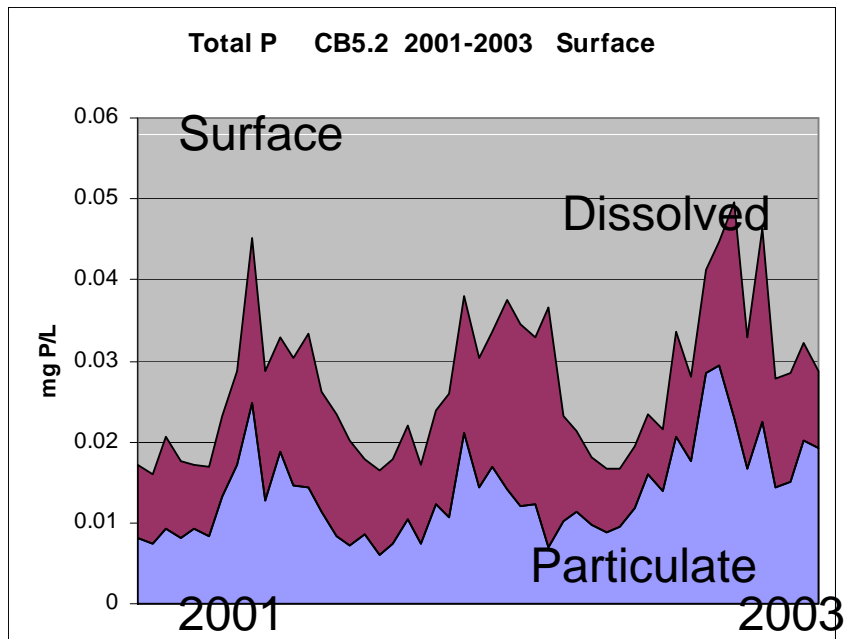
Mean: 23.3%

Range: 10-65%

Chesapeake Bay 2001-2003

Upper Bay

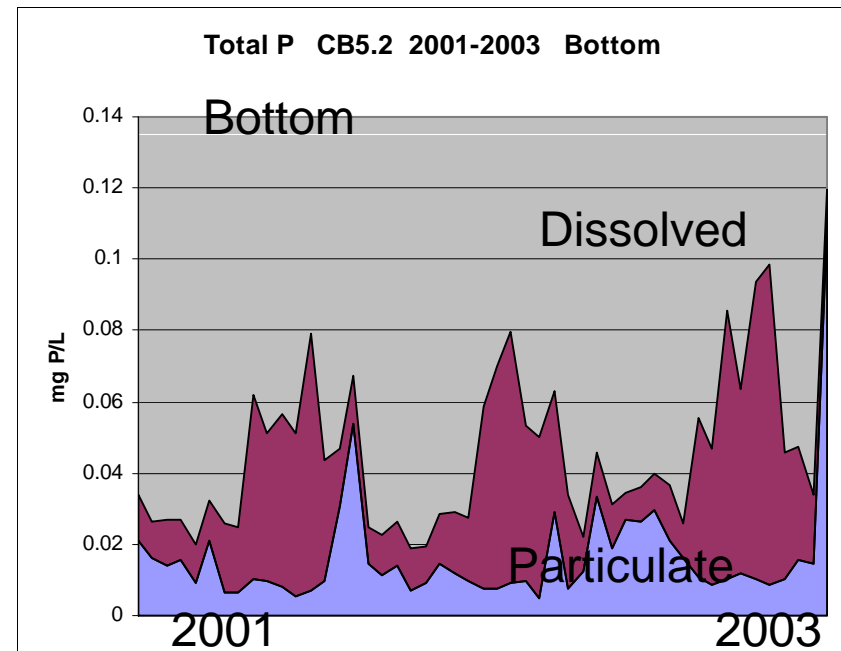
Total P



Particulate Fraction

Mean: 50%

Range: 18-70%



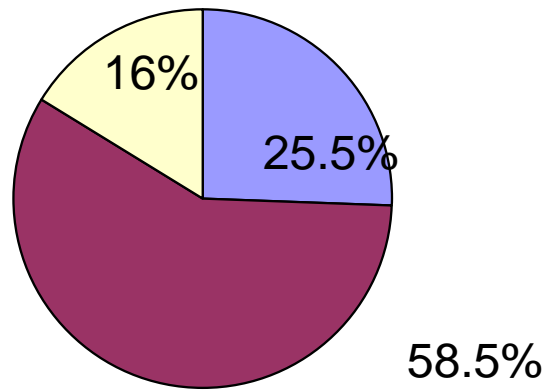
Particulate Fraction

Mean: 39.8%

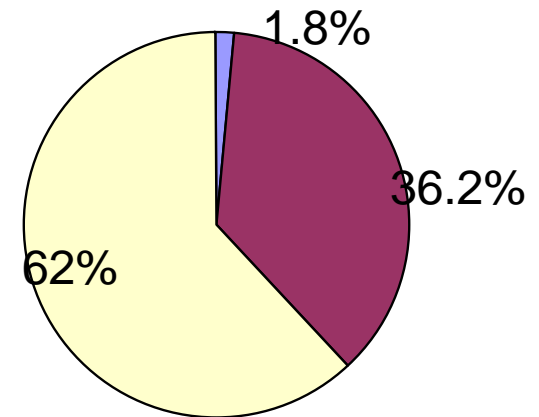
Range: 10-90%

Nitrogen Partitioning Fresh Water Pond

Nitrogen Partitioning November



Nitrogen Partitioning August



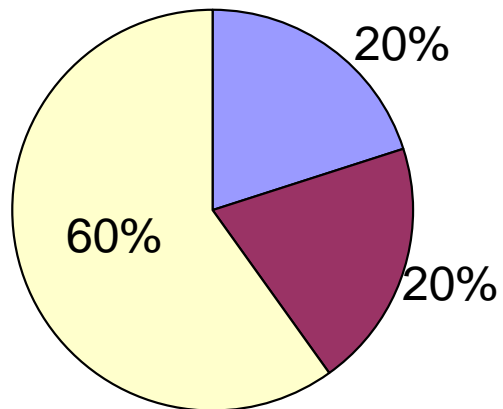
DIN= Blue

DON= Purple

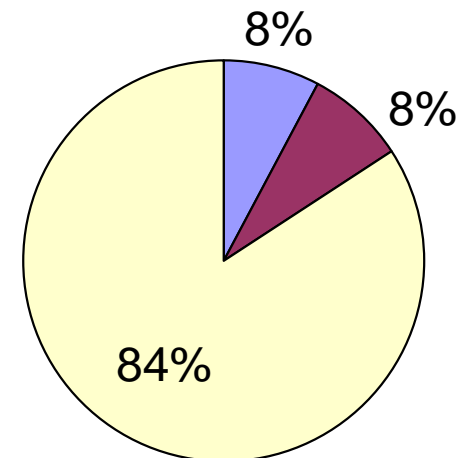
Particulate N= Beige

Phosphorus Partitioning Fresh Water Pond

Phosphorus Partitioning November



Phosphorus Partitioning August



DIP= Blue

DOP= Purple

Particulate P= Beige

Determining Accuracy and Precision of Direct Particulate Measurements

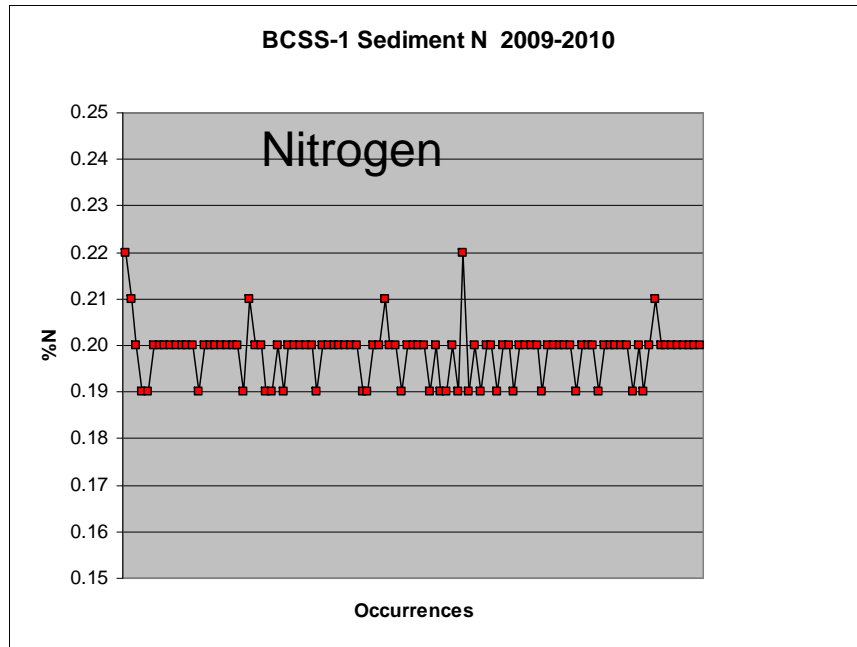
- Determining Accuracy in the Lab
- Chesapeake Bay Split Sample Program
- Chesapeake Bay Blind Audit Program

No Commercially Available SRM for Particulate N and P

BCSS-1 Marine Sediment (Gulf of St. Lawrence) National Research Board of Canada.

Historical Value of N: 0.2%

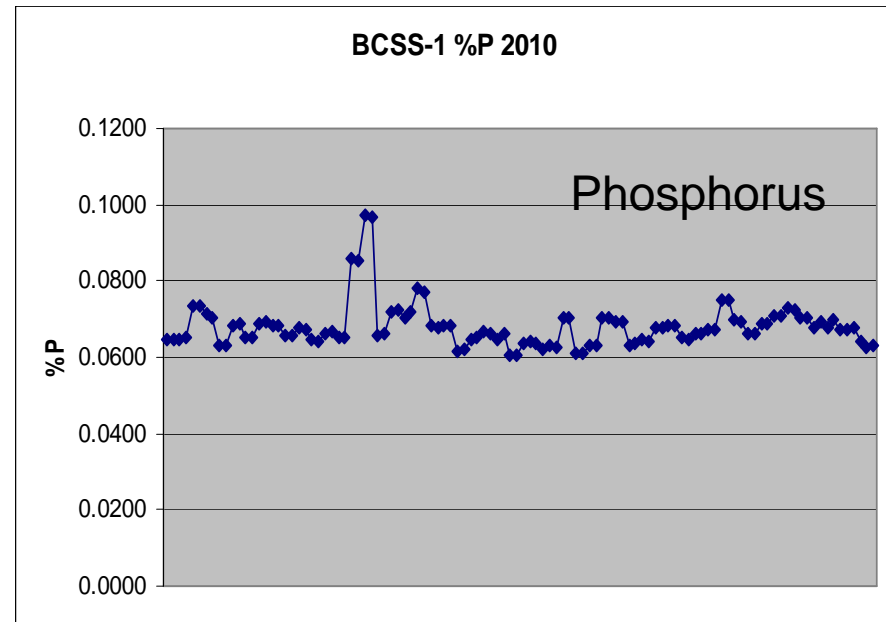
Reliable Value of P: 0.0672%



Mean= 0.20%

Std. Dev.= 0.0057

%CV= 2.8



Mean= 0.068%

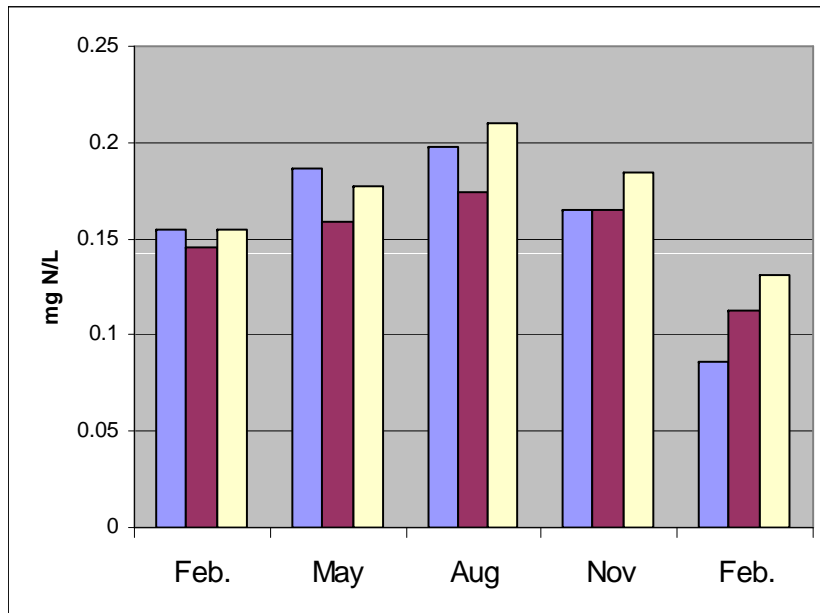
Std. Dev.: 0.0059

%CV= 8.7

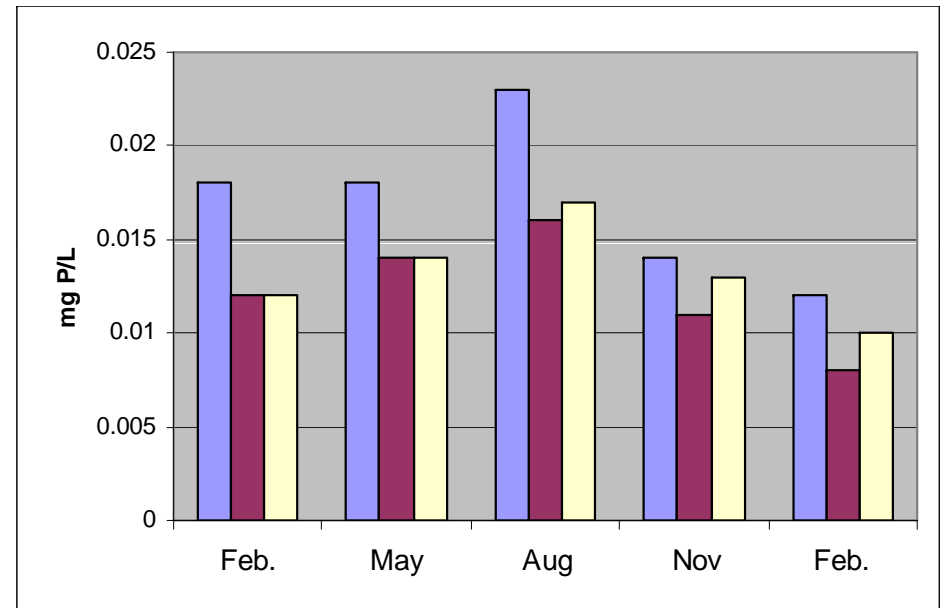
Chesapeake Bay Coordinated Split Sample Program

- Quarterly split samples collected
- Delivered to laboratories same day
- Samples processed by groups the following day
- Results indicative of processing and analytical variability

Particulate N and P Mainstem CSSSP 2010



Particulate N



Particulate P

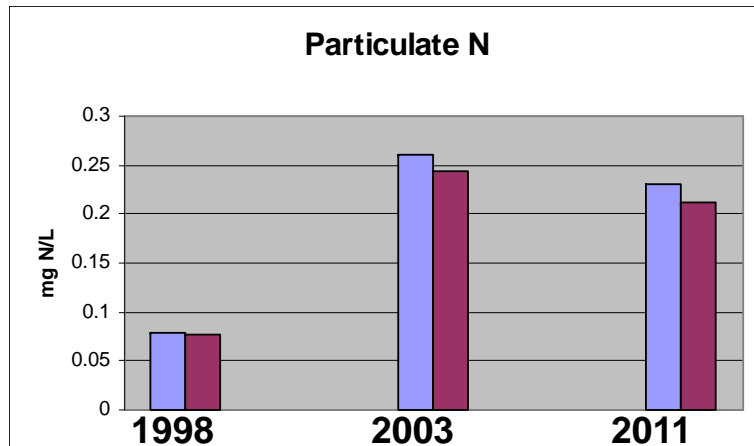
Chesapeake Bay Blind Audit Program

- Particulate and Dissolved Unknowns Sent to Participating Laboratories Semi-annually.
- Prepared Concentrations Approximate Estuarine Levels

Blind Audit Particulates

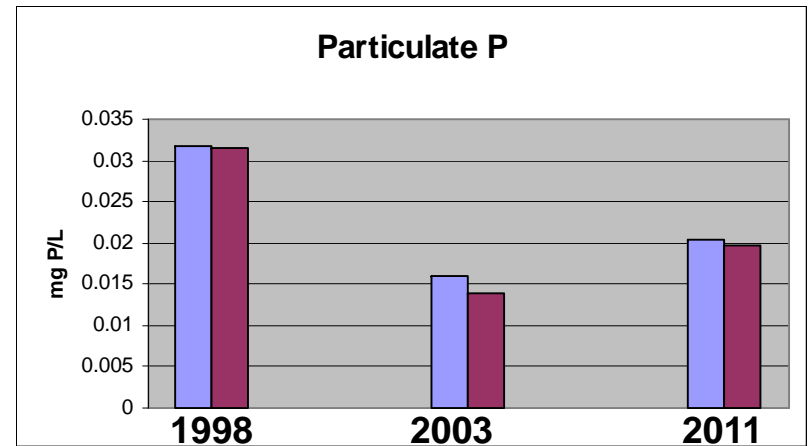
- Natural Population Samples Collected From End of CBL Pier.
- Filtered and Dried
- Several Replicates Analyzed At CBL To Provide Estimate of Analytical and Processing Variability.
- Eliminates other laboratories processing variability

Apparent vs Reported



Blue:
Multiple
Replicates

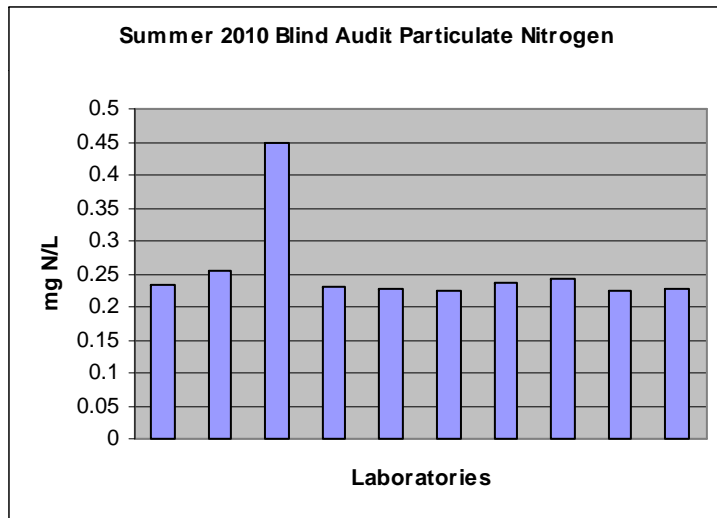
Purple:
Laboratory
Results



<u>Particulate N</u>	CBL	Labs
<i>1998</i>		
Mean	0.078	0.0733
SD	0.004	0.0087
%CV	5.1	11.9
<i>2003</i>		
Mean	0.26	0.243
SD	0.0048	0.0223
%CV	1.8	9.2
<i>2011</i>		
Mean	0.23	0.221
SD	0.0079	0.0131
%CV	3.4	5.9

<u>Particulate P</u>	CBL	Labs
<i>1998</i>		
Mean	0.0318	0.0316
SD	0.001	0.0005
%CV	3.1	1.6
<i>2003</i>		
Mean	0.0159	0.014
SD	0.001	0.0008
%CV	3.1	1.6
<i>2011</i>		
Mean	0.0203	0.0197
SD	0.0018	0.0026
%CV	8.9	13.2

CBP Blind Audit Summer 2010

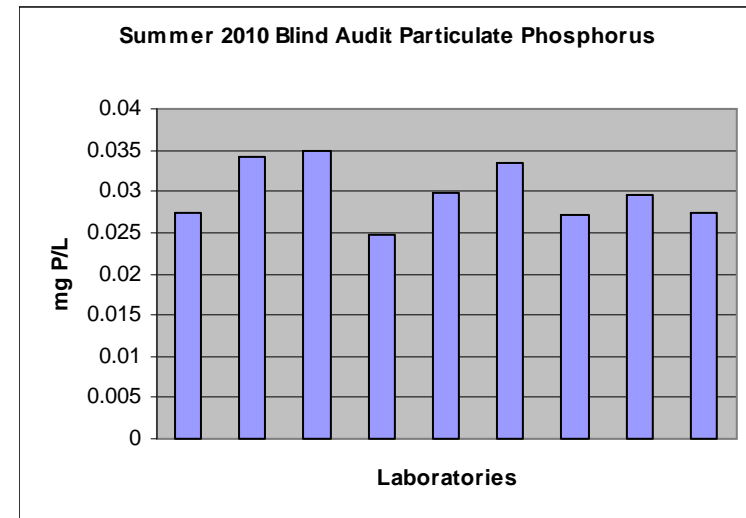


Particulate N

Mean: 0.255 mg N/L

Std. Dev.: 0.068

%CV: 26.9



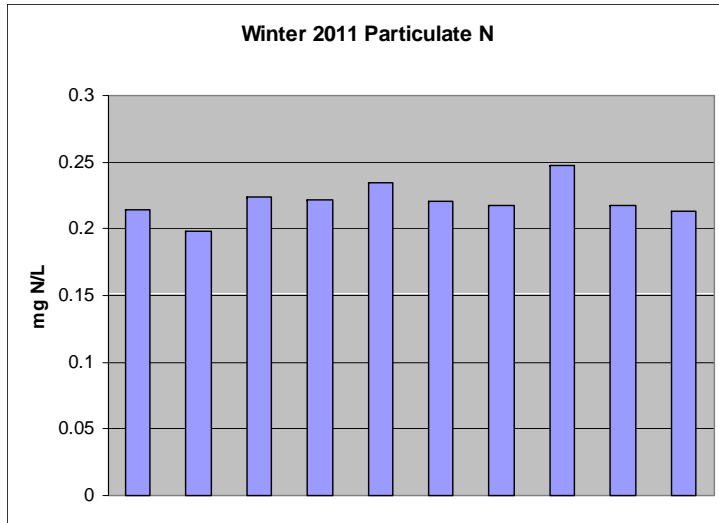
Particulate P

Mean: 0.0298 mg P/L

Std. Dev.: 0.0036

%CV: 12.03

CBP Blind Audit Winter 2011

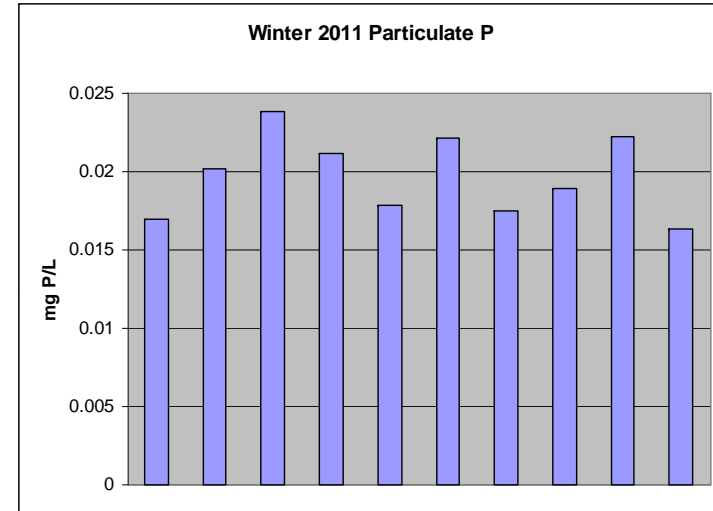


Particulate N

Mean: 0.221 mg N/L

Std. Dev.: 0.014

%CV: 5.9



Particulate P

Mean: 0.0197

Std. Dev.: 0.0026

%CV: 13

Conclusions

- Direct measurement of particulates preferred over the “by-difference” technique.
- Particulate analysis gives an estimate of biological fraction
- Cost
- Chesapeake Bay Program has programs in place to adequately address precision and accuracy of these fractions