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The composition and bioavailability of phosphorus transport through the Changjiang (Yangtze) River during the 1998 flood

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Abstract. Water and suspended sediment (SS) samples were collected from the Changjiang River at the Datong Hydrological Station (DHS), five times from May 1997 through January 1999 in order to evaluate transport, composition and bioavailability of phosphorus (P) during a 1998 flood. Transport of most of the phosphorus compositions was substantially higher during the 1998 flood than at other sampling dates. Phosphorus associated with suspended sediment (TPP) accounted for more than 85% of total phosphorus (TP) transport during periods of preflood and flood. The high transport of TPP during the flood was due to unusually high concentrations of TPP and sediment discharge. The potentially bioavailable phosphorus in SS (PBAP) accounted for about 10% of TPP. PBAP with dissolved inorganic phosphorus (DIP) consisted of 15–89% of TP. For all the sampling dates, the concentrations of potential bioavailable phosphorus (BAP) ranged from 0.035–0.08 mg L^{-1}, significantly higher than the limiting concentration for eutrophication. Therefore, the increasing temporal trends of TP concentration and high bioavailability of TP appear to support more frequent algal blooms in receiving East China Sea coastal waters in recent years. Hence, the underestimate of TPP transport by large rivers may also underestimate the biogeochemical cycling of other associated nutrients, such as nitrogen and carbon.

Abbreviations: Al-P – Aluminum-bound Phosphorus, BAP – Bioavailable Phosphorus, Ca-P – Calcium-bound Phosphorus, DHS – Datong Hydrologic Station, DIP – Dissolved Inorganic Phosphorus, DOP – Dissolved Organic Phosphorus, TDP – Total Dissolved Phosphorus, Fe-P – Iron-bound Phosphorus, SS – Suspended Sediment, PBAP – Particulate Bioavailable-P in Suspended Sediment, PIP – Particulate Inorganic-P in Suspended Sediment, POP – Particulate Organic-P in Suspended Sediment, TPP – Total-P in Suspended Sediment, TP – Total Phosphorus

Introduction

Phosphorus (P) is a key nutrient limiting the primary production of many aquatic systems (Howarth 1988; Schindler 1977; Vollenweider 1968). It has been estimated that the worldwide use of P fertilizers is rising exponentially (Beaton et al. 1995), and the transport of inorganic P (IP) by the rivers to the world oceans has increased several fold over the last 150–200 years (Howarth et al. 1995; Meybeck 1982; Turner and Rabalais 1991). Several studies show that the overfertilization of P can result in many aquatic environmental issues (Daniel et al. 1998; Munn et al. 1999; Sharpley et al. 1994), such as eutrophication and toxic coastal algal blooms. Although the cause of eutrophication varies somewhat for different aquatic systems: rivers behave somewhat differently than lakes, while estuaries and coastal waters differ from rivers and lakes, excessive concentration of P is the most common cause of eutrophication in lakes, rivers, estuaries and coastal waters (Correll 1998). Furthermore, phosphorus flux through long-distance river transport is the ultimate links in the continental land and ocean interaction, and may constitute a sensitive indicator of global change. Therefore, studies on the transport of P to oceans by the world's rivers can provide useful information not only for global P budgets, but also for nutrient management in the coastal waters (Howarth et al. 1996). Studies made in USA indicated that rivers were often highly polluted with P (Smith et al. 1987), and that P is a key element controlling productivity of rivers (Correll 1998). Other studies showed that concentrations and forms of riverine P vary greatly and have been related to human activities such as land use, population density, and chemical fertilizer application. For example, McKee et al. (2000) found that TPP was the dominant form, accounting for more than 40% of TP transport during storm discharge; while Russell et al. (1998) reported that TPP loads accounted for 26–75% of the annual TP transport in various rivers in Britain. Nevertheless, the influence of human activity on riverine particulate P fluxes is poorly known (Howarth et al. 1995). Since TPP in suspended sediment, brought by a river into a receiving water body, begins to revisit with the receiving water's TDP and becomes bioavailable, it is necessary to re-estimate TPP transport and its effect on algal growth. There are several studies estimating bioavailable-P in suspended sediments by chemical extraction with 0.1 N NaOH solution (Logan et al. 1979; Sharpley et al. 1991; Yan et al. 1999). However, NaOH solution can not extract P from Ca-P compounds in suspended sediments. Therefore, when Ca-P compounds are the dominant forms of P in suspended sediments, extraction with NaOH solution will greatly underestimate bioavailable-P in suspended sediments. The method of iron-oxide paper strips developed by Sharpley (1993a, b) has proven to be a better representation of bioavailable-P in suspended sediment. In China, compared with riverine transport of nitrogen (Duan et al. 2000; Yan et al. 2001b), the study of P transport has been very limited, especially TPP transport in a river as large as the Changjiang River under extreme hydrologic conditions, such as floods and droughts. The objective of this study was to investigate P transport and forms of particulate P and the roles they play in P transport through the Changjiang River. To our knowledge, this paper is the first to address Changjiang River transport of P in various different forms and P bioavailability during the 1998 Changjiang River flood.

Materials and methods

Study site

The Changjiang River (also called the Yangtze River) is the largest river in China, draining almost one fifth of the total area of the country (Figure 1). In terms of length (6300 km), SS load (500×10^9 kg yr^{-1}), and water discharge (900 km^3 yr^{-1}), the river channel is the third, fourth, and fifth largest river in the world, respectively (Milliman et al. 1984; Chen and Shen 1987). During the modernization process, the Changjiang drainage basin has been and continues to be significantly affected by human activities, such as fertilizer application, population growth, and land use changes (Table 1). As such, the Changjiang River is perhaps the best region to study land and ocean interaction in East Asia. In this paper, we chose Datong Hydrologic Station (DHS) (117°37′ E, 30°46′ N, Figure 1) which is located on the lower reaches of the river and is free from tidal effects and industrial pollution associated with cities (Chen and Shen 1987). It drains a wide area of nearly 1.71×10^6 km^2, representing more than 95% of the basin area. The 30-year annual average precipitation is 1100 mm (Guo and Jiang 1999) at DHS.

Sampling and methods

Water and suspended sediment (SS) samples were collected from the Changjiang River at DHS five times during a 1-day period in each of May 1997, June 1998, August 1998, November 1998, and January 1999. Water discharge and SS concentrations were recorded from DHS. At each sampling time, the same sampling profile was used; and three sampling points at fixed positions from the right bank of the river (260, 1050 and 1590 meters, respectively) were used. At each point, water was collected (3 L each) from three different depths of 0.2, 0.6, 0.8 meter. A total of nine samples (3 points × 3 depths) were taken and then mixed up thoroughly as one composite sample. Then duplicate water samples (500 mL each) were collected from the composite. After sampling, 300-mL aliquots of each water sample were filtered through 0.45 μm filters. All the filtered and unfiltered water samples were digested with $K_2S_2O_4$ solution at the DHS laboratory and stored at 4 °C until analysis. The digested unfiltered water samples were analyzed for total-P (TP), the digested filtered water samples were analyzed for dissolved-P (TDP), and the undigested filtered water samples were analyzed for dissolved inorganic-P (DIP). TP, TDP and DIP in water samples were determined by the method of Murphy & Riley in duplicate (Murphy and Riley 1962). Suspended sediment samples were isolated and collected by filtering 20 liters of water through 0.45 μm filters. The samples were air-dried and stored at 4 °C until analysis. Suspended sediment samples were analyzed for TPP (Olsen and Sommers 1982) and inorganic-P content (PIP), including Al-P, Fe-P, and Ca-P (Chang and Jackson 1957), respectively. Bioavailable-P associated with the SS samples (PBAP) was determined using the method of iron oxide paper strips (Sharpley 1993a, 1993b).

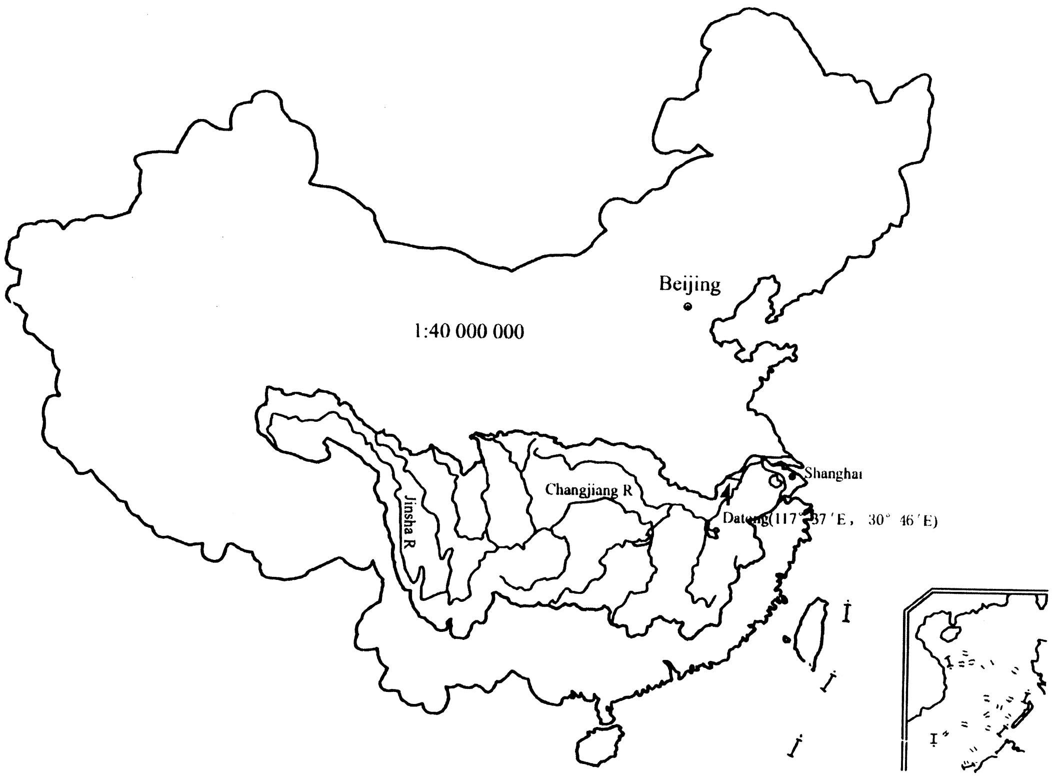

Figure 1. Map of the Changjiang River basin showing general areas of flooding (June–August 1998), and the sample site at DHS, Anhui Province.

Table 1. The regional characteristics of the Changjiang basin at DHS.

Drainage area (10^6 km^2)	Land Use* (10^6 km^2)						Population density* (ind. km^{-2})	Fertilizer usage* (10^9 kg)		Water discharge (10^9 m^3 yr^{-1})
	Arable	Forest	Grass	Fallow	Surface water	Urban & others		P	N	
1.71	0.45	0.52	0.08	0.05	0.03	0.58	240	1.0	7.0	900

*Values for the Changjiang basin are for the year 1997.

Calculations of phosphorus fractions

The concentrations of different P forms in water and SS samples were calculated according to the following equations:

$$TP = TPP + TDP$$

$$TPP = PIP + POP$$

$$PIP = Al\text{-}P + Fe\text{-}P + Ca\text{-}P$$

$$BAP = DIP + PBAP$$

Where POP is the organic-P content in SS, BAP is total bioavailable-P in water and SS. In this study, TP, TDP, DIP, Al-P, Fe-P, Ca-P, PBAP were measured directly.

Results and discussion

Characteristics of water and SS discharges

The annual rainfall in the Changjiang basin, average monthly water discharge and SS transport through DHS for a 30-year (1968–1997) period are shown in Figure 2. The annual rainfall varied somewhat with an average of 1100 mm yr^{-1} (Figure 1, Top). The temporal trend of water discharge through DHS varied little over 30 years with an average of 9.0×10^{11} m^3 yr^{-1}, corresponding to 5.3×10^5 m^3 km^{-2} yr^{-1}. Water discharge varied greatly over the course of the year (Figure 2, Middle). The highest discharge, generally occurred in July, was about 3 times the lowest discharge in January. The average monthly water discharge is about 3.0×10^4 m^3 s^{-1}. A water discharge (Q in m^3 s^{-1}) model, $Q = 27700 + 19500 \times \sin [\pi/6 \times (t - 3)]$, fit the monthly data well except for extreme flood events (Duan 2000). The pattern of SS discharge was similar to that of water discharge (Figure 2, Bottom). The annual SS discharge through DHS varied little with an average of 4.4×10^{11} kg yr^{-1}, corresponding to 2.6×10^5 kg km^{-2} yr^{-1}.

During the first sampling date on May 28, 1997, and the second on June 15, 1998, water discharges were 33000 and 33300 m^3 s^{-1}, respectively; SS discharges were 33000 and 8600 kg s^{-1}, respectively. These water discharges are close to the 30-year average monthly discharge (30000 m^3 s^{-1}), water and SS discharges determined at these times are considered a normal seasonal flow. From June through August 1998, unusually heavy summer rains produced severe flooding throughout the entire Changjinag River basin (Yuan et al. 1999). The extensive flooding persisted for almost 100 days (Wang and Wang 1999). Water discharge on the third sampling date (August 19, 1998) was near the highest peak (82300 m^3 s^{-1}) of the 1998 flood passing through DHS (Figure 3). Water and SS discharges were 75200 m^3 s^{-1} and 32000 kg s^{-1}, respectively. During this flood, the total water discharges

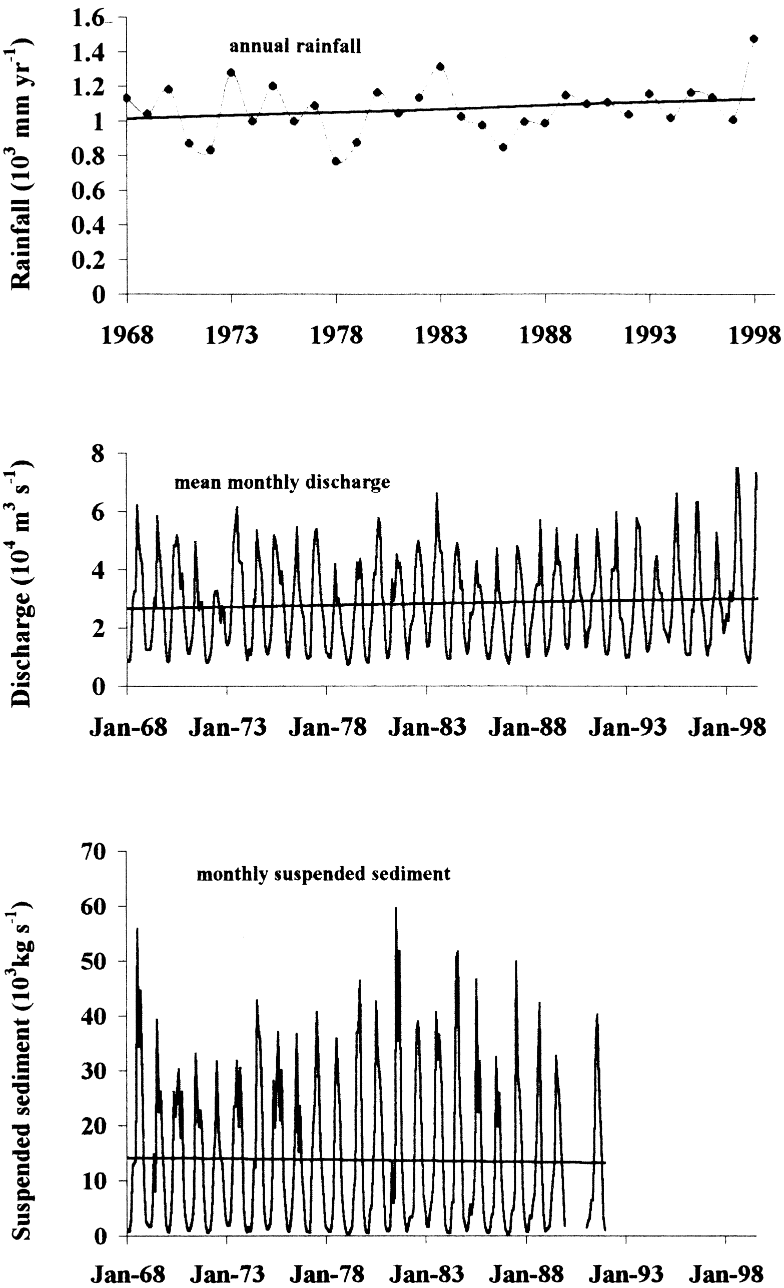

Figure 2. Annual rainfall (top), Monthly average of water (middle) and suspended sediment (bottom) discharges of Changjiang River at DHS, based on 30 years (1968–1997) of unpublished data from annual hydrological reports of China.

at DHS were 2.0×10^{11} m^3 and 4.0×10^{11} m^3 for 30 and 60 days, respectively (Li 1999). Water and SS discharges for the 5 months from May to September were about 7.8×10^{11} m^3 and 3.2×10^{11} kg, respectively, accounting for 63.0% of total water discharge and 79.0% of total SS discharge, respectively, in 1998. This was the second largest flood event during the 20th Century (Figure 3), and has a 1:30–100 return period since Song Dynasty (960) (Ji 1999). During the fourth sampling (November 14, 1998), water discharge was 23500 m^3 s^{-1}, much lower than that in the third sampling, indicating that the river was in the recession stage of the flood. Suspended sediment discharge was about 1960 kg s^{-1}, significantly lower than the 30-year monthly average and minimum values in November. During the fifth sampling (January 19, 1999), water discharge was 10400 m^3 s^{-1}, similar to the monthly average values for January, reflecting the seasonal low flow condition. However, SS discharge was about 230 kg s^{-1}, significantly lower than the monthly minimum values for January. During the sampling periods in 1998, SS concentrations increased from June 15 to August 19, 1998, and peaked on August 12, then decreased due to depletion of SS supply (Table 2).

Phosphorus fractions and bioavailability

Concentrations and distributions of different P fractions are listed in Table 2 and presented in Figure 4. The TDP concentration was highest in water discharge on January 19, 1999, followed by November 14, August 19, June 15, 1998 and May 18, 1997 (Table 2). TDP accounted for 42–86% of TP during the recession stage and 8–14% of TP during preflood and flood periods, indicating that TDP concentrations were negatively correlated with water discharges ($r = 0.83$), partly because of a dilution effect. Both TP and TPP concentrations were significantly higher during preflood and flood periods than during the recession stage. The TP and TPP concentrations were closely related to water and SS discharges ($r > 0.9$), which is consistent with the findings of other studies (e.g. Kronvang (1992) and Ng et al. (1993)). The strong correlation between SS and TPP suggests that P transport in particulate form (more than 90% of TP) was the dominant mechanisms for riverine P transport. The high correlation between TP and SS was due to the obvious relationship between TPP and SS. This pattern was similar to observations of P transport in surface runoff from various cropland soils (Uusitalo et al. 2000; Yan et al. 2001a). TPP contents were 677, 806, 707, 624, 596 mg kg^{-1} SS (Table 3) for the five sampling times, respectively. These values are almost 50% lower than the average value (1350 mg kg^{-1}) for world rivers estimated by Meybeck and Froelich (Howarth et al. 1995). However, a study made by Chinese Environmental Protection Agency (1990), showed that the average P contents in sediment columns of three lakes along the Upper and Middle Changjiang River ranged from 580–810 mg kg^{-1} for almost 150 years (from 1840 to 1987), which is consistent with our findings. These consistently low TPP concentrations strongly suggest that basin geology has a great influence on P concentrations in SS. For all sampling dates, PIP concentrations accounted for more than 60% of TPP, while POP concentrations accounted for less than 40% of TPP. POP/TPP ratios varied greatly demonstrating the

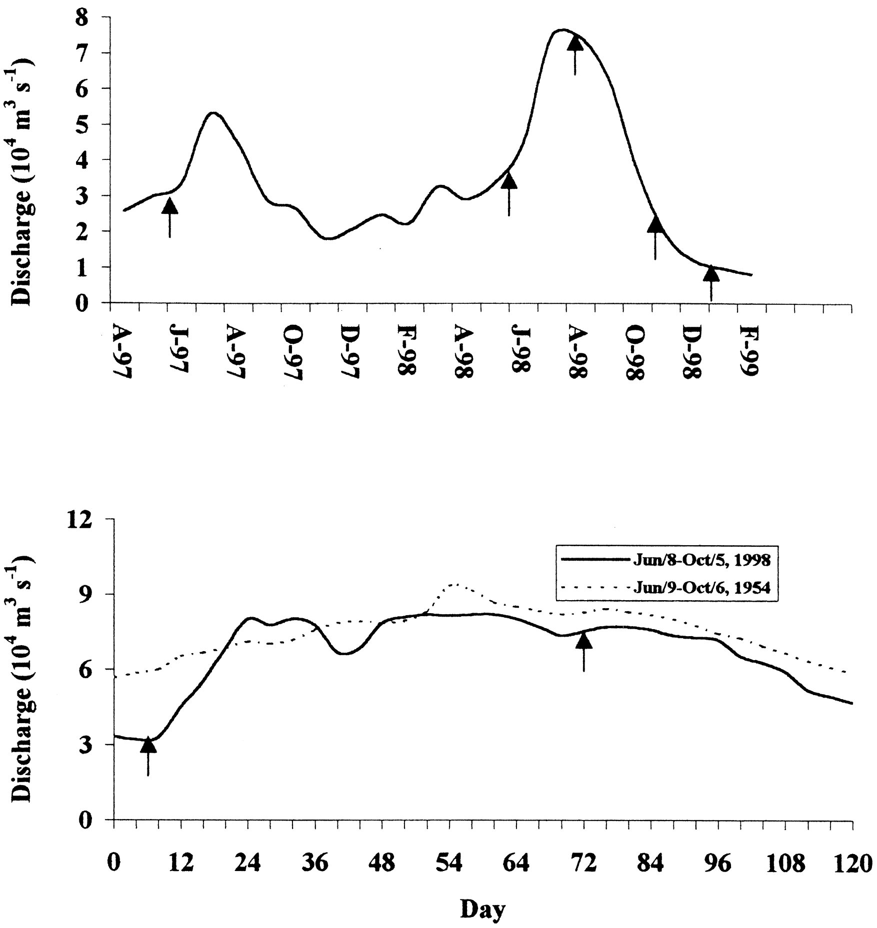

Figure 3. Monthly average of water discharges of the Changjiang River at DHS (top), and water flow hydrograph over the entire flood period of the two largest floods of the Changjiang River at DHS in the 20th Century (bottom), showing the sampling dates with arrow.

following trend: preflood season > flood season > dry season. Ca-P was the dominant fraction of PIP, representing more than 80% of PIP (Figure 4), while both Fe-P and Al-P fluctuated between 2–9% of PIP. A strong relationship was observed between Ca-P fraction and SS concentration (r = *0.9*). The relative magnitudes PIP fractions during the flood period were as follows: Ca-P > Al-P > Fe-P, which is similar to the order of chemical weathering of phosphate minerals (Ca-P $\rightarrow$ Al-P $\rightarrow$ Fe-P) in the acidified areas of the Upper River basin. This implies that TPP may originate from soil erosion in the Upper and Middle Changjiang River basin during flood events. Therefore, the percentage distribution of inorganic-P fractions in river SS should be a better indicator of P origin than the distributions in river bed sediments (Weng 1993).

Table 2. Water discharge, suspended sediment concentration, and concentrations of various P fractions through the Changjiang River at DHS.

Sample date	Water discharge ($m^3\ s^{-1}$)	SS (mg L^{-1})	Phosphorus concentration (mg L^{-1})								
			Al-P	Fe-P	Ca-P	POP	TPP	PBAP	DIP	TDP	TP
May 28, 1997	33000	260	0.005	0.009	0.110	0.052	0.176	0.025	0.011	0.017	0.193
June 15, 1998	33300	170	0.002	0.005	0.078	0.053	0.137	0.013	0.018	0.022	0.159
Aug. 19, 1998	75200	430	0.006	0.005	0.190	0.103	0.304	0.024	0.021	0.025	0.329
Nov. 14, 1998	23500	83.4	0.002	0.002	0.043	0.005	0.052	0.006	0.035	0.038	0.09
Jan. 19, 1999	10400	21.8	0.001	0.001	0.010	0.001	0.013	0.003	0.054	0.077	0.09

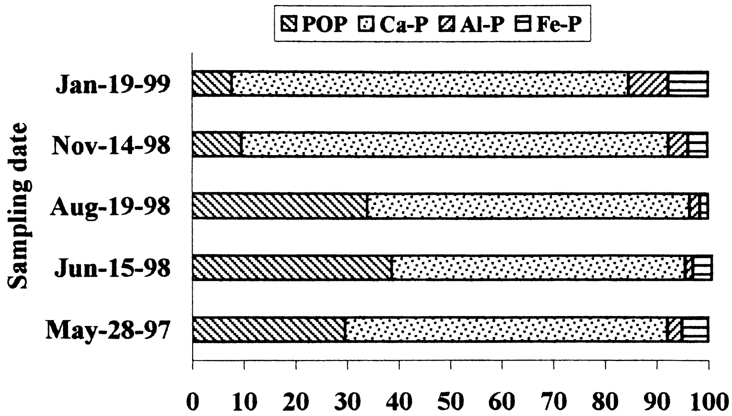

Figure 4. Percentage distribution of different P fractions making up suspended sediment-P (TPP). TPP = P content in suspended sediment, POP = organic-P content in suspended sediment, PIP = inorganic-P content in suspended sediment = Ca-P + Al-P + Fe-P.

Table 3. Phosphorus contents in SS through the Changjiang River at DHS.

Sample date	Phosphorus content (mg kg^{-1} SS)							PBAP/TPP (%)	POP/TPP (%)
	Al-P	Fe-P	Ca-P	PIP	POP	TPP	PBAP		
May 28, 1997	19.2	34.6	423	477	200	677	96.2	14.2	29.5
June 15, 1998	11.8	29.4	458	498	311	806	76.5	9.5	38.6
Aug. 19, 1998	13.9	11.6	442	467	240	707	55.8	7.9	33.9
Nov. 14, 1998	24.0	24.0	516	564	56.0	624	71.9	11.5	9.0
Jan. 19, 1999	45.9	45.9	459	551	45.9	596	137.6	23.1	7.7

The potential bioavailable-P contents in SS (PBAP) were 96.2, 76.5, 55.8, 71.9, 137.6 mg kg^{-1} for the five sampling periods, respectively, indicating a significant variation ($p = 0.01$). The proportion of PBAP over TPP expresses the contribution of SS to potentially bioavailable-P. This ratio ranged from 8% during floods to 23% during the recession stages (Table 3). PBAP plus DIP constitutes total BAP. The BAP concentrations varied from 0.031–0.057 mg L^{-1}, accounting for 14–63% of TP. This study showed that both the PBAP/TPP and BAP/TP ratios decreased when SS discharges increased, suggesting that more biologically unavailable TPP was transported during floods. The study found that BAP concentrations through DHS for all sampling dates were higher than 0.02 mg L^{-1}, the critical concentration limit for eutrophication of receiving water bodies (Bock et al. 1999; Correll 1998; Hakanson and Jansson 1983; Schindler 1977). Therefore, the values for riverine transport of potentially bioavailable-P may be severely underestimated if PBAP is not taken into account. This indicates a even greater potential for coastal eutrophication from Changjiang River transport of P, when TPP is taken into account.

Amount of P transport

The P load can be calculated by multiplying P concentration by water discharge (kg day^{-1}). The TP transport by the Changjiang River at DHS was 5.5, 4.6, 21.4, 1.8, 0.81 × 10^5 kg day^{-1} for the five sampling times, respectively. The amount of P transport during the 1998 flood (8/98) was about 4 times higher than that during preflood period (6/98), and about 10 times higher than during the recession stage (11/98). The transport of TPP was 19.8 × 10^5 kg day^{-1}, about 4 times higher than the transport measured preflood, and 19 times higher than that measured during the recession stage. TPP was the predominant P fraction, accounting for more than 85% of TP during periods of preflood and flood (Figure 5). During the recession stage, the TPP/TP percentage decreased from about 60% to 15%. According to Duan (2000), the total wastewater discharge from point sources between 1985 and 1998 varied little in the basin, (9.5 × 10^9 m^3 yr^{-1}) with an average P concentration of 6 mg L^{-1}. Thus, we estimate P load from point sources to be 5.7 × 10^7 kg yr^{-1}, corresponding to 1.6 × 10^5 kg day^{-1}. Therefore, P load from point sources account for less than 8% of P transport during the flood, and more than 90% of P transport during the recession stage through the Changjiang River at DHS. This suggested that the major source of P in the Changjiang River at DHS originated from soil erosion during the flood, and from urban and industrial point discharge during the recession stage. The amount of BAP transported by Changjiang River at DHS during the flood was 3.18 × 10^5 kg day^{-1}, which was about 3 times higher than that transported during periods of preflood and recession stage (Figure 5). However, the BAP/TP percentage was lower during periods of preflood and flood than that during the recession stage. The extremely high transport of BAP during the flood was likely due to unusually high concentrations of TPP and unusually high discharges of water and SS. The normal transport of BAP during the recession stage was due to the usual concentration of dissolved organic-P (DOP), which can turnover to the preferentially-available form of dissolved inorganic-P (DIP) (Benitez-Nelson and Buesseler 1999; Clark and Ingall 1998). Phosphorus associated with SS in the Changjiang River is ultimately flushed into the East China Sea coastal waters, potentially serving as a substrate for phytoplankton and bacterial utilization. Since P has no stable gaseous state (Chameides and Perdue 1997), P input to the East China Sea by atmospheric deposition is extremely low. Thus, it can be assumed that Changjiang River transport of P is the dominant P input to the East China Sea. Compared to P concentrations transported through the Changjiang River at DHS during 1970's (Wang et al. 1990) and 1980's (Duan and Zhang 1999), our study showed an increasing temporal trend in P transport due to an increasing P concentration. The transport of large quantities of TPP may be responsible for the more frequent algal blooms in East China Sea coastal waters in recent years. The data also imply that an underestimate of TPP transport may also underestimate the transport of other associated nutrients, such as nitrogen and carbon.

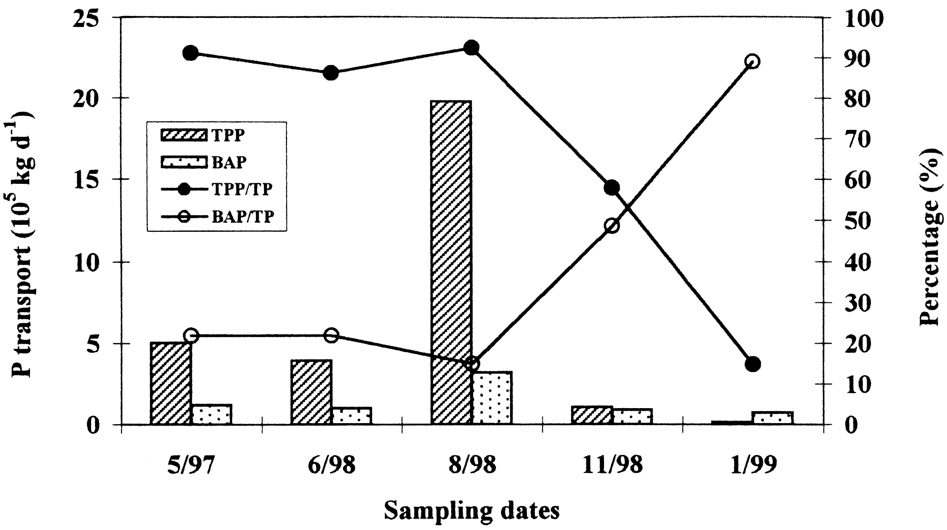

Figure 5. Transport of TP, TPP and BAP, and BAP/TP, TPP/TP percentage through Changjiang River at DHS.

Conclusions

Routine monitoring of P in the Changjiang River is not commonly undertaken. Occasionally, DIP is measured; However, TP, TPP and other forms of P are never measured during Changjiang River flood events. This study showed that concentrations of TP and TPP were 0.329 and 0.304 mg L^{-1}, respectively, during the 1998 flood period, and were significantly higher than during preflood and recession periods. The amount of TP transported by the Changjiang River at DHS during the flood was 4–10 times greater than that during periods of preflood and recession stage. The transport of TPP during the flood was 4–19 times greater than that during preflood and recession periods. In terms of both concentration and transport, TPP was predominant P fraction, accounting for more than 85% of TP during periods of preflood and flood. For all sampling dates, PBAP, accounted for about 10% of TPP, and together with DIP, consisted of 15–89% of TP. BAP concentrations ranged from 0.035–0.08 mg L^{-1}, significantly higher than the limiting concentration for eutrophication, suggesting that Changjiang riverine transport of P may be responsible for the more frequent algal blooms in the East China Sea in recent years. This study has demonstrated that an underestimate of TPP transport may not only underestimate the TP and potential BAP transport, but also the transport of other associated nutrients, such as nitrogen and carbon. Further study is required to comfirm the temporal and spatial variation of P transport through the Changjiang River in order to evaluate the riverine P contribution to receiving East China Sea eutrophication.

Acknowledgements

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