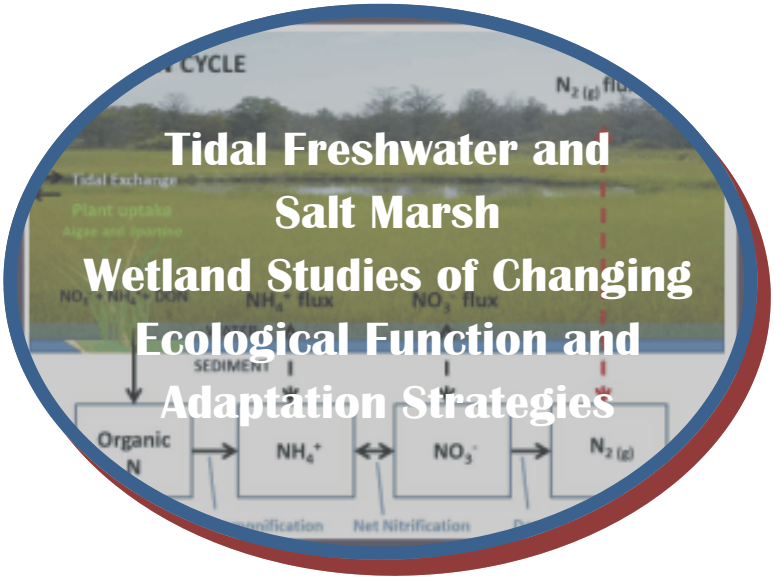
Barnegat Bay—Year 3



Dr. David Velinsky, Academy of Natural Sciences of Drexel University, Principal Investigator

Tracy Quirk, Academy of Natural Sciences of Drexel University, Co-Investigator

Michael Piehler, and Ashley Smyth Institute of Marine Sciences, University of North Carolina, Co-Investigators

Project Manager: Dorina Frizzera, Division of Science, Research and Environmental Health

Thomas Belton, Barnegat Bay Research Coordinator

Dr. Gary Buchanan, Director—Division of Science, Research & Environmental Health

Bob Martin, Commissioner, NJDEP

Chris Christie, Governor

February 2016

Phosphorus Dynamics in the Barnegat Bay, New Jersey (Year 3)

FINAL REPORT

Phosphorus Dynamics in the Barnegat Bay, New Jersey (Year 3)

Submitted to

Donna Frizzera, Project Manager
New Jersey Department of Environmental Protection
Office of Science
428 East State Street
PO Box 420
Trenton, NJ 08625-0420

PCER Report No. 2015-4
(NJSG Number 49040009/ NJDEP No. SR14-012; DU 243554)

Submitted by:

Drs. David Velinsky, Nathaniel Weston[1], and Bhanu Paudel
Patrick Center for Environmental Research
The Academy of Natural Sciences of Drexel University, Philadelphia, PA 19103

[1]Villanova University
Department of Geography and the Environment Villanova, PA

November 20, 2015

Table of Contents

List of Figures

List of Tables

Executive Summary

Both phosphorus (P) and nitrogen (N) are essential nutrients for the plants and animals that make up the aquatic food web in the bay. Since phosphorus is thought to be the nutrient in short supply in most fresh and saline waters, even a modest increase in phosphorus can, under the right conditions, increase algal production and biomass, alter the structure of aquatic food-webs, and potentially increase the chance for low dissolved oxygen (i.e., eutrophication).

Phosphorus can be found in soluble inorganic forms readily available to primary producers (soluble reactive phosphorus, orthophosphate, polyphosphate), as well as dissolved organic phosphorus and particulate phosphorus that are not as readily available. There are many sources of phosphorus to aquatic systems, both natural and human. These include the weathering of soils and rocks, wastewater treatment plants, runoff from fertilized lawns and croplands, septic systems, runoff from animal manure storage areas, disturbed land areas, drained wetlands, and commercial cleaning operations. Application of inorganic fertilizers is an important source of phosphorus in runoff and in surface waters.

The objective of this project is t*o determine the potential mechanism(s) that result in higher ambient P levels* in the southern portions of Barnegat Bay. The loadings of P from tributaries to the Bay tends to be higher in the northern Bay (above ~ Barnegat Inlet) due to higher concentrations of developed land use in the northern watershed, but ambient water column levels of P are higher in the southern Bay despite lower P inputs from the less-developed watershed. We proposed to investigate the mechanism(s) driving elevated concentrations of P in the lower Bay. Differences in nutrient availability in the Bay impact algal production, water quality, and food web structure.

Water column SRP: We confirmed previous observations that soluble reactive phosphorus (SRP) concentrations were higher in southern Barnegat Bay than in northern Barnegat Bay. The stations in the bay south of Barnegat inlet had concentration as high as 53.9 μg P/L (ranging from 29.1 to 53.9 μg P/L); while above the inlet concentrations ranged in the bay ranged from below detection to 21.2 μg P/L. The tributaries station Trib-5 had the highest concentration of the all stations, i.e. 55.1 μg P/L in the July sample. In all three samplings, there was clear evidence of a north-south SRP concentration gradient.

Sediment-bound P and sediment grain size: The sediment-bound P concentration gradient was evident in the main bay stations (MB1 – MB6). Similar to water column P concentration, sediment-bound total phosphorus (TP) was higher in the southern bay stations versus northern bay stations, however organic-bound PP concentrations at northern bay Stations MB1 and MB2 were comparable to the organic bound P concentrations from southern bay stations. A higher percentage of TP was bound to the inorganic fraction of sediments, whereas loosely sorbed P was of the lowest percentage of TP fraction. The northern bay stations had coarser sediments than the southern bay stations; the presence of fine-grained particles in the southern bay stations may have provided adsorption sites that resulted in higher P concentration at those southern stations.

Benthic SRP flux: Sediments were collected in the main portion of the bay, brought back to the laboratory to determine the flux of P from or to sediments under oxic and anoxic conditions. Exchange of SRP between the sediments and water was low and variable. There was no north-south

gradient of P release, and anoxic conditions did not appear to promote release of SRP from sediments. Rather than a source of SRP to the water, P uptake by sediments was identified in the southern main bay stations in October. Ancillary data from July measurements suggested that the water column may have been acting as a source of SRP under anoxic conditions, though field sampling did not identify low DO levels in the water column of Barnegat Bay. The sediments do not appear to be the source of the SRP in the southern Bay.

Nutrient Limitation: It was thought that water column uptake and recycling of nutrients by algae and bacteria could be a factor in the north to south distribution of dissolved P in the Bay. Changes in oxygen and chlorophyll-*a* concentrations at MB5 (southern station) clearly indicated N-limitation, while P addition made little difference in rates of primary production and changes in chlorophyll-*a*. However, station MB2 (northern station) demonstrated little response with addition of either P or N, and a response was evident only with the addition of both N+P together. These results indicate that N limitation in the Southern Bay may result in the excess SRP. There was not overwhelming evidence for P limitation in the northern bay, although co-limitation or limitation of another nutrient (for example, silica) may be important in the northern bay.

Conclusions: We have determined that sediment-water exchange of dissolved P is not an important source of P to the waters of the southern Bay compared to the northern Bay, and the sediments instead appear to be an important sink for P. Nutrient uptake experiments suggest that nitrogen limitation of phytoplankton growth may leave excess P in the water column in the southern Bay.

Management Recommendations:

Specific NJDEP management objectives can be addressed or considered from this study includes areas such as water quality, biological endpoints for the development of nutrient criteria and ecosystem based management.

This study attempted to determine the cause(s) for the distribution of dissolved phosphorus in the bay that appear to be disconnected from the sources of phosphorus to the bay. Results shows that a benthic source of phosphorus is not evident in the lower bay, and that water column processes, such as uptake and remineralization, might result in higher phosphate concentrations in the lower bay (below Barnegat Inlet) compared to the upper bay. Nutrient uptake experiments indicate that concentrations of co-limitation of N and P as well as silica might limit algal production in the lower bay and the change in nutrient ratios could impart a change in algal species composition in both the north and south sections of the bay. Additional nutrient addition experiments using waters from the north and southern sections could help determine if nutrient limitation is occurring. The data does help in the development of nutrient-stressor models but additional information is required.

1. Introduction

In an aquatic ecosystem, insoluble minerals of less than 0.2%, present in the eroded continental rocks, are the main source of available dissolved phosphate. The probability of transport of those insoluble minerals to the coastal regions in the dissolved state is less than 0.1, with the remaining being transported with fluvial sediments as inert phosphorus (Froelich 1988). Phosphorus, as phosphate, also has low bonding affinity towards water molecules compared to high bonding affinity towards inorganic minerals, which makes phosphorus adhere to the sediment. Thus, to transport phosphorus from one place to another, sediment has to move, and this is one of the main reasons for the slow movement of phosphorus compared to nitrogen (Bennett et al. 2001).

The transported particulate phosphorus (PP) is mainly composed of the following chemical fractions: loosely bonded P, oxide bonded P, calcite and carbonate bonded P, detritus P and organic matter bonded P (Hartzell et al. 2010). This transported phosphorus in organic-rich freshwater-sediment forms a complex with iron and aluminum ions and adheres to the sediments. When sediments get to the more saline estuary water (generally from freshwater to oligo-haline region), phosphorus desorbs due to the increase in electrolytes (e.g., sulfate) and negatively charged metal oxide (Sundareshwor and Morris, 1999). As organic sediment is transported farther up in the estuary, it flocculates with more saline water (salinity equivalent to 18 ppt or greater), retaining the P-load sediment in the bed (Howarth et al. 1995). A laboratory experiment using sediments from the Guadalupe and Nueces identified adsorption of added orthophosphate in sediment organic matter at all salinities over the course of the 48-hr experiment (Paudel et al. 2015). This and other studies by Paudel et al. indicate that organic matter and salinity alter sediment-orthophosphate fluxes.

1.1. Background

Both phosphorus and nitrogen are essential nutrients for the plants and animals that make up the aquatic food web in the Bay. Modest increase in phosphorus can, under the right conditions, increase algal production and biomass and potentially increase the chance for low dissolved oxygen (i.e., eutrophication). There are many sources of phosphorus, both natural and human; in general the highest concentrations are present in inorganic forms (orthophosphate and polyphosphates). These include soil and rocks, wastewater treatment plants, runoff from

fertilized lawns and cropland, failing septic systems, runoff from animal manure storage areas, disturbed land areas, drained wetlands, water treatment, and commercial cleaning preparations. Application of inorganic fertilizers is an important source of phosphorus in runoff and in surface waters.

The P cycle in estuaries can be complex, involving many forms and various biogeochemical reactions. In brief, P inputs, as dissolved inorganic P (or soluble reactive P or ortho-phosphate), can enter the Bay from tributary inputs or atmospheric deposition. Dissolved inorganic phosphate (DIP) can be taken up by algae to form particulate organic forms of P. DIP can be particulate-bound in freshwater systems, or associated with various solid phases (Smith and Longmore 1980; Lucotte and d'Anglejan 1985; Lebo 1991; Huanxin et al. 1997). Sediments typically are the dominant source of P to the overlying water column, especially at the mix of favorable pH and/or redox conditions (Seitzinger 1991; Froelich et al. 1982; Froelich 1988). While surface-bound iron-P, calcium-P and aluminum-P can play an important role in the P "buffer" mechanism in many marine and freshwater systems (Smith and Longmore, 1980; Caraco et al., 1990), the controls of P cycling in sediments are directly linked to C, Fe and S cycling. Changes in microbial processes within sediments, such as those associated with salt-water intrusion could release sediment-bound P to overlying waters (Caraco et al. 1989; Lamers et al. 2001). Release of P from sediments can be attributed to changes in pH (Seitzinger 1991), ion exchange (Fox 1989; Hawke et al. 1989), and reduction of iron oxides (Callendar 1982; Sundareshwar and Morris 1999). In addition, increases in SO_4^{2-} concentrations have been shown to remobilize sediment-bound P (Caraco et al., 1989; Lamers et al., 2001). As bacteria degrade organic material, P can be released as both dissolved inorganic and organic forms to the overlying water to be re-incorporated to biomass by algae.

When the water or sediments become anoxic (e.g., iron/manganese reduction), the adsorbed inorganic P is also released to the porewaters of the sediments and potentially overlying waters. In Northern Gulf of Mexico, P release in the water column during hypoxic events was positively correlated with Fe/Al bound P that release contributed to the bioavailable P (Adhikari et al 2015). Mississippi River sediments had higher Fe/Al and loosely bound P, while lower Ca/Mg and Inorganic bound P than Gulf of Mexico Shelf. The decrease in Fe/Al bound P in river to sea water gradient was associated with anoxic condition in the shelf floor (Sutula et al. 2004; Adhikari et al. 2015). Barnegat bay, a shallow estuary with oxic condition throughout a year, may have similar Fe/Al bound P. In addition, freshwater sediments (bottom or suspended) have

ample sites for P to be bound.Once these particles are transported to estuarine waters (salinities of > 1-5 ppt), the bound inorganic P can be exchanged with sulfate, for example, and released into the water column. Moreover, the solubilization of sediment-bound P from tidal marshes could provide a feedback for higher primary production rates in the estuary (altering nutrient ratios).

We studied the forms and changes of P in the Barnegat Bay and explored the observed distribution in the water column. Our ultimate goal was to determine the mechanism(s) supporting higher concentrations of dissolved P in the southern bay (Pang 2013) despite lower watershed inputs of P to this region (Baker et al. 2014), with a focus on sediments as a reservoir of P. Our hypothesis was that sediment in the Bay is a major reservoir of P, and that conditions in the southern Bay promote higher rates of P release to the water column. These processes can alter the concentration and form of P in waters of the Bay and change the N to P distribution. This can result in alteration of nutrient limitation in the Bay and algal productivity (and algal speciation).

1.2. Project Objectives

The objective of this project was to determine the potential mechanism(s) that result in higher ambient P levels in the lower sections of Barnegat Bay. Loadings of P from tributaries to the Bay tend to be higher in the upper areas of the Bay (above ~ Barnegat Inlet), but ambient water column levels of P are higher in the lower sections. We investigated these levels to determine the mechanism(s) or cause(s) of the elevated levels in the lower Bay. Changes in P concentrations could impact levels of algal production and water quality by altering the N to P ratio and nutrient limitation.

2. Methods

2.1. Water Column Sampling

Surface and bottom water samples were collected during three sampling events using Van Dorn sampler from 20 different stations in the Bay (Fig. 1). Those samples were stored on ice and filtered for chlorophyll and nutrients. Water samples were filtered through GF/F filters for chlorophyll-*a* and TSS analyses, and polycarbonate filters for nutrient analyses. Water quality parameters of dissolved oxygen, salinity, temperature, and pH were measured using a YSI Sonde.

The top 3 cm of surface sediments were collected from all of the 20 stations in the Bay during July and October samplings for the phosphorus speciation study, but only from MB2 and MB5 in the May sampling.

2.2. Sediment Fluxes

Larger diameter (10 cm i.d.) sediment cores to a depth of 20 cm, and 20 L of site water were collected from six selected main bay sites (MB1 – MB6); three in the northern region and three in the southern region, during July and October samplings, whereas only from MB2 and MB5 during May sampling. In the laboratory, the sediment cores were filled with site water, and capped. Two cores from each station were filled with oxygenated water (site water bubbled with air for approximately 0.5 hr), while another two cores from each station were filled with anoxic site water (water bubbled with N_2 gas for >0.5 hr). The custom gas-tight lids were constructed with ports to allow sampling of the water overlying the sediment surface and were equipped with magnetic stir-bars (driven by a magnet external to the core) to keep the water well mixed (Fig. 2). Oxygen concentrations were monitored (in the oxic cores only) and samples were collected from the overlying water at 5 time points over approximately 1 day incubation period and analyzed for soluble reactive phosphorus (SRP) and dissolved inorganic carbon (DIC) to determine the rates at which SRP and DIC were exchanged between the sediment and overlying water column. Site water (both oxic and anoxic) was placed into gas-tight glass stoppered bottles (BOD bottles) that were sampled at the beginning and end of an approximately one day incubation to assess changes in oxygen, SRP, and DIC in the water column irrespective of the benthic influence. The main goal of this portion of the research was to evaluate whether the sediments were a major source of SRP to the water column in Barnegat Bay. Oxygen and DIC were used to evaluate total sediment metabolism (oxygen uptake and DIC release). By measuring SRP release under oxic and anoxic conditions, we hoped to determine the amount of

sediment-bound but easily available SRP (such as Fe-P precipitates that become soluble under anoxic conditions).

2.3. Phosphorus Speciation on Solids

Phosphorus "sorbed" to surfaces of Fe-, Ca- and Al-rich particles can play an important role in the phosphate "buffer" mechanism in marine and freshwater systems (Caraco et al. 1990). Phosphorus is also found in lattice-bound Fe, Ca, and Al phases that are less available for exchange with the overlying waters (Froelich 1988). Fox (1989), for example, showed that dissolved phosphate concentrations can be in partial equilibrium with iron phosphate and hydroxide phases, but can also be controlled by hydrolysis reactions with hydroxyapatite ($Ca_5(PO_4)_3(OH)$).The solubility and partitioning of P can be very dependent on the pH and redox condition of the sediments (Fox 1989). In fact, Sietzinger (1991) demonstrated that the occurrence of algal blooms in the tidal Potomac River was related to the release of P under high pH (9–10) conditions. The release of P from the sediments was postulated to be from desorption or dissolution of P bound in iron oxides or phosphates. In addition, as salinity increases sulfate increases thus P can be released from the exchangeable sites on particles and sediments.

In brief, sediment and suspended particles were subjected to a modified extraction scheme used by Ruttenberg (1992). In the present study, five different fractions: exchangeable P (loosely sorbed), Fe/Mn oxide-bound P, Ca-bound P, inorganic P, and organic P were extracted from the surface sediments (see brief description in Table 1). The first fraction was identified by leaching the sediment with $MgCl_2$ solution and the resultant extract analyzed for phosphate. The residue was extracted with Citrate-Dithionite-Bicarbonate (CDB) solution to reduce oxides of Fe and Mn to identify Fe/Mn-bound P. This fraction looks at the amount of P released from solids under "reducing" conditions. Acetate buffer was used to extract calcium-bound P, and 1N hydrochloric acid was used to extract inorganic and organic- bound P. A separate fraction of sediment was analyzed for total P using the method of Asplia et al. (1976). In order to prevent resorption of phosphorus onto solid surfaces during extraction, each step of extraction was followed by $MgCl_2$ wash. It should be noted that these methods only provide an approximate fractionation of P on particles and each method has it strengths and drawbacks. A schematic of the extraction process is depicted in Fig. 3. The extraction process provided a fractionation that indicates how much P was stored in sediments throughout the Bay, and potentially released from sediments to the water

column under various conditions. Once extraction was completed samples were stored frozen.

2.4. Nutrients and Chlorophyll-*a* Analysis

Water samples from Barnegat Bay and laboratory experiments were analyzed for nitrite+nitrate ($NOx = NO_2+NO_3$), ammonium ($NH4^+$) and soluble reactive phosphorus (SRP). Water was filtered and stored frozen in pre-cleaned bottles. Nitrate-nitrite and ammonium concentrations were determined using an Alpkem 300 segmented flow autoanalyzer with a detection limit of 0.006 and 0.005 mg/L for NOx and NH_4, respectively, while SRP had a detection limit of 0.002 mg P/L. Phosphorus samples were analyzed by an ascorbic acid and molybdate colorimetric method using an Alpkem Segmented Flow analyzer and Westco Smartchem 200. Chlorophyll-*a* was analyzed by a fluorometric detection method using acetone as the extract solution.

2.5. Sediment Characteristics

Sediment total organic carbon and total nitrogen were measured using a CE Instruments, Flash EA 1112 Series following the guidelines in EPA 440.0, manufacturer's instructions and ANSP-PC SOP. Samples were ground to a powder, pre-treated with fuming HCl to remove inorganic carbon, re-dried and ground. Samples were weighed into tin boats using a microbalance (in duplicate) and analyzed using the FLASH 1112 elemental analyzer. Sediment grain size of greater and less than 63 micron were identified by wet sieve method using a 2 mm and 63 micron sieves to separate gravel/sand portions of the sediments from silt/clay.

2.6. Revised Work Plan

Our findings from the first two sediment-flux samplings indicated that the sediments were not the source of SRP to the water column in the southern bay which resulted in higher water column SRP distribution versus the northern bay. Therefore, we suggested a revised approach to identify phosphorus dynamics in Barnegat. In our third sampling, we hypothesized that differences in nutrient input along the Bay and phytoplankton uptake of nitrogen and phosphorus in the Bay drive the observed patterns in water-column nutrients along the north-south gradient.

Nutrient (both nitrogen and phosphorus) inputs are higher to the northern bay due to greater concentrations of development in the northern region (Fig. 4; Baker et al. 2014).

Higher nutrient concentrations in the northern bay likely fueled greater phytoplankton production in the north, as suggested by our results for water column particulate organic carbon (POC; largely phytoplankton; Fig. 5). While total rates of both nitrogen and phosphorus loading are higher in the northern portion of the Bay, the *relative* loadings of nitrogen and phosphorus vary along the axis of Barnegat Bay, with higher nitrogen loadings in the north and relatively higher phosphorus loadings in the south, with a decrease in the N:P ratio from 12.6 in the northern Bay to 11 in the southern Bay (Fig. 4). The patterns of nitrogen and phosphorus inputs to the Bay and the results of our incubation experiment indicate that differential nutrient limitation of primary production is the major mechanism driving differences in water-column nutrient concentration. Therefore, we suggest that greater nitrogen availability in the north fuels high rates of production in the water column drawing down SRP concentrations, so that SRP becomes limiting for growth. In contrast, lower overall nutrient availability and higher relative concentrations of SRP in the southern bay draw down available nitrogen (NOx and NH4+) resulting in nitrogen limitation and higher water column SRP. The differences in relative nutrient availability (Fig. 4; nitrogen versus phosphorus) and differential demand for these nutrients by producers in the water column may drive observed patterns of water column nutrient concentrations throughout the Bay. This could also result in changes in algal species between northern and southern parts of the Bay.

Our revised approach for May 2015 field and laboratory work was to evaluate differences in nutrient availability and demand as the mechanism driving phosphorus dynamics in Barnegat Bay. We reduced the number of benthic flux measurements we made to two stations, i.e., MB2 and MB5, and redirected our efforts towards water-column incubations under light and dark conditions and with nutrient (nitrogen and phosphorus) additions.

We focused that work at two main bay stations (MB2 and MB5) that have distinct differences in water-column and sediment P concentrations (Figs. 6 and 10) and received different watershed loadings (Fig. 4), and therefore represent the northern and southern bay conditions, respectively. Briefly, we:

1. conducted benthic flux experiments using established methodology at two stations (MB2 and MB5),

2. collected water-column samples from the main bay and bay sites using established methodology,
3. collected large volumes of water at two stations (MB2 and MB5) and incubated

this water in BOD bottles to establish rates of oxygen consumption, and

4. performed sediment speciation for P bound in different fractions.

2.6.1. Methodology for BOD Incubations

Large volumes (20 L) of whole surface water were collected from stations MB2 and MB5 (Fig. 1) during the May 2015 sampling. Water samples were stored on ice and brought to the laboratory. A portion of each water sample was vacuum-filtered through pre-weighed GF/F glass fiber filters for measurement of water-column chlorophyll-*a* (n = 3 per site), particulate carbon, nitrogen (PC/PN; n = 3 per site), and particulate phosphorus (PP; n = 3 per site). Chlorophyll filters was preserved with $MgCl_2$ (3 drops of a saturated $MgCl_2$ solution) and frozen for later analysis. PC/PN filters and PP filters were dried at 60°C and weighed to determine the suspended matter content of the water. The PC/PN was determined on a CE Flash elemental analyzer, and the PP content was measured following combustion and an acid digestion. Another portion of the water was filtered (0.2-µm nylon filters) for dissolved inorganic carbon (DIC; 8 ml in a glass vial preserved with 10 µl of saturated $HgCl_2$ solution) and SRP, NOx, and NH_4^+ (30 ml in a plastic vial and frozen).

For the incubations, 15 glass 250-ml BOD bottles were filled with water from each station to achieve triplicates of five treatments:

a. Light
b. Light + SRP
c. Light + $NO3^-$
d. Light + SRP + $NO3^-$
e. Dark

The SRP bottles (treatments b and d) received 10 µl of a 1 mg/L potassium phosphorus stock solution to achieve a 40 µg/L SRP amendment, and the NOx treatments (c and d) received 10 µl of a 10 mg/L potassium nitrate stock solution to achieve a 400 µg/L NOx amendment. The nutrient amendments were targeted to achieve approximate SRP concentrations observed in the southern bay (Fig. 6) and NOx concentrations observed in the northern bay at both the MB2 and MB5 stations (note: the amendment level was specifically determined using previous monitoring data collected by NJ DEP). The light and dark bottles (treatments a and e) received no

amendments. Just prior to the start of the incubation, samples for initial nutrient and DIC concentrations were taken from the bottles (as described above) and initial oxygen concentrations were measured in each BOD bottle.

The BOD bottles were capped, headspace- free, with gas-tight glass stoppers and incubated for approximately 24 hr. The light bottles (a-d) were incubated at ambient temperature in the light. Light was provided by a high pressure sodium lamp that produces approximately 1000 μE of photosynthetically active radiation. Dark bottles were incubated in the dark at ambient temperature.

Following the incubation period, the BOD bottles were sampled for final oxygen concentrations, nutrients, DIC, chlorophyll-*a*, PC/PN, and PP as described above. The change in these variables allowed us to assess rates of phytoplankton net primary production (oxygen production and DIC consumption) in the light bottles with and without added SRP and NOx, and rates of respiration in the dark bottles (oxygen consumption and DIC production).

3. Results

3.1. Water Quality

Salinity was similar at all stations during the three samplings, except for a low salinity at MB3 during the October sampling (3.06 ppt) versus July sampling (28.3 ppt). Chlorophyll-*a* concentrations for the three samplings ranged from 3 to 32.5 μg/L in July, 1.3 to 24.1 μg/L in October and 2.8 to 8.2 μg/L in May. The average temperatures in the Bay were 21.4˚C in July, 18.2˚C in October, and 20.9˚C in May. Dissolved oxygen was similar for the three samplings, with some of the stations having slightly lower DO in the May sampling as compared to July and October. Most of the time pH in the Bay ranged from 7.5 to 8. In the July and October samplings, TSS was highest at Station MB5 (Table 2). Dissolved nitrogen was variable in the Bay. The highest NH_4 concentration (199 μg N/L) was identified at Station MB5 in the October sample, while the lowest concentration (0.8 μg N/L) was also identified at the same station in the May 2015 sample. Nitrate+nitrite (NOx) concentration was highest (199 μg N/L) at tributary 3 (trib 3) in the July 2014 sample (Table 2).

3.2. Sediment Characteristics

Sediments at the main bay stations that are north of the Barnegat inlet are coarser than those south of the inlet, i.e. average grain size of <63 μm in Stations MB1 – MB3 was 28.5% versus 67.9% in Stations MB4 – MB6. In all samplings, sediment organic contents were higher in the tributary stations than in the bay stations. The organic contents ranged from 0.87 to 15.05 in the tributaries' stations, while those ranged from 0.61 to 4.68 in the bays' stations (Table 3). The tributaries stations had higher TN and TP than the Bay stations, whereas southern main bay stations had higher sediment TP than northern main bay stations (Table 3).

3.3. Surface Water Phosphate

A dissolved phosphorus concentration gradient was identified from northern to southern stations. Northern bays and tributary stations had low dissolved phosphorus compared to the southern bay. In July, Station MB6 had the highest dissolved P (53.4 μg P/L) whereas Station MB2 had the lowest dissolved P (1.1 μg P/L) (Fig. 7). In October 2014 and May 2015, SRP in some of the northern bay stations were less than the detection limit (Figs. 8 and 9). During the May 2015 sampling, SRP concentrations were not detected in Station MB2. In all three samplings, stations south of Barnegat inlet had higher SRP concentrations.

3.4. Sediment Phosphate

The sediment total phosphorus was higher in southern bay stations compared to northern bay stations (Fig. 10). Total phosphorus in the surface sediments of Barnegat Bay was in the range from 222 to 1282 μg P/g with the dominant fractions being iron and inorganic or detrital apatite bound P (Table 4 & 5; Figs. 11a & 11b). The average total sediment phosphorus collected from July and October samplings in the three northern bay stations (MB1 – MB3) were 577 and 399 μg P/g, respectively, whereas for southern bay stations (MB4 – MB6), they were 526 and 593 μg P/g, respectively. The organic bound P was higher in the tributaries and stations closer to tidal inlets (Figs. 11a & 11b). The central bay stations were lower in organic-bound P as compared to other bay stations (Figs. 11a &b). In all stations, the loosely-bound fraction of phosphorus was the lowest. Iron bound P decreased from 86 to 33%, whereas inorganic or detrital P increased from 4 to 33% along the north south gradients of the bay (Fig. 12).

3.5. Phosphate Flux Experiment

Benthic phosphorus exchange and water column P production under oxic and anoxic conditions in the northern and southern bay were almost similar (Figs. 13 to 15). P uptake was higher in October 2014 benthic flux and water column SRP production experiments (Fig. 13). July experimental results suggested release of water column P during anoxic condition (Fig. 14).

3.6. Nutrient Limitation Experiment

Rates of production and changes in nutrient concentrations in the light bottles (likely nutrient consumption) allowed us to evaluate the role of nutrient availability on rates of phytoplankton production and the nutrient limiting production in the northern and southern bay. We hypothesized that SRP limits production in the northern bay (MB2) and rates of production will be highest in the bottles with added SRP (b and d), while NOx limits production in the southern bay (MB5) and that production will be greatest in the bottles with added NOx (c and d). We further hypothesized that the particulate matter in the Bay water column is a major source of SRP and NOx upon decomposition, and that concentrations of SRP, NOx, and NH_4^+ will increase in the dark bottles.

Oxygen and chlorophyll-*a* concentrations in the five treatments were identified (samples for nutrients, DIC, PC/PN, and PP are yet to be analyzed) to analyze results for the incubations. Net

change in oxygen concentration was identified in the dark, control, +P, +N, and +N+P treatments at Stations MB2 and MB5 (Fig. 16a). Changes in oxygen concentration also identified gross primary production in the four treatments (except dark) (Fig. 16b). Addition of N and N+P increased oxygen concentration in Station MB5 as compared to Station MB2; however P addition did not affect the net primary production at Stations MB2 and MB5. Rate of change in chlorophyll-*a* was greatest in the Station MB5 N+P treatment, though +N treatment of the same station also had a comparable change in chlorophyll-*a* (Fig. 16c). Station MB2 had 1 mg/L per day change in chlorophyll-*a* concentrations in the N+P treatment.

4. Discussion

Surface runoff due to overland flow alters SRP concentrations in an estuary. In Barnegat Bay, loading of P was higher at the northern part compared to the southern part (Baker et al. 2014). The present study has identified higher surface water P concentration in the southern part of the Bay versus the northern part, thus, in contrast to Baker et al. (2014). Similar to water column P concentrations, sediment TP concentrations were higher in the southern part of the Bay, although organic-bound P at Stations MB1 and MB2 during July were comparable to concentrations at southern stations. Different fractions of P bound in the sediment are potential sources of P to the water column. These P fractions are released at the sediment water interface under different environmental conditions, i.e., at variable DO, pH, temperature, and bacterial activities. The present study identified a higher percentage of inorganic or detrital P and iron-bound P as compared to loosely bound P in the sediments of the northern and southern bay. Calcium bound sediment phosphorus or authigenic P was higher than loosely sorbed P in all sites but was lower in comparison to other fractions. In some samples calcium bound P was below detection levels (i.e. 0.014 mg/L). Sutula et al. (2004) identified decrease in Fe bound P as Mississippi River sediments transport from river to continental shelf. Similarly, Hartzell et al. (2010) identified Fe bound sediment P decreased from freshwater to mesohaline water of the Patuxent River, a sub-estuary of the Chesapeake Bay. In Barnegat Bay, we did not identify decrease in Fe bound sediment P from tributary to main bay stations, however we did identify decrease in Fe bound P in the suspended sediments along north south main bay stations collected during October sampling (Figs 11 and 12). The decrease in iron bound P in the suspended sediments along north south gradient of Barnegat bay was not associated with increase in anoxic condition as was identified by Sutula et al. (2004). That could be because of the decrease in riverine source of suspended sediment along the transport from north to south. The high iron bound P concentration in the tributaries' sediment confirms the presence of iron in the riverine sediment transport. In the suspended sediments inorganic bound P increases from north to south salinity gradient, this is in agreement of Sutula et al. (2004) findings. Differences in sediment grain size, especially more fine grain particles in an estuary, and suspended clay particles, affect P by altering adsorption sites (Wang and Li 2010; Garcia-Luque et al. 2006).The sediment grain size analysis identified finer particles at the southern stations as compared to the northern stations, which may enhance adsorption in the southern bay.

Generally, P is recycled to the water column by remineralization of organic matter. Our initial hypothesis was that sediment phosphorus in the southern Bay was a source of SRP to the water-column, supporting the relatively high water-column SRP. However, the results of our sediment core incubations indicated that very little sediment phosphorus was released to the overlying water in either oxic or anoxic conditions throughout the Bay (Figs. 14 & 15). Similarly, Seitzinger (1993) identified little recycling of sediment phosphorus to the water column by diffusive flux in Barnegat Bay. Despite higher sediment P in the southern Bay, P in sediments throughout the Bay is tightly bound in minerals, sediment particles, and in organic matter complexes. The present study found that a higher percentage of P was bound to inorganic minerals, which may be difficult to release to the water column.

Benthic metabolism (oxygen uptake and DIC release) was similar throughout the Bay. Instead of sediment being a source of P to water, it appeared that the southern bay is a sink of P (Fig. 14). However, a standout result was SRP production in water at anoxic conditions and we have not identified anoxic conditions in the Bay. The results of benthic SRP flux and P production lead to the possibility of difference in water column activity at the northern and southern bay causing the north-south SRP gradients.

The field and laboratory experiments conducted using sediments collected during the first two samplings (July and October) identified sediment as a sink of P rather than a source. We thus tested the hypothesis that N limitation in the southern bay and P limitation in the northern bay of water-column primary production as the mechanism that drives observed differences in nutrients in the Bay. We incubated water from the MB2 (northern) and MB5 (southern) bay sites in the dark and in the light with added SRP, NOx, SRP+NOx in combination, and under control conditions with no nutrient addition (Fig. 16a and b). At site MB2, with higher ambient SRP (Fig. 16a), we observed rapid uptake of SRP than the MB5 site when SRP was added (+SRP treatment; Fig. 16c), supporting the hypothesis that SRP was limiting in the northern bay. In contrast, the addition of NOx stimulate much higher rates of NOx uptake at site MB5 than at site MB2 (Fig. 16d), indicating N limitation in the southern bay. When NOx and SRP were added together, rates of SRP uptake and NOx uptake were similar at both sites (Figs. 16c and d).

$$MB2: GPP = (11.97 \times SRP) + (8.70 \times NO_3^-) + 0.92$$
$$R^2 = 0.69; p = 0.005$$
$$MB5: GPP = (6.51 \times SRP) + (38.14 \times NO_3^-) + 0.46$$
$$R^2 = 0.99; p < 0.001$$

Rates of net primary and gross primary production measured at site MB5 further indicated that when NOx was available, rates of primary production increased (Figs. 17a and b) and the standing stock of chlorophyll-α in the water increased strongly (Fig. 17c). Rates of production and the change in chlorophyll-α did not appear to respond strongly to either SRP or NOx alone and only increased notably with the addition of both nutrients (Fig. 17). GPP (mg/L-d), equal to the rate of photosynthesis, was found to be correlated with the starting concentrations of SRP and NOx (µg/L) in the water-column incubations at both sites.

Nutrient enrichment experiments during summer and fall in Barnegat bay identified that addition of N and P together increased the production and phytoplankton biomass more than the input of one single nutrient (either N or P only) (Seitzinger 1993). In our study, note that while GPP responds to both SRP and NOx at both sites, the response is stronger to SRP at the MB2 site, and to NOx at the MB5 site. These results again support the hypothesis that SRP limits primary production in the northern Bay (site MB2), while NOx limits production in the lower Bay (site MB5). N limitation in the southern Bay may therefore result in 'excess' P relative to the demands of the phytoplankton community, leading to higher concentrations of SRP in the water-column.

The results of this water-column incubation experiment lend support to our hypothesis that variable demand for nutrients by the primary producers relative to availability is at least partially responsible for the spatial pattern of nutrient concentrations in Bay water.

<u>Major findings of this study include:</u>

- Even though watershed loadings of phosphorus are higher in the northern part of the Barnegat bay, phosphorus are higher in the water column of southern bay than in the northern Barnegat bay.
- Sediments in Barnegat bay are the sink of phosphorus and sediment total phosphorus is higher in the southern bay compared to northern bay.

- Iron bound and detrital or inorganic bound phosphorus were higher in Barnegat bay, while loosely sorbed was the lowest fractions of sediment phosphorus.
- Benthic flux experiment did not identify flux of phosphorus from sediments to the water column under oxic and anoxic condition
- Water column in the northern bay may be phosphorus limiting, while water column in the southern bay may be nitrogen limiting.
- Nutrient limitation experiments also identified limitation of both (N and P) nutrients in the Barnegat Bay.

Management Recommendations:

Specific NJDEP management objectives can be addressed or considered from this study includes areas such as water quality, biological endpoints for the development of nutrient criteria and ecosystem based management.

This study attempted to determine the cause(s) for the distribution of dissolved phosphorus in the bay that appear to be disconnected from the sources of phosphorus to the bay. Results shows that a benthic source of phosphorus is not evident in the lower bay, and that water column processes, such as uptake and remineralization, might result in higher phosphate concentrations in the lower bay (below Barnegat Inlet) compared to the upper bay. Nutrient uptake experiments indicate that concentrations of co-limitation of N and P as well as silica might limit algal production in the lower bay and the change in nutrient ratios could impart a change in algal species composition in both the north and south sections of the bay. Additional nutrient addition experiments using waters from the north and southern sections could help determine if nutrient limitation is occurring. The data does help in the development of nutrient-stressor models but additional information is required.

<u>Recommendations for Future Research and Monitoring</u>

- Determine loads from specific sub-watersheds to bay
- Monitor seasonal changes of dissolved silica in bay
- Nutrient addition experiments using N and P as well as Si
- We have not studied phosphorus input to the bay from the Atlantic oceanic, which may be an important source of P.

Acknowledgment

We would like to thank Paul Kiry, Melissa Bross, Paula Zelanko George Keighton, Roger Thomas, and Sylvan Klein at the Academy for field and laboratory assistance as well data interpretation. In addition, Dr. Lori Sutter and students at Villanova assisted in field and laboratory experiments during this project. Tom Belton (NJ DEP) provided background, field and editorial support throughout this project. Robin S. Davis provided assistance with final report preparation and review. Funds for this project were provided by NJ DEP.

References

Adhikari, P. L., J. R. White, K. Maiti, and N. Nguyen. 2015. Phosphorus speciation and sedimentary phosphorus release from the Gulf of Mexico sediments: Implication for hypoxia. Estuarine, Coastal and Shelf Science 164: 77-85.

Asplia, K.I., H. Agemian and A.S.Y. Chau. 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101: 137-197.

Baker, R.J., C.M. Wieben, R.G. Lathrop and R.S. Nicholson. 2014. Concentrations, loads, and yields of total nitrogen and total phosphorus in the Barnegat Bay-Little Egg Harbor watershed, New Jersey, 1989 – 2011, at multiple spatial scales: U.S. Geological Survey Scientific Investigations Report 2014-5072, 64 pp.

Bennett, E.M., S.R. Carpenter and N.F. Caraco. 2001. Human impact on erodible phosphorus and eutrophication: A global perspective. Bioscience 51: 227-234.

Callendar, E. 1982. Benthic phosphorus regeneration in the Potomac River Estuary.

Caraco, N.F., J. Cole. 1990. A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems. Biogeochemistry 9: 277-290

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

Fox, L.E. 1989. A model for inorganic control of phosphate concentration in river waters.

Froelich, P.N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnolology and Oceanography 33: 649-668.

Froelich, P.N., M.L. Bender, N.A. Luedtke, G.R. Heath and T. DeVries 1982. The marine phosphorus cycle. American Journal of Science 282: 475-511.

Garcia-Luque, E., J. M. F. Pajares, and A. Gomez-Parra. 2006. Assessing the geochemical reactivity of inorganic phosphorus along estuaries by means of laboratory simulation experiments. Hydrol. Process 20: 3555-3566.

Geochimica et Cosmochimica Acta 53: 417-428.

Hartzell, J.L., T.E.Jordon and J.C. Cornwell. 2010. Phosphorus burial in sediments along the salinity gradient of the Patuxent River, a subestuary of the Chesapeake Bay (USA).

Hawke, D., P.D. Carpenter, and K.A. Hunter. 1989. Competitive adsorption of phosphate on goethite in marine electrolytes. Environ. Sci. Technol. 23: 187-191.

Howarth, R.W., H.S. Jennesen, R. Marino, H. Postma. 1995. Transport to and processing of Phosphorus in near-shore and oceanic water. *In* H. Tiessen (ed.), Phosphorus in the Global Environment: Transfers, Cycles and Management. John Wiley and Sons, Chichester, England. pp 323-345.

Huanxin, W., B.J. Presley and D.J. Velinsky. 1997. Distribution and sources of phosphorus in tidal river sediments in the Washington, D.C. area. Environmental Geology 30(3/4): 224-230.

Hydrobiologia 92: 431-446.

Lamers, L.P.M., G.E. Ten Dolle, S.T.G. Van Den Berg, SS.P.J. Van Delft, and J.G.M. Roelofs.

2001. Differential responses of freshwater wetland soils to sulphate pollution. Biogeochemistry 55: 87-102.

Lebo, M.E. 1991. Particle-bound phosphorus along an urbanized coastal plain estuary. Marine Chemistry 34: 225-246.

Lucotte, M. and B. d'Anglejan. 1985. A comparison of several methods for the determination of iron hydroxides and associated orthophosphates in estuarine particulate matter. Chemical Geology. 48: 257-264.

Pang, H., T. Ingelido, A. Giudicelli, B. Hirst, A. Lotto, and J. Lipoti. Barnegat Bay water quality and quantity monitoring program. 2013. Delaware Estuary Science and Environmental Summit.

Paudel B., P.A. Montagna and L Adams. 2015 Variations in the release of silicate and orthophosphate along a salinity gradient: Do sediment composition and physical forcing have roles? Estuarine, Coastal and Shelf Science 157:42-50.

Ruttenberg, K.C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnology and Oceanography. 37: 1460-1482.

Seitzinger, S. P. 1993. Eutrophication and nutrient loading in Barnegat Bay: N or P limitation of primary production. Final Report#93-2F. Academy of Natural Sciences, Division of Environmental Research, Philadelphia, PA.

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

Smith, J.D. and A. R. Longmore 1980. Behavior of phosphate in estuarine water. Nature 287: 532-534.

Sundareshwar, P.V. and J.T. Morris. 1999. Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient. Limnology and Oceanography 44: 1693-1701.

Sutula, M., T. S. Bianchi, and B. A. McKee. 2004. Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico. Limnol. Oceanogr. 49: 2223-2235.

Wang, Q. and Y. Li. 2010. Phosphorus adsorption and desorption behavior on sediments of different origins. J Soils Sediments 10: 1159-1173.

Figures

Figure 1. Map of the study sites with all 20 sampling

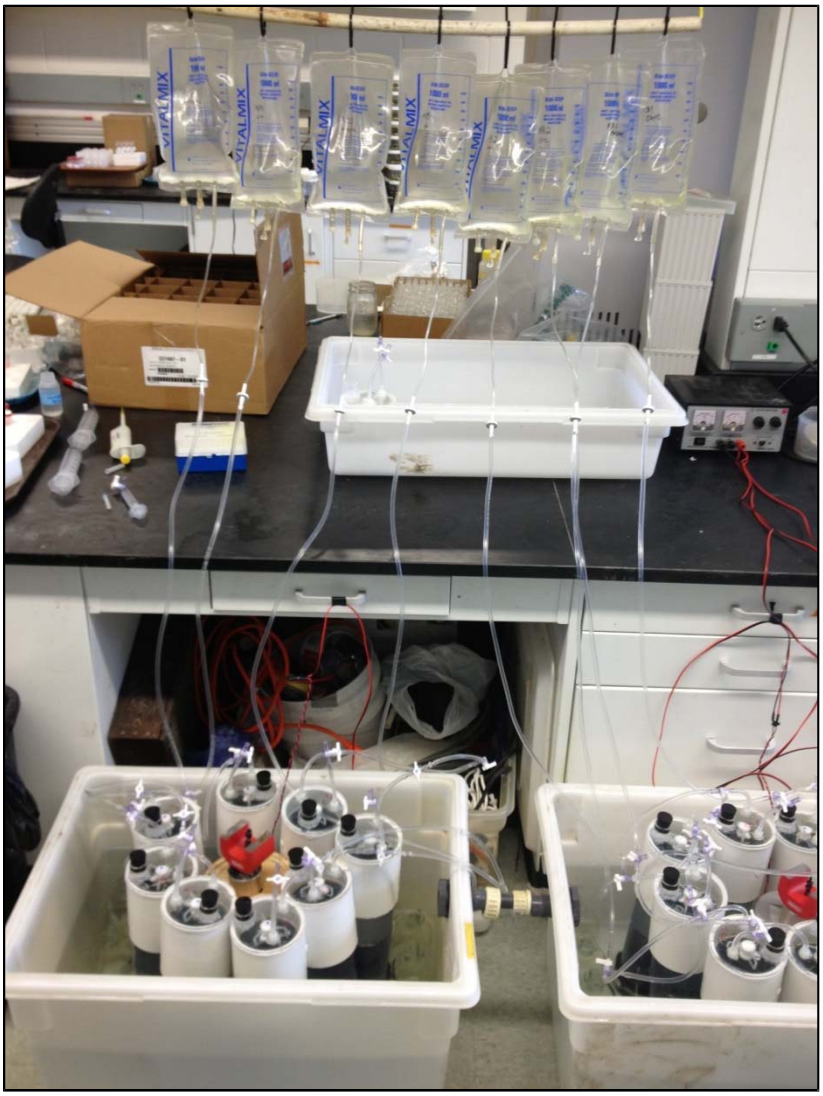


Figure 2. Flux experimental set up.

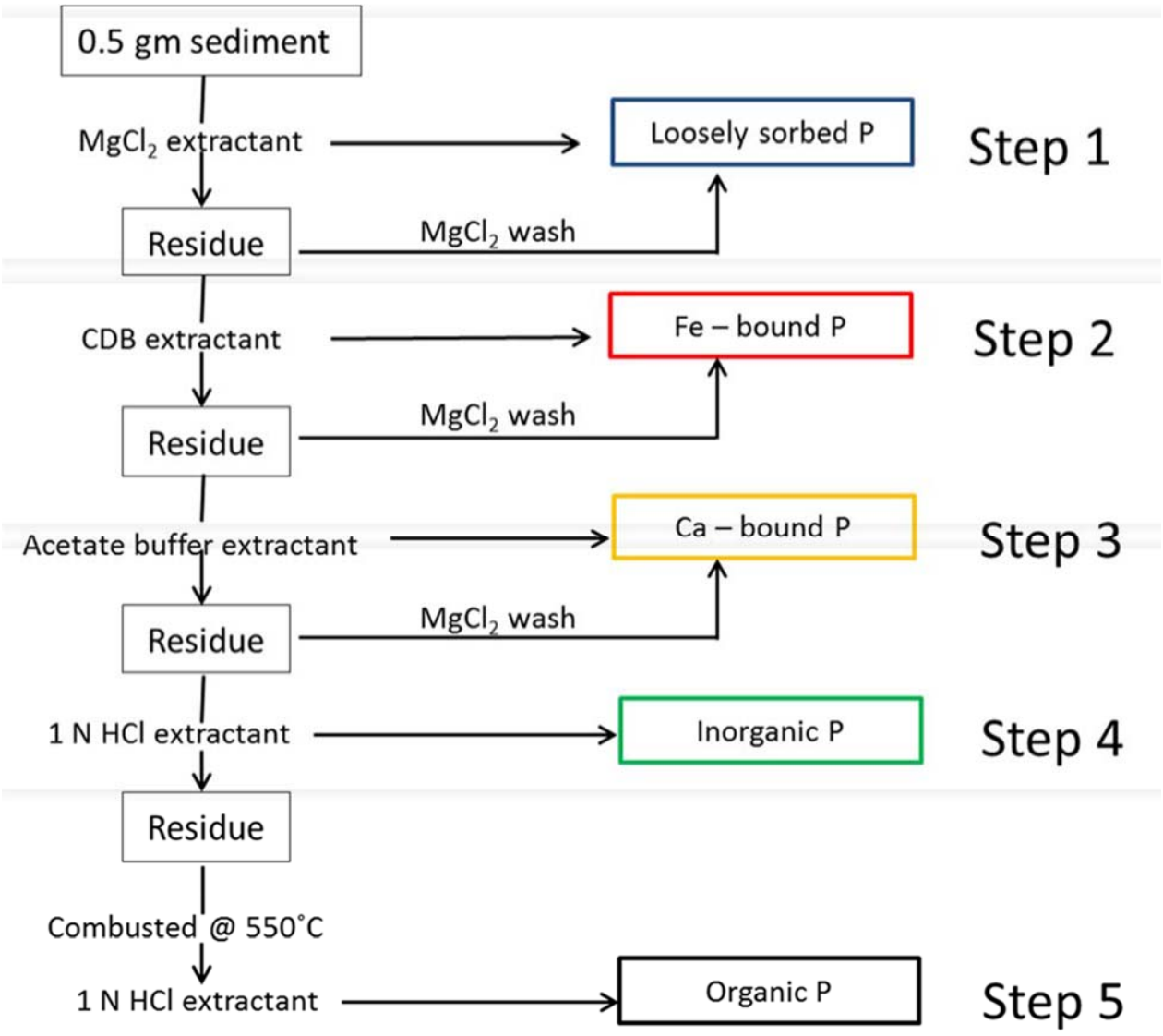


Figure 3. Five different steps required for sequential P extraction from sediments.

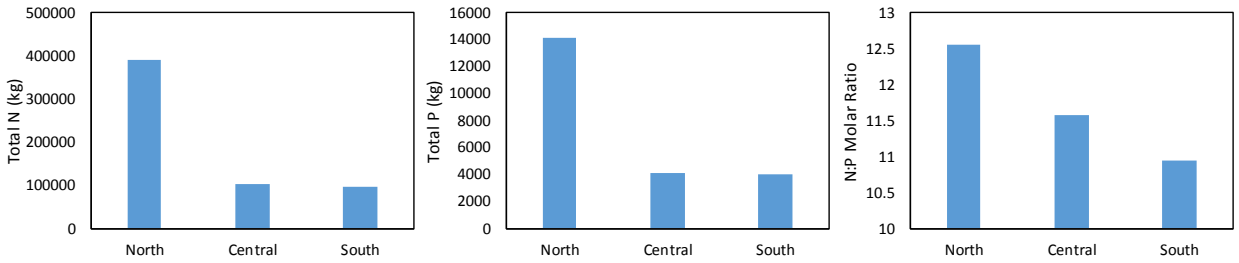


Figure 4. Annual nitrogen and phosphorus loading and the molar nitrogen : phosphorus loading ratio from watershed regions to Barnegat Bay (derived from Baker et al. 2014 Table 14; loading estimates from 1989-2011).

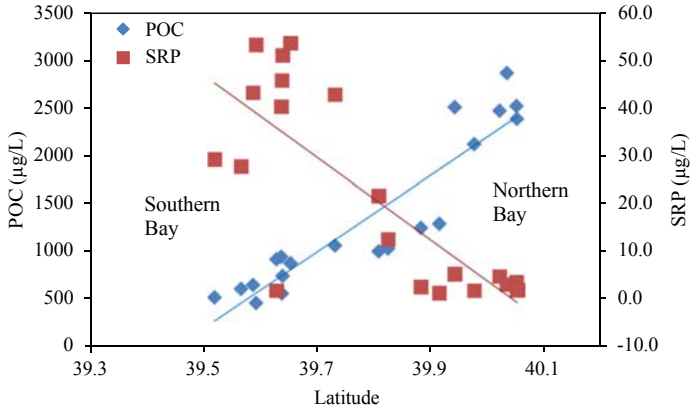


Figure 5. Water-column soluble reactive phosphorus (SRP) and particulate organic carbon (POC) in Barnegat Bay stations along a latitude gradient.

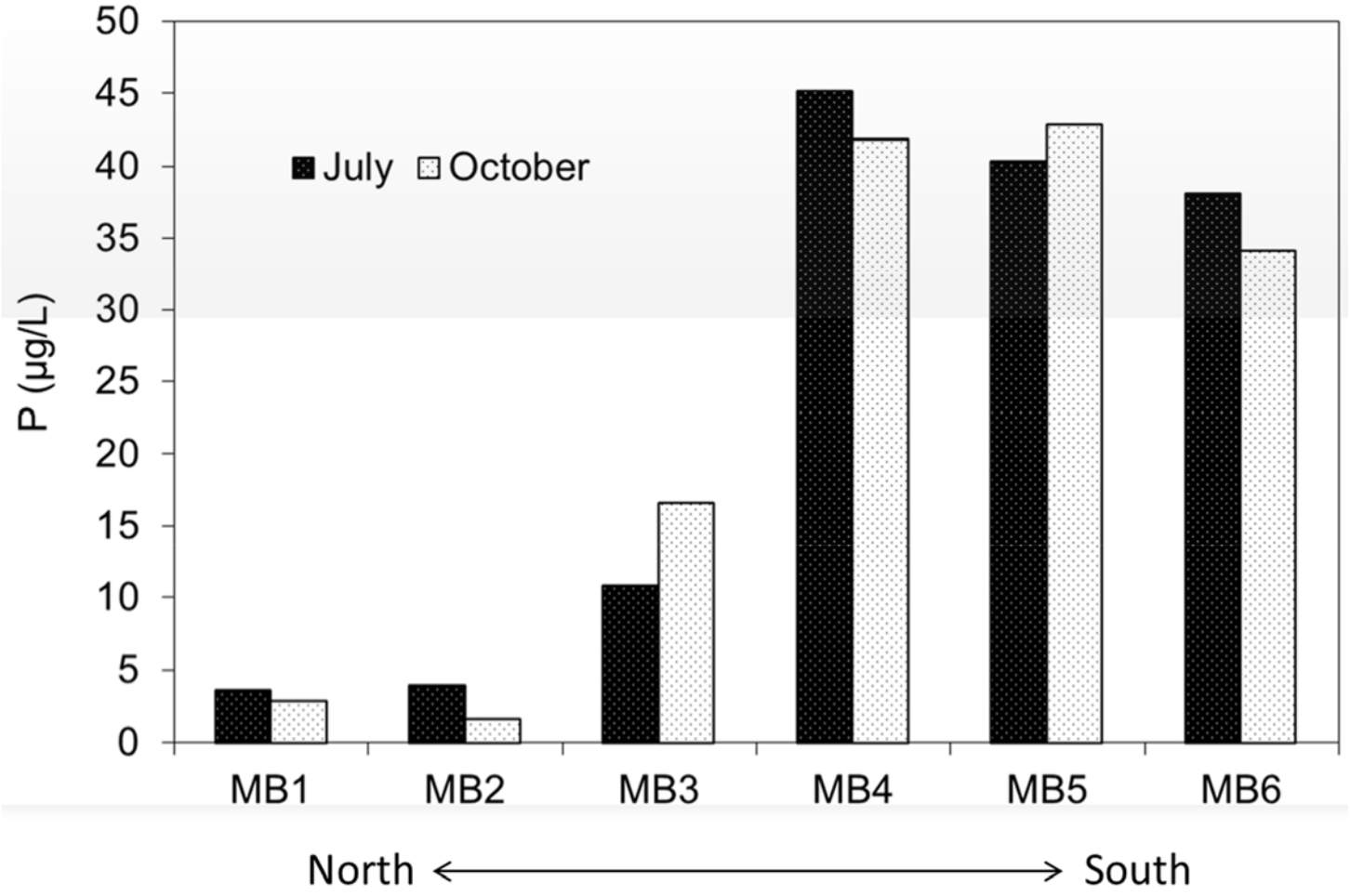


Figure 6. Water column phosphate concentrations in the main bay (flux sites) stations.

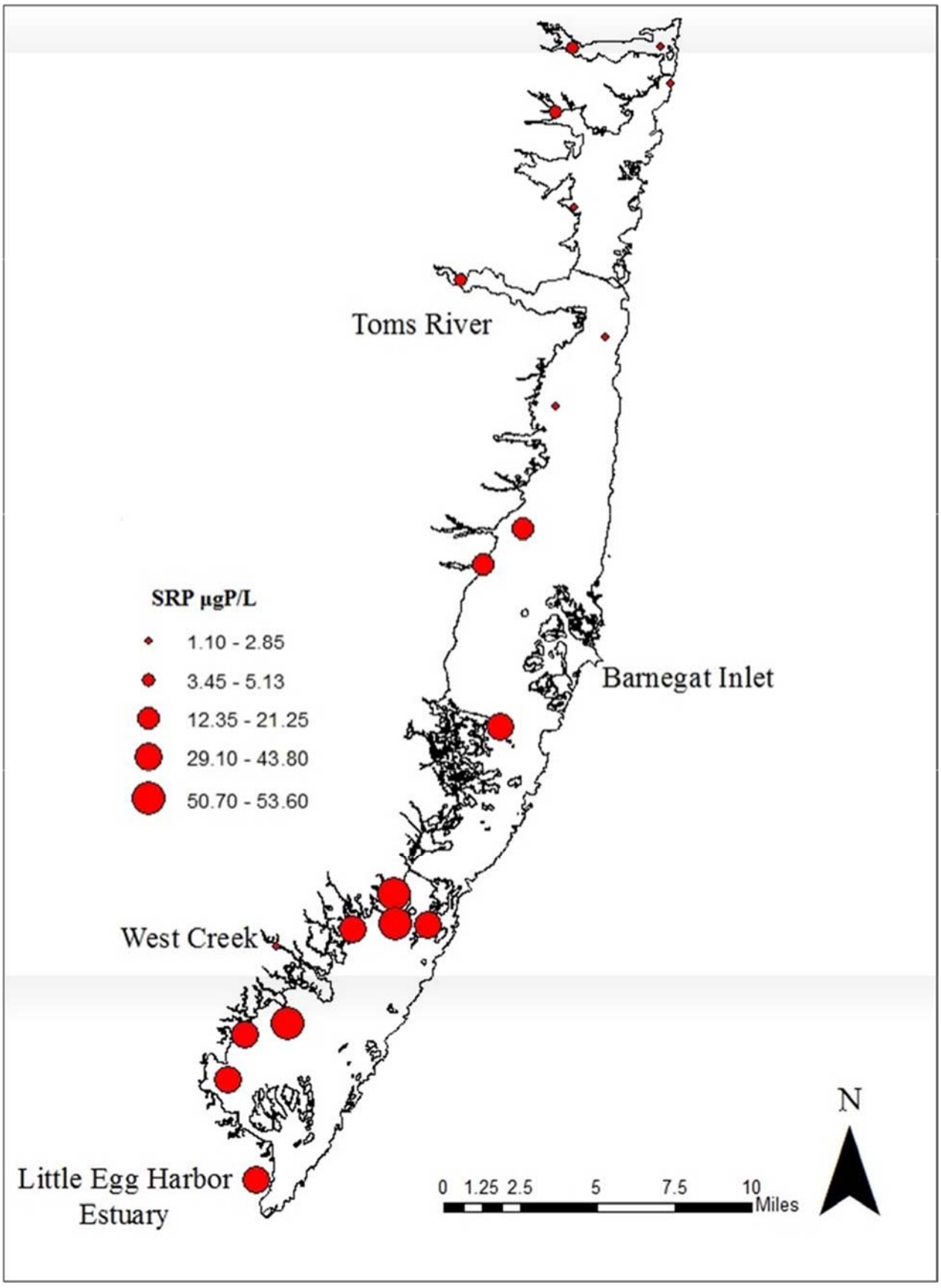


Figure 7. SRP concentrations in 20 different sampling stations during July 2014.

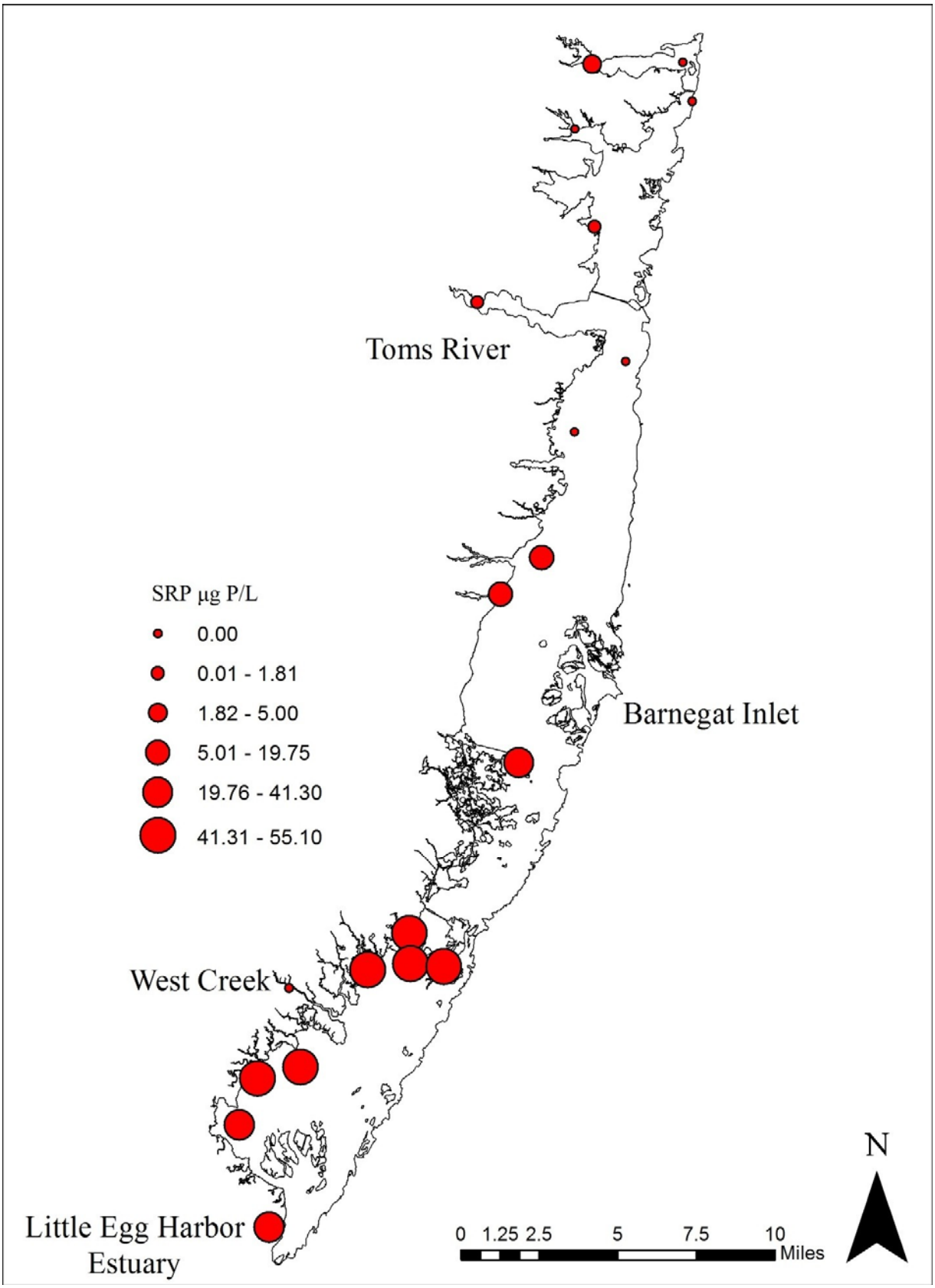


Figure 8. SRP concentrations in 20 different sampling stations during October 2014. Stations that are depicted with 0.00 µg P/L are the ones with below detection limit of SRP concentration.

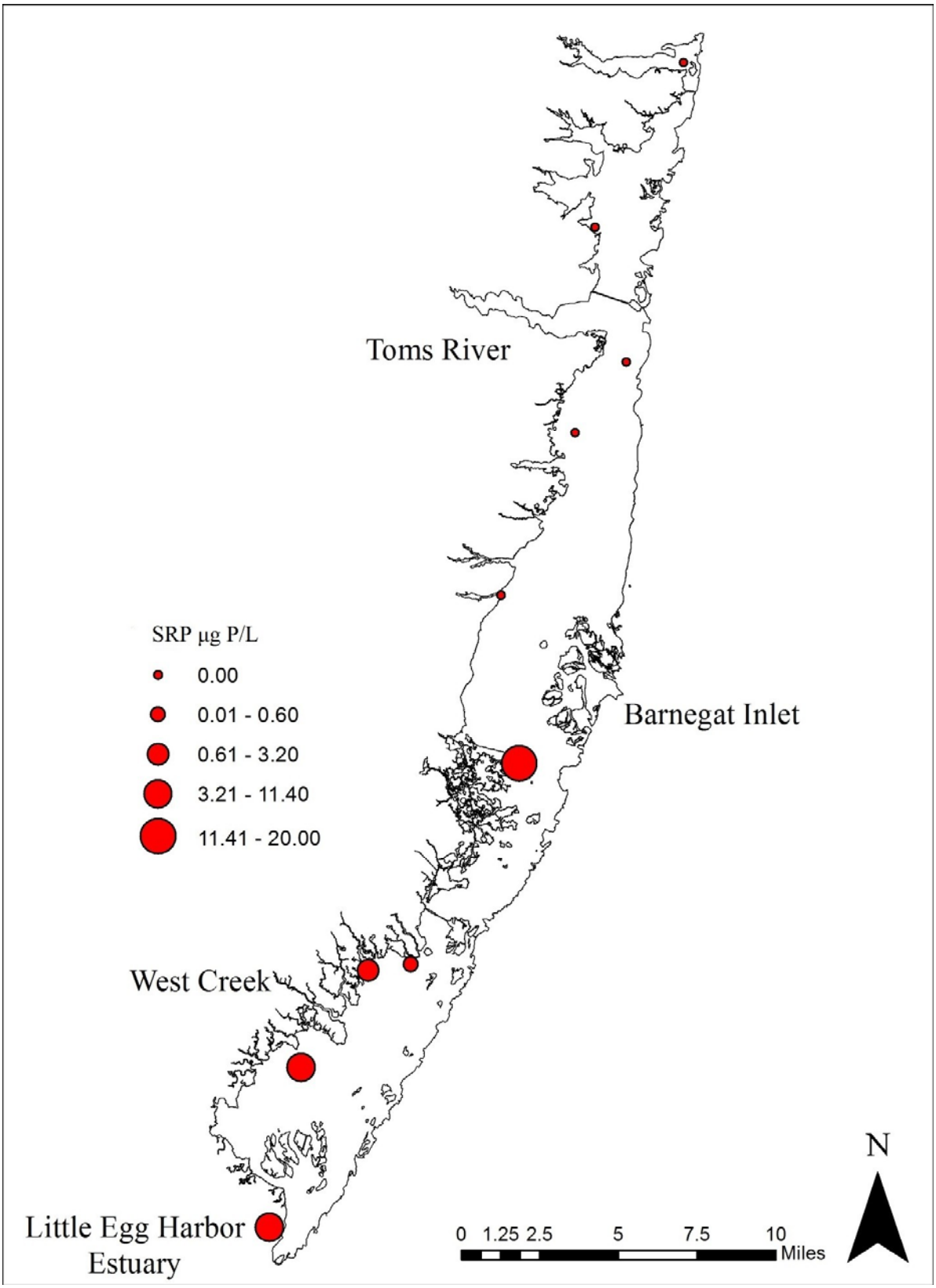


Figure 9. SRP concentrations in 10 different sampling stations during May 2015. Stations that are depicted with 0.00 µg P/L are the ones with below detection limit of SRP

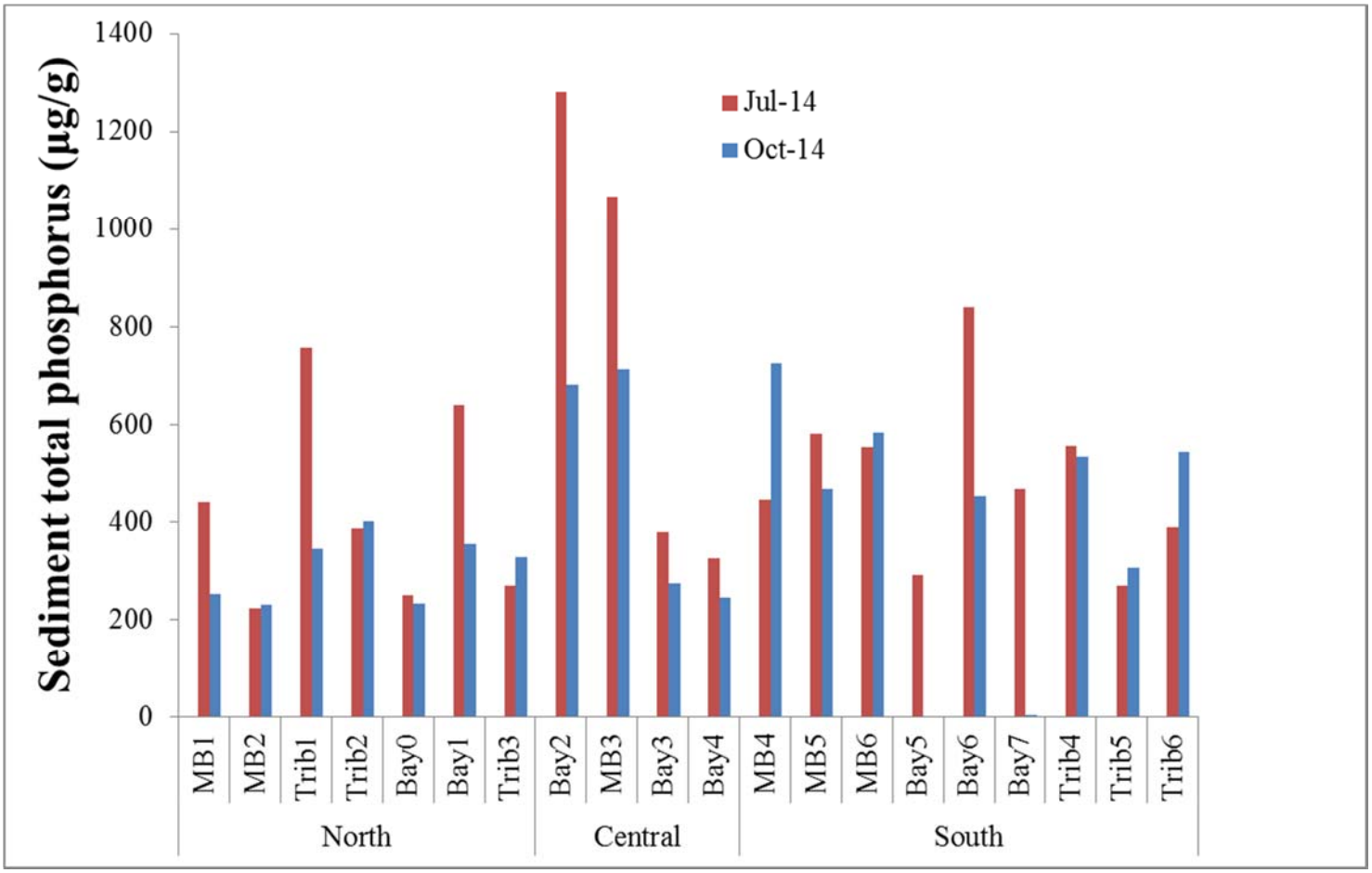


Figure 10. Total phosphorus extracted from sediments collected from all bay and tributaries stations during July and October 2014.

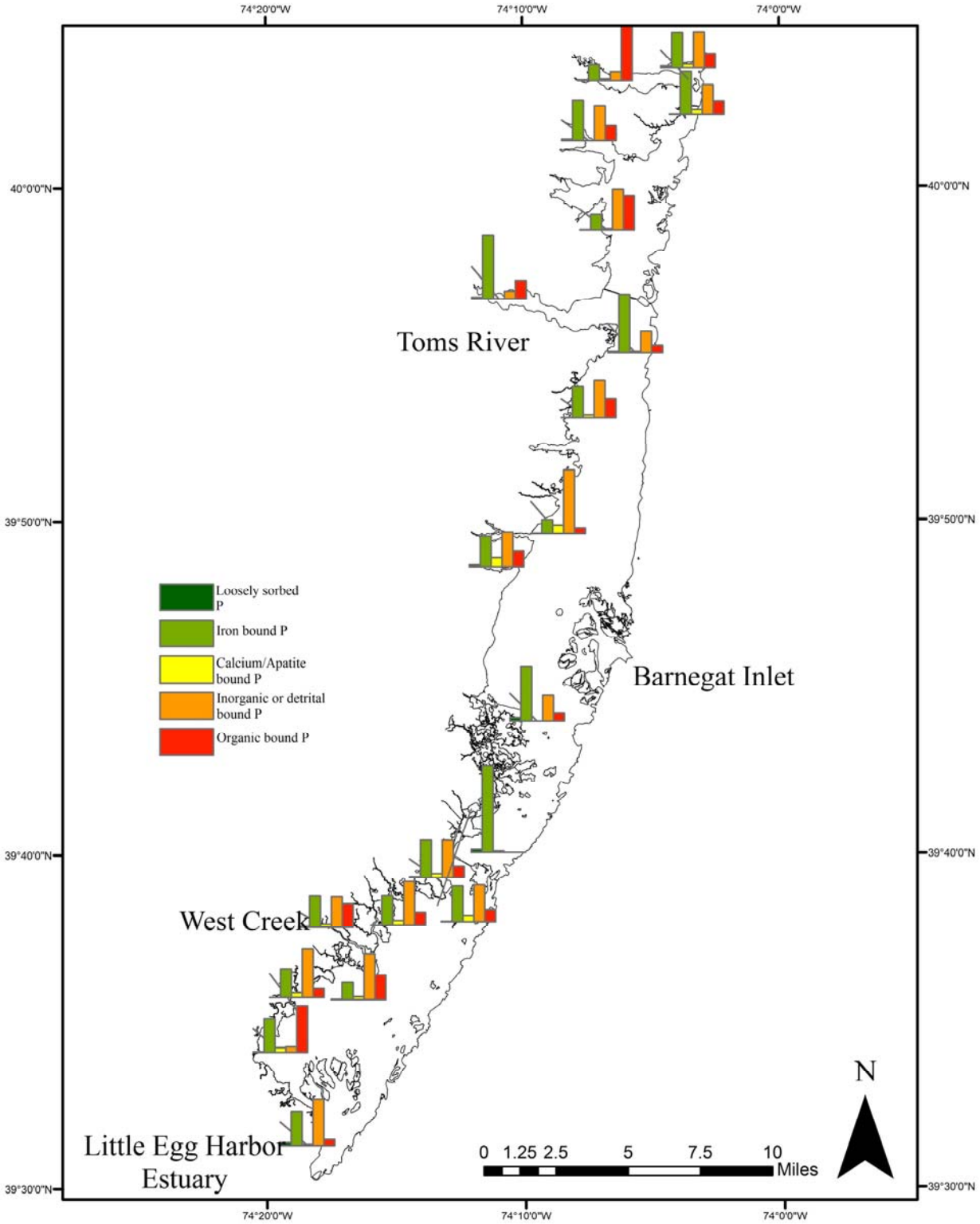


Figure 11a. Five different fractions of phosphorus extracted from sediments collected during July sampling from all bay sites.

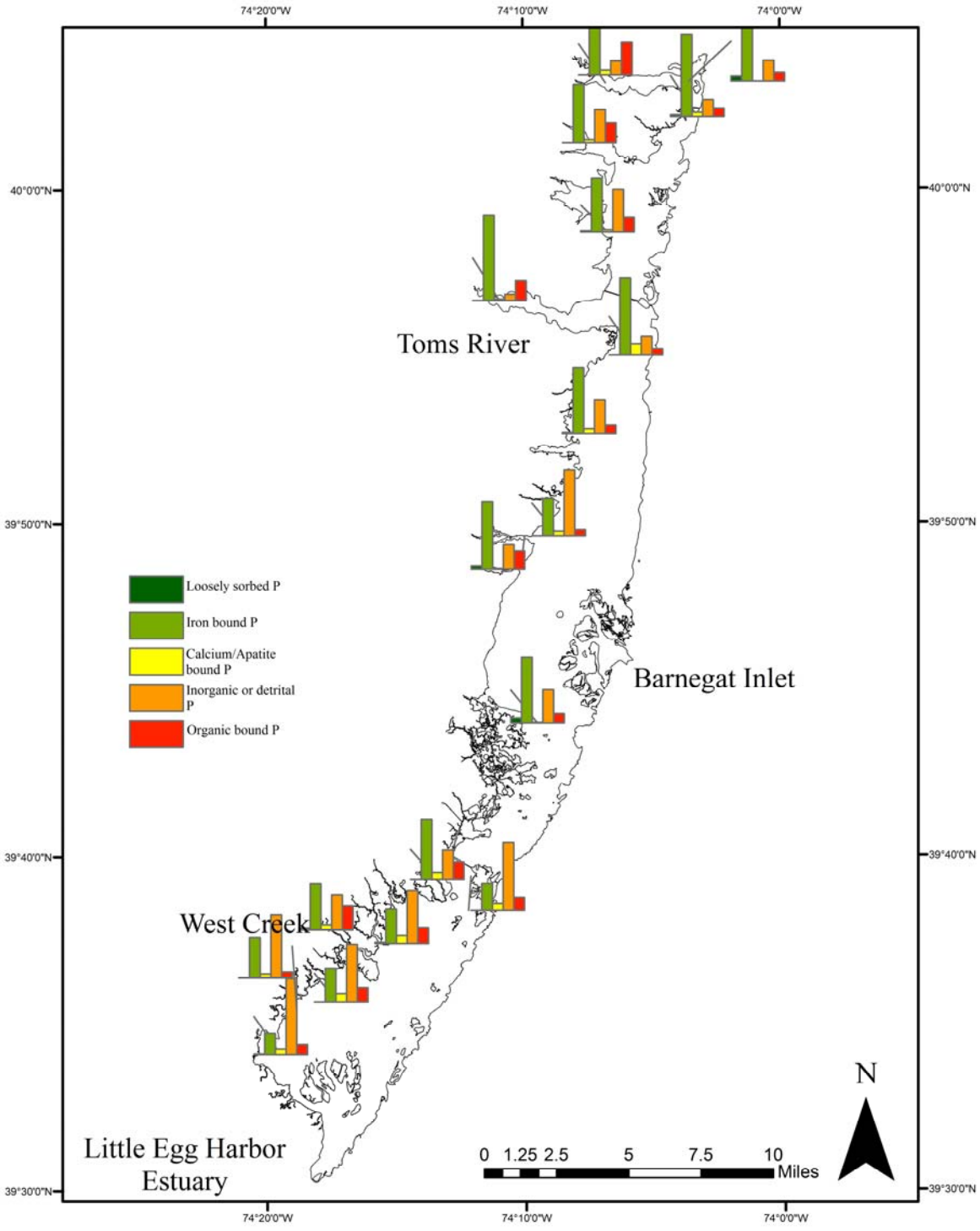


Figure 11b. Five different fractions of phosphorus extracted from sediments collected during October sampling from all bay sites.

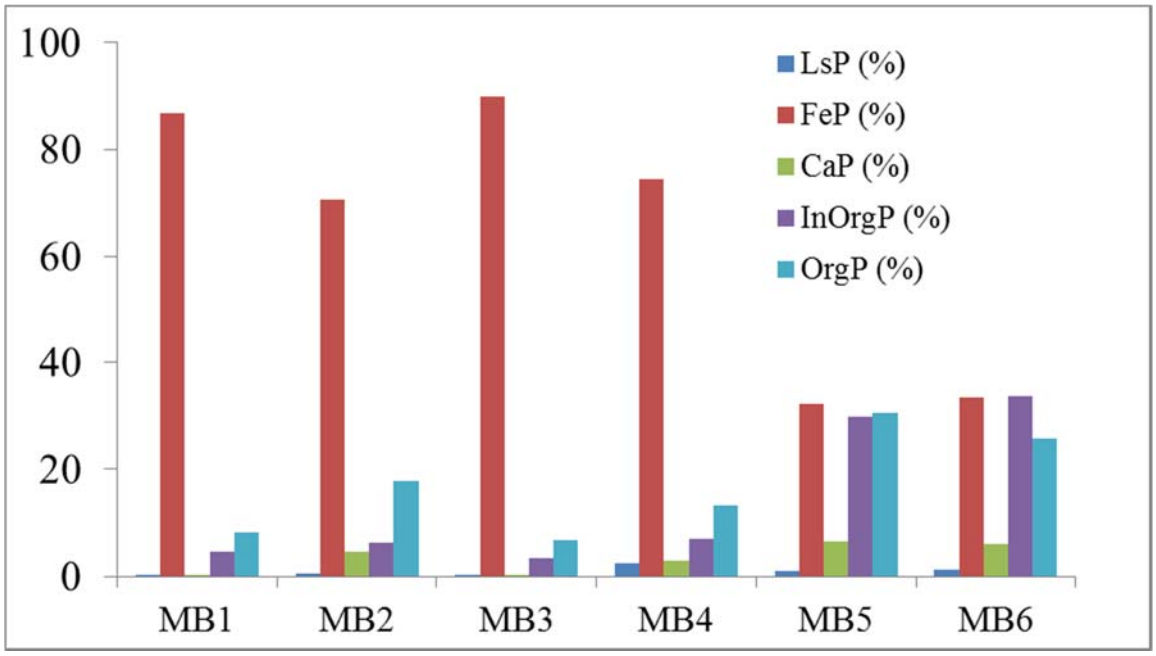


Figure 12. Five different fractions of P in the suspended sediments collected from main bay stations during October 2014 sampling. Abbreviations: LsP = Loosely sorbed P; FeP = Iron bound P; CaP = Calcium/Apatite bound P; InOrgP = Inorganic or detrital P; OrgP = Organic bound P

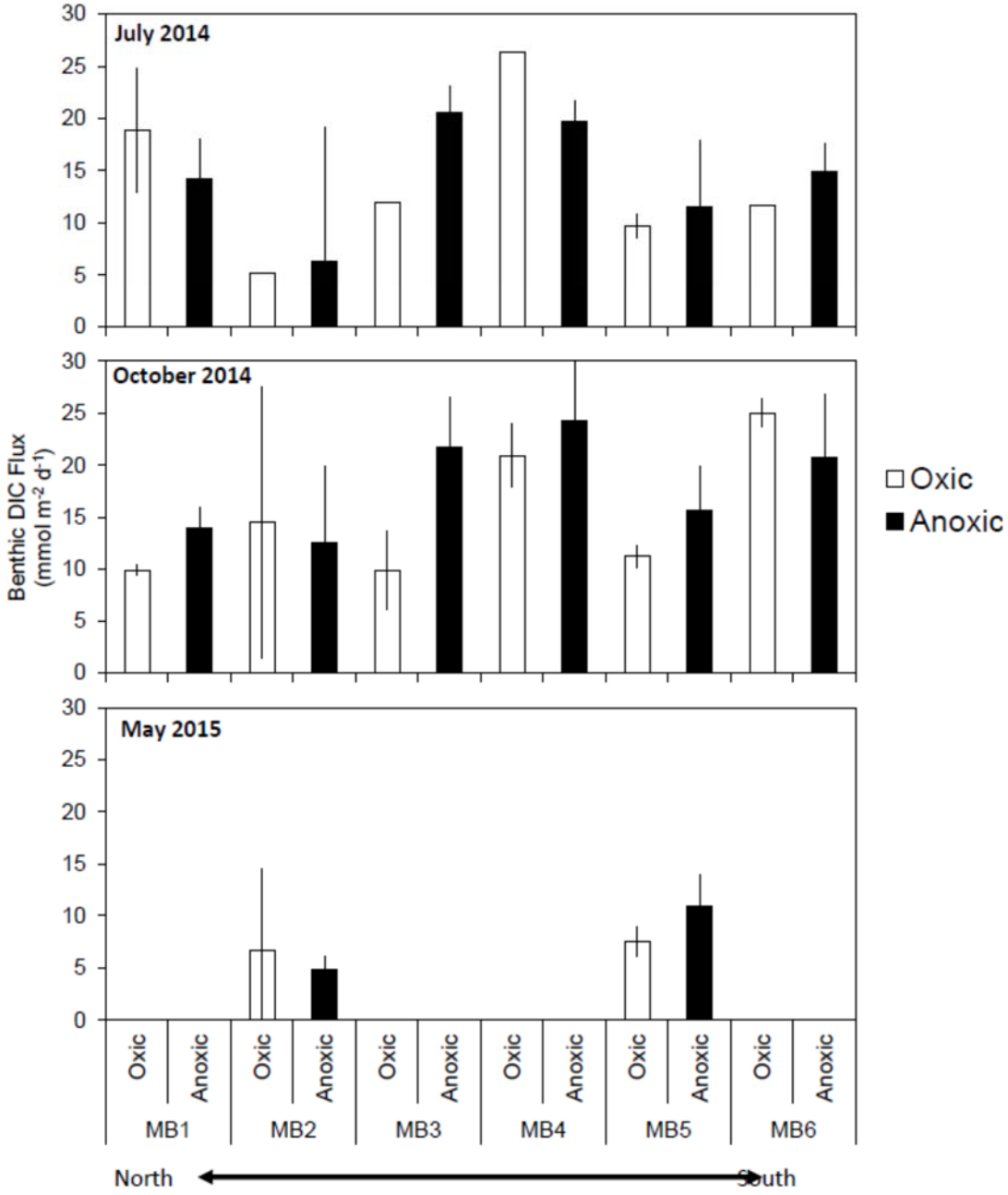


Figure 13. Benthic metabolism (measured using change in dissolved inorganic carbon) in sediment cores collected on July and October 2014 and May 2015 under oxic and anoxic condition.

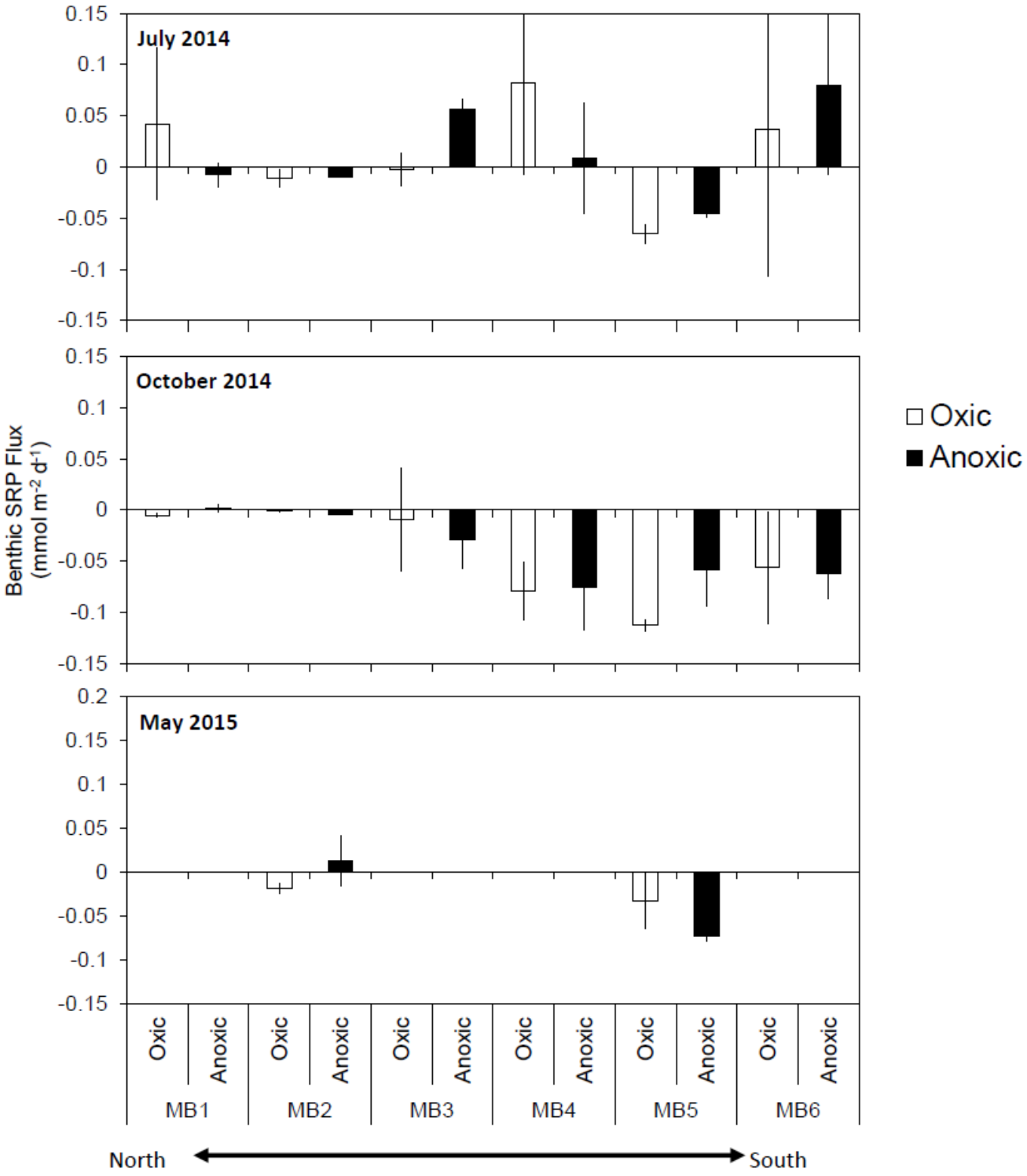


Figure 14. Benthic SRP fluxes identified in the sediment cores collected during July and October 2014 and May 2015 samplings.

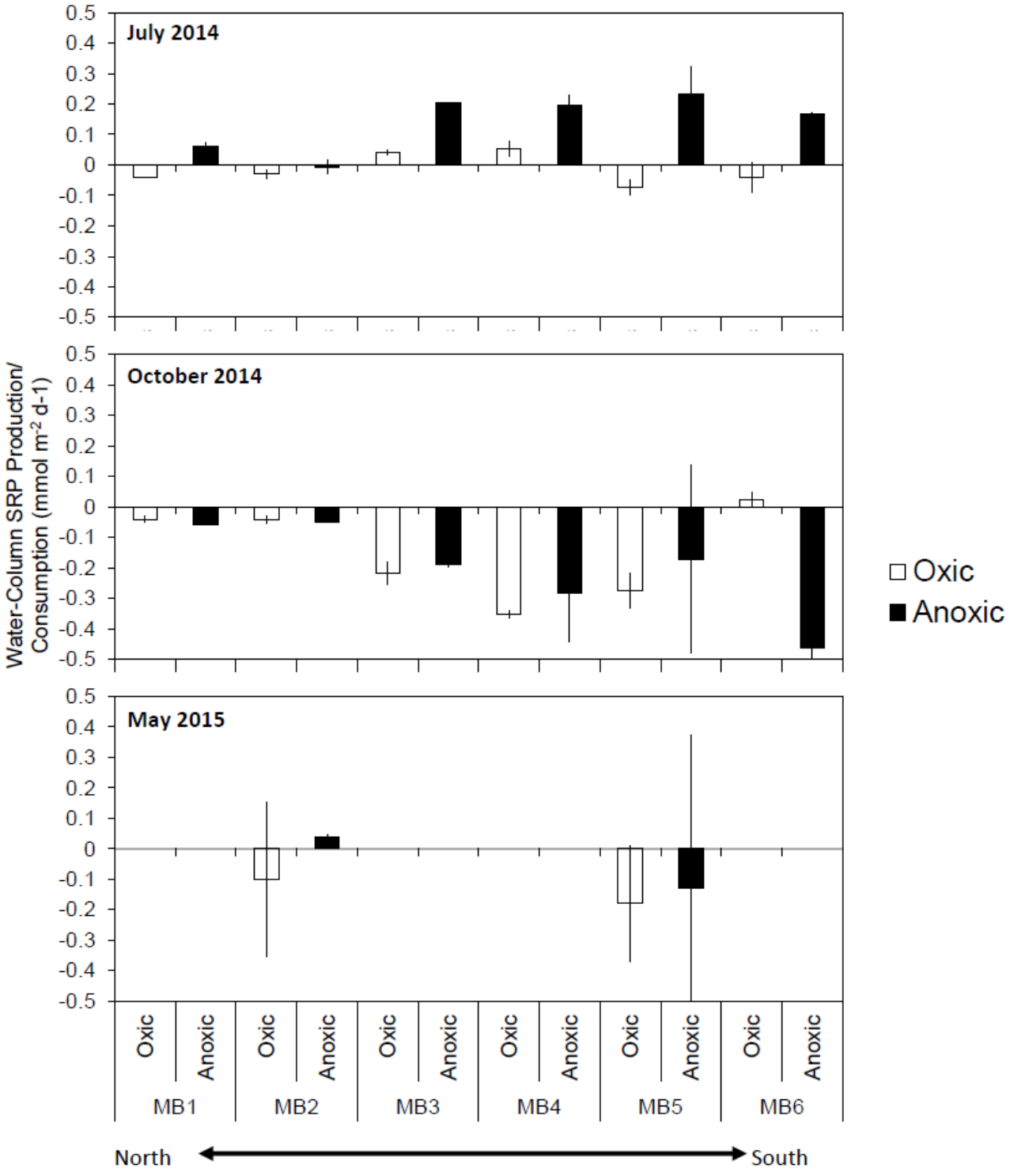


Figure 15. Production and consumption of SRP in the water column under oxic and anoxic conditions.

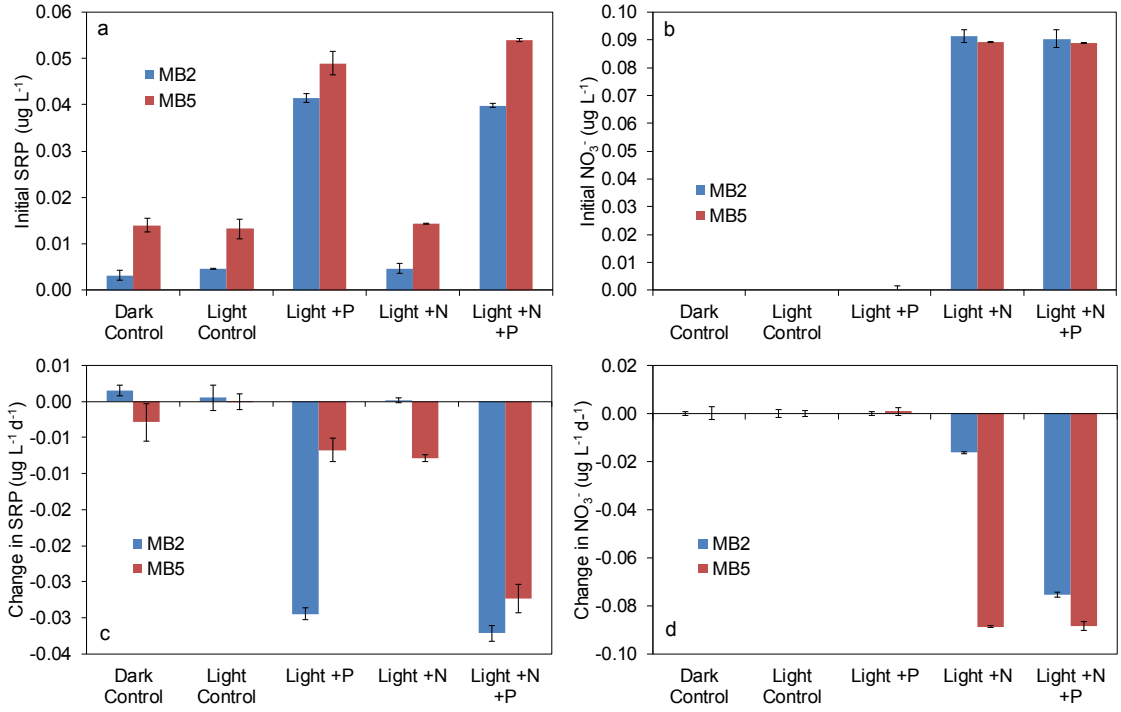


Figure 16. Initial concentrations (top row) of soluble reactive phosphate (SRP; a) and nitrate (NOx; b), and changes of SRP (c) and NOx (d) during 1 day incubation of water from the MB2 and MB5 sites in the May 2016 nutrient limitation experiment.

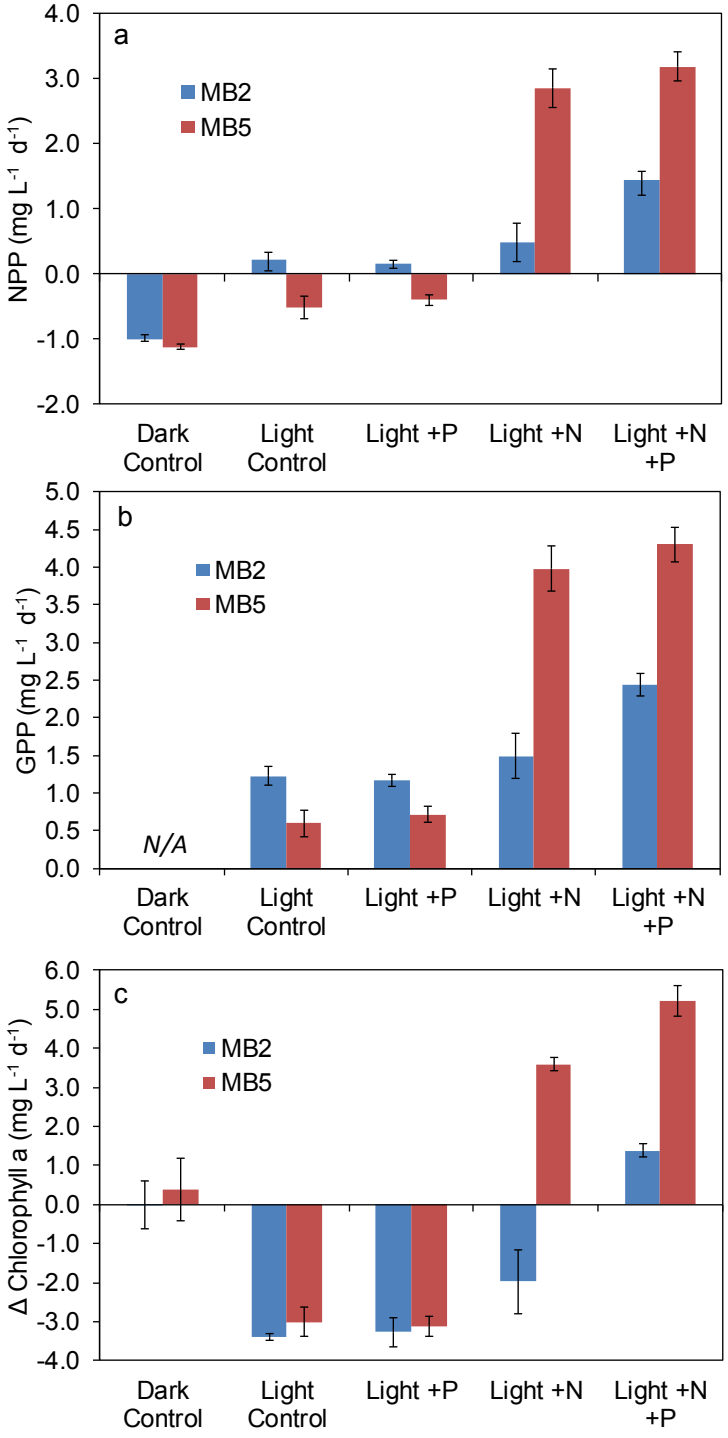


Figure 17. Rates of net primary production (NPP; a), gross primary production (GPP; b), and the change in chlorophyll a (c) for water from sites MB2 and MB5 incubated in the dark and light with varying nutrient additions.

Tables

Table 1. Nomenclature and characteristics of the various sediment fractions of bound P.

Fraction Name	Label	Characteristics
Loosely sorbed P	LsP	Exchangeable forms of P that forms complexes of $MgPO_4^-$ when reacted with $MgCl_2$
Iron bound	FeP	Reducible Fe/Al/Mn-bound P – reduced by dithionite and subsequent chelation by sodium citrate
Calcium bound P	CaP	Apatite + $CaCO_3$ bound P that dissolutes at low pH when extracted by acetate
Inorganic bound P	InorP	Apatite bound P or detrital P that dissolutes with the addition of acid
Organic bound P	OrgP	Organic matter bound P that was dry oxidized and extracted with acid

Table 2 Surface water quality variables during three sampling events in the Barnegat Bay. Abbreviation: NS – No Sample

	Jul-14						Oct-14						May-15					
Stations	Sal (ppt)	Chl (µg/L)	DO (mg/L)	pH	Temp (°C)	TSS (mg/L)	Sal (ppt)	Chl (µg/L)	DO (mg/L)	pH	Temp (°C)	TSS (mg/L)	Sal (ppt)	Chl (µg/L)	DO (mg/L)	pH	Temp (°C)	TSS (mg/L)
Bay 0	21.63	17.6	8.3	7.9	23.6	25.98	23.39	9.3	8	7.57	20.1	30.2	22.27	3.7	6.61	7.65	20.06	8.93
Bay 1	19.26	11.3	8.19	7.9	24.1	18.87	20.27	13.9	9.03	7.97	16.6	33.7	17.22	3.7	7.22	7.76	22.24	4.9
Bay 2	24.93	10.5	7.46	7.9	24.2	15.52	23.1	10	8.28	7.87	16.2	47.5	21.85	4.8	7.66	8	21.82	7.68
Bay 3	28.54	9.9	6.78	7.8	25.9	49.78	26.64	4.7	7.93	7.81	17	38.8	26.54	3.4	7.26	8.02	21.11	6.95
Bay 4	28.73	3.9	6.43	7.7	23.3	47.53	-----	2.1	7.82	7.72	15.7	35.6	27.39	6.6	7.12	7.9	23.05	11.57
Bay 5	28	10.5	8.09	7.9	24.2	38.19	26.75	3.8	7.76	7.74	18.91	53.5	26.8	8.2	7.36	7.95	22.62	6.47
Bay 6	29.72	3.6	6.74	7.9	23.6	48.83	27.67	2.4	7.74	7.73	27.67	27.3	28.9	7.3	7.54	7.91	22.31	23.7
Bay 7	30.13	3	6.99	7.8	19.8	37.13	29.62	2.1	7.84	7.84	18.43	25.6	30.46	4.5	7.93	7.95	17.14	17.83
Trib 1	17.53	21	9.44	8	24.4	33.7	24.1	24.1	9.15	8.03	19	35.0	NS	NS	NS	NS	NS	NS
Trib 2	16.42	12.8	9.11	8	25	42.3	19.26	15.1	8.95	7.78	17.6	32.9	NS	NS	NS	NS	NS	NS
Trib 3	12.88	32.5	8.63	7.7	23.9	26.15	6.7	11.6	9.11	7.33	18.2	20.7	NS	NS	NS	NS	NS	NS
Trib 4	26.37	20.5	8.11	7.9	24.8	48.76	24.49	7.5	8.25	7.69	18	72.8	NS	NS	NS	NS	NS	NS
Trib 5	17.3	6	7.4	7.4	23.3	12.44	1.46	11.5	8.99	6.84	19.17	11.8	NS	NS	NS	NS	NS	NS
Trib 6	29.2	3	7.96	8	22.7	30.93	28.35	1.3	8.49	7.88	18.25	20.6	NS	NS	NS	NS	NS	NS
MB1	20.73	18.8	9.01	8	24.1	47.82	22.35	9.4	8.87	7.98	17.2	34.5	NS	NS	NS	NS	NS	NS
MB2	23.07	5.2	7.89	8	23.7	32.9	21.6	12.1	8.93	7.97	16.5	30.4	21.26	2.8	7.41	8.04	22.1	6.25
MB3	28.34	10.4	7.22	7.9	23.8	32.58	3.06	6.9	8.18	7.88	16.1	32.8	NS	NS	NS	NS	NS	NS
MB4	29.6	2.3	9.5	8.2	24.1	38.77	27.44	1.6	9.45	7.98	17.5	36.5	NS	NS	NS	NS	NS	NS
MB5	27.8	10.9	7.59	7.8	23.9	57.06	26.14	5.8	7.41	7.66	18.85	92.5	25.21	5.3	7.33	7.85	23.26	8.82
Bay 7 (original)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	31.26	7.9	8.05	7.99	13.84	6.80
MB6	29.47	4.3	6.65	7.9	23.6	33.15	27.7	2.9	7.57	7.71	17.93	55.1	NS	NS	NS	NS	NS	NS

Table 2 Contd.

	Jul-14		Oct-14		May-15	
Stations	NH4+ (µgN/L)	NO2+3(µgN/L)	NH4+ (µgN/L)	NO2+3(µgN/L)	NH4+ (µgN/L)	NO2+3(µgN/L)
Bay 0	5.4	0.8	13	20.6	37.5	14.1
Bay 1	4.5	0.5	8.2	3.6	29.3	10.5
Bay 2	5.4	0.4	7.2	3.9	1.6	2.4
Bay 3	34.9	5.9	92.1	29.4	3.1	1.6
Bay 4	59.2	6.1	84	26.2	4.6	1.7
Bay 5	17.2	19.6	193.9	63.6	3.2	1.1
Bay 6	78.4	23.5	154	52.6	5.7	1.9
Bay 7	36.9	14.7	86.5	28.2	6.5	5.4
Trib 1	4.1	0.4	6	0.4	NS	NS
Trib 2	5.2	0.4	6.1	13.8	NS	NS
Trib 3	4.9	199.3	24.2	350	NS	NS
Trib 4	26	28.6	178.4	51	NS	NS
Trib 5	5.8	24.1	4.6	61.5	NS	NS
Trib 6	11.3	19.3	110.5	32	NS	NS
MB1	5.2	0.4	7.5	1.7	NS	NS
MB2	4.2	0.4	7.5	3.8	2.3	3.0
MB3	8.3	0.4	24.9	11.6	NS	NS
MB4	15.7	8.4	77.3	24.6	NS	NS
MB5	13.8	20.8	199.5	60.7	0.8	1.1
Bay 7 (original)	NS	NS	NS	NS	18.7	8
MB6	38.2	6.8	141.4	43	NS	NS

Table 3 Sediment characteristics identified from July and October 2014 sediment samples.

	Jul-14				Oct-14			
Stations	GS (<63um %)	OC (%)	TN (%N)	TP (%P)	GS (<63um %)	OC (%)	TN (%N)	TP (%P)
Bay 0	27.4	0.98	0.10	0.02	15.7	0.61	0.09	0.01
Bay 1	75.8	2.25	0.21	0.04	74.1	2.13	0.20	0.04
Bay 2	49.4	1.26	0.12	0.04	55.9	1.67	0.18	0.06
Bay 3	74.2	4.44	0.28	0.03	78.6	4.68	0.23	0.03
Bay 4	15.9			0.01	12.5			0.01
Bay 5	44.75	1.13	0.12	0.25	55.6	1.24	0.13	0.03
Bay 6	78.8	1.43	0.15	0.08		2.03	0.19	0.07
Bay 7	30.9			0.03	29.4	0.80	0.11	0.04
Trib 1	96.6	9.80	0.68	0.10	95.2	9.31	0.63	0.09
Trib 2	97.3	4.22	0.32	0.06	96.5	4.58	0.35	0.07
Trib 3	25.15	2.12	0.16	0.02		2.44	0.18	0.02
Trib 4	91.4	3.63	0.30	0.08		3.75	0.30	0.08
Trib 5	95.6	15.05	0.73	0.11	96.4	7.07	0.49	0.08
Trib 6	51.3	0.87	0.10	0.04	53.3	2.16	0.13	0.06
MB1	29	2.13	0.13	0.02	19.6	2.08	0.15	0.01
MB2	7.3			0.01	4.2			0.01
MB3	53.7	1.06	0.12	0.04	57.1	1.13	0.13	0.05
MB4	52.6	1.40	0.14	0.04		1.32	0.14	0.35
MB5	72.2	1.97	0.16	0.05				
MB6	79.2	1.39	0.12	0.04				

Table 4 Different fractions of sediment phosphorus analyzed from July-2014 sediment samples

Date	Station	LsP(%)	FeP(%)	CaP(%)	InorgP(%)	OrgP(%)
Jul-14	MB1	0.22	46.56	5.34	32.71	15.17
Jul-14	MB2	1.44	64.30	1.48	24.27	8.50
Jul-14	MB3	0.29	14.98	9.09	69.53	6.11
Jul-14	MB4	0.29	39.00	6.93	40.42	13.36
Jul-14	MB5	0.18	32.16	5.29	48.19	14.17
Jul-14	MB6	0.22	31.61	5.13	53.09	9.95
Jul-14	Bay0	2.08	38.66	4.20	39.14	15.92
Jul-14	Bay1	0.24	16.62	0.86	44.61	37.67
Jul-14	Bay2	0.15	34.79	2.87	41.25	20.94
Jul-14	Bay3	1.93	33.60	9.69	37.88	16.90
Jul-14	Bay4	3.69	59.66	0.00	27.94	8.71
Jul-14	Bay5	3.36	95.22	1.42	0.00	0.00
Jul-14	Bay6	0.34	18.78	3.22	50.32	27.34
Jul-14	Bay7	3.12	37.83	1.14	51.29	6.62
Jul-14	Trib1	0.89	17.64	1.97	9.58	69.93
Jul-14	Trib2	1.52	44.22	0.00	38.15	16.11
Jul-14	Trib3	1.68	69.62	0.01	8.62	20.08
Jul-14	Trib4	1.29	40.75	4.57	40.75	12.65
Jul-14	Trib5	1.68	34.70	3.91	33.61	26.10
Jul-14	Trib6	0.81	36.90	5.21	6.13	50.95

Table 5 Different fractions of sediment phosphorus analyzed from July-2014 sediment samples

Date	Station	LsP(%)	FeP(%)	CaP(%)	InorgP(%)	OrgP(%)
Oct-14	MB1	1.72	71.74	3.92	15.10	7.53
Oct-14	MB2	2.04	66.60	9.69	16.20	5.50
Oct-14	MB3	1.34	32.20	4.18	56.90	5.40
Oct-14	MB4	1.36	23.3	5.99	58.20	11.2
Oct-14	MB5	1.12	30.62	7.18	46.85	14.23
Oct-14	MB6	1.31	35.00	3.36	55.00	5.30
Oct-14	Bay0	4.40	69.86	0.01	18.14	7.60
Oct-14	Bay1	0.78	47.27	1.81	37.46	12.68
Oct-14	Bay2	0.94	58.02	4.27	29.41	7.36
Oct-14	Bay3	2.68	59.27	0.57	21.62	15.87
Oct-14	Bay4	4.23	57.76	0.51	29.19	8.30
Oct-14	Bay6	1.78	29.20	7.09	49.70	12.20
Oct-14	Trib1	2.77	53.40	3.95	11.90	27.90
Oct-14	Trib2	1.34	50.10	2.63	28.60	17.30
Oct-14	Trib3	1.94	73.70	1.29	5.70	17.40
Oct-14	Trib4	0.83	52.40	6.05	25.50	15.20
Oct-14	Trib5	1.98	40.85	4.71	30.99	21.47
Oct-14	Trib6	0.58	18.55	4.87	67.16	8.85