

Nutrients and chlorophyll at the interface of a watershed and an estuary

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Abstract

We investigated the fates of nutrients entering the Rhode River estuary from its watershed and from atmospheric deposition. Production or consumption of materials in the upper estuary was calculated from a mixing model with chloride as a conservative tracer. The upper estuary produced chlorophyll and dissolved PO_4^{3-} (DPO_4^{3-}) but consumed particulate PO_4^{3-} (PPO_4^{3-}), total inorganic N, dissolved organic N, and particulate organic C. These net fluxes were influenced more by shallow, open-water areas than by the tidal marshes which cover two-thirds of the area of the upper estuary. Ratios of chlorophyll to organic C, N, and P suggest that most of the suspended particulate organic matter in the upper estuary was produced by phytoplankton rather than derived from watershed inputs. The consumption of nitrate due to phytoplankton production and the production of DPO_4^{3-} due to release from particulate P after deposition in sediments resulted in low inorganic N:P ratios, contrasting sharply with the lower estuary and adjacent Chesapeake Bay. Dissolved inorganic N and P entered the upper estuary from the watershed at an atomic ratio of 26 but left the upper estuary at a ratio of 2.7. The release of DPO_4^{3-} from watershed-derived sediments may be a common feature among estuaries and could promote N limitation of primary production in estuarine and coastal waters.

Estuaries function as important sinks and transformers of nutrients, thus altering the quantity and quality of nutrients transported from the land to the sea. The processes that govern the fates of N and P in estuaries differ. Consequently, the ratios of inorganic N to P in estuaries, unlike those in the ocean (Redfield 1958), may vary widely with time and space and may deviate greatly from the ratio of N to P in phytoplankton (e.g. D'Elia et al. 1986). The relative abundance of inorganic N in estuaries may be decreased by denitrification (Seitzinger 1988), by inhibition of N fixation (Howarth and Cole 1985), or by hydrologic factors (Smith 1984). In contrast, abundance of inorganic P may be increased by enhanced release from sediments in the presence of high salinity and SO_4^{2-} (Caraco et al. 1989). These processes may explain why N is the nutrient that most often limits primary production in estuaries (Boynton et al. 1982). In some estuaries, however, high inputs of NO_3^- from water-

sheds may increase the ratio of inorganic N to P and lead to P limitation (D'Elia et al. 1986). Thus, the processes governing the fates of nutrients entering estuaries not only determine the ultimate delivery of nutrients to adjacent coastal waters but also influence which, if any, may limit primary production within the estuary.

In many estuarine systems, tidal marshes are thought to play an important role in the flux and transformation of nutrients, but the nature and significance of their role is controversial. Some studies suggest that marshes may be important sources of organic matter for coastal ecosystems, while others suggest that marshes are relatively unimportant (Nixon 1980). In addition, marshes have been described both as sinks and sources of inorganic nutrients (Nixon 1980). Their role in nutrient flux remains obscure due to difficulties in measuring nutrient exchanges and due to real differences among marshes (Jordan et al. 1983). Moreover, it is difficult to evaluate the significance of marshes without comparative knowledge of nutrient fluxes in adjacent subtidal ecosystems, and such comparative information is often lacking. In fact, there is a paucity of information on nutrient exchanges among linked watershed, estuary, and marsh sys-

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tems because these systems are usually studied separately.

We have studied the flow of N, P, and organic C through the hydrologically linked ecosystems in the Rhode River watershed and estuary. They include several terrestrial ecosystems, tidal marshes, and subtidal estuarine waters (Jordan et al. 1986a). Our goals were to determine the fates of nutrients entering the estuary from the watershed, to compare the uptake and transformation of nutrients in the estuary to the rates of input from the watershed, and to evaluate the role of tidal marshes in nutrient flows. This report focuses on seasonal changes, spatial patterns, and fluxes of nutrients and chlorophyll in the estuary. We describe how N, P, and organic C fluxes from the watershed are altered in transit through the upper estuary and how the role of the tidal marshes compares to that of subtidal, open-water areas.

Methods

Study site—The Rhode River estuary (38°51'N, 75°36'W, Fig. 1) is one of several tributary embayments or subestuaries on the western shore of Chesapeake Bay. It is 550 ha in area and averages 2 m deep with a maximal depth of 4 m. The mean tidal range is 30 cm, but weather conditions often cause more extreme changes in water level. Salinity varies from 0‰ at the head of the estuary in spring to almost 20‰ at the mouth in fall during years with low runoff. As in many subestuaries, water exchanges between the lower Rhode River and Chesapeake Bay are driven by changes in salinity in the Bay (Han 1974), but water in the upper estuary is measurably diluted by discharge from the local watershed. Accordingly, we focused on the upper estuary as the site where nutrient effluxes from the watershed would have the greatest effect.

The 2,300-ha watershed of the upper estuary (Fig. 1) is 63% forest, 18% cropland, 13% pasture, and 7% residential. Most N and P discharged from the watershed originates from cropland (Jordan et al. 1986a). The upper estuary includes 23 ha of shallow mudflat and creek areas bordered by 12 ha of low marsh and 22 ha of high marsh. The low marsh is vegetated primarily by *Typha*

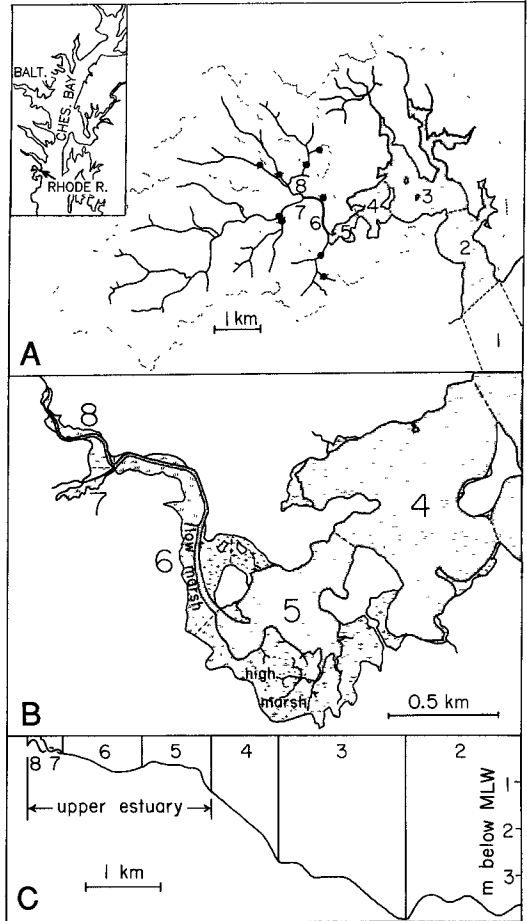


Fig. 1. A. The Rhode River and its watershed. Numbered segments of the river relate to sampling (see text). Dotted lines indicate the subwatersheds of the upper estuary. Dots indicate automated watershed monitoring stations. Inset shows location of Rhode River on upper Chesapeake Bay. B. Detail of upper segments of estuary showing marshes. C. Depth below mean low water along the channel of the estuary.

angustifolia and the high marsh by *Spartina patens*, *Distichlis spicata*, *Scirpus olneyi*, and several other species. The mudflats and creeks are exposed by < 1% of the low tides, so they are essentially subtidal.

Sampling and analysis—For sampling purposes we divided the estuary into eight segments with lengths greater than a tidal excursion and boundaries corresponding to constrictions in the width of the estuary (Fig. 1, Table 1). Although we began sampling in 1971, our most intensive sampling was from 1980 to 1986 and focused on segments 4–

Table 1. Areas and volumes of segments of the Rhode River at mean tide, and the area of watershed draining directly into each segment. Data on segments 1, 2, and 3 from Han (1974).

Segment	Area (ha)	Volume (10^3 m ³)	Watershed (ha)
1	408	6,970	150
2	185	4,070	184
3	324	6,430	717
4	54.2	862	115
5	19.1	129	237
6	2.90	14.2	42.3
7	0.170	0.593	1,260
8	0.398	1.32	746

8. During those years we took spatially integrated samples each week from March to November by pumping surface water continuously while cruising the lengths of the segments. We also measured vertical profiles of salinity and temperature at the boundaries and centers of the segments with a Beckman RS5-3 salinometer.

Samples to be analyzed for dissolved substances were filtered with prewashed 0.45- μ m Millipore filters. Total P in filtered and unfiltered samples was digested to orthophosphate with perchloric acid (King 1932). Orthophosphate was analyzed by reaction with stannous chloride and ammonium molybdate (Am. Public Health Assoc. 1976). Internal standards were used to correct phosphate concentrations for chloride interference. Samples for total Kjeldhal N were digested with H₂SO₄, Hengar granules, and H₂O₂ (Martin 1972). The resultant NH₃ was distilled and analyzed by Nesslerization (Am. Public Health Assoc. 1976). Dissolved NH₄⁺ was oxidized to NO₂⁻ by alkaline hypochlorite (Strickland and Parsons 1972), dissolved NO₃⁻ was reduced to NO₂⁻ by Cd amalgam, and NO₂⁻ was analyzed by reaction with sulfanilamide (Am. Public Health Assoc. 1976). PO₄³⁻ and NH₄⁺ bound to particles were extracted by collecting particles on 0.4- μ m Nuclepore filters, and then rinsing with 1 M KCl (Keeney and Nelson 1982) to extract NH₄⁺, or with 0.5 N H₂SO₄ to extract PO₄³⁻ (Correll and Miklas 1975). From results of the above analyses, we calculated particulate organic N (PON) and P (POP), and dissolved organic N (DON) and P (DOP).

Before 1983 dissolved and particulate or-

ganic C (DOC and POC) were analyzed by drying samples at 60°C, followed by reaction with potassium dichromate in 67% H₂SO₄ at 100°C for 3 h (Maciolek 1962) with HgSO₄ added to complex halides (Dobbs and Williams 1963). Organic C was calculated from the amount of unreacted dichromate measured colorimetrically (Maciolek 1962; Gaudy and Ramanathan 1964). Since 1983 organic C has been analyzed by persulfate digestion in sealed ampoules (Strickland and Parsons 1972) and measurement of the resulting CO₂ with a Coulometric carbon analyzer. For 4 yr we used both methods to ensure their comparability.

Chl *a* was measured spectrophotometrically (Strickland and Parsons 1972; Jeffrey and Humphrey 1975) after collecting particles on Schleicher and Schuell glass-fiber filters, macerating the filters, and extracting the pigments with a mixture of acetone and DMSO (Shoaf and Lium 1976). Chloride was measured directly with a Dionex model 16 ion chromatograph until 1986, when it was measured with a Technicon autoanalyzer (method 696-82 W). Total suspended particulate matter (TSP) was measured by filtering through prewashed, preweighed, 0.4- μ m Nuclepore filters, rinsing with distilled water to remove salts, drying, and reweighing.

Since 1974 we have monitored discharges from the watershed of Muddy Creek at the head of the Rhode River with a network of automated samplers (Fig. 1) that measure water flow and take samples in volumes proportional to the flow rate (Jordan et al. 1986a). These samples were composited weekly and analyzed for total N, P, organic C, PO₄³⁻, NO₃⁻, and NH₄⁺. Since 1973, we have monitored bulk atmospheric precipitation of NH₄⁺, NO₃⁻, NO₂⁻, PO₄³⁻, and total N and P (Correll et al. 1984; Weller et al. 1986).

Mixing model—To estimate production and consumption of nutrients and chlorophyll in the upper estuary (segments 5–8), we constructed a model of mixing using chloride as a conservative tracer. The rate of change of chloride content of the upper estuary was modeled as the rate of input from the watershed, plus the rate of input

from segment 4 (the downstream end-member), minus the rate of output to segment 4:

$$V \, dC_u/dt = RC_r + QC_c - (R + Q)C_u$$

where V is the volume of water in the upper estuary, C_u is the concentration of chloride in the upper estuary, C_c is the concentration in segment 4, C_r is the concentration in watershed runoff, R is the rate of water discharge by the watershed, and Q is the rate of water mixing from segment 4 to the upper estuary. Every variable except Q was calculated from consecutive measurements that were no more than 16 d apart. Q was a constant fitted to all the data such that the measured change in chloride content of the upper estuary would, on average, equal the calculated change. In other words, we found a single value for Q which would satisfy the requirement that chloride be conserved.

The variables for the model were determined as follows. The chloride concentration in the upper estuary was calculated as a volume-weighted average of concentrations in the integrated samples from the separate segments 5–8. Water discharge from 36% of the watershed was measured by the automated samplers (Fig. 1). Discharge rate per unit area from the unmonitored watershed was estimated from the average from monitored areas. The rate of discharge was averaged over each period defined by consecutive samplings. We assumed that watershed discharge contained a constant concentration of 0.3 mM chloride—an approximate average of previous measurements (Correll et al. 1984). Inputs of chloride from the watershed, however, were usually trivial. The volumes of the segments were calculated from bathymetric data and from the tidal height at the time of sampling. To minimize differences in volume between samplings, we generally sampled at high tide. When there were differences in volumes between samplings, however, we estimated what the chloride content of segments 5–8 would have been on the second sampling had volume remained constant. We did so by either adding or subtracting an amount of chloride equal to the volume difference times the average of the chloride concentration in segment 4 and in segments 5–8.

To estimate the rates of production or consumption of nonconservative materials in the upper estuary, we substituted their concentrations into the mixing model with the value of Q determined from the chloride data. A term for the rate of production (or consumption) was added to the right-hand side of the equation defining the rate of change of the amount of material in the upper estuary. Inputs from the watershed were measured with the automated sampling stations. The proportions of dissolved and particulate materials in watershed inputs were estimated for each automated station from a regression model using time of the year and instantaneous water flow rate as independent variables (Weller et al. in prep.). For some forms of N, the input from atmospheric precipitation directly onto the upper estuary influenced the production estimates. In these cases we subtracted the amount of material entering from precipitation to obtain net production. Our calculations of fluxes based on the mixing model used only data from 1980 to 1986 when sampling was generally weekly. Fluxes were calculated from concentration data from each pair of consecutive samplings no more than 16 d apart.

Results

Spatial and seasonal patterns—Because seasonal and spatial patterns were similar from year to year, we graphed concentrations averaged by week of the year across all years to illustrate the general patterns (Figs. 2–4). Salinity was lowest in spring and highest in fall due to seasonal changes in watershed discharge (Fig. 2). Salinity decreased upstream from segment 4 and was often zero in the most upstream segments in spring. Horizontal salinity gradients downstream of segment 4 were relatively slight. The vertical and horizontal gradients in salinity were steepest from late fall to spring (Fig. 2). From May through October there were only slight vertical gradients in salinity, however, suggesting that the water column was relatively well mixed at that time of the year.

The contrasting seasonal and spatial patterns of dissolved PO_4^{3-} (DPO_4^{3-}) and $\text{NO}_3^- + \text{NO}_2^-$ (NO_3^-) concentrations (Fig. 3) in-

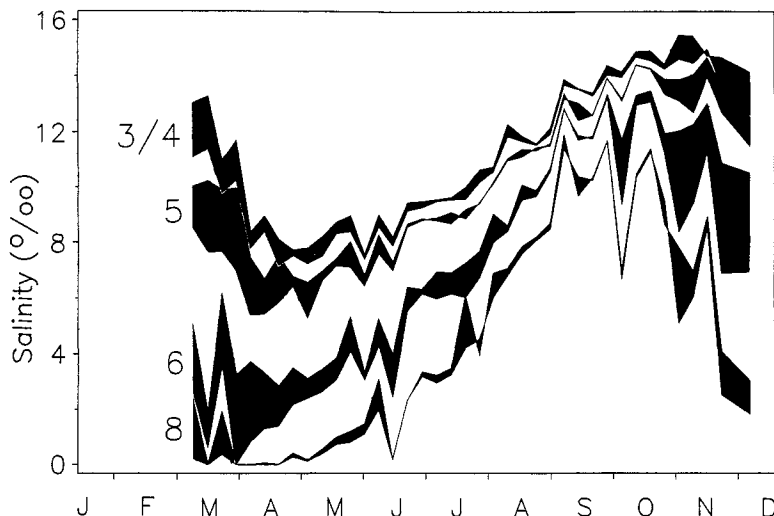


Fig. 2. Salinity vs. time of year at the boundary of segments 3 and 4, and at the centers of segments 5, 6, and 8. Data are weekly means from 1980 to 1986. The upper edge of the bold lines indicates salinity at the bottom of the water column; the lower edge indicates salinity at the surface.

dicade that very different processes govern their fates in the upper estuary. For example, DPO_4^{3-} peaked in summer when watershed discharge was lowest, but NO_3^- peaked in spring when watershed discharge was highest (Fig. 3). Concentration gradients suggest that DPO_4^{3-} is produced in the upper estuary, especially in summer, because DPO_4^{3-} concentrations are higher in segment 5 than in upstream or downstream segments. In contrast, NO_3^- appears to be consumed in the upper estuary, especially in spring, because NO_3^- concentrations are lower in segment 5 than at the mouth of the estuary or in segments 7 and 8 (Fig. 3) where most of the watershed inputs enter (Fig. 1). Spatial and seasonal patterns in the variations of dissolved NH_4^+ (DNH_4^+) were less clear, with peaks in the fall and spring differing among the segments (Fig. 3).

The ratio of dissolved inorganic N (DIN) to P (DIP) varied spatially and seasonally, reflecting the contrasting patterns of NO_3^- and DPO_4^{3-} variation. For example, at segment 1 (the mouth of the Rhode River) the median atomic ratio of DIN to DIP was 165 (123–362, 25th–75th percentiles) in March and 23 (8.1–85.6) in August, while at segment 5 the median ratio was 40 (21–84) in March and 1 (0.74–1.63) in August. Thus, comparison to the Redfield (1958) ratio

(N:P = 16) suggests that phytoplankton growth could be limited by either N or P depending on location and season. It is also possible that neither nutrient is limiting. The ratio simply indicates which is in shorter supply relative to the demands of phytoplankton growth.

Seasonal patterns of Chl *a* concentrations (Fig. 3) were generally the opposite of those for NO_3^- , suggesting that the seasonal depletion of NO_3^- is due to assimilation by phytoplankton. Spatial patterns of chlorophyll concentration varied with season, probably in response to variations in flushing by watershed discharge. In spring Chl *a* concentration decreased with distance upstream of segment 4, but in summer it increased with distance upstream. Patterns for particulate and dissolved organic P, N, and C were very similar to those for Chl *a*.

A large fraction of the total PO_4^{3-} in the water column was bound to suspended particles, and the partitioning of PO_4^{3-} between dissolved and particulate forms varied spatially. Particulate phosphate (PPO_4^{3-}) concentrations were higher than DPO_4^{3-} concentrations in the upstream segments, but lower than DPO_4^{3-} concentrations in the downstream segments (Figs. 3 and 4). The seasonal patterns of PPO_4^{3-} were similar to those of DPO_4^{3-} , as would be expected if

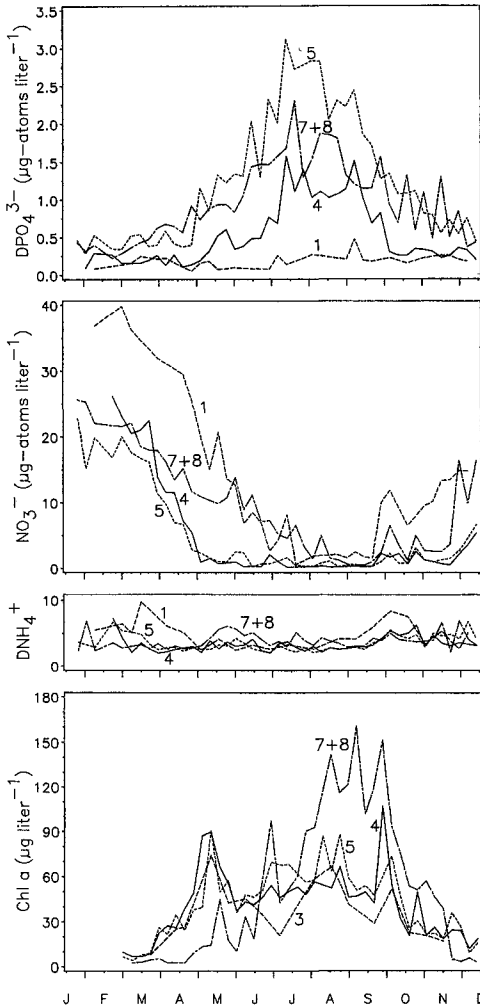


Fig. 3. DPO_4^{3-} , NO_3^- , DNH_4^+ , and $\text{Chl } a$ concentrations vs. time of year in numbered segments of the estuary. Data are means of all available measurements within each week and represent 7–16 yr of measurements.

the particulate and dissolved fractions were in equilibrium. Their spatial gradients differed, however. PPO_4^{3-} concentrations were always higher in segments 7 and 8 than in downstream segments, while DPO_4^{3-} concentrations peaked in segment 5 in summer. This pattern partly reflected the distribution of suspended particles, which decreased in concentration with distance downstream (Fig. 4), but the distribution of particles did not account completely for the gradient in PPO_4^{3-} . The amount of PPO_4^{3-} per mass of particulate matter at given concentrations

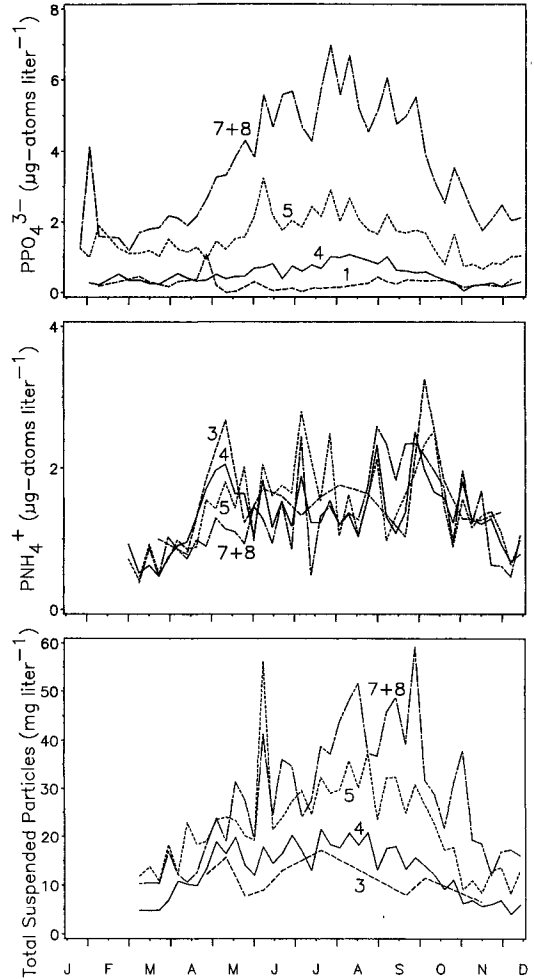


Fig. 4. As Fig. 3, but of PPO_4^{3-} , PNH_4^+ , and TSP concentrations.

of DPO_4^{3-} was greater in segments 7 and 8 than in downstream segments (Fig. 5). This disparity suggests either that suspended particles release bound PO_4^{3-} to solution as they move downstream or that different types of suspended particles are present in the different segments.

Particulate NH_4^+ (PNH_4^+) concentrations were generally much lower than DNH_4^+ concentrations (Figs. 3, 4). They were highest in summer and showed no clear spatial gradients. Surprisingly, the amount of PNH_4^+ per mass of particulate matter was not correlated with the concentration of DNH_4^+ , suggesting that the two fractions

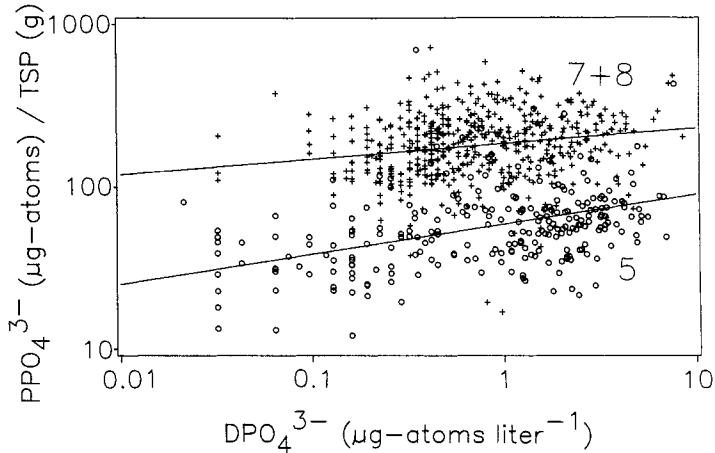


Fig. 5. PPO_4^{3-} vs. DPO_4^{3-} concentration in segments 5 (O), 7 (+), and 8 (+). Data are from 1980 to 1986. Lines were fitted by principal components analysis. The correlations were statistically significant ($P < 0.05$), but explained only 15% of the variance for segment 5 and 5% of the variance for segments 7 and 8 combined.

were not in equilibrium or that the binding sites for PNH_4^+ were always saturated.

Fluxes—To calculate the fluxes of nutrients between the upper and lower estuary, we used a mixing model that combined segments 5–8 as one compartment representing the upper estuary. Despite differences in concentrations among these segments, there were advantages to combining them in the flux analysis. Segments 6–8 are of such small volumes (Table 1) that they are often completely flushed by watershed discharge, eliminating upstream mixing. Segments 7 and 8 receive most of the direct watershed inputs. Combining them with segment 5 simplified the flux analysis while permitting the summing of the watershed inputs from segments 5–8. Moreover, the concentration data indicated that segment 5 is a site of active nutrient transformation, and comparative data on nutrient exchanges from tidal marshes in segments 5 and 6 are available (Jordan et al. 1983).

We used a constant upstream mixing rate (Q) in our model. To confirm that it adequately represented mixing, we used the model to predict the chloride concentration in segments 5–8 from the measurements of concentration in segment 4 and water inflow from the watershed. In general, the model predictions came close to the measured concentrations despite the use of a constant Q (Fig. 6). There were a few instances, how-

ever, where an abrupt change in chloride concentration was not well predicted (e.g. in June and November 1985, Fig. 6). Also, the model systematically overestimated chloride concentrations during summer and fall 1980 and underestimated them during spring 1982 and 1983. Undoubtedly, there were transient conditions and changes in upstream mixing rates that the model could not simulate.

We also tested models in which Q was permitted to vary among pairs of samplings, but they produced extremely variable estimates of Q that were sometimes negative, implying mixing against the concentration gradient. One problem is that the value of Q is difficult to estimate when the salinity gradient is slight. We concluded that the model with a constant Q gave the most useful estimate of mixing from our data.

The upstream mixing rate that produced the best representation of conservative mixing of chloride was $51,000 \text{ m}^3 \text{ d}^{-1}$. Given this rate, we estimate that the half-life of a conservative tracer in segments 5–8 would be about 2.5 d during periods of low watershed flow ($0\text{--}5,000 \text{ m}^3 \text{ d}^{-1}$) and about 0.5 d during periods of unusually high flow ($\sim 200,000 \text{ m}^3 \text{ d}^{-1}$).

Using a constant value for Q , we calculated nutrient fluxes from concentration data for each pair of consecutive samplings < 16 d apart. Among the various nutrient frac-

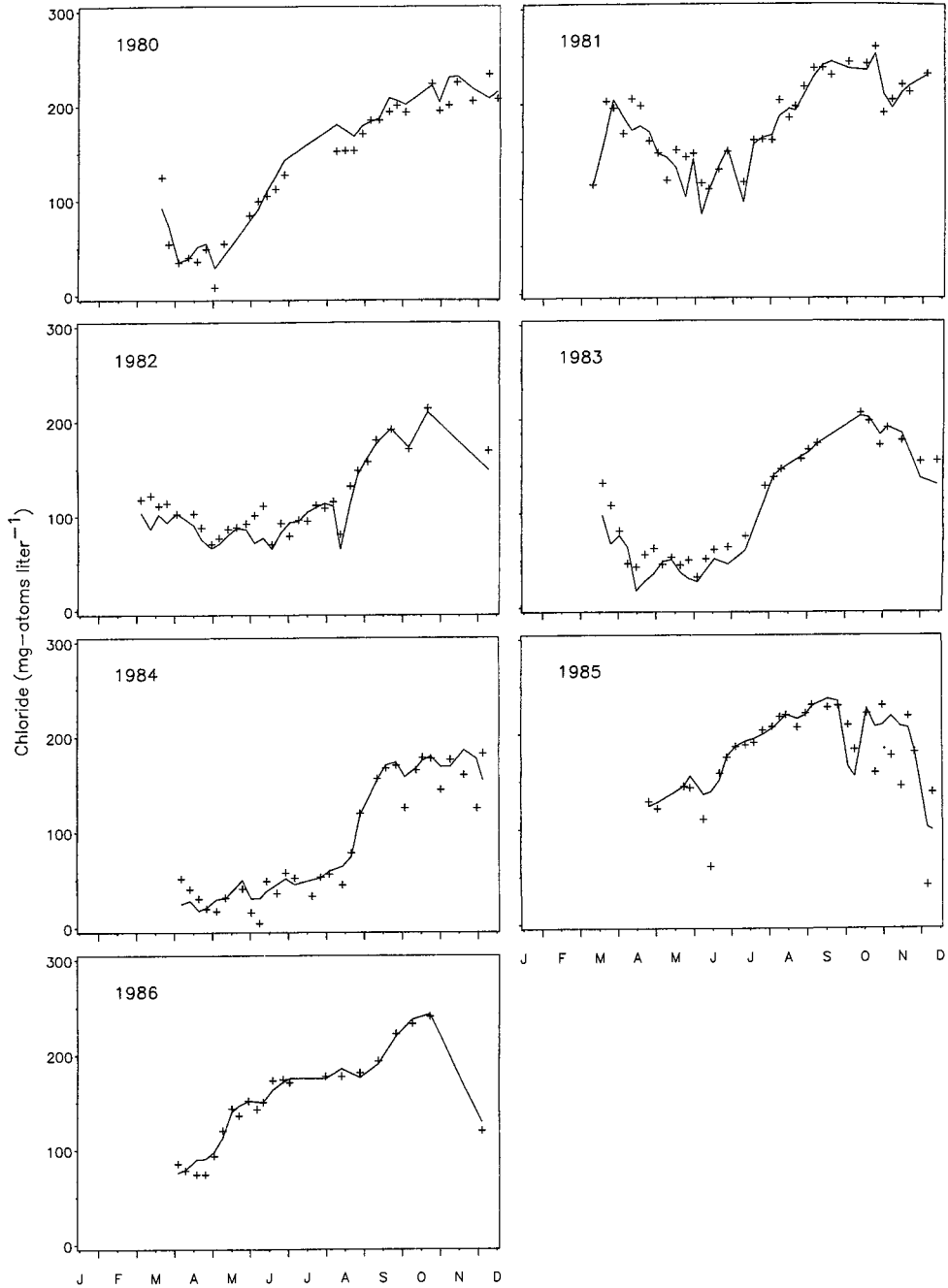


Fig. 6. Chloride concentration in the upper estuary calculated as a volume-weighted average of concentrations in segments 5-8 vs. time. Lines indicate values predicted from mixing model. Plus signs indicate measured values.

tions, NO_3^- and DPO_4^{3-} showed the clearest seasonal patterns of production (or consumption) in segments 5–8. As suggested by the concentration gradients (Fig. 3), there was a net in situ consumption of NO_3^- peaking in spring and a net production of DPO_4^{3-} peaking in summer (Fig. 7). In contrast to DPO_4^{3-} , PPO_4^{3-} was, on average, consumed. The consumption of PPO_4^{3-} followed a different temporal pattern than the production of DPO_4^{3-} , with most of the consumption coinciding with episodes of high watershed input occurring randomly throughout spring and summer (Fig. 7). Except for these episodes of high consumption, there was usually slight production of PPO_4^{3-} (Fig. 7). Also, there was usually net production of Chl *a* with a vague peak in summer (Fig. 7). The seasonal patterns of fluxes of other materials were less clear.

To summarize the fluxes, we averaged all the weekly flux observations from March to November (1980–1986) and used the variation among these observations to estimate the precision of the mean fluxes. The estimates of precision are probably conservative because there are sources of variation among observations besides measurement error. For example, seasonal variability is important in some cases, such as DPO_4^{3-} production and NO_3^- consumption (Fig. 7). An even larger source of variation is the variability of watershed discharges caused by variability of rainfall. This can lead to differences in flux rates among years as well as among weeks. Such interannual differences are discussed elsewhere (Jordan et al. in press). Here we focus on the average fluxes throughout the 7-yr span of weekly sampling.

We used the bootstrap technique (Efron 1982) to estimate the 95% C.L. of the means because the individual observations were not normally distributed. The bootstrap technique begins by creating 1,000 sets of data by selecting data points at random from the original data set, replacing the selected points so they can be chosen again. Each of the sets created by the bootstrap procedure has the same number of samples as the original data set. The means of these sets are calculated, and the 2.5 and 97.5 percentiles of these means represent the 95% C.L. of

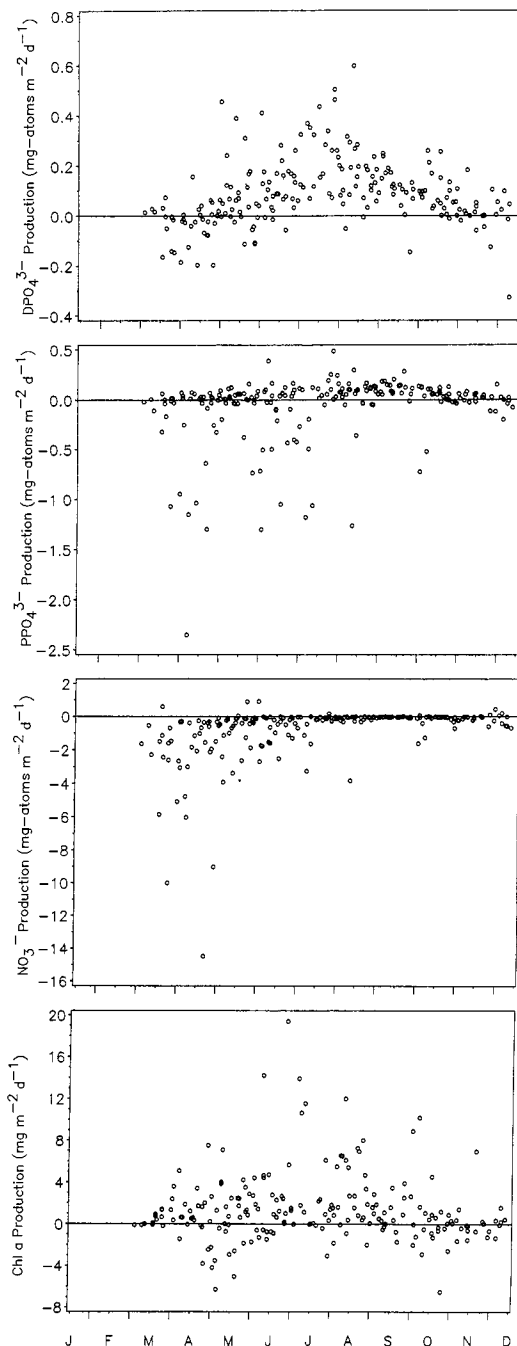


Fig. 7. Net production of DPO_4^{3-} , PPO_4^{3-} , NO_3^- , and Chl *a* in the upper estuary (segments 5–8) calculated with the mixing model from sequential concentration measurements and plotted vs. time of the year. All data from 1980 to 1986 (>200 weekly or biweekly observations) are plotted together. Units are m^{-2} of area of upper estuary including marshes (56.7 ha). Negative production is equivalent to consumption.

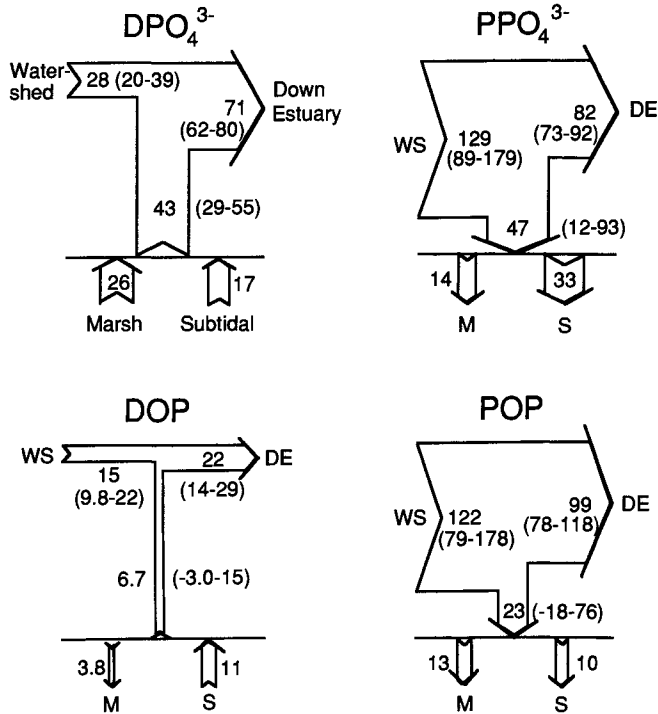


Fig. 8. Average flux rates (g-atoms d^{-1}) for forms of P in the upper estuary (segments 5–8) from March to November (95% C.L. in parentheses). Watershed inputs (WS) were measured with automated monitors. The sum of marsh and subtidal fluxes were calculated from the model of mixing. Marsh fluxes (M) are from Jordan et al. (1983). Subtidal fluxes (S) were calculated by difference. Exports to the lower estuary (DE) were calculated by summing watershed inputs and estuarine production or consumption from the model of mixing.

the original mean, after applying a correction for possible bias in the original data set (Efron 1982).

On average, from March through November, there was net production of DPO_4^{3-} in the upper estuary and a nearly equal consumption of PPO_4^{3-} (Fig. 8). On the basis of their 95% C.L., the apparent net production of DOP and net consumption of POP were not statistically significant. Using previous measurements of tidal exchanges of nutrients by the high and low marshes of the upper estuary (Jordan et al. 1983), we estimated how much of the total flux in the upper estuary was due to the marshes that cover two-thirds of its area. We then subtracted these estimates to infer how much flux was due to the subtidal area (Fig. 8). The direction of fluxes of forms of P other than DOP was the same for the marshes and the subtidal area. The magnitude of the fluxes per unit of area was less, however, for the marshes than for the subtidal areas.

The upper estuary consumed NO_3^- , DNH_4^+ , PNH_4^+ , and DON (Fig. 9). The apparent production of PON was not statistically different from zero. Nearly all of the NO_3^- entering in bulk precipitation and watershed discharge was consumed in the upper estuary. The marshes, unlike the subtidal areas, released DNH_4^+ and DON and took up PON. The release of DNH_4^+ from the marshes was about a third the uptake by the subtidal areas, and the exchanges of DON and PON by the marshes were about half those by the subtidal areas.

The upper estuary consumed POC, but DOC production was not statistically significant (Fig. 10). Evidently, the trapping of POC inputs from the watershed exceeded the production of POC associated with the net production of Chl *a*. The upper estuary (56.7 ha, including marshes) trapped total suspended particles at a rate of $2.6 \text{ g m}^{-2} \text{ d}^{-1}$ (95% C.L.: 1.0–4.5)—about two-thirds the rate of input from the watershed. How-

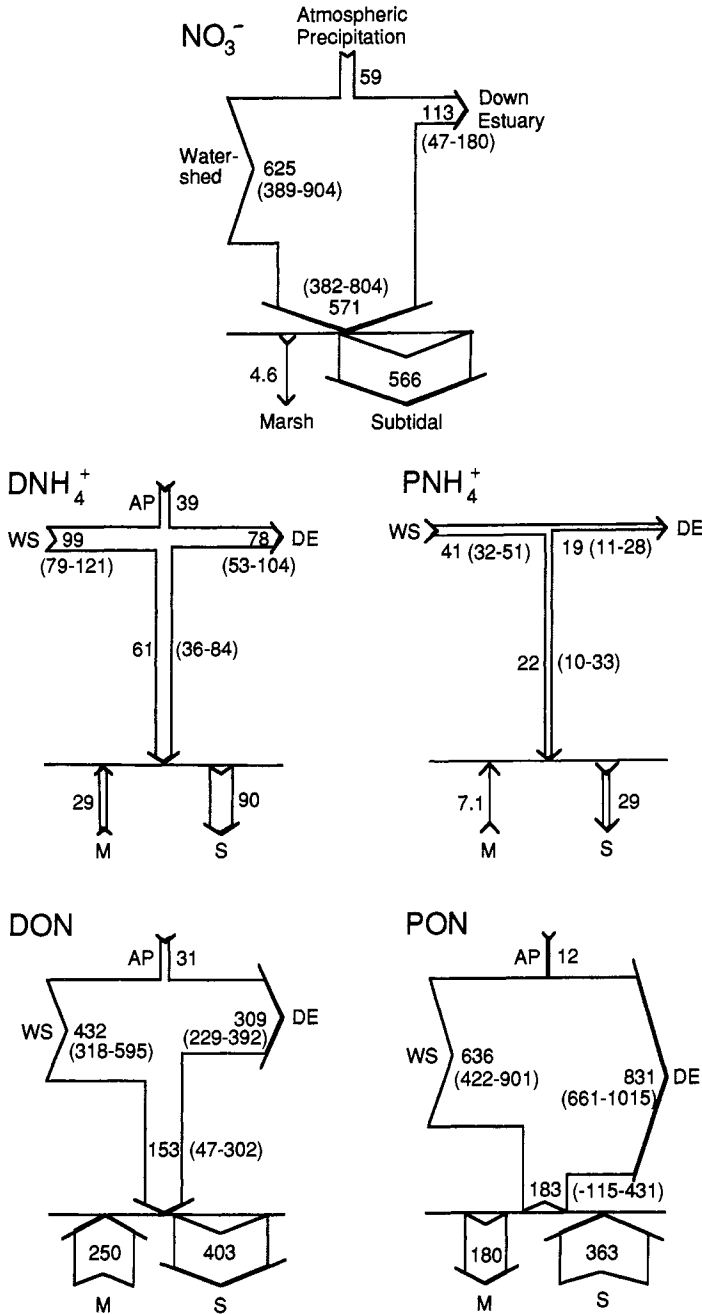


Fig. 9. Average flux rates (g-atoms d⁻¹) of forms of N in the upper estuary from March to November. Calculations and abbreviations as in Fig. 8. Inputs from atmospheric precipitation (AP) also shown for NO₃⁻, DNH₄⁺, DON, and PON. Atmospheric inputs for other forms of N, P, and organic C were negligible.

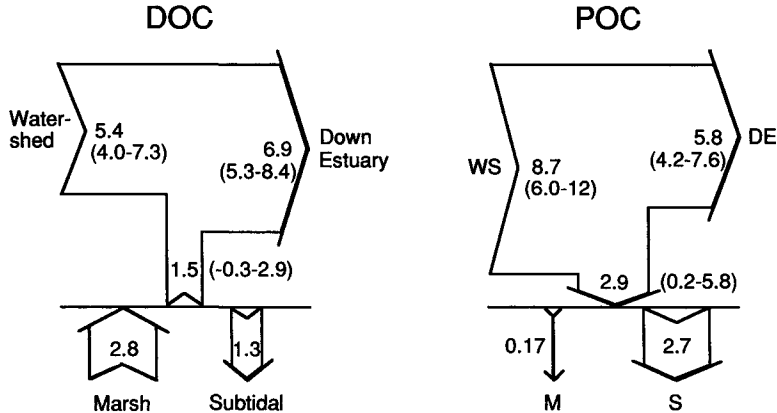


Fig. 10. Average flux rates (kg-atoms d⁻¹) of forms of organic C in the upper estuary from March to November. Calculations and abbreviations as in Fig. 8.

ever, the upper estuary produced and exported 1.3 mg m⁻² d⁻¹ Chl *a* (95% C.L.: 0.7–1.8).

Discussion

Phosphorus—The production of DPO₄³⁻ is the most pronounced feature of P flux in the upper estuary (Fig. 8). It shifts the ratio of available N:P downward, thus creating the potential for N limitation. This phenomenon occurs in the headwaters of many estuaries. DPO₄³⁻ concentrations in estuaries are commonly elevated above levels that would be predicted from conservative mixing of freshwater and seawater end-members (Froelich 1988). Also, a summer peak in DPO₄³⁻ concentration is typical of shallow estuaries (Pomeroy et al. 1965), and

similar peaks occur in other tributary estuaries of Chesapeake Bay, such as the Wye (Kunishi and Glotfelty 1985) and Patuxent Rivers (D'Elia et al. 1986). In the Wye River, as in the Rhode, the high concentration of DPO₄³⁻ in the headwaters cannot be attributed to runoff but is apparently due to release from sediments (Kunishi and Glotfelty 1985).

In the Rhode River, the differences in the temporal patterns of PPO₄³⁻ consumption and DPO₄³⁻ production (Fig. 7) suggest that DPO₄³⁻ production is not due to release of DPO₄³⁻ from PPO₄³⁻ in suspension, but more likely to release from particulate P deposited in the sediment (Fig. 11). Most deposition occurs after episodes of high runoff (Jordan et al. 1986b). The trapping of PPO₄³⁻ was similarly episodic and correlated with the trapping of TSP (Spearman correlation, $r = 0.53$, $P < 0.0001$), but DPO₄³⁻ production was not. The maximal rate of DPO₄³⁻ production is ~0.6 mg-atoms m⁻² d⁻¹ for the whole upper estuary, including marshes (Fig. 7). This rate is plausible for DPO₄³⁻ release from the sediments. It is relatively high, but within the range of DPO₄³⁻ release rates from sediments in other estuaries (e.g. Nixon et al. 1980).

DPO₄³⁻ is released from sediments by mineralization of POP and dissolution of iron oxyhydroxides that bind PPO₄³⁻. Both processes accelerate as temperature increases. Thus, release of DPO₄³⁻ from sediments is most rapid in summer, and consequently

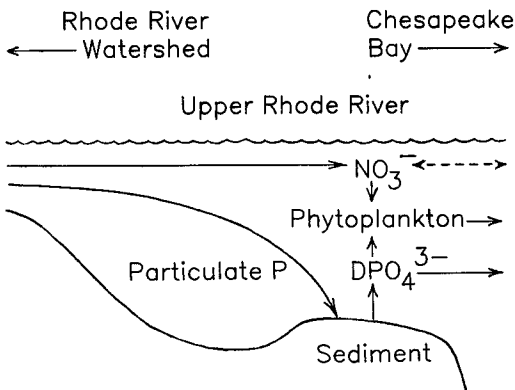


Fig. 11. Summary of the major net nutrient fluxes in the upper estuary.

DPO_4^{3-} concentrations in estuarine waters peak in summer (Nixon et al. 1980). Dissolution of Fe oxyhydroxides occurs when oxidized Fe is reduced (Krom and Berner 1980). Sediments become more reducing as higher temperatures increase metabolic rates. Occasionally, the water column of the upper estuary becomes anoxic before dawn in late summer and fall (unpubl. data). When overlying waters are anoxic, rapid release of DPO_4^{3-} from sediments takes place in both freshwater and salt-water environments (Krom and Berner 1980).

Anoxia of the overlying waters is probably less important for DPO_4^{3-} release in salt-water than in freshwater because salinity may play an important role in promoting DPO_4^{3-} release from sediments. In freshwater sediments, when PO_4^{3-} -binding Fe oxyhydroxides are reduced in anoxic sediment, the PO_4^{3-} and Fe dissolve and diffuse upward until they encounter aerobic conditions, where the Fe oxyhydroxides may reprecipitate and rebind PO_4^{3-} (Carignan and Flett 1981). In salt-water sediments, however, reduced Fe can precipitate as sulfides (Krom and Berner 1980) and thus be prevented from diffusing to aerobic layers where it might otherwise reoxidize and bind PO_4^{3-} . In addition, formation of vivianite, a stable, reduced Fe- PO_4^{3-} mineral, is less likely in sulfidic sediments than in freshwater sediments (Postma 1982). Therefore, as salinity increases in an estuary, increasing the supply of SO_4^{2-} for reduction to sulfide, the ability of the sediments to retain PO_4^{3-} may diminish. This effect may explain the observations of Upchurch et al. (1974) and Strom and Biggs (1982) that concentrations of P and associated Fe oxyhydroxides in sediments decrease with increasing salinity along estuarine salinity gradients. Similarly, Caraco et al. (1989) compared several systems with anaerobic sediments overlain by aerobic water and found that marine sediments retained less P than freshwater sediments. They also suggested that SO_4^{2-} reduction in marine sediments accounts for the difference.

The release of DPO_4^{3-} from sediments in the upper Rhode River is roughly matched by the uptake of PPO_4^{3-} (Fig. 8). Thus, particulate P entering from the watershed is

converted to DPO_4^{3-} after deposition in anoxic, saline sediments. Such conversion is probably common in estuaries because they generally function more efficiently as sediment traps than as P traps (e.g. Nixon 1987). The resulting enrichment of coastal waters with DPO_4^{3-} may partly explain why P seldom limits primary production. N, rather than P, is generally thought to limit primary production in estuarine waters (Boynton et al. 1982). N appears to be limiting in the Rhode River since phytoplankton blooms are triggered by high flow from the Susquehanna River which increases NO_3^- (but not PO_4^{3-}) influx from the adjacent Chesapeake Bay (Jordan et al. in press). Explanations for N limitation have focused on depletion of N through denitrification (e.g. Seitzinger 1988), inhibition of N fixation (Howarth and Cole 1985), or rapid water exchanges (Smith 1984). However, conversion of particulate P to DPO_4^{3-} in sediments may also promote N limitation. In contrast to marine water, production in freshwater is often P limited, perhaps because lack of SO_4^{2-} favors PO_4^{3-} retention in freshwater sediments (Caraco et al. 1989).

Another important factor controlling DPO_4^{3-} concentrations in estuarine water is adsorption to suspended particles. Increasing salinity may decrease the binding of PO_4^{3-} to suspended particles due to competition of anions for exchange sites (Pomeroy et al. 1965; Froelich 1988). This effect may explain why the amount of PPO_4^{3-} per unit of weight of suspended particles decreases downstream as salinity increases (Fig. 5). Alternatively, some of the suspended particles may be resuspended sediment that has undergone diagenesis.

Our flux calculations (Fig. 8) suggest that the upper Rhode River trapped total P at a rate of 20 g-atoms d^{-1} . Considering the imprecision of the estimates, this is in reasonably good agreement with previous studies which suggest a net accretion of P at a rate of 97 g-atoms d^{-1} in sediments of the upper estuary (Table 2). Our flux calculations would be expected to underestimate the annual rate of P trapping because they are based on data that do not include winter, when DPO_4^{3-} release and export of P in phytoplankton biomass are probably minimal.

Table 2. Accretion of N and P in sediments.

	Subtidal (22.6 ha)	Low marsh (12.0 ha)	High marsh (22.1 ha)
Sediment accretion			
g m ⁻² yr ⁻¹	3,200*	730*	550*
Phosphorus			
μg-atoms (g sediment) ⁻¹	32†	71‡	52‡
mg-atoms m ⁻² yr ⁻¹	100	52	29
kg-atoms yr ⁻¹	23	6.2	6.3
Nitrogen			
μg-atoms (g sediment) ⁻¹	190†	710§	1,600†
mg-atoms m ⁻² yr ⁻¹	590	520	910
kg-atoms yr ⁻¹	130	62	200

* Jordan et al. 1986b.

† Unpublished data.

‡ Jordan et al. 1983.

§ Jordan et al. 1989.

Discrepancies may also arise from the variability of particulate inputs. Inputs of particulate matter from the watershed are highly episodic (Jordan et al. 1986b), so it is possible that particulate P delivered after one storm may be released gradually from the sediments as DPO₄³⁻ over a period of years.

The waters of the upper Rhode River are much richer in P than those of adjacent Chesapeake Bay (Fig. 3). This disparity probably reflects differences in the watersheds. Upper Chesapeake Bay is dominated by inputs from the Susquehanna River. These inputs are enriched in NO₃⁻, mostly due to agricultural N applications (Clark et al. 1974) and depleted in P due to sediment trapping by dams (Donoghue et al. 1989) and the low P content of the Appalachian soils of the Susquehanna watershed compared with the coastal plain soils of the Rhode River watershed (Correll 1987).

Nitrogen—Among the forms of N, NO₃⁻ was affected most by transit through the upper estuary. Two factors appeared to control NO₃⁻ concentrations: input from the watershed, which accounted for the spring peak in concentration; and uptake by phytoplankton, which depleted NO₃⁻ as Chl *a* concentration rose (Fig. 3). Apparently phytoplankton production consumes nearly all of the NO₃⁻ entering the upper estuary from the local watershed (Figs. 9, 11). Phyto-

plankton generally take up DNH₄⁺ rather than NO₃⁻ if DNH₄⁺ concentrations are > 1.5 μg-atoms liter⁻¹, but NO₃⁻ is sometimes taken up at DNH₄⁺ concentrations as high as 40 μg-atoms liter⁻¹ (Pennock 1987). DNH₄⁺ concentrations in the Rhode River were usually > 2 μg-atoms liter⁻¹ (Fig. 3). This level would generally favor DNH₄⁺ uptake but not preclude NO₃⁻ uptake. DNH₄⁺ concentrations were less variable seasonally and thus were probably controlled by the balance between phytoplankton uptake and mineralization of organic N. The seasonal pattern of DIN concentrations, dominated by NO₃⁻, and the seasonal pattern of DPO₄³⁻ concentrations lead to a seasonal change in the inorganic N : P ratio as found in another subestuary of Chesapeake Bay, the Patuxent River (D'Elia et al. 1986).

Our flux measurements indicate a small net export of NO₃⁻ from the upper estuary (Fig. 9), but the gradient of NO₃⁻ concentration, with a minimum at segment 5 (Fig. 3), suggests some influx of NO₃⁻ from Chesapeake Bay (Fig. 11). Such influx is also suggested by correlations between changes in NO₃⁻ concentration in segment 5 and changes in Susquehanna River flow (Jordan et al. in press). Influxes of NO₃⁻ from Chesapeake Bay to segment 5 may be episodic, accompanying high Susquehanna flow, yet on average there may still be export of NO₃⁻ from the upper estuary as inputs from the local watershed force downstream advection. Net downstream advection would be relatively small, however, beyond the upper estuary. Therefore, Chesapeake Bay is likely to be the main source of NO₃⁻ input to the lower estuary (segments 1–4).

Total N flux comes close to balancing accretion, suggesting that there is little net exchange of gaseous N by the upper estuary, unlike many estuaries that exhibit large net losses of N to the atmosphere due to denitrification (Seitzinger 1988). As with P, our flux calculations (Fig. 9) suggest that the upper estuary was a net sink for N, trapping 620 g-atoms d⁻¹. However, using data from other studies we estimate that 1,100 g-atoms d⁻¹ N accretes in sediments, with high-marsh sediments being the largest sink (Table 2). Most of the difference could be accounted for by the trapping of watershed

Table 3. Atomic ratios of C, N, and P in particulate organic matter based on slopes of geometric regression (e.g. POC vs. POP). The 95% C.L. are indicated and the coefficients of determination are given in parentheses. Ratios of C, N, and P in phytoplankton biomass are based on slopes of geometric mean regressions of Chl *a* vs. POC, PON, and POP. The 95% C.L. for ratios in phytoplankton are based on the C.L. for regression slopes of the nutrients vs. chlorophyll and the assumption that variances are additive. Ratios for oceanic phytoplankton from Redfield (1958) are shown for comparison.

	C:P	N:P	C:N
Particulate			
Watershed	57±3 (0.33)	4.0±0.2 (0.37)	14±1 (0.58)
Estuary	98±7 (0.37)	12±1 (0.42)	8.1±0.6 (0.40)
Phytoplankton			
From Chl	89±6	11±1	8.3±0.5
Redfield 1958	106	16	6.6

and precipitation inputs during winter, when the export of N in phytoplankton biomass is probably minimal.

Organic matter—POC : PON : POP ratios suggest that much of the particulate organic matter (POM) in the estuary is produced in situ by phytoplankton. POM in the upper estuary was much richer in N and poorer in P than was POM in watershed discharges (Table 3). The C : N ratio of POM in the estuary was close to that expected for phytoplankton (Table 3), while the C : N ratios of POM from the watershed were more like that of terrestrial plant detritus (e.g. Berg and Staaf 1981). POM from both the estuary and watershed was relatively rich in P compared to average oceanic phytoplankton (Redfield ratios). C : N : P ratios for POM in the estuary were similar, however, to estimates for phytoplankton in the estuary from slopes of geometric mean regressions of POC, PON, and POP vs. Chl *a* ($r^2 = 0.50$, 0.70 , and 0.58). These regressions suggest ratios of 5.0 g-atoms C, 0.60 g-atoms N, and 0.054 g-atoms P (g Chl *a*)⁻¹. We used geometric mean regression (Sokal and Rohlf 1981) because there are errors in the measurements of both Chl *a* and POM. Estimates of elemental ratios to Chl *a* based on regression slopes must be interpreted cautiously because the amount of POM that is not phytoplankton biomass may correlate with the amount of phytoplankton biomass (Banse 1977). Nevertheless, it seems likely that much of the POC, PON, and POP in the upper estuary is in phytoplankton biomass.

From the export of Chl *a* (0.72 kg d⁻¹), we estimated that export of phytoplankton

biomass from the upper estuary could account for ~62% of the export of POC (Fig. 10). PON and POP must also be exported in phytoplankton, but their net exports were not significantly different from zero (Figs. 8, 9), possibly because their net flux reflects deposition of particulate matter from watershed inputs as well as phytoplankton exports. Another subestuary of Chesapeake Bay, the Gunpowder River, also exports phytoplankton biomass (Sellner 1983).

Tidal marshes—On an areal basis, nutrient fluxes into and out of the marshes were generally less than fluxes into and out of the subtidal area of the upper estuary, but the marshes still had important effects. Exchanges of DOP, DON, PON, and DOC by the marshes offset those by the subtidal area, while exchanges of DPO₄³⁻, PPO₄³⁻, and POP by the marshes augmented them (Figs. 8–10).

The importance of tidal exchanges of materials from marshes has been the subject of much research (reviewed by Nixon 1980). One central hypothesis—the “outwelling” hypothesis—suggests that marshes contribute to the productivity of nearshore waters by exporting particulate organic detritus. This hypothesis does not seem to hold for the marshes of the Rhode River, which generally import particulate nutrients and export dissolved nutrients, except NO₃⁻ (Jordan et al. 1983).

The relative importance of marsh exchanges is influenced by the adjacent waters. Marsh exchanges in the upper Rhode River may be comparatively less important because of the high phytoplankton productivity of the tidal waters. Also, tidal exchanges

by Rhode River marshes may be low due to the relatively low tidal amplitude (30 cm).

The effects of the upper estuary as a whole on NO_3^- and DPO_4^{3-} alter the ratio of dissolved inorganic N:P flux from 26 in watershed discharge to 2.7 in export from the upper estuary (Figs. 8, 9). Although the marshes had relatively little effect on NO_3^- , they contributed substantially to the release of DPO_4^{3-} . The release of DPO_4^{3-} from terrigenous sediments may be a feature common to many estuaries and may partly explain why N, rather than P, is usually limiting in coastal waters.

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