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Journal
Estuarine Coastal and Shelf Science, 34(3)

ISSN
0272-7714

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Publication Date
1992-03-01

DOI
10.1016/s0272-7714(05)80080-0

Peer reviewed

Estuarine, Coastal and Shelf Science (1992) **34**, 213–233

Geochemistry and Loading History of Phosphate and Silicate in the Hudson Estuary

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Received 19 February 1991 and in revised form 25 July 1991

Keywords: phosphorus cycle; silicon cycle; time series; waste water disposal; Hudson estuary

The loading history and geochemistry of soluble reactive phosphorus (SRP) and dissolved silica (DSi) are evaluated in the Hudson estuary using 16 years of axial transect data. SRP behaves atypically in the estuary. Profiles show conservative mixing between a large mid-salinity source and the freshwater and seaward end members. Order of magnitude calculations indicate that waste water treatment facilities (WWTFs) are the dominant mid-salinity SRP source. DSi profiles display behaviour more typical of other estuaries in the northeastern United States, showing conservative mixing during periods of high flow and a mid-salinity source during periods of low flow. A single layered multi-box model is used to evaluate the loading history of SRP and DSi. Shortly after the New York State phosphate detergent ban of 1972, the SRP load dropped to two-thirds of that typical of the early 1970s. Loading of SRP remained at this level until the mid-1980s when construction began at the largest point source. During the construction phase (1984–1986), SRP loading returned to the early 1970s level. Upon completion, the total load declined once again and by the end of the 1980s it reached a level approximately one-third of that existing prior to the detergent ban. Model calculations of observed DSi profiles do not show a similar time-trend. They suggest that during summer months dissolution of diatom tests is a major source of DSi; however, WWTF DSi loads also appear to be a significant source to the Hudson estuary.

Introduction

Years of industrial and municipal waste discharge to riverine, estuarine and coastal waters have deteriorated the quality of these waters and of their corresponding habitats. Nutrient concentrations in water near large urban centres have increased as the result of discharge from waste water treatment facilities (WWTFs). Higher nutrient concentrations enhance biomass productivity, that can lead to hypoxia and eutrophication. Much of the effort put

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forth to improve water quality has concentrated on increasing dissolved oxygen levels by reducing the loading of biological oxygen demand (BOD) and nutrients. Legislation which reduced the concentration of phosphorus in detergents and promoted the construction of sewage treatment facilities are examples of these efforts. Here, we examine soluble reactive phosphorus (SRP) and dissolved silica (DSi) profiles collected from the lower Hudson estuary since the early 1970s to evaluate the effectiveness of these efforts in the New York City metropolitan area.

Although dissolved oxygen, BOD, and inorganic nitrogen concentrations are often used to assess the quality of estuarine water, we have chosen to use SRP and DSi to monitor changes in the Hudson because their chemistries lack complications such as gas exchange or transformations between different inorganic forms (i.e. nitrification and denitrification).

The general behaviour of SRP and DSi in estuaries is well known. Both show seasonal variations on concentration *vs.* salinity plots. Uptake of SRP is observed in spring while relatively small mid-salinity SRP sources are commonly found during the remainder of the year. These trends have been observed both near (Sharp *et al.*, 1982) and away from (Edmond *et al.*, 1981; Kaul & Froelich, 1984; Fox *et al.*, 1986) industrial and agricultural sources. Two types of mid-salinity sources have been postulated: seasonal regeneration of organic material (Edmond *et al.*, 1981; Kaul & Froelich, 1984) and desorption from suspended material (Sharp *et al.*, 1982; Fox *et al.*, 1986; Froelich, 1988).

DSi also displays similar seasonal changes in concentration *vs.* salinity plots (Sharp *et al.*, 1982; Kaul & Froelich, 1984; Anderson, 1986). Anderson (1986) showed in transects from three river-estuary systems which flow into Chesapeake Bay that the seasonal behaviour is regulated primarily by diatom activity upstream of the salt/freshwater interface. During the winter when the diatom activity was at a minimum, DSi mixed conservatively in the salt intruded reach. During the summer, DSi concentration decreased to values near zero in the area of the diatom activity. Seaward of the salt/freshwater interface, the diatom activity dropped off by an order of magnitude and the DSi concentration increased. From these data Anderson concluded that removal of DSi upstream of the salt intrusion is caused by diatom blooms and addition of DSi in the saline reach of the estuary results from the dissolution of freshwater diatom tests that have been carried seaward.

The Hudson estuary

The Hudson estuary (Figure 1), as defined here, extends from the Narrows (mp -8)[a] north to the up-stream limit of tidal influence at the Federal Dam at Green Island (mp $+154$). North of Manhattan, the axial trend is north–south and nearly linear. Along the axis, little variation is found in the cross-sectional area, which averages $1{\cdot}5 \times 10^4$ m^2. Mean depths are generally 10 m, although regions can be shallower than 3 m or deeper than 35 m. South of Manhattan, the Upper Bay has a width of 5 km and is partially isolated from the sea by the Narrows which has a width slightly greater than 1·5 km. Tidal channels, the Kill Van Kull and East River, enter the estuary south of Manhattan providing other indirect connections with the ocean and other drainage basins.

The general circulation of estuaries has been understood for some time (see Pritchard, 1969; Abood, 1974; Bowden, 1980). The Hudson estuary is a partially-mixed estuary.

[a]Axial distance along the Hudson River has traditionally been recorded in mile points, mp, which designate the number of statute miles north (+) or south (−) from the Battery at the southern tip of Manhattan.

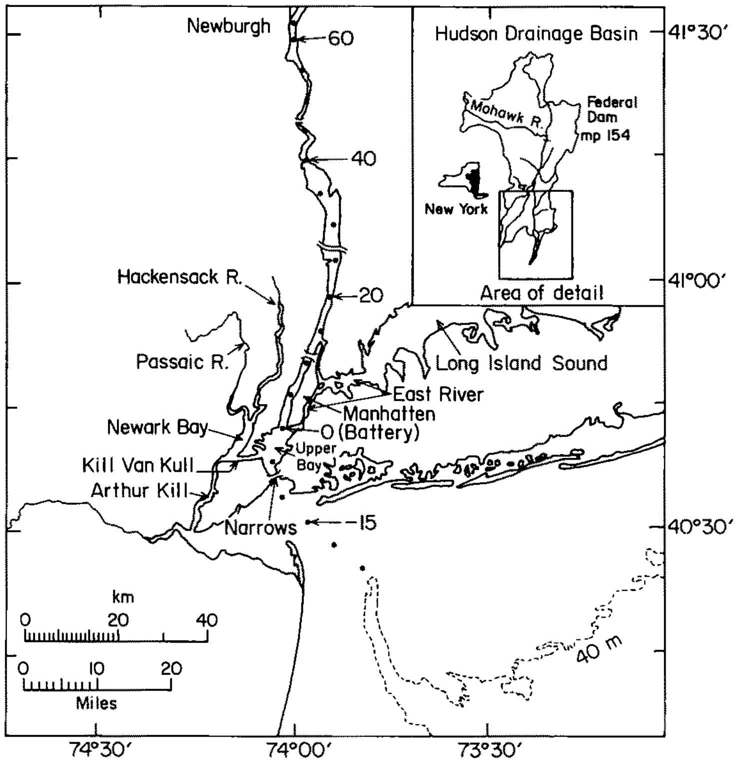

Figure 1. Hudson River and estuary with mile points (mp) indicated at intervals of 5 miles.

Generally the difference between surface and bottom salinities are less than 10 ppt. Freshwater discharge usually reaches a maximum during the spring and a minimum during late summer. Typical seasonal extreme values of the discharge at the Battery (mp 0) are 1200 $m^3 s^{-1}$ and 200 $m^3 s^{-1}$, respectively. Lower basin (down stream of the Federal Dam) tributary discharge averages about 35% of the total discharge at the Battery, but can vary from <15% to more than half of the total discharge during summer months. More than 90% of the total freshwater flow at the Battery enters the estuary up-stream of the salt/freshwater interface. During late summer, the saline water can extend as far north as Newburgh (mp +60) while during late spring saline water extends to just north of Manhattan (mp +15). Freshwater replacement times (total equivalent volume of freshwater divided by freshwater discharge at the Battery) are inversely related to discharge (Figure 2). During high discharge (>600 $m^3 s^{-1}$), freshwater replacement times are less than 15 days while during low flow conditions (150–250 $m^3 s^{-1}$) replacement times are typically between 45 and 60 days although they can be greater than 75 days during extreme dry periods.

More than 30 WWTFs serving the greater New York City metropolitan area treat roughly 10 billion litres of waste water per day (Mueller *et al.*, 1976; Brosnan *et al.*, 1987). In the early 1970s, half of the discharge was secondary treated and one quarter was primary treated. The remaining quarter passed directly into the estuary untreated (Mueller *et al.*, 1976). Much of the effort since the early 1970s to improve the quality of Hudson estuary water involved up-grading and construction of new treatment facilities.

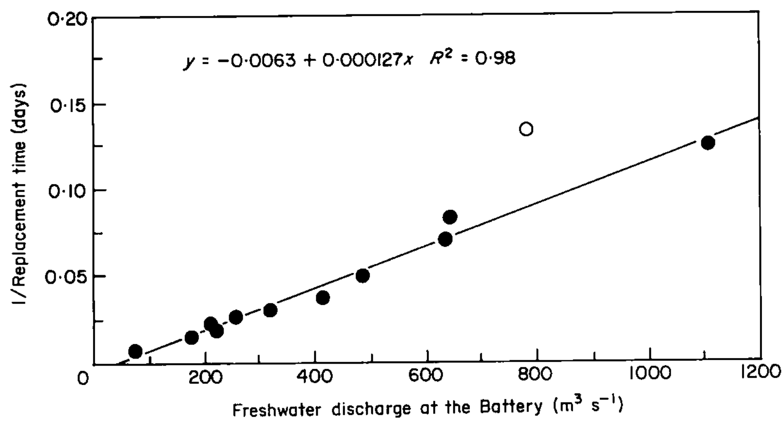

Figure 2. Freshwater replacements times were calculated for different discharge rates from the observed salinity distributions. The open circle off the line was not included in the fit.

As the result of these improvements, by the late 1980s dry weather waste water discharge into the Hudson was more than 85% secondary, about 15% primary, and less than 5% untreated (raw) (Brosnan *et al.*, 1987; Interstate Sanitation Commission, 1989).

Methods

Since the early 1970s, researchers at the Lamont-Doherty Geological Observatory have collected axial transects of Hudson estuary water. Though the investigators have changed over the years, the collection and nutrient analysis procedures have remained reasonably consistent. Samples 1 m below the surface and 1 m above the bottom were collected using a Niskin bottle. They were immediately filtered and brought to the laboratory for nutrient analysis. In addition to SRP and DSi, total dissolved phosphate (TDP), nitrogen species, oxygen, and carbon species have been determined in a number of the transects. Except for TDP, which was determined using the high temperature decomposition procedure of Solorzano & Sharp (1980), the nutrient analyses followed procedures outlined by Strickland & Parsons (1972). In this study we define SRP as molybdate-reactive phosphate.

Most of the transects discussed here are combinations of two or more sets of samples collected over a period of up 2 weeks. The profiles were composed of individual samples collected in sequence from a small boat and thus were neither synoptic nor averaged over an entire tidal cycle at each location. Thirty miles of the estuary could usually be sampled in about 4 h.

Results

Typical SRP profiles taken during periods of high and low freshwater discharge in 1974 are shown in Figure 3(a). The profiles show that the SRP maxima are at mid-salinities and that during high freshwater discharge, the peak is lower and broader. The maxima indicate a source which, after making the transformation from salinity to mile point reference frame, lies for these profiles between mp −8 (the Narrows) and mp 14 (the northern tip of

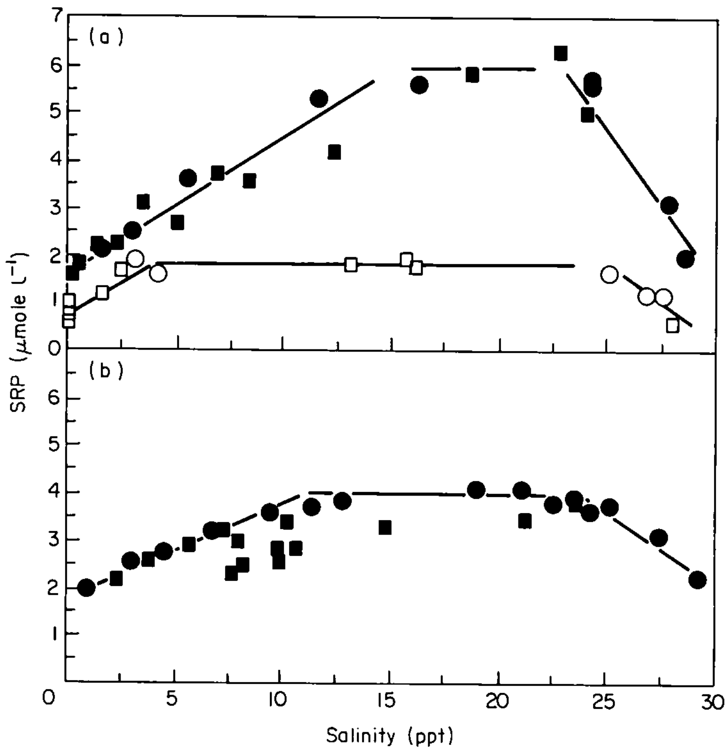

Figure 3. (a) Hudson estuary SRP profiles collected 2–3 March and 27–28 August 1974. The freshwater discharges at the Battery (mp 0) were 850 $m^3 s^{-1}$ and 210 $m^3 s^{-1}$ for the spring and summer transects, respectively. ■, Surface August; ●, Bottom August; □, Surface March; ○, Bottom March. (b) Hudson estuary SRP profile collected 23–26 August, 1988. The freshwater discharge at the Battery (mp 0) was 176 $m^3 s^{-1}$ during this transect. ■, Surface Samples; ●, Bottom Samples.

Manhattan). Surface and bottom samples fall on similar conservative mixing lines between the mid-salinity source and the fresh and seaward end members. This behaviour has been previously reported for the Hudson estuary by Simpson *et al.* (1975) and others who have described it as quasi-conservative. Quasi-conservative behaviour is used to indicate the dominance of rapid mixing and discharge to coastal waters with little evidence for biological uptake within the estuary.

Figure 3(b) shows a SRP transect collected during a period of low freshwater flow 14 years after the transects shown in Figure 3(a). Similar to the earlier profiles, there is a maximum in SRP at mid-salinities. However, in the low salinity reach of the estuary (between 7–12 ppt) there are significant deviations of samples from the conservative mixing trend, as well as a systematic separation between surface and bottom samples, suggesting that substantial net uptake of SRP was occurring. Away from this area, SRP appears to behave conservatively. In a transect collected 2 weeks prior to the one shown in Figure 4, Ammerman (1989) measured SRP, chlorophyll *a*, and SRP uptake rates. His SRP profile also showed deviations below the conservative mixing line, although the region was slightly fresher and spread over a larger salinity range (3–12 ppt) than we observed 2 weeks later. In this region, chlorophyll *a* concentrations and SRP turnover rates, respectively 30 $\mu g\ l^{-1}$ and 3% h^{-1}, were five- to seven-fold greater than in the region of quasi-conservative mixing.

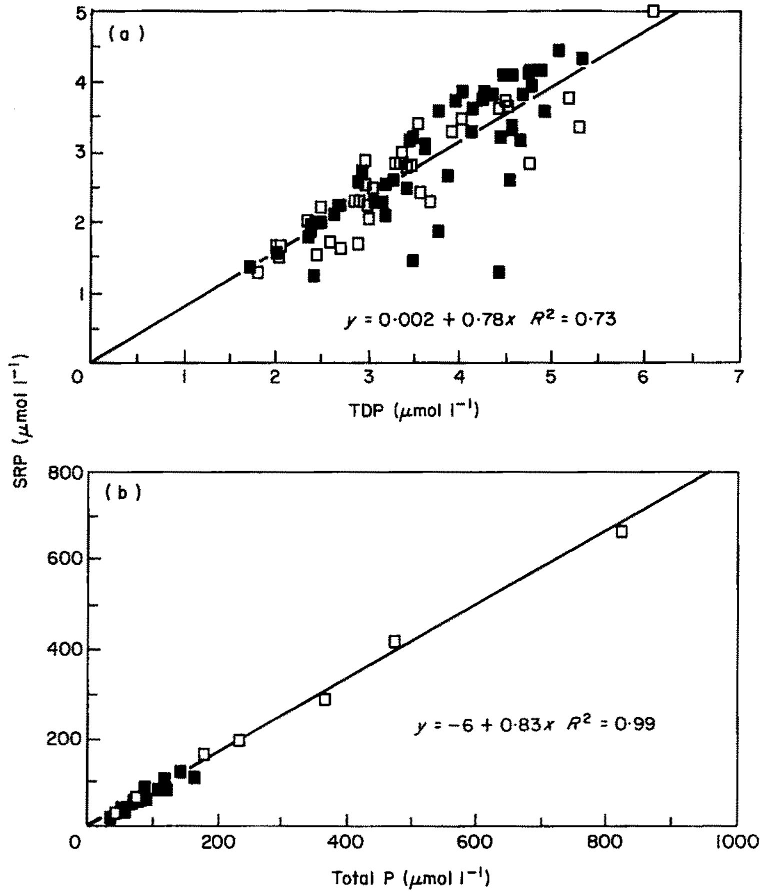

Figure 4. SRP concentrations plotted against (a) TDP for estuary transect samples collected after 1980. □, Surface Samples; ■, Bottom Samples. (b) Total-P for WWTF. The WWTF data were derived from Mueller *et al.* (1982). □, Primary Treatment Facilities ($n=7$); ■, Secondary Treatment Facilities ($n=19$).

About one quarter of the profiles in our data set showed some evidence of SRP deviations from quasi-conservative mixing lines. Typically, they occurred in a restricted salinity window, 5–10 ppt, in the fresher reaches of the estuary. However, because many of our profiles did not include the fresher stations (i.e. salinity less than 10 ppt) and half of the transects were collected during the summer (July–September) the overall frequency of net SRP-uptake during the course of a year is difficult to infer from our data set.

TDP concentrations, which were also measured after 1980, show similar quasi-conservative behaviour and mid-salinity maxima to those of SRP, as was initially reported for the Hudson estuary by Ketchum (1969). SRP and TDP concentrations from Hudson estuary samples [Figure 4(a)] correlate with a slope of approximately 0·8. A similar concentration ratio between SRP and total-P concentrations from WWTF samples [Figure 4(b)] is also observed.

The concentrations of SRP and total-P in effluent from different WWTFs vary considerably [Figure 4(b)]. SRP concentrations differed by more than an order of magnitude, ranging for primary plants between 30 and 650 μmol l^{-1} and for secondary plants between

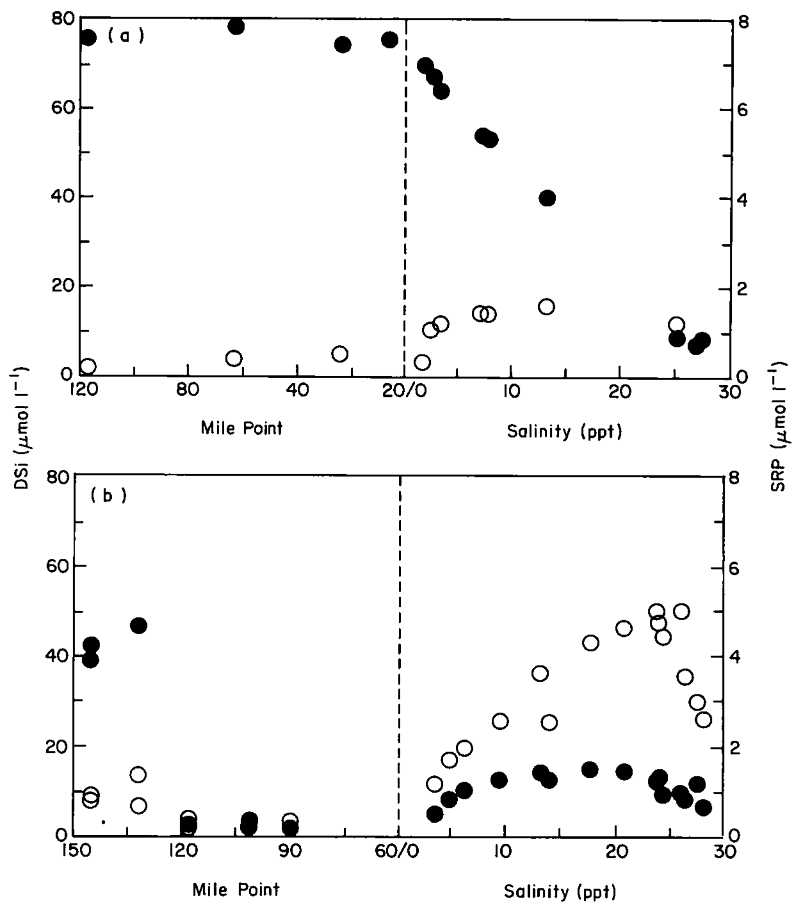

Figure 5. Typical dissolved DSi (●) and SRP (○) profiles for the Hudson estuary during (a) high (1340 $m^3 s^{-1}$, 22–26 April 1977) and (b) low (225 $m^3 s^{-1}$, 14–21 July 1977) freshwater discharge. The (¦) splits the plots into two regions. On the right hand side, DSi is plotted against salinity while on the left it is plotted against mile point. During the April transect, saline water intruded to mp +20 while during the July transect it intruded to mp +60.

20 and 110 μmol l^{-1}. (The range during the late 1970s was greater than during the earlier 1970s. See Mueller *et al.*, 1976 and 1982). The variations in mean effluent SRP concentrations reflect differences in treatment procedures and also the quality of waste water reaching the facilities.

While SRP showed relatively little variation in behaviour between periods of different freshwater discharge rates, DSi had much larger seasonal variations. During winter and early spring transects (periods of high flow), DSi concentrations in freshwater were greater than 70 μmol l^{-1} and samples from within the salinity intrusion fell on a conservative mixing line between the freshwater and the seaward end members. On the other hand, during summer transects (periods of low flow), freshwater DSi concentration drop to less than 20 μmol l^{-1} in the region just up-stream of the salt/freshwater interface. Further upstream concentrations typical of winter are observed. Downstream of the interface a mid-salinity DSi maximum appears.

TABLE 1. Single layer model box dimensions as estimated by Deck (1981)

Box number	Box length (mp to mp)		Surface area (10^6 m^2)	Volume (10^6 m^3)	Mean depth (m)
10	−8	−4	12·8	216	16·8
9	−4	0	22·4	259	11·6
8	0	8	16·7	189	11·4
7	8	16	18·2	169	9·4
6	16	24	23·7	184	8·0
5	24	32	47·7	258	5·4
4	32	40	46·3	260	5·7
3	40	48	12·9	193	15·8
2	48	56	13·1	178	14·8
1	56	64	22·7	199	9·0
Total			237	2105	

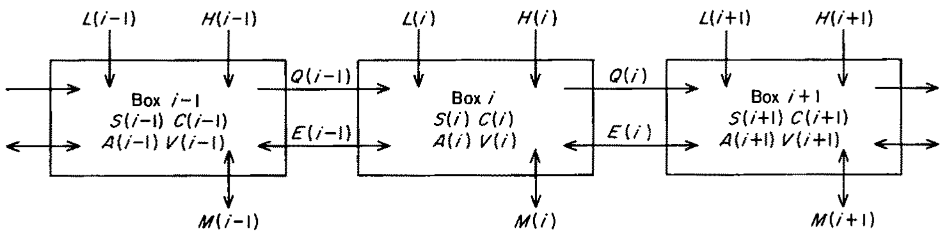

Figure 6. Diagrammatic representation of the single layer model used for the calculations. (See text for a description of the parameters used in the model).

A typical DSi seasonal cycle from 1977 is plotted along with SRP in Figures 5(a) and 5(b). During the summer, samples collected between the salt/freshwater interface and mp 130 show removal of DSi and SRP relative to samples collected upstream of mp 130. DSi concentrations drop from 40–50 μmol l^{-1} to less than 3 μmol l^{-1}, while SRP concentrations declined from approximately 0·9 μmol l^{-1} to 0·3 μmol l^{-1}. The average DSi/SRP net uptake ratio in this region was 70.

Single-layer box model

Model calculations can provide valuable insights on the trends of DSi and SRP profiles over the past 2 decades. Deck (1981) developed two multiple-box models of the Hudson estuary to predict nutrient distribution patterns. His first model assumed the water column to be vertically homogeneous; the second assumed it to be stratified. The former is represented by a single layer of boxes while the latter is described by two layers. He showed that during periods of low discharge the single and two-layer models represented longitudinal variations of nutrient concentrations in the Hudson estuary equally well. Here we will employ Deck's single-layer model representation to the lower estuary from the Narrows (mp −8) to Newburgh (mp +60).

Model description

We have divided the lower estuary into 10 boxes whose dimensions are listed in Table 1. The boxes are 8 miles in length (approximately the excursion distance of a parcel of water

TABLE 2. Model parameters and nutrient transects used to estimate the WWTF SRP and DSi loading trends

Collection period	Federal dam[a] (mp +154; $m^3 s^{-1}$)	Battery[a,b] (mp 0; $m^3 s^{-1}$)	Federal dam (%)	No. of boxes	Maximum SRP ($\mu mol\ l^{-1}$)	SRP load[c,d] % of early 1970s	DSi flux[c] ($mol\ s^{-1}$)
16–18 Aug. 1973	171	318	54	10	5·3	100	
27–28 Aug. 1974	169	210	80	10	6·5	100	
2–4 Oct. 1974	302	414	73	7	4·7	80[e]	12
15 Oct. 1975	418	634	66	7	2·9	60	
14–21 Jul. 1977	188	225	84	10	5·0	70	6
25 Aug. 1977	153	183	84	8	5·3	60	12
2–4 Aug. 1978	141	185	76	5	3·4	45	17
26 Aug.–13 Sept. 1981	141	160	88	8	5·1	55	
21–23 Jul. 1982	162	255	64	8	3·3	65	17
13–15 Sept. 1982	114	156	73	7	3·5	45	
10–13 Jul. 1984	286	523	55	8	2·7	60	
14–15 Aug. 1984	184	279	66	8	3·8	60–100	8
2–31 Jul. 1985	134	223	60	5	4·2	90	
8–30 Aug. 1985	103	184	56	5	5·1	95	
11–12 Aug. 1988	120	223	54	10	3·6	40	
23–26 Aug. 1988	109	176	62	9	4·0	33	5
29 Aug.–8 Sept. 1989	44	76	58	10	4·4	33[e]	3
Mean $\pm\sigma$	173 ± 89	260 ± 142	68 ± 11				

[a]Discharges are 25–30 day averages calculated from daily discharges (U.S.G.S., 1973–89).
[b]Discharges are calculated from gauged tributaries and basin area.
[c]Results from our single-layer model calculations. DSi flux is the sum of dissolution of diatom tests and diffusive flux from the sediment pore waters.
[d]Assumes WWTF discharges listed in Table 4.
[e]To fit the observed profiles, the sediment SRP flux had to be changed in the model calculations.

TABLE 3(a). SRP discharge rates, treatment level, and location of WWTF in the lower Hudson estuary in the early 1970s

MP	Treatment facility	Treatment level	Freshwater discharge ($m^3 s^{-1}$)	SRP load[c] ($mol s^{-1}$)	SRP ($\mu mol l^{-1}$)
64–56	Box 1 (five WWTF)[a]	S	0·59	0·09	150
56–48	Box 2 (two WWTF)[a]	S	0·10	0·03	300
48–40	Box 3 (three WWTF)[a,b]	P,S	0·25	0·04	160
40—32	Box 4 (four WWTF)[a]	P,S	0·29	0·09	310
32–24	Box 5 (three WWTF)[a]	P	0·24	0·05	210
24–16	Box 6 (two WWTF)[a]	S	1·6	0·09	60
16	Yonkers[a]	P	3·9	0·24	60
9	Edgewater[a]	P	0·11	0·02	180
7	Woodcliff–N. Bergen	P	0·07	0·01	140
5	West New York	P	0·42	0·05	120
2	Hoboken[a]	P	0·76	0·02	30
0–13	West Manhattan	R	8·8	0·35	40
0–4	Red Hook	R	3·1	0·12	40
0	East River facilities[d]	R,S	19·5	1·2	60
−1	Jersey City East[a]	P	1·6	0·06	40
−3	Passaic Valley S.C.[a]	P	11	3·0	270
−4	Kill Van Kull facilities[e]	P	4·8	0·37	80
−4	Owl's Head[a]	S	4·2	0·35	80
−6	Staten Island	R	2·6	0·10	40
		Total	64	6·3	100

[a]Calculated from total-P assuming a SRP/total-P of 0·8.
[b]No data; calculated from freshwater discharge assuming average treatment concentration.
[c]The phosphate loads of the primary and secondary treatment facilities were estimated by Mueller *et al.* 1976. The untreated or raw discharges were estimated from the freshwater discharge rate by assuming the average concentration, 40 $\mu mol\ l^{-1}$, Hammond (1975) measured at the 125th Street outflow.
[d]Only 50% of the East River WWTF discharge is assumed to enter the estuary and subsequently be flushed out through the Narrows; the remainder is assumed to flow into Long Island Sound [see Table 3(b) listing of WWTF entering the East River].
[e]Discharge from facilities discharging into the Kill Van Kull and Newark Bay are assumed to enter the Hudson estuary [see Table 3(b) listing of WWTF entering Kill Van Kull and Newark Bay].
S, Sec; P, Pri; R, Raw.

during the semi-diurnal tidal cycle) except in the harbour area where they are 4 miles long. All box volumes are within a factor of two of each other. Figure 6 illustrates the fluxes and properties incorporated in the model calculations. Each box is assumed to have a uniform value of salinity, S_i, and nutrient concentration, C_i. Similar to the two-layer box model of Pritchard (1969), mixing along the axis of the estuary has been lumped into a single parameter, the box exchange coefficient, E_i. The inter-box fresh water flow, Q_i, is distinguished from additional freshwater inputs, L_i, due to tributary inflows and waste water discharge. The net flow of freshwater is always seaward. The nutrient loads to each box associated with WWTFs and tributaries are described by H_i. The flux from the sediment is represented by M_i. In this representation of the Hudson estuary, we have not explicitly included adsorption/desorption from suspended particles or *in situ* (water column) uptake as sources or sinks of either SRP or DSi.

TABLE 3(b). SRP discharge rates, treatment level, and location of WWTF in the lower Hudson estuary tidal channels in the early 1970s

Channel	Treatment facility	Treatment level	Freshwater discharge ($m^3 s^{-1}$)	SRP load[c] ($mol s^{-1}$)	SRP ($\mu mol l^{-1}$)
K.V.K.	Bayonne	P	0·32	0·03	100
K.V.K.	Port Richmond[a]	P	0·72	0·14	190
K.V.K.	Jersey City West[a]	P	0·75	0·08	110
K.V.K.	Kearny[a]	P	0·20	0·02	100
K.V.K.	N. Bergen + Bergen[a]	P	2·8	0·10	30
	Total (Kill Van Kull)		4·8	0·37	80
E.R.	East Manhattan	R	6·6	0·26	40
E.R.	Bowery Bay	S	4·7	0·40	80
E.R.	Hunts Point	S	6·8	0·40	60
E.R.	Tallsman Island	S	2·7	0·33	120
E.R.	Newton Creek	S	7·6	0·42	60
E.R.	Wards Island	S	10·6	0·66	60
	Total (East River)		38·9	2·47	60

The footnotes are the same as in Table 3(a). K.V.K., Kill Van Kull and Newark Bay; E.R., East River.

Deck (1981) showed that concentrations of conservative constituents could be calculated if the volume, freshwater flow, salinity, external sources and sinks, and end member concentrations for each box are specified. By assuming that the system is in steady state with respect to salt transport, the box exchange coefficients, E_i, can be calculated from the observed salinity distribution and rate of freshwater discharge.

Model calculation input parameters

There are three dominant sources of freshwater to the tidal Hudson: (1) gauged upper river discharge over the Federal Dam at mp +154, (2) lower basin tributary run-off, and (3) WWTF discharge. The USGS maintains a number of discharge gauge stations on the main stem of the Hudson River upstream of tidal influence and on many of its tributaries. The most seaward station on the Hudson River is at the Federal Dam (mp +154). About half of the tributary area downstream of the Federal Dam is gauged. Discharge from the remainder was estimated using discharge per square kilometer from gauged areas. Only tributaries which lack significant perturbations (e.g. reservoirs and/or WWTF discharge) have been used to derive the mean tributary runoff rate. Following Garvey's (1989) approach, gauges north of Poughkeepsie (mp +75) were used to estimate tributary discharge between there and mp +154 and gauges to the south were used to estimate non-gauged tributary discharge further downstream. In all cases it was assumed that non-gauged tributary discharge was not perturbed significantly by municipal water works.

Table 2 lists discharges at the Federal Dam and at the Battery (Federal Dam plus tributary discharge) for each sampling period used in the model calculations of SRP and DSi distributions. The choice of suitable periods of time over which to average discharges was somewhat arbitrary. Because we were interested in simulating equilibrium late summer nutrient profiles, the replacement time for fresh water was relatively long

(Figure 2) and sometimes exceeded the time since the last high discharge episode. For profiles in this category we have averaged discharges following the last significant runoff event. The mean discharge rates used in the model calculations are averages of daily inflows for 25–30 days preceding collection of the estuary samples. Tributary flows were added to appropriate boxes in the model simulations.

Discharge from WWTF is the third category of major fresh water influx to the estuary below the Federal Dam. Tables 3(a) and 3(b) list the treatment facilities considered in the model calculations, along with their place of entry and discharge rates. The list includes inputs from facilities along the tidal Hudson downstream of Newburgh (mp +60), Kill Van Kull, Newark Bay, and the East, Passaic, and Hackensack Rivers. Although individual facilities have been modified signficantly during treatment level upgrading, later estimates of the discharge rate of water from WWTF (Mueller *et al.*, 1982; Brosnan *et al.*, 1987) do not differ much from those of earlier estimates. We have chosen to use the data of Mueller *et al.* (1976), because the corresponding nutrient data is more complete and hold these WWTF water discharge rates constant for the model calculations representative of later years. The total freshwater input from WWTF to the estuary as modeled here is $64\,m^3\,s^{-1}$, which is comparable, during our 17 collection periods, to the mean summer tributary input, $87 \pm 63\,m^3\,s^{-1}$, and one third of the mean summer Hudson discharge, $173 \pm 89\,m^3\,s^{-1}$, over the Federal Dam.

Net evaporation is a minor loss of freshwater in the tidal Hudson. Average reservoir evaporation rates vary throughout the year, reaching a maximum in July of 13 cm $month^{-1}$, and minimum in January of 1·5 cm $month^{-1}$ (Todd, 1970). During the summer months, an average of approximately $15\,m^3\,s^{-1}$ of freshwater is lost. Except for the 29 August–8 September collection, this loss is less than 10% of the Battery discharge (mp 0) for the transects discussed here. Freshwater discharge was not corrected for evaporative loss when used in the model calculations.

The mean salinity for each box was determined from a third order polynomial fit of the depth-averaged salinities plotted against mile point observed during each transect. The salinity calculated at the midpoint of each box from this fit was used. Rather than extrapolating from the observed salinity profile to regions not sampled, we have decreased the number of boxes used in the model runs. The number of boxes used for the model calculations for each estuary transect are listed in Table 2.

While the freshwater SRP and DSi end members were chosen by extrapolating from conservative mixing lines, the seaward end member concentrations have been fixed by the most saline data point in each transect. Usually this was the sample collected 1 m above the bottom at the Narrows (mp −8).

The SRP loading rates from WWTF [Tables 3(a) and (b)] have been estimated from compilations by Mueller *et al.* (1976) and Hammond (1975). For many of the primary and secondary treatment facilities, Mueller *et al.* (1976) reported only total-P discharge rates. In these cases, we have assumed a SRP/total-P ratio of 0·8 [Figure 5(b)] to calculate the SRP discharge rate. Mueller *et al.* (1976) did not include loading estimates for untreated sources. We have estimated these loads from their water discharge rates and an assumed SRP concentration of $40\,\mu\,mol\,l^{-1}$, which is the average value for untreated outflow from Manhattan at 125th Street measured by Hammond (1975). There are a number of assumptions built into our loading terms and they differ from other estimates. For example, Hammond (1975) estimated the total WWTF SRP load to the tidal Hudson to be 4·6 mol s^{-1} which is approximately 75% of our estimate (6·3 mol s^{-1}). However, because we are primarily interested in comparing temporal trends of observed nutrient profiles, the absolute loading term is not so important. By scaling the total WWTF SRP discharge to match observed profiles, each year's SRP loading can be quantified relative to conditions in the early 1970s.

Although our order of magnitude calculations (see discussion and Table 4) suggest that the sediment flux of SRP is minor, we have included a source term for this input in our model calculations. The sediment flux (0·2 mol s^{-1}) was assumed to be constant throughout the estuary, based on the mean flux calculated from observed pore water profile gradients, (Deck, 1981; 1×10^{-7} μmol cm^{-2} s^{-1}).

The DSi discharges from WWTF have been calculated from water discharge rates at these facilities and an assumed DSi concentration of 80 μmol l^{-1} which corresponds to average New York City reservoir water (Bopp, unpubl. data). Published values (Hammond, 1975; Garside *et al.*, 1976) and measurements we have made on New York City WWTF effluent also average approximately 80 μmol l^{-1} of DSi.

The sensitivities and resolution of the model calculations have been checked by varying the magnitudes of input parameters. Model results using SRP loads and freshwater flows varied by amounts up to $\pm 10\%$ cannot be distinguished from results using our best estimates of these parameters. However, loading and freshwater discharges which differ by more than 10% can be resolved. Changes in SRP and DSi concentrations of the seaward end member significantly affect predicted model concentrations; an increase in these concentrations leads to higher calculated maximum values and a decrease to lower maximum values. We hope by choosing observed values, we have minimized the uncertainties dependent on the magnitude of this critical parameter.

Discussion

While DSi displays behaviour typical of a number of Atlantic coast estuaries (Sharp *et al.*, 1982; Anderson, 1986) SRP displays atypical behaviour. The two unusual features of the Hudson estuary SRP profiles are the large increases in concentrations at mid-salinities (two-to-six-fold) and the quasi-conservative behaviour throughout most of the salt intruded reach.

SRP behaviour

The Hudson estuary SRP–salinity profiles differ from those of most other estuaries in that the mid-salinity maxima are more pronounced and apparent throughout the year, independent of freshwater discharge. The maximum concentrations, however, are inversely proportional to the freshwater discharge rate (Table 2). The differences between SRP *vs.* salinity profiles in the Hudson and those from other estuaries could reflect different flushing rates, a larger suspended particle load, or the presence of significant external point sources (WWTF). A comparison of loading terms shows that the discharge of the WWTFs dominates (Table 4), with more than 85% of the mid-salinity inputs coming from this source in the early 1970s.

Lacking from Table 4 are inputs from the regeneration of nutrients from organic material in the water column. The interaction of nutrients and phytoplankton has been previously examined in the Hudson south of the northern tip of Manhattan (Garside *et al.*, 1976; Malone, 1977; Malone *et al.*, 1980; Ammerman, 1989, 1991). All of these studies suggest that SRP concentrations should not be dramatically affected by biological activity in the Hudson. Despite the presence of elevated nutrient levels (SRP$>$1·3 μmol l^{-1} and total dissolved inorganic nitrogen $>$35 μmol l^{-1}), these studies have shown that chlorophyll *a* concentrations are usually low (non-bloom summer chlorophyll *a* concentrations

TABLE 4. Calculated mid-salinity non-biological SRP fluxes for the Hudson estuary. The freshwater discharge data correspond to high, low, and annual average flows

	High flow	Mean flow	Low flow
Suspended particle load (mg l^{-1})	40	30	20
Federal Dam flow ($m^3 s^{-1}$)	1200	350	200
Lower basin tributary discharge ($m^3 s^{-1}$)	200	60	25
Freshwater end member SRP (μmol l^{-1})	1·0	1·5	2·0
Sediment SRP flux (mol s^{-1})[a]	0·2	0·2	0·2
Lower basin tributary SRP flux (mol s^{-1})[b]	0·2	0·1	0·1
Desorption SRP flux (mol s^{-1})[c]	0·5	0·1	0·04
WWTF SRP in early 1970s (mol s^{-1})[d]	6·3	6·3	6·3
Total	7·2	6·7	6·6
WWTF loading (%)	88%	94%	95%

[a]Sediment diffusion rates were determined by Deck (1981) from sediment pore water profiles. In our calculations we have used a sediment diffusional flux equal to 1×10^{-7} μmol cm^{-1} s^{-1}, Deck's mean, and have assumed it to be constant over the lower estuary which has an area of $2{\cdot}4 \times 10^8$ m^2 (mp −8 to mp 64).
[b]The tributary flux is calculated only for the discharge that enters seaward of the fresh/salt water interface, which averages 25% of the total tributary flow to the tidal Hudson.
[c]Particle reactive phosphorus (i.e. the amount of SRP which can be desorbed from the suspended material) is assumed to equal 10 μmol SRP g^{-1} of suspended material (Froelich, 1988). The flux is calculated assuming all of the particle reactive phosphorus is desorbed.
[d]Our model calculations show that the discharge during the late 1980s was closer to 2·1 mol s^{-1} and hence, during the late 1980s, WWTF loading was 70, 84 and 88% of the total load for the high, mean, and low discharge conditions respectively.

are between 5–10 μg l^{-1}). Variations in biomass rarely perturb dissolved nutrient concentrations and neither phosphorus nor nitrogen limit primary production. It is generally thought that primary production in the saline Hudson is light limited (Malone, 1977). Microbial biomass may also be limited by its relatively short residence time within the estuary.

Microbial involvement in the phosphorus cycle in the Hudson has been examined by Ammerman (1989, 1991). His experiments indicated that SRP turnover rates (uptake rate/SRP concentration) were as high as 3% h^{-1} in the region of net SRP-uptake, but were less than 0·5% h^{-1} elsewhere. He also found that the uptake rate was generally balanced by the microbial SRP regeneration rate.

These earlier studies and our order of magnitude calculations suggest that the majority of the dissolved phosphorus added to the Hudson estuary originates from WWTFs and is rapidly mixed throughout the estuary with relatively little perturbation by the microbial community. The estuary retains a similar SRP to TDP ratio as that of the WWTFs [Figure 4(b); WWTF total-P is assumed to approximately equal TDP] showing little net uptake or regeneration within the water column. The quasi-conservative behaviour of SRP seems to result from a relatively low microbial turnover rate due to high concentrations of dissolved SRP.

DSi behaviour

DSi/SRP ratio *vs.* salinity plots of our Hudson profiles demonstrate that summer mid-salinity sources are significantly different in location for these two nutrients. A typical plot

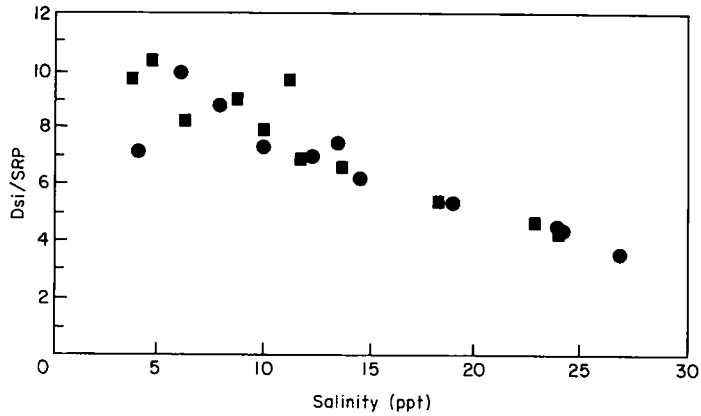

Figure 7. DSi/SRP ratios plotted against salinity for the 25 August 1977 profile. The decrease of the ratio at higher salinities indicates that an important component of DSi input occurs at lower salinity than the dominant SRP source, WWTFs. ■, Surface; ●, Bottom.

(Figure 7) shows that a substantial portion of the DSi is added to the water at lower salinities than for SRP. Therefore, a source other than WWTFs must be involved as an important input of DSi. A process similar to that outlined by Anderson (1986) appears to be occurring in the Hudson estuary [Figures 5(a) and (b)] in addition to any DSi derived from WWTFs.

SRP loading history

To estimate the loading history of SRP over a period of 16 years we will assume it behaves quasi-conservatively within the Hudson estuary and match model simulations to observed nutrient profiles by varying the total loading rate from the WWTF sources. Late summer profiles have been chosen because steady-state salinity conditions are most likely after long periods of low freshwater discharge, the differences between surface and bottom salinities are minimized, and because the differences between mid-salinity SRP and end member concentrations are greatest. Freshwater discharge, sediment source, salinity distribution, and end member nutrient concentrations, are used as fixed input parameters.

Figures 8(a)–(c) show SRP transect data from 16–18 August, 1973, 27–28 August, 1974 and 23–26 August, 1988 and model calculated profiles using loads which are based on the WWTF input values listed in Table 3(a), fresh water discharges listed in Table 2, and a sediment flux of 1×10^{-7} μmol cm^{-2} s^{-1}. Model calculated profiles from the loads listed in Table 3(a) matched the observed data of the 1973 and 1974 transects. On the other hand, Figure 8(c) shows that these loads are much too high to account for the observed data in 1988. However, when the WWTF loads are reduced by 66%, the model calculation results are consistent with the observed SRP data.

For an additional 14 profiles we have estimated the WWTF SRP loading by scaling the early 1970s loads to fit observed SRP transect data. The results of these models runs are listed in Table 2 and plotted in Figure 9. While most of the error bars represent the resolution of single-layer model calculations ($\pm 10\%$), for the 14–15 August 1984 profile the uncertainty was estimated to be $\pm 25\%$. In this profile, the seaward end member was not well defined. Two samples were collected at different locations in the Upper Bay with salinities of 25 ppt and significantly different SRP concentrations ([SRP] = 2·6 and

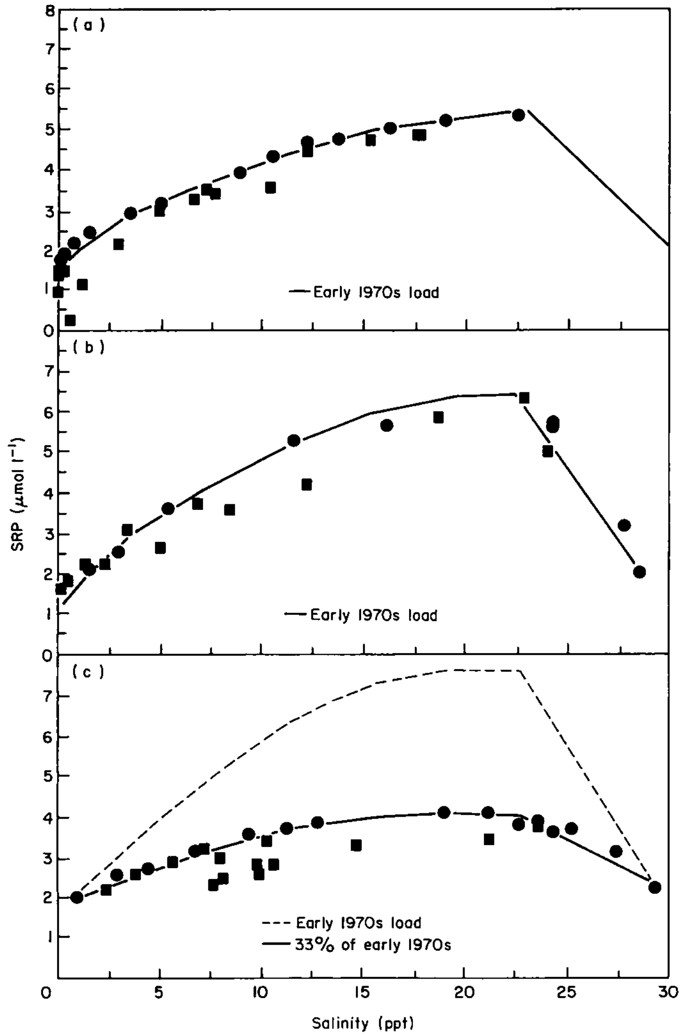

Figure 8. Model results plotted with observed SRP data for the (a) 16–18 August 1973 (b) 27–28 August 1974 and (c) 23–26 August 1988 profiles. The freshwater discharges for these transects are listed in Table 3. ■, Observed surface data; ●, observed bottom data.

$1{\cdot}5\ \mu mol\ l^{-1}$). The model was run using each of these SRP concentrations as an end member; the range of calculated WWTF SRP loads are represented by the larger error bar. For two of the profiles, 2–4 October 1974 and 29 August–8 September 1989, the model calculated curves could not be fit to the observed data without changing the sediment flux; the rest of the profiles could be fit reasonably well by varying the WWTF SRP discharges alone. The inability of the model to predict the observed data from 2–4 October 1974 and 29 August–8 September 1989 profiles probably reflects non-steady state conditions for the salinity distribution. For 3 weeks prior to early October 1974, the freshwater discharge had been increasing. During the late August 1989 collection, the freshwater discharge was much lower than during any of the other collection periods, with a freshwater residence time of 170 days. In Figure 9, these points are plotted in brackets

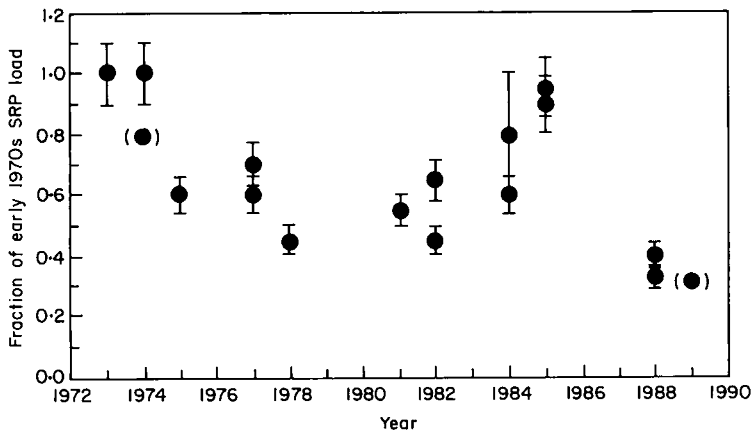

Figure 9. Model predicted SRP loads plotted as a function of collection years for Hudson estuary profiles. The loads are reported as fractions of the early 1970s total WWTF load components (which are listed in Table 4(a)].

because we believe the WWTF loads based on model calculations have greater uncertainty than for the other sets of transect data.

Figure 9 indicates that the SRP loading from WWTFs has decreased significantly over the 16 years represented here by nutrient transect data. Some of the variability in the time trend may reflect storm pulses from combined sewer overflows (CSOs) which can double the total WWTF SRP discharge immediately following a heavy rain. There is some evidence from lower basin tributary discharges that storms passed prior to all collections periods. However, the CSO discharges are episodic pulses and do not account for a high proportion of the loading over extended periods of time.

Part of the decrease of WWTF SRP discharge after 1974 to 55% of the early 1970s load probably reflects the replacement of phosphorus in detergents as well as upgrading of treatment facilities. WWTFs which were not upgraded between 1974 and 1979 had a systematic decline in SRP discharge concentrations which averaged 33% (Mueller *et al.*, 1976, 1982) in both New York and New Jersey facilities (despite the fact that NJ does not have a legal limit on phosphorus in detergents). The New York State ban of phosphorus detergents (end of 1972) occurred prior to our earliest transect but the largest decline in SRP in the Hudson estuary appears to have occurred a few years later. At present we do not have a well documented explanation for the lag between the decline of SRP levels in the Hudson estuary and New York State's ban. The return to loading conditions typical of the early 1970s in the mid-1980s probably reflects construction at the Passaic Valley Sewerage Commission treatment facility, which accounts for nearly half of the SRP load to the Hudson estuary. From 1983–86 new primary clarifiers were installed at the plant causing a period of reduced treatment (Interstate Sanitation Commission, 1983–86). Similarly the most recent reduction of SRP loading may reflect the new primary clarifiers coming on line at the Passaic Valley Sewerage Commission facility. Another factor which may have affected SRP loading over the years was changes in industrial releases, but we do not have empirical data relevant to this issue.

New York City Department of Environmental Protection summer 'average' Hudson Harbor SRP concentrations show roughly similar trends with time since the mid 1970s (Brosnan, 1987). However, these average values have not been corrected for differences in

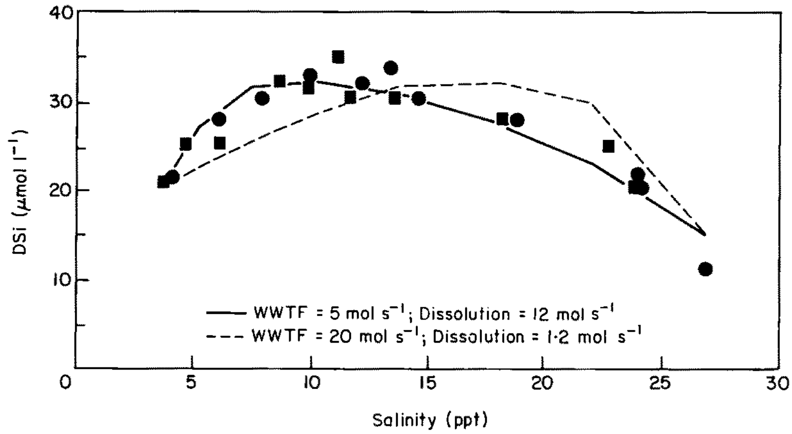

Figure 10. Model calculation results plotted with observed DSi data for the 25 August 1977 transect. The shape of the solid line is more consistent with the observed data, indicating that the dissolution of diatom tests is a major source of DSi to the salt intruded estuary and probably exceeds WWTF as a source of DSi during this sampling period. ■, Surface; ●, Bottom.

freshwater discharge between the collection periods. Some of the variability observed in their time trend probably results from variable summer freshwater discharge.

Transects collected prior to 1973 (Ketchum, 1969; Interstate Sanitation Commission, 1971) displayed higher maximum SRP concentrations than observed during our 1973 and 1974 transect. The maxima from SRP transects on 7 July, 1964 (Ketchum, 1969) and 2–12 August, 1971 (Interstate Sanitation Commission, 1971) transects were 8·4 and 7·2 $\mu mol\, l^{-1}$, respectively. However both transects were collected during periods of low freshwater discharge, (100 and 220 $m^3\, s^{-1}$ at the Battery, respectively). Model calculations suggests that SRP loading at the time of these two transects were not significantly different than during the early 1970s.

DSi loading history

The summer DSi loading history is estimated by assuming the dissolution of diatom tests can be simulated as a sediment source and by matching the model calculations to observed profiles. Freshwater discharge, WWTF DSi discharge, salinity distribution, and end member nutrient concentrations, are used as fixed input parameters.

Figure 10 illustrates several attempts to simulate a representative observed DSi profile using the single-layer model. The dashed line was calculated using DSi fluxes from the sediments based on pore water concentration gradients (Deck, 1981) and WWTF DSi fluxes proportional to their water discharge rates (using a constant DSi = 320 $\mu mol\, l^{-1}$). The DSi maximum of the model calculations lies seaward of the observed values indicating that WWTF discharge is not the only important source of DSi within the estuary. The most likely candidate for a second major source is provided by the dissolution of diatom tests (Anderson, 1986). The solid line represents model calculations assuming that the dissolution rate of diatoms per square metre is constant throughout the estuary and the WWTF discharge has a DSi concentration of 80 $\mu mol\, l^{-1}$. All eight observed transects could be matched using these assumptions. The calculated dissolution fluxes are 2–14 times the average sediment diffusive flux, $5 \times 10^{-7}\, \mu mol\, cm^{-2}\, s^{-1}$, calculated by Deck

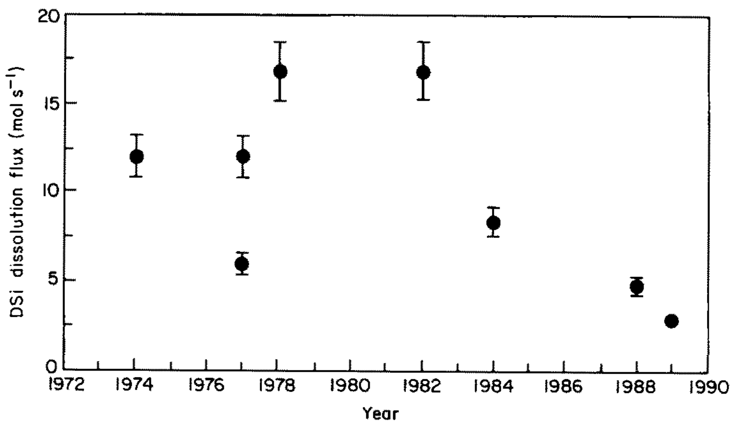

Figure 11. DSi influxes calculated with model simulations plotted as a function of year of collection for the Hudson estuary profiles.

(1981) from pore water profiles, indicating that the dissolution of diatom tests is an important DSi flux during the summer in the Hudson estuary. Mass balance calculations indicate that this flux, which ranges between 3 and 17 mol s^{-1}, is the same order of magnitude as the total WWTF discharge, 5 mol s^{-1}. Thus the results of the model calculations suggest that WWTF discharge supplies a significant but not dominant portion of the DSi to the Hudson estuary during summer months.

Although there appears to be some correlation between the temporal history of total DSi dissolution flux and SRP WWTF discharge, the co-variation is not strong. Rather than showing an initial reduction in the mid 1970s followed by high discharges in the mid 1980s as occurred for SRP loading, DSi shows a relatively high and variable input flux through the early 1980s followed by a decline in the mid to late 1980s (Figure 11). Plots of dissolution *vs.* time of year or freshwater discharge do not reveal consistent relationships, suggesting the observed variation of DSi may reflect episodic strong and weak diatom blooms or downstream transport of tests.

The regeneration of SRP from the transported diatoms can be estimated from the model-derived DSi fluxes. Assuming that the regeneration rate of DSi and SRP from the transported diatom tests is the same as the observed uptake ratio upstream of the salt/freshwater interface (DSi-uptake/SRP-uptake = 70), the maximum SRP regeneration rate from diatoms would be 0·25 mol s^{-1} in the saline Hudson. This flux is small compared to the total WWTF discharge rate, but is comparable to the diffusive flux of SRP from the sediment pore waters (Table 4).

Conclusions

In the Hudson estuary, the effects of phytoplankton activity upstream of the salt/freshwater interface were apparent in the SRP and DSi profiles collected during low summer discharge but not during high flow spring conditions. In some of the profiles downstream of the interface, appreciable SRP uptake was observed in surface water samples at relatively low salinities. The uptake occurred episodically throughout the year in narrow salinity windows at relatively low salinities. The lack of observable SRP uptake in the saltier water (Harbor and Upper Bay regions, mp +10 to mp −8) is consistent with the observations of Garside *et al.* (1975) and Malone (1977), who found changes in phytoplankton activity from that section of the estuary were not reflected in nutrient *vs.* salinity profiles. DSi profiles never showed a net uptake of DSi downstream of the salt/freshwater interface.

Excluding these episodic periods of net uptake, SRP displays behaviour in the saline reach of the Hudson atypical of most other estuaries. Biological and particle exchange processes are overwhelmed by the addition of SRP from WWTF near the downstream end of the system. The dominance of these external sources leads to SRP displaying quasi-conservative behaviour within the estuary. On the other hand, the behaviour of DSi in the Hudston estuary is more similar to that of other estuaries along the Atlantic coast of the U.S.A. Diatoms blooms upstream of the salt/freshwater interface followed by downstream transport and dissolution of the tests appear to regulate critical features of the distribution of DSi in the saline reaches of the estuary.

During low freshwater discharge (summer) conditions SRP and DSi have profiles with similar shapes, although the mid-salinity maximum for DSi is upstream of that for SRP. Loading estimates indicates that WWTF is a major source for both nutrients. While the WWTF DSi discharges account for 20–65% of the total lower estuary loads during summer months, the SRP discharges accounted for more than 85% of the net influx. Efforts to improve coastal water quality are reflected in the SRP WWTF loading history over the period of nearly two decades. In addition to the phosphate detergent ban in New York State, construction of secondary treatment facilities and improved primary systems appear to have substantially reduced the total loading of SRP. The history of DSi loading has not been the same as for SRP. The variations from one summer to another as well as between months of the same summer appear episodic and controlled by some combination of diatom blooms upstream of the salt/freshwater interface and downstream transport followed by dissolution of diatom tests, rather than changes in discharge amounts of DSi from WWTFs.

Acknowledgements

The authors are thankful for many discussions with W. Broecker and the helpful comments made on the original text by P. N. Froelich, J. Marra and K. Hunkins. The many hours spent collecting and analysing the transect samples by David Robinson are greatly appreciated. Financial support for this study was provided by the Hudson River Foundation (grant no. 010/88A/027). This is contribution no. 4804 from Lamont-Doherty Geological Observatory of Columbia University.

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