

Response of summer chlorophyll concentration to reduced total phosphorus concentration in the Rhine River (Netherlands) and the Sacramento – San Joaquin Delta (California, USA)

Erwin E. Van Nieuwenhuysse

Abstract: Reductions in wastewater loading led to significant declines in mean summer total phosphorus (TP) and chlorophyll concentration (Chl) in two large flowing water systems despite their initially shallow (<2 m) euphotic depth and continually high (>40 mg·m⁻³) soluble reactive P concentration. In the Rhine River, a gradual 2.7-fold reduction in TP resulted in a 4-fold decline in Chl. In the Sacramento – San Joaquin Delta, an abrupt 1.5-fold reduction in TP led to an equally abrupt 2.6-fold reduction in Chl. Neither response could be attributed to coincidental changes in flow, light, or nitrogen concentration. The slope of the response (Chl:TP) in both systems paralleled the average trajectory calculated using an among-system TP–Chl relationship for a broad cross section of flowing waters. The results suggest that TP was the principal determinant of Chl in both systems and that control of phosphorus loading may be an effective tool for managing eutrophication in other flowing water systems with relatively high (10–100 mg·m⁻³) soluble reactive P concentrations.

Résumé : La réduction des apports d'eaux usées a entraîné un déclin important dans les concentrations moyennes de phosphore total (PT) et de chlorophylle (Chl) en été dans deux grands systèmes d'eau courante malgré la faible profondeur initiale de leur zone euphotique (<2 m) et leurs concentrations de départ constamment élevées (>40 mg·m⁻³) de P réactif soluble. Dans le Rhin, une réduction graduelle du PT par un facteur de 2,7 a causé un déclin de la Chl par un facteur de 4. Dans le delta Sacramento – San Joaquin, une réduction subite du PT par un facteur de 1,5 a aussi résulté en un déclin rapide de la Chl par un facteur de 2,6. Ni l'un, ni l'autre de ces phénomènes ne s'explique par des changements parallèles dans le débit, la lumière ou les concentrations d'azote. La pente de la réaction (Chl:PT) dans les deux systèmes suit en parallèle la trajectoire moyenne calculée à l'aide d'une relation PT–Chl obtenue sur un large éventail de milieux d'eau courante. Ces résultats laissent croire que le PT est la principale variable explicative de la Chl dans les deux systèmes et que le contrôle des apports de phosphore peut être un outil efficace pour gérer l'eutrophisation dans d'autres systèmes d'eau courante possédant des concentrations relativement élevées (10–100 mg·m⁻³) de P réactif soluble.

[Traduit par la Rédaction]

Introduction

The response of average chlorophyll concentration to reduced phosphorus loading is well documented in individual lakes (Smith and Shapiro 1981; Sas 1989) and is consistent with the positive relationship between chlorophyll and total phosphorus concentration among lakes (e.g., Sakamoto 1966; Jones and Bachmann 1976). Recent studies indicate that phosphorus may also determine the chlorophyll concentration of tidal lakes, estuaries, and nearshore coastal waters (Meeuwig et al. 2000; Hoyer et al. 2002; Smith 2003). This body of evidence demonstrates the dependence of suspended algal biomass on phosphorus supply and provides the scientific basis for managing eutrophication in many parts of the world. Much less is known about the phosphorus–chlorophyll relationship in flowing waters.

It is commonly assumed that phosphorus limitation is unlikely in systems where soluble reactive P concentrations rou-

tinely exceed the half-saturation constants of algae grown in phosphorus-limited cultures, i.e., in the 1–10 mg·m⁻³ range (e.g., Chapra 1997). Such low concentrations are common in phosphorus-limited lakes, especially during phytoplankton blooms (Sas 1989), but are rare in high-order flowing water systems (Harrison et al. 2005). Consequently, most studies of suspended algal production in large, turbid rivers assert that algal growth rate depends primarily on light rather than phosphorus (e.g., Friedrich and Viehweg 1984; Reynolds and Descy 1996; Jassby 2005). In some systems, nitrogen and silica limitation have also been invoked (Ball and Arthur 1979; Admiraal et al. 1993).

Other studies, however, document strong positive relationships between total phosphorus concentration (TP) and chlorophyll concentration (Chl) among flowing water systems (Jones et al. 1984; Basu and Pick 1996; Van Nieuwenhuysse and Jones 1996). These among-system relationships for flowing waters are analogous to the TP–Chl relationships

Received 22 September 2006. Accepted 29 June 2007. Published on the NRC Research Press Web site at cjfas.nrc.ca on 25 October 2007.
J19553

E.E. Van Nieuwenhuysse. US Bureau of Reclamation, Division of Environmental Affairs, 2800 Cottage Way, MP-150, Sacramento, CA 95825, USA (e-mail: evannieuwenhuysse@mp.usbr.gov).

Table 1. Physical and chemical characteristics of the Rhine River at Lobith (1977–2005) and the Sacramento – San Joaquin Delta (1975–2005): catchment area (A), mean annual discharge (Q_{ave}), and mean summer (May–September) discharge for study period (Q), mean depth (z), and mean summer specific conductance (EC).

System	A (km ²)	Q_{ave} (m ³ ·s ⁻¹)	Q (m ³ ·s ⁻¹)	z (m)	EC (μS·cm ⁻¹)
Rhine River at Lobith	185 000	2355	2052	6 ^a	760
Sacramento – San Joaquin Delta	90 650	918 ^b	560	5.5 ^c	308
Sacramento River at Freeport	55 000	653	511	6.6 ^d	162
San Joaquin River near Vernalis	35 060	133	105	2.3 ^d	656

^aJulien et al. 2002.

^bSum of “net Delta outflow” and “total exports” in DAYFLOW model (<http://www.iep.ca.gov/dayflow/output/index.html>).

^cVolume (~1100 × 10⁶ m³) divided by wetted area (~200 × 10⁶ m²).

^dFrom US Geological Survey rating curve data (<http://nwis.waterdata.usgs.gov/usa/nwis/measurements>).

Fig. 1. Mean summer phosphorus concentrations in the Rhine River at Lobith: (a) total phosphorus (TP, squares) and discharge at Lobith (broken line); (b) total particulate P (TPP, open squares), soluble reactive P (SRP, solid squares), and the SRP:TP ratio (open diamonds, right axis); and (c) total suspended solids (solid squares) and the TPP:TSS ratio (open squares, right axis). Broken vertical line splits the time series in half for before-and-after comparisons.

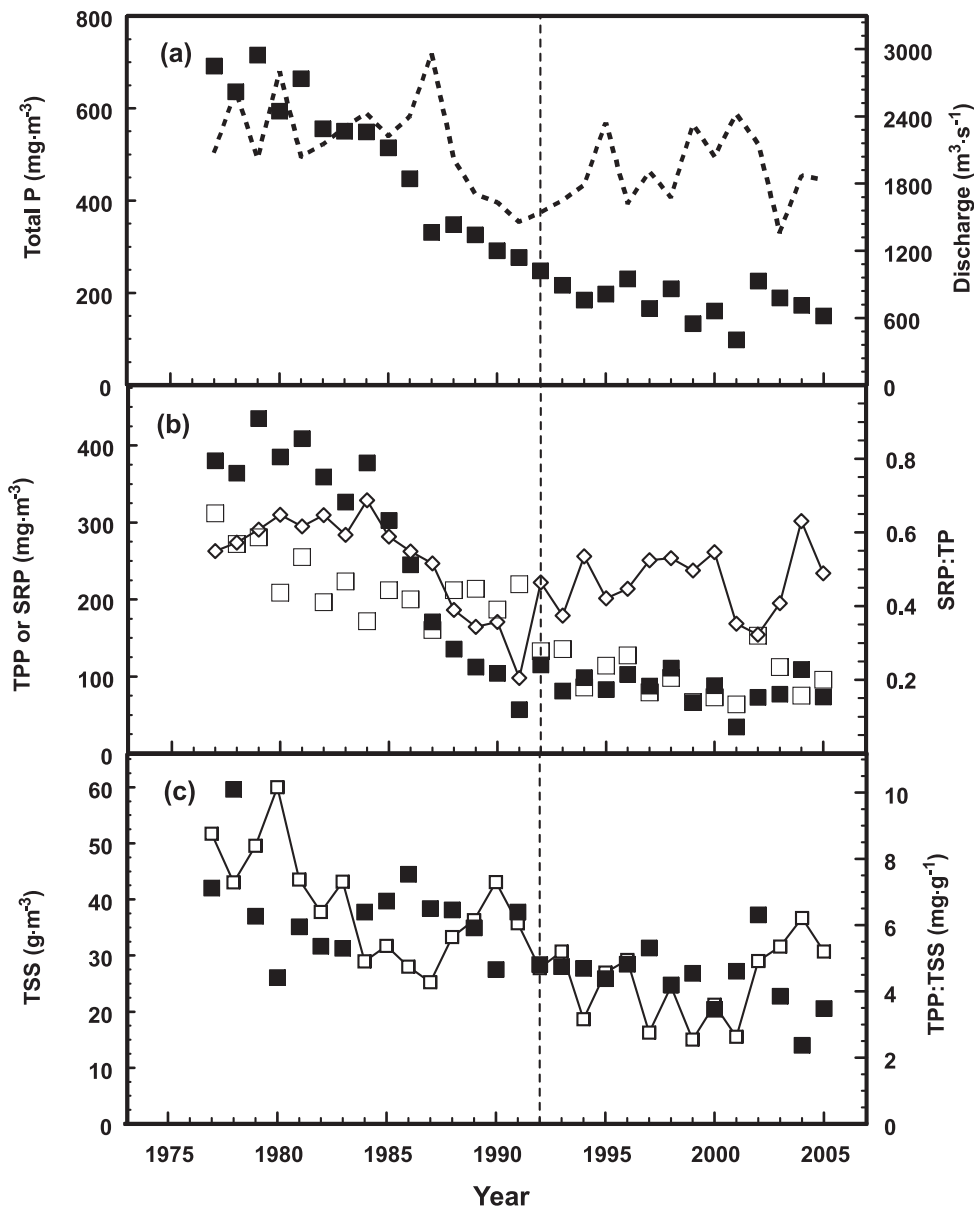


Table 2. Summary statistics for summer average water quality conditions in the Rhine River and the Sacramento – San Joaquin Delta before and after phosphorus load reduction.

Variable	Rhine River				Delta			
	1977–1991		1992–2005		1975–1993		1994–2005	
	Mean±SE	Min–Max	Mean±SE	Min–Max	Mean±SE	Min–Max	Mean±SE	Min–Max
Discharge, Q ($\text{m}^3\cdot\text{s}^{-1}$)	2189±108	1458–2959	1895±87	1359–2423	458±47	211–1084	595±66	314–1025
Total P, TP ($\text{mg}\cdot\text{m}^{-3}$)	499±39	277–716	184±11	98–248	127±4	76–150	87±3	73–104
Total particulate P, TPP ($\text{mg}\cdot\text{m}^{-3}$)	222±11	160–312	101±8	64–153	52±2	37–68	37±2	28–47
Soluble reactive P, SRP ($\text{mg}\cdot\text{m}^{-3}$)	278±33	57–435	86±6	35–115	75±4	39–104	51±2	41–66
SRP:TP (unitless)	0.53±0.04	0.20–0.69	0.47±0.02	0.32–0.63	0.59±0.02	0.46–0.70	0.58±0.02	0.45–0.67
Total suspended solids, TSS ($\text{g}\cdot\text{m}^{-3}$)	37±2	26–60	26±2	14–37	19±2	10–38	8.7±0.6	4.5–12
TPP:TSS ($\text{mg}\cdot\text{g}^{-1}$)	6.7±0.4	4.3–10.2	4.3±0.3	2.5–6.2	3.2±0.2	1.2–4.5	5.3±0.5	3.9–9.1
Total N, TN ($\text{mg}\cdot\text{m}^{-3}$)	4967±83	4413–5573	3297±150	2496–4327	638±22	488–795	602±29	483–783
Dissolved nitrate–nitrite N, $\text{NO}_3\text{--NO}_2\text{-N}$ ($\text{mg}\cdot\text{m}^{-3}$)	3538±68	3104–3914	2568±120	1978–3326	223±15	111–353	249±18	169–344
Dissolved ammonium N, $\text{NH}_4\text{-N}$ ($\text{mg}\cdot\text{m}^{-3}$)	335±35	158–666	70±11	23–176	43±4	23–82	46±3	27–65
TN:TP (unitless)	11±1	7.7–18	20±1	15–28	5.2±0.2	3.4–7.9	7.0±0.3	5.4–9.3
DIN:SRP (unitless)	24±6	9.5–80	41±5	29–99	3.7±0.2	2.4–5.9	6.1±0.4	3.6–8.0
Dissolved silica, $\text{SiO}_2\text{-Si}$ ($\text{mg}\cdot\text{m}^{-3}$)	1.3±0.11	0.6–1.9	1.7±0.06	1.3–2.0	6.4±0.2	4.7–7.9	6.2±0.2	5.3–7.0
Euphotic depth, z_{eu} (m)	1.6±0.06	1.06–1.97	2.0±0.1	1.53–2.9	2.5±0.11	1.5–3.3	3.6±0.10	3.1–4.4
Chlorophyll, Chl ($\text{mg}\cdot\text{m}^{-3}$)	56±6	14–89	14±1	6.3–24	15±1	10–23	5.7±0.4	3.7–7.7
Chl:TP (unitless)	0.11±0.01	0.04–0.18	0.09±0.01	0.03–0.20	0.12±0.01	0.07–0.30	0.07±0.01	0.04–0.10

Note: SE, standard error; Min, minimum; Max, maximum.

developed for lakes. This analogy implies that phosphorus may limit suspended algal biomass in large flowing water systems despite their relatively high soluble reactive phosphorus concentrations and low light intensities at depth (Mainstone and Parr 2002). If so, management actions aimed at reducing a particular river's TP may, as in inland and tidal lakes, lead to a concomitant reduction in Chl. To test this hypothesis, I used data from long-term (~30 years) monitoring programs to document how TP and Chl in two large, flowing water systems, one inland (the Rhine River at Lobith) and one tidal (the Sacramento – San Joaquin Delta), responded to substantial reductions in their external phosphorus supply.

Materials and methods

Study sites

Rhine River

The Rhine River at Lobith ($51^{\circ}52'0''\text{N}$, $6^{\circ}7'0''\text{E}$) is 1320 km long and drains some 185 000 km^2 . Historically, mean daily discharge has ranged from 790 to 12 000 $\text{m}^3\cdot\text{s}^{-1}$, with a long-term annual mean of 2300 $\text{m}^3\cdot\text{s}^{-1}$ (Van Dijk et al. 1996; Nienhuis et al. 2002). The high flow season is during November through April, whereas relatively low flows prevail from May through October. During the period of study (1977–2005), mean summer (May–September) discharge ranged from 1359 to 2959 $\text{m}^3\cdot\text{s}^{-1}$ and averaged 2047 $\text{m}^3\cdot\text{s}^{-1}$. The mean depth at this discharge is about 6 m (Julien et al. 2002). Summer water temperature, pH, and

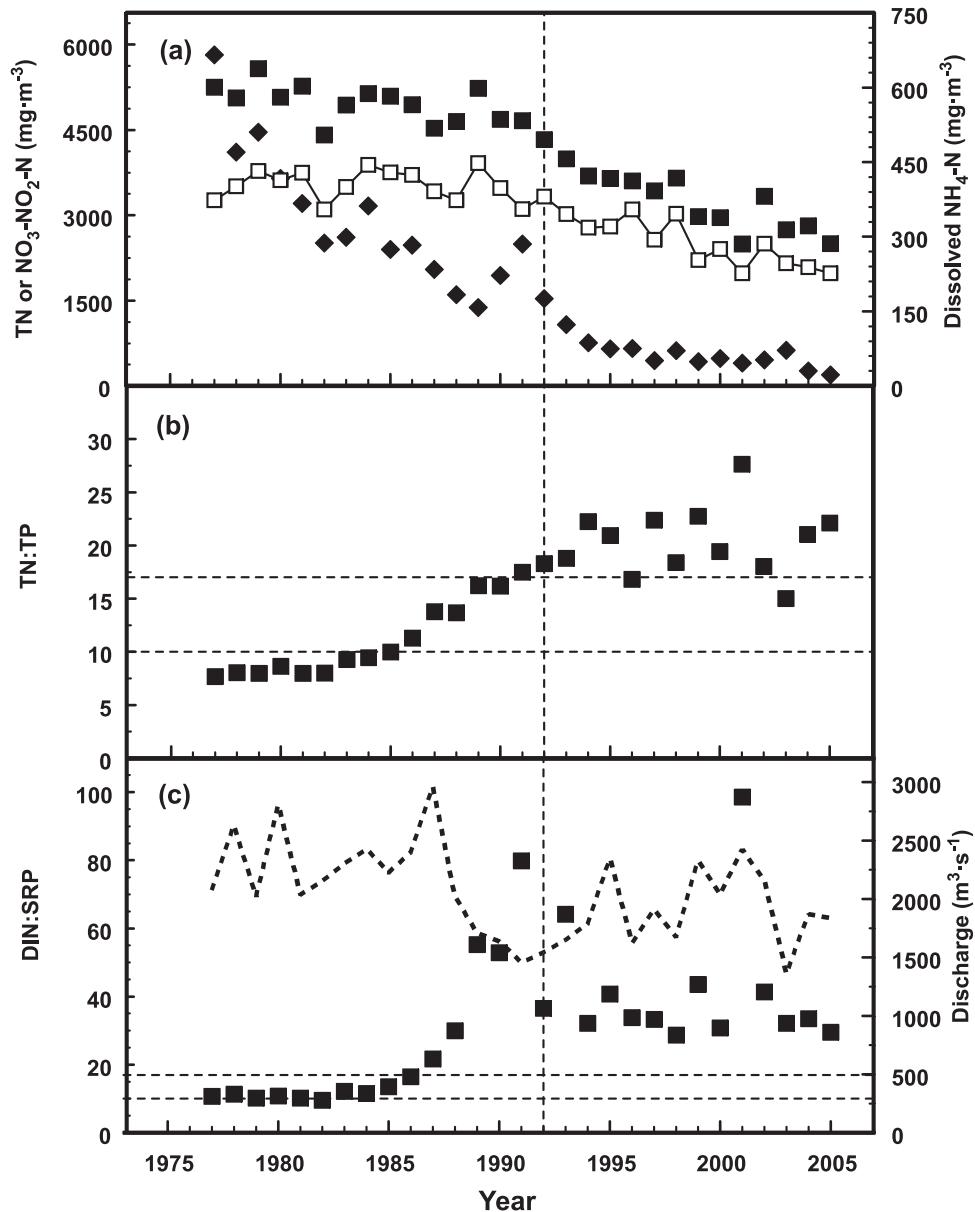
specific conductance average 20 °C, 7.7, and 760 $\mu\text{S}\cdot\text{cm}^{-1}$, respectively (Table 1). The relatively high salinity at Lobith is the result of mining and industrial activities in the catchment, not salt intrusion from the sea (Nienhuis et al. 2002).

In the 1970s, the Netherlands, Germany, and other countries bordering the Rhine River initiated a cooperative program to reduce wastewater loading from municipal and industrial facilities. One result of this program was a gradual decline in total phosphorus concentration (Van Dijk et al. 1996).

Sacramento – San Joaquin Delta

The Sacramento – San Joaquin Delta (the Delta) is an inverted delta (its apex points seaward) formed by the confluence of the Sacramento and San Joaquin rivers. Its natural outlet empties into Suisun Bay, a euryhaline subembayment of the San Francisco Bay (Jassby and Cloern 2000). The Sacramento River enters the Delta from the north and accounts for some 82% (62%–97%) of the Delta's total inflow. The San Joaquin River flows in from the south and accounts for most of the inflow balance (Table 1). In wet years, some of the Sacramento River flow is diverted around the main gaging station at Freeport (US Geological Survey gage 11447650) via a floodway that empties into the Delta near its outlet. Mean daily flow during summer varies considerably in both rivers. During the study period, flow in the Sacramento River at Freeport ranged from 131 to 2509 $\text{m}^3\cdot\text{s}^{-1}$, with a median of 445 $\text{m}^3\cdot\text{s}^{-1}$. Flows were even more variable in the San Joaquin River (USGS gage 11303500), ranging from 1.6 to 1056 $\text{m}^3\cdot\text{s}^{-1}$, with a median of 55 $\text{m}^3\cdot\text{s}^{-1}$. In addi-

Fig. 2. Mean summer nitrogen concentrations in the Rhine River at Lobith: (a) total nitrogen (TN, solid squares), dissolved nitrate–nitrite N ($\text{NO}_3\text{--NO}_2\text{-N}$, open squares), and dissolved ammonium N ($\text{NH}_4\text{-N}$, solid diamonds, right axis); (b) TN:TP; (c) ratio of dissolved inorganic nitrogen ($\text{NO}_3\text{--NO}_2\text{-N} + \text{NH}_4\text{-N}$) to soluble reactive P (DIN:SRP, solid squares) and discharge at Lobith (broken line, right axis). Broken horizontal lines mark the threshold for phosphorus limitation (>17) and nitrogen limitation (<10) using the criteria of Forsberg and Ryding (1980) and Sas (1989). Broken vertical line splits the time series in half for before-and-after comparisons.

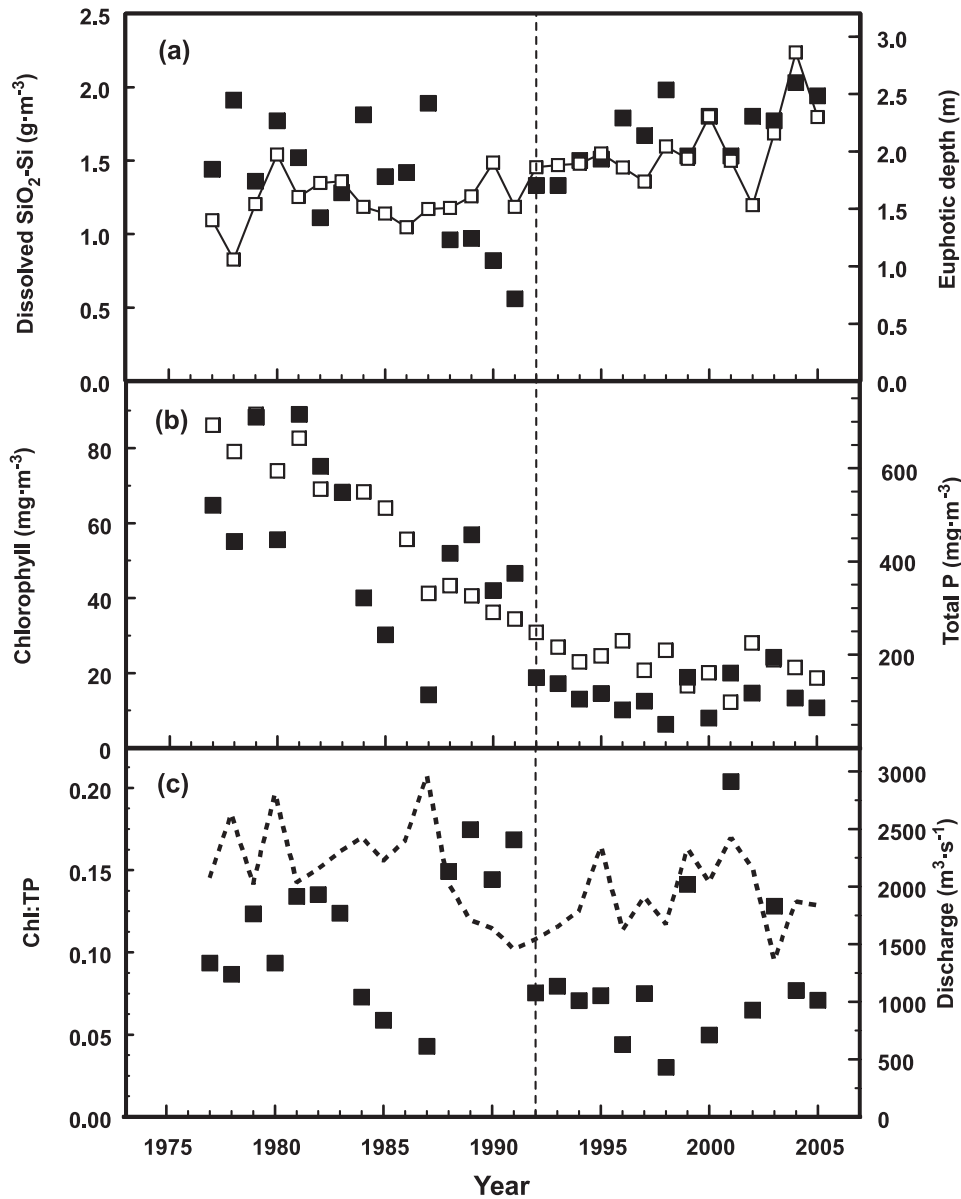


tion to the Delta's outflow to the Bay, two large ($\sim 350 \text{ m}^3\cdot\text{s}^{-1}$) pumping facilities export water from the southern Delta to supply irrigation and raw drinking water to farms and cities south of the Delta (Ball and Arthur 1979; Arthur et al. 1996).

The water diverted for export from the Delta during summer includes most of the outflow from the San Joaquin River and a large percentage of the outflow from the Sacramento River. The Sacramento River water is conveyed across the Delta by several large channels and a complex network of smaller channels. Water quality in some of these channels has been monitored off and on since the 1960s (Ball and Arthur 1979), but only three sta-

tions within this strictly freshwater corridor (station codes D26, D28A, and MD10) have an uninterrupted record for the period 1975–2005. The pooled data for these three stations were used for this analysis. Channel depths at these stations fluctuate within a roughly 1 m tidal amplitude, but average 12.5 m (D26), 5.8 m (D28A), and 5 m (MD10). By comparison, the average volume of the Delta as a whole is $\sim 1100 \times 10^6 \text{ m}^3$ and its wetted surface area is $\sim 200 \times 10^6 \text{ m}^2$. Thus, mean depth is roughly 5.5 m. Summer water temperature, pH, and specific conductance among the three stations average $23 \text{ }^\circ\text{C}$, 7.6, and $365 \mu\text{S}\cdot\text{cm}^{-1}$, respectively. A detailed map, station metadata, and links

Fig. 3. Mean summer chlorophyll concentration in the Rhine River at Lobith: (a) dissolved silica ($\text{SiO}_2\text{-Si}$, solid squares) and euphotic depth (open squares, right axis); (b) chlorophyll (Chl, solid squares) and total P (open squares, right axis); and (c) Chl:TP (solid squares) and discharge at Lobith (broken line, right axis). No chlorophyll data were collected in 1986. Broken vertical line splits the time series in half for before-and-after comparisons.



to each station's historical data sets are available at <http://www.baydelta.water.ca.gov/emp/>.

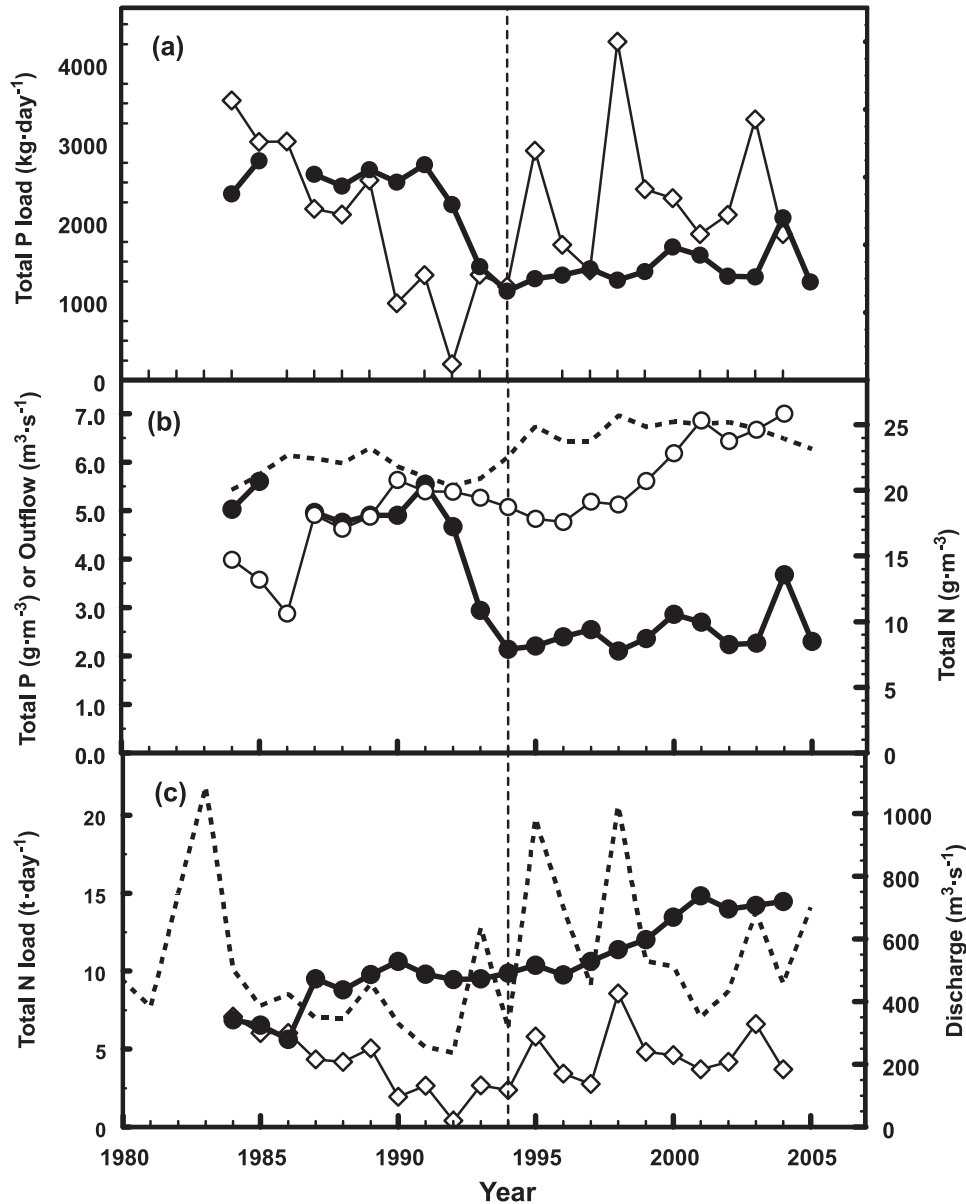
The Delta stations are located ~70 km downstream from the Freeport flow gage and from the outfall of a large (~7 m³·s⁻¹) wastewater treatment facility (38°27'15"N, 121°29'54"W). The facility treats the consolidated municipal and industrial waste of the Sacramento metropolitan area and discharges its effluent into the Sacramento River some 100 m downstream of Freeport. The facility was completed in 1984 and began discharging some 2400 kg·day⁻¹ of phosphorus up through 1991. Then, within the span of 2 years, the phosphorus output was roughly halved because of a sudden twofold reduction in the effluent's total phosphorus con-

centration. It was this perturbation that provided an opportunity to study the effect of phosphorus loading on the Delta's phosphorus and chlorophyll concentrations.

Data sets

Water quality, mean daily discharge data, and associated metadata for the Rhine River at Lobith were downloaded from an online data base maintained by the Dutch Governmental Institute on inland water management and wastewater treatment (<http://www.waterbase.nl/>). Although some variables have been monitored at this site for >100 years, routine monitoring of chlorophyll concentration began in 1977. In most years, phosphorus and chlorophyll samples

Fig. 4. Mean summer nutrient discharge from the Sacramento regional wastewater treatment facility: (a) total P discharge from the facility (solid circles) and total P load in the Sacramento River at Freeport ~100 m upstream from the facility's outfall (open diamonds); (b) discharge of effluent from the treatment facility (broken line) and the effluent's total P concentration (solid circles) and total N concentration (open circles, right axis); and (c) total N discharge from the facility (solid circles), total N load (tonnes (t)·day⁻¹) in the Sacramento River at Freeport (open diamonds), and mean summer discharge at Freeport (broken line, right axis). Effluent total P was not measured in 1996. Broken vertical line marks the beginning of the period of reduced phosphorus discharge from the wastewater facility (1994–2005).

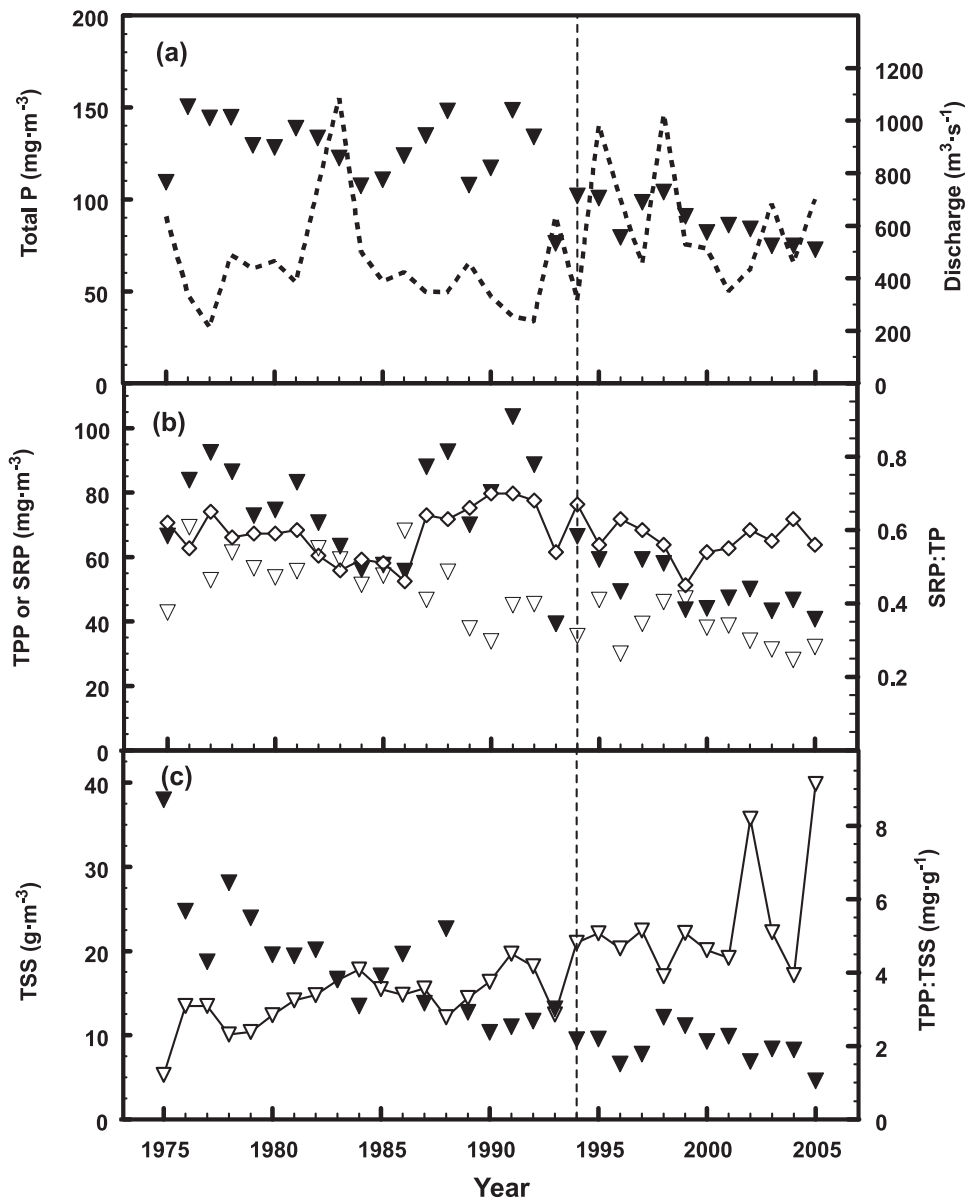


were collected twice a month. Arithmetic mean summer concentrations of total and soluble reactive phosphorus, total nitrogen, dissolved nitrate–nitrite N, dissolved ammonium N, chlorophyll, and total suspended solids were calculated using only individual samples for which chlorophyll and total phosphorus concentration had been measured. Multiple samples or duplicate entries for a given day were averaged before calculating the seasonal average.

Seasonal mean flow at Lobith was calculated using all the daily average discharge values during May–September, as opposed to just the days when water samples were collected. I used the May–September interval to be consistent with among-system TP–Chl relationships. The resulting data set had 298 individual observations (Supplemental Table S1, available from the NRC Data Depository)¹ and 28 summer mean values.

¹Supplementary data for this article are available on the journal Web site (<http://cjfas.nrc.ca>) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Building M-55, 1200 Montreal Road, Ottawa, ON K1A 0R6, Canada. DUD 5228. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml.

Fig. 5. Mean summer phosphorus concentrations in the Sacramento – San Joaquin Delta: (a) total phosphorus (TP, solid triangles) and discharge in the Sacramento River at Freeport (broken line); (b) total particulate P (TPP, open triangles), soluble reactive P (SRP, solid triangles), and SRP:TP (solid line, right axis); and (c) total suspended solids (TSS, solid triangles) and TPP:TSS (open triangles, right axis). Broken vertical line splits the time series into pre- and post-phosphorus loading reduction periods (see Table 2 for before-and-after comparisons).



Water quality data and metadata for the Delta were downloaded from a data base maintained by the California Department of Water Resources and the Interagency Ecological Program (<http://www.iep.ca.gov/emp/>). Summer mean values for the 31 years of record (1975–2005) were calculated for the same constituents and in the same way as for the Rhine. In most years, the frequency of sampling was once per month. The resulting data set had 487 individual observations (Supplemental Table S2, available from the NRC Data Depository)¹.

Water quality and effluent discharge data for the Sacramento regional wastewater treatment facility were provided by Mr. Milton Preszler (Water Quality Division, Sacramento Regional County Sanitation District, Administrative Office,

10545 Armstrong Avenue, Mather, CA 95655, USA, personal communication, 2006). Loading rates were calculated as the product of effluent discharge and the effluent’s discharge-weighted mean concentration.

I used Cloern’s (1987) empirical relationship between total suspended solids concentration (TSS) and the total vertical extinction coefficient of photosynthetically active radiation (k_z) to estimate the average depth of the euphotic zone (z_{eu}):

$$(1) \quad z_{eu} = 4.605/k_z$$

where z_{eu} is expressed in metres, and k_z (per metre, natural log) = $0.77 + 0.06(TSS)$, where TSS is expressed in grams per cubic metre.

Table 3. Analysis of covariance results, $\log Y = a + b_1(\log Q) + b_2(I)$, where Y is the dependent variable, Q is the mean summer discharge ($\text{m}^3\cdot\text{s}^{-1}$) in the Sacramento River at Freeport (USGS gage 11447650), and I is an indicator variable (0 for pre-phosphorus loading reduction, 1 for post-phosphorus reduction years).

Variable (Y)	$a \pm \text{SE}$	$b_1 \pm \text{SE}$	p^a	$b_2 \pm \text{SE}$	p^a	SE	Adj R^2
Total P, TP ($\text{mg}\cdot\text{m}^{-3}$)	2.41±0.19	0.11±0.07	0.11	-0.15±0.03	<0.0001	0.06	0.60
Total particulate P, TPP ($\text{mg}\cdot\text{m}^{-3}$)	1.46±0.24	0.10±0.09	0.30	-0.16±0.03	<0.0001	0.08	0.42
Soluble reactive P, SRP ($\text{mg}\cdot\text{m}^{-3}$)	2.51±0.24	-0.24±0.09	0.01	-0.14±0.03	0.0002	0.08	0.54
SRP:TP (unitless)	0.16±0.13	-0.15±0.05	0.005	0.008±0.02	0.65	0.05	0.21
Total suspended solids, TSS ($\text{g}\cdot\text{m}^{-3}$)	0.82±0.04	0.16±0.15	0.29	-0.34±0.05	<0.0001	0.14	0.57
Chlorophyll, Chl ($\text{mg}\cdot\text{m}^{-3}$)	1.21±0.32	-0.02±0.12	0.88	-0.41±0.04	<0.0001	0.11	0.76
Chl:TP (unitless)	-1.20±0.43	0.10±0.16	0.55	-0.27±0.06	0.0001	0.15	0.39

Note: SE, standard error; p , probability that the value of a coefficient does not differ significantly from 0 (t test, $n = 31$); Adj, adjusted.

^aAdjusted for serial correlation using eq. 3.

Data analysis

I used a simple analysis of covariance model to make before-and-after comparisons that corrected for possible flow effects. The years prior to the abrupt reduction in phosphorus loading from the wastewater treatment facility (1975 through 1993) constituted the “before” condition for the Delta, whereas for the Rhine, I used the first half of the time series (1977 through 1991). The general form of the model was

$$(2) \quad Y_i = a + b_1 Q_i + b_2 I$$

where Y_i is the variable of interest (e.g., TP, Chl, TSS) during year i , Q_i is the mean summer discharge during year i , I is an indicator variable equaling 0 for the before condition and 1 for after, and a , b_1 , and b_2 are the intercept and regression coefficients associated with each variable, respectively. If b_2 differed significantly from 0 (t test, $p < 0.01$), I concluded that the average value of Y differed significantly between the two conditions and that the difference was not due to differing flow conditions. In most cases, \log_{10} -transformation of Y and Q was necessary to stabilize variance and normalize the distributions. It was also necessary to confirm that the residual values were normally distributed (Shapiro–Wilk test, $p > 0.01$) and that their average value did not differ significantly from 0 (t test, $p > 0.01$).

Use of this model also required me to determine if the residual values were autocorrelated and, if so, to adjust the t statistic associated with b_2 accordingly. First, I calculated the correlation between the residuals for a given year and the residuals for prior years. If any of the resulting autocorrelation coefficients exceeded $1.96(\sqrt{n})$, where n is the number of observations in the time series (Brockwell and Davis 2002), I adjusted the value of the t statistic as follows:

$$(3) \quad t_{\text{adj}} = t / \sqrt{(1 + \rho^i) / (1 - \rho^i)}$$

where t_{adj} is the adjusted value of the t statistic associated with b_2 and ρ^i is the autocorrelation coefficient for adjacent years ($i = 1$), for lags of 2 years ($i = 2$), and so on (van Belle 2002). This adjustment was necessary because positive autocorrelation can inflate the value of the t statistic thereby increasing the chances of rejecting the null hypothesis (in this case, the hypothesis that the coefficient associated with i did not differ significantly from 0) when it is true. In other words, this precaution further reduced the likelihood of concluding, for example, that a before-and-after difference in Chl resulted

from a before-and-after difference in TP when the change was more likely a consequence of differing flow conditions.

Results

Rhine River

Mean summer TP in the Rhine River declined 2.7-fold over the nearly three decades of record (Fig. 1a). The decline in mean summer soluble reactive P concentration (SRP) roughly paralleled the gradual decline in TP, whereas mean summer total particulate P concentration (TPP) declined at a slower rate (Fig. 1b). Consequently, SRP:TP declined rapidly during the first half of the time series to a minimum of 0.20 by 1991, but then increased to values near its initial average value (Table 2). The 2.2-fold decline in TPP was associated with a less rapid 1.4-fold average decline in mean summer total suspended solids concentration (TSS). Consequently, the apparent phosphorus content of the suspended solids (TPP:TSS) declined over time (Fig. 1c).

Mean summer total nitrogen (TN), dissolved nitrate–nitrite N ($\text{NO}_3\text{--NO}_2\text{--N}$), and dissolved ammonium N ($\text{NH}_4\text{--N}$) concentrations also declined between 1977 and 1991 and continued to decline during subsequent years (Fig. 2a). These declines were less rapid than for TP and SRP. Consequently, TN:TP and the ratio of dissolved inorganic nitrogen ($\text{NO}_3\text{--NO}_2\text{--N} + \text{NH}_4\text{--N}$) to SRP (DIN:SRP) increased after 1991 from values indicative of potential nitrogen limitation to values consistent with exclusive phosphorus limitation (Figs. 2b, 2c).

The summer mean concentration of dissolved silica ($\text{SiO}_2\text{--Si}$) averaged $1.5 \text{ g}\cdot\text{m}^{-3}$ overall, but declined to potentially limiting levels ($\sim 0.5 \text{ g}\cdot\text{m}^{-3}$) during the low flow year of 1991 (Fig. 3a). The average $\text{SiO}_2\text{--Si}$ was 1.3 times higher during the second half of the time series than during the first half (Table 2).

Accompanying the negative trend in TSS was a positive trend in the summer average depth of the euphotic zone (z_{eu} ; Fig. 3a). On average, the z_{eu} was 10% deeper during the second half of the time series than during the first (Table 2). Assuming a constant mean depth of 6 m, the ratio of euphotic to mean depth ($z_{\text{eu}}:z$) ranged from 0.18 to 0.48, averaging about 0.30.

Along with the 2.7-fold reduction in average TP came a 4-fold decrease in the mean summer chlorophyll concentration (Chl) between the first and second halves of the study period (Table 2). The decline in Chl roughly paralleled the TP tra-

jectory but was more sensitive to abrupt changes in discharge. For example, between 1987 and the four subsequent years of relatively low flow conditions, a 1.7-fold decrease in Q had little effect on TP but was associated with a 3.5-fold increase in Chl (Fig. 3b). Consequently, there was considerable interannual variation in the Chl:TP ratio, but it bore no consistent relationship with the variation in flow (Fig. 3c).

Sacramento – San Joaquin Delta

The abrupt 2-fold decline in phosphorus loading from the regional wastewater treatment facility (Fig. 4a) led to an abrupt 1.5-fold decrease in the average TP and SRP in the Delta (Fig. 5; Table 2). Superimposed on the step-like decline in SRP was a gradual reduction in TPP (Fig. 5b). The net result was a nearly constant SRP:TP of ~0.59 throughout the study period (Table 2). The TPP decline accompanied an even steeper decline in TSS (Fig. 5c). Consequently, there was a 1.7-fold increase in TPP:TSS.

As flow to the Delta increased, SRP tended to decline, whereas TPP and TP bore no significant relationship with flow (Table 3). Consequently, SRP:TP declined slightly under high flow conditions (Fig. 5b). Analysis of covariance indicated, however, that flow was not responsible for the step declines in TP, TPP, or SRP (Fig. 6a; Table 3).

In contrast with TP, there was no evidence of an abrupt decline in TN in the Delta. Despite a gradual increase in TN loading from the wastewater treatment facility (Fig. 4c), there was no positive trend for any form of nitrogen in the Delta (Fig. 7a). The relatively stable nitrogen concentrations in the Delta combined with the substantial reductions in TP and SRP resulted in generally higher TN:TP and DIN:SRP after the reduction in phosphorus loading (Figs. 7b, 7c). Both indices, however, indicated the possibility of continual N limitation. By contrast, SiO₂-Si remained relatively high throughout the study period, averaging 6.3 g·m⁻³ overall (Fig. 8a).

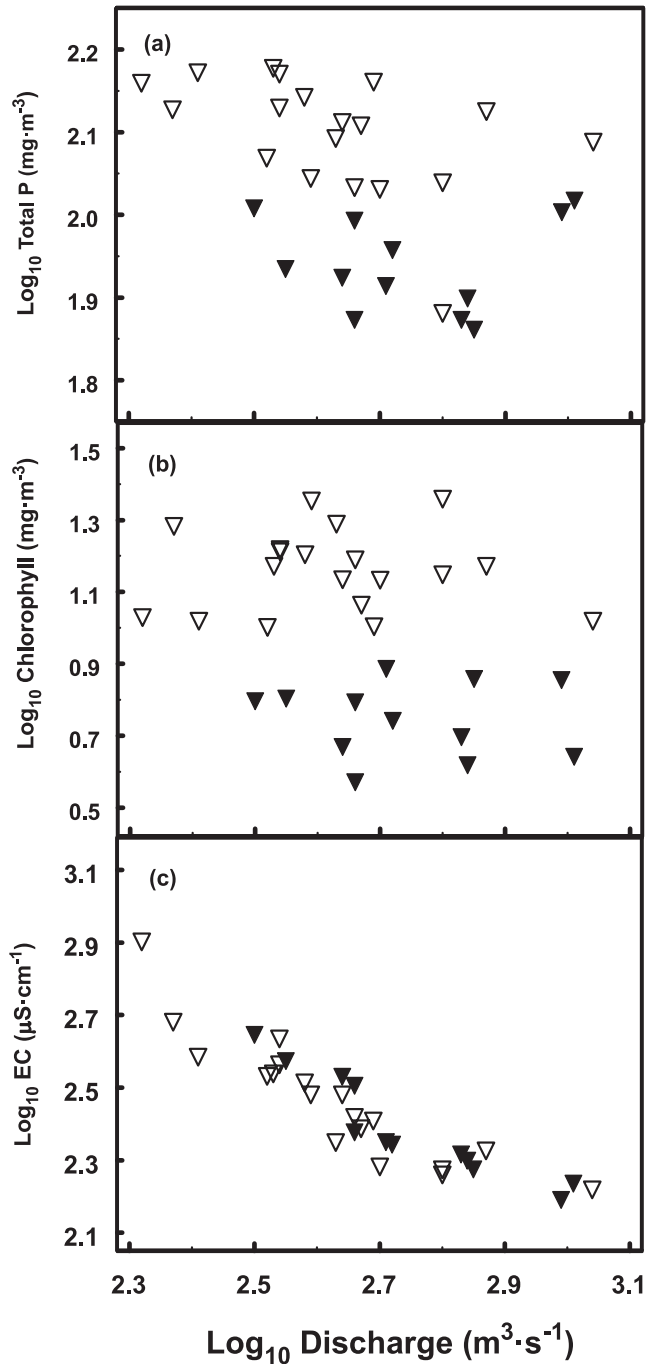
The 2.2-fold average decline in TSS resulted in a gradual 1.5-fold increase in z_{eu} (Fig. 8a; Table 2). Assuming a constant mean depth of 5.5 m, $z_{eu}:z$ thus increased from 0.45 to 0.65.

One year after the rapid and persistent reduction in TP, Chl in the Delta also declined abruptly and remained low thereafter (Fig. 8b). On average, the 1.5-fold reduction in TP led to a 2.6-fold reduction in Chl. The decline in Chl was not a result of differing flow conditions (Fig. 6b). Similarly, although Chl:TP varied from year to year, it too bore no systematic relationship with flow (Table 3).

Discussion

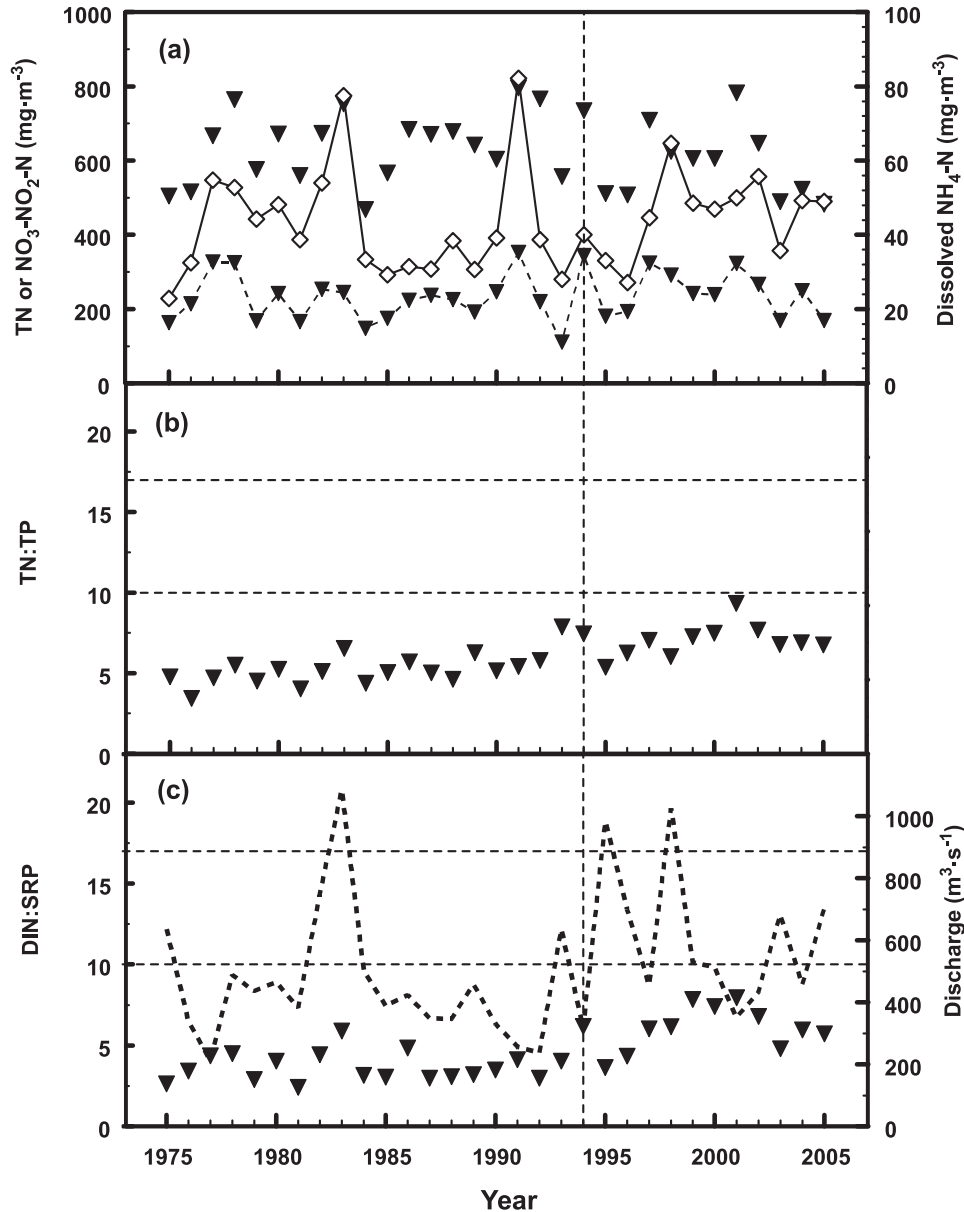
The TP decline in the Delta differed in several ways from the TP decline in the Rhine. The decline in the Delta was abrupt, whereas in the Rhine it was gradual. The 1.5-fold reduction in the Delta's TP was subtle compared with the 2.7-fold decline in the Rhine. Both systems had relatively high SRP:TP, a property consistent with the large contribution wastewater loading made to their total P loads (Jarvie et al. 2006). In the Delta, however, the proportionate change in SRP and TPP were identical, whereas in the Rhine, SRP declined more rapidly than TPP. Consequently, SRP:TP de-

Fig. 6. Analysis of covariance plots for the Sacramento – San Joaquin Delta: mean summer (a) total P concentration, (b) chlorophyll concentration, and (c) specific conductance (EC) as a function of mean summer discharge in the Sacramento River at Freeport. Phosphorus and chlorophyll concentrations were significantly higher during 1975–1993 (open triangles) than during 1994–2005 (solid triangles). There was no significant difference in the intercept of the flow–EC relationship between periods ($t = 0.96, p = 0.35$).



clined in the Rhine, especially during the first half of the time series, whereas in the Delta, SRP:TP remained about the same. Similarly, in both systems, most of the particulate P was associated with nonalgal particulate matter. But, TPP

Fig. 7. Mean summer nitrogen concentrations in the Sacramento – San Joaquin Delta: (a) total nitrogen (TN, solid triangles), dissolved nitrate–nitrite N ($\text{NO}_3\text{-NO}_2\text{-N}$, solid triangles with broken line), and dissolved ammonium N ($\text{NH}_4\text{-N}$, open diamonds, right axis); (b) TN:TP; (c) ratio of dissolved inorganic nitrogen ($\text{NO}_3\text{-NO}_2\text{-N} + \text{NH}_4\text{-N}$) to soluble reactive P (DIN:SRP, solid triangles) and discharge in the Sacramento River at Freeport (broken line, right axis). Broken horizontal lines mark the threshold for phosphorus limitation (>17) and nitrogen limitation (<10) using the criteria of Forsberg and Ryding (1980) and Sas (1989). Broken vertical line splits the time series into pre- and post-phosphorus loading reduction periods (see Table 2 for before-and-after comparisons).

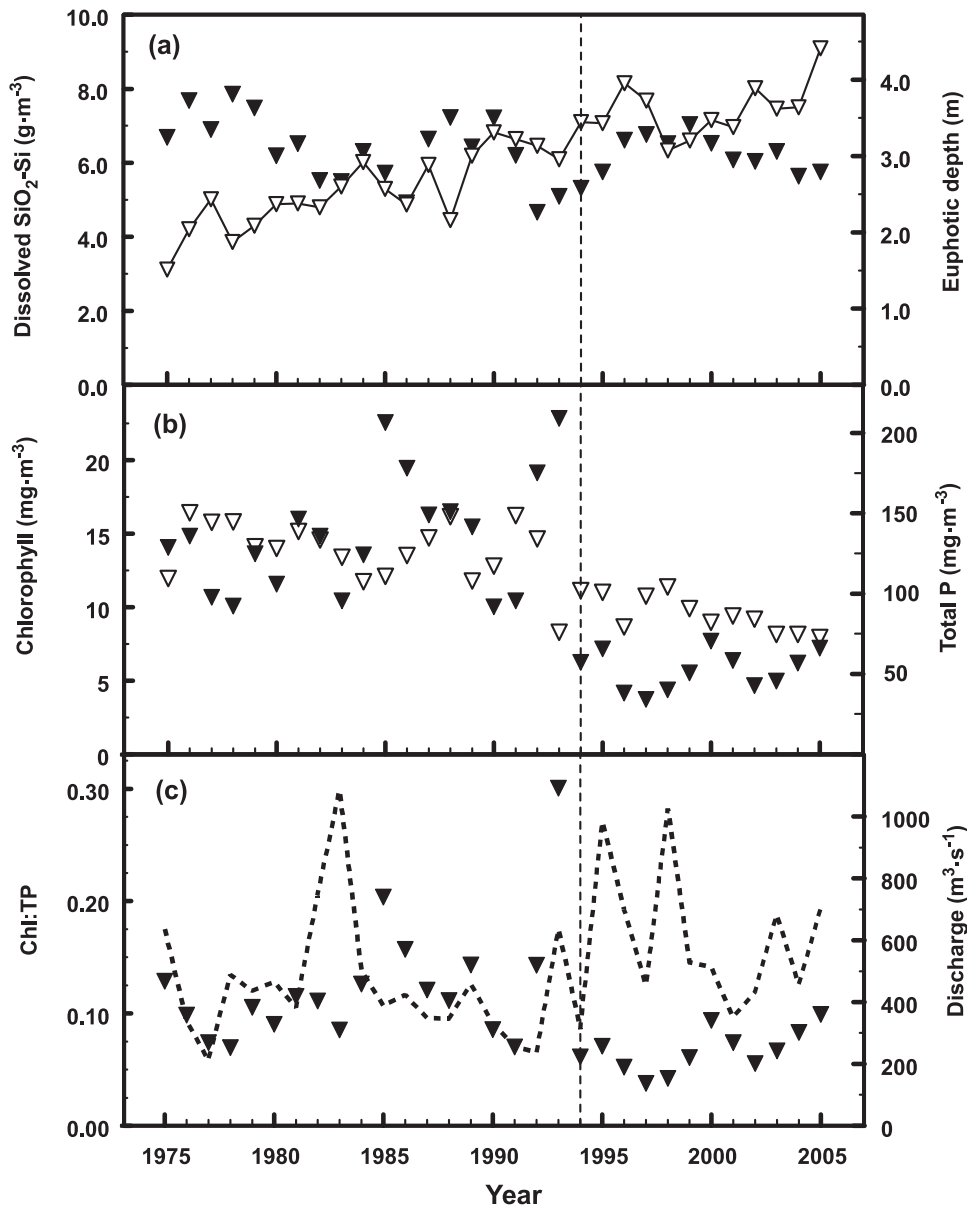


declined more rapidly in the Rhine than in the Delta, whereas TSS declined more rapidly in the Delta than in the Rhine. Consequently, the apparent P content of the suspended solids (TPP:TSS) increased in the Delta but decreased over time in the Rhine. The TP declines in both systems also shared two important similarities, however. First, neither decline could be attributed to changes in average flow conditions. And second, the TP declines in both systems led to substantial declines in Chl.

The negative response of Chl to TP reduction in the Rhine and the Delta suggests that phosphorus was the principal determinant of Chl in both systems. In both cases, the Chl tra-

jectory paralleled the average response calculated using an empirical TP–Chl relationship for a broad cross section of flowing waters (Fig. 9). In the Delta, mean Chl declined from 15 to 6 $\text{mg}\cdot\text{m}^{-3}$, whereas TP declined from 127 to 87 $\text{mg}\cdot\text{m}^{-3}$. The observed change in Chl per unit change in TP (Chl:TP) was thus 0.23 . This value is nearly identical to the maximum instantaneous Chl:TP predicted by the among-system model (Fig. 9c). Similarly, the initial Chl:TP in the Rhine (0.13) was identical to the instantaneous average Chl:TP predicted by the among-system model for $\text{TP} = 600$ $\text{mg}\cdot\text{m}^{-3}$. A lower Chl:TP in the Rhine than in the Delta is consistent with the curvilinear form of the TP–Chl rela-

Fig. 8. Mean summer chlorophyll concentration in the Sacramento – San Joaquin Delta: (a) dissolved silica ($\text{SiO}_2\text{-Si}$, solid triangles) and euphotic depth (open triangles, right axis); (b) chlorophyll (Chl, solid triangles) and total P (open triangles, right axis); and (c) Chl:TP (solid triangles) and discharge in the Sacramento River at Freeport (broken line, right axis). Broken vertical line splits the time series into pre- and post-phosphorus loading reduction periods (see Table 2 for before-and-after comparisons).

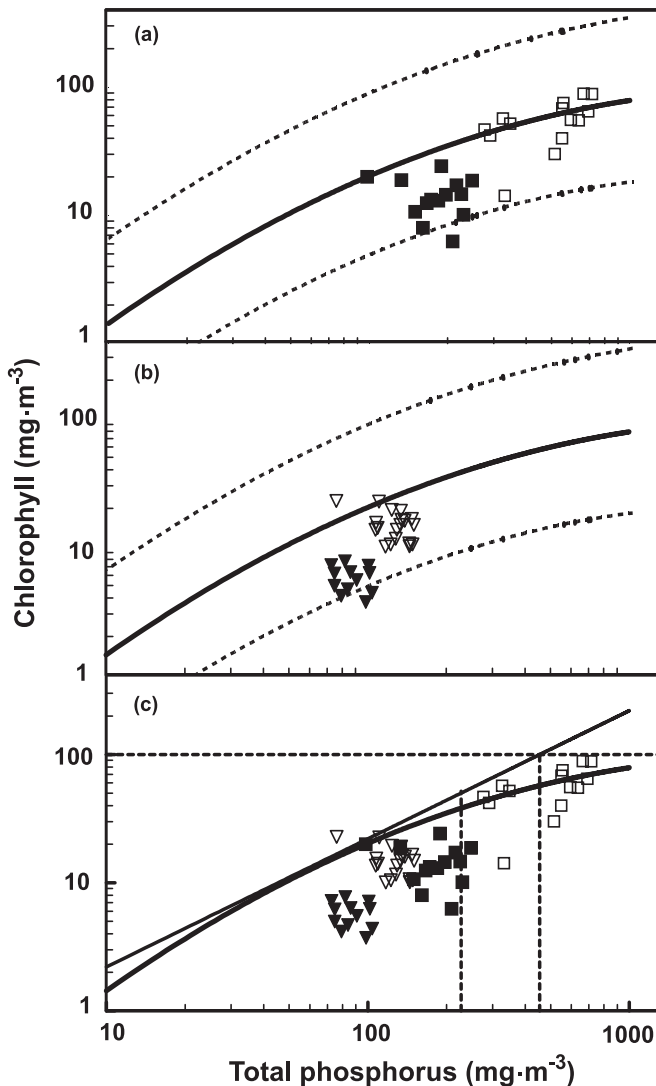


relationship and indicates that there is a point of diminishing returns beyond which further increases in phosphorus loading will have less and less effect on Chl. Initially, TP in the Rhine was near this point of diminishing returns, whereas the Delta was functioning at TP levels well within the range at which Chl would have been most sensitive to changes in phosphorus loading.

The sensitivity of both systems to changes in their phosphorus supply, despite their initially high SRP, calls into question the use of very low ($<10 \text{ mg}\cdot\text{m}^{-3}$) SRP values to determine whether or not a system is likely to respond to phosphorus management actions. The among-system model indicates that the average maximum Chl (Chl_{max}) among flowing waters generally is about $100 \text{ mg}\cdot\text{m}^{-3}$. Dividing this

value by the average maximum Chl:TP predicted by the model (0.22) yields an estimate of the average threshold TP beyond which Chl would be relatively insensitive to further increases in TP, i.e., $100/0.22$ or $455 \text{ mg}\cdot\text{m}^{-3}$ (Fig. 9c). An operational estimate of the “half-saturation constant” for TP is thus $455/2$ or $227 \text{ mg}\cdot\text{m}^{-3}$ and for SRP (assuming SRP:TP ~ 0.5) is about $114 \text{ mg}\cdot\text{m}^{-3}$. In the Rhine, SRP did not decline to this level until 1989, roughly halfway through the time series, whereas the maximum SRP in the Delta was $104 \text{ mg}\cdot\text{m}^{-3}$. Although Chl_{max} , Chl:TP, and thus the half-saturation constant for phosphorus will vary among individual systems, these results indicate that phosphorus control may be an effective tool for managing eutrophication in other flowing waters where SRP routinely exceeds $10 \text{ mg}\cdot\text{m}^{-3}$.

Fig. 9. Response of mean summer chlorophyll concentration (Chl) to reduced total P concentration (TP) in (a) the Rhine River (squares) and (b) the Sacramento – San Joaquin Delta (triangles). Open symbols are for the before-TP-reduction period, solid symbols are after. Solid line is the average trajectory calculated using an empirical model for a broad cross section of flowing waters (eq. 1 in Van Nieuwenhuysse and Jones (1996)). Broken lines encompass the 95% confidence interval for individual predicted values. Straight solid line in (c) is the maximum slope (Chl:TP) predicted by the empirical model (0.22), broken horizontal line approximates the model's predicted average maximum Chl. Broken vertical lines define the average critical TP ($455 \text{ mg}\cdot\text{m}^{-3}$) and the predicted "half-saturation constant" for TP ($227 \text{ mg}\cdot\text{m}^{-3}$).



Nitrogen concentrations declined in the Rhine, whereas they remained about the same in the Delta. In both systems, however, N:P ratios increased over time. The proportionate increase in DIN:SRP (1.7-fold) was about the same for both systems. Still, there was little evidence of nitrogen limitation in the Rhine, whereas N:P ratios in the Delta remained <10 throughout the study. This indication of N limitation seems inconsistent with the Delta's Chl response to TP reduction. Or more accurately, perhaps, the N:P criteria seem to be in-

consistent with the Delta's observed behavior. If the Delta had been N-limited, one would not expect an abrupt decline in Chl without a concomitant decline in TN. Perhaps the problem is with the assumptions underlying the criteria. The N:P criteria assume that the relative demand for both resources is fixed and that all of the N and P is potentially available for uptake by individual algal cells. In reality, both the stoichiometry of algal production (Rhee and Gotham 1980; Hecky and Kilham 1988; Geider and La Roche 2002) and the availability of nutrients (Claesson and Forsberg 1980; Bradford and Peters 1987) are highly variable properties under natural conditions. So, it is not unreasonable to suggest that either ratio might have indicated a relative shortage of nitrogen when in fact the nutrient supply was balanced or even phosphorus deficient. This line of reasoning suggests that N:P ratios, like the $\text{SRP} < 10 \text{ mg}\cdot\text{m}^{-3}$ criterion, may not provide a sufficient basis for determining whether or not a system is likely to respond to changes in its phosphorus supply.

Although in one year (1991) $\text{SiO}_2\text{-Si}$ in the Rhine declined to levels that could have limited diatom growth ($<0.5 \text{ g}\cdot\text{m}^{-3}$; Lund 1950), there was no overall downward trend in $\text{SiO}_2\text{-Si}$ paralleling the long-term decline in TP, and in the Delta, $\text{SiO}_2\text{-Si}$ was never $<4.7 \text{ g}\cdot\text{m}^{-3}$. Thus, the Chl declines were almost certainly not a consequence of a reduced silica supply.

It also seems unlikely that light played any role in the Chl declines. Even the initial $z_{\text{eu}}:z$ in both systems (>0.20) would have provided enough light to maintain a positive carbon balance (Cloern 1987; Cole et al. 1992) and the $z_{\text{eu}}:z$ only increased over time. If light had been limiting algal growth rate, then the gradual increase in euphotic depth should have led to a gradual increase in Chl unless all of the putative incremental production resulting from the increased light supply had been consumed by a concomitant increase in algal respiration or some other loss process. Even under this extraordinary circumstance, Chl would have remained about the same rather than decline.

Perhaps, however, the Chl decline in the Rhine was not caused by the reduced supply rate of P or any other resource capable of limiting algal growth rate but by a coincidental increase in the algal loss rate. Given the lack of any consistent trend in flow, it is unlikely that it was the average wash-out or settling rate that changed. However, the loss rate imposed by herbivores could have increased over time. Sudden declines in Chl and Chl:TP following the introduction and proliferation of filter-feeding invertebrates are well documented for several other systems (e.g., Mellina et al. 1995; Meeuwig et al. 1998; Nicholls et al. 1999). So conceivably, it could have been the proliferation of, say, the filter-feeding amphipod *Corophium curvispinum* between 1987 and 1991 (van den Brink et al. 1993) that caused or at least contributed to the Chl decline in the Rhine after 1991. Similarly, a sudden increase in the density of some other herbivore could have been responsible for the decline after 1977. On the other hand, a recent modeling study suggests that it is the density of suspended algae in the Rhine that limits the density of the benthic herbivores rather than the reverse (Schol et al. 2002).

The sudden acceleration of some loss process could also have been responsible for the abrupt Chl decline in the Delta,

but unlike the Rhine, there is no evidence yet to suggest that this process was biological. Zooplankton densities have declined precipitously since the 1970s (Orsi and Mecum 1996) and there is no evidence of a sudden increase in benthic grazing after 1993. On the contrary, the limited data available suggest that the average summer densities of *Corbicula fluminea*, the dominant filter feeder in the freshwater reaches of the Delta, have steadily declined since the 1970s, presumably because their growth rate too became food-limited (Foe and Knight 1985). Such a decline would help explain why these clams no longer form dense beds along the canals that convey water diverted from the Delta. Before 1975, these clam beds reduced water velocities severely enough to require periodic removal and disposal (Prokopovich 1969), but have not achieved such nuisance levels of abundance since then.

Given that Chl in the Delta was independent of flow, it also seems unlikely that the Chl decline resulted from a sudden increase in the net washout rate of suspended algae toward the Bay, and the lack of any change in the relationship between flow and specific conductance in the Delta indicates that the Chl decline did not result from an abrupt increase in tidal exchange with the Bay. It is plausible, however, that the Chl decline was somehow related to changes in reservoir storage and release patterns in the San Joaquin River after 1982 (Jassby 2005) or to changes in the amount and timing of export pumping after 1995 (Arthur et al. 1996).

In summary, reductions in wastewater loading led to substantial reductions in mean summer total phosphorus concentration (TP) and chlorophyll concentration (Chl) in the Rhine River and in the Sacramento – San Joaquin Delta despite their continually high (>40 mg·m⁻³) soluble reactive phosphorus concentration and initially shallow (<1.5 m) euphotic depth. The slope of the response in both systems paralleled the average trajectory calculated using an among-system TP–Chl relationship for a broad cross section of flowing waters. Neither response could be attributed to coincidental changes in flow, light, or nitrogen supply. The results suggest that TP was the principal determinant of Chl in both systems and that phosphorus control may be an effective tool for managing eutrophication in other systems with relatively high (1–100 mg·m⁻³) soluble reactive P concentrations.

Acknowledgements

The Interagency Ecological Program for the San Francisco Bay Estuary provided funding for this research. I thank the two anonymous reviewers whose comments greatly improved an earlier version of this manuscript. I also thank Ken Lentz, Chief, Applied Sciences Branch, Bureau of Reclamation, Mid-Pacific Region, for his patient guidance and encouragement.

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