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UNIVERSITY OF MARYLAND CENTER for ENVIRONMENTAL SCIENCE
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AND
HORN POINT ENVIRONMENTAL LABORATORY (HPL)

SEDIMENT PHOSPHORUS FLUX: PH INTERACTIONS IN THE TIDAL FRESHWATER POTOMAC RIVER ESTUARY

FINAL REPORT

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Sediment Phosphorus Flux: pH Interactions in the Tidal Freshwater Potomac River Estuary

Final Report

Prepared by:
E. M. Bailey[1], Sr. Faculty Research Assistant
M. Owens[2], Sr. Faculty Research Assistant
W. R. Boynton[1] Principal Investigator
J. C. Cornwell[2], Principal Investigator
E. Kiss[2], Faculty Research Assistant
P. W. Smail[1], Sr. Faculty Research Assistant
H. Soulen[1], Sr. Faculty Research Assistant
E. Buck[1], Laboratory Assistant
M. Ceballos[1], Laboratory Assistant

Prepared for the:
Interstate Commission on the Potomac River Basin
6110 Executive Blvd.
Suite 300
Rockville, MD 20852

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University of Maryland System
Center for Environmental Science

[1]Chesapeake Biological Laboratory (CBL)
P.O. Box 38, Solomons, MD 20688-0038

[2] Horn Point Laboratory (HPL)
2020 Horns Point Road
P.O. Box 775, Cambridge, MD 21613

TABLE OF CONTENTS

Report Summary

1. The primary objective of this research program was to develop a better understanding of the influence of water column pH conditions on sediment phosphorus fluxes in the tidal freshwater portion of the Potomac River estuary. The program had a total of five research components which included a mixture of field measurements and laboratory experiments, both of which were needed to produce a better understanding of the role of sediment phosphorus flux in the ecology of the Potomac River estuary.

2. Field work and laboratory experiments were conducted in April, May, July, September and October of 2004 and July 2005. All measurements were made in the tidal freshwater portion of the Potomac River estuary.

3. Field work included:

1) collection of sediment mapping samples (solid phase analyses)
2) sediment pore water samples
3) *in situ* flux measurements
4) water column profiles
5) surficial sediment sampling

Laboratory experiments included:

1) ambient flux measurements
2) pH response flux measurements
3) sediment microelectrode profiles
4) denitrification measurements

4. Bottom water nutrient concentrations (NO_3, NH_4 and PO_4) were typical of those found in this area of the Potomac River estuary. There was a general increase in concentrations at the end of the study in September, 2004.

5. The chemistry of surface sediments was determined at 40 sites to provide spatial information on percent water, grain size, total and inorganic P concentrations, iron and manganese. These data are useful in the extrapolation of site-specific rate measurements to larger sediment areas. The highest water content and the finest grain size was found below Occoquan Bay; HCl-extractable Mn and Fe concentrations generally follow the grain size distribution. Inorganic P was fairly constant through the upper Potomac, but organic P was much higher in the upper part of the estuary above Mattawoman Creek. Overall, organic P and inorganic P fractions were similar. The expected positive relationship between inorganic P and Fe was evident.

6. Ambient sediment fluxes of oxygen, ammonium and nitrate in the tidal fresh Potomac were very large in comparison to such measurements made in other portions of Chesapeake Bay and in a wider selection of estuaries. The first two of these fluxes have been shown to be largely regulated by the supply rate of labile organic matter available for either aerobic or anaerobic decomposition. The upper

Potomac estuary is heavily enriched with organic matter from both external and *in situ* sources. Hence, the pattern we have seen of large fluxes, based on biological respiratory processes, makes a good deal of sense. The decline in ammonium fluxes in a downriver direction is also consistent with a longitudinal decrease in available organic matter which is likely the case in the Potomac. Sediment phosphorus fluxes were not responsive to this gradient in organic enrichment. Rather, *in situ* PO_4 fluxes were generally small, consistent with observations in other tidal freshwater estuarine zones. This suggests that other mechanisms are controlling P fluxes in this region of the estuary.

7. Denitrification rates were determined on four dates, with a total of 9 rate measurements generated on triplicate cores. Overall rates averaged 99 ± 74 μmoles m^{-2} h^{-1}, with a range from 35-261 μmoles m^{-2} h^{-1}. These high rates reflect an abundance of water column nitrate and the additional supply of nitrate from sediment nitrification.

8. Results of experimental pH elevation on sediment P releases indicated that while there were temporal and spatial differences in responses to pH elevation there were also strong patterns of pH response. With very few exceptions, sediment P fluxes were low (< 25 μmoles m^{-2} hr^{-1}) at pH levels less than about 9.2. In fact, the majority of these fluxes were less than about 10 μmoles m^{-2} hr^{-1} and about 50% were either zero or were directed into sediments, again at small rates. At these pH levels (7 -9) sediment P fluxes are not sufficient to support major phytoplankton bloom formation. However, under pH conditions higher than about 9, sediment P fluxes did increase and at pH levels of greater than 10 reached high levels capable of supporting very large phytoplanktonic nutrient demand. In one experiment there was a clear indication that sediments responded to pH increases within several hours. Experimental measurements made in July responded to pH elevation more than those conducted in May. Measurements made in September responded least to pH increases. Some of this variability might be associated with *in situ* conditions prior to measurement, seasonal variation in sediment P availability, seasonal variations in sediment structure, animal community characteristics influencing bioirrigation or some other factor, or combination of factors, we have yet to consider. However, there remains the fact that there was a strong experimental response to elevated pH and the magnitude of the response was sufficient to supply a great deal of P to the water column.

9. The microelectrode data generally showed oxygen penetration depths of 1.5-2.0 mm; this small aerobic zone is consistent with the high rates of sediment oxygen demand. The sediment pH data showed a rapid response to increased pH in the overlying water. Within a week, elevated pH values were found below 1 cm of sediment depth. Pore water soluble reactive phosphorus also responded quickly, with > order of magnitude increases in concentration. Large gradients in pore water P drive the increased P fluxes observed in our experiments. The pore water data indicate that increased pH has an impact below the sediment surface and that

a large pool of sediment P is susceptible to release with increased pH over a long duration.

10. Results of these investigations suggest the following issues relevant to management:

1) Ambient sediment water P releases are generally small in the tidal freshwater portion of the estuary when pH conditions are also near ambient (pH=7-8).

2) Sediment consumption of dissolved oxygen and nitrate and releases of ammonium are large to very large, indicating that this is a very enriched estuarine zone.

3) There is a very large potential source of P adsorbed to sediments, particularly in the upper portion of the tidal freshwater estuary.

4) At pH levels of 9 or greater sediments released large amounts of P under laboratory conditions and these releases were large enough to support very high rates of primary production, such as those associated with algal bloom formation.

11. Examination of river morphology, suspended sediment conditions and vertical profiles of chlorophyll and pH in the upper Potomac River estuary suggested an additional mechanism for internally generated DIP supply. There are substantial sections of the upper Potomac where shoal (<2 m depth) areas dominate the river cross-section. The importance of shoal areas is that they are vulnerable to sediment re-suspension events caused both by tidal action and modest wind events. Resuspended sediments in the upper estuary are relatively rich in Fe-bound phosphorus. Thus, there is a potentially large source of P associated with resuspended sediments. Vertical profiles of algal biomass indicate that concentrations are higher in near-surface waters and lower, or much lower, at depth. Similarly, pH values were much higher during daytime periods in surface waters than at depth. Surface water pH values can be elevated for 10 or more hours per day and at times reach very high values (pH>10.0). Thus, a likely additional source of DIP involves regular resuspension of bottom sediments from shoal areas. These sediments mix into the upper euphotic layer and for some hours come into contact with waters having high or very high pH conditions. Elevated pH leads to Fe-bound P going into solution and becoming immediately available to phytoplankton. Repeated events reinforces this cycle of enhanced P release, increased phytoplanktonic activity, further pH increase in the water column and more release of P into solution. If further investigations of P sources in the upper Potomac River are to be conducted our research suggests that effort should be directed at clarifying the role of resuspended sediments in shallow embayments as a source of DIP.

ACRONYMS AND ABBREVIATIONS

CBL	Chesapeake Biological Laboratory
CSO	Combined sewer overflow
DGPS	Differential Global Positioning System
DIP (or PO_4^{-3})	Dissolved inorganic phosphorus (or PO_4)
DO	Dissolved oxygen
Eh	Redox potential of sediment porewater
EPA	Environmental Protection Agency
HPL	Horn Point Laboratory
IAN	Integration and Application Network
ICES	International Council for the Exploration of the Sea
KCl	Potassium chloride
m	Meters
MINI-SONE	Abbreviated SONE measurements
mV	Millivolts
µM	micromoles per liter (unit of concentration)
NASL	Nutrient Analytical Services Laboratory
NH_4^+	Ammonium (or NH_4)
NI	Not interpretable
NIST	National Institute of Standards and Technology
NO_2^-	Nitrite (or NO_2)
$NO_2^- + NO_3^-$	Nitrite plus nitrate ($NO_2 + NO_3$)
NPS	Nonpoint source
ODU	Old Dominion University
P	Phosphorus
PC	Particulate carbon
PI	Principal Investigator
PN	Particulate nitrogen
PP	Particulate phosphate
PO_4^{-3}	Dissolved inorganic phosphorus (or PO_4)
ppt	Parts per thousand
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RFO	Research Fleet Operations
SOC	Sediment oxygen consumption
SOD	Sediment oxygen demand
SONE	Sediment Oxygen and Nutrient Exchanges
TMDL	Total maximum daily loads
UMCES	University of Maryland Center for Environmental Science
VIMS	Virginia Institute of Marine Science
WQD	Water Quality Division
YSI	Yellow Springs Instrument

ANALYSIS PROBLEM CODES

ANALYSIS PROBLEM CODE	DESCRIPTION
A	Laboratory accident
B	Interference
C	Mechanical/materials failure
D	Insufficient sample
N	Sample Lost
P	Lost results
R	Sample contaminated
S	Sample container broken during analysis
V	Sample results rejected due to QA/QC criteria
W	Duplicate results for all parameters
X	Sample not preserved properly
AA	Sample thawed when received
BB	Torn filter paper
EE	Foil pouch very wet when received from field, therefore poor replication between pads, mean reported
EN	Value corrupted by electronic noise
FF	Poor replication between pads; mean reported
HD	Particulate and chlorophyll-*a* samples only taken at -1.0 cm of the Eh profile
HH	Sample not taken
JJ	Amount filtered not recorded (Calculation could not be done)
LL	Mislabeled
NI	Data for this variable are considered to be non-interpretable
NN	Particulates found in filtered sample
PP	Assumed sample volume (pouch volume differs from data sheet volume; pouch volume used)
QQ	Although value exceeds a theoretically equivalent or greater value (*e.g.*, PO4F>TDP), the excess is within precision of analytical techniques and therefore not statistically significant.
SD	All sampling at station discontinued for one or more sampling periods
SS	Sample contaminated in field
TF	Dissolved oxygen probe failure
TL	Instrument failure in research laboratory
TS	Dissolved oxygen probe not stabilized
TT	Instrument failure on board research vessel
UU	Analysis discontinued
WW	Station was not sampled due to bad weather conditions, research vessel mechanical failure, VFX array lost or failure of state highway bridge to open or close

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF TABLES

Sediment Phosphorus Flux- pH Interactions in the Tidal Freshwater Potomac River Estuary

Introduction

Background

During the last several decades a great deal has been learned about the importance of exchanges of oxygen and nutrients across the sediment-water interface and the dynamics of these interactions in estuarine ecosystems. Sediment oxygen consumption can be an important sink for oxygen in estuarine environments and sediment nutrient releases can be a large internal source of both nitrogen and phosphorus to the water column (Boynton *et al.* 1991; Kemp and Boynton 1992). Both of the latter compounds are essential for phytoplankton growth, which can become excessive when nutrient supplies are large. Thus, sediment processes can play an important role in determining water quality conditions by lowering oxygen levels and promoting excessive algal growth.

Estuarine water quality conditions can influence fluxes of nutrients from sediments, especially in summer when temperature is high, hypoxic and anoxic events typically occur and pH excursions, especially in poorly buffered tidal freshwaters, can also be large. The magnitude of these sediment oxygen and nutrient fluxes also appear to be directly influenced by nutrient and organic matter loading to estuarine systems (Kemp and Boynton 1992). Both annual and interannual patterns demonstrate that when these external nutrient and organic matter loadings decrease, the cycle of organic matter deposition to the sediments, sediment oxygen demand, and the release of nutrients into the water column also decrease and water quality and habitat conditions improve (Boynton *et al.* 1995). Evaluation of these processes (*i.e.* exchanges between sediment and the water column) as well as mechanisms influencing these processes (e.g., sediment characteristics, dissolved oxygen concentrations and pH levels) provides some of the important information necessary to diagnose water quality status of an estuary. These data can be used in a variety of diagnostic and forecasting tools, including static nutrient budget computations and for calibration and verification of dynamic water quality models.

The Potomac River estuary has been the focus of intense management efforts for several decades. In earlier periods (1960's and early 1970's) water quality in the tidal fresh portion of the river was very degraded, largely from excessive point and non-point nutrient and organic matter inputs. Upgrades in sewage treatment plant operations lead to some substantial improvements in the upper estuary but little change in the mesohaline portion of the ecosystem. In addition, occasional large algal blooms continue to occur in the tidal fresh portion of the estuary and are a cause for concern. This program addresses the role of estuarine sediments as a source of phosphorus to overlying waters in the tidal fresh portion of the estuary and the influence of elevated pH on the release of phosphorus from sediments.

Previous Studies of Sediment Fluxes in the Potomac River Estuary

There have been several earlier examinations of sediment fluxes in various portions of the Potomac River estuary and we have summarized these in Table 1. All but two (Callender 1982 and Seitzinger 1991) were largely monitoring activities wherein a variety of fluxes were measured at fixed sites along the river. Some had limited spatial resolution but were continued for multiple years (Boynton *et al*. 1992) while others emphasized spatial gradients but were conducted for limited periods of time (Bailey *et al.* 2003) or were based on a single set of measurements (Callender and Hammond 1982).

Table 1. Summary of previous Potomac River sediment flux investigations.

Focus of Study	General Locations	Time Span	Authors
1. Longitudinal gradient of fluxes and comparison of gradient and *in situ* fluxes	Tidal Fresh to Chesapeake Bay	Summer 1979	Callender and Hammond (1982)
2. Sediment P-fluxes	Tidal Fresh to Chesapeake Bay	Summer 1979	Callender (1982)
3. Chesapeake Bay Monitoring Program	Mesohaline and transition zone	1985 – 1992 4-6 times per year	Boynton *et al.* (1992)
4. Sediment Flux Monitoring	Tidal Fresh to Oligohaline	Summer 1985 - 1988	Boynton *et al.* (1997)
5. Effects of pH on P-Flux	Tidal Fresh	Fall 1985	Seitzinger (1991)
6. Sediment Flux Monitoring	Anacostia River and Upper Potomac River	Spring and Summer May – August 1990	Sampou (1990)
7. TMDL Sediment Flux Monitoring	Anacostia River	Summer 2002	Bailey *et al.* (2003a)
8. TMDL Sediment Flux Monitoring	Tidal Fresh to Chesapeake Bay	Summer 2002	Bailey *et al*. (2003b)

Two studies examined, to varying degrees, the effect of pH on sediment fluxes of phosphorus (Callender 1982 and Seitzinger 1991). Both concluded that elevated pH enhanced sediment releases of phosphorus and that these conditions occurred in the Potomac River estuary. However, neither study examined, to any significant degree, the mechanisms underlying the pH-sediment P flux relationship, the probable seasonal pattern such a relationship might have, the locations in the estuary (i.e., deep versus shallow areas) where enhanced P fluxes might occur most often, or the temporal characteristics of pH-sediment P fluxes (e.g., sediment response time to elevated pH). This study takes advantage of the earlier studies as a source of background information and as a guide for selecting sampling sites. This program is more comprehensive than previous studies and emphasizes development of a better understanding of the mechanisms listed above.

Recent Experience

During the summer of 2002 our research group at the University of Maryland's Center for Environmental Science conducted sediment-water nutrient exchange studies along the

length of the Potomac River, Anacostia River and Washington Channel. These studies were in support of modeling efforts necessary for the development of total maximum daily loads (TMDL) and were supported by the District of Columbia, Department of Health, Environmental Health Division, Bureau of Environmental Quality, Water Quality Division and Maryland Department of the Environment. Our recent experience in the Potomac was valuable in selecting sampling locations and for judging the ecological significance of fluxes, especially those obtained early in the research program.

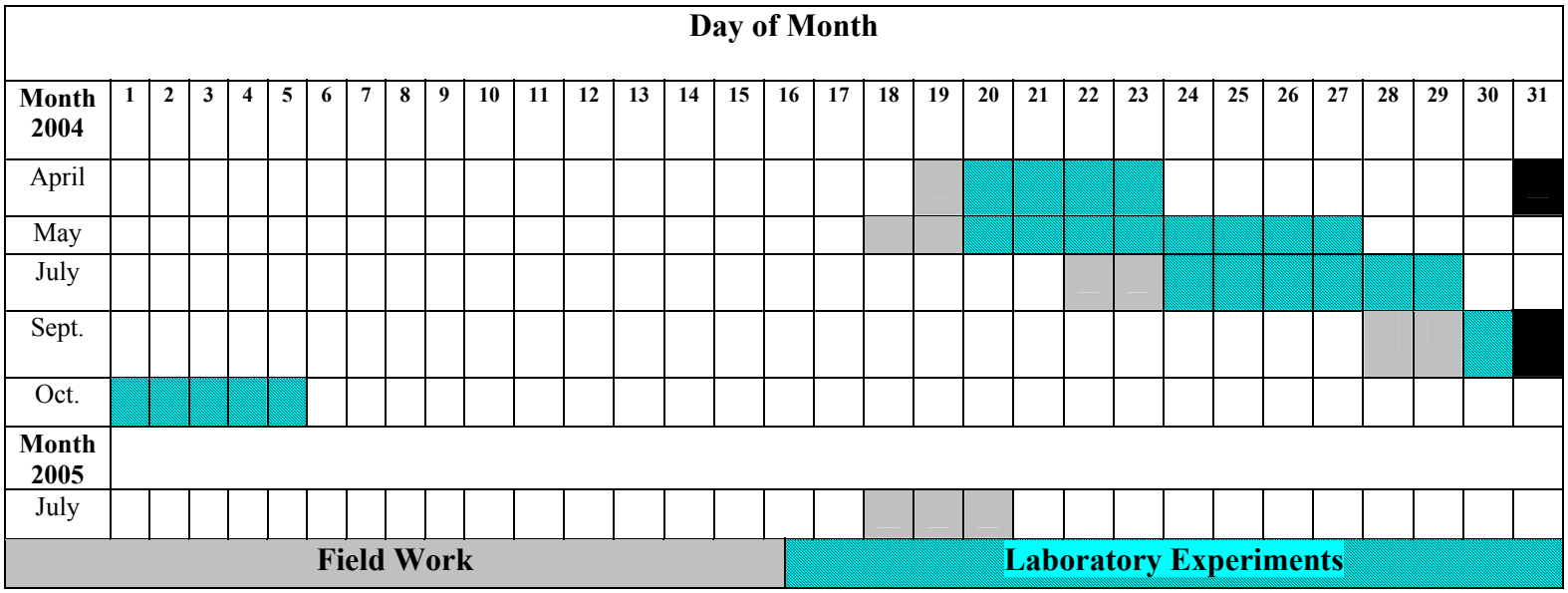
General Project Objectives

The overarching objective of this research program was to develop a better understanding of the influence of pH conditions on sediment phosphorus fluxes in the tidal freshwater portion of the Potomac River estuary. The program had a total of five research components which included a mixture of field measurements and laboratory experiments, both of which were needed to produce a better understanding of the role of sediment phosphorus flux in the ecology of the Potomac River estuary. This research has been designed such that these results will be of direct use to those implementing water quality models of this estuarine system.

Sampling Schedule

Field work and laboratory experiments were conducted in April, May, July, September and October of 2004 and July 2005. We have summarized all sampling dates in Table 2.

Table 2. Summary of field sampling and laboratory experiment schedule, 2004-2005



Field work included:

1) collection of sediment mapping samples (solid phase analyses)
2) sediment pore water samples

3) *in situ* flux measurements
4) water column profiles (water quality parameters and dissolved nutrients)
5) surficial sediment sampling

Laboratory experiments included:

1) ambient flux measurements
2) pH response flux measurements
3) sediment microelectrode profiles
4) denitrification measurements

Description of Study Area

Sampling locations for sediment mapping were distributed between channel, shelf and shoal locations between the Wilson Bridge and Aquia Creek (see Figure 1). Eight stations located between the Wilson Bridge and Smith Point were chosen for sediment pore water sampling, *in situ* flux measurements, water column profiling and surficial sediment sampling. In May sediment mapping samples were collected at the eight main stations. All station location coordinates are included in Table 3.

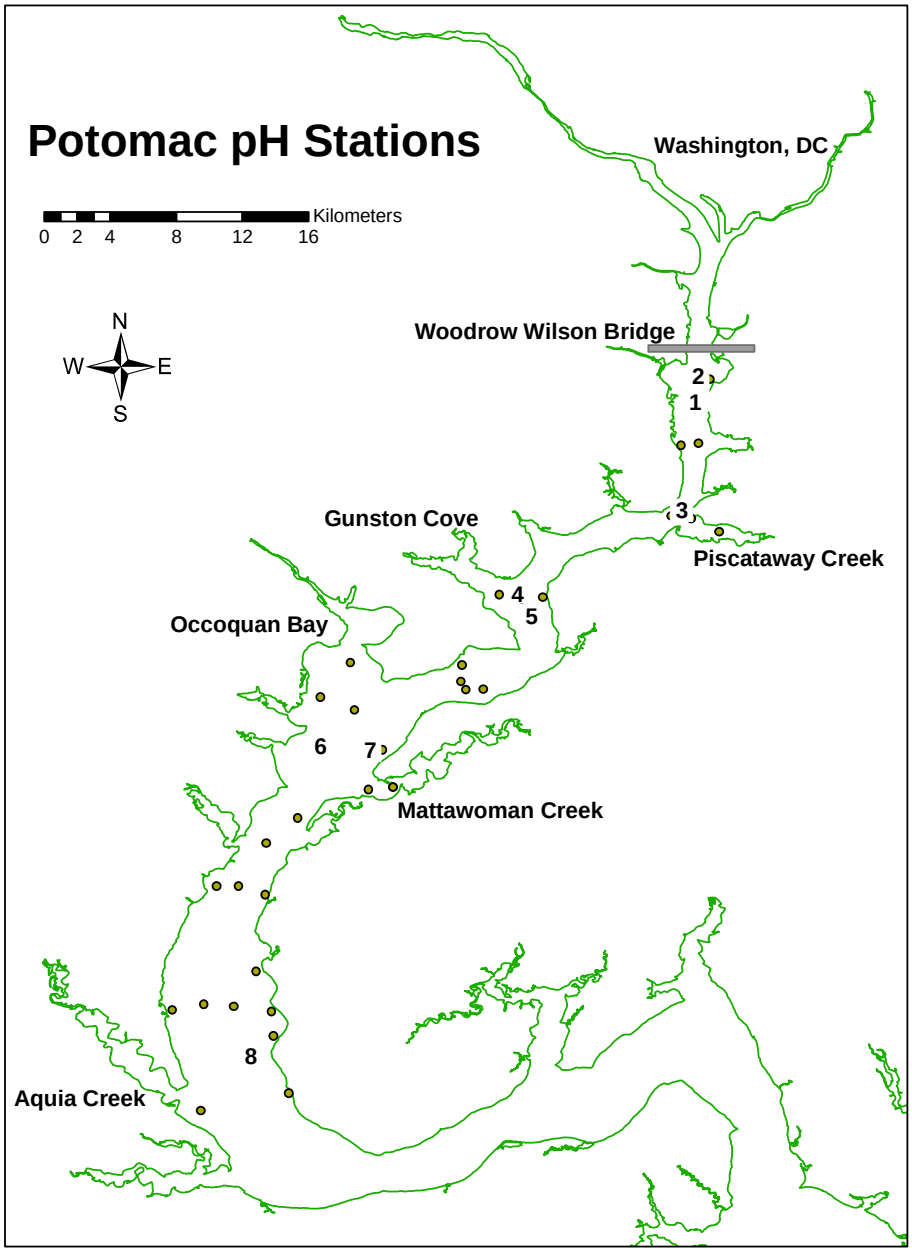


Figure 1. A map of the upper Potomac River Estuary showing the eight main sampling stations (number) and sediment mapping stations (●).

Table 3. Station number, name and grid locations of Potomac sampling stations.
Datum NAD 83.
Latitude and longitude values are expressed as decimal degrees.

Station	Name	Latitude	Longitude	Depth (m)
		Degrees	Degrees	
1	Hunting Creek	38.7705	77.0338	8.6
2	Rosier Bluff	38.7781	77.0333	4.0
3	Piscataway Creek	38.7108	77.0423	3.1
4	Gunston Cove	38.6665	77.1320	6.5
5	Fenwick	38.6538	77.1240	2.9
6	Freestone Point	38.5821	77.2388	5.3
7	Deep Point	38.5805	77.2118	5.0
8	Smith Point	38.4136	77.2765	4.5
M1A	Mapping Station 1A	38.5601	77.1992	2.0
M2A	Mapping Station 2A	38.6020	77.2202	2.4
M3A	Mapping Station 3A	38.6279	77.2224	1.9
M4A	Mapping Station 4A	38.6648	77.1413	1.5
M5A	Mapping Station 5A	38.6635	77.1177	1.6
M6A	Mapping Station 6A	38.7077	77.0480	1.6
M7A	Mapping Station 7A	38.7471	77.0332	1.2
M8A	Mapping Station 8A	38.7461	77.0425	1.7
M1B	Mapping Station 1B	38.5601	77.1993	1.8
M2B	Mapping Station 2B	38.5590	77.2125	2.2
M3B	Mapping Station 3B	38.6131	77.1595	2.3
M4B	Mapping Station 4B	38.6175	77.1622	2.8
M5B	Mapping Station 5B	38.6265	77.1618	2.2
M6B	Mapping Station 6B	38.6626	77.1294	2.4
M7B	Mapping Station 7B	38.6990	77.0219	0.5
M8B	Mapping Station 8B	38.7063	77.0371	1.0
1	Mapping at Station 1	38.7703	77.0335	9.0
2	Mapping at Station 2	38.7820	77.0267	2.1
3	Mapping at Station 3	38.7108	77.0423	3.1
4	Mapping at Station 4	38.6647	77.1328	6.8
5	Mapping at Station 5	38.6536	77.1239	3.0
6	Mapping at Station 6	35.5818	77.2388	5.4
7	Mapping at Station 7	38.5804	77.2049	4.2
8	Mapping at Station 8	38.4135	77.2769	4.6
M1	Mapping Station M1	38.4599	77.2737	8.5
M2	Mapping Station M2	38.5298	77.2682	9.4
M3	Mapping Station M3	38.6091	77.2388	10.7
M4	Mapping Station M4	38.7781	77.0333	4.5
M9	Mapping Station M9	38.5435	77.2510	6.5
M10	Mapping Station M10	38.5064	77.2953	2.4
M11	Mapping Station M11	38.5065	77.2832	6.3
M12	Mapping Station M12	38.5017	77.2687	2.1
M13	Mapping Station M13	38.4388	77.3193	3.0
M14	Mapping Station M14	38.4420	77.3020	4.3
M15	Mapping Station M15	38.4410	77.2860	4.5
M16	Mapping Station M16	38.4383	77.2653	1.8
M17	Mapping Station M17	38.3841	77.3037	2.0
M18	Mapping Station M18	38.3938	77.2559	2.7
M19	Mapping Station M19	38.4250	77.2642	1.8
M20	Mapping Station M20	38.4729	77.2712	2.1

Methods

Coring

Four different coring approaches were used during this project. In shallow waters (< 2.5 m) pole-coring devices suited to 2.5" or 4" ID cores were used. When the R/V Aquarius was used, we used a modified Bouma box corer that was sub-sampled. We also used a 6" Soutar-designed box corer for deployment from small boats. Finally, in very shallow waters, we collected sediment cores by hand.

Sediment Mapping

The top 2 cm of sediment ("surficial") from a 4" core was extruded into a plastic bag and were transported to Horn Point Laboratory (HPL) on ice. The remainder of the sediment core (to 10 cm) was saved for grain size analysis. Sediments were dried at 65 °C, ground with a mortar and pestle, and analyzed for solid phase chemistry (Table 4).

Pore Water Collection

Pore water was collected by centrifugation, with all sediment sectioning in an N_2-filled glove bag to minimize oxidation artifacts (Bray *et al*. 1973). Samples were extruded using a hydraulic piston-driven device. Sectioning was relatively fine near the sediment water interface (0.0-0.5, 0.5-1.0, 1.0-1.5, 1.5-2.0 cm), with coarser sections at greater depth (2-3, 3-4, 5-7, 9-11 cm). After centrifugation, samples were filtered and preserved for analysis. Cores for Br^- diffusion experiments were held with 1 mmol L^{-1} Br^- in overlying water for ~36 hours, with pore water analysis on the same sections as above; use of a glove bag was not necessary for this analysis.

Microelectrode Techniques

The microelectrode system manufactured by Unisense (www.unisense.com) was used for pore water profiling. We have successfully used their O_2 and N_2O micro-sensors in Chesapeake Bay sediments. This profiling has a minimum resolution of 0.1 mm. These electrodes are typically 0.05 mm in diameter at the tip and are quite fragile and expensive, requiring their use in a laboratory setting. Cores were brought back to the laboratory for this analysis. For this program, O_2 electrodes with a 50 μm tip diameter were used to examine sediment oxygen penetration. Profiles were done at 0.2 mm depth intervals. Microelectrode pH profiles were measured with a 50 μm tip electrode, with 0.2 mm depth intervals.

Sediment Pore Water and Solid-phase Analyses

All sediment pore water and related solid phase analyses were carried out in Horn Point Laboratory analytical laboratories.

Table 4. Laboratory analytical procedures used at HPL.

Analyte	Procedure	Preservative	Reference
Pore Water Analysis			
soluble reactive P	manual colorimetric	freezing	Parsons *et al.* (1984) EPA 365.2
nitrate, sulfate, chloride, bromide	ion chromatography	freezing	EPA 300.0

Analyte	Procedure	Preservative	Reference
dissolved iron	manual colorimetric	acidification	Gibb (1979)
Ammonium	manual colorimetric	freezing	Parsons *et al*. (1984)
pH	Electrode	immediate analysis	EPA 150.1
Ca, Mg, Na, K	Ion chromatography	freezing	
Dissolved inorganic C	Gas chromatography	Acidification	Stainton (1973)
Solid Phase Analysis			
total C, N	Elemental Analyzer	drying	Cornwell *et al*. (1996)
inorganic C	Acidification, headspace	drying	Stainton (1973)
inorganic C	CO_2 analysis		
total P	HCl extraction of ashed sediment, colorimetry	drying	Aspila *et al*. (1976)
inorganic P	HCl extraction of unashed sediment, colorimetry	drying	Aspila *et al*. (1976)
HCl-Fe	Analysis of 1.0 N HCL extract by flame AAS	drying	Leventhal (1990)
chlorophyll a	acetone extraction, HPLC	freezing	Sun *et al*. (1991)
grain size	sieving, settling	Refrigeration	Sweet *et al*. (1993)
Water content	Drying at 65º C	None	Cornwell *et al*. (1996)

In Situ Sediment Flux Measurements

The protocols used in Potomac River *in situ* flux estimates are an abbreviated set of measurements of the standard SONE techniques. We used a single sediment core with no blank. Intact sediment cores constitute a benthic microcosm where changes in oxygen, nutrient and other compound concentrations are determined.

A single intact sediment core was collected at each station using a modified Bouma box corer. These cores were then transferred to one of two types of Plexiglas cylinder and inspected for disturbances from large macrofauna or cracks in the sediment surface. If the sample was satisfactory, the core was fitted with an O-ring sealed top containing various sampling ports, and a gasket sealed bottom (Figure 2). The core was then placed in a darkened, temperature controlled holding tank where overlying water in the core was slowly replaced by fresh bottom water to ensure that water quality conditions in the core closely approximated *in situ* conditions.

During the period in which the flux measurements were taken, the cores were placed in a darkened temperature controlled water bath to maintain ambient temperature conditions. The overlying water in a core was gently circulated with no induction of sediment resuspension via stirring devices attached to oxygen probes. Oxygen concentrations were recorded and overlying water samples (35 ml) extracted from each core every 60 minutes during the incubation period. Cores were incubated and sampled using standard MINI-SONE station protocol (incubated for 3 hours with a total of 4 measurements taken). As a water sample was extracted from a core, an equal amount of ambient bottom water was added to replace the lost volume. Water samples were filtered and immediately frozen for later analysis for ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$) and dissolved inorganic phosphorous (PO_4^{-3}). Oxygen and nutrient fluxes were estimated by

calculating the mean rate of change in concentration during the incubation period; volumetric rates were converted to a flux using the volume to area ratio of each core.

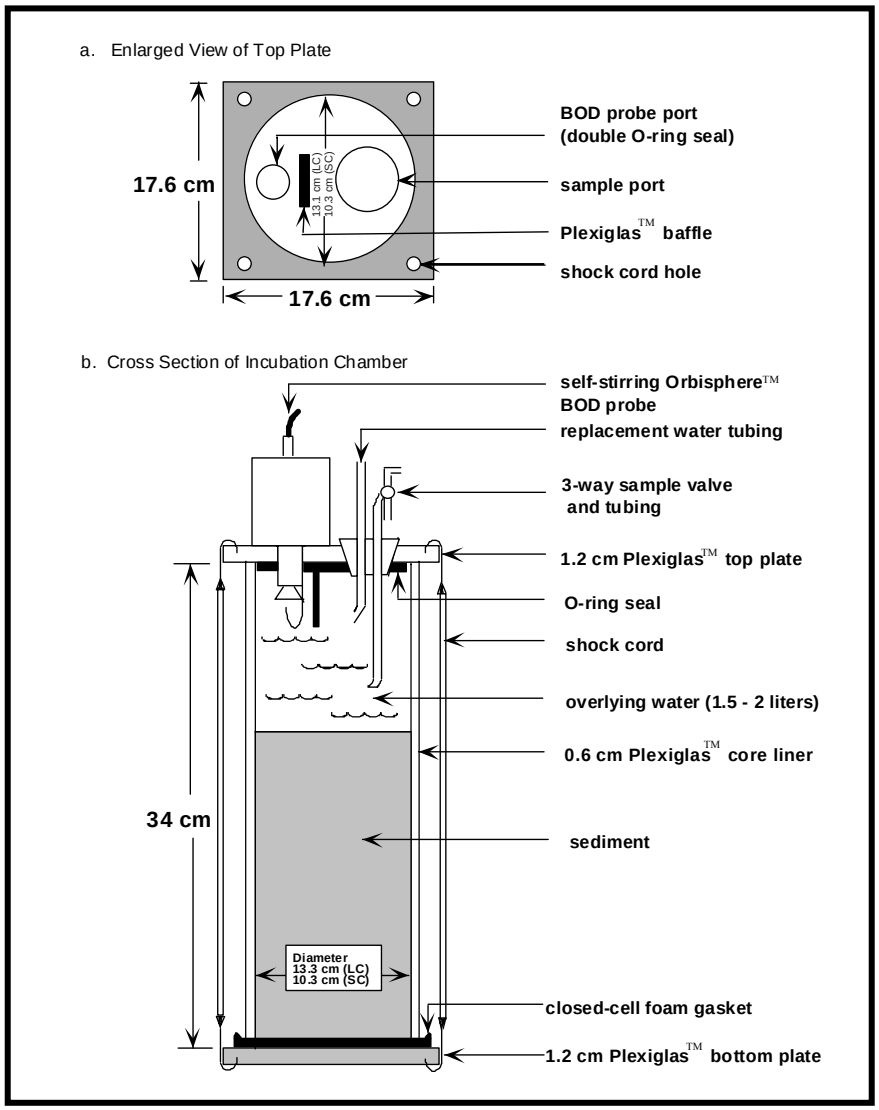


Figure 2. Schematic diagram of the incubation chamber.
a. Enlarged View of Top Plate
b. Cross Section of Incubation Chamber
Small Core (SC): 10.3 cm x 34 cm = 83.3 cm^2
Large Core (LC): 13 cm x 34 cm = 139 cm^2

Water Column Profiles

Vertical water column profiles of temperature, salinity, pH, chlorophyll-*a*, turbidity and dissolved oxygen were measured at 2 m intervals from 0.5 m below the surface to 0.5 m above the bottom at each station using a Yellow Springs Instrument (YSI) 6600 DataSonde®. Turbidity of surface waters was also measured using a Secchi disc.

Water Column Nutrients

Surface (~ 0.5 m) and near bottom (~0.5 m above sediment surface) water samples were collected using a high volume submersible pump system. Samples were filtered using

GF/F (0.7 μm) filter pads and immediately frozen. Samples were analyzed by CBL's Nutrient Analytical Services Laboratory (NASL). Methods for the determination of dissolved and particulate nutrients are as follows: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), and dissolved inorganic phosphorus (DIP or PO_4^-) are measured using the automated method of EPA (1979); particulate carbon (PC) and particulate nitrogen (PN) samples are analyzed using an Elemental Analyzer; particulate phosphorus (PP) concentration is obtained by acid digestion of muffled-dry samples (Aspila *et al.*, 1976); methods of Strickland and Parsons (1972) and Parsons *et al.* (1984) are followed for chlorophyll-*a* analysis. All analytical (laboratory) parameters are measured at the University of Maryland's Chesapeake Biological Laboratory (CBL), Nutrient Analytical Services Laboratory (NASL). See table 5 below for details.

Surficial Sediments for *In Situ* Sediment Flux Measurements

Surficial sediments were sampled using a small core (sub-core of larger cores) for total and active sediment chlorophyll-*a*, particulate carbon (PC), nitrogen (PN) and phosphorus (PP) to a depth of 1 cm. Samples were immediately frozen and returned to Nutrient Analytical Services (NASL) for analyses. Methods for the determination of dissolved and particulate nutrients are as follows: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), and dissolved inorganic phosphorus (DIP or PO_4^-) are measured using the automated method of EPA (1979); particulate carbon (PC) and particulate nitrogen (PN) samples are analyzed using an Elemental Analyzer; particulate phosphorus (PP) concentration is obtained by acid digestion of muffled-dry samples (Aspila *et al.* 1976); methods of Strickland and Parsons (1972) and Parsons *et al.* (1984) are followed for chlorophyll-*a* analysis. All analytical (laboratory) parameters are measured at the University of Maryland's Chesapeake Biological Laboratory (CBL), Nutrient Analytical Services Laboratory (NASL). See table 5 below for details.

Table 5. Laboratory analytical procedures used at CBL (see Rohland *et al.* 2003 for further details).

Matrix	Variable	Analytical Method	MDL (Mean Detection Limit)	Precision (% CV)*	Accuracy (% spike recovery)
Water	Ammonium (NH_4^+)	Berthelot Reaction	0.0030 mg l^{-1}	< 5%	90-110%
Sediment	Active Chlorophyll-*a*	Fluorescence after acidification	0.6 μg l^{-1}	-	-
Sediment	Total Chlorophyll-*a*	Fluorescence before acidification	0.51 μg l^{-1}	-	-
Water	Dissolved Inorganic Phosphorus (DIP)	Antimony-phospho-molybdate complex	0.0006 mg l^{-1}	< 5%	90-110%
Water	Nitrite (NO_2^-)	Diazo compound	0.0002 mg l^{-1}	< 5%	90-110%
Water	Nitrate + Nitrate ($NO_2^- + NO_3^-$)	Copper-cadmium reduction	0.0002 mg l^{-1}	< 5%	90-110%
Sediment	Sediment Particulate Carbon	Combustion in O_2	0.13%	< 5%**	-
Sediment	Sediment Particulate Nitrogen	Combustion in O_2	0.0084%	< 5%**	-
Sediment	Sediment Particulate Phosphorus	Antimony-phospho-molybdate complex	0.008%	< 5%**	-

* Concentration dependent

** BCSS-1 Coastal marine sediment: Standard reference material

Denitrification Measurements

Denitrification measurements were carried out in 7 cm id acrylic cores. Upon collection, cores were bubbled with air to maintain aerobic conditions. Cores were transported to the Horn Point Laboratory in Cambridge, Maryland where they were placed in a constant temperature, dark environmental chamber. Cores were preincubated overnight with air lift pumps in each core used to prevent anoxia and to recirculate the overlying water with a large reservoir water bath. This preincubation also ensures thermal equilibrium between surface sediments and the overlying water; this is critical to the measurement of denitrification. Incubations were started on day 2, with addition of a sealed magnetic stirring unit to the top of the cores and insertion into the incubator. A control core without sediment was used to correct for any water-column effects. The incubator has a central stirring disk that stirs cores in the annular chamber outside the disk. Water temperatures are maintained by using a circulating cooler/heater unit to maintain temperature to within one degree of ambient temperature. An inlet tube and outlet tube is attached to the top of the flux core and ambient replacement water in a carboy is attached to that tube. On the outlet tube, a 2 way valve is attached for sampling. Stirring is carried out at a rate below that required for sediment resuspension. Temperature is monitored at each sample point.

We sampled the cores 4 times at ~2 hour intervals, for a total of 6 hours incubation. Sampling consisted of opening a valve to the replacement water, opening the sampling valve, and sampling using gravity (the replacement water was placed 0.7 m above the cores). For gas analysis (i.e. N_2 and O_2), we added a small sample tube and filled 7 mL stoppered glass tubes to 2 times overflowing (i.e. like a BOD bottle fill). We add 0.010 mL 50% saturated $HgCL_2$ to each vial to preserve the sample; this preservation has worked well on the order of 3 weeks. After stoppers were added, vials are submerged under water and stored at a temperature lower than the incubation temperature; this minimized drying of the stopper/vial joint. For nutrient analysis, a 30 mL syringe was attached to the sampling valve without the plunger; when full, the plunger is added and the sample filtered through a 0.4 μm pore size 25 mm syringe filter. Samples were stored frozen in plastic vials until analysis. At the end of the experiment, the water column heights were recorded to calculate the volume of overlying water.

A membrane inlet mass spectrometer was used for the gas analysis. This instrument resides at Horn Point Laboratory in Dr. Todd Kana's laboratory. This instrument, also known as the Dissolved Gas Analyzer or DGA, provides high precision analysis of gases based on gas ratios (Kana *et al*. 1994; 1998). Argon, a gas not involved in biological processes, is used as a conservative constituent and minor changes in O_2:Ar or N_2:Ar ratios indicate biological or chemical activity. This approach has been the most recent advance in the measurement of denitrification in coastal ecosystems (Cornwell *et al.* 1999). More information may be found at (http://www.hpl.umces.edu/dga/DGAhome.htm).

Sediment P Flux Responses to pH Changes

In all experiments, water from each site was used to treat cores from that specific site. In the first experiment (May 2004), sediment cores were collected from 3 sites (3 cores/site plus one blank core) and returned to the laboratory. Sediment cores were subjected to continuous and elevated pH treatments (pH ~10.0) lasting for 4-5 days using a combination of batch-mode (see Ambient Sediment Flux Measurements below) and flow-through (see Flow-through Sediment Flux Measurements below) incubation techniques. Cores were incubated in the dark and at ambient Potomac River temperatures. Blank cores (cores without sediment) were utilized to correct for any net nutrient concentration changes due to water column processes. Flux measurements were made prior to pH adjustments (to establish flux magnitude under ambient conditions) and then daily for the 4-5 day period of the experiment.

In the second experiment (July 2004), sediment cores were collected from one site (no blanks) and triplicate cores were continuously exposed to waters having a pH of ambient (~7.5), 9.5 or 10.5. Flux measurements were made daily using the batch-mode incubation technique over the course of the 5-6 day experiment. In the third experiment (September 2004), sediment cores were collected from 3 sites and duplicate cores were continuously exposed to waters having a pH of 9.0 or 10.0. Flux measurements were made daily using the batch-mode incubation technique over the course of the 5-6 day experiment. pH was measured using combination electrodes calibrated against NIST-traceable standards. pH response flux experiments treatments are summarized in Table 6 below.

Table 6. Treatment design for Potomac River pH sediment experiments during 2004.

Month	Station	pH Treatment	Core (n)	Blank (n)
May	2	10.0	2*	1
	5	10.0	3	1
	7	10.0	1*	1
July	3	Ambient	4	0
	3	9.5	4	0
	3	10.5	4	0
September	3	9.0	2	0
	3	10.0	2	0
	5	9.0	2	0
	5	10.0	2	0
	8	9.0	2	0
	8	10.0	2	0

* Some replicate cores lost during experiment.

Flow-through Sediment Flux Measurements

After completion of the initial ambient sediment flux and denitrfication incubation the experimental cores were connected to a flow-through system (Figure 4). Water collected from each site was pumped from reservoirs using a peristaltic pump at a rate of about 60 ml min^{-1}. Outflow collection containers were used to measure exact flow rates for individual cores. Water samples were taken at timely intervals for dissolved gases and nutrients and to determine water column pH. After cores had reached desired pH levels

flow-through mode was stopped and batch mode flux measurements were made (described in Ambient Sediment Flux Measurements). We continued alternating between flow-through and batch mode measurements for 4-5 days.

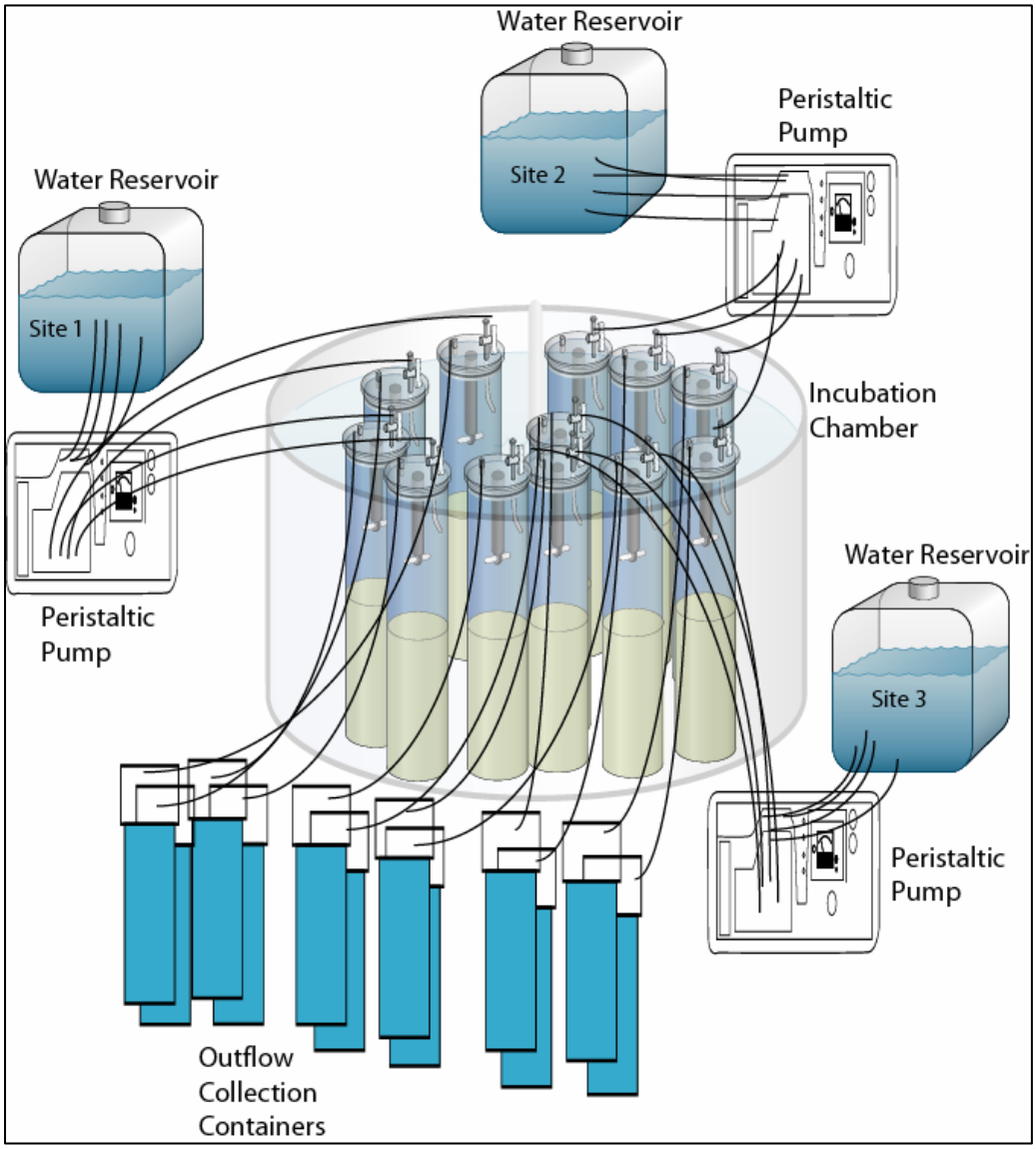


Figure 3. Diagram of flow-through incubation system (symbols from UMCES IAN Symbol Library).

Ambient Sediment Flux Measurements (Batch Mode Incubations)

Ambient sediment flux and dentrification incubations were performed prior to initiating pH treatments (first experiment) and separately from batch mode incubations (second and third experiments). Initial incubation of the experimental cores occured within 24 hours of core collections. From each site, 3 replicate cores plus one blank core that contains bottom water were incubated. Upon arrival to our temperature controlled (± 0.5 °C) chamber at Horn Point Laboratory, the cores were immersed in bottom water which is continually exchanged with the cores to 1) assure saturation with respect to oxygen and

2) equilibrate the plastics so that other gases (N_2, Ar) and O_2 have a minimum incubation artifact (i.e. no change imposed by gases in the plastic). After ~ 12 hours of exchange, stirring tops were placed on the cores, a replacement water line was attached to each core, and incubations were started. Incubations were carried out in the dark. Using gravity, replacement water was added to the cores and sample water collected in 1) glass tubes for gas analysis and 2) 20 mL plastic syringes for nutrient analysis.

Batch mode incubations were performed during the second and third experiments. Cores were returned to our lab at the Chesapeake Biological laboratory and placed in bottom water filled incubation chambers located in a temperature controlled (± 0.5 °C) environmental room (Figure 4). Upon initial arrival, all cores were gently flushed (total overlying water volume exchanged > 4 times) with water from each core's specific site and then bubbled overnight with air. Water from each site was treated to achieve the desired pH (titration with 1N NaOH) and bubbled overnight with air to maintain oxygen levels. Within 24 hours of collection, cores were treated with pH adjusted water by gentle continual flushing. Every 24 hours flushing was halted in order to perform static flux measurements (see methods above for *In Situ* Sediment Flux Measurements) for 3 hours.

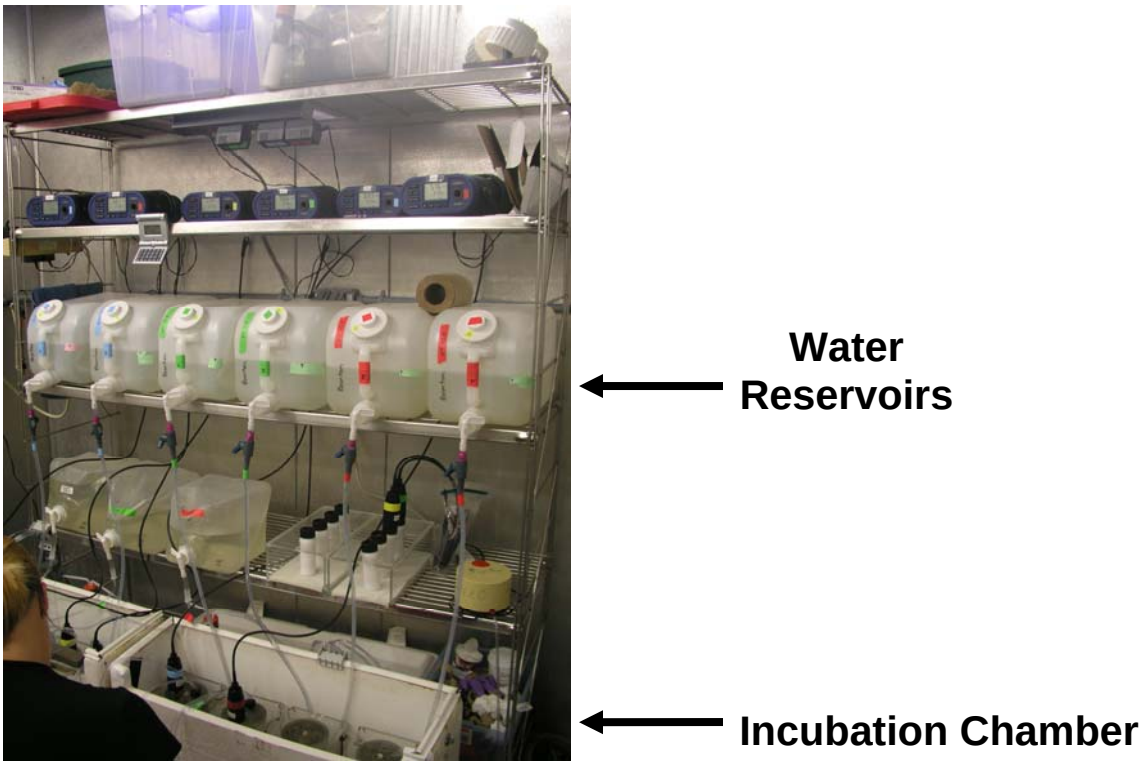


Figure 4. Picture of batch mode sediment flux incubation system.

Results

Water Column Conditions

Water quality conditions at the study sites are summarized in a series of tables (7, 8, 9 and 10) and Figure 4. The nearest Chesapeake Bay Program Monitoring Station has been listed for reference (http://www.chesapeakebay.net/pubs/maps/2004-149.pdf**).** Depths at the eight main flux stations ranged from about 3 to 9 m (Table 7). As expected, salinity of surface waters was very low at all stations during the full study period (Table 7). All stations were basically tidal-fresh (0.1 to 0.5) with no vertical stratification (Table 8). Water temperatures were generally warm with surface and bottom water averages ranging from 24 to 26 ºC, well within the range of typical summer values in shallow temperate estuarine ecosystems (Table 8). Dissolved oxygen levels were moderate to high at all stations and depths over the entire study period (Table 8). Dissolved oxygen ranged from 6.4 to 9.4 mg L^{-1} in surface waters and from 6.3 to 8.1 mg L^{-1} in bottom waters. Average pH values across all cruises ranged from 7.5 to 8.7 in surface waters and from 7.6 to 8.4 in bottom waters (Table 8). Average turbidity ranged from 21 to 66 NTU in surface waters and 30 to 94 NTU in bottom waters (Table 8).

Table 7. Basic descriptions of characteristics at 8 routinely sampled stations (averages from all cruises n=3).

Station	Name	Depth (m)	Salinity (surface water)	Nearest CBP Monitoring Station*
1	Hunting Creek	8.6	0.1	PMS48
2	Rosier Bluff	4.0	0.1	PMS48
3	Piscataway Creek	3.1	0.1	XFB1986
4	Gunston Cove	6.5	0.1	TF2.2
5	Fenwick	2.9	0.1	TF2.2
6	Freestone Point	5.3	0.1	IH1
7	Deep Point	5.0	0.1	IH1
8	Smith Point	4.5	0.5	RET2.1

***http://www.chesapeakebay.net/pubs/maps/2004-149.pdf**

Table 8. Water quality conditions at 8 routinely sampled stations (averages from all cruises n=3).

Station	Temperature (°C)		Salinity		DO (mg L^{-1})		pH		Turbidity (NTU)	
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	26.2	25.9	0.1	0.1	7.04	6.37	8.00	7.92	32.5	86.6
2	25.8	25.6	0.1	0.1	6.88	6.54	7.90	7.82	21.9	30.2
3	26.0	26.0	0.1	0.1	6.49	6.31	7.77	7.74	20.9	53.7
4	25.8	25.6	0.1	0.1	6.41	6.32	7.67	7.66	35.3	90.0
5	24.1	24.0	0.1	0.1	6.39	6.36	7.56	7.56	65.6	88.3
6	25.8	25.4	0.1	0.1	9.42	8.15	8.74	8.39	31.9	52.5
7	25.6	25.2	0.1	0.1	8.55	7.26	8.29	7.80	37.8	57.3
8	25.0	25.0	0.5	0.7	7.53	7.20	8.00	7.86	42.3	93.5

Surface: 0.5 m below water surface.
Bottom: 0.5 m above sediment surface.

Figure 5 shows water column pH values for the three 2004 Potomac cruises. During the May 2004 cruise the highest surface water pH value (8.7) occurred at station 6 (Freestone Point). pH values rose to their highest levels in surface waters during July with values reaching close to 10 at stations 6 and 7. Bottom water pH values were also highest in July with the highest value of 9.4 occurring at station 6. In September, pH at all stations in both surface and bottom waters, had dropped to around 7.5.

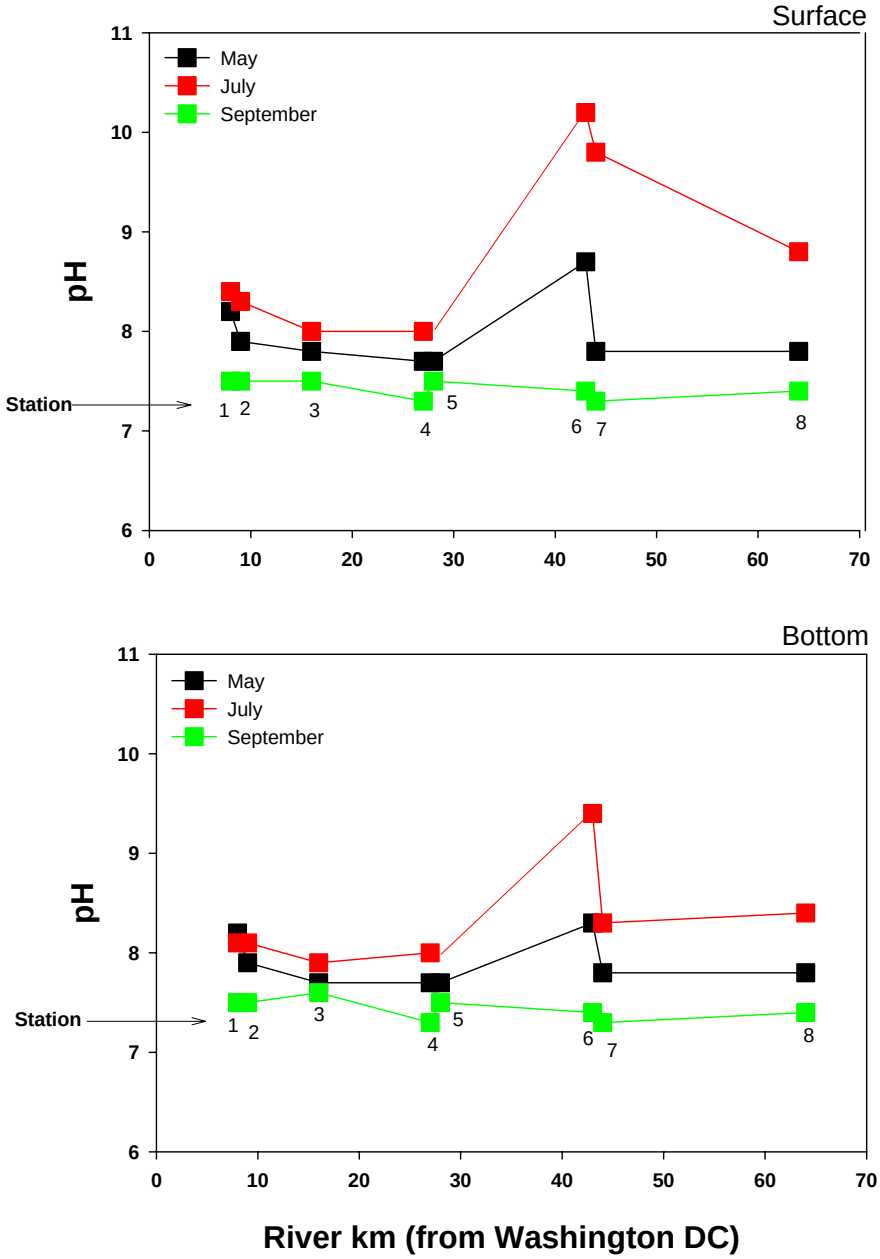


Figure 5. Water column pH during 2004 Potomac cruises. Numbers denote stations.

Bottom water nutrient concentrations are summarized in Figure 6. Ammonium concentrations were moderate (5-10 µM) at most stations during all months. During the September cruise, ammonium concentrations were quite high (~30 µM) at station 2 (Rosier Bluff). Nitrate concentrations were generally high at all stations during all cruises ranging from around 20 µM to about 100 µM. Nitrate concentrations remained high during each cruise and showed only moderate decreases at the three downriver stations (6, 7 and 8) during the May cruise. Dissolved inorganic phosphate concentrations were generally low (~ 0.5 µM) at most stations during all three cruises. The notable exceptions were the higher values (> 1.0 µM) seen at the 5 most upstream stations during the September cruise.

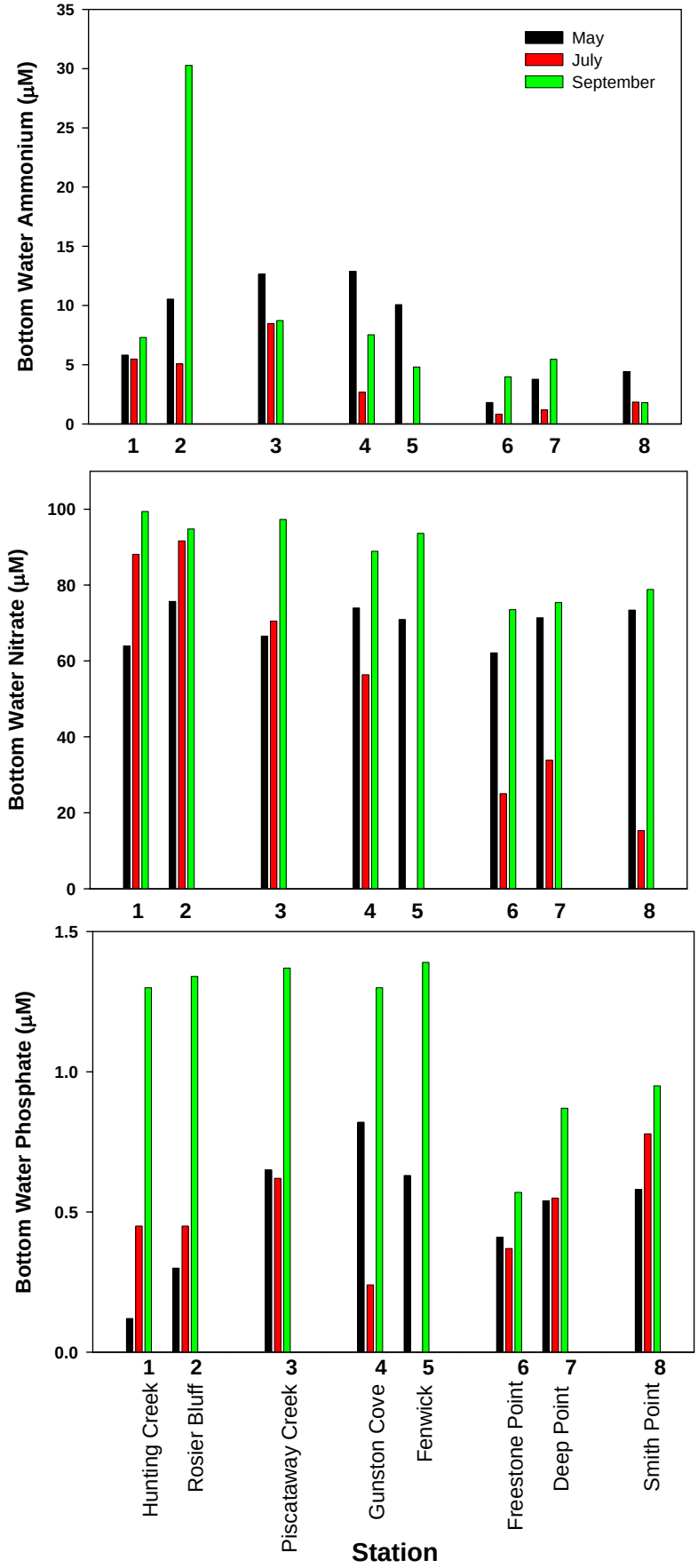


Figure 6. Bottom water nutrient concentrations observed during 2004 Potomac River estuary cruises.

Surficial Sediment Conditions

Sediment organic matter content was characterized with measurements of particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP) and two measures of labile organic matter based on total and active chlorophyll-*a* content of surface sediments (Table 9). Average sediment PC values were typical of those observed in enriched areas of the Chesapeake Bay ranging from about 2.5 to 5 % of dry sediment weight. Both sediment PN and PP values were moderate with little variation ranging from 0.22 – 0.33 % and 0.08 to 0.1 % dry sediment weight respectively. Sediment concentrations of total (active chlorophyll-*a* plus chlorophyll-*a* degradation products) and active chlorophyll-*a* are used as indicators of labile organic matter. Average total sediment chlorophyll-a values ranged from 49 to 75 mg m^{-2} with between 20 to 40% of total chlorophyll-*a* in the active form.

Table 9. Surficial (top 1 cm) sediment particulate concentrations at 8 main sampling stations (averages from all cruises n=3).

Station	(PC) Carbon % (wt)	(PN) Nitrogen % (wt)	(PP) Phosphorus % (wt)	Total Chl-*a* (mg m^{-2})	Active Chl-*a* (mg m^{-2})
Up River▼					
1	3.87	0.327	0.088	58.2	21.3
2	3.16	0.260	0.080	74.6	29.6
3	2.91	0.293	0.100	68.6	23.0
4	2.47	0.220	0.082	66.6	20.0
5	5.01	0.335	0.086	48.6	17.1
6	2.93	0.327	0.094	58.3	20.0
7	3.32	0.333	0.104	65.3	21.3
8	2.79	0.327	0.104	59.9	12.7
Down River					

Sediment Mapping

The surficial (0-2 cm) mapping data were examined for 1) the spatial distribution of grain size, P, Fe and Mn distributions and 2) data inter-relationships. Using the NAD 83 Horizontal Datum, data were interpolated using the Ordinary Kriging routine in the Geostatistical Analyst extension for ArcGIS 8.3. This produced a rectangular layer which was then cropped to the extent of the study area on the Potomac. Core composition figures, represented by percentage, were classified manually to reflect a scale from 0-100% in 10% increments. Concentrations were classified using a Smart Quantile method in the Geostatistical Analyst. This method follows natural breaks within the distribution of the data, and is useful for exploring these types of datasets since it represents a compromise in highlighting changes within middle values and accurate representation of extreme values. The product of this effort is a series of sediment maps of percent water, percent sand, percent silt, percent clay, total P, inorganic P, organic P, HCl-extractable Fe and HCl-extractable Mn (Figures 7 – 15).

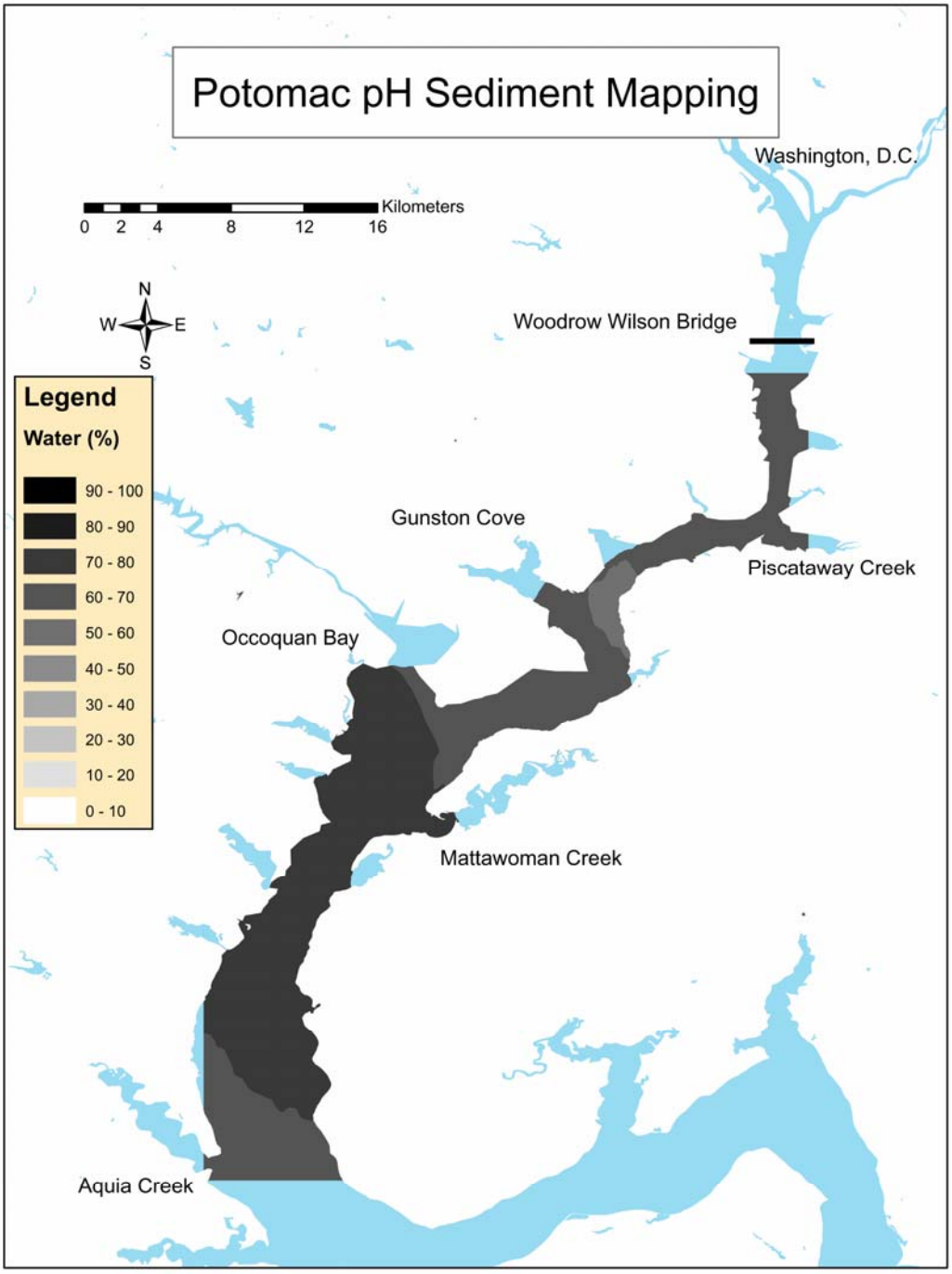


Figure 7. Sediment map of percent water in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

Percent water in surficial sediments is generally higher in fine-grained sediments; in the upper Potomac, the samples below Occoquan Bay tended to be higher (> 80% by weight) in water content (Figure 7). Mean percent water in this study was 67±10%. The coarse

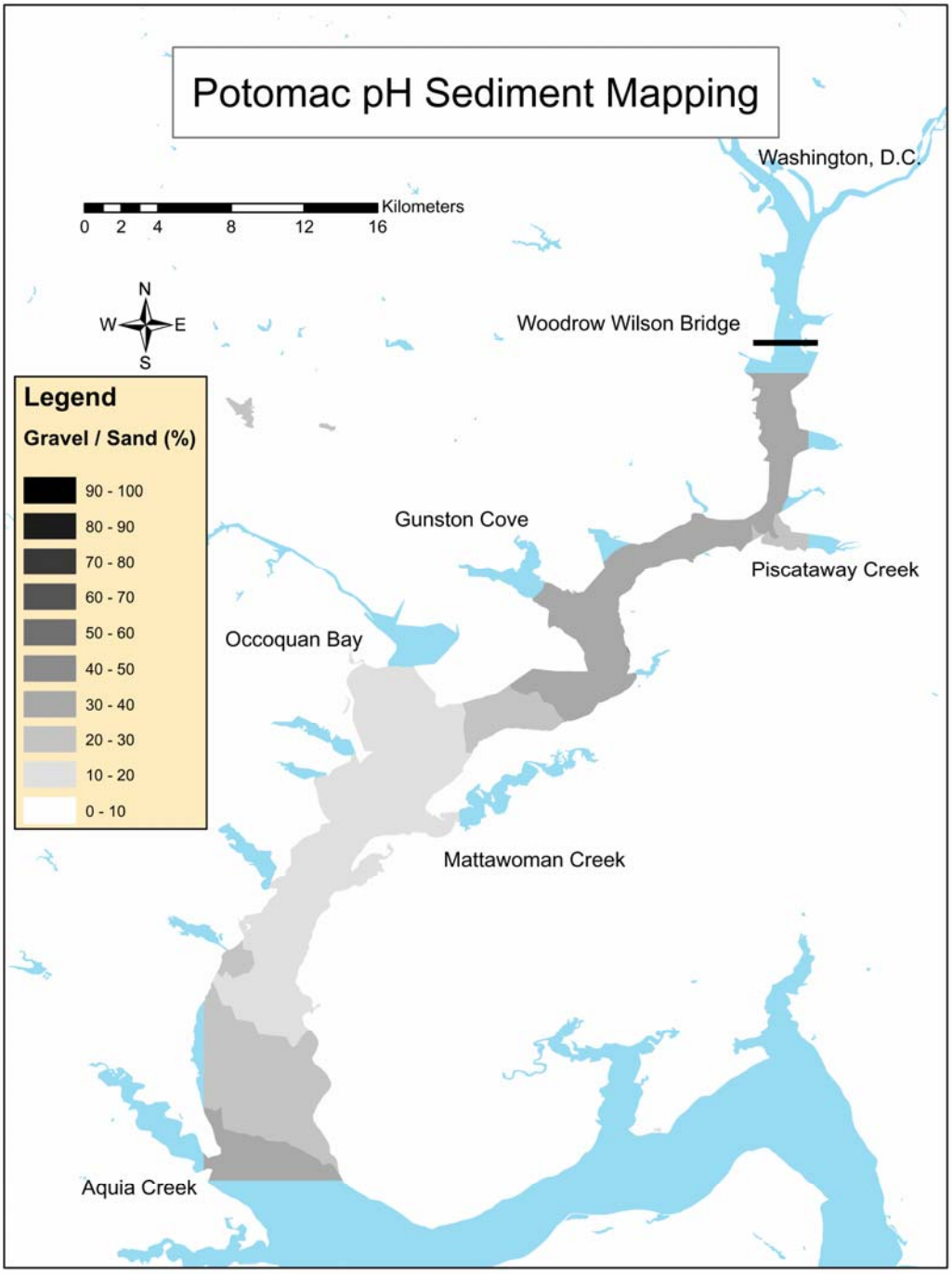


Figure 8. Sediment map of percent gravel/sand in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

grained fraction (gravel/sand) was higher at the upper and lower part of the spatial domain of this study (Figure 8), with the lowest concentration below Occoquan Bay. Sand/gravel averaged 25±22%. The silt content was highest in the Occoquan area, while

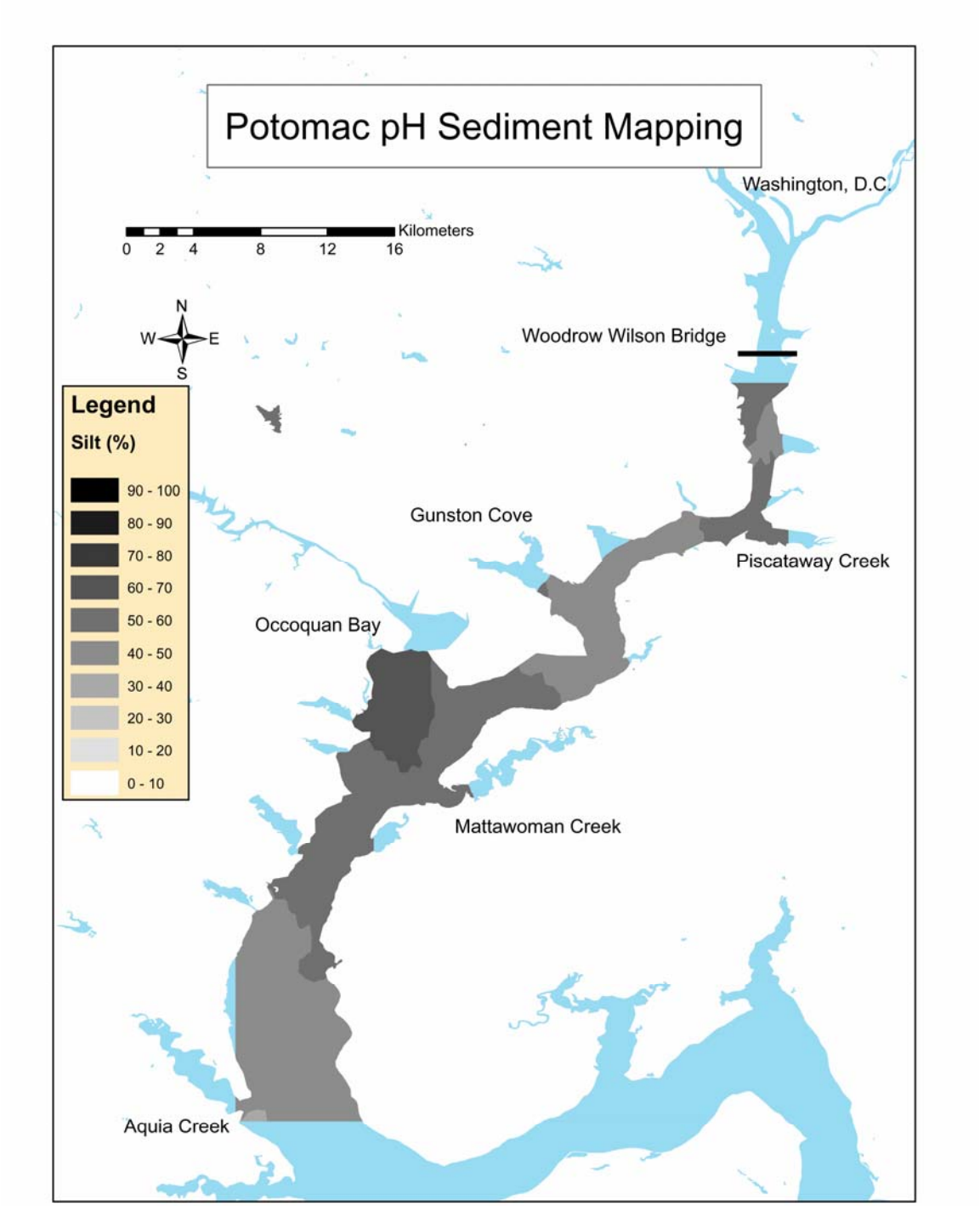


Figure 9. Sediment map of percent silt in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

the percentage clay was highest in the reach below Mattwoman Creek (Figures 9 and 10). Silt was the dominant fraction overall (51±14%), with clay content similar to the coarse fraction (24±9%).

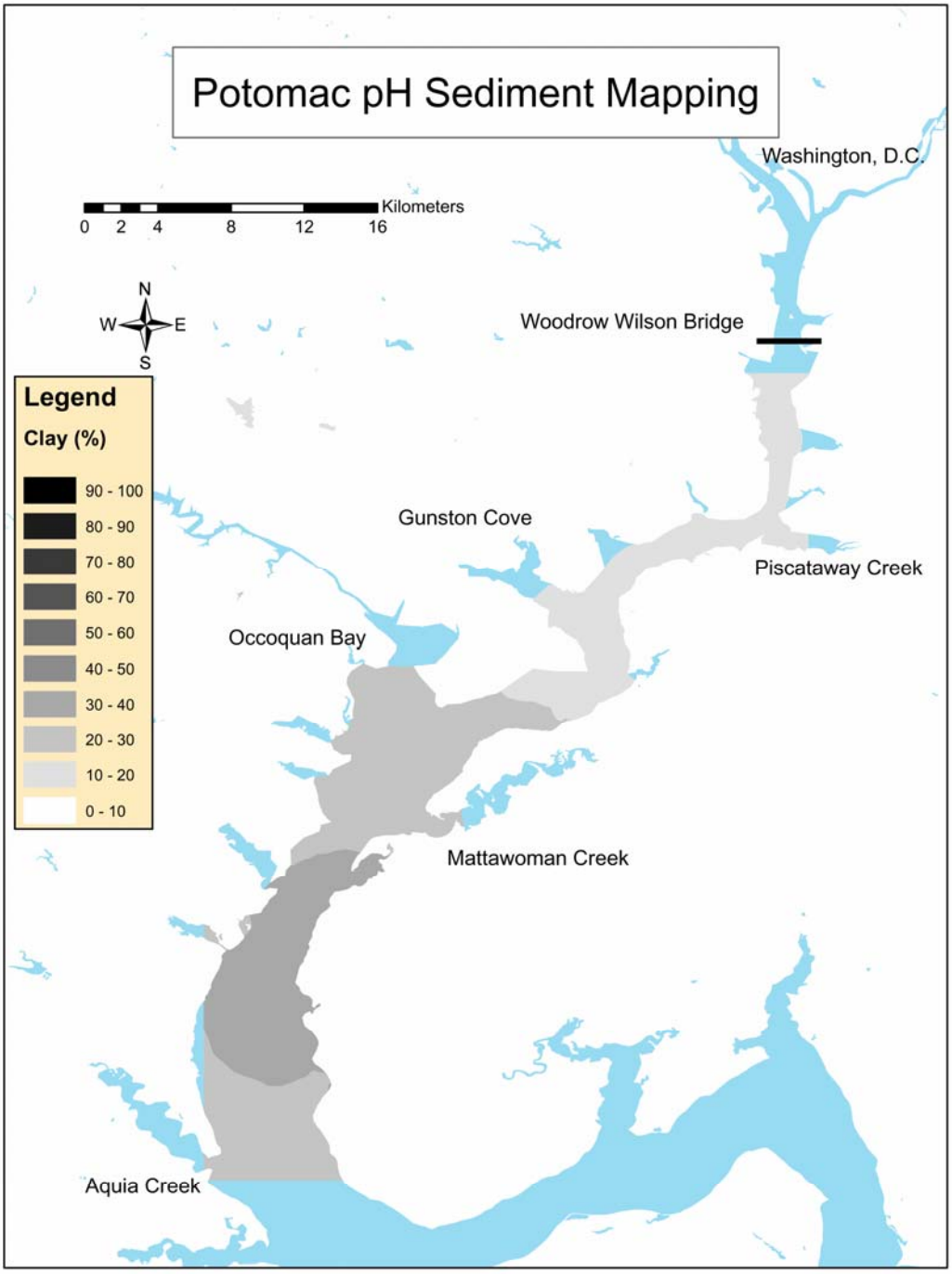


Figure 10. Sediment map of percent clay in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

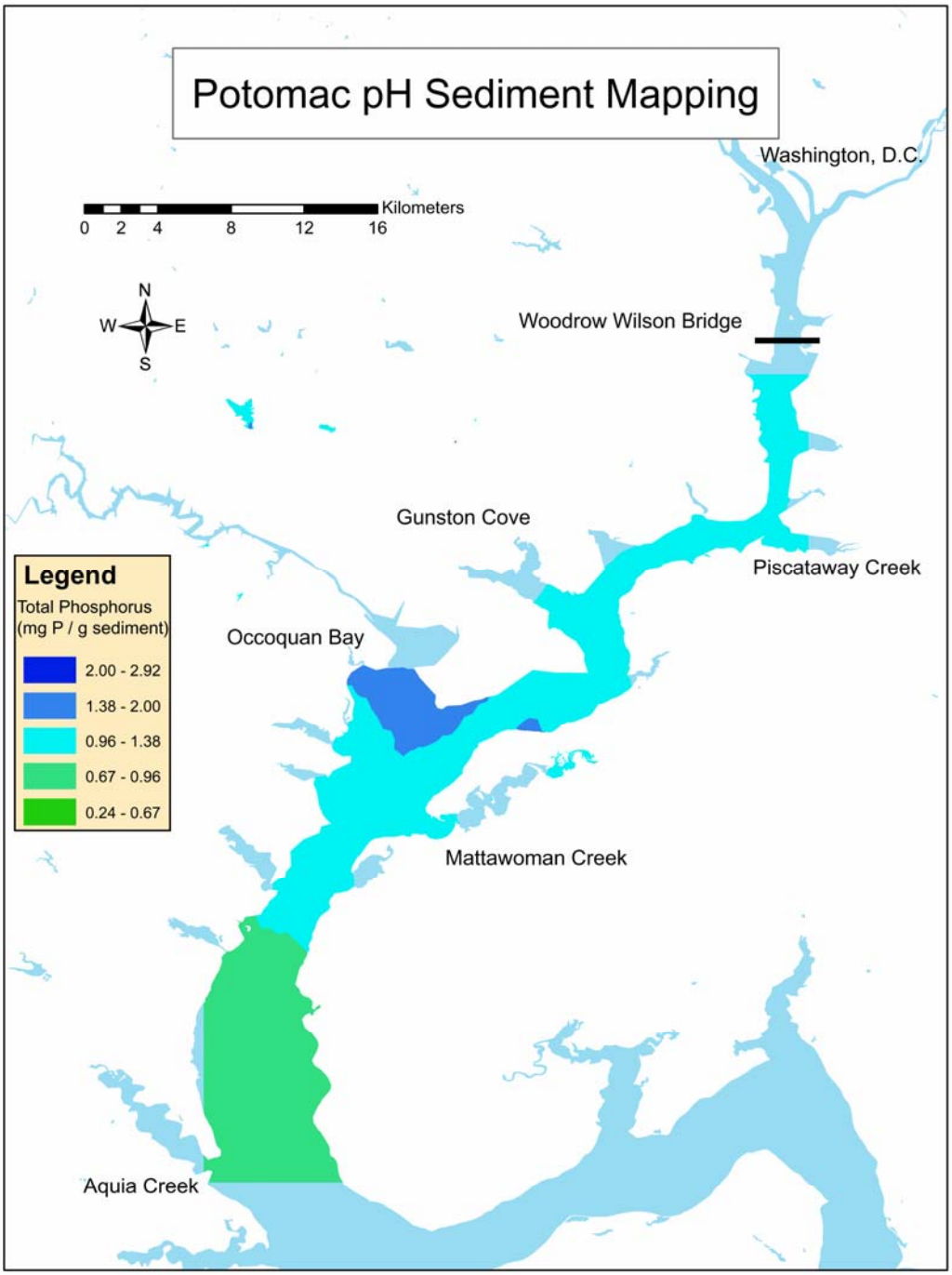


Figure 11. Total phosphorus concentrations (mg g^{-1}) in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

Total phosphorus concentrations ranged from 0.24 to 2.92 mg g^{-1}, averaging 1.1±0.5 mg g^{-1}. The lowest concentrations were found in the lower part of the sampling domain,with the highest concentrations in the vicinity of Occoquan Bay (Figure 11). Inorganic P

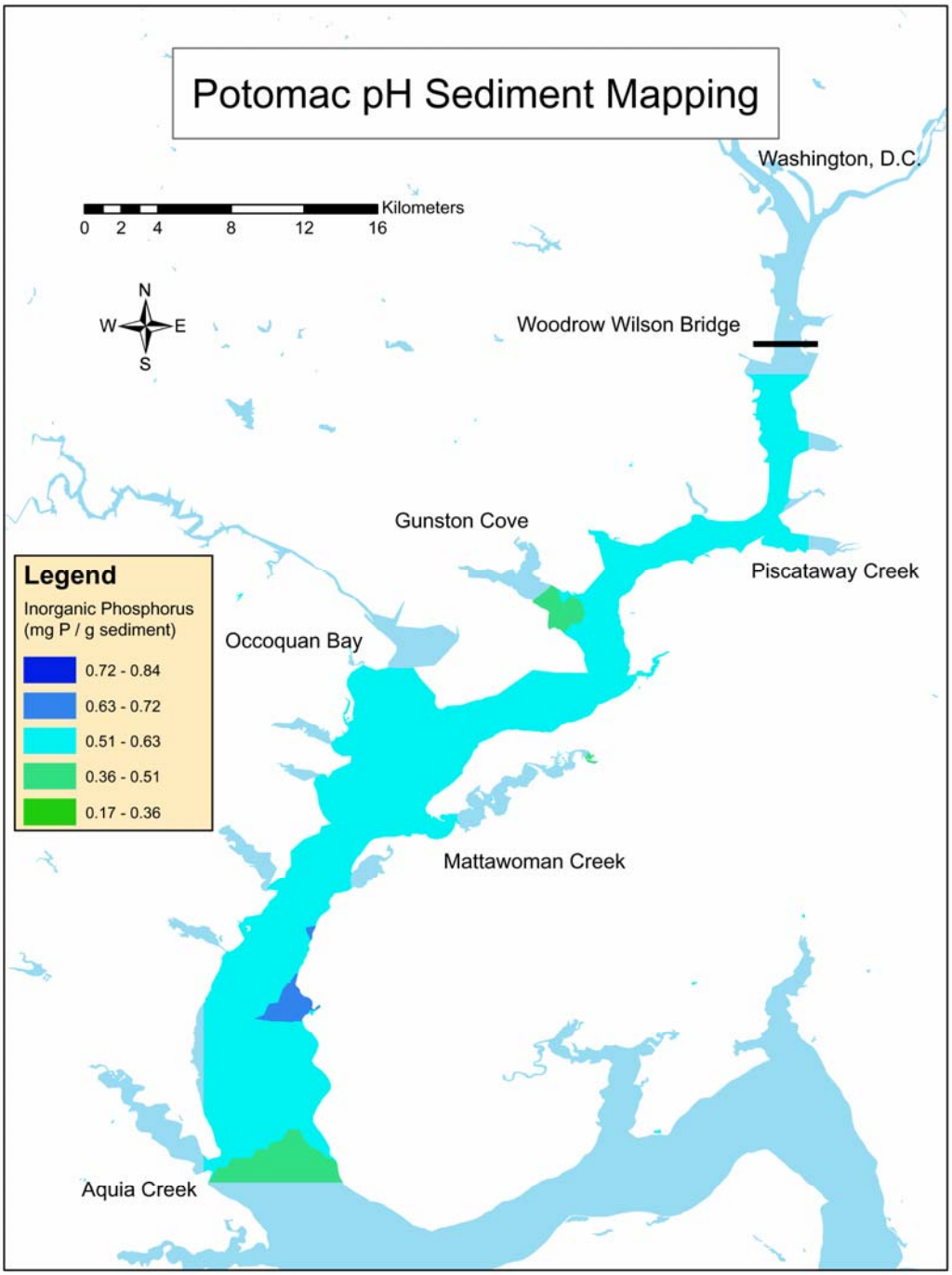


Figure 12. Inorganic phosphorus concentrations (mg g^{-1}) in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

generally lower (average = 0.6±0.2 mg g^{-1}), with a fairly uniform distribution in this part of the Potomac (Figure 12). Slightly lower values were found in Gunston Cove. The concentrations of organic P decreased down-estuary (Figure 13), with an average similar

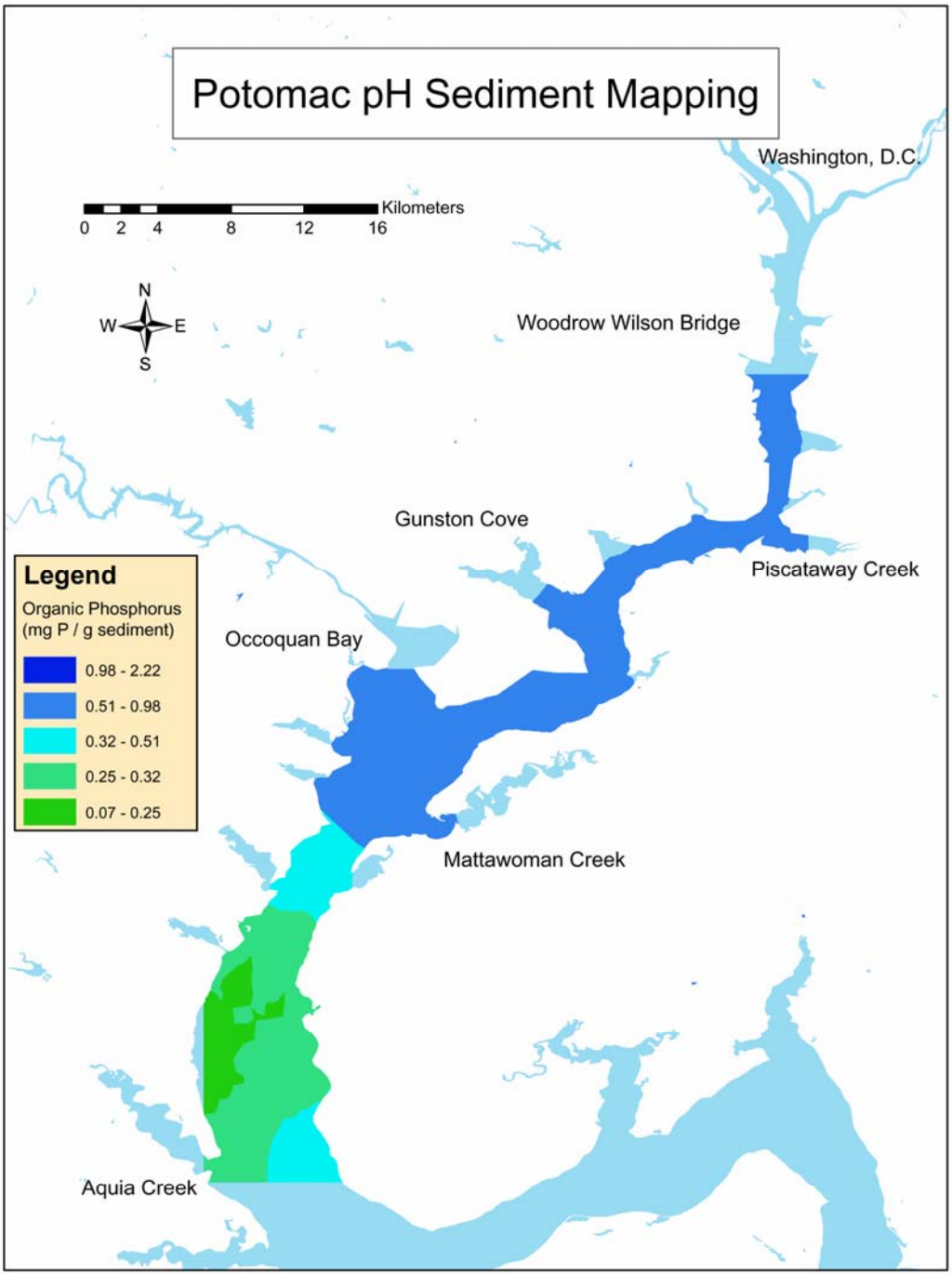


Figure 13. Organic phosphorus concentrations (mg g^{-1}) in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

to the inorganic P (0.6±0.4 mg g^{-1}). The spatial pattern is suggestive of an organic P source from the upper watershed.

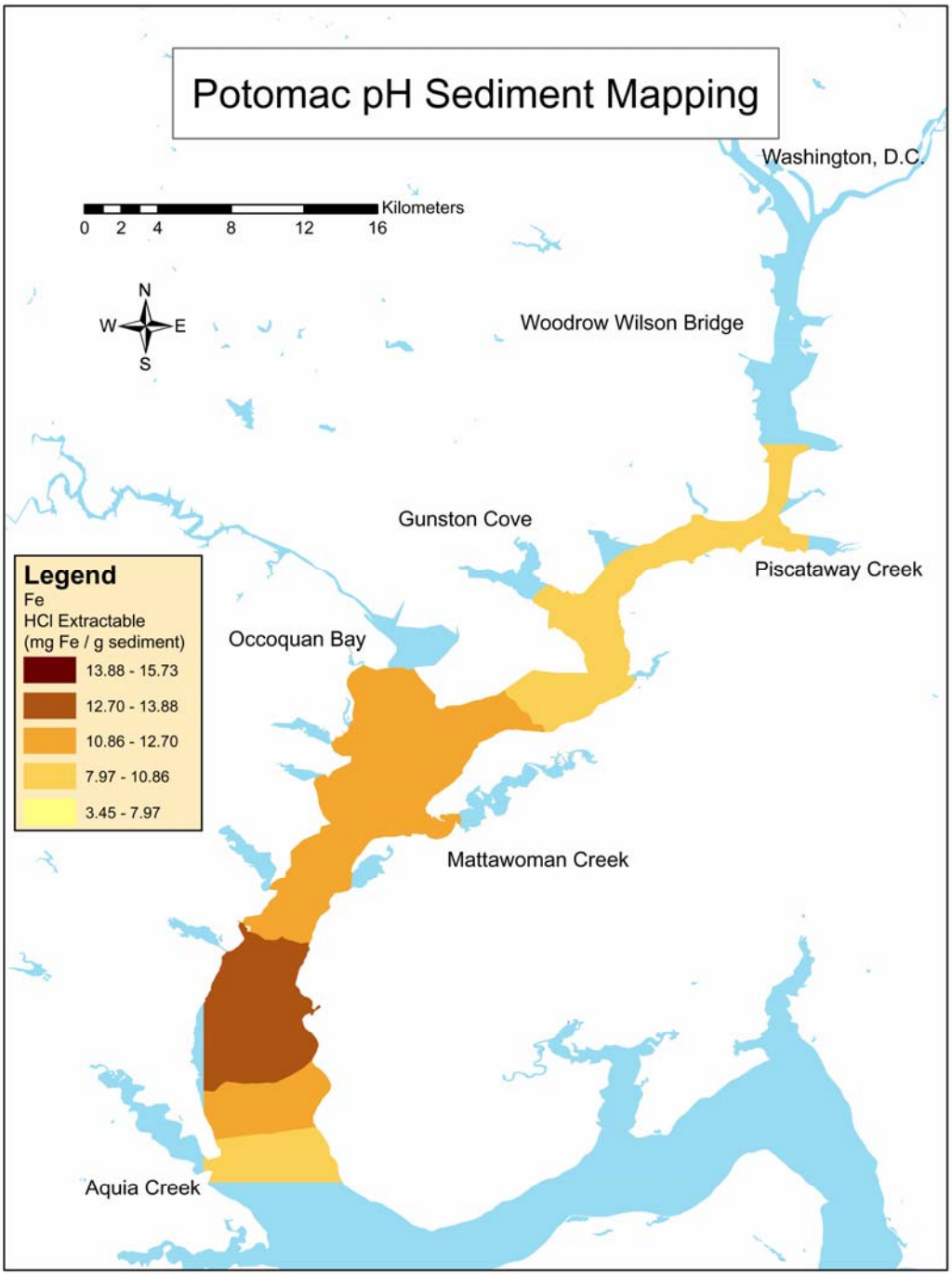


Figure 14. Iron concentrations (mg g^{-1}) in surficial sediments (0-2 cm) in Potomac study area. See text for full details.

Iron concentrations increased down estuary, with highest concentrations in the region of finest sediment grain size (figure 14). Overall Fe concentrations were high, averaging

11±3 mg g^{-1}. Manganese distribution was similar to Fe, with higher concentrations below Mattawoman Creek ((Figure 15). The average Mn concentration was 1.1±0.6 mg g^{-1}.

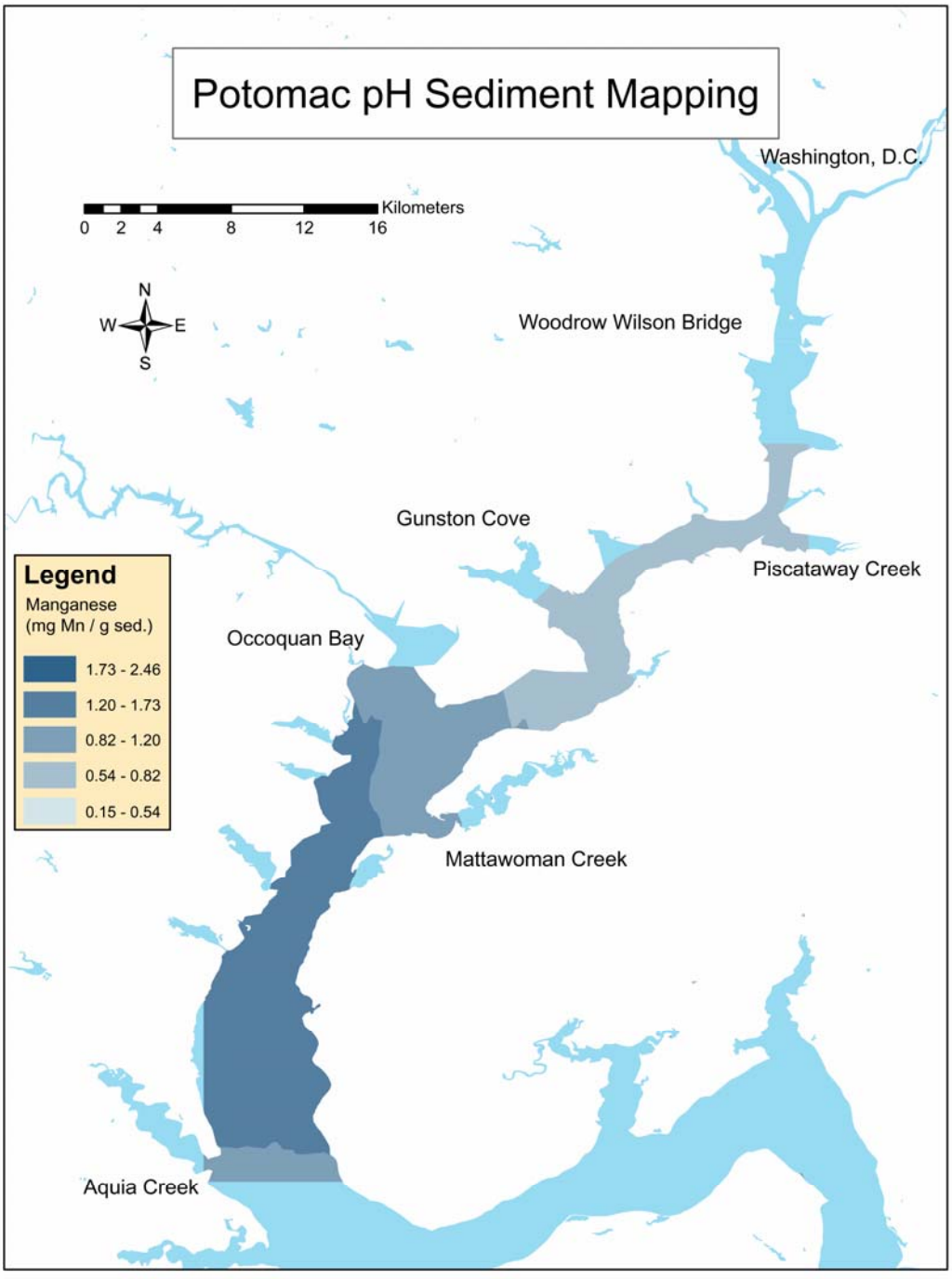


Figure 15. Manganese concentrations (mg g^{-1}) in surficial sediments (0-2 cm) in Potomac study area. See full text for details.

Property-property plots show a number of expected relationships in the mapping data. The correlation between inorganic P and Fe ($P < 0.01$; Figure 16a) is typical of sediments in many environments; similar relationships are found in the Patuxent River subestuary (Cornwell unpublished). Total P is not correlated with other parameters, including inorganic P (Figure 16b; the line corresponds to 100% inorganic P). Inorganic P is highly correlated ($P < 0.01$) to the fine grained sediment concentration (Figure 16c), as is HCl-Fe (Figure 16d). The relationships between HCl-Fe – HCl-Mn and HCl-Mn – inorganic P are significant at the $P < 0.05$ level.

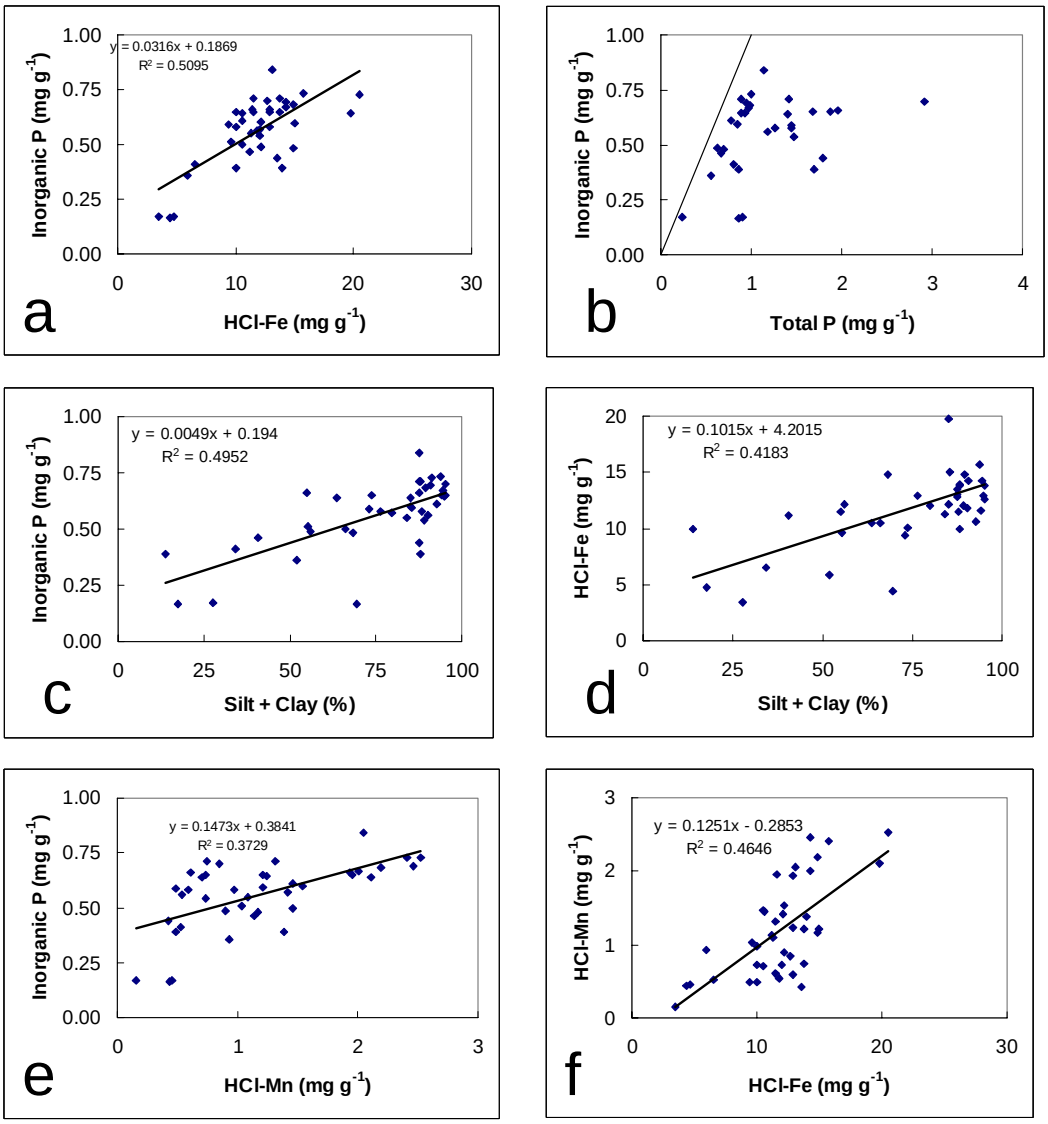


Figure 16. Property-property scatter plots of selected Potomac River estuary sediment paratmeters. See text for details.

Ambient Sediment Fluxes

In situ sediment flux data are plotted as a series of clustered bar graphs in Figures 17 and 18. Sediment oxygen consumption (SOC) rates ranged from around 1 to 3 g O_2 m^{-2} d^{-1}. Sediment oxygen consumption rates of this magnitude are comparable to those observed in the Potomac previously (Bailey *et al*. 2003b) and in other enriched estuarine systems (Bailey *et al*. 2003a). The majority of the highest rates occurred in July however there were neither strong seasonal or station location patterns in SOC rates.

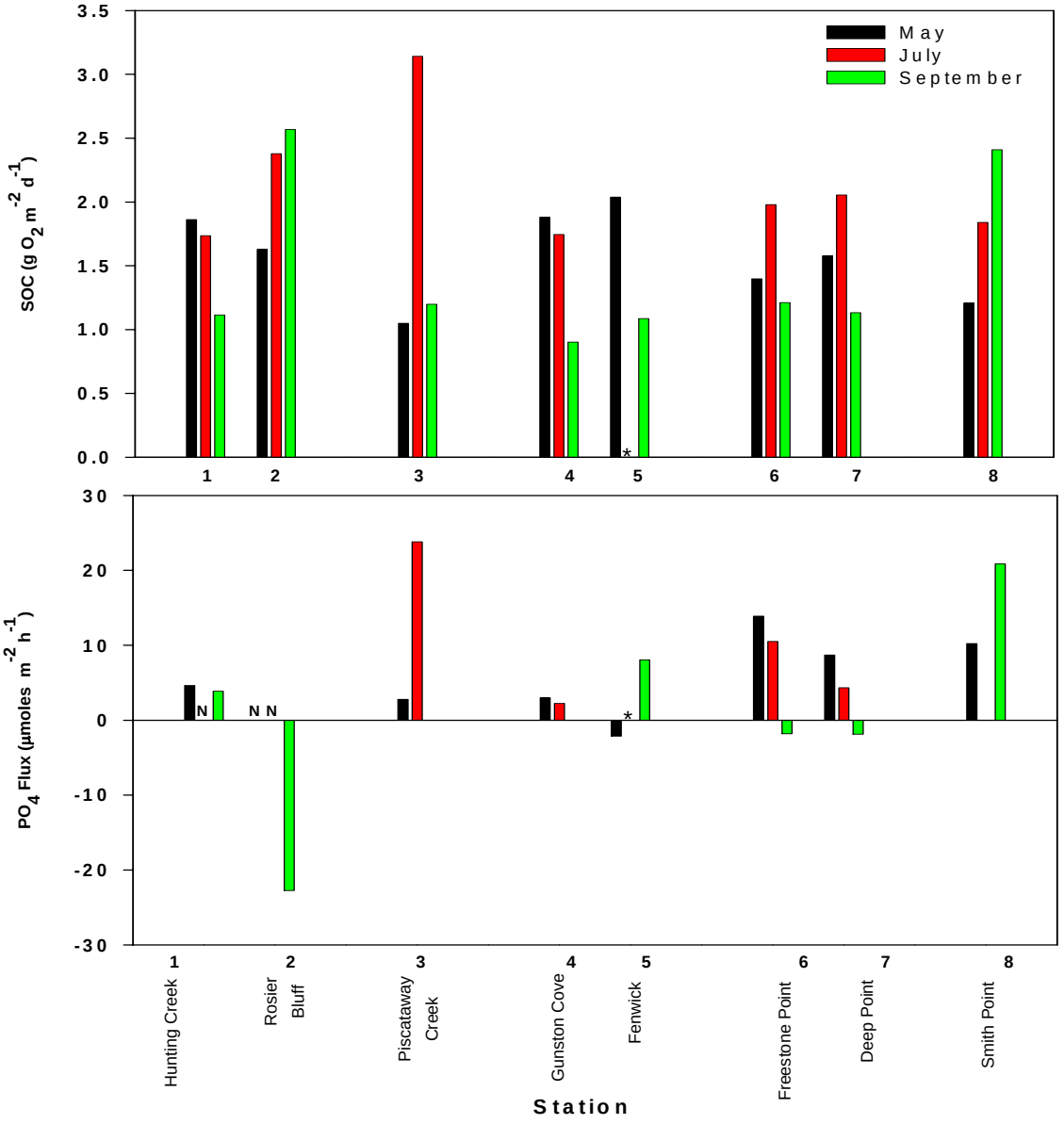


Figure 17. Sediment oxygen consumption (SOC) and phosphorus (PO_4) fluxes at the eight main sampling stations for 2004 Potomac studies (numbers denote station number with station names along bottom axis).

*** = WW (station not sampled)**

N = NI (data for this variable considered to be non-interpretable)

Ambient sediment phosphorus fluxes varied among months and stations (Figure 17). Rates were very low ranging from zero to around 25 µmoles m^{-2} h^{-1} either into or out of the sediments. Ambient sediment ammonium fluxes were mostly releases with

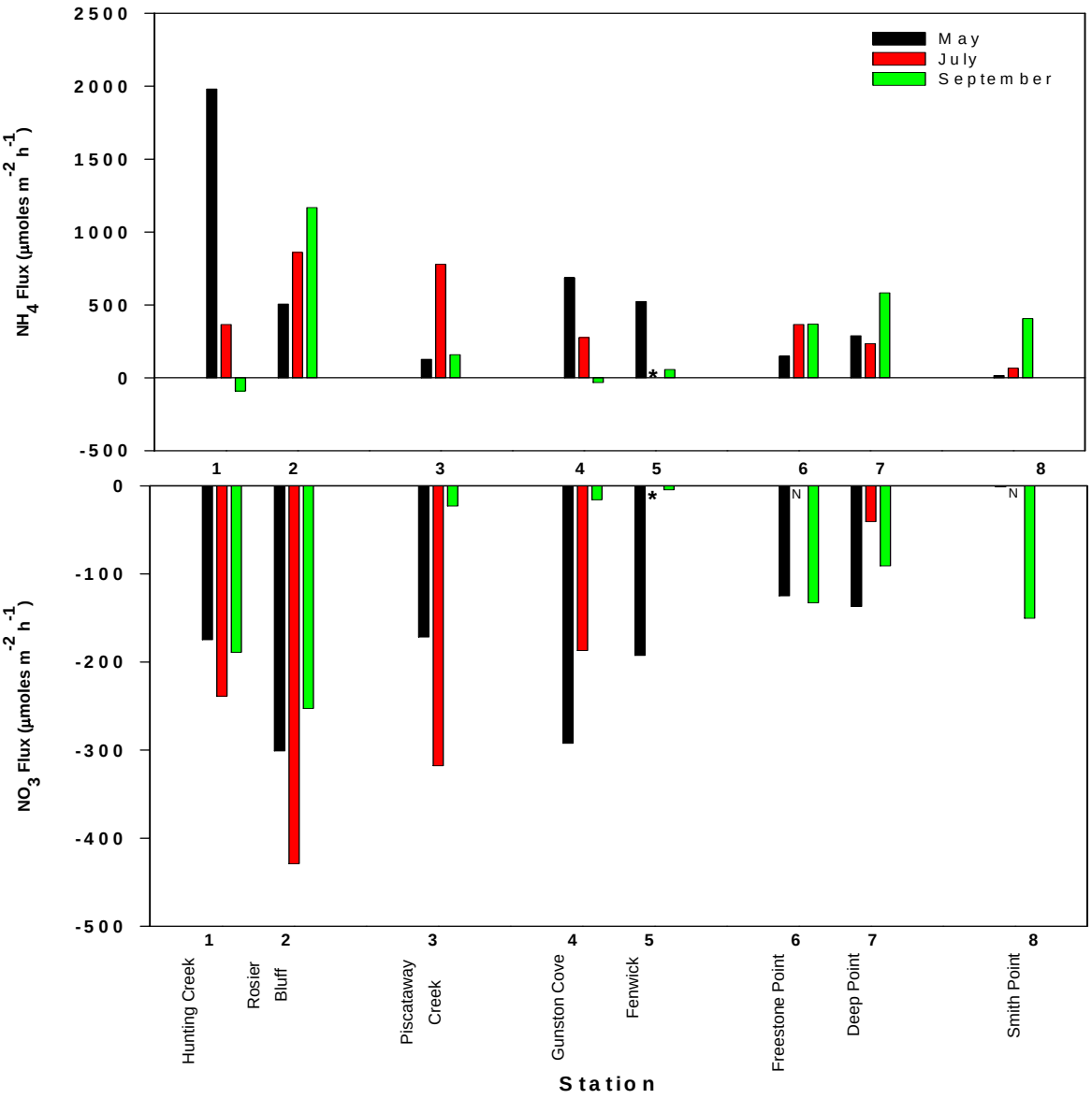


Figure 18. Sediment ammonium (NH_4) and nitrate (NO_3) fluxes at the eight main sampling stations for 2004 Potomac studies (numbers denote station number with station names along bottom axis).

*** = WW (station not sampled)**

N = NI (data for this variable considered to be non-interpretable)

ammonium flux directed into the sediments in July at stations 1 and 4 (Figure 18). No seasonal patterns were observed in ambient sediment ammonium fluxes, but the larger fluxes occurred at stations closer to the upriver end of the sampling area. In general, large ammonium fluxes were observed at all stations.

Ambient sediment nitrate fluxes showed net uptake of nitrate into sediments at all stations for all months. The majority of theses fluxes were substantial, measuring over 150 μmoles m^{-2} h^{-1}. The largest of these fluxes (> 200 μmoles m^{-2} h^{-1}) were observed at the stations closer to the upriver end of the sampling area. In general, ambient *in situ* sediment oxygen consumption, phosphate, ammonium and nitrate fluxes measured during the Potomac study were comparable to both previous work in the Potomac River (Bailey *et al.* 2003b) and other enriched estuarine systems (Bailey *et al.* 2003a).

Denitrification

Denitrification measurements were made on 4 occasions, with 1-3 sites analyzed per time (Figure 19). The Kana *et al*. (1994; 1998) approach to denitrification measures net N_2 fluxes using the changes in the N_2:Ar ratio. Rate measurements above 25 μmol N m^{-2} h^{-1} can be made reliably; at lower rates, alternative techniques are useful (i.e. Nielsen 1992). The higher rates of denitrification are typical of rates found in nitrate-rich estuaries. We observe rates over 100 μmol m^{-2} h^{-1} in the Choptank and Patuxent subestuaries, both nitrate-enriched systems. Nitrate concentrations were generally in the range of 70-100 μmol L^{-1}; at Station 7 in July, concentrations were 35 μmol L^{-1}. This small program was designed to provide a snapshot of rates, and provides an indication that rates are very high at some stations. We cannot readily distinguish between the denitrification depending on water column nitrate from that supported by nitrification in surface sediments. The higher rates, such as those measured at Station 8 in September, generally require more nitrate than the 82 μmol L^{-1} found at that site.

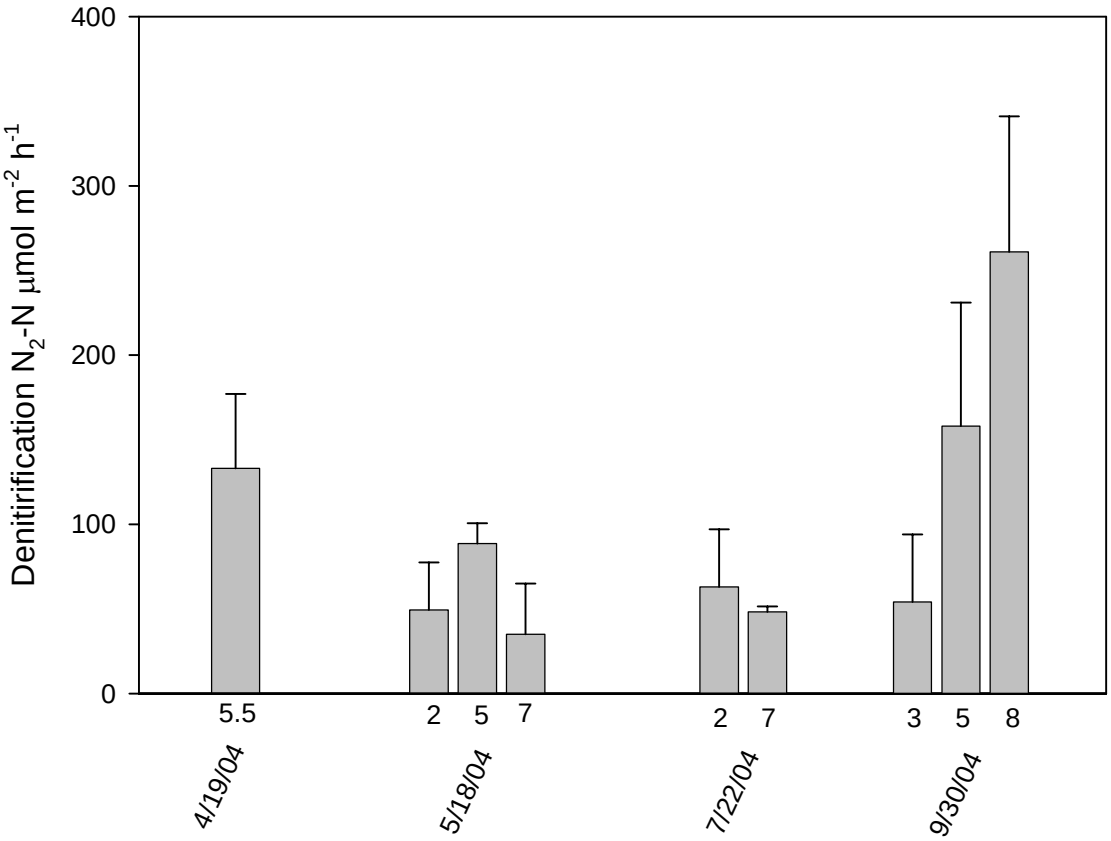


Figure 19. Denitrification rates from 4 time periods in the Potomac River. The error bars are standard deviations of the rate data from 3 cores.

Pore Water Profiles - Microelectrodes

Pore water microelectrode profiles can reveal processes at the sediment-water interface which control N and P cycling. In many sediments, the presence of oxygen in the top few mm of sediment is enough to fuel high rates of nitrification and to limit P efflux. In this study, we show such O_2 profiles as well as profiles of pH from our experimental incubations.

The oxygen profiles from the September, 2004 sample period (Figure 20) show uniformly shallow oxygen penetration depths (OPD).These profiles are typical of sediments with high metabolic rates and show an exponentially decreasing oxygen concentration. With the exception of core 3, replicate profiles are virtually identical. With the exception of Core 3, OPD's are in the 1.5-2.0 mm range. The general absence of deeper penetration suggests a minimal role for bioirrigation at these sites.

The final pH values for the May pH addition experiments were quite surprising to us (Figure 21); elevated pH values penetrated to about 1 cm, suggesting that the depth of effect of pH increase was quite large. We repeated this work in July (Figure 22) with cores from 5 sites. A time course of pH penetration was developed for all cores; as in the May experiment, 1 cm depths of penetration were attained. In September, we examined

the ambient pH profiles at 8 sites (Figure 23); while there also was a pH increase evident at the surface of the cores, pH's did not exceed 8.5. With the addition of high pH overlying water (Figure 24), we observed a substantial increase in pH within the pore water. Considerable core to core variability was observed in these fall experiments.

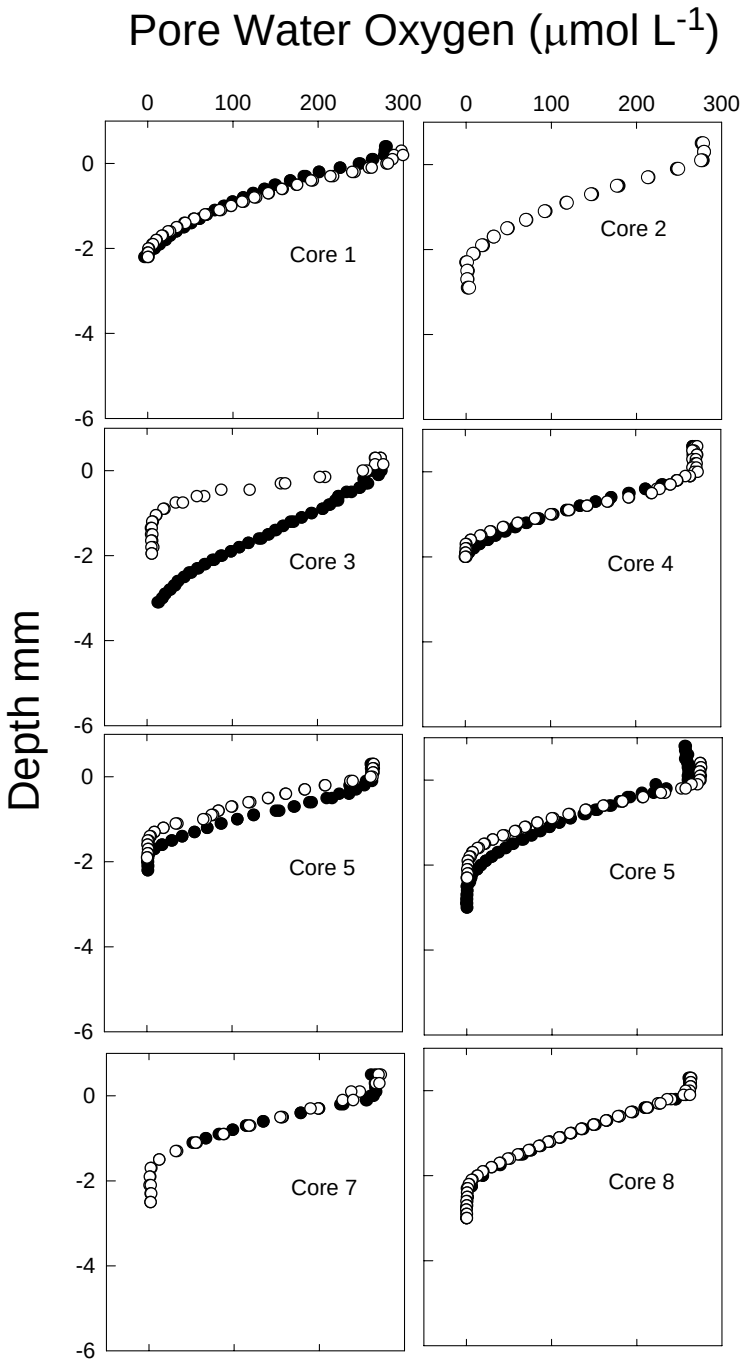


Figure 20. September 2004 pore water profiles of dissolved oxygen for all sampling sites. Duplicate profiles in a single core are shown. In this case, cores 1-8 correspond to sampling stations 1-8.

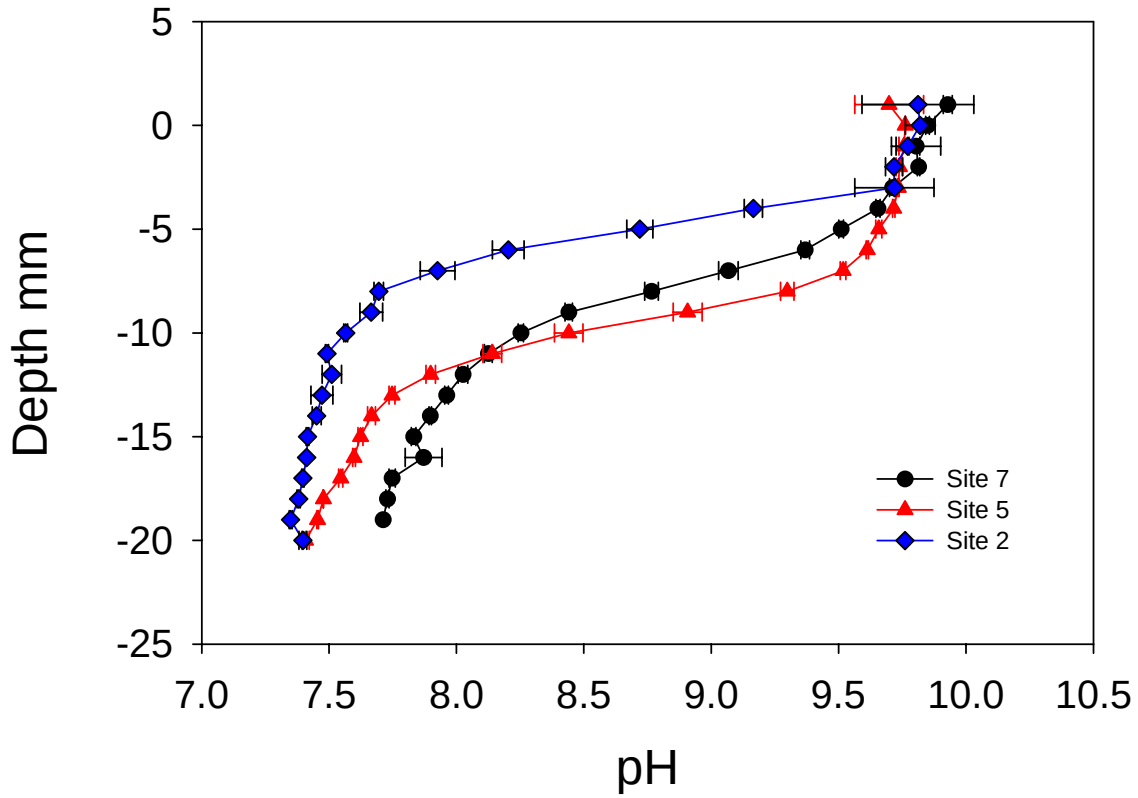


Figure 21. May 2004 pH profiles in experimental flux cores. The experimental pH of the overlying water was 10.0. These cores correspond to the flux data in Figure 28.

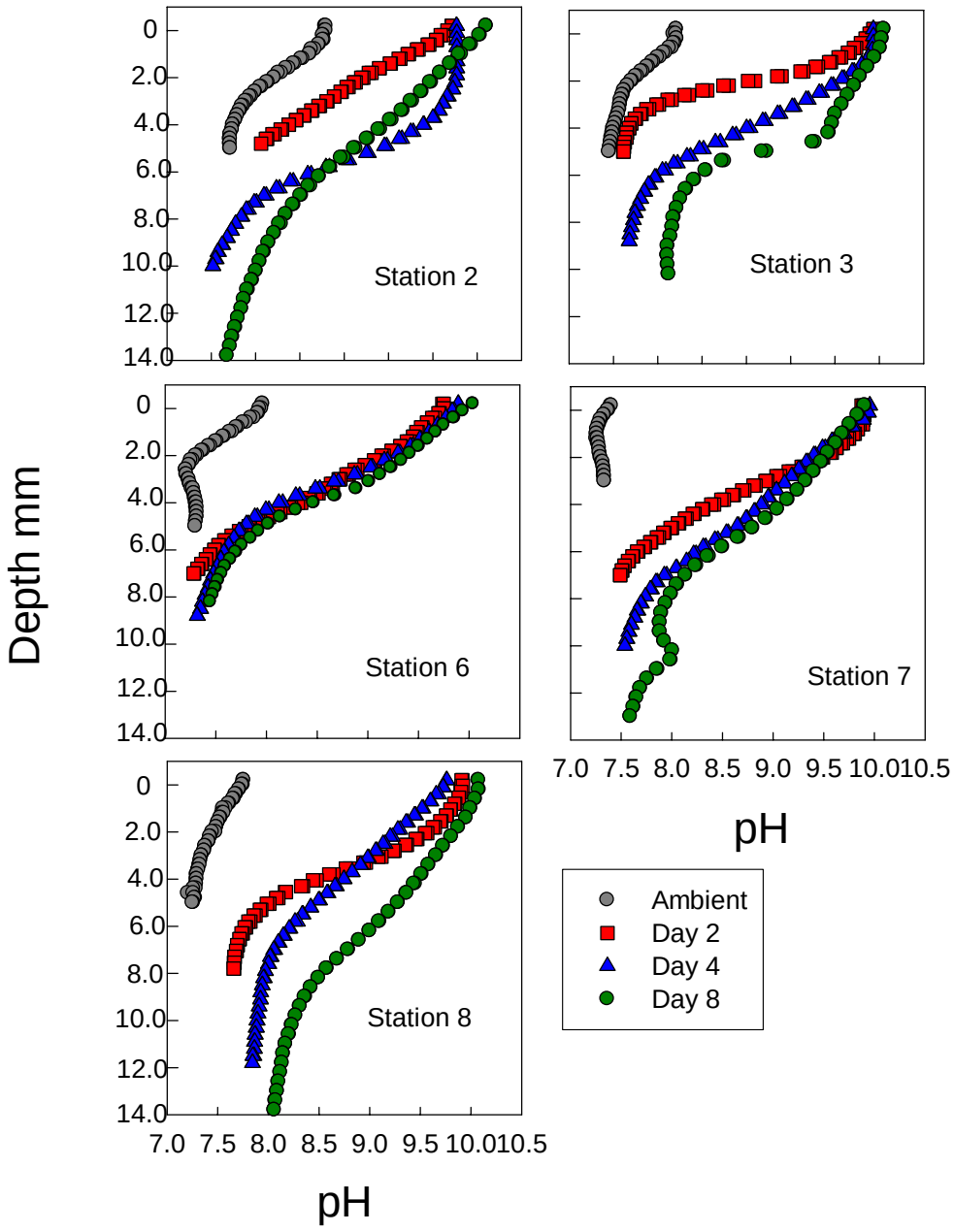


Figure 22. Time course cores for pH profiling, July 2004. The pH was set to 10 in the overlying water.

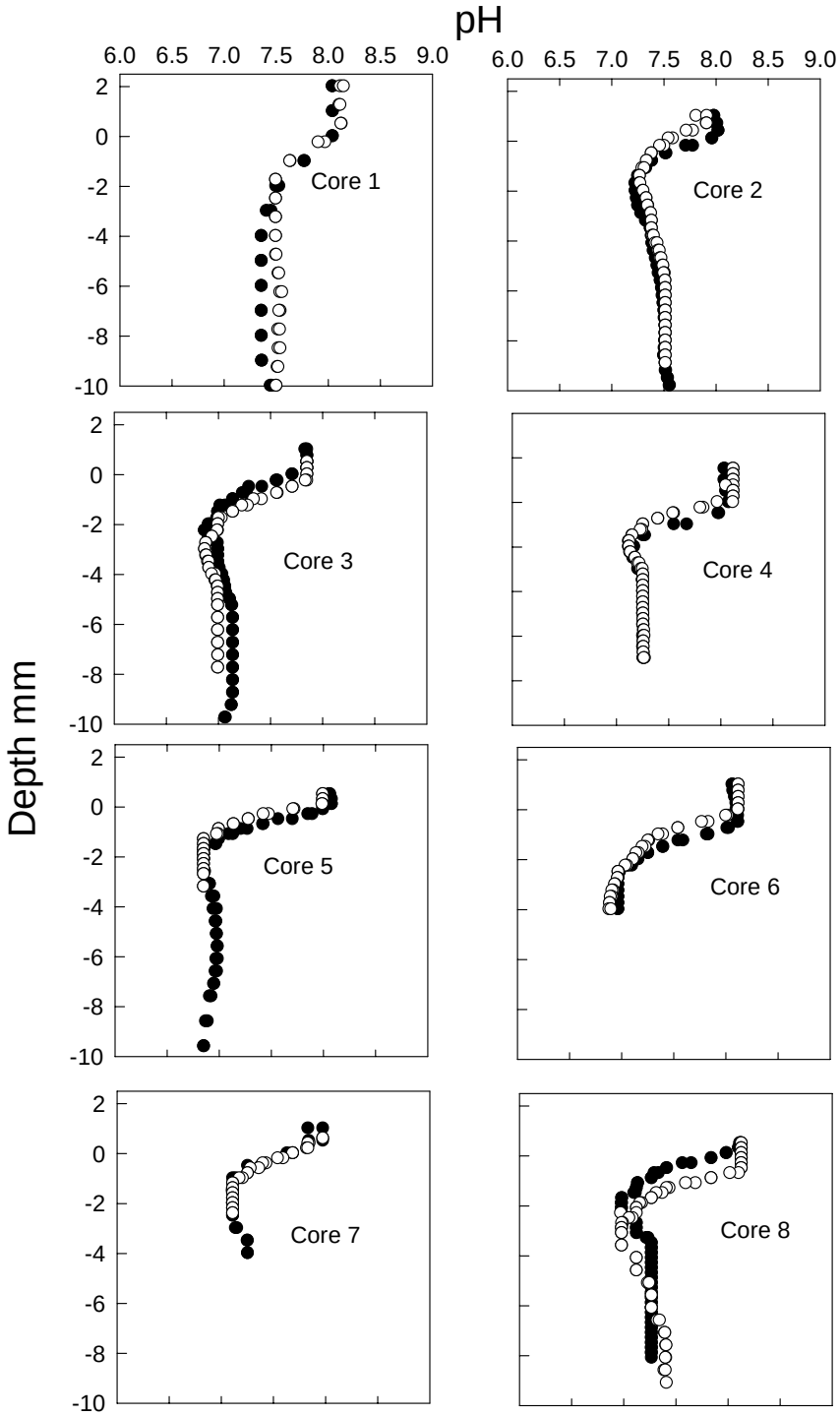


Figure 23. Ambient pH's in cores from all 8 sampling stations. Duplicate profiles from a single core are shown. In this case, cores 1-8 correspond to sampling stations 1-8.

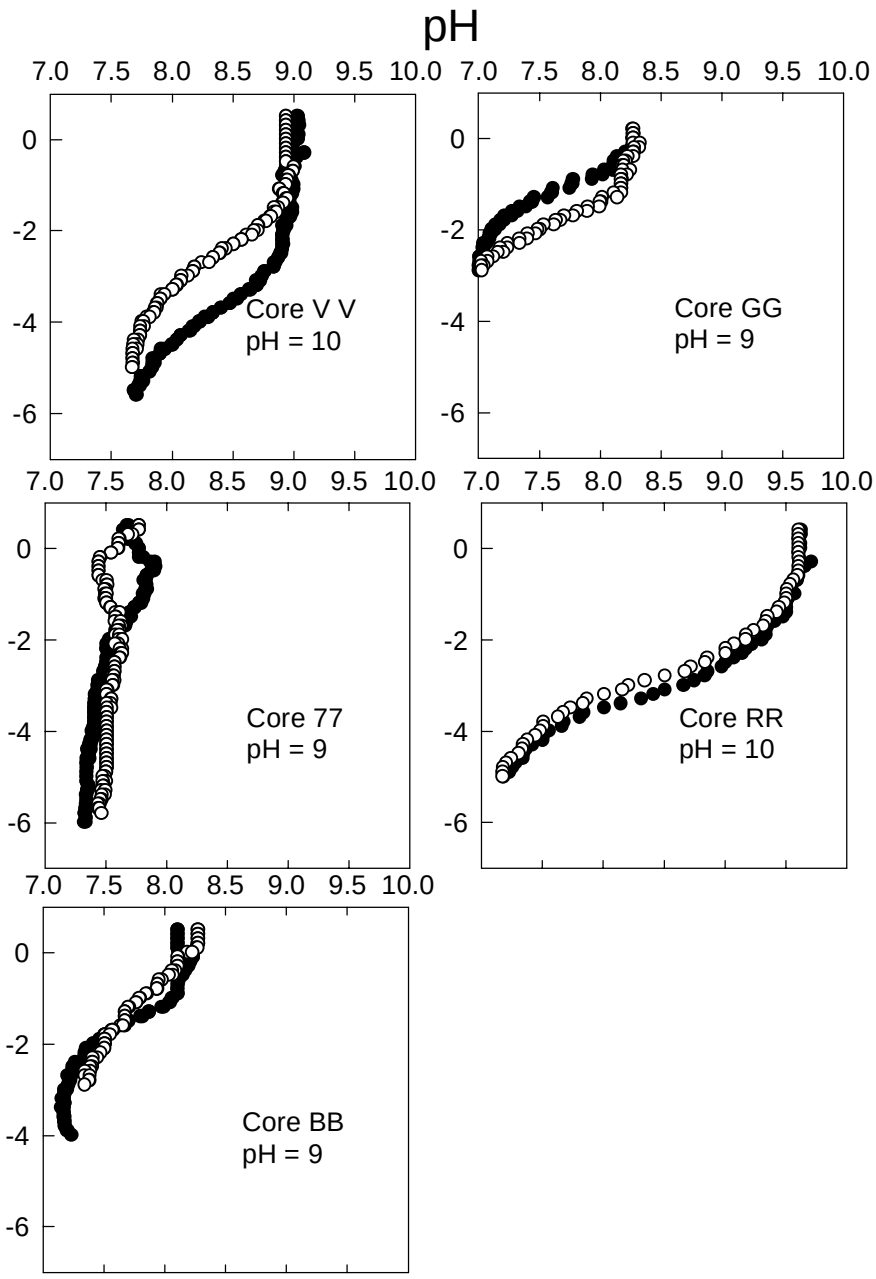


Figure 24. Profiles of pH in sediment cores after > 1 week exposure to elevated pH. Cores were collected during the September 2004 cruise.

Pore Water Profiles – Solutes

The pore water chemistry of Potomac River sediments has been examined previously using techniques similar to the ones employed here (Callender 1982). In Figure 25, we show a representative pore water profile, all with substantial increases in SRP, ammonium and Fe concentrations below the top 1-2 cm of sediment. Sulfate is depleted in the top ~3 cm. These profiles are consistent with Callender's (1982) data and with the position of these sediment in a relatively Fe-rich (Lovley and Phillips 1986), sulfate poor environment. While there is site to site variability in pore water chemistry, the processes which control N and P cycling in the tidal fresh part of the Potomac River will not change across this sampling domain.

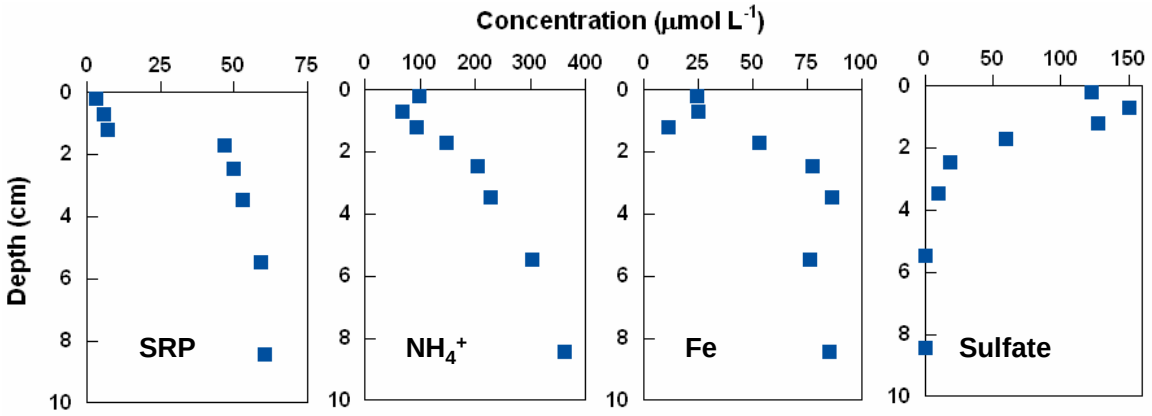


Figure 25. Pore water profiles of SRP, ammonium, iron and sulfate from May 2004 at Station 9 (Freestone Point). This figure illustrates the main characteristics of Potomac River pore water chemistry.

The response of pore water SRP to increased pH is readily evident from our experiments (Figure 26). The increase of SRP concentration in the top 2-3 cm is relatively high; the flux of SRP across the sediment-water interface is driven by the SRP gradient at the sediment-water interface. In the May 2004 pH experiment, deeper SRP concentration changes are not large in the experiment time frame of < 1 week. The increase of pH always resulted in a large SRP increase in our experimental cores (Figure 27), with the largest response at Station 3 in July, 2004.

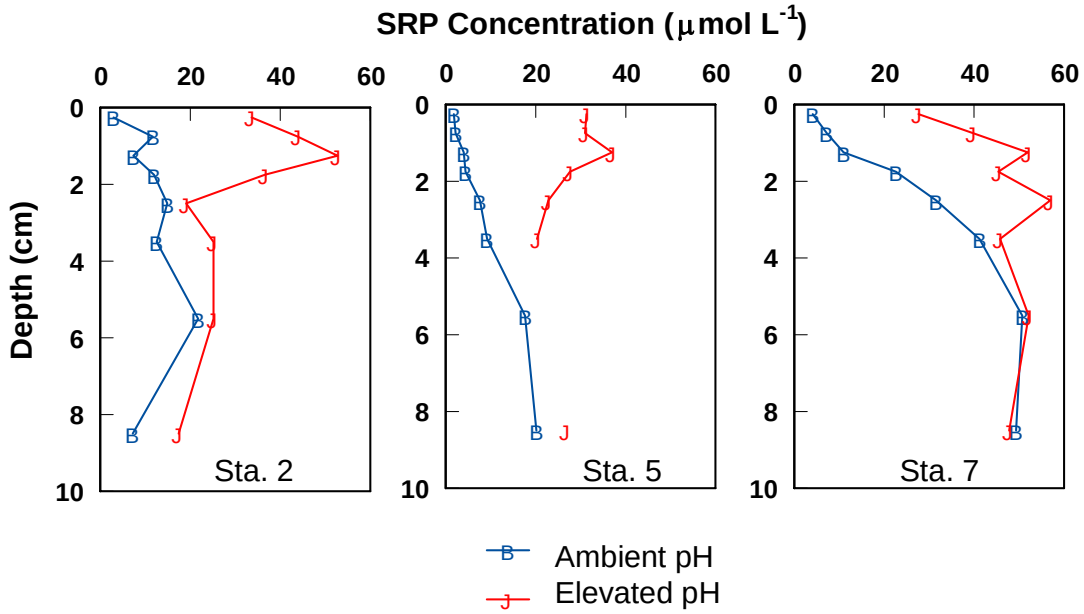


Figure 26. SRP profiles from three sites in May 2004. The ambient pH data is from the unamended cores; the elevated pH cores are from a pH 10 treatment of 1 week duration.

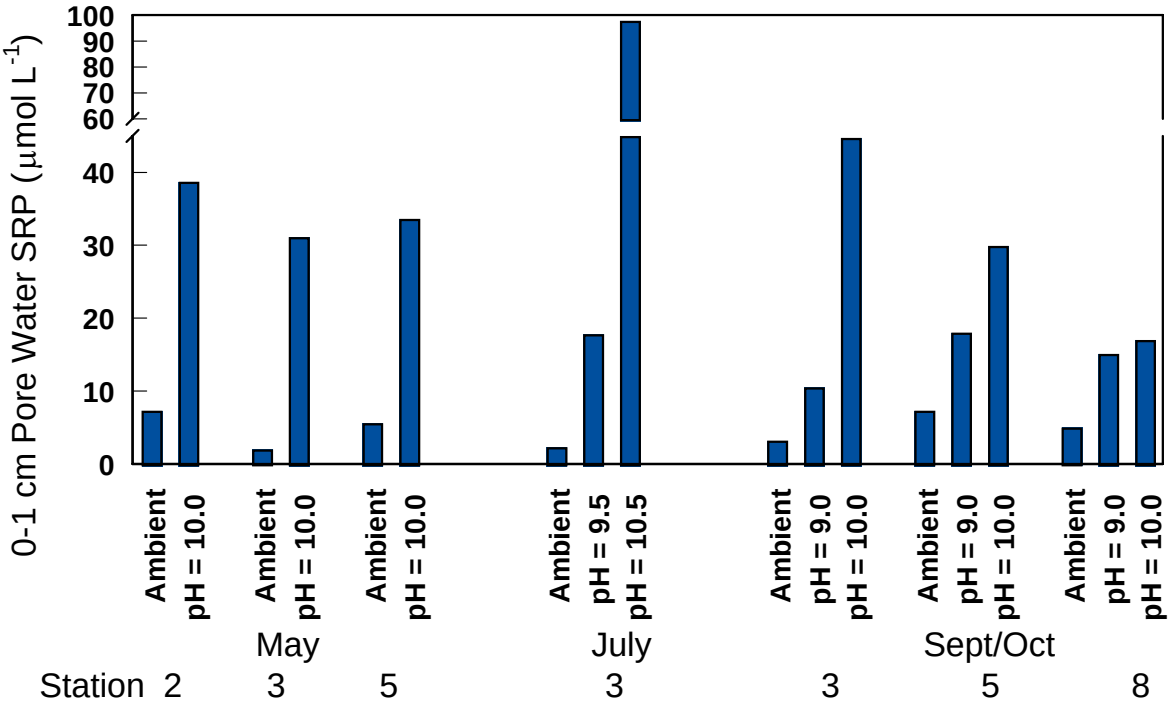


Figure 27. Average pore water SRP concentrations in ambient pH (generally 7.0-7.5) and elevated pH experiments. The average of the 0.0-0.5 and 0.5-1.0 cm pore water sections are presented; on the time frame of the experiments, this depth is where the largest response to increased pH occurs.

Sediment P Flux Responses to pH Changes

In May 2004 sediment phosphorus flux response to pH changes were conducted using sediment cores from stations 2, 5 and 7. Figure 28 shows fluxes measured *in situ* and after 5 and 7 days of treatment with water adjusted to a pH of 10. *In situ* fluxes were low and after 5 days of treatment, all three stations showed an increase in phosphorus fluxing out of the sediments (Figure 28). After 7 days of treatment all stations had large phosphorus fluxes ranging from 40 to over 60 µmoles m^{-2} h^{-1}.

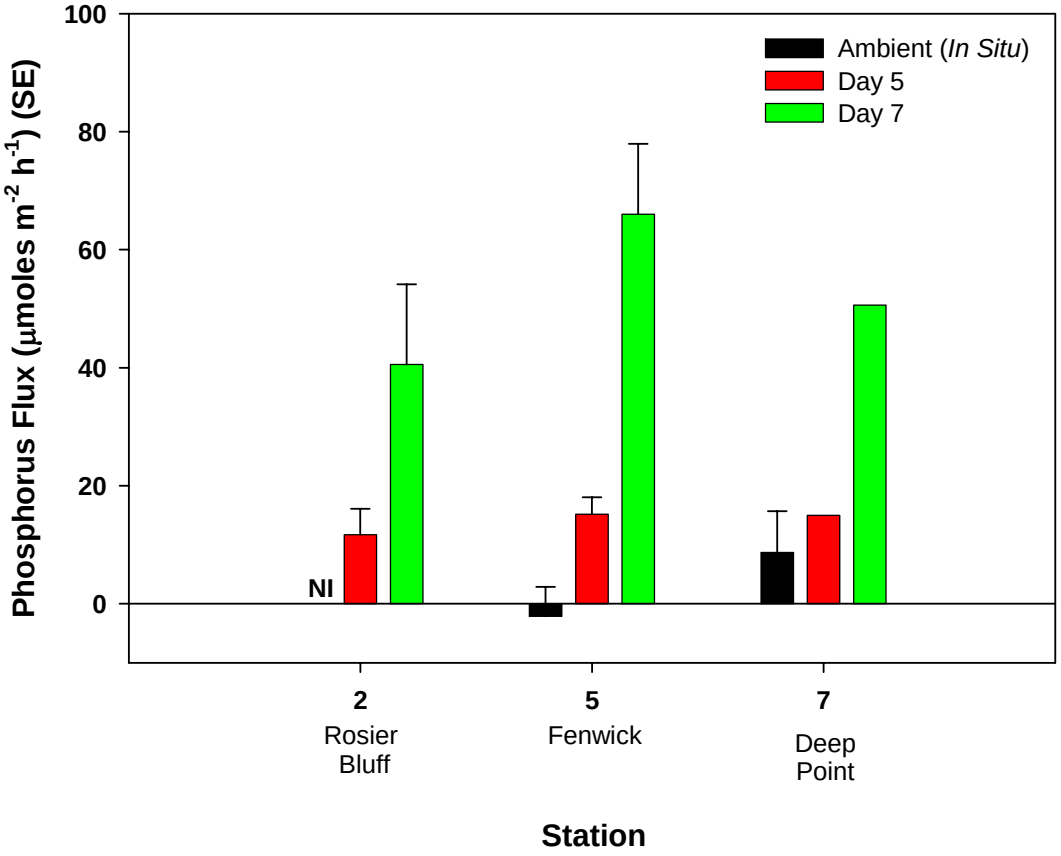


Figure 28. May 2004 static flux pH response measurements (NI= data for this variable considered to be non-interpretable). Measurements were made with cores collected at stations 2, 5 and 7.

In July 2004 sediment phosphorus flux response to pH change was measured using sediments from station 3. Treatments included ambient pH (~7.5), pH 9.5 and pH 10.5. Figure 29 shows static phosphorus flux measurements plotted against exposure time to pH adjusted water. *In situ* fluxes were low (~20 µmoles m^{-2} h^{-1}) measured the day prior to the experiment. After only 2 hours of exposure to pH adjusted water, sediment phosphorus flux rates rose to around 30 µmoles m^{-2} h^{-1} in the pH 10.5 treatment (Figure 29). A little over a day later this rate had more than doubled and by day 4 the rate increased to over 120 µmoles m^{-2} h^{-1}. Ambient and pH 9.5 treatment fluxes remained low (< 20 µmoles m^{-2} h^{-1}) during the course of the experiment.

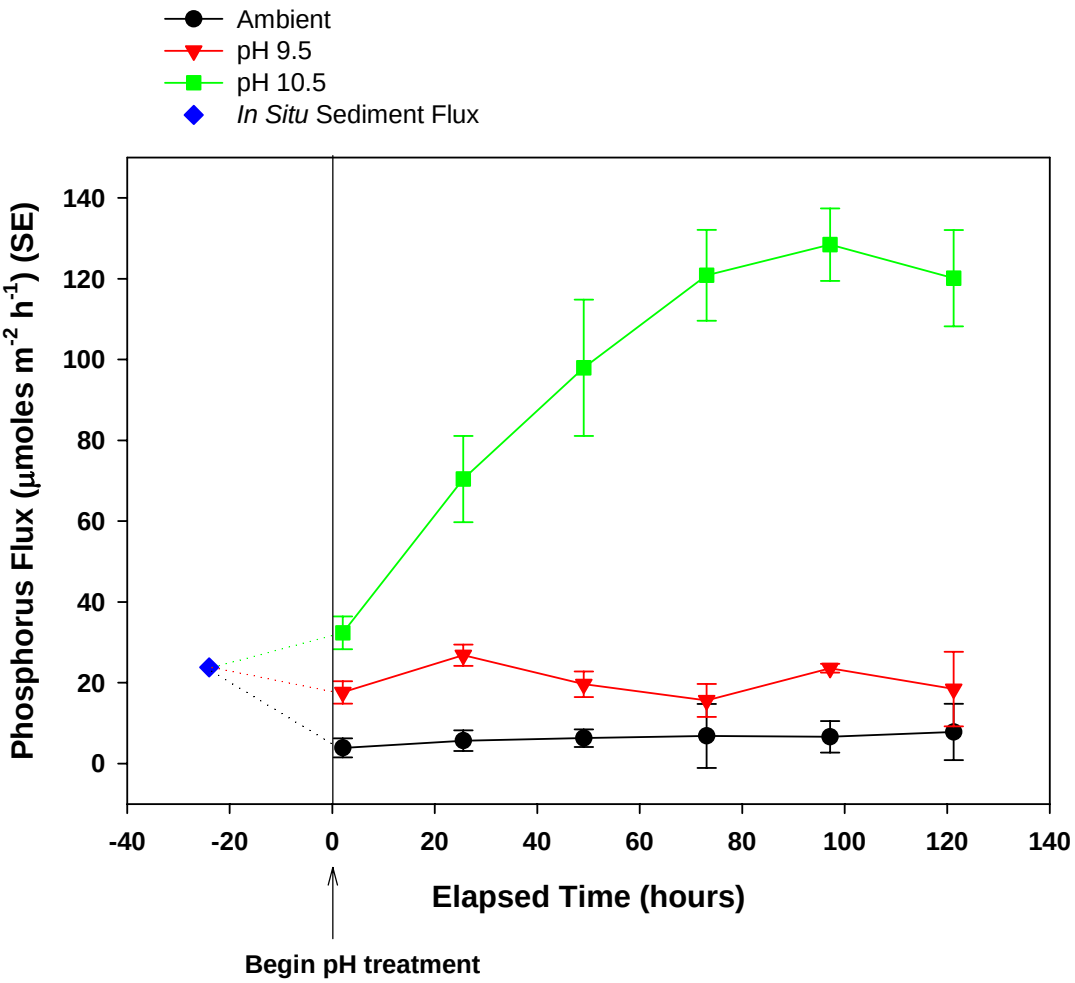


Figure 29. July 2004 static flux versus pH response measurements (Station 3).

In September 2004 sediment phosphorus flux response to pH change was measured using sediments from stations 3, 5 and 8. Treatments included pH 9 and 10. Figure 30 shows static phosphorus flux measurements plotted against exposure time to pH adjusted water. At all three stations *in situ* fluxes were low. Treatment with pH adjusted waters only elicited a response at station 8 (Figure 30). Phosphorus fluxes began increasing after a day of exposure to pH 10. The increase continued for two more days reaching a maximum rate of around 60 µmoles m^{-2} h^{-1}.

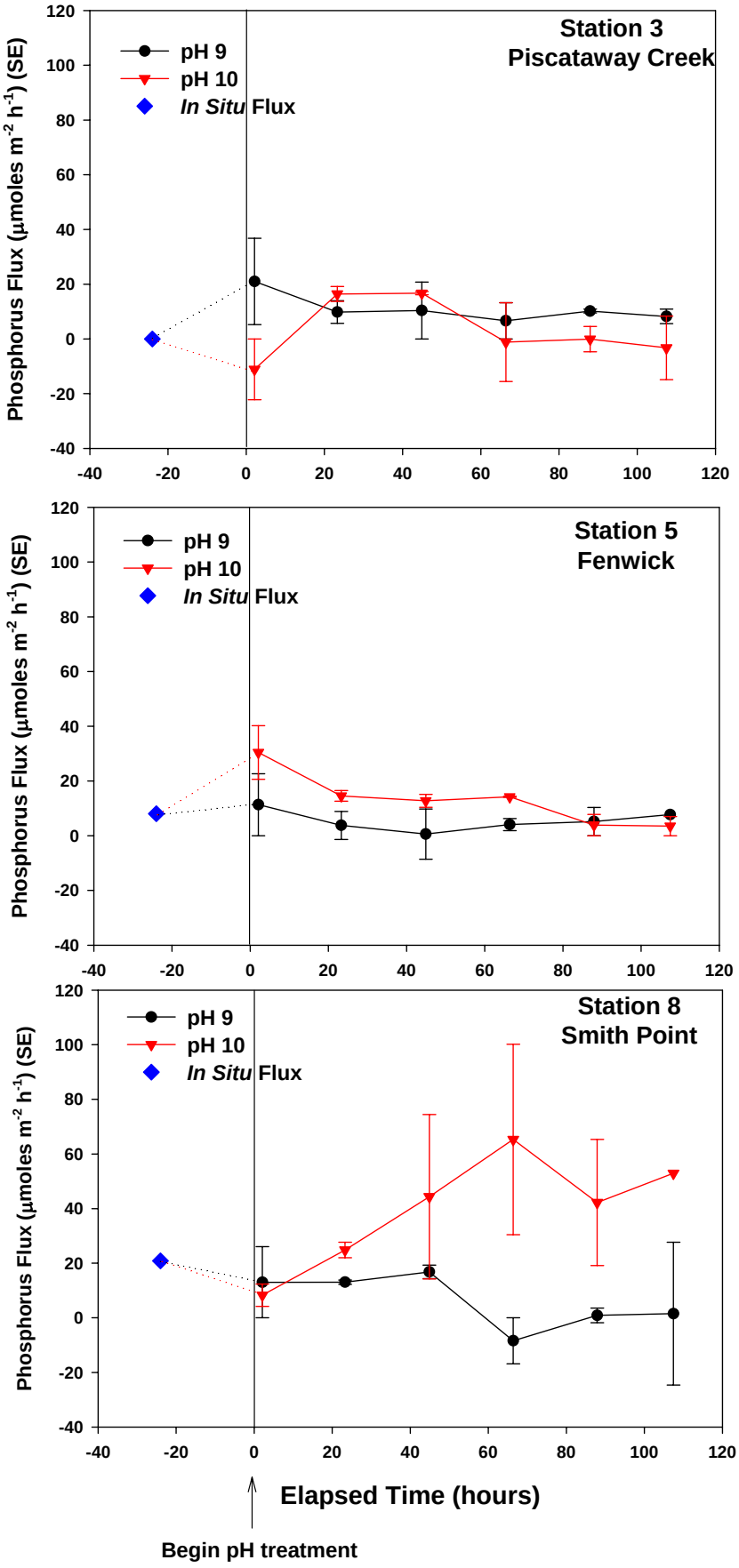


Figure 30. September 2004 static flux versus pH response

Discussion

Ambient Sediment Fluxes of Oxygen and Nutrients

We begin this discussion by comparing sediment fluxes of oxygen and nutrients to those observed in earlier studies conducted in the Potomac River estuary and in other estuaries. For this comparison we rely heavily on the recent review developed by Bailey (2005) in which sediment flux data were organized and examined for a total of 48 estuarine systems and included SOC, NH_4 and PO_4 fluxes. These results are summarized in Figure 31 for easy reference.

SOC fluxes in the tidal fresh portion of the Potomac ranged from about 1 to 3 g O_2 m^{-2} day^{-1} and averaged during the summer of 2004 about 1.5 g O_2 m^{-2} day^{-1}. These rates were distinctly higher than those reported by Bailey where about 90% of observations of SOC were < 1 g O_2 m^{-2} day^{-1}. Bailey (2005) also examined SOC in relation to depth, salinity zone and bottom water temperature. SOC rates observed in the Potomac were about 50% greater for comparable depths, twice as high as those observed elsewhere in comparable salinity zones and similar to fluxes observed elsewhere when water temperature was in excess of 20 °C.

Ammonium (NH_4) fluxes in the tidal fresh portion of the Potomac ranged from about 2000 to -50 μmoles N m^{-2} hr^{-1} and averaged during the summer of 2004 about 300 μmoles N m^{-2} hr^{-1}. There was also a substantial longitudinal gradient in flux wherein fluxes tended to be higher upriver and decrease in a downriver direction. We should note that almost all NH_4 flux measurements yielded large values relative to those routinely measured in estuarine ecosystems, a point that can easily be missed because the highest rates were very large. Ammonium fluxes in the Potomac study area were distinctly higher than those reported by Bailey where about 80% of observations of ammonium flux were less than 100 μmoles N m^{-2} hr^{-1}. Bailey (2005) also examined ammonium flux in relation to depth, salinity zone and bottom water temperature. Ammonium fluxes observed in the Potomac were about double for comparable depths, an order of magnitude higher than those observed elsewhere in comparable salinity zones and about 50% greater than fluxes observed elsewhere when water temperature was in excess of 20 °C.

Sediment fluxes of nitrate (NO_3) were very large relative to measurements made elsewhere in Chesapeake Bay. Unfortunately, Bailey (2005) did not include this parameter in the flux review and hence we can not make broader comparisons. However, nitrate fluxes measured in the tidal fresh Potomac were primarily directed from overlying water into sediments and fluxes, as with ammonium, tended to decrease in a downstream direction. In terms of these fluxes alone, this represents a loss of nitrate from the water column. It is possible, and has often been suggested (e.g., Boynton and Kemp 1985; Cowan and Boynton 1996), that the fate of this nitrate is to be denitrified. If that is the case, then denitrification rates based solely on nitrate derived from the water column (generally referred to as direct denitrification) are quite large. However, other fates for this nitrate are also possible and include autotrophic uptake by phytoplankton and reduction to ammonium by sediment bacteria. Fortunately, denitrification was also

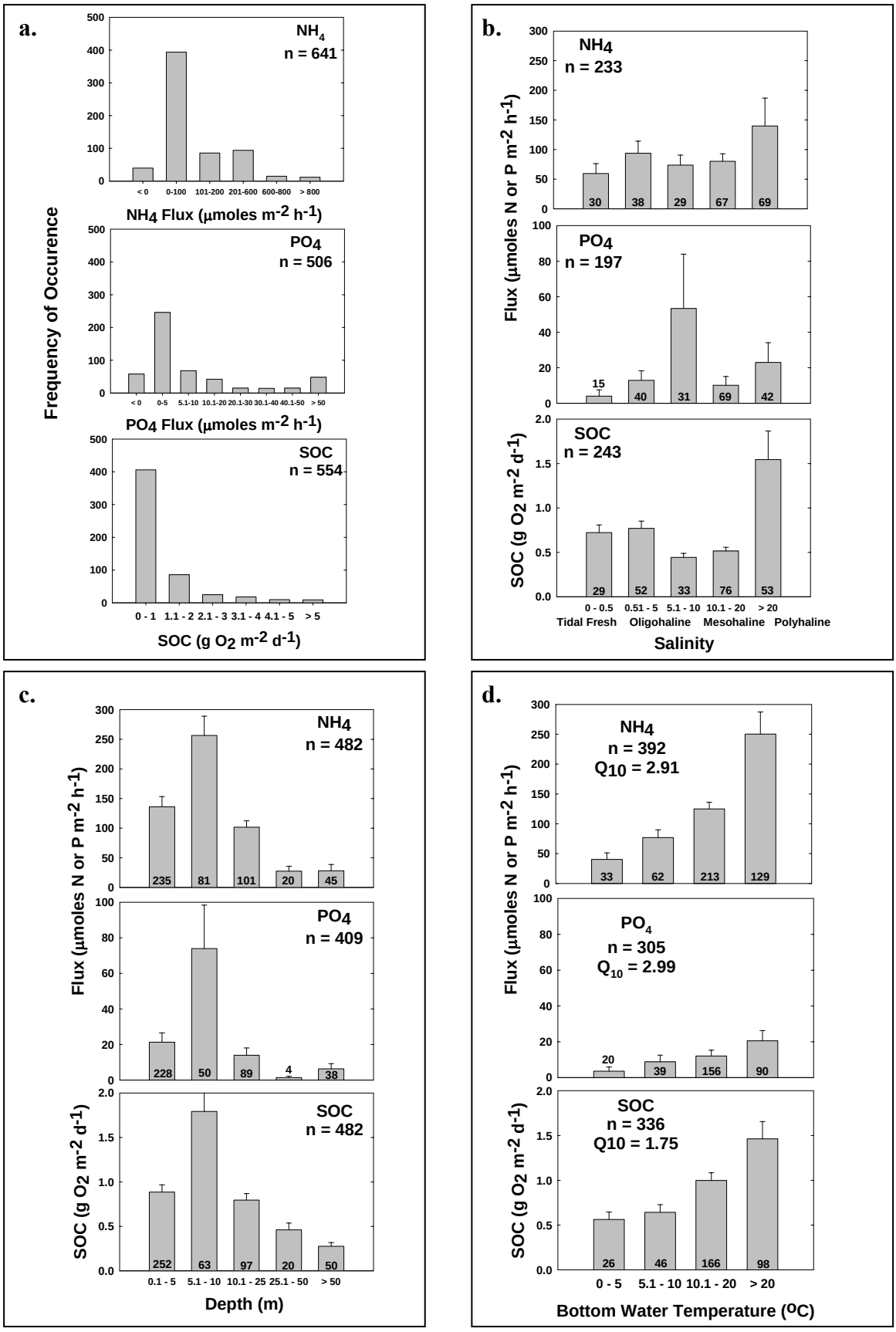


Figure 31. Flux histograms developed by Bailey (2005).Histograms were developed for a) frequency of occurance; b) salinity zone; c) depth; d) water temperature.

measured in this study so a more direct examination of this process is possible, as well as a better understanding of nitrate flux, and these are discussed later in this report.

Sediment phosphate (PO_4) fluxes in the tidal fresh portion of the Potomac are of central interest in this study. *In situ* fluxes ranged from about -23 (flux directed into sediments) to 25 μmoles P m^{-2} hr^{-1} and averaged during the summer of 2004 about 5 μmoles P m^{-2} hr^{-1}. There was also a weak longitudinal gradient in flux wherein fluxes tended to be lower upriver and increase in a downriver direction. Phosphorus fluxes in the Potomac study area were similar to those reported by Bailey where about 50% of all observations of phosphorus flux were less than 5 μmoles P m^{-2} hr^{-1}. Bailey (2005) also examined phosphorus flux in relation to depth, salinity zone and bottom water temperature. Phosphorus fluxes observed in the Potomac were about 25% of those observed at comparable depths, very similar to those observed elsewhere in comparable salinity zones and only about 25% as large as fluxes observed elsewhere when water temperature was in excess of 20 °C.

Several important points seem to emerge from this comparative examination of *in situ* sediment-water oxygen and nutrient exchanges. First, oxygen, ammonium and nitrate fluxes in the tidal fresh Potomac were very large in comparison to such measurements made in other portions of Chesapeake Bay (Cowan and Boynton 1996) and in a wider selection of estuaries (Bailey 2005). The first two of these fluxes have been shown to be largely regulated by the supply rate of labile organic matter available for either aerobic or anaerobic decomposition. The upper Potomac estuary is heavily enriched with organic matter from both external and *in situ* sources. Hence, the pattern we have seen of large fluxes, based on biological respiratory processes, makes a good deal of sense. The decline in ammonium fluxes in a downriver direction is also consistent with a longitudinal decrease in available organic matter which is likely the case in the Potomac. Second, phosphorus fluxes were not responsive to this gradient in organic enrichment. Rather, *in situ* PO_4 fluxes were largely small, consistent with observations in other tidal fresh estuarine zones. This suggests that other mechanisms are controlling P fluxes in this region of the estuary.

Because the emphasis of this work was focused on the influence of pH conditions on sediment phosphorus flux, we have organized all *in situ* flux data as a function of *in situ* pH values (Fig. 32) and also combined data from the present study with data from several other Potomac River estuary programs (Fig. 33). Scatter plots of ambient sediment fluxes versus *in situ* pH values do not suggest any strong relationships to pH conditions at the time of measurement. It does appear that *in situ* bottom water pH was lowest in September (<7.5), intermediate in May (7.6 – 8.4) and highest in July (7.9 – 9.4). While we did not anticipate strong relationships between oxygen or nitrogen fluxes and pH it was possible that P fluxes would exhibit a response to *in situ* pH conditions. However, this was not the case. In general, *in situ* bottom water pH values were not sufficiently elevated at the time of measurement to expect such a response. The highest pH value observed in bottom waters was about 9.4 during July, 2004 and the associated sediment P flux was not large. In fact, three higher fluxes were observed at lower pH values, two of them at less than a pH of 8. Thus, there is little in the ambient field measurement data set

to suggest that bottom water pH values were sufficiently elevated to enhance P release from sediments, at least during the three field cruises conducted during May – September, 2004. Sediment P flux data from several Potomac River estuary studies were

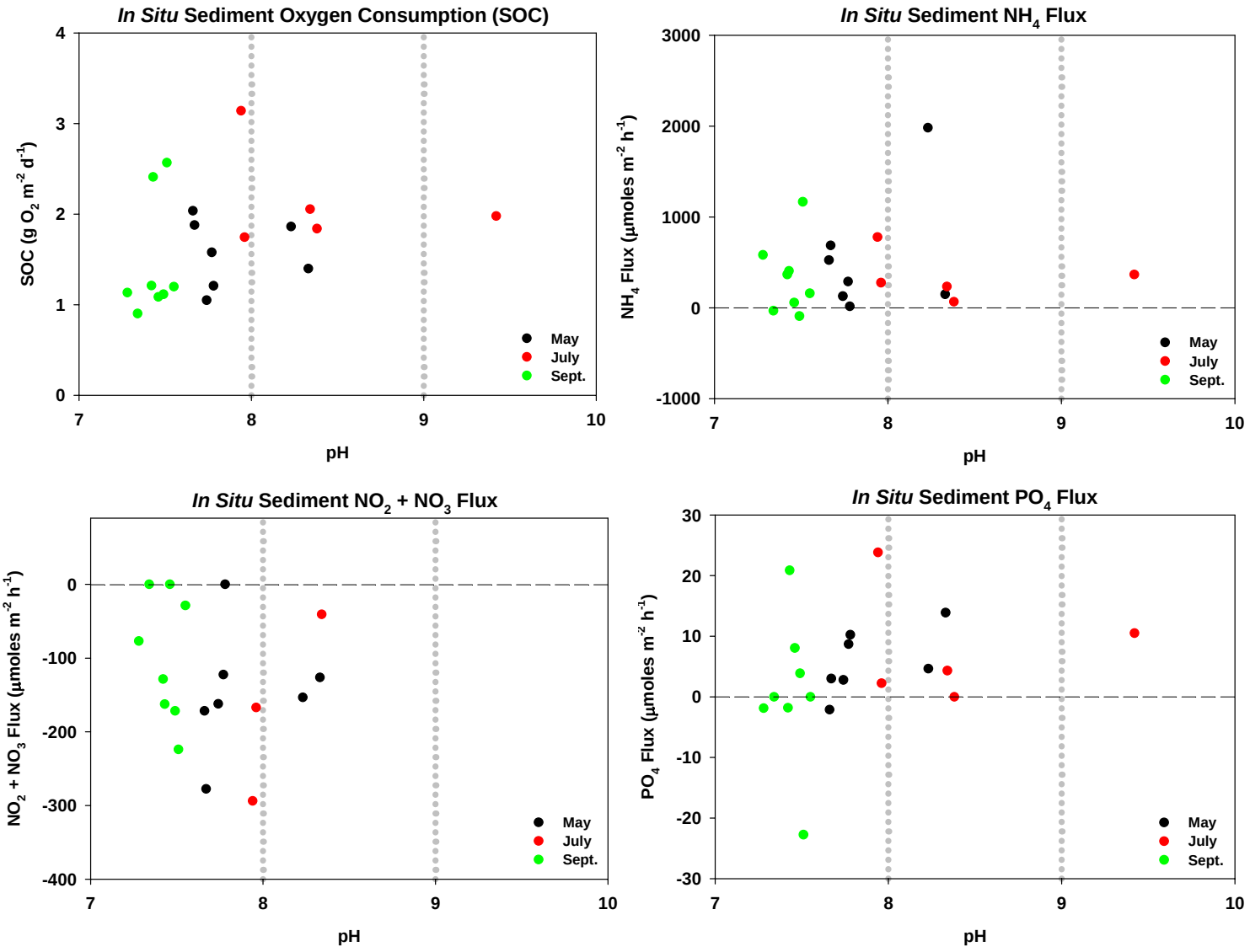


Figure 32. *In situ* sediment fluxes of oxygen (SOC), ammonium, nitrite + nitrate and phosphate measured in the tidal fresh Potomac River estuary during 2004 plotted as a function of bottom water pH measured concurrently with sediment fluxes.

also combined and plotted as a function of the full estuarine salinity regime to further explore the role of sediments as a source of P available to support algal bloom formation (Fig. 33). In this diagram P fluxes were low (~ 10 µmoles P m^{-2} hr^{-1}) in the tidal fresh region and in the low mesohaline region and about 2 and 2.5 times as high in the oligohaline and high mesohaline zones, respectively. The two regions of elevated P flux correspond to the region of most intense algal bloom formation and to the region characterized by severe summer season hypoxia/anoxia. In the first case there is the possibility that bloom formation elevated pH sufficiently so that P was released from Fe-

rich sediments and became available to support further bloom growth/persistence. In the high mesohaline area of the estuary high sediment P releases were very likely caused by reactions between reduced S and iron-bound P wherein P is released into solution and moves from sediment porewater into the water column. Thus, in this estuary there may be two zones prone to high P release from sediments (both deposited and suspended sediments) and that the mechanisms of release involve elevated pH in the low salinity zone and hypoxia/anoxia in the higher salinity zone.

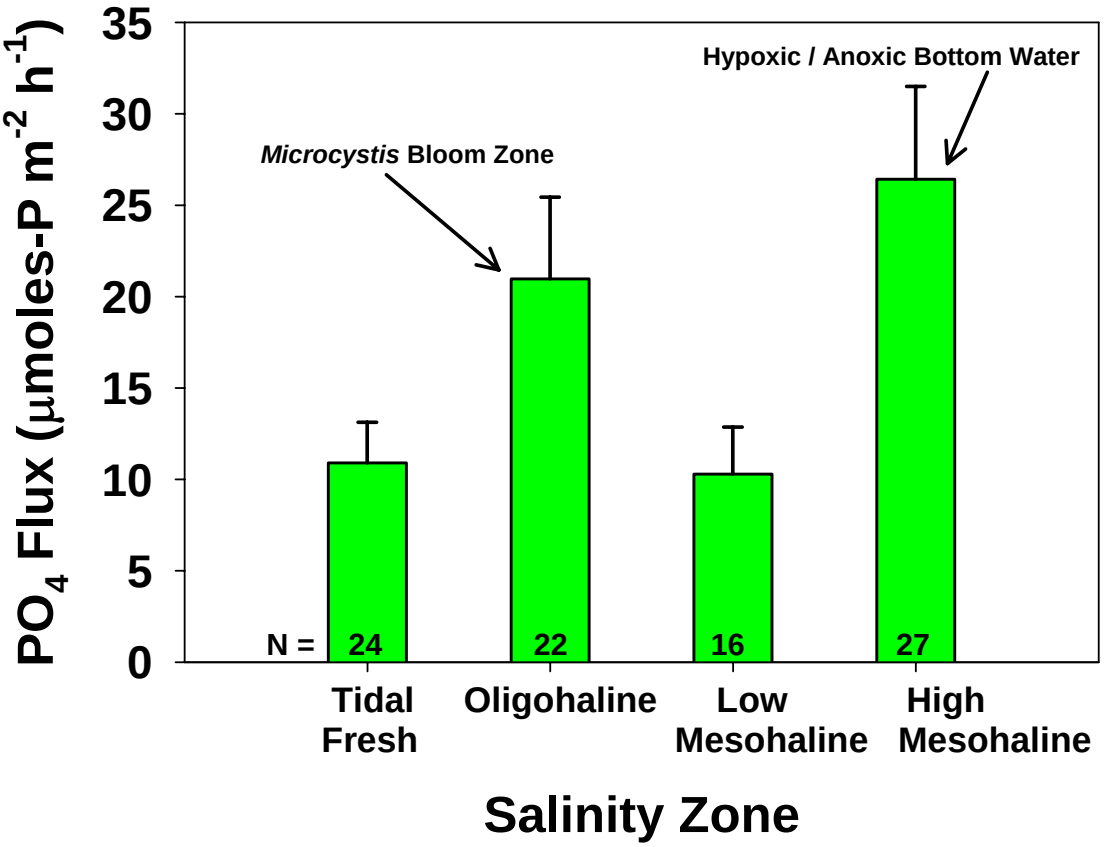


Figure 33. A summary of *in situ* Potomac River estuary sediment fluxes of phosphorus during warm seasons collected along the Potomac salinity gradient. Data were from Callender 1982, Potomac TMDL 2002 (Bailey *et al.* 2003b) and this study.

Denitrification

The measurement of denitrification has generally not been a routine measurement in most studies of nutrient flux in estuaries. Direct measures of denitrification using N_2 are difficult (Seitzinger *et al.* 1993), though the recent development of $^{15}N_2$ (Nielsen 1992) and N_2:Ar (Kana *et al*. 1994; 1998, 2006 (in press) approaches appear to provide better measurements than in the past (e.g. Cornwell *et al.* 1999). Excellent replication indicates that our denitrification experiment worked quite well. Denitrification requires a source of oxidized nitrogen such as nitrate. Nitrate can be supplied from the overlying water or from the process of nitrification within aerobic sediments. In high nitrate environments such as the Potomac River, elevated rates of denitrification would be expected. In

particular, the high rates of sediment metabolism evidenced by high SOD should lead to very high rates.

Our Potomac denitrification rate data are the first for this ecosystem; direct comparisons to other nitrate-rich subestuaries of the Chesapeake are not available. However, our unpublished data on the upper Choptank River and Patuxent Rivers show rates that exceed that of the Potomac River; these two systems have higher water column nitrate concentrations. The average rate of all sites (~100 μmoles m^{-2} h^{-1}) is consistent with high organic matter and nitrate loading rates. The overall importance of denitrification to the Potomac River N budget depends on residence time of the water and area of sediment which can denitrify. Boynton *et al.* (1995) used lower rates, but concluded that these sediments in the upper estuary removed only a small part of the nitrogen load. Though these rates are higher than the rates assumed by Boynton *et al*. (1995), it seems unlikely that sediments are a large N sink on an annual basis. In a low flow year with longer water residence time, summer denitrification may affect the nitrate concentration substantially. Under higher flow conditions, the effect would be minimal. We observe the same phenomena in the Choptank River, where high rates in the upper estuary are a low proportion of the overall denitrification in that system. This happens because most of the estuarine sediment surface area is in the lower estuary. We expect the same relationship in the Potomac.

Sediment Characteristics and Relationships to Potential Sediment P Fluxes

The mapping data showed strong statistical relationships between a number of parameters. Of prime interest to this project is the Fe-P relationship. Both inorganic P and Fe are correlated with grain size as well. Our original goal of using mapping data for extrapolation was sound, but the range of sediment concentrations at our flux core sites was not large. For example, inorganic P ranged from 0.51-0.73 mg g^{-1}, organic P ranged from 0.30-0.49 mg g^{-1} and Fe from 10-20 mg g^{-1}. This low range, combined with an absence of large spatial differences in P fluxes, minimizes the need for such spatial extrapolation. These data, especially the grain size data, will be of great use to the sediment transport modeling efforts on the Potomac.

Sediment P Fluxes in Relation to Experimental pH Modifications

One of the central goals of this work was to examine the influence of elevated pH conditions on P release from estuarine sediments in the tidal freshwater portion of the Potomac River estuary. It has long been suspected (e.g. Seitzinger 1991) that P derived from estuarine sediments plays a central role in supplying P needed to stimulate and maintain blue-green algal blooms (*Microcystis aeruginosa*) in this region of the Potomac. The current work re-visited this issue and in this section we examine the results of experimental studies wherein pH conditions were modified, to mimic conditions during a *Microcystis* bloom, with direct measurements made of sediment P fluxes under enhanced pH conditions.

There are several mechanisms that can promote movement of P from estuarine sediments to the water column. Under low oxygen situations (hypoxic or anoxic), common in some estuaries, sediments become reduced and Fe(III) oxides are also reduced to Fe(II) with

the resultant release of adsorbed P into solution. Increased salt content of bottom waters also promotes this process. Second, sediment pore waters can be transported fast enough from deeper in the sediment column to the surface to bypass P adsorption to iron oxides; generally this mechanism is associated with bioirrigation. Third, P can be released directly to the water column associated with infaunal (e.g., dense bivalve communities) metabolism. Finally, under increased pH conditions (>9.0), P adsorbed to Fe(III) oxides can be released into solution. It is this final mechanism that was investigated using experimental cores with pH elevation of overlying waters.

There have been, it appears, relatively few investigations of pH influences on sediment P flux in estuarine systems. Such investigations have been conducted in lakes and it appears that pH influences are clearly operative (e.g., Anderson 1974; Istvanovics 1988). In the case of estuarine systems such examinations have rarely been conducted, probably because in most estuaries there is sufficiently strong carbonate system buffering to prevent pH increases to the extent needed for sediment P responses.

However, one such study was conducted in the Potomac River estuary in the same general salinity zone as the present study. During fall of 1985 Seitzinger (1991) conducted a series of pH enhancement measurements using sediment microcosms with pH control using direct additions of a strong base. Results indicated that sediment P fluxes were small (< 25 μmoles m^{-2} hr^{-1}) when pH was <9.0. At some sites sediment P fluxes increased when pH was elevated to 9.5 and all sites exhibited larger sediment P fluxes at a pH of 10. Increases in pH to 10.5 did not further increase sediment P release rates.

Several other points are of relevance here as well. In the Seitzinger (1991) study, up-river sites (Stations 1 – 4) exhibited higher sediment P releases at elevated pH levels than did more downriver sites (Stations 5 -8) at similarly increased pH levels. At the up-river sites sediment P release rates ranged from about 50 to 113 μmoles m^{-2} hr^{-1}, very substantial rates, while at downriver sites rates were between 34 to 46 μmoles m^{-2} hr^{-1}, still large but closer to ambient rates. Finally, during the 1985 study, high pH levels were reported as being characteristic of the full water column so that sediment surfaces were in contact with high pH water. In our study, this did not appear to be the case, at least based on vertical water column profiling data collected during cruises in May, July and September, 2004. High pH in bottom water was the exception rather than the rule during those cruises. However, it is also clear that in near-shore (shallow) areas where high frequency measurement devises were located, surface water (~1 m depth) pH values often were in excess of 9, at times reached 10.5, and exhibited extremely strong diel patterns with high pH values persisting for 10 or more hours per day. Finally, in the Seitzinger (1991) work, pH enhanced sediment microcosms were exposed to elevated pH conditions for 5 days (with appropriate water replacement during this period of incubation) and then a sediment P flux measurement was obtained. Thus, there was a substantial time of exposure to elevated pH conditions. In the present study this approach was used to a limited extent; we relied more on a time-series approach to better understand both the ultimate effect of elevated pH on sediment P fluxes but also the shorter term (hours to day) responses of sediments to pH fluctuations.

Three major experiments were conducted, the details of which have already been presented. In the first experiment a single pH level was selected (pH = 10), sediment cores collected from the upper, middle and lower portions of the study area and sediment P fluxes measured after 5 and 7 days of incubation. Except for the fact that different methods of pH adjustment were utilized, these measurements were conducted in a fashion similar to those of Seitzinger (1991). Indeed, results were also qualitatively similar (Fig. 9). Ambient (i.e., non-pH adjusted cores) fluxes were very small, fluxes were larger after 5 days exposure to elevated pH and after 7 days fluxes were very substantial at all sites. Thus, these results indicate that the potential for elevated sediment P release is high during spring throughout the study area. This approach, however, teaches us little about the time-course of pH effect on estuarine sediments other than after an extended period of exposure sediment P fluxes can be large. During July 2004 sediment cores were collected from a site in the middle of the study zone (Station 3) and sub-sets of cores exposed to ambient pH conditions, pH 9.6 and pH 10.5 with sediment P flux measurements made as a time-series during a 5 day period in all treatments. In this case there was a clear indication of response to pH elevation almost immediately (2 hrs post-treatment) for both the pH 9.5 and 10.5 treatment cores (Fig. 10). Sediment P fluxes did not respond further in the pH 9.5 treatments but continued to increase to extremely high levels (> 100 μmoles m^{-2} hr^{-1}) in the pH 10.5 treatment core after 48 hours. Thus, these data suggest that response to pH can be very rapid, well within the diel pH cycle observed with shore-based high frequency measurement systems, and that the magnitude of response is proportional to the degree of pH elevation. The final experiment utilized sediment cores collected in September, 2004 from sites in the upper, middle and downstream zones of the study area (Stations 3, 5, and 8) with sub-sets of cores exposed to pH conditions of 9 and 10. For reasons that remain unclear at this point, sediment P flux responses to pH elevation were not consistent. The time-series of response fluxes at the upper and middle study area sites were quite small and at times the lower pH treatment caused a greater response than did the higher pH treatment. At the remaining sampling site (Station 8) the pH 9 treatment effect was very small while the pH 10 treatment elevated sediment P fluxes but not to the same degree as did similar pH treatments in July. While we may yet discover a convincing mechanistic explanation for September results, at present they suggest some significant seasonality in the potential for sediments to respond to elevated pH conditions.

While there were temporal and spatial differences in sediment P fluxes in response to pH elevation there were also strong patterns of pH response when the full sediment flux data set was examined as a function of pH. In Figure 34 both *in situ* and experimental sediment P fluxes were plotted as a function of pH at the time of measurement. Data from May, July and September are color coded and *in situ* measurements are indicated by circles and experimental measurements indicated by triangles. With very few exceptions, sediment P fluxes were low (< 25 μmoles m^{-2} hr^{-1}) at pH levels less than about 9.2. In fact, the majority of these fluxes were less than about

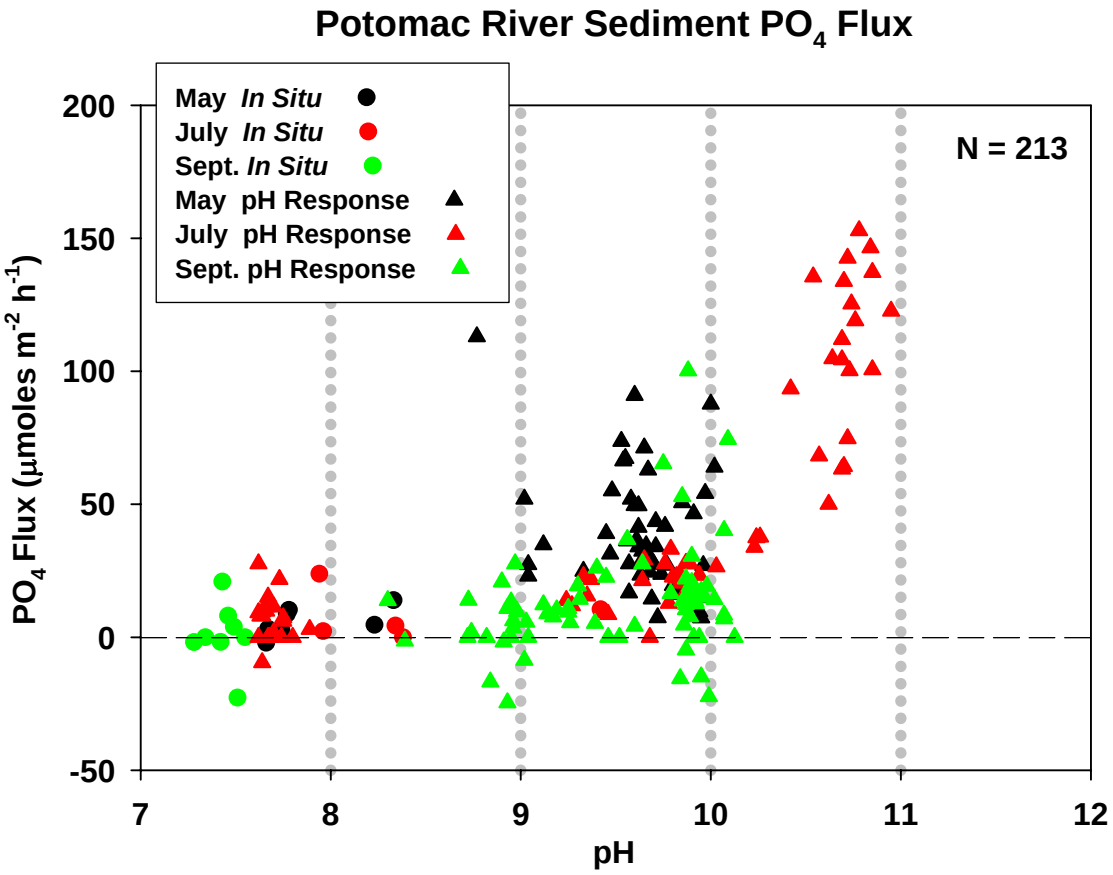


Figure 34. A scatter plot of sediment P flux as a function of water column pH at the time of measurement. *In situ* fluxes are shown as circles and experimental fluxes are triangles. Month of measurement is color coded.

10 µmoles m^{-2} hr^{-1} and about 50% were either zero or were directed into sediments, again at small rates. We make this point because at these pH levels (7 -9) sediment P fluxes are not sufficient to support major phytoplankton bloom formation. Later in this report we discuss the quantitative significance of various levels of sediment P release rates. However, under pH conditions higher than about 9.2, sediment P fluxes did increase and at pH levels of between 10.5 and 10.9 reached very high levels capable of supporting very large phytoplanktonic nutrient demand. There is also an indication in Figure 34 of temporal variability. Experimental measurements made in July responded to pH elevation more than did cores similarly exposed in May. Measurements made in September responded least to pH increases. Some of this variability might be associated with *in situ* conditions prior to measurement, seasonal variation in sediment P availability, seasonal variations in sediment structure, animal community characteristics influencing bioirrigation or some other factor, or combination of factors, we have yet to consider. However, there remains the fact that there was a strong experimental response to elevated pH and the magnitude of the response was sufficient to supply a great deal of P to the water column.

One of the issues yet to be fully addressed concerns spatial and temporal prediction of sediment P and other fluxes. There have been some successes in modeling sediment

biogeochemistry (see, for example, DiToro 2004 for a review of simulation modeling approaches). In Chesapeake Bay, Cowan and Boynton (1996) found very strong statistical relationships between the amount of labile organic matter at the sediment surface during spring (following deposition of the spring phytoplankton bloom) and subsequent oxygen, nitrogen, phosphorus and silica fluxes during summer along the salinity gradient of mainstem Chesapeake Bay. Later, Cowan *et al*. (1996) extended these analyses to include data from Mobile Bay with similar results. More recently, Stankelis *et al*. (1998) developed multiple regression models of sediment nutrient fluxes for the mesohaline portion of the Patuxent River estuary and important predictive variablies included such things as sediment redox status, bottom water oxygen and nutrient concentrations, and sediment organic matter content. However, neither of these studies included tidal freshwater portions of the estuary. We have started to examine this data set for relatively simple, useful statistical models for predicting sediment nutrient releases (or uptake). As an exploratory step we have used a technique called Classification and Regression Tree analysis which is a non-parametric multivariate approach for prediction of both categorical (classification) and continuous (regression) variables. Within these analyses both categorical and continuous predictors can be used. We used the TREES module in the Systat® 10.2 software package with the least squares estimate for the loss function. The results of two preliminary analyses are provided in Figure 35. Major "splitting factors" classifying sediment nitrate plus nitrite fluxes included water column DO concentrations and water column nitrate plus nitrite concentration. The mechanistic basis for DO being a splitting variable are, at this point, obscure but may become clearer as we pursue these analyses. The influence of water column nitrate plus nitrite concentration on sediment nitrate plus nitrite flux has been observed previously (e.g. Boynton and Kemp 1985) and this N going into sediments has been generally thought to be denitrified. This could be the case here as well. The second analysis considered sediment P flux and in this case water column pH was the first splitting variable and bottom water dissolved oxygen concentration the second splitting variable. In both cases, mechanistic explanations are available. The pH influence has already been discussed in previous sections of this report. The dissolved oxygen influence may actually be an indicator of redox conditions in the surficial sediments where more reduced sediments (as indicated by lower water column dissolved oxygen concentrations) favor larger sediment P release rates. We expect to further elaborate these analyses in the future with the ultimate goal being multivariate models useful in prediction of sediment P fluxes based on readily measured water column and sediment properties.

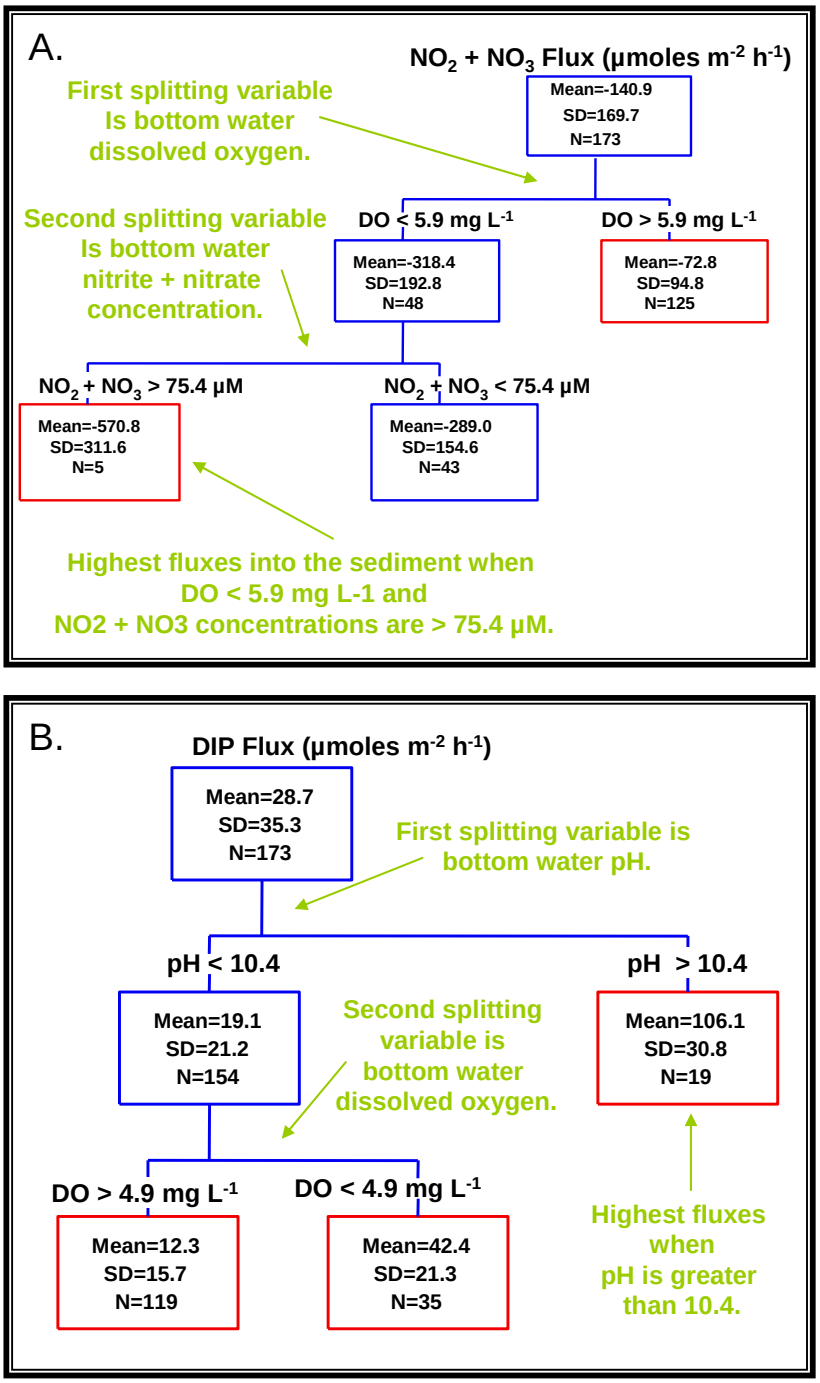


Figure 35. Preliminary results of classification and regression TREE analysis. (A) Sediment nitrite plus nitrate flux regression tree; (B) Sediment DIP flux regression tree.

Mechanisms Regulating Sediment P Fluxes

The mobilization of P from aquatic sediments can arise from a variety of mechanisms. For the purposes of this discussion, we will not consider that case of calcareous sediments which have a considerably different biogeochemical behavior. In "normal" watershed-derived sediments, the chief mechanisms for P release include:

- Low redox is a key part of P release from most aquatic sediments (i.e. Einsele 1936; Mortimer 1941). Under aerobic, neutral pH conditions, Fe(III) oxides in sediment retain SRP by physical-chemical adsorption (Krom and Berner 1980; Cornwell 1987). Iron oxides often have high surface area and present a key barrier to diffusion of SRP to overlying water. In freshwater sediments, the efficiency of P release is not as high as in saline sediments (i.e. Caraco *et al.* 1989) because of the importance of sulfate/sulfate reduction on the surface area of Fe(III) oxides. Keys to redox-related P release are 1) dissolved oxygen concentrations in overlying water (i.e. Cowan and Boynton 1996), 2) organic matter metabolic rates which affect rates of P mineralization and redox zonation, 3) the influence of benthic organisms which can either rapidly transport SRP out of sediments (i.e. Aller 1980) and 4) modifying factors such as temperature and concentrations of alternate electron acceptors such as nitrate (i.e. Anderson 1982).
- Animals such as bivalves may help P bypass sediment biogeochemical processes by direct excretion into the water column. We have directly observed this in lake sediments (Cornwell and Owens 1999); cores with bivalves had > 10 fold increases in SRP fluxes. Less is known about this mechanism and it will not be discussed further.
- Elevated pH can be an efficient mechanism of P release (Seitzinger 1991). The enhancement of P release under the elevated pH conditions found in eutrophic lakes results in enhanced SRP fluxes (i.e. Andersen 1974; Drake and Heaney 1987; Jensen and Andersen 1992; Xie *et al*. 2003).

We will discuss the relevance of all of these mechanisms for Potomac River sediments. In the Potomac River, high sediment Fe(III) oxide concentrations (see mapping data), particularly at the sediment-water interface (Lovley and Phillips 1986), result in the presence of a large surface barrier for the diffusion of SRP across the sediment-water interface. While aerobic conditions generally extend < 2 mm into the sediment, Fe oxides generally are found to greater depths. Most of our pore water Fe(II) profiles indicate that while there is a substantial increase downcore, gradients within the sediment suggest that the Fe is retained. Rapid oxidation of Fe(II) occurs either through exposure to oxygen (i.e. Stumm and Morgan 1981) or via electron exchange with other oxidants (such as Mn(IV) or nitrate; Postma 1985; 1990). Low SRP fluxes under normal pH conditions are consistent with Fe retention of SRP.

Despite the dissolution of Fe oxides in Potomac River sediments, evident because of pore water Fe(II) accumulation, SRP cannot readily diffuse past the near-surface Fe(IIII) oxide diffusive barrier. Reprecipitation of Fe(II) in the sediments results in a high surface area oxide coating, often visually distinguished by its reddish color. The effect of Fe redox changes can be the redistribution of Fe and associated SRP (i.e. Carignan and Flett 1981;

Cornwell 1987); enhanced fluxes across the sediment-water interface are often not a result of such redistribution. Higher concentrations of nitrate in the tidal freshwater Potomac River can also promote the retention of SRP. Nitrate can serve as an oxidant, and delay the reduction of Fe(III) until nitrate is depleted. In several lake studies, high overlying water nitrate or experimental nitrate amendments has been shown to limit SRP release (i.e. Anderson 1982; Bostrom and Pettersson 1982), though in at least one study it promoted P remineralization and enhanced SRP fluxes (Jensen and Andersen 1992). We did not experiment with nitrate effects, but it seems likely that high Fe(III) alone would keep SRP fluxes low.

The physical chemistry of SRP desorption is well described; competition of OH^- for Fe(III) oxide binding sites, as well as changes in H_3PO_4 speciation can result in desorption at higher pH's. One of the key questions is not the physical chemistry of the release, but the combination of diffusion, depth of pH change and P availability may drive the flux rates. Drake and Heaney (1987) showed high SRP releases from sediment at ph = 10.5 (~ 100 mmoles m^{-2} h^{-1}), with the suggestion that the flux was primarily from near-surface sediments. In the lake they investigated, high pH in the overlying water did not extend all the way to the sediment surface, with sediment pH buffering suggested. Jensen et al. (1992) suggested that pH-enhanced fluxes required desorption somewhat deeper into the sediments. In neither case were detailed sediment pH profiles carried out.

In our experiments, we observed a rapid and continuing increase in pore water pH in the sediment. We did not expect such a rapid increase because of presumed pH buffering by the sediments. Nevertheless, pH penetration resulted in enrichment of the pore water with SRP; this enrichment created a strong gradient between the sediment and overlying water. We can generally show how pore water concentration changes can determine upward fluxes by using Ficks first law (Berner 1980; Cornwell 1987):

$$F = \Phi D_s \partial C/\partial x$$

$$D_s = D_t * \Phi^2$$

where Φ is porosity (volume of water/volume of wet sediment), C is the concentration of SRP, x is depth (cm), Dt is the temperature corrected diffusion coefficient and Ds is sediment diffusion coefficient. We estimated D_s as a function of porosity following Ullman and Aller (1982) using the diffusion coefficients of Li and Gregory (1974). Using a porosity of 0.9 (about 80% water by weight, assuming dry density of 2.5 g cm^{-3}), T = 25º, a 25 μmol L^{-1} concentration change between the water and the 0.0-0.5 cm top section SRP value, and a diffusion coefficient of 0.00000535 cm^2 s^{-1}, we calculate a upward flux of 19 μmol m^{-2} h^{-1} based on the pore water gradient.. This calculation shows fluxes a little smaller than from sediment-water exchange work. The somewhat lower flux estimate can arise if 1) the SRP gradient is much higher in the top few mm than in the bulk sediment we sample or 2) there is bioirrigation leading to pore water advection. Nevertheless, the pore water shows a substantial increase in upward flux when pH is increased.

If we consider the top 1 cm of sediment, with 80% water content (by weight), we can estimate about 2000 g of dry sediment per m^2 (again assuming a dry density of 0.25 g cm^{-3}). If we take the average inorganic P concentration from mapping (0.56 mg g^{-1} P) and assume it is all mobile, we can sustain a flux of 60 μmoles m^{-2} h^{-1} for ~20-25 days. Not all inorganic P would be mobile. The 1 cm depth may be too shallow if high pH is sustained for weeks. On the time frame of our experiments (1 week), it seems likely that significant P depletion would not strongly affect our experimental results. Lower flux rates (i.e. lower pH's) could be sustained for months. Continual additions of new sediment and P would also support longer-term rates.

The key to pH-driven SRP release is the actual level of pH and the duration of high pH. There is a large pool of available P in sediments and a sustained bloom should be able to "mine" a considerable proportion of surface sediment. Drake and Heaney (1987) have suggested that available P is rapidly depleted under high pH (~10) conditions. Such depletion of inorganic P should be observable under sustained bloom conditions, such as the Potomac River *Microcystis* bloom and similar blooms elsewhere (Xie *et al*. 2003).

Estuarine-Scale Impact of P Fluxes Responding to Elevated pH

One important issue that needs to be addressed in environmental studies such as the Potomac pH-Phosphorus work has to do with reconciling observations made *in situ* with those derived from laboratory experiments. In the present study we have shown that under laboratory conditions sediment P fluxes can be enhanced, more so at some times of the year than during others, and that at least in some locations of the Potomac (e.g., shoal areas of the tidal fresh zone) *in situ* pH values can reach levels where Fe-bound P could be released into solution and thereby be available to support phytoplanktonic growth and biomass increase.

An additional issue involves the supply of dissolved inorganic P (DIP) available to support phytoplanktonic growth. In a simple fashion, DIP can come from external sources, such as non-point or point sources, or from some more internal source, such as P bound to Fe-rich sediment particles. It is possible to make a preliminary estimate of the importance of various sources of DIP and thus place in perspective the relative importance of pH-driven P release from sediments, either from bottom or suspended sediments.

In Figure 36 we have summarized point and diffuse DIP loads from the Potomac River and from sewage treatment plants downstream of the fall line of the Potomac. During the drought year of 2002 average daily loads amounted to about 590 kg P day^{-1}. In sharp contrast, DIP loads during 2003, an especially wet year, amounted to about 3,000 kg P

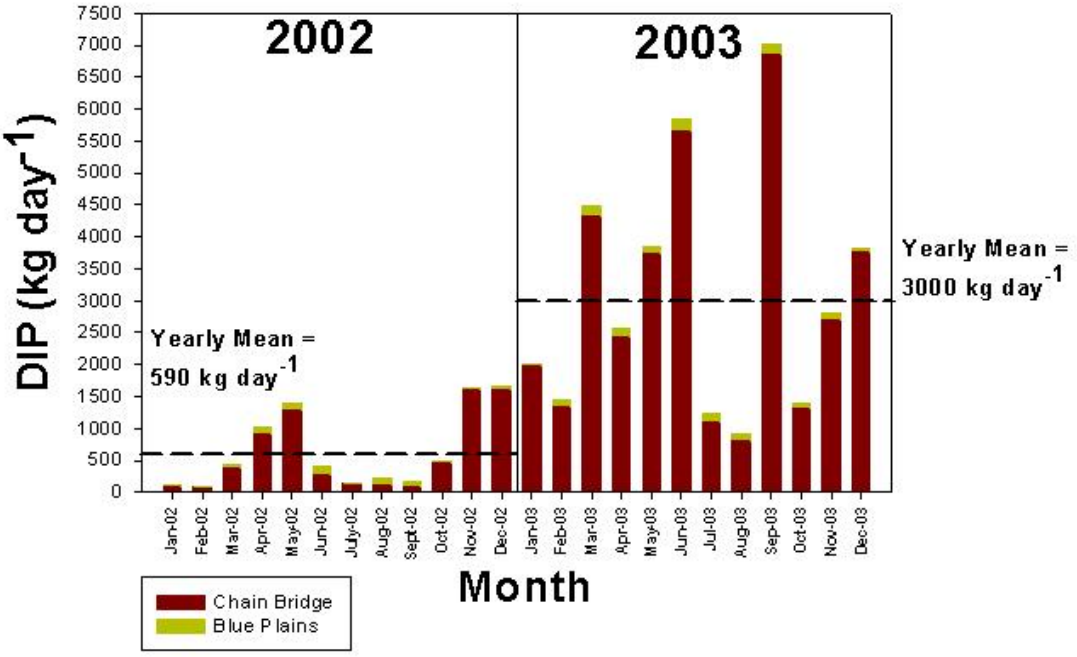


Figure 36. Monthly average dissolved inorganic P (DIP) loading rates from 2002 and 2003. Note the 5X difference in P loads between extreme dry (2002) and wet (2003) years. (CIMS; CBP Nutrient Point Source Database).

day^{-1}, an increase of about 5-fold over the previous year. Boynton and Kemp (2000) and Hagy *et al.* (2004) have made the point that interannual-scales of input variability can have very important influences of ecosystem dynamics; this is very likely the case in the Potomac as well.

In Table 10 we have taken external DIP inputs from Figure 36 and pro-rated these loads over the spatial extent of the upper estuary, thereby estimating an areal DIP load. Then, these P loads were used in conjunction with Redfield ratios of phytoplankton composition (Redfield 1934) to estimate rates of potential phytoplankton production. The first three rows of Table 10 have such production estimates, several for multiple years. The final row of this table has direct estimates of production (C^{14}-based technique) and can be used as a benchmark value. Several important whole ecosystem-scale points emerge from these simple calculations. First, while of management concern, external inputs of DIP are

not nearly large enough to directly support daily rates of primary production. During the drought year of 2002 external inputs could support 6% of production observed during 2004 and even during the high flow year of 2003 only about 28% of daily production could be attributed to external sources. Thus, internal sources, mainly the liberation of Fe-bound P, must play a significant role in providing P needed for production. In the upper portion of the Potomac we have two estimates of the production that could be supported based on ambient sediment releases of DIP (0.5 and 0.2 g C m^{-2} day^{-1}). The first of these was based on DIP releases measured during the TMDL evaluation conducted on the Potomac during 2002 and the second based on measurements made during 2004 (this study). In both cases, ambient sediment DIP releases did no generate production close to that directly measured in this zone of the estuary; percentages were similar to those calculated for external inputs. However, sediment DIP releases estimated from laboratory-based experiments, especially those where pH was elevated to about 10, indicate that rates of primary production well in excess of measured rates could be supported, the type of conditions likely needed to start and sustain algal bloom conditions.

Table 10. Estimates of phytoplankton productivity supported by various sources (both external and internal) of P. Production in the first three rows was estimated by converting areal P loads (g P m^{-2} d^{-1}) to carbon using Redfield ratios (C:N:P = 106:16:1). In the last row, primary production rates were available from the Chesapeake Bay Biomonitoring Program.

	2002	2003	2004
	g C m^{-2} d^{-1}		
External P Inputs	**0.1**	**0.5**	**----**
Ambient Sediment P Fluxes	**0.5**	**----**	**0.2**
pH Induced P Fluxes (@ pH 10)	**----**	**----**	**3.7**
Computed P Demand (plankton monitoring)	**----**	**----**	**1.8**

However, before reaching the conclusion that pH-induced P releases from estuarine sediments is the sole, or even primary, mechanism supporting excessive algal growth we need to remember several things that make this conclusion unlikely. First, sustained very high pH values are generally seen in surface waters. A time-series of such measurements are shown in Figure 37 and clearly indicate that in the surface meter of the water column really high pH values do occur on a regular basis. However, during routine cruises in May, July and September, 2004 we observed very few elevated pH conditions in near-bottom waters at stations generally deeper than 2 meters. Thus, there may be a disconnect between the potential for sediment DIP release and the conditions needed for such an event to happen on a sustained basis. Second, most of our routine measurement sites were in waters deeper than one meter and they may not be routinely exposed to elevated pH conditions. Unfortunately, except for shallow shoreline sites, we have no detailed time-series measurements of pH at greater depths. While these considerations cast some doubt

on bottom sediments in deeper areas of the upper estuary as a primary source of DIP, the relatively large expanse of shallow shoals (~2 m depth) in the Potomac may be an important source of high pH-induced DIP.

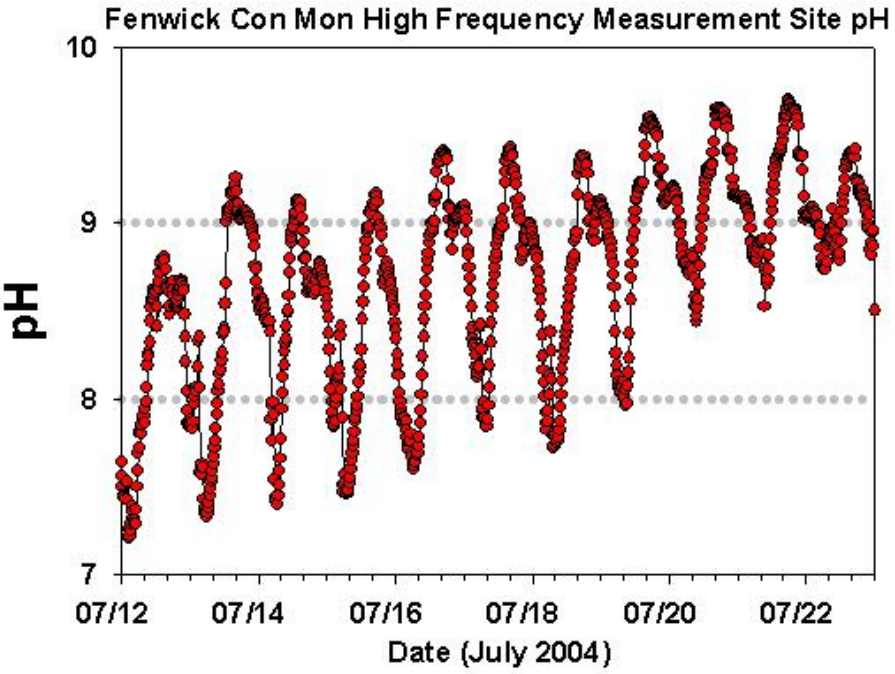


Figure 37. A time series (12 – 23 July, 2004) of pH measurements from a shallow, shore line site of the upper Potomac River estuary. Measurements were made about 1 m below the water's surface. Data from http://mddnr.chesapeakebay.net/eyesonthebay/index.cfm.

Additional Sources and Mechanisms Regulating P-availability

The focus of this research has been on the possible role of bottom sediments as a source of DIP when these sediments are exposed to elevated pH conditions. In addition, detailed measurements were made of pore water conditions and these measurements helped reveal the mechanistic basis for enhanced DIP fluxes under conditions of elevated pH. In short, elevated pH, caused by algal growth in these relatively poorly buffered waters, initiates a positive feedback cycle wherein DIP is released from sediments (probably at modest rates when pH elevation is modest) because Fe-P complexes become soluble at elevated pHs. This DIP supports additional algal growth and biomass accumulation leading to further pH increases which, in turn, serves to stimulate further releases of Fe-bound phosphorus from estuarine sediments. This cycle apparently can become very active, in part because in this zone of the estuary various forms of N (NH_4 and NO_3) are always abundant and would not serve to limit production (e.g. Figure 6) as they do in many estuarine systems

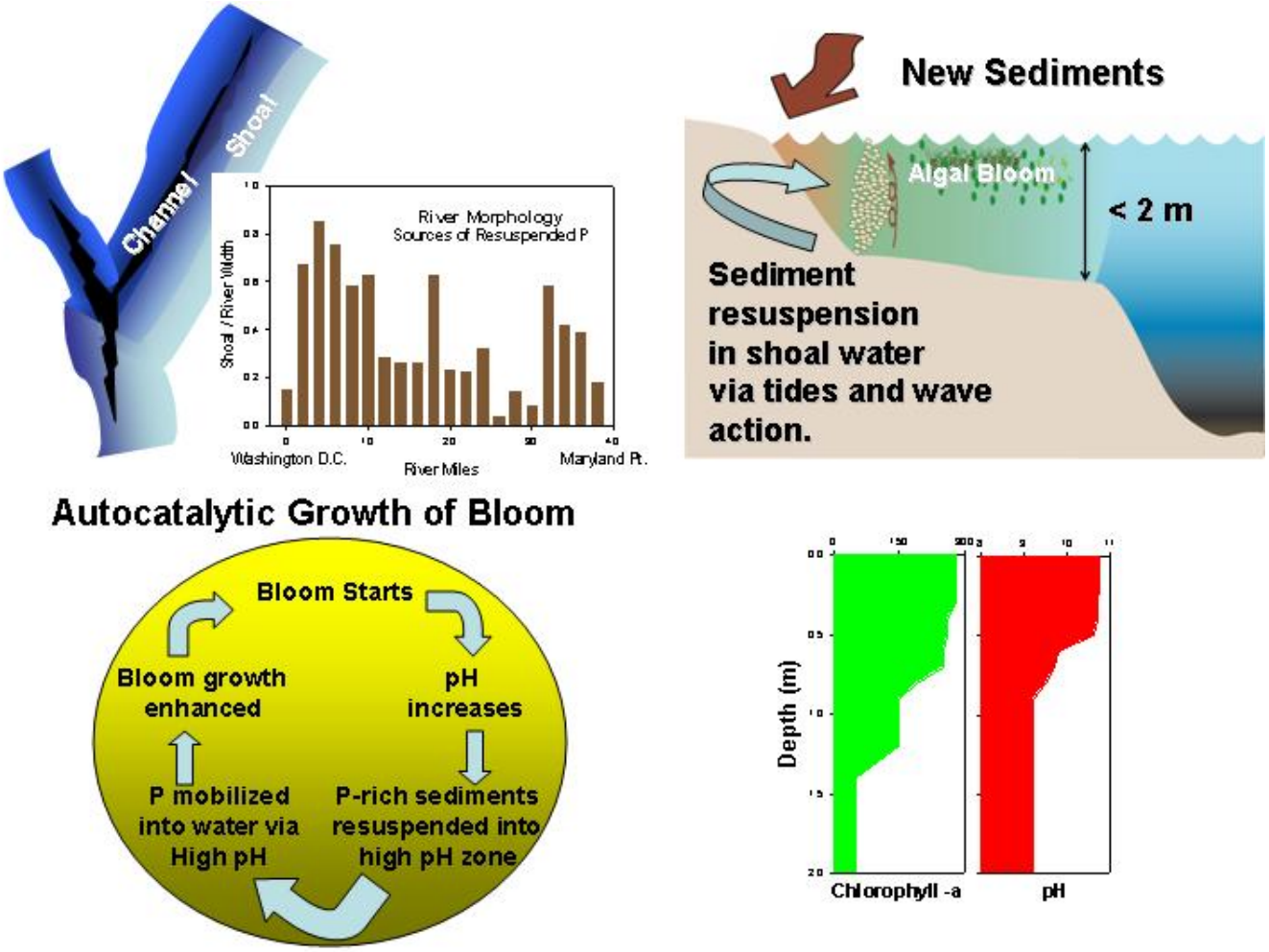


Figure 38. A pictorial representation of features and processes likely responsible for supplying P to autotrophs. See text for full description.

(e.g. Kemp *et al.* 2005). However, a key element of this argument requires that elevated pH conditions extend to bottom sediments and persist for sufficient time to increase the pore water DIP pool enough to result in substantial DIP release from estuarine sediments. It is not clear that this is the case, at least in some of the deeper portions of the tidal Potomac freshwater system. What is clear is that DIP must be supplied from some source to maintain the high, and at times very high, rates of phytoplanktonic production and it does not appear that external inputs of P are nearly large enough to meet this demand. Examination of the morphology, suspended sediment conditions and vertical profiles of chlorophyll and pH in the upper Potomac River estuary suggested an alternative, or additional, mechanism for internally generated DIP supply. The main features of this are shown in Figure 38 as a cartoon-like drawing and as a conceptual model in Figure 39. As indicated in Figure 38 there are substantial sections of the upper Potomac where shoal (<2 m depth) areas dominate the river cross-section. For example, in the upper 10

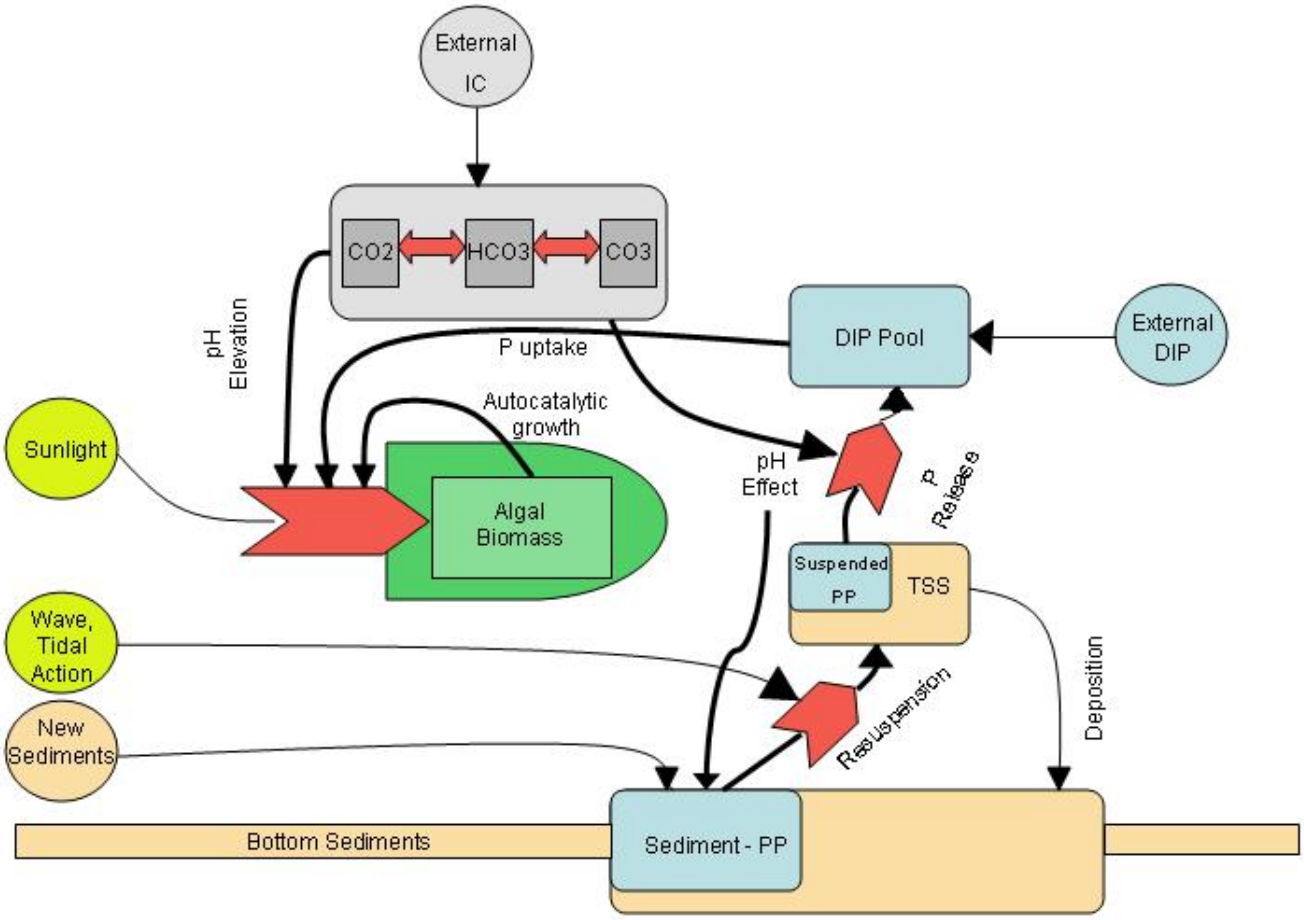


Figure 39. A conceptual model focusing on pH influence on P dynamics in sediments and the water column and showing the likely autocatalytic nature of these processes. See text for full details.

miles of the estuary, about 80% of the cross-section is shoal water. Several other zones in the next 30 miles of the estuary also have extensive shoal areas. The importance of shoal areas is that they are vulnerable to sediment re-suspension events caused both by tidal action and modest wind events. In effect, deposited sediments appear to be routinely resuspended and these resuspension events are caused by frequent events rather than by infrequent and more severe storm events. Because resuspended sediments in the upper estuary are of recent origin (mainly from upland sources) they are relatively rich in Fe-bound phosphorus, as indicated by the sediment mapping work reported earlier. Thus, there is a potentially large source of P associated with resuspended sediments. Furthermore, vertical profiles of algal biomass, as indicated by chlorophyll-a concentrations, indicates that concentrations are higher, or much higher, in very near-surface waters and lower, or much lower, at depth. Similarly, pH values were much higher during daytime periods in surface waters than at depth, in response to photosynthetic activity of phytoplankton which, because of the generally turbid conditions of the upper estuary, are largely restricted to the near-surface portion of the

water column. As indicated earlier, surface water pH values can be elevated for 10 or more hours per day and at times reach very high values (Figure 37). Thus, a likely additional source of DIP involves regular resuspension of bottom sediments from shoal areas. These sediments mix into the upper euphotic layer and for some hours come into contact with waters having high or very high pH conditions. Elevated pH leads to Fe-bound P going into solution and becoming immediately available to phytoplankton. Repeated events reinforces this cycle of enhanced P release, increased phytoplanktonic activity, further pH increase in the water column and more release of P into solution. Figure 39 combines, in a schematic form, both bottom sediment and suspended sediment P releases in response to elevated pH conditions.

If further investigations of P sources in the upper Potomac River are to be conducted our research suggests that effort should be directed at clarifying the role of resuspended sediments as a source of DIP that acts to support the development of nuisance algal blooms.

References

Aller, R. C. 1980. Diagenetic processes near the sediment-water interface of Long Island Sound. I. Decomposition and nutrient element geochemistry (S, N, P). Advances in Geophysics 22: 237-350.

Andersen, J. M. 1974. Nitrogen and phosphorus budgets and the role of sediments in six shallow Danish lakes. Archiv fur Hydrobiologia 74: 528-550.

Anderson, J. M. 1982. Effect of nitrate concentration in lake water on phosphate release from the sediment. Water Research 16: 1119-1126.

Aspila K. I., H. A. Agemian, A. S.Y. Chau. 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101: 187-197.

Bailey, E. M. 2005. Measurements of Nutrient and Oxygen Fluxes in Estuarine and Coastal Marine Sediments: Literature Review and Data Report. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES] CBL 05-091.

Bailey, E. K. M, R. M. Stankelis, P. W. Smail, S. Greene, F. M. Rohland and W. R. Boynton. 2003a. Dissolved Oxygen and Nutrient Flux Estimation from Sediments in the Anacostia River. Report prepared for The Health Department, Environmental Health Administration, The Government of the District of Columbia, Bureau of Environmental Quality, Water Quality Division. Technical Report Series No. TS-423-03-CBL, Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES] CBL 03-352.

Bailey, E. K. M, P. W. Smail, F. M. Rohland, B. Bean, M. Ceballos, M. Kaumeyer and W. R. Boynton. 2003b. Monitoring of Sediment Oxygen and Nutrient Exchanges in the Potomac River Estuary in Support of TMDL Development. Report prepared for the Maryland Department of the Environment, Chesapeake Bay and Special Projects. Technical Report Series No. TS-437-03-CBL, Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES] CBL 03-396.

Bailey, E. M., M. Owens, E. Kiss, H. Soulen, W. R. Boynton and J. C. Cornwell. 2005. Sediment Phosphorus Flux: pH Interactions in the Tidal Freshwater Potomac River Estuary. Data Report. Technical Report Series No. TS-480-05-CBL, Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. Ref. No. [UMCES] CBL 05-037.

Berner, R. A. 1980. *Early Diagenesis A Theoretical Approach.* Princeton University Press.

Bostrom, B., and K. Pettersson. 1982. Different patterns of phosphorus release from lake sediments in laboratory experiments. Hydrobiologia 92: 415-429.

Boynton, W.R. and W.M. Kemp. 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Marine Ecology Progress Series 23:45-55.

Boynton, W. R. and W. M. Kemp. 2000. Influence of river flow and nutrient loads on selected ecosystem processes: A synthesis of Chesapeake Bay Data, p. 269-298. In: J. E. Hobbie (ed.) *Estuarine Science: A Synthetic Approach to Research and Practice.* Island Press, Washington, DC.

Boynton, W. R., W. M. Kemp, J. M. Barnes, L. L. Matteson, J. L.Watts, S. Stammerjohn, D. A. Jasinski and F. M. Rohland. 1991.Ecosystem Processes Component Level 1 Interpretive 8. Chesapeake Biological Laboratory (CBL), University of Maryland Center for Environmental Science, Solomons, MD 20688-0038. Ref. No. [UMCES] CBL 91-110a.

Boynton, W. R., W. M. Kemp, J. M. Barnes, L. L. Matteson, J. L. Watts, S. Stammerjohn, D. A. Jasinski and F. M. Rohland. 1992. Ecosystem Processes Component Level 1 Interpretive Report No. 9. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. [UMCEES] CBL Ref. No. 92-042.

Boynton, W. R., J. H. Garber, R. Summers, and W. M. Kemp. 1995. Inputs, transformations and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. Estuaries 18:285-314.

Boynton, W. R., L. L. Magdeburger, B. J. Weaver and J. M. Barnes. 1997. The effects of Macrobenthos on Sediment-Water Oxygen and Ammonium Fluxes. Prepared for the U.S. Army Corps. Of Engineers, Waterways Experimental Station, Vickburg, MI 39180-6199. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. [UMCEES] CBL Ref. No. 97-039.

Bray, J. T., O. P. Bricker and B. N. Troup. 1973. Phosphate in interstitial waters of anoxic sediments: oxidation effects during the sampling procedure. Science 180:1362-1364.

Callender, E. 1982. Benthic phosphorus regeneration in the Potomac River Estuary. Hydrobiologia 92: 431-446.

Callender, E. and D. E. Hammond. 1982. Nutrient exchange across the sediment-water interface in the Potomac River Estuary. Estuarine, Coastal and Shelf Science (15): 395-413.

Caraco, N. F., J. J. Cole, and G. E. Likens. 1989. Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. Nature 341: 316-318.

Carignan, R., and R. J. Flett. 1981. Post-depositional mobility of phosphorus in lake sediments. Limnology and Oceanography 26: 361-366.

Cornwell, J. C. 1987. Phosphorus cycling in arctic lake sediment: adsorption and authigenic minerals. Archiv fur Hydrobiologia 109: 161-179.

Cornwell, J. C., and M. S. Owens. 1999. Benthic Phosphorus Cycling in Lake Champlain: Results of an Integrated Field Sampling/Water Quality Modeling Study. Part B: Field Studies. June 1999, Lake Champlain Basin Program Technical Serives. UMCES Horn Point Laboratory.

Cornwell J. C., J. C. Stevenson, D. J. Conley and M. S. Owens. 1996. A sediment chronology of Chesapeake Bay eutrophication. Estuaries 19: 488-499

Cornwell, J. C., W. M. Kemp, and T. M. Kana. 1999. Denitrification in coastal ecosystems: environmental controls and aspects of spatial and temporal scale. Aquatic Ecology 33: 41-54.

Cowan, J. L. W., and W. R. Boynton. 1996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors and ecological significance. Estuaries 19: 562-580.

Cowan, J. L., J. R. Pennock and W. R. Boynton. 1996. Seasonal and interannual patterns of sediment-water nutrient and oxygen fluxes in Mobile Bay, Alabama (USA): regulating factors and ecological significance. Mar Ecol Prog ser 141: 229-245

DiToro, D. M. 2001. *Sediment Flux Modeling*. John Wiley and Sons, NY. vii-624.

Drake, J. C., and S. I. Heaney. 1987. Occurrence of phosphorus and its potential remobilization in the littoral sediments of a productive English lake. Freshwater Biology 17: 513-523.

Einsele, W. 1936. Ueber die Beziehungen des Eisenkreislaufes zum Phosphatkreislauf im Eutrophen See. Archiv fur Hydrobiologia 29: 664-686.

Environmental Protection Agency (EPA). 1979. Methods for Chemical Analysis of Water and Wastes. USEPA-6000/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

Environmental Protection Agency (EPA). 1989. Sediment data management plan. Chesapeake Bay Program. CBP/TRS 29/89.

Gibb, M. M. 1979. A simple method for the rapid determination of iron in natural waters. Water Research 13: 295-297.

Hagy, J. D., W. R. Boynton, C. W. Keefe and K. V. Wood. 2004. Hypoxia in Chesapeake Bay, 1950-2001: Long-term change in relation to nutrient loading and river flow. Estuaries 27(4): 634-658.

Istvanovics, V. 1988. Seasonal variation of phosphorus release from sediments of shallow lake Balaton (Hungary). Water Research 22: 1473-1481.

Jensen, H. S., and F. O. Andersen. 1992. Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes. Limnology and Oceanography 37: 577-589.

Kana, T. M., and D. L. Weiss. 2004. Comment on "Comparison of isotope pairing and N-2: Ar methods for measuring sediment denitrification" by B. D. Eyre, S. Rysgaard, T. Daisgaard, and P. Bondo Christensen. 2002. Estuaries 25: 1077-1087. Estuaries 27: 173-176.

Kana, T. M., C. Darkangelo, M. D. Hunt, J. B. Oldham, G. E. Bennett, and J. C. Cornwell. 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N2, O2, and Ar in environmental water samples. Analytical Chemistry 66: 4166-4170.

Kana, T. M., M. B. Sullivan, J. C. Cornwell, and K. Groszkowski. 1998. Denitrification in estuarine sediments determined by membrane inlet mass spectrometry. Limnology and Oceanography 42: 334-339.

Kana, T. M., J. C. Cornwell, and L. Zhong. 2006. Determination of denitrification in the Chesapeake Bay from measurements of N_2 accumulation in bottom water. Estuaries: accepted.

Kemp, W. M. and W. R. Boynton. 1992. Benthic-Pelagic Interactions: Nutrient and Oxygen Dynamics. In: D.E. Smith, M. Leffler and G. Mackiernan [Eds.], *Oxygen Dynamics in the Chesapeake Bay: A synthesis of Recent Research*. Maryland Sea Grant Book, College Park, MD, pp. 149-221.

Kemp, W. M., W. R. Boynton, J. E. Adolf, D. F. Boesch, W. C. Boicourt, G. Brush, J. C. Cornwell, T. R. Fisher, P. M. Glibert, J. D. Hagy, L. W. Harding, E. D. Houde, D. G. Kimmel, W. D. Miller, R. I. E. Newell, M. R. Roman, E. M. Smith, and J. C. Stevenson. 2005. Eutrophication of Chesapeake Bay: Historical trends and ecological interactions. Mar Ecol Prog Ser 303: 1-29.

Krom, M. D., and R. A. Berner. 1980. Adsorption of phosphate in anoxic marine sediments. Limnology and Oceanography 25: 797-806.

Leventhal, J. C. Taylor. 1990. Comparison of methods to determine degree of pyritization. Geochimica et Cosmochimica Acta 54: 2621-2625.

Li, Y.-H., and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochimica et Cosmochimica Acta **38:** 703-714.

Lovley, D. R., and E. J. P. Phillips. 1986. Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac River. Applied and Environmental Microbiology 52: 751-757.

Mortimer, C. H. 1941. The exchange of dissolved substances between mud and lake water. Journal of Ecology 29: 280-329.

Nielsen, L. P. 1992. Denitrification in sediment determined from nitrogen isotope pairing. FEMS Microbiology Ecology 86: 357-362.

Parsons T. R, Y. Maita and C. M. Lalli. 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, New York.

Postma, D. 1985. Concentration of Mn and separation from Fe in sediments---I. Kinetics and stoichiometry of the reaction between birnessite and dissolved Fe(II) at 10oC. Geochimica et Cosmochimica Acta 49: 1023-1033.

Postma, D. 1990. Kinetics of nitrate reduction by detrital Fe(II)-silicates. Geochimica et Cosmochimica Acta 54: 903-908.

Redfield, A. C. 1934. On the proportions of organic derivatives in seawater and their relation to the composition of plankton. In: James Johnstone Memorial Volume. University Press. Liverpool, p. 176-192.

Rohland, F. M., W. R. Boynton, R. M. Stankelis, E. K. Machelor Bailey and P. W. Smail. 2003. Quality Assurance Project Plan for Water Quality Monitoring in the Anacostia River, FY 2002. Chesapeake Biological Laboratory (CBL), University of Maryland Center for Environmental Science, Solomons, MD 20688-0038. Technical Report Series No. TS-349-02-CBL.

Sampou, P. 1990. Sediment/Water Exchanges and Diagenesis of Anacostia River Sediments. Prepared for Metropolitan Washington Council of Governments, 777 North Capitol Street, N.E. Suite 300, Washington, D.C. CEES, Horn Point Environmental Laboratory (HPL), University of Maryland System, Cambridge, MD 21613. Under Grant Identification No. 90-040-PE-4845.

Seitzinger, S. P. 1991. The effect of pH on the release of phosphorus from Potomac Estuary sediments: implications for blue-green algal blooms. Estuarine, Coastal and Shelf Science 33: 409-418.

Seitzinger, S. P., L. P. Nielsen, J. Caffrey, and P. B. Christensen. 1993. Denitrification measurements in aquatic sediments: A comparison of three methods. Biogeochemistry 23: 147-167.

Stainton, M. P. 1973. A syringe gas-stripping procedure for gas-chromatographic determination of dissolved inorganic and organic carbon in fresh water and carbonates in sediments. Journal of the Fisheries Research Board of Canada. 30:1441-1445.

Stankelis, R. M., W. R. Boynton, J. M. Frank and F. M. Rohland. 1998. Sediment-water oxygen and nutrient exchanges: Mini-SONE and high resolution mapping. Chesapeake Bay Water Quality Monitoring Program, Level One Report No. 16. Technical Rept Ser. No. TS-190-99. Chesapeake Biological Laboratory, Solomons, MD. p. 1-164.

Strickland, J. D. H. and T. R. Parsons. 1972. A practical handbook of seawater analysis. Fish. Res. Bd. Can. Bull. 167 (second edition).

Stumm, W., and J. J. Morgan. 1981. *Aquatic Chemistry*, Second ed. John WIley & Sons, Inc.

Sun M., R. C. Aller and C. Lee. 1991. Early diagenesis of chlorophyll-a in Long Island Sound sediments: a measure of carbon flux and particle reworking. Journal of Marine Research 49: 379-401.

Sweet S. T., J. M. Wong, J. M. Brooks and T. L. Wade. 1993. Sediment grain size analysis. In: Lauenstein GG, Cantillo AY (eds) Sampling and Analytical Methods of the National Status and Trends Program. NOAA, Silver Spring, Maryland, pp II.23-II.26.

Ullman, W. J., and R. C. Aller. 1982. Diffusion coefficients in nearshore marine sediments. Limnology and Oceanography 27: 552-556.

Vaas, L. H., R. N. J. Comans, H. A. Das, J. M. M. Reith, and C. H. van der Weijden. 1987. Isotopically exchangeable phosphate in freshwater sediments: effects of u.v.-irradiation, formaldehyde, solid/solution ratio, and pH on its experimental determination. Water Research 21: 1135-1142.

Xie, L. Q., P. Xie, and H. J. Tang. 2003. Enhancement of dissolved phosphorus release from sediment to lake water by *Microcystis* blooms - an enclosure experiment in a hyper-eutrophic, subtropical Chinese lake. Environmental Pollution 122: 391-399.

Additions to:
APPENDICES A - I
Potomac River pH Study
2004 to 2005

Data Set Addendums

Data Sets
These appendices include new data files (*) and files with new data added ("**add" added to end of filename**). The original files are found in Bailey *et al.* 2005.

The data from this study are contained in these files:

Name	Description	Appendix
POTPHPR01	Water Column Profiles-May	A-1
POTPHPR02	Water Column Profiles-July	A-2
POTPHPR03	Water Column Profiles-September	A-3
POTPHNT01	Water Column Nutrients-May	B-1
POTPHNT02	Water Column Nutrients-July	B-2
POTPHNT03	Water Column Nutrients-September	B-3
POTPHPO01add	Pore Water Profiles-May	C-1
*POTPHPO01a	Pore Water Profiles-June	C-1a
POTPHPO02add	Pore Water Profiles-July	C-2
POTPHPO03add	Pore Water Profiles-September	C-3
POTPHCD01	Core Data for *In Situ* Mini-SONE Fluxes-May	D-1
POTPHCD02	Core Data for *In Situ* Mini-SONE Fluxes-July	D-2
POTPHCD03	Core Data for *In Situ* Mini-SONE Fluxes-September	D-3
POTPHFL01	*In Situ* Mini-SONE Fluxes-May	E-1
POTPHFL02	*In Situ* Mini-SONE Fluxes-July	E-2
POTPHFL03	*In Situ* Mini-SONE Fluxes-September	E-3
POTPHRC01a	Core Data for pH Response Flow-through Fluxes-May	F-1
POTPHRC01b	Core Data for pH Response Static Fluxes-May	F-1
POTPHRC02	Core Data for pH Response Fluxes-July	F-2
POTPHRC03	Core Data for pH Response Fluxes-September	F-3
POTPHRL01a	pH Response Flow-through Fluxes-May	G-1
POTPHRL01b	pH Response Static Fluxes-May	G-1
POTPHRL02	pH Response Fluxes-July	G-2
POTPHRL03	pH Response Fluxes-September	G-3
POTPHSP01	Surficial Sediment Characteristics-May	H-1
POTPHSP02	Surficial Sediment Characteristics-July	H-2
POTPHSP03	Surficial Sediment Characteristics-September	H-3
POTPHMA01	Sediment Mapping Data-April	I-1
POTPHMA02	Sediment Mapping Data-July	I-2
POTPHMA03add	Sediment Mapping Data-September	I-3
*POTPHMA04	Sediment Mapping Data- July 2005	I-4

TABLE C-1. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 1
FILENAME: POTPHPO01add
REVISED: 20060118

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
1	20040518	0.25	3.58	941.0	21.0	1539.0	279.4	7972.0	91.2	7.17
		0.75	2.21	1351.9	112.9	1945.1	125.3	1759.2	176.8	7.24
		1.25	1.12	1636.8	120.8	2329.6	48.0	588.7	229.9	7.24
		1.75	0.03	1632.1	438.0	2266.4	69.9	743.5	147.3	7.14
		2.50	11.94	1768.3	143.1	2565.5	19.1	510.1	421.8	7.14
		3.50	2.24	1679.5	352.1	2377.1	13.3	424.6	349.0	7.19
		5.50	13.12	1670.3	26.2	2715.0	16.1	394.9	448.3	7.12
		8.50	13.91	1919.0	552.4	2921.3	10.6	432.8	623.5	6.79
2	20040519	0.25	2.93	352.4	42.8	853.3	81.2	517.8	45.9	7.17
		0.75	11.71	317.5	195.1	988.9	77.2	664.4	62.6	7.25
		1.25	7.35	359.1	232.9	1020.6	33.5	492.4	61.7	7.04
		1.75	11.90	477.5	37.8	1217.1	16.1	484.2	116.8	7.02
		2.50	14.90	588.8	40.6	1421.6	9.8	506.1	173.8	6.97
		3.50	12.53	713.1	35.0	1550.6	D	435.9	227.9	6.97
		5.50	21.83	788.1	52.5	1800.4	D	401.1	315.5	7.00
		8.50	7.19	900.6	223.9	2269.6	D	502.2	393.2	6.87
3	20040518	0.25	3.73	154.7	557.2	808.5	124.5	457.3	19.4	6.91
		0.75	5.57	201.4	39.6	859.1	127.2	545.0	44.9	6.76
		1.25	9.92	258.4	251.3	902.1	59.2	360.2	70.5	6.80
		1.75	12.99	395.8	554.8	997.9	28.9	471.9	130.5	6.69
		2.50	30.53	482.2	250.1	1118.8	13.0	384.0	213.2	6.74
		3.50	23.61	626.7	602.9	1192.7	6.2	393.2	247.6	6.88
		5.50	22.82	802.9	236.5	1417.1	D	406.7	303.7	6.70
		8.50	16.49	950.9	712.5	1540.6	D	429.9	360.8	6.70
4	20040518	0.25	1.80	244.7	51.0	1213.2	81.2	441.1	27.2	7.29
		0.75	5.77	D	802.5	1540.7	82.7	457.4	12.5	7.39
		1.25	6.66	247.7	50.6	1617.0	25.1	141.5	19.4	7.35
		1.75	15.07	292.7	236.1	1986.0	11.3	407.6	54.8	7.29
		2.50	13.72	504.7	650.2	2163.2	7.7	488.1	115.8	7.11
		3.50	22.03	532.0	49.4	2462.7	9.7	380.6	201.4	7.14
		5.50	20.05	876.9	925.7	3252.0	D	446.6	302.7	7.07
		8.50	11.74	1235.1	1042.8	4534.0	D	463.8	453.3	7.08
5	20040519	0.25	1.85	138.1	852.7	1024.7	187.4	558.0	2.6	7.13
		0.75	2.21	117.4	44.9	1002.2	152.2	442.0	2.6	7.21
		1.25	3.99	212.2	823.3	1455.7	127.1	498.6	6.6	7.28
		1.75	4.39	283.3	313.6	2036.2	54.6	423.8	33.1	7.18

TABLE C-1. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 1
FILENAME: POTPHPO01add
REVISED: 20060118

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
		2.50	7.58	496.4	705.4	2450.1	11.4	436.8	124.6	7.16
		3.50	9.17	668.1	860.1	2690.6	9.8	473.6	264.4	7.14
		5.50	17.67	912.4	814.5	2796.5	9.6	357.5	475.9	6.80
		8.50	20.24	945.0	954.7	2722.1	D	486.8	604.8	6.76
6	20040518	0.25	3.18	99.0	338.2	872.5	123.1	519.9	24.3	7.20
		0.75	5.87	67.0	355.1	862.7	150.3	699.3	25.3	7.10
		1.25	6.86	92.6	887.0	761.4	127.1	748.2	11.5	7.07
		1.75	46.92	147.1	1030.0	922.0	59.2	722.3	52.8	7.02
		2.50	49.72	203.9	74.1	881.2	18.7	922.3	77.4	7.08
		3.50	53.08	226.4	1376.5	839.6	9.7	1257.5	86.3	6.95
		5.50	59.02	302.6	1645.9	775.5	D	1420.7	76.4	7.05
		8.50	60.60	361.8	971.3	817.1	D	2085.0	85.3	7.12
7	20040519	0.25	4.07	123.3	985.0	950.9	123.1	761.4	3.6	7.15
		0.75	7.15	142.2	841.7	1133.2	114.3	542.1	4.6	7.21
		1.25	11.01	202.7	60.4	1280.9	60.2	453.3	17.4	7.28
		1.75	22.59	270.2	933.8	1432.6	17.1	454.6	46.9	7.23
		2.50	31.52	284.4	796.3	1549.6	7.5	504.2	76.4	7.29
		3.50	41.22	247.7	970.1	1505.7	8.8	543.6	113.8	7.15
		5.50	50.71	421.0	1073.6	1455.0	D	673.8	162.0	7.12
		8.50	49.33	574.9	1582.6	1623.1	D	1071.2	258.4	6.99
8	20040518	0.25	1.60	42.8	917.9	803.7	156.5	596.7	5.6	7.13
		0.75	1.91	29.1	921.8	798.7	187.9	663.0	3.6	7.21
		1.25	2.11	47.6	1069.3	829.1	199.1	771.8	2.6	7.33
		1.75	2.21	59.4	76.4	886.4	204.1	911.7	1.6	7.31
		2.50	4.02	78.4	1400.4	857.4	157.8	977.4	5.6	7.13
		3.50	13.12	95.0	98.3	766.3	116.4	1326.7	15.4	7.14
		5.50	27.76	113.1	187.7	660.7	85.8	2758.6	11.5	7.21
		8.50	68.91	169.3	4265.8	587.8	12.0	3972.5	3.6	7.39

TABLE C-1a. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 1a
FILENAME: POTPHPO01a
REVISED: 20051209

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
1	20040623	0.25	11.49	112.4	221.1	1119.2	222.7	1017.9	31.10	HH
		0.75	21.45	168.9	154.9	1132.1	101.8	537.5	67.35	HH
		1.25	20.86	139.3	D	D	61.5	455.5	365.39	HH
		1.75	33.85	448.4	844.4	1938.0	43.8	460.0	240.54	HH
		2.50	33.45	712.4	1160.5	7706.3	18.6	439.5	644.30	HH
		3.50	30.61	876.5	816.5	3361.6	20.3	485.1	649.33	HH
		5.50	47.38	630.6	682.3	3579.8	n.a.	454.4	809.21	HH
		8.50	0.00	D	2068.3	7614.4	15.6	484.8	1253.25	HH
2	20040623	0.25	5.65	77.4	723.5	1314.3	D	D	16.00	HH
		0.75	17.67	213.5	1512.0	3962.8	83.3	465.7	117.69	HH
		1.25	30.19	440.1	194.3	1758.8	56.7	558.9	190.19	HH
		1.75	49.44	365.2	D	D	19.1	501.5	791.08	HH
		2.50	57.78	783.8	2186.7	3299.0	17.4	645.2	642.29	HH
		3.50	58.25	1025.1	532.4	3033.8	14.4	491.6	713.78	HH
		5.50	64.62	1165.7	1781.8	3480.9	D	490.2	827.33	HH
		8.50	61.55	904.1	146.7	4276.2	D	544.2	896.81	HH
3	20040623	0.25	11.90	89.3	2519.0	504.9	160.3	472.8	26.07	7.25
		0.75	38.10	185.0	2702.1	1092.0	131.9	531.1	85.47	6.83
		1.25	40.22	567.3	1022.8	1622.4	63.5	608.3	273.76	6.93
		1.75	4.92	530.5	2168.4	2070.3	10.2	456.6	284.84	6.86
		2.50	47.86	1385.4	938.1	3513.5	10.2	569.7	679.54	6.93
		3.50	38.17	825.4	1043.2	3308.5	18.4	565.4	713.78	6.80
		5.50	52.11	1320.3	75.0	3909.0	12.4	555.9	827.33	6.83
		8.50	41.01	972.4	1220.8	17489.6	16.3	766.4	1706.35	6.74
4	20040623	0.25	13.91	125.5	16168.3	2134.9	140.1	497.4	45.20	7.57
		0.75	39.28	311.6	3311.9	779.6	77.8	462.8	122.73	7.04
		1.25	46.13	287.9	7392.6	3747.7	21.7	486.1	589.93	6.86
		1.75	32.43	710.0	4287.8	2470.3	10.9	504.5	440.91	6.84
		2.50	25.18	1021.6	2069.6	2482.9	18.2	568.9	528.51	6.82
		3.50	15.26	1196.4	3240.6	3341.3	16.1	576.1	568.78	6.81
		5.50	39.35	1959.4	1623.9	3540.6	18.2	595.9	788.06	6.73
		7.75	29.67	1543.2	1366.0	5039.3	D	D	815.25	6.77
5	20040623	0.25	14.21	242.6	D	D	149.3	539.5	D	7.99
		0.75	32.31	319.9	7154.8	1887.2	73.3	451.8	116.69	7.19
		1.25	36.33	499.6	4554.2	2806.3	24.0	475.0	349.28	7.01
		1.75	33.61	554.3	3889.7	2175.8	16.5	492.2	402.65	6.94

TABLE C-1a. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 1a
FILENAME: POTPHPO01a
REVISED: 20051209

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
		2.50	33.21	1045.3	3445.5	2884.7	17.7	543.1	559.72	6.92
		3.50	50.22	1160.7	1797.8	3795.2	20.5	622.8	772.96	6.86
		4.75	19.51	651.4	2263.5	4846.3	18.6	648.5	717.80	6.80
6	20040623	HH	HH	HH	HH	HH	HH	HH	HH	HH
7	20040623	HH	HH	HH	HH	HH	HH	HH	HH	HH
8	20040623	HH	HH	HH	HH	HH	HH	HH	HH	HH

TABLE C-2. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 2
FILENAME: POTPHPO02add
REVISED: 20051209

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
1	20040722	0.25	5.35	179.6	366.1	1189.1	157.7	1074.3	25.06	8.48
		0.75	7.92	245.0	406.4	1868.7	76.4	848.4	63.32	8.33
		1.25	10.79	323.6	723.0	2429.6	32.8	797.2	119.71	8.41
		1.75	4.95	610.1	509.1	3385.6	25.4	733.0	123.74	8.40
		2.50	7.13	559.0	543.9	3421.7	14.0	630.7	214.36	8.21
		3.50	D	905.0	544.8	3571.9	26.1	700.5	199.25	8.13
		5.50	7.13	1153.8	942.5	3523.2	22.8	679.8	355.32	8.03
		8.50	8.32	1308.4	202.7	3368.4	14.6	587.1	467.09	7.88
2	20040722	0.25	0.45	287.2	1179.4	1273.1	208.5	1177.1	13.98	7.99
		0.75	0.59	373.4	898.9	1702.0	91.6	781.4	35.13	8.08
		1.25	0.40	503.1	915.3	1911.0	31.8	770.4	95.54	7.98
		1.75	0.10	565.0	724.6	2099.9	30.6	724.3	145.89	8.06
		2.50	2.57	611.3	423.9	2464.8	28.7	737.9	386.54	7.81
		3.50	0.40	800.4	842.7	3520.2	12.0	626.0	548.65	7.85
		5.50	9.11	1980.2	648.9	5147.1	11.5	588.2	987.43	7.82
		8.50	1.58	2128.8	928.9	8273.3	11.2	551.4	1144.50	7.85
3	20040723	0.25	6.24	102.9	990.1	1621.0	249.1	1049.5	25.06	7.06
		0.75	10.79	130.3	920.9	973.0	222.4	791.0	46.21	6.85
		1.25	6.93	166.6	1079.8	1511.5	168.1	759.8	65.34	7.03
		1.75	8.81	171.4	673.0	1005.9	117.9	817.1	67.35	6.83
		2.50	11.68	341.4	2609.8	6235.9	38.5	771.0	D	7.00
		3.50	11.88	513.8	847.0	1437.2	16.9	736.1	199.25	6.97
		5.50	31.29	428.4	401.9	1641.2	33.9	726.0	272.76	6.97
		8.50	15.25	996.2	1023.5	1661.4	20.8	665.7	388.55	6.92
4	20040722	0.25	1.34	222.4	792.3	2120.4	196.9	872.1	6.94	8.46
		0.75	1.88	320.5	1003.7	2517.7	87.5	796.4	6.94	8.45
		1.25	1.39	347.4	963.6	4085.3	11.5	676.0	47.21	8.38
		1.75	0.99	600.6	1018.9	4094.4	3.6	665.9	33.12	8.35
		2.50	12.08	750.5	630.0	4865.5	10.5	650.5	187.17	8.33
		3.50	10.30	914.6	1143.2	5459.6	8.8	613.0	269.74	8.25
		5.50	8.71	856.5	850.5	5936.4	11.5	628.1	419.76	8.21
		8.50	11.49	1133.0	2506.0	19600.9	11.6	610.8	D	8.07
5	WW	WW	WW	WW	WW	WW	WW	WW	WW	WW
		WW	WW	WW	WW	WW	WW	WW	WW	WW
		WW	WW	WW	WW	WW	WW	WW	WW	WW
		WW	WW	WW	WW	WW	WW	WW	WW	WW

TABLE C-2. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 2
FILENAME: POTPHPO02add
REVISED: 20051209

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
		WW	WW	WW	WW	WW	WW	WW	WW	WW
		WW	WW	WW	WW	WW	WW	WW	WW	WW
		WW	WW	WW	WW	WW	WW	WW	WW	WW
		WW	WW	WW	WW	WW	WW	WW	WW	WW
6	20040722	0.25	2.82	127.3	1178.3	1799.8	186.3	951.3	26.07	8.35
		0.75	6.83	193.3	1931.7	2017.7	89.8	1061.4	75.41	8.29
		1.25	5.84	362.8	1756.6	1302.5	31.4	1256.3	51.24	8.06
		1.75	6.54	438.9	1594.7	1440.4	11.7	1635.7	78.43	8.10
		2.50	38.62	487.7	2507.0	1412.2	12.2	1991.2	152.94	8.02
		3.50	15.05	587.6	2341.3	1398.6	6.6	2371.4	97.56	8.16
		5.50	27.53	484.9	3732.0	1408.7	12.2	3056.3	118.70	8.10
		8.50	11.68	577.1	4321.8	1353.0	3.1	3866.1	64.33	8.23
7	20040722	0.25	4.01	174.9	1677.8	983.9	171.0	931.7	16.00	8.28
		0.75	6.54	302.1	1177.8	1351.0	65.5	1115.4	18.01	8.36
		1.25	4.75	323.6	970.7	1872.9	43.4	1157.5	25.06	8.20
		1.75	2.28	670.8	1539.2	2313.4	41.0	1253.6	54.26	8.22
		2.50	12.28	716.0	1633.0	2848.0	41.8	1416.7	206.30	8.12
		3.50	1.39	977.6	2073.0	2541.9	10.9	1521.7	156.96	8.13
		5.50	1.19	612.7	2413.5	2374.0	7.8	1801.7	172.07	8.11
		8.50	8.71	1040.8	2645.4	2222.9	8.1	2333.8	289.87	8.03
8	20040722	0.25	0.69	3.0	638.5	561.6	376.5	2179.3	2.91	8.39
		0.75	1.39	62.5	1933.9	546.3	375.7	2796.9	2.91	8.54
		1.25	2.67	51.3	3687.2	486.2	486.6	5015.1	3.92	8.31
		1.75	4.55	64.4	7921.9	617.6	531.4	6951.3	7.94	8.29
		2.50	11.49	89.3	9221.8	700.6	594.9	10165.6	10.96	8.26
		3.50	22.77	128.6	27132.3	2181.4	D	D	62.32	8.34
		5.50	56.64	208.5	14460.2	1248.0	418.8	14795.1	9.96	8.56
		8.50	67.14	345.2	11978.0	826.9	D	D	1.90	9.18

TABLE C-3. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 3
FILENAME: POTPHPO03add
REVISED: 20060113

STATION	DATE	CORE DEPTH (cm)	DIP (µM)	$NH4^+$ (µM)	Na^+ (µM)	Ca^{2+} (µM)	SO_4^{2-} (µM)	Chloride (µM)	Fe (µM)	pH
1	20040928	0.25	1.7	94.8	3217.0	1534.8	160.1	410.4	6.9	6.79
		0.75	1.7	159.6	3256.9	2025.4	40.6	394.9	15.0	7.67
		1.25	1.7	163.9	2317.9	2288.3	114.4	481.6	5.9	7.80
		1.75	4.8	196.9	2652.0	1547.5	64.4	354.8	19.0	7.73
		2.50	7.0	320.5	3914.3	2090.0	28.7	352.7	54.3	7.65
		3.50	20.4	426.9	3201.3	2538.8	30.1	481.4	123.7	7.64
		5.50	43.5	501.5	2027.6	1531.2	D	360.1	3.9	7.42
		8.50	49.0	1021.4	3224.4	2662.1	D	419.0	334.2	7.28
2	20040929	0.25	2.0	133.9	3733.5	1723.8	89.4	408.5	10.0	7.52
		0.75	4.0	157.8	3275.3	2195.8	62.2	405.6	34.1	7.54
		1.25	D	D	4031.1	2315.1	27.9	377.9	57.3	7.48
		1.75	2.5	231.3	D	D	20.7	384.1	D	7.67
		2.50	0.9	313.8	D	D	54.4	444.7	D	7.36
		3.50	D	D	D	D	D	D	D	7.31
		5.50	D	D	D	D	D	D	D	D
		8.50	D	D	D	D	D	D	D	D
3	20040929	0.25	1.7	74.6	3761.7	1016.8	204.8	435.2	12.0	6.87
		0.75	4.7	112.5	3456.1	903.2	170.6	506.1	19.0	7.06
		1.25	5.0	144.3	3365.6	982.4	159.4	474.9	33.1	7.03
		1.75	9.5	170.0	3667.9	1277.6	102.1	373.8	63.3	6.98
		2.50	19.8	276.5	4016.0	1231.9	48.3	449.9	107.6	7.00
		3.50	26.7	347.4	3790.8	1563.9	15.1	434.8	180.1	6.69
		5.50	43.8	645.3	4291.7	1796.4	D	544.1	266.7	6.82
		8.50	35.8	880.7	3568.3	2127.6	D	557.4	347.3	6.78
4	20040928	0.25	8.1	186.5	3656.8	2705.9	135.6	454.0	56.3	7.38
		0.75	27.3	367.0	3923.8	2109.3	52.6	386.8	77.4	7.34
		1.25	29.8	415.9	3972.7	1949.1	19.9	397.8	113.7	7.28
		1.75	36.6	566.4	3285.0	2283.9	D	460.4	183.1	7.24
		2.50	9.2	733.9	3815.9	2808.1	D	411.6	173.1	7.14
		3.50	56.9	834.2	4051.8	3218.5	D	541.5	340.2	7.12
		5.00	50.3	822.6	4763.1	2953.8	28.4	565.1	380.5	7.01
		7.50	56.9	1367.0	4008.7	4528.4	D	582.0	687.6	6.93
5	20040929	0.25	4.6	488.1	4173.2	1163.6	160.6	603.6	84.5	6.83
		0.75	9.9	838.5	4610.6	1603.9	94.4	599.3	232.5	6.72
		1.25	20.3	1136.4	6051.6	5025.3	42.8	458.1	987.4	6.79
		1.75	20.1	1000.6	5119.5	2809.7	15.3	461.2	649.3	6.75

TABLE C-3. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES
Potomac River: Pore Water Profiles
Vertical sediment profiles of pH and dissolved nutrients in sediment pore waters.

Potomac River Cruise: 3
FILENAME: POTPHPO03add
REVISED: 20060113

STATION	DATE	CORE DEPTH (cm)	DIP (μM)	$NH4^+$ (μM)	Na^+ (μM)	Ca^{2+} (μM)	SO_4^{2-} (μM)	Chloride (μM)	Fe (μM)	pH
		2.50	40.5	1086.2	3617.1	1852.8	D	554.3	514.4	6.65
		3.50	40.7	831.8	4756.6	2561.6	24.0	568.5	745.8	6.50
		5.50	47.8	1256.9	3794.9	2445.2	D	556.7	733.7	6.63
		8.50	46.2	2006.1	4300.0	2580.0	D	668.3	806.2	6.74
6	20040928	0.25	1.1	79.5	5526.5	1090.4	203.5	717.2	15.0	6.78
		0.75	7.5	125.4	6016.0	888.8	184.7	878.9	58.3	6.75
		1.25	17.2	253.2	5751.7	1062.1	114.9	1165.4	143.9	6.75
		1.75	21.2	326.6	4797.9	1129.7	47.3	1288.4	110.6	6.96
		2.50	22.8	392.7	6049.9	1253.0	23.1	1591.8	111.7	7.07
		3.50	15.7	494.2	6525.2	1501.5	D	2068.8	88.5	7.06
		5.00	19.0	480.1	6800.7	1418.0	D	2597.1	87.5	7.05
		7.50	37.2	495.4	7771.7	1538.0	D	3336.1	92.5	7.04
7	20040928	0.25	1.7	164.5	5165.4	1507.2	D	D	6.9	7.27
		0.75	4.3	332.1	5207.4	2119.9	73.9	602.1	19.0	7.30
		1.25	10.8	549.2	5029.6	1981.1	21.5	622.0	73.4	7.13
		1.75	13.5	666.7	4791.2	2301.8	26.0	821.7	113.7	7.20
		2.50	28.9	677.7	7916.1	9534.4	D	751.6	1150.5	7.02
		3.50	29.5	1159.6	5491.5	2673.1	D	957.6	398.6	6.97
		5.50	33.8	1220.2	5236.9	2927.5	D	1174.7	552.7	6.74
		8.50	33.2	1470.9	6123.2	2881.5	D	1816.1	710.8	6.81
8	20040929	0.25	1.9	121.7	5176.6	635.2	207.1	1363.1	0.9	7.30
		0.75	8.1	59.3	6383.1	669.4	227.2	1876.6	11.0	7.20
		1.25	28.5	93.0	7569.1	656.0	D	D	21.0	7.44
		1.75	27.8	127.2	D	D	129.2	3069.4	D	7.45
		2.50	45.4	124.8	9668.6	585.0	91.1	4091.7	9.0	7.50
		3.50	57.6	151.7	7918.3	496.7	46.6	4379.1	5.9	7.40
		5.50	69.7	165.1	8825.3	479.5	40.0	5169.7	6.9	7.42
		8.50	78.3	269.1	11998.1	619.8	16.6	9188.1	10.0	7.29

TABLE I-3. SEDIMENT MAPPING DATA

Potomac River: Sediment mapping core characteristics.
Solid phase analyses.

Potomac River Sediment Mapping Cruise: 3 (Potomac River Cruise 3)
FILENAME: POTPHMA03add
REVISED:20060118

CORE	DATE	H_2O (%)	Gravel / Sand (%)	Clay (%)	Silt (%)	Total Phosphorus (mg P / g sediment)	Inorganic Phosphorus (mg P / g sediment)	Organic Phosphorus (mg P / g sediment)	Fe HCl Extractable (mg Fe / g sediment)	Manganese (mg Mn / g sediment)
M1	20040928	79.55	9.23	42.05	48.72	0.95	0.69	0.26	14.30	2.46
M2	20040928	66.00	12.49	32.42	55.09	1.14	0.84	0.29	13.06	2.05
M3	20040928	66.87	7.40	24.67	67.93	0.77	0.61	0.16	10.57	1.46
M4	20040928	69.65	48.14	11.00	40.85	0.56	0.36	0.20	5.89	0.93

TABLE I-4. SEDIMENT MAPPING DATA
Potomac River: Sediment mapping core characteristics.
Solid phase analyses.

Potomac River Sediment Mapping Cruise: 4 (Potomac River Cruise 4)
FILENAME: POTPHMA04
REVISED: 20060118

CORE	DATE	H_2O (%)	Gravel / Sand (%)	Clay (%)	Silt (%)	Total Phosphorus (mg P / g sediment)	Inorganic Phosphorus (mg P / g sediment)	Organic Phosphorus (mg P / g sediment)	Fe HCl Extractable (mg Fe / g sediment)	Manganese (mg Mn / g sediment)
M9	20050718	72.82	5.99	30.27	63.74	0.92	0.65	0.28	11.55	1.95
M10	20050718	66.08	59.43	21.33	19.24	0.66	0.46	0.20	11.18	1.13
M11	20050718	70.62	5.03	36.08	58.89	0.89	0.65	0.25	12.91	1.24
M12	20050718	65.01	12.27	36.87	50.86	0.89	0.71	0.18	11.53	1.31
M13	20050718	71.85	31.69	30.40	37.90	0.69	0.48	0.21	14.85	1.16
M14	20050718	72.93	14.68	33.55	51.77	0.85	0.59	0.25	14.97	1.21
M15	20050718	76.93	6.16	34.95	58.89	1.00	0.73	0.26	15.73	2.41
M16	20050718	64.17	44.06	20.80	35.14	0.63	0.49	0.14	12.16	0.90
M17	20050718	45.95	82.50	9.20	8.30	0.24	0.17	0.07	4.70	0.46
M18	20050718	70.19	30.39	28.74	40.87	0.86	0.17	0.69	4.40	0.43
M19	20050718	73.43	10.54	32.51	56.94	0.99	0.68	0.31	14.85	2.20
M20	20050718	75.50	5.54	32.22	62.24	0.98	0.67	0.31	14.27	2.00