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RESEARCH ARTICLE

Particle-size distribution and phosphorus forms as a function of hydrological forcing in the Yellow River

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Abstract Samples were collected monthly from January to December in 2010, and daily observations were made during the water–sediment regulation event in June–July 2010. Sequential extractions were applied to determine the forms of P in different particle-size fractions and to assess the potential bioavailability of particulate phosphorus (PP). The results indicated that exchangeable phosphorus, organic phosphorus, authigenic phosphorus, and refractory phosphorus increased with the decreasing of particulate size; conversely, detrital phosphorus decreased with the decreasing of particulate size. The content of bioavailable particulate phosphorus (BAPP) varied greatly in different sizes of particles. In general, the smaller the particle size, the higher the content of bioavailable phosphorus and its proportion in total phosphorous was found in these particles. Hydrological forcing controlled the variability in the major P phases found in the suspended sediments via changes in the sources and the particle grain-size distribution. The variation of particle sizes can be attributed also to different total suspended sediment (TSS) sources. Water–sediment regulation (WSR) mobilized only particulate matter from the riverbed, while during the rainstorm soil erosion and runoff were the main source. The BAPP fluxes associated with the "truly suspended" fraction was approximately 200 times larger than the dissolved inorganic phosphorus (DIP) flux. Thus, the transfer of fine particles to the open sea is most probably accompanied by BAPP release to the DIP and can support greater primary and secondary production.

Keywords Phosphorus forms · Particle size · Hydrological forcing · Yellow River

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Introduction

Major rivers play a dominant role worldwide in transferring both particulate and dissolved materials from the land to the coastal ocean. The total suspended sediment delivered to the ocean by all rivers is approximately 1.5×10^{10} metric tons annually, of which Asian rivers discharge nearly 70 % (Milliman and Syvitski 1992; Syvitski et al. 2005). Most of these sediments, however, are trapped in estuaries or deposited on adjacent continental shelves; only 5–10 % of the fluvial sediments presently reach the deep sea (Meade 1996; Liu et al. 2006). The riverine sediments play a significant role in nutrient biogeochemical cycles. Additionally, the study of the speciation and fluxes of nutrients from large rivers is crucial to connecting land and sea in terms of global biogeochemistry (Mebeck 1982; Giraud et al. 2008; Gao et al. 2012).

As a key nutrient, phosphorus (as the species phosphate) represents an important regulating factor in primary productivity, not only in freshwater but also in transient zones such as estuaries and coastal environments (Bauerfeind et al. 1990; Harrison et al. 1990). 87 %–90 % of river-borne phosphorus (P) that is transported into estuarine and coastal regions exists as particulate P species (Mebeck 1982; Jensen et al. 2006). Upon delivery to estuaries from rivers, the river-borne P experiences large changes in salinity, pH, and sometimes redox potential. Phosphorus mobility in these changing environments is related to the P speciation. The importance of particles as a potential source of phosphorus has also been highlighted in lakes and shallow coastal

areas (Fisher et al. 1982). The bioavailability of PP is affected by chemical processes such as adsorption–desorption, precipitation–dissolution, and reduction–oxidation reactions, which regulate the amount of dissolved inorganic P that is released into the water body and/or sorbed to particles (Ellison and Brett 2006). Exchangeable phosphate can escape to the overlying water when fine particles are put back into suspension by bottom currents, and Fe(III)-bound phosphate can dissolve under reducing conditions. The bioavailability of PP may be relatively high if P is bound to clays or easily degradable organic matter or if it is only weakly sorbed to particles (Pacini and Gächter 1999; Reynolds and Davies 2001). Phosphorus is potentially available when bound to redox-sensitive iron and manganese or pH-sensitive aluminum oxides but is almost completely unavailable when co-precipitated with calcium carbonate or bound with more resistant forms of organic matter, such as humic acids (Reynolds and Davies 2001). Particle size plays an important role in the transport and settling of particulate P (Andrieux-Loyer and Aminot 2001; Koch et al. 2001). Different particle-size classes, with different P contents, are remobilized and transported by different hydraulic conditions (Andrieux-Loyer and Aminot 2001; Koch et al. 2001; He et al. 2010). Although P species have been studied in sediments with respect to particle size (Andrieux-Loyer and Aminot 2001), little information is available for SPM. The Yellow River is known for its high sediment discharge with the averaged value of 1.6×10^9 t/year, approximately an order of magnitude greater than the Yangtze River (Dai et al. 2011). The upper reaches of the Yellow River drains the northeastern part of the Qinghai–Tibet Plateau with at about 3000–4000 m supplying ~60 % of the river discharge but only ~10 % of the sediment load. This area mainly comprises sandstone, dolomitic limestone, and minor volcanics (Yang et al. 1986). Due to the effects of climatic change and human activities in recent years, the eco-hydrological processes, along with the mass and energy transport, have changed (Wang et al. 2008). Since the 1970s, the Yellow River has experienced a new historical period characterized by low discharges and drying up due to the decrease of annual precipitation and the increase of water extraction (Saito et al. 2001; Xu 2002; Wang et al. 2007). The consequences include frequent flow cutoff, riverbed elevation, and lower flood control capabilities (Wang et al. 2005). Since 2002, the Yellow River Conservancy Commission has instituted a water–sediment regulation (WSR) scheme at the beginning of every flood season to avoid situations in which there is no water flow and to improve the relationship between water and sediment transport by flushing the reservoirs and reducing sediment deposition in the lower reaches of the river (Li 2002; Wang et al. 2005). A vast amount of water and sediment are delivered to the sea during the WSR. The WSR has caused a profound alteration of the hydrological regime, e.g., in July 2002, more than 64 % of the annual water and 84 % of the annual sediment discharges were delivered to the sea during a WSR event (Wang et al. 2005). This management could results in the Yellow River water discharge to attain a very high value within a short period and is expected to influence substance transports and the ecosystem of the Yellow River Estuary and the adjacent sea (Li et al. 2009; Yang and Liu 2007; Liu et al. 2012), but it is not clear how the nutrient species and transports are affected by the WSR. The high levels of particulate matter in the Yellow River make it the extreme end-member among major world rivers for high input of suspended particles. This suspended sediment is coincident with a high total phosphorus (TP) input to the river (Duan and Zhang 1999; Meng et al. 2007; He et al. 2010; Pan et al. 2013) and is potentially important for buffering dissolved inorganic phosphate (DIP). Few studies foucused on the forms of phosphorus in different particle-size fractions. Moreover, since the fine particle fractions are often preferentially transported to offshore area, they are more harmful to the marine environments.

This paper reports the results of biogeochemical observations in the Yellow River in 2010. Dissolved and particle phosphorus were measured for samples collected from monthly observations in the Yellow River from January to December in 2010 and daily observation during the water–sediment regulation event in June–July 2010. The purpose of the investigation was to understand the hydrological regime controls on particle size, phosphorus forms, and phosphorus transport in the Yellow River.

Materials and methods

Sample collection

The Lijin Hydrographic Station, located 100 km upstream from the Yellow River estuary, is the last station before the river debouches into the Bohai Sea, and the records at Lijin represent the standard figures of the contributions of the Yellow River to the sea (Fig. 1). Therefore, the water and suspended sediment samples collected at the Lijin Station can be used to examine phosphorus concentrations in the suspended sediments delivered by the river to the sea.

Water samples from the Yellow River were collected along a transect at sites located 70, 120, 150, 180, and 210 m (marked with A, B, C, D, and E) from the river bank at the Lijin Station between January and December 2010 (Fig. 1). During a water–sediment regulation event in the summer of 2010, daily observations were conducted at Lijin in the river from 19 June to 13 July. Approximately 1 L of surface water was filtered through pre-cleaned 0.45-μm Millipore filters within 8 h of collection and stored frozen before the measurement of dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP). The filters were kept frozen until the analyses of total suspended sediment (TSS) and particulate P species were performed.

In this study, a custom-built water elutriation apparatus, built according to Walling and Woodward (1993) as illustrated

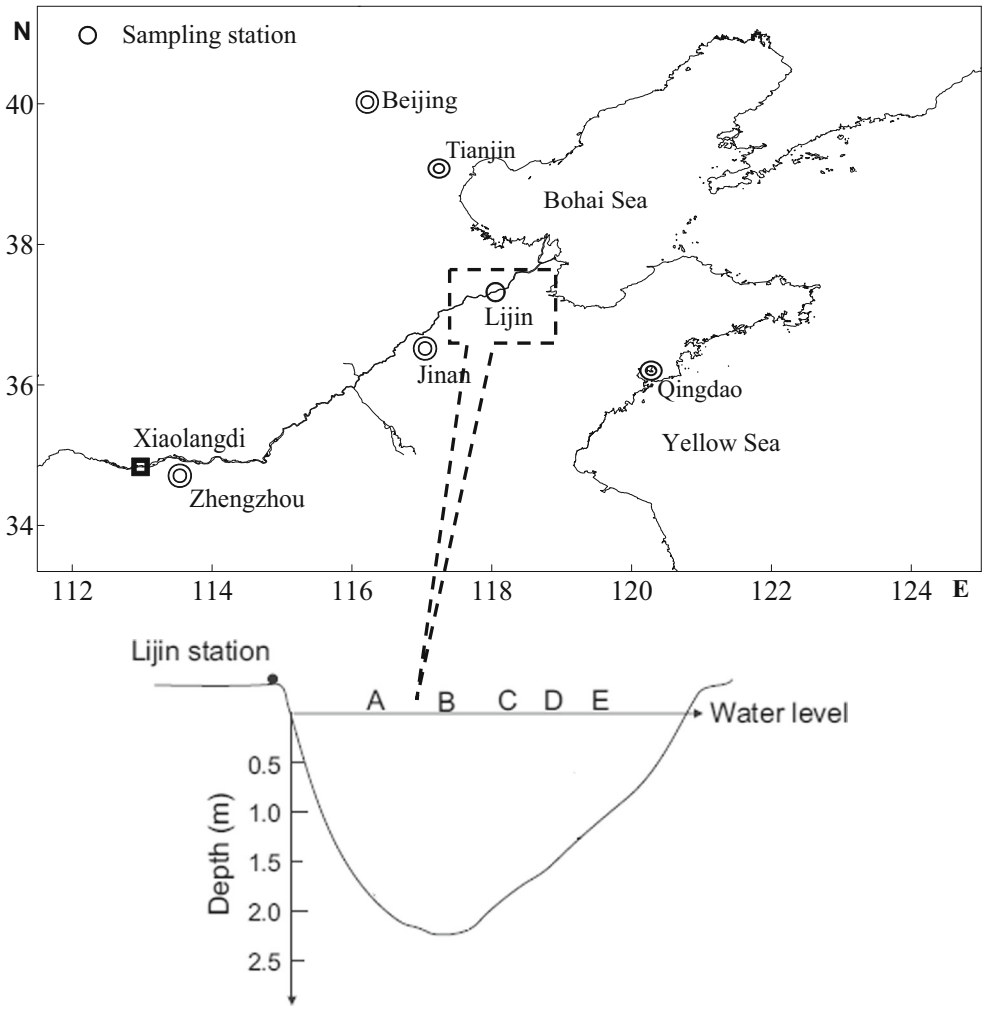

Fig. 1 Sampling transects and sites of samples at Lijin Station. Samples from Lijin at sites located 70, 120, 150, 180, and 210 m away from the river bank

in Fig. 2, was used to separate suspended sediments into clay-very fine silt (<8 μm), fine silt (8–16 μm), medium silt (16–32 μm), coarse silt (32–63 μm), and sand (>63 μm) (He et al. 2009). Approximately 100 to 150 L of surface water sample was collected. After allowing particulates to settle for approximately 24 h, the clear water was decanted and stored for use as carrier water in the elutriation process, and the sediment that remained in the container was used for elutriation.

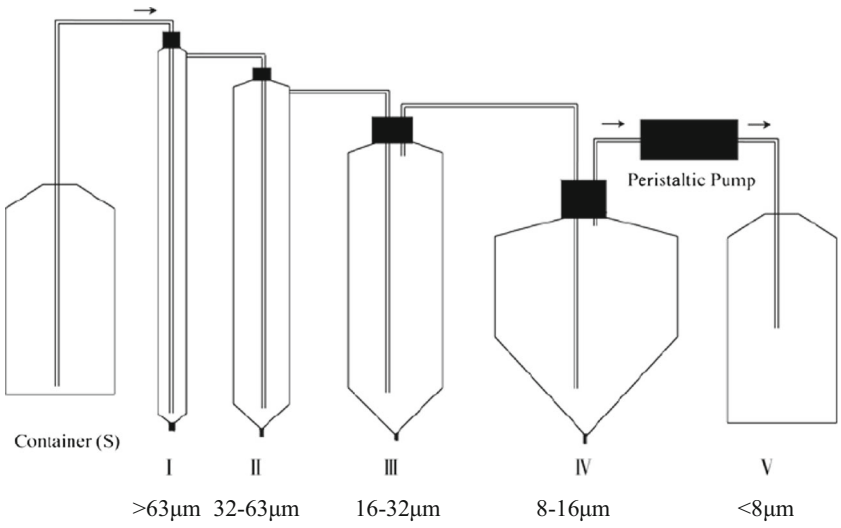

Fig. 2 Water elutriation apparatus (modified from He et al. 2009)

When a sampling run was initiated, the water elutriator was filled with clear water that was just drawn from the container. After enough slurry was drawn into the apparatus, the clear water was drawn through the system until the sedimentation chambers were completely flushed. The sediment samples collected from each sedimentation chamber were filtered through 0.45-μm pore-size acid-washed Millipore filters and frozen. The slurry collected in the outflow containers was left to settle for approximately 72 h and was then decanted. The sediment was collected on filters and frozen.

Analytical methods

The DIP in the filtrates was determined using an AAIII Continuous-Flow Analyzer (BRAN + LUEBBE, Germany). Wet chemical oxidation with $K_2S_2O_8$ in an autoclave (2 h) was applied to the filtered TDP and PP samples, and they were stored in a cool room at 4 °C (Yu 1999; Yu et al. 2004). The digested TDP and PP were analyzed as DIP using an AAIII Continuous-Flow Analyzer (Grasshoff et al. 1999). The concentration of DOP is the difference between the TDP and the DIP. The data quality was monitored by inter-calibrations with an international standard and by repeated analyses of samples for DIP at the micromole level. The detection limit of DIP was 0.030 μmol/L. The precision for dissolved and total P (TP) was 5–10 % at <1–10 μmol/L.

The suspended sediments were freeze-dried and then crushed and ground. The PP forms were determined using a modified SEDEX (Table 1), introducing the extraction of surfactant sodium dodecyl sulfate (SDS) to extract organic phosphorus (Vink et al. 1997). The six-step extraction scheme separated total PP into six pools, including exchangeable P, organic P, Fe-bound P, authigenic apatite P, detrital P, and refractory P. The acid extractions were neutralized with 1 mol/L NaOH. The molybdenum blue method was used as the final detection method for soluble reactive phosphorus extracted by the scheme (Murphy and Riley 1962). The phosphorus in the citrate–dithionite–bicarbonate (CDB) extraction was determined using the solvent extraction method after the following treatment: 0.25 mL of 1 mol/L $FeCl_3$ was added to 25 mL CDB + rinse solution and allowed to sit for 1 week to destroy the excess dithionite (Ruttenberg 1992; Anschutz et al. 1998). The P in the supernatant was analyzed with a UnicoTM 2000 spectrophotometer. The reproducibility of the measured P fractions ranged from 4 to 13 %.

Results

Hydrology

The distribution of water discharge and total suspended sediment (TSS) near the mouth of the Yellow River between January and December 2010 is presented in Fig. 3. The water discharge of the Yellow River was related to strong seasonal variations in rainfall. The water flow rate was very low between January and May, averaging only 198 m^3/s. A sharp increase was observed during the period from May to August, followed by a decrease from August to December. The water flow of the Yellow River increased from 168 m^3/s in May to 919 m^3/s in June to 1850 m^3/s in August and then decreased sharply to 1070 m^3/s in September and 101 m^3/s in December. The maximum monthly discharge occurs in August and is about 18 times that of the minimum in December, reflecting a substantial water input from precipitation during the flood season.

The Xiaolangdi Reservoir, located on the mainstream of the middle river section and 870 km upriver from the study site (Fig. 1), began discharging the stored water in 19 June, which resulted in a response at Lijin Station 5 days later. Water discharge recorded at Lijin Station rapidly increased from about 300 m^3/s in 20 June to 2980 m^3/s in 25 June. After maintaining a water discharge around 3000 m^3/s for 14 days, water discharge decreased from 3290 m^3/s in 8 July to less than 1000 m^3/s in 11 July (Fig. 4a).

The TSS concentrations varied between 0.29 to 14.8 kg/m^3. The highest concentration of TSS was found in August, and the lowest was in December. No obvious variations in the TSS were found during the period of January to May. The TSS increased dramatically from 0.64 kg/m^3 in May to 10.3 kg/m^3 in June, reaching 14.8 kg/m^3 in August. A dramatic decreasing

Table 1 The determined method of particulate phosphorus (PP) forms (Ruttenberg 1992; Vink et al. 1997)

Steps	Reagents and conditions	Particulate phosphorus (PP) forms
1	1 M $MgCl_2$, 2 h, pH 8, 25 °C	Exchangeable P
2	1 % SDS, HCO_3^- buffer, pH 8.6, 2 h (×6)	Organic P
3	1 M citrate dithionite bicarbonate buffer, pH 7.6, 8 h, 25 °C	Fe-bound P
4	1 M Na acetate, acetic Acid buffered, pH 4, 6 h, 25 °C	Authigenic apatite P
5	1 M HCl, 16 h, 25 °C	Detrital P
6	Ash 500 °C, 2 h, 1 M HCl, 16 h, 25 °C	Refractory P

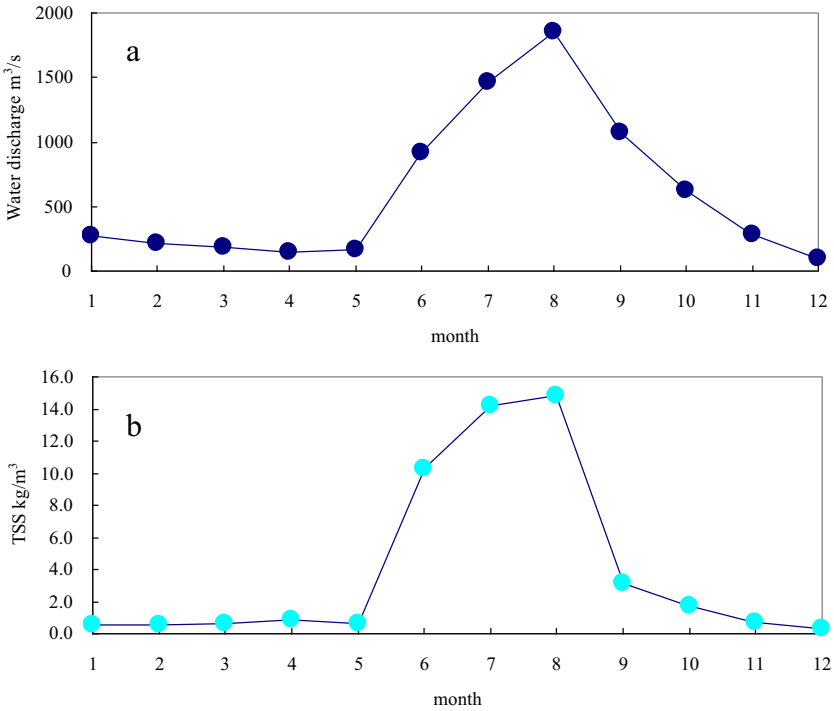

Fig. 3 Water discharges (**a**) and total suspended sediment (TSS) concentrations (**b**) at Lijin (Yellow River) in 2010. These data are from government reports and documents (http://www.yellowriver.gov.cn/nishagonggao)

trend was found during the period of August to December. TSS decreased sharply to 3.15 kg/m^3 in September and reached 0.29 kg/m^3 in December (Fig. 3b).

The TSS concentration ranged from 0.6 to 63 kg/m^3 during the WSR period. TSS increased rapidly from 0.6 kg/m^3 in 20 June to 11.6 kg/m^3 in 23 June. After maintaining around 12.0 kg/m^3 for 14 days, TSS increased rapidly from 12.0 kg/m^3 in 8 July to 63.2 kg/m^3 in 10 July, then decreased to less than 10.0 kg/m^3 in 15 July (Fig. 4b).

Suspended sediment characteristics

The contributions of various size fractions to the total suspended sediment of each sample are shown in Fig. 5.

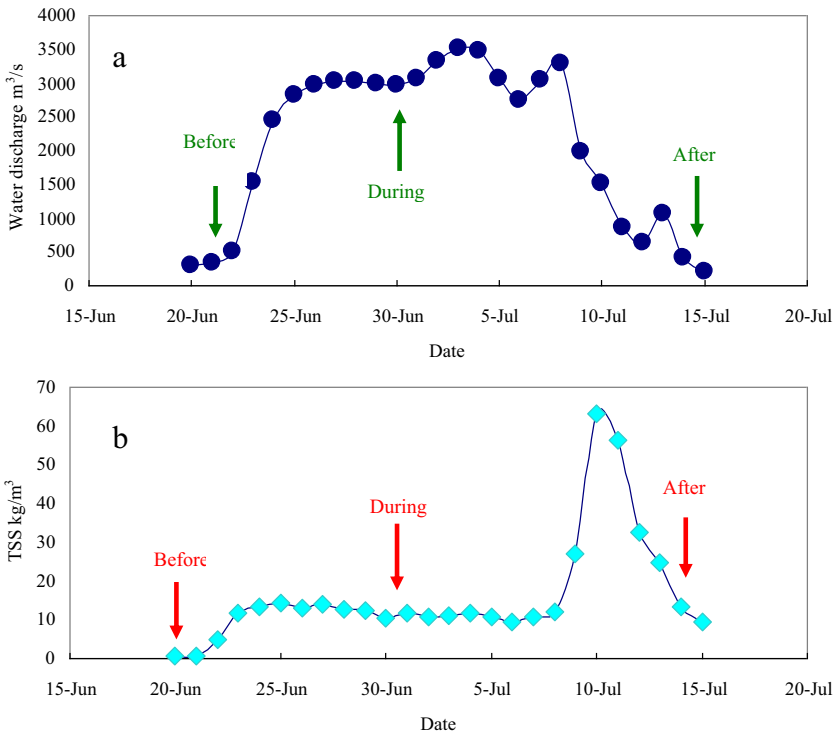

Fig. 4 Water discharges (**a**) and total suspended sediment (TSS) concentrations (**b**) at Lijin (Yellow River) during WSR in 2010

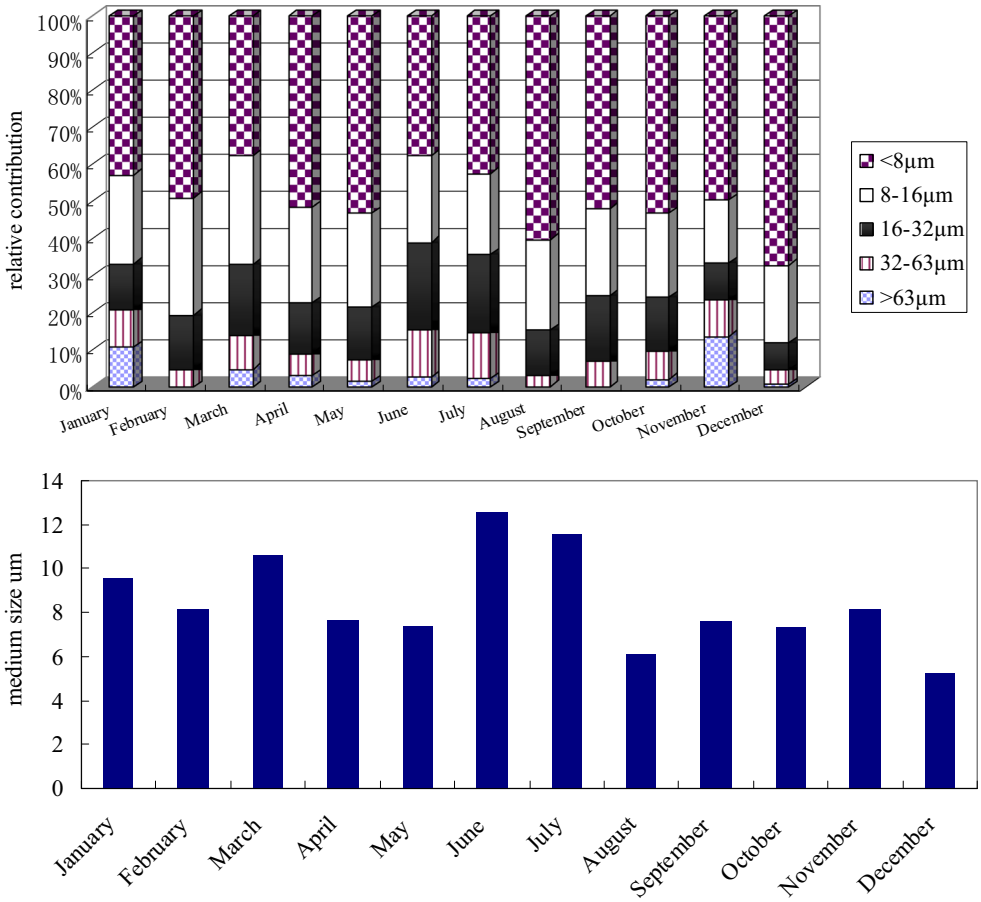

Fig. 5 Medium size and contribution of various size fractions to the TSS in the Yellow River in 2010

Clay and very fine silt dominated among the five TSS fractions, representing 37–67 % of the TSS, while the sand fraction never exceeded 13 %. The contribution of the fine silt fractions ranged from 17 to 32 %, whereas medium silt ranged from 10 to 30 %, and coarse silt ranged from 7 to 24 %. The increase in clay–very fine silt was accompanied by a decrease in medium silt, coarse silt, and sand fractions. The contributions of >32-μm-sized particles were higher in June and July than those of other months. The median particle size was highest in June and July and was about twice the median particle size in August (the lowest). The contributions of various size fractions to the total suspended particles and median particle size during the WSR event were different to those in other times of this year (Fig. 6a, b). The increase in sand and medium silt fractions were accompanied by increases in water discharge and TSS (R^2=0.45, n=27) (Fig. 6c).

Phosphorus speciation

The concentrations of DIP, DOP, PP, and TP ranged from 0.04 to 0.36, 0.25 to 0.65, 6.14 to 322.1, and 6.79 to 322.6 μmol/L, respectively, with averages of 0.14, 0.38, 92.8, and 93.3 μmol/L, respectively. The DOP accounted for 40.6–89.9 % of the TDP, with an average of 74.5 %. The PP accounted for 83.2–99.9 % of the TP, with an average of 96.7 %. The DOP was the predominant species of the TDP, and the PP was the predominant species of the TP (Table 2).

The concentrations of DIP and DOP show seasonally stable levels, while there were significant seasonal changes in the concentrations of PP that correlate with water discharge and sediment load. No obvious variations in the PP contents were found during the period of January to May, but the PP increased dramatically from 14.8 μmol/L in May to 322.1 μmol/L in June, 278.9 μmol/L in July, and 315.7 μmol/L in August, then decreased sharply to 73.5 μmol/L in September and 6.14 μmol/L in December. The maximum monthly PP content occurred in June, July, and August and was approximately 100 times that of the minimum in December, reflecting high suspended sediment contents during the summer flood season.

Forms of phosphorus in the suspended sediments

The content of PP in the suspended sediment ranged from 18.3 to 28.3 μmol/g. The PP remained stable during most months, except in June and July (the WSR period) (Fig. 7). The PP contents were obviously higher in June and July than in other months. The contents of different phosphorus

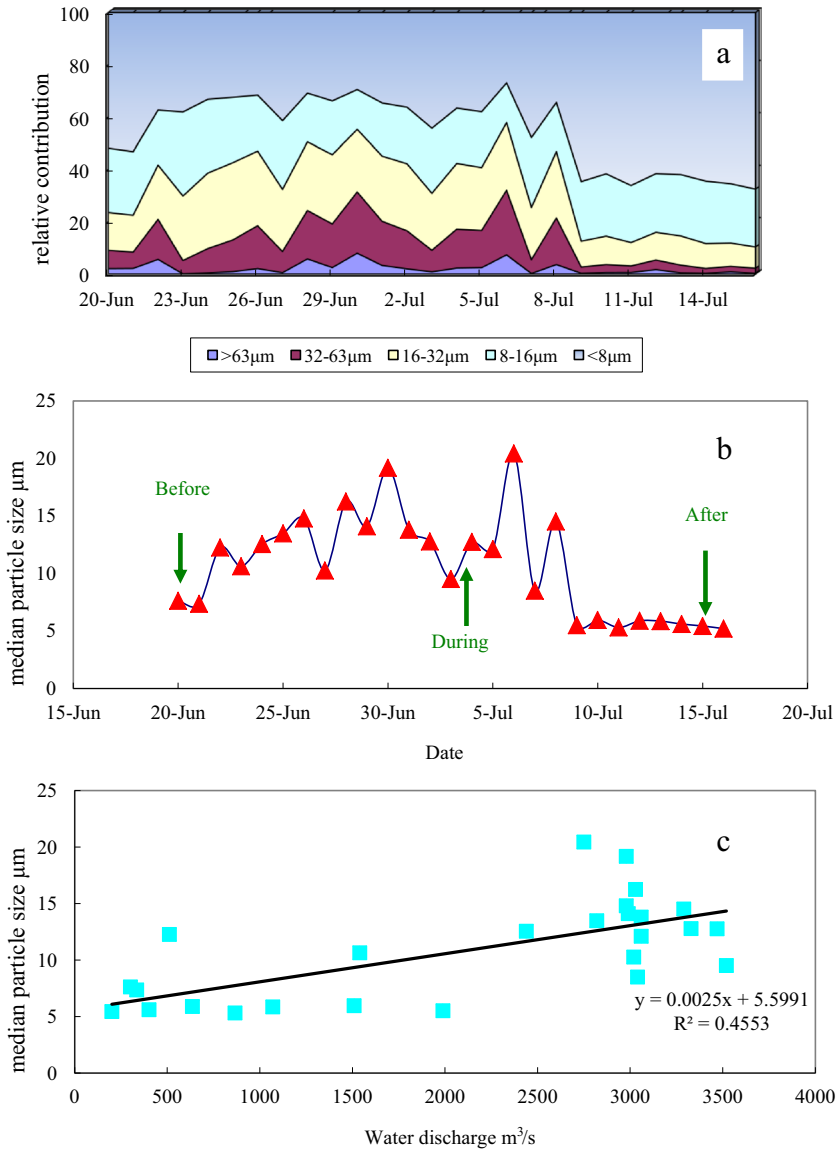

Fig. 6 **a**–**c** Medium size and contribution of various size fractions to the TSS in the Yellow River during WSR

Table 2 Concentrations of phosphorus speciation in the Yellow River (μmoI/L)

	DIP	DOP	TDP	PP	TP
January	0.08	0.32	0.39	9.48	9.88
February	0.08	0.34	0.41	12.3	12.7
March	0.06	0.36	0.42	14.8	15.2
April	0.04	0.35	0.38	18.8	19.2
May	0.13	0.34	0.47	14.5	15.0
June	0.13	0.35	0.47	322.1	322.6
July	0.12	0.38	0.51	278.9	279.4
August	0.19	0.36	0.55	315.7	316.3
September	0.36	0.25	0.61	73.5	74.1
October	0.23	0.65	0.87	35.5	36.4
November	0.11	0.39	0.50	14.5	15.0
December	0.04	0.50	0.65	6.14	6.79

fractions in the suspended sediment are presented in Fig. 7. The order of P fractions was detrital P > refractory P > authigenic P > organic P > exchangeable P > Fe-bound P. The Fe-bound P represented the smallest P fraction, which made up approximately 5 % of the PP. The Fe-bound P contents in June (3.65 μmol/g) and July (1.28 μmol/g) were higher than those in other months (<0.60 μmol/g), while its percentage contributions to PP were lower in these 2 months than in other months. The exchangeable P content in suspended sediment was low (1.70 μmol/g) and represented <6 % of the TPP. The organic P proportions related to PP remained roughly between 7.9 and 24.6 %, with lower proportions in June and July. The detrital P was the most significant fraction of PP, with higher values found in June and July (44.5 and 45.4 %, respectively). The refractory P and authigenic P showed little seasonal variation and represented 24.9 and 17.8 % of the TPP, respectively.

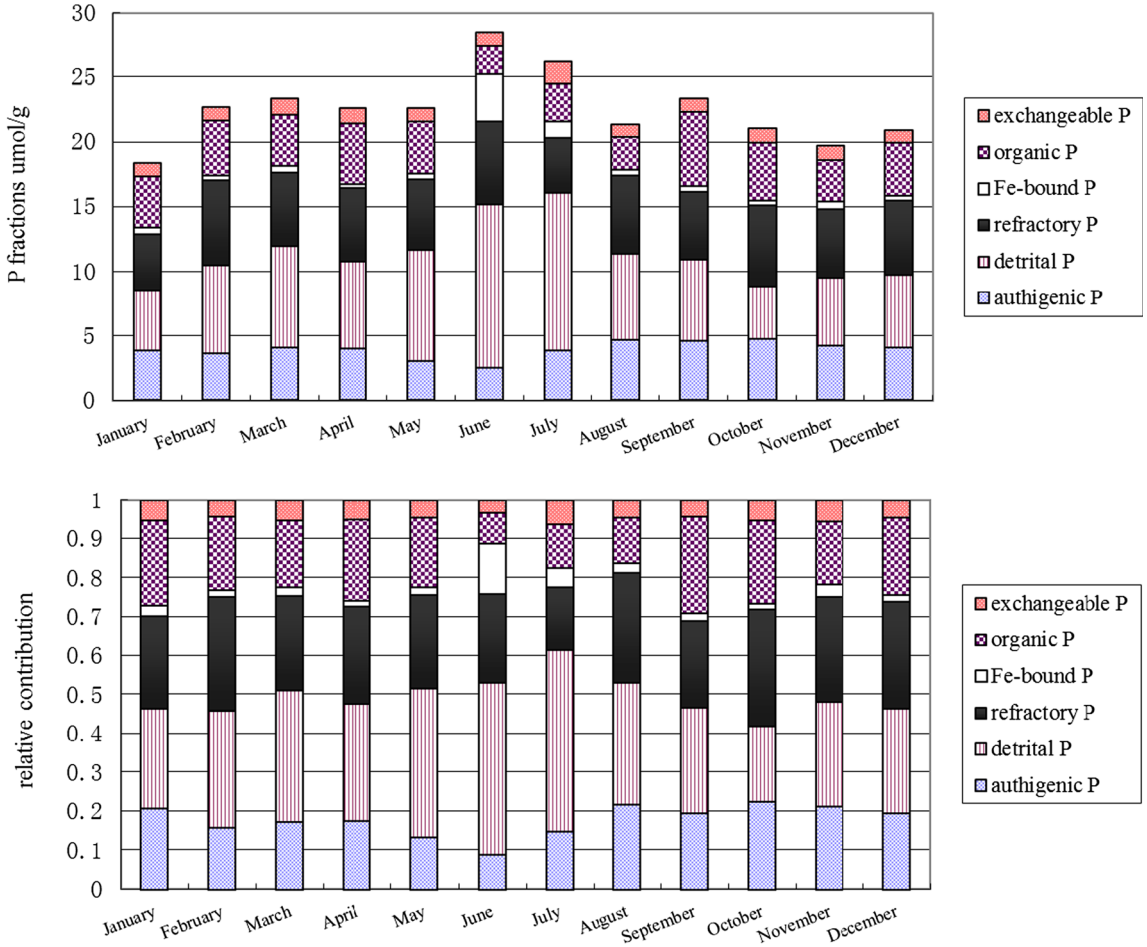

Fig. 7 Content of P fractions and their relative contribution to PP in suspended particles

Discussion

Influence of particle size on P forms

Several studies have shown that PP increases with decreasing particle size and that this relationship is determined by particle surface and mineralogy (Viner 1982; Stone and Mudroch 1989; Pacini and Gächter 1999; He et al. 2010). Particle size influences not only the total P content but also its forms, as observed in the analysis of a size fractionated sample (Figs. 7 and 8). The exchangeable P, organic P, authigenic P, and refractory P increased with decreasing particulate size. Conversely, the detrital P decreased with decreasing particulate size. The authigenic P was the major P form in the silt and clay fractions, while detrital P was the dominant P form in the >32-μm particle-size fraction (Figs. 7 and 8). In addition to their size, small particles offer structural advantages. Clays are weathered, laminated, secondary minerals offering large internal surfaces available for interactions with organic matter, metal oxy-hydroxides, and nutrients (Pacini and Gächter 1999). Fe and Al oxides are often regarded as phosphorus scavengers and are known to associate with surfaces and therefore become enriched in small particles (Pacini and Gächter 1999). Particle size is often correlated with various particulate phosphorus fractions of sediment, which is attributed to increasing Fe and Al oxides with decreasing particle sizes (Stone and English 1993). The enrichment of organic P in the fine TSS was related to the high content of organic matter in the TSS. The smaller the particles, the more particulate organic carbon was observed (Bergamaschi et al. 1997; Keil et al. 1997). More than 80 % of the POC was concentrated in the finest particles (<16 μm) (Zhang et al. 2009).

Effects of hydrological forcing on the P content in suspended sediment

The TSS concentrations were most influenced by the flow state, and the TSS concentrations were higher during storms than baseflow conditions (Fig. 9a). Both the TP and PP concentrations were higher in the flood season samples (Table 2, Fig. 9d, e), and the average TP and PP concentrations during storms were nearly 50 times those measured during the lowest discharge. In contrast, the TDP concentrations were similar between the two flow conditions (Fig. 9c) and were not significantly related to the flow state, which agrees with previous observations (Ellison and Brett 2006). PP was the dominant P

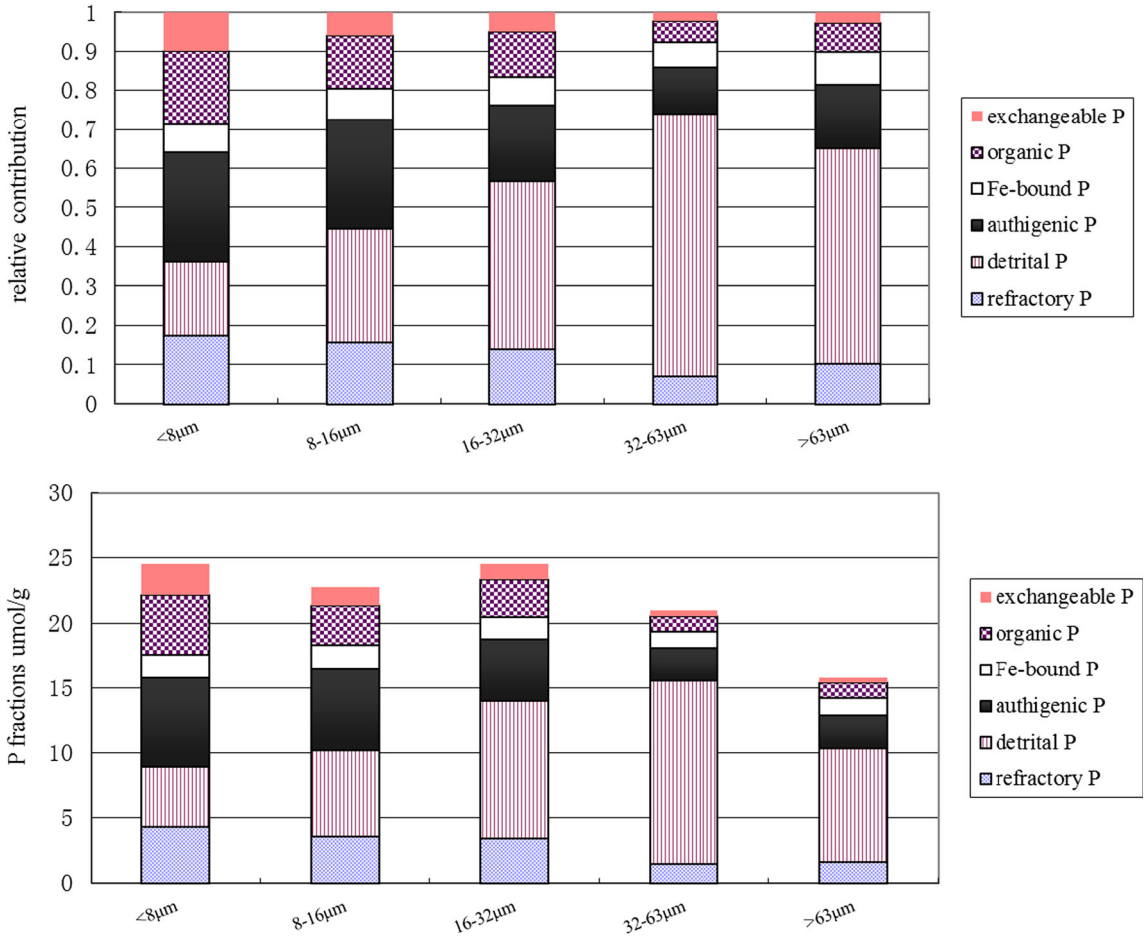

Fig. 8 Annual average contents of each P phases and its relative contributions to PP in the different size suspended particles

fraction during the two flow conditions. Therefore, the fluctuations in the TP over time were driven by the PP concentrations. This differs from the results of Ellison and Brett (2006), who found that the TDP was the dominant P fraction during base flow, and PP was the dominant P fraction during storms. This is most likely because of the high TSS concentrations in the Yellow River. The PP is associated with TSS transport, as shown by the high correlation between the two parameters (R^2=0.99, n=35) (Fig. 9f). The concentration of DIP in river water is known to be buffered by interaction with inorganic particulate matter. Much of the P input was removed by adsorption in the Yellow River, which was due to the high TSS. The sediment was a sink for P in the middle to lower reaches (Pan et al. 2013). Pan et al. (2013) studied the adsorption-desorption behavior of P in the Yellow River through adsorption experiments. The result showed that TSS of 0.2–1 kg/m^3 was a critical threshold for the Yellow River, below which most of the phosphate input cannot be removed by the particles and may cause eutrophication. The TSS concentrations varied between 0.29 to 14.8 kg/m^3 in the Yellow River in 2010. So the low TDP was due to the high TSS.

To reduce the siltation of the lower river channel and to transport both the sediment released from the Xiaolangdi Reservoir and the sediment derived from channel erosion to the sea via floodwaters, the Yellow River Conservancy Commission has instituted a WSR scheme at the beginning of every flood season since 2002. For the last eight WSR events (2002–2009), the freshwater discharges during the WSR events have represented 14–55 % of the annual river water discharge, with an average of 28 %. The sediment loads during the WSR events have accounted for 26–66 % of the annual sediment load, with an average of 41 % (Wang et al. 2005; Liu et al. 2012). This is significantly different from the previous long-term monthly average freshwater discharge, which exhibited high values during August to October. This pattern has resulted in earlier and greater discharges of Yellow River water into the Bohai Sea and has extended the period of higher discharge by several months. The higher monthly average water discharges and sediment loads have advanced to as early as June, i.e., at least 60 days earlier than before this management was implemented. The ninth WSR started in 19 June and ended in 7 July (http://politics.people.com.cn/GB/1026/12200414.html). During this period, the Yellow River freshwater discharge and sediment content exhibited higher values in June and July, which were related to only the water–sediment regulation event, than in the other months.

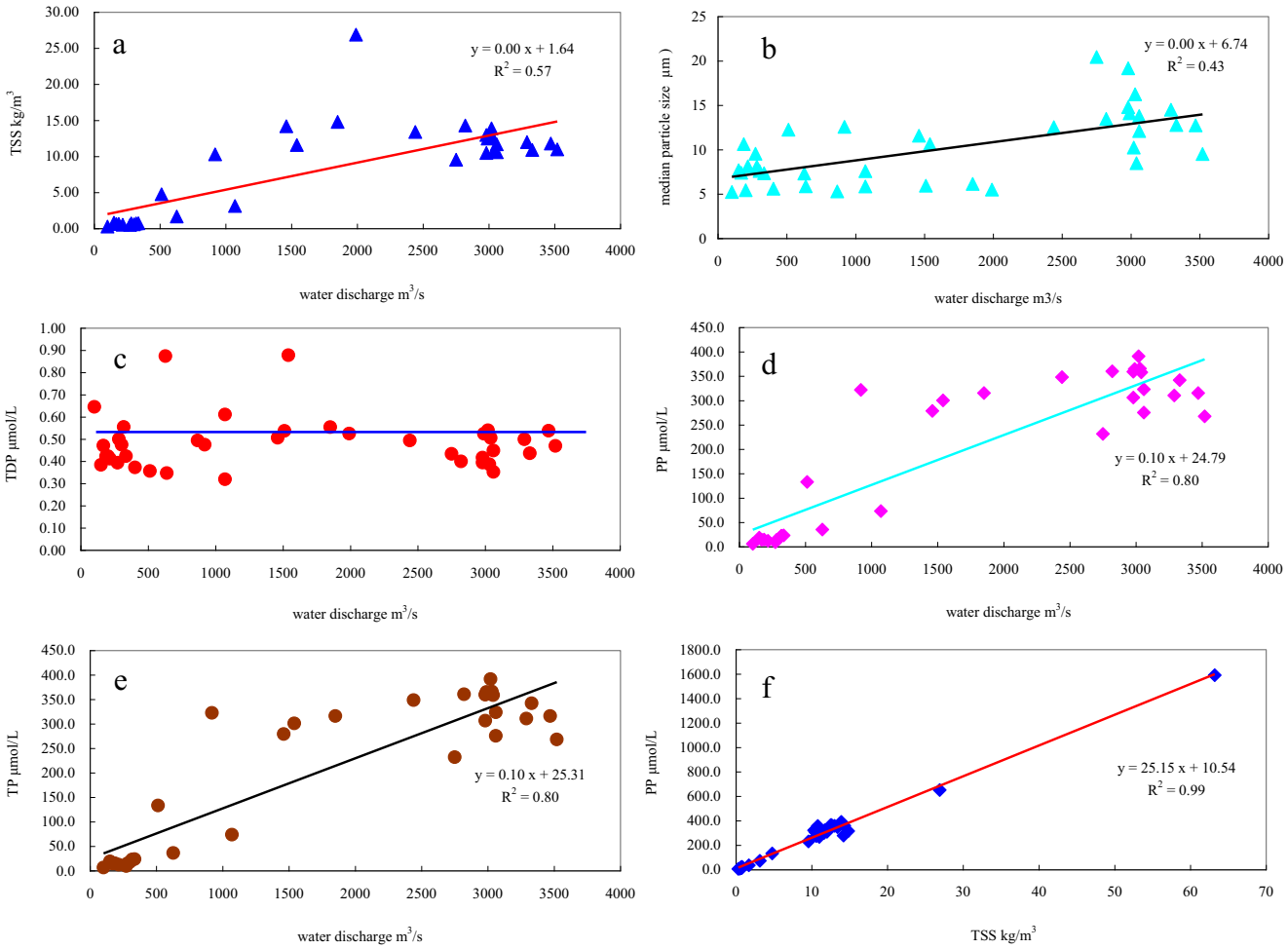

Fig. 9 Power function fits for water discharge and TSS (**a**), water discharge and medium size (**b**), water discharge and TDP (**c**), water discharge and PP (**d**), water discharge and TP (**e**), and TSS and PP (**f**)

However, the highest water discharge and sediment content were found in August and were due to heavy rain in the Yellow River basin.

During the low discharge periods from January to May and from October to December, the suspended sediments were finer grained (67–88 %, <16 μm). During the high discharge periods of June and July, the suspended sediment featured a greater percentage of coarse particles (nearly 40 %, >16 μm) than the low discharge periods (Figs. 3 and 4). However, the highest discharge and suspended sediment load were found in August, and the percentage of fine particles (<16 μm) reached 85 %. The variation in the suspended sediment size under different hydrological regimes can be attributed to the changes in the TSS sources (Pacini and Gächter 1999). While the WSR (in June and July) was operated by the facilities of the Xiaolangdi and the other large reservoirs on the main stream and the controlled water release was regulated, the rainstorm (in August) can be considered a natural event. During the period of the WSR (June and July), the sudden release of water from the reservoir into the channel formed artificial density currents. The controlled water release from the dam caused resuspension and remobilization of the bottom sediment, while the rainstorm mainly increased the soil runoff and transported terrestrial TSS to the river (He et al. 2010). Thus, the suspended sediments transported in June and July was mainly sourced from the channel, while the suspended sediments in August were mainly sourced from the soil in the river basin.

The seasonal hydrodynamic sorting of sediment in the Yellow River exerted a major control on the source and the particulate grain-size distribution. This, in turn, influenced the P fraction in suspended sediment. The changes in particle-size distribution and source associated with the variations in water discharge may explain the observed changes in the P content of the suspended sediment. The particle P content is correlated with the median particle diameter of size-fractionated samples (Figs. 5 and 8). As shown in Fig. 5, the percentage of fine particles was higher (i.e., in April). Accordingly, the relative content of exchangeable P, organic P, authigenic P, and refractory P concentrated in the fine particles were higher, while the concentration of detrital P, which was related to the coarser particle sizes, were lower (Figs. 7 and 8). The P content in

suspended sediment in June and July was higher than in the other months, and the contents and percentages of detrital P and Fe-bound P to TPP were higher. The suspended sediments in June and July mainly originated from the channel and feature the largest median particle diameters and highest percentages of 16- to 63-μm particles. However, the suspended sediments in August mainly originate from the soil in the river basin and feature the smallest median particle diameter. The P content in the suspended sediments in August was obviously lower than the P content in July and June.

Potential bioavailable particulate phosphorus

The sequential extraction allowed us to gain information on the forms of the particulate phosphorus, which was necessary to understand the potential bioavailability of the total PP in the coastal waters. Among different forms of particulate phosphorus, exchangeable phosphorus is readily released to ambient water by desorption and thereby becomes available to water column (Liu et al. 2004; Andrieux and Aminot 1997). Organic P could become bioavailable through remineralization (Andrieux-Loyer and Aminot 2001). Phosphorus is also potentially available when bound to redox-sensitive iron and manganese. Therefore, exchangeable P, organic P, and Fe-bound P represent the amount of potentially bioavailable PP (BAPP) (Andrieux and Aminot 1997; Zhang et al. 2004), and these three forms constitute approximately 19–31 % of the TPP (4.00–7.24 μmol/g) transported by the Yellow River. The average percentages of exchangeable P, organic P, and Fe-bound P in the BAPP were 18.2, 68.3, and 13.5 %, respectively. Organic P was the predominant form of BAPP. The content of BAPP varied greatly between different sizes of particles (Fig. 10). In general, the smaller the particle size, the higher the BAPP content and its proportion of TPP in these particles.

Importance of particle phosphorus in the transport of P to the Bohai Sea

According to the monthly concentrations of DIP, TDP, PP, and TP and the monthly water discharges in 2010, the DIP, TDP, PP, and TP fluxes were 3.82×10^6, 10.6×10^6, 3.60×10^9, and 3.61×10^9 mol/year, respectively (Table 3). The PP flux accounted for 99 % of the TP flux. The detrital P was the

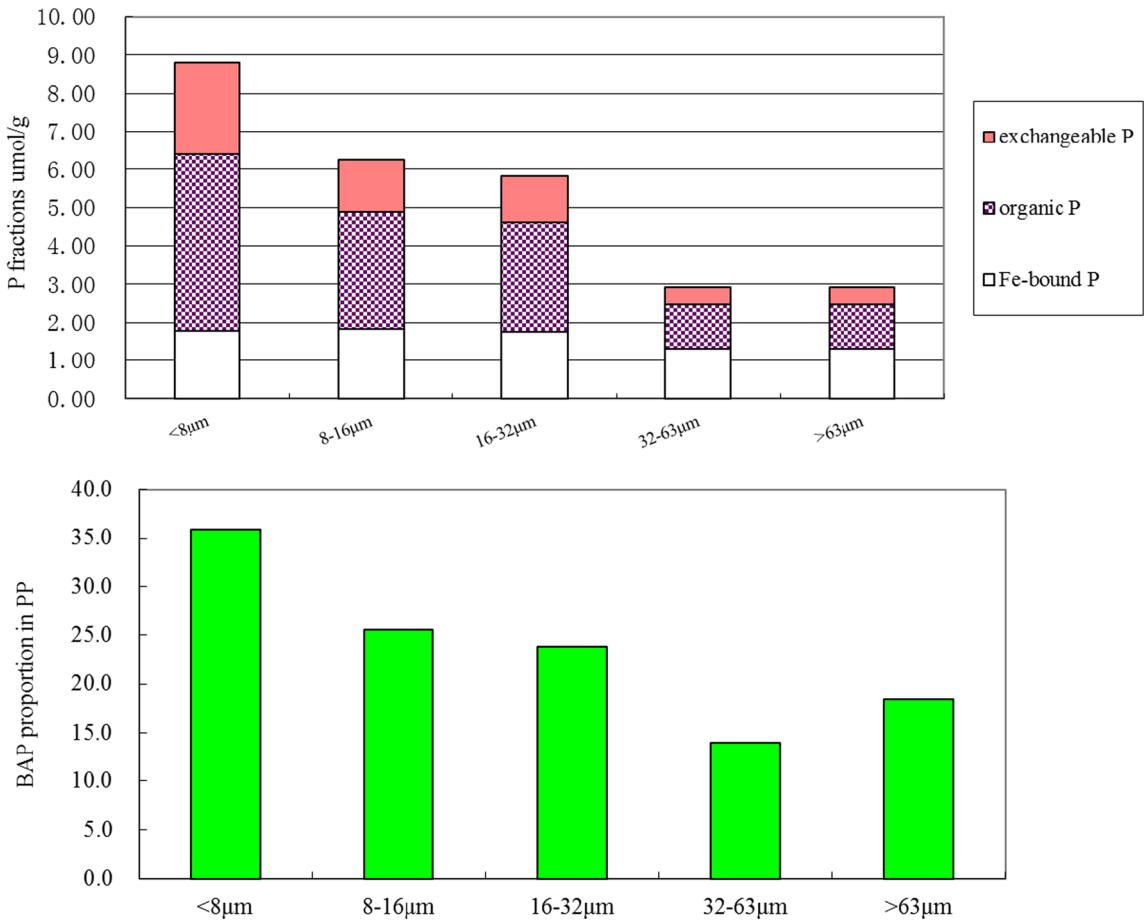

Fig. 10 BAP content and its relative contribution to PP in different size suspended particles

Table 3 Annual fluxes of particle P and dissolved P in the Yellow River ($\times 10^6$ mol/year). (Exchangeable P, Fe-bound P, and organic P of particulate P is BAP and therefore could be released into the water column.)

P forms	Truly suspended	Settleable				Total
	<8 μm	8–16 μm	16–32 μm	32–63 μm	>63 μm	
TP						3606.5
TDP						10.6
DIP						3.82
Exchangeable P	267.3	58.2	24.6	1.12	2.17	353.4
Organic P	419.6	75.2	48.3	7.1	1.26	551.5
Fe-bound P	59.3	18.5	11.9	2.47	0.7	92.9
Authigenic P	641.6	139.1	66.2	9.24	2.08	858.2
Detrital P	502.3	260.3	205	72.1	8.1	1047.8
Refractory P	503.9	108.2	66.8	11	2.36	692.3
PP	2393.9	659.5	422.8	103	16.7	3595.9
BAP	746.2	151.9	76.1	10.7	4.13	989.0

predominant fraction of P (29.2 % of the particulate P flux) among the pools of particulate P. The authigenic P, refractory P, and organic P were the next largest fractions and accounted for 23.9, 19.3, and 15.4 % of the particulate P flux, respectively. The exchangeable P and Fe-bound P composed less than 10 % of the particulate P flux. The BAPP flux was 9.89×10^8 mol/year, which was approximately 260 times larger than the SRP flux.

When the velocity of water flow is lower, most riverine suspended sediments are deposited in the estuary, and due to differences in settling velocities, the different particle sizes of the suspended sediment are deposited in different parts of the estuary (Gibbs et al. 1989). The coarse suspended sediments (such as sand and coarse silt) are deposited closer to the land, whereas fine suspended sediments (such as fine silt) are transported a greater distance seaward, and the finest suspended sediments (such as clay) are delivered to the sea. Alber (2000) operationally separated suspended sediments into "truly suspended" and "settleable" fractions with a cut-off velocity of 0.006 cm/s and found that all measured parameters (Chl-*a*, organic carbon, and nitrogen) were largely associated with the "truly suspended" fraction. Alber hypothesized that the more organic-rich, biologically active material associated with the suspended fractions likely had a different fate in the estuary because "truly suspended" particles will be readily transported, but "settleable" particles will settle and be resuspended with each tide. According to the diameters of the elutriator chambers and the flow rate, the settling velocities of particles with size ranges of <8, 8–16, 16–32, 32–63, and >63 μm were <0.004, 0.004–0.016, 0.016–0.064, 0.064–0.256, and >0.256 cm/s, respectively. Thus, the <8-μm particle fraction could be regarded as "truly suspended" particles.

Based on the particulate P fractions in various particle-size classes, the suspended sediment-size distribution, the TSS, and the water discharge, the riverine fluxes of particulate P to the Bohai Sea could be calculated in terms of total suspended sediments and various particle-size classes. The results are shown in Table 3. Approximately 2.39×10^8 mol/year of particulate P was associated with the "truly suspended" fraction, and 1.20×10^8 mol/year was transported with the "settleable" fraction. In other words, 66.6 % of particulate P was readily transported to the Bohai Sea. The BAP flux was approximately 9.89×10^8 mol/year (27.5 % of the particulate P flux), which was much greater than the flux of the DIP. Of the BAPP flux, approximately 7.46×10^8 mol/year was associated with the "truly suspended" fraction and approximately 2.43×10^8 mol/year was transported by "settleable" particles. Thus, approximately 75.4 % of the bioavailable P was readily transported to the sea, which was approximately 200 times higher than the flux of the SRP.

Conclusions

The biogeochemical observations in the Yellow River indicate that DOP was the predominant species of TDP, and PP was the predominant species of TP. The TSS, TP, and PP were all higher during flood season, while the TDP varied little. Two factors, the hydrologically controlled sources and the distributions of suspended sediment, controlled the relative distribution of the major pools of P found in the suspended sediments. The seasonal hydrodynamic sorting of sediment in the Yellow River exerted a major control on the sediment source and the particulate grain-size distribution, which influenced the P fraction in suspended sediment. The suspended sediment originated from the riverbed during the WSR period (in June and July) but from soil erosion and runoff during the rainstorm (in August).

The particle-size distribution influenced not only the total P content but also its forms, as observed in the analysis of a size-fractionated sample. The exchangeable P, organic P, Fe-bound P, authigenic P, and refractory P were concentrated in the small

particle-size classes, whereas more detrital P was found in the coarse silt and very coarse silt fractions. Authigenic P was only in major form in the fine silt and clay, and detrital P in the >32-μm fraction. The content of BAP varied greatly between the different sizes of particles. Organic P was the predominant form of BAP. In general, we found that the smaller the particle size, the higher the content of BAP and its proportion of the TPP.

Approximately 99 % of the TP flux transported from the Yellow River to the Bohai Sea was particulate P. The BAP flux was approximately 260 times larger than the DIP flux. Of the BAP flux, approximately 7.46×10^8 mol/year was associated with the "truly suspended" fraction, and approximately 2.43×10^8 mol/year was transported by "settleable" particles. Thus, approximately 75.4 % of the bioavailable P was readily transported to the sea, which was approximately 200 times higher than the flux of the DIP. Thus, the transfer of fine particles to the open sea is most probably accompanied by BAPP release to the DIP and can support greater primary and secondary production.

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