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Impact of suspended inorganic particles on phosphorus cycling in the Yellow River (China)

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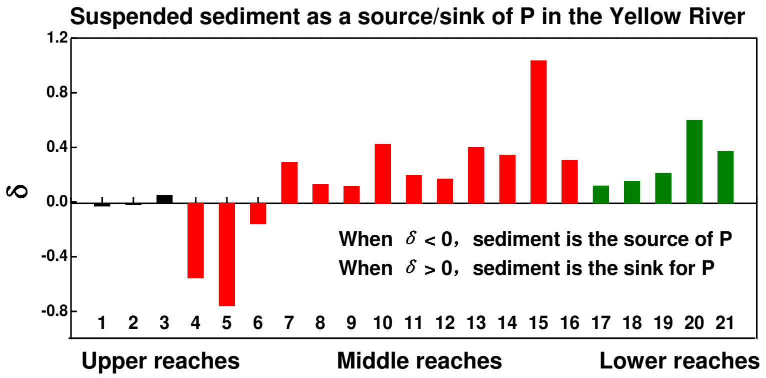
Abstract

Phosphorus (P) in water and sediment in the Yellow River was measured for 21 stations from the source to the Bohai Sea in 2006-2007. The average total particulate matter (TPM) increased from 40 mg/L (upper reaches) to 520 mg/L (middle reaches) and 950 mg/L in the lower reaches of the river. The average dissolved PO_4 concentration (0.43 μmol/L) was significantly higher than that in 1980's but lower than the world average level despite high nutrient input to the system. Much of the P input was removed by adsorption, which was due to the high TPM rather than the surface activity of the particles since they had low labile Fe and low affinity for P. The sediment was a sink for P in the middle to lower reaches but not in the upper to middle reaches. TPM has been reduced by more than an order of magnitude due to artificial dams over recent decades. Modeling revealed that TPM of 0.2~1 g/L 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. These findings are important for river management and land-ocean modeling of global biogeochemical P cycling.

TOC:



Introduction

Phosphorus (P) is an essential nutrient for biological productivity and in most freshwater systems it limits primary production.[1] It is also a common pollutant. In river systems, adsorption of dissolved phosphate onto inorganic particles, particularly amorphous iron oxyhydroxides, is considered the key process buffering bioavailable phosphate concentrations to relatively low values and making it the limiting nutrient.[2] While the importance of P as a limiting nutrient is well established, our understanding of global scale control on P cycling on the continents and how this affects riverine fluxes of bioavailable P is still incomplete.

The Yellow River (China) has the highest suspended sediment concentration of any major river in the world (22-65 g/L) ,[3-5] and the second largest sediment load (Qs) of 1.08 Gt/yr,[3] which represents 6% of the estimated global river sediment flux to the ocean. This high sediment load is because the middle reaches of the river drain the Chinese Loess Plateau. This is a region subject to extensive soil erosion mostly as a result of agricultural practices which started ~200BC.[6] In addition, there are five large deserts (Ulan Buh, Kubuqi, Mu Us, Badain Jirin and Tenggeli Desert) in the surrounding region which also contribute sediment load to the river. The high levels of particulate matter in the Yellow River make it the extreme end-member amongst major world rivers for high input of suspended particles. This suspended sediment is coincident with high total phosphorus (TP) input to the river [7, 8], and is potentially important for buffering dissolved inorganic phosphate (DIP) . However, it is not well understood whether and to what extent the total particulate matter (TPM) in the Yellow River is chemically active and hence how much it controls dissolved phosphorus.

Equilibrium phosphorus concentration (EPC_0), a parameter obtained from phosphate-sediment adsorption experiments, has been used to provide quantitative information on whether sediments remove or release P to the overlying water,[9, 10] to calculate the P flux between sediment and the overlying waters [10] and to estimate the exposure history of sediment to anthropogenic inputs of P.[11] The nature and history of the particulate matter is a crucial factor influencing P cycling. Most of the particulate matter in the Yellow River comes from soil erosion from the Loess plateau.[12] This soil has undergone physical erosion with a minimum of chemical weathering.[13] It is not clear how the P activity is affected by the physicochemical nature of TPM in the Yellow River, or whether the TPM is a source or sink of P.

Adsorption processes are important for regulating the dissolved P levels in rivers when there are significant amounts of suspended particles. The total phosphate removed by the particles depends on both the surface activity of the solids to P and the total amount of TPM available (i.e. particle concentration).[10] Surface activity and adsorption capacity, which can be quantified by equilibrium adsorption constants, are determined by the chemical composition of the particles.[14] Experimentally measured equilibrium adsorption constants generally reflect metastable equilibrium,[15, 16] which can be affected by both adsorbent concentration and adsorbate concentration depending on the adsorption reversibility.[17-20] Adsorption reversibility is important in regulating the uptake and release (the buffering effect) of DIP especially when water conditions (e.g. pH and salinity) change along a river. No studies to date have integrated all these adsorption properties to determine their effects on P concentration at the scale of an entire river.

One of the most important recent environmental changes is the widespread damming of many rivers. Between 2000 and 2005, the sediment load delivered from the Yellow River to the sea decreased to only 14% of the previous flux of 1.08×10^9 t/yr.[21] This decrease is continuing,[22] raising the possibility that eventually the particle load in parts of the river will decrease below a threshold required to maintain low bioavailable P concentration, resulting in increased eutrophication in the catchment. However, no quantitative method has been found to predict such a threshold, which is essential for science based river management including eutrophication control and also for coupled land-ocean modeling in global biogeochemical P cycling.

In this study detailed geochemical measurements of dissolved and particulate P were made at 21sampling stations from the source to the estuary of the Yellow River (Figure 1). EPC_0 was used to identify the role of TPM as a source or sink of P throughout the entire river. The aim was to understand the nature and controls on P cycling in this most extreme particle-rich end-member amongst major world rivers. Having defined the present baseline conditions of the river, laboratory experiments were carried out to predict how current and future changes in TPM might affect the phosphate level in the river and its impact on water quality problems such as eutrophication.

Materials and methods

Study sites and sample collection. Surface sediment samples were collected from the river bed at 21 sites along the Yellow River from the source to the Bohai Sea during low flow periods in November 2006 (mid to lower reaches) and April 2007 (upper reaches) (Figure 1). Samples were air dried at room temperature and sieved to < 63μm as this size fraction is the most geochemically reactive and approximates most closely to the suspended particulates in the Yellow River.[23] Water samples (20-40 cm bellow surface) were also collected at each site. Additional water samples were collected in November 2011 at 3 stations (Stations A, B and C) in the lower reaches (Figure 1). TPM was calculated from filtering (0.45μm cellulose acetate filters) as the weight of dry particulate matter per unit volume of water. Conductivity, pH and oxidation reduction potential (ORP) were analyzed in the field with a portable meter YSI-556 (YSI, USA). Details about the sample collection methods and sample analysis are presented in the SI 'Sample collection and analysis'.

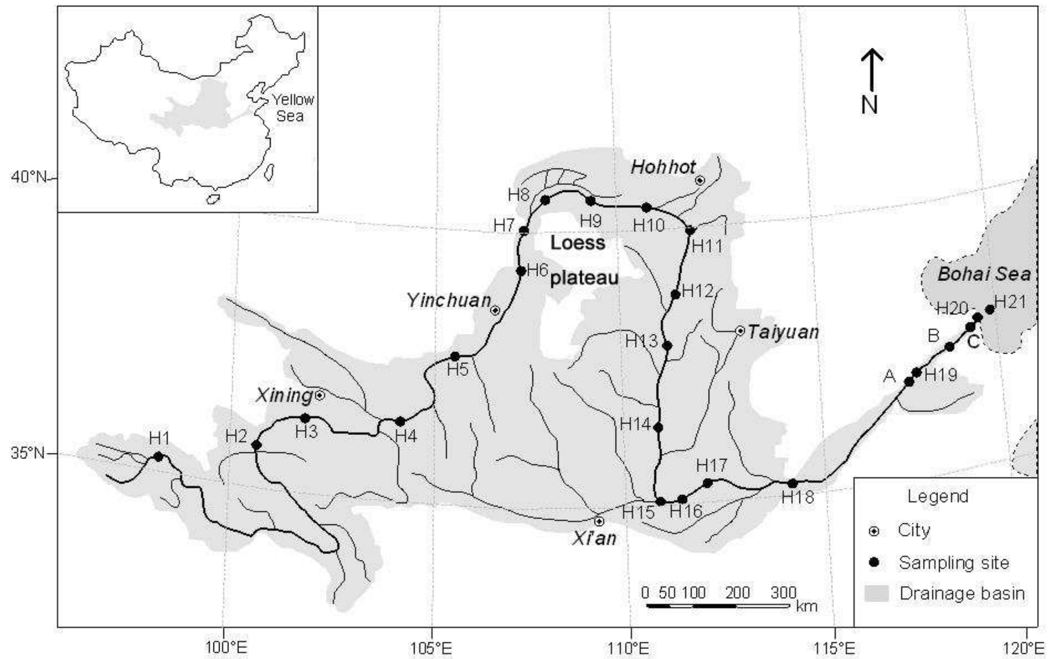


Figure 1. Map of the Yellow River Basin showing its geographical position in China and the location of sampling stations. The stations are approximately equally spaced along 5464 km of the river.

Phosphorus speciation in sediment samples. Phosphorus fractions in the sediment samples were analyzed using the standard measurement and test (SMT) procedure of phosphorus forms in freshwater sediments.[14] The SMT method consists of five steps and the following forms were determined: NaOH- P (P bound to Fe, Al, and Mn oxides and hydroxides), HCl- P (P associated with Ca- principally apatite), inorganic P (IP; NaOH-P & HCl-P), organic P (OP), and concentrated HCl-extractable P (total P, TP).[14] Details of the procedures used are given in Supplementary Information.

The concentration of DIP in water samples, the P extracts obtained from each chemical fraction separated during the P speciation experiments of particulate matter and the supernatant obtained during sorption experiments, were all analyzed colorimetrically after filtration, using an adaptation of the molybdate-blue method.[24] Concentrations of dissolved total phosphorus (DTP) were analyzed after acid-persulfate digestion using the same method.[25] The dissolved organic phosphorus (DOP) was calculated by subtracting DIP from DTP.

Adsorption experiments. EPC_0 is the measured DIP concentration at which there is no net adsorption or release of dissolved P from sediment.[11] In order to determine EPC_0 for each sediment sample, 0.03 grams of sediment was placed in each of seven polypropylene centrifuge tubes with 30 ml of filtered water collected from the same sample location (TPM=1 g/L). All but one of the tubes was spiked with KH_2PO_4 to provide a range of initial phosphorus (P) concentrations (0 – 19.3 μmol/L). The centrifuge tubes were placed in a shaking bath at 150 rpm and 25℃ for 50 h, maintaining the pH at 8.35 ± 0.05 with 0.01 mol/L HCl or NaOH during the incubation period. After 50 h, each tube was centrifuged and the supernatant filtered through 0.45 μm and analyzed for DIP. Adsorption isotherms were plotted for all 21 stations.

In a 2nd set of adsorption experiments, a series of TPM (1, 5, 10, 30, 50 g/L sediment) were used to determine the threshold of TPM which leads to reduction of the phosphate level. These TPM conditions were chosen to bracket the known changes of TPM over the past decades in the Yellow River. The sediment sample came from the lower reach Jinan station (H19), and tubes were spiked with KH_2PO_4 to provide a range of initial phosphorus concentrations (C_0, 0.51 to 25.8 μmol P/L) designed to simulate the typical condition of P input to the Yellow River.[26] The remaining details of the experiments are the same as described above.

Phosphorus adsorption was described by a Freundlich crossover-type equation [10]. The crossover-type equation is expressed as

$$Q = K \times C_p^{-n} \times \left(C_{eq}{}^{\beta} - EPC_0^{\beta}\right) \quad (1)$$

where Q (μmol P/g) is the amount of P adsorbed during the experiment, K (L/μmol) is a sorption constant reflecting the sorption affinity of the sediment for P, β is an empirical constant, and Ceq (μmol P/L) is the equilibrium concentration of P. The Cp effect index (n) was assumed to be 0 here to simplify the analysis. The measured crossover adsorption isotherms were used to determine the EPC_0. Model parameters were estimated by a Marquardt nonlinear least-squares fitting routine.

In order to judge whether the sediment acts as a source or sink of phosphorus for the water body, Pan et al.[10] defined a criterion of λ=C/EPC_0 and Jarvie et al.[11] defined EPC_{sat} = (EPC_0 − DIP)/EPC_0× 100%. However, both of the methods could easily enlarge the measurement error especially when EPC_0 is low since EPC_0 is in the denominator in both equations. Here, we developed a new simple criterion δ. According to equation (1), for adsorption isotherm under constant TPM condition, we define:

$$\delta = C_{eq}{}^{\beta} - EPC_0^{\beta} \quad (2)$$

When $\delta < 0$, Q < 0 (desorption), sediment is a source of P.

When $\delta > 0$, Q >0 (adsorption), sediment is a sink for P.

Results and Discussion

Water quality changes from upper reaches to the estuary. The Yellow River can be divided into three sections based on TPM load and water chemistry (Figure 2). The stations are grouped into Upper Reaches (H1-H3), Middle Reaches (H4-H12) and Lower Reaches (H13-H21). The upper reaches of the river (H1-H3), before it reaches the Loess plateau, are characterized by relatively low TPM (41±22 mg/L, Figure 2A), dissolved calcium (1.05±0.12 mmol Ca/L, Figure 2B) and conductivity (455±173 μS/cm, Figure 2C) typical of chemical weathering in temperate rivers.[27]

The DIP and DOP concentrations are low (0.27±0.02 and 0.06±0.09 µmol/L respectively) (Figure 2D and Table S1a). In the upper reaches of the river which flow through the desert regions of eastern China, there is relatively little influence of human activities, with only relatively minor influxes of anthropogenic nutrients.

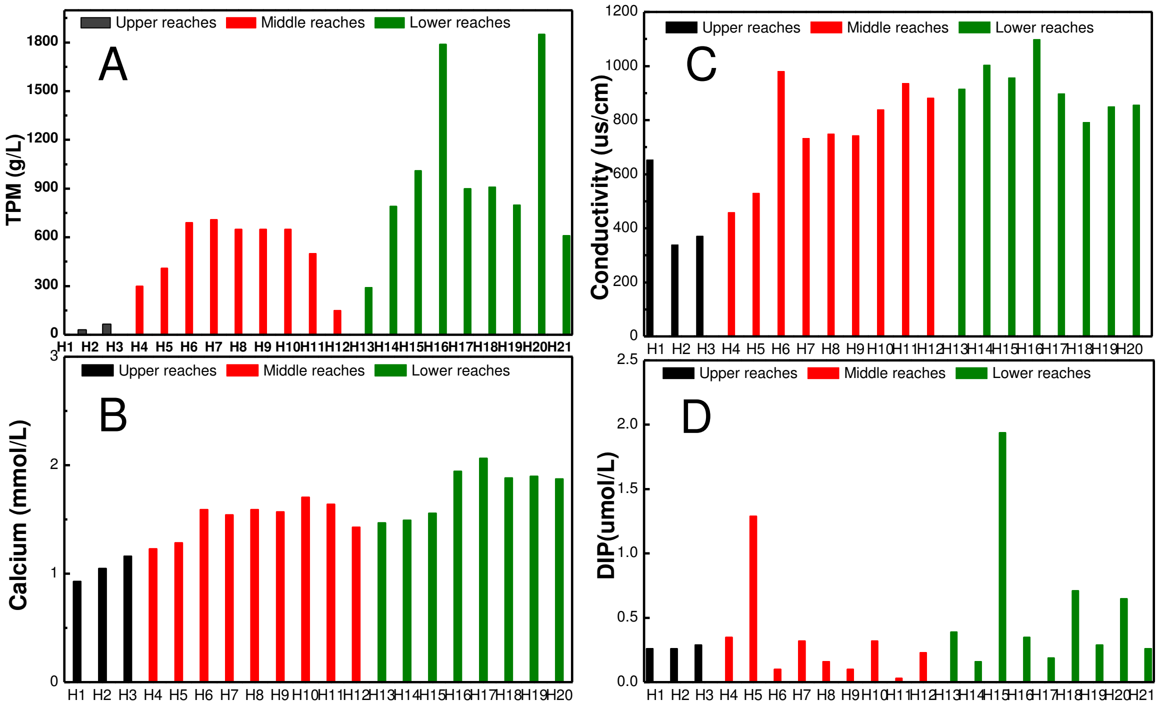


Figure 2. Total Particulate Matter (TPM; A), Calcium concentration (mmol Ca/l; B) , conductivity (µS/cm; C) and DIP concentrations (µmol/L; D) in surface water of the Yellow River from Maduo (Station 1) to the Bohai Sea (Station 21). The stations are grouped into Upper Reaches (H1-H3), Middle Reaches (H4-H12) and Lower Reaches (H13-H21).

In the middle reaches (H4 to H9), the river flows to the east of the Loess plateau and receives major inputs of particulate matter from tributaries flowing off the plateau. The river now also reaches the most highly populated areas. As a result, the TPM concentration in the river increases by an order of magnitude to 520±200 mg/L (Figure 2A). Weathering in the Yellow River catchment is dominated by physical weathering (159 mg/cm^2) with very low levels of chemical weathering (2.7 mg/cm^2), a ratio of 59:1.[13] This compares for example to a ratio of 2.8 in the Yangtze catchment.[13] Nonetheless the total chemical weathering in the catchment is large enough to result in changes in major ion water chemistry, so conductivity and dissolved calcium increase by ~50%, becoming similar to those reported in the Yangtze river.[27] Between stations H10 and H12, the TPM concentration decreases mainly due to the hydrological changes of slower flow.

In the lower reaches (H12 to H16), the river flows south and then east and receives further input from the Loess plateau. This results in an increase in TPM from 150 mg/L at station H12 to a maximum value of 1790 mg/L at station 16. After station H16, the TPM again decreases downstream until there is a final peak of 1850 mg/L associated with the turbidity maximum in the estuary at station H20. The dissolved calcium increases in the lower reaches compared to the middle reaches. However, the increase in calcium due to chemical weathering is relatively small (<25%), as is expected from a system where physical weathering dominates over chemical weathering. The measured DIP increases in general from upper to lower reaches with the exception at stations H5 and H15 (Figure 2), which are both located in a grain producing area and might be polluted by phosphorus-rich run-off following agricultural irrigation. The average DIP of the Yellow River is 0.43±0.44 μmol/L, which is slightly lower than the world river background levels.[5, 28] Similar low concentrations for DIP (0.09-0.19 μmol/L) and DOP (0.42-0.56 μmol/L) were obtained from the samples collected in 2011.

The concentration of dissolved phosphate in river water is known to be buffered by interaction with inorganic particulate matter.[2] The phosphate is held reversibly on adsorption sites and then exchanges with the water column and with biota. This is the principle reason why primary productivity in many rivers is phosphorus limited. The Yellow River is an extreme example with high TPM in the middle and lower reaches of the river (22-65 g/L) in the past [3-5] and very low phosphate levels (~ 0.3 μmol/L) [7,8] before the 1980's. In this study, the average phosphate concentration is about 0.43 μmol/L, which has increased since the 1980's but is still lower than (or close to) many other world major rivers (Figure 5). This change coincides with a current average TPM of 0.76±0.45 g/L in the middle to lower reaches, which has been reduced by more than an order of magnitude compared to pre-1980 but is still higher than many rivers. The average TPM for the world's 10 largest rivers defined by annual flow rate is 0.35 g/L with a range of 0.02 g/L- 1.7 g/L.[27] Our values of TPM are lower than previously published values both because of the overall decrease in TPM in the river with time (see below) and because only the surface river water was sampled during a period of low flow in this study.

P activity of particles and its effect on phosphate adsorption. The surface activity of Yellow River TPM is governed by the chemical composition of the particles. The measured values for P speciation and total P of the particles for all 21 stations are presented in Figure 3 and Table S2. The relative proportion of various forms of phosphorus is similar to untreated Loess.[29] In particular the majority of the TP in the sediments is present in the form of HCl-P (apatite-P, average value 89.3 %, Figure 3). There is very little NaOH-P (2.5 %) or OP (6.9%) in the Yellow River particles (Figure 3). NaOH-P which measures P bound to Fe and other oxyhydroxides is equivalent to P bound to labile Fe (Fe-P) measured in previous studies using a citrate-dithionite extraction.[30] The Fe-P and OP phase are considered to be most important in the buffering of DIP in natural waters.[2] In comparison, particulate matter in the Nile and Mississippi contains 43-46 % Fe-P [10, 31] and in the Amazon 28-33%.[32] The Yangtze River is closest to the Yellow River with 18 %.[33] Fe-P is formed by the interaction of P with labile iron oxy-hydroxides which are mainly produced as a result of chemical weathering of rocks and soil formation. Our previous experimental study suggests that for

Yellow River particles, phosphate is mainly taken up within the Fe-P phase.[18] The labile Fe measured in the Yellow River TPM in the middle and lower reaches is only 2.3 % ± 0.8 % (Table S2) which is similar to previous studies which found that labile Fe of Yellow River TPM is low compared to most other rivers.[34] Thus the amount of P which can be adsorbed per gram of sediment is relatively low in the Yellow River. The buffering phenomenon observed in the past and to a lesser extent at present is thus due principally to the high levels of TPM in the river.

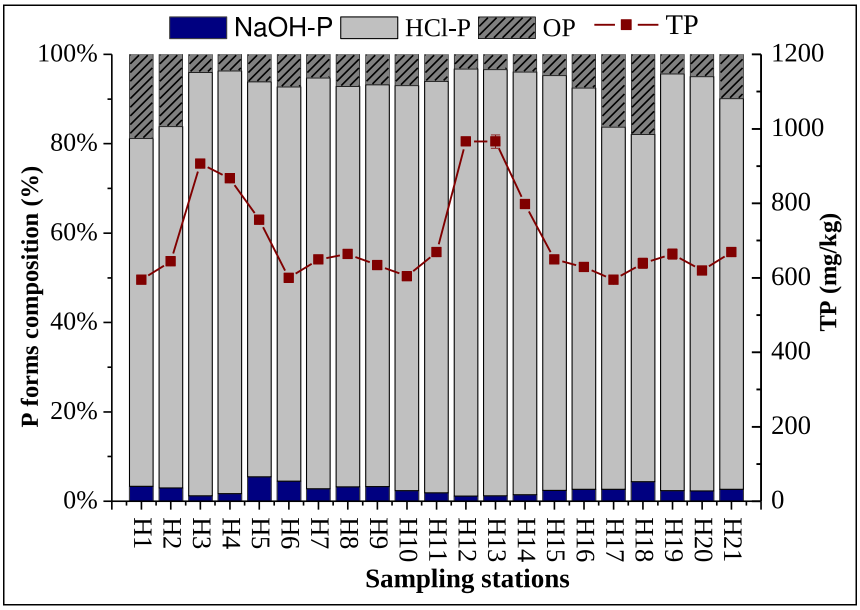


Figure 3. Relative proportion of various forms of phosphorus and total phosphorus concentrations in sediments from the Yellow River.

The role of TPM as a source or sink in the Yellow River. Table 1 lists the DIP, equilibrium adsorption constant (k), EPC_0 , and the criterion δ values calculated using equation 2 for all 21 sediment samples. Adsorption isotherms for all 21 station samples are presented in Figure S1. In the upper reaches with relatively low TPM and anthropogenic nutrient input, DIP is in equilibrium with the sediment (δ values close to zero). At the beginning of the middle reach there is an increase in anthropogenic input of phosphate together with increased particulate (Loess) input. As the P level in the upper river is relatively low, the input of land-borne particles plays a role as a source of P, i.e.

δ is negative (Table 1 and TOC). After the major input of loess in the middle reach, the water borne suspended particles become a weak sink of P as the δ values become positive from the middle to lower reaches (Table 1). Since TPM is still high, the suspended particles in the mid-to-lower reach can still remove most P and act as a sink for additional phosphate input. The phosphate level in the river is therefore not high (average 0.43 μmol/L) given the significant TP input. However, due to the reduction in TPM over recent decades, the phosphate level in the Yellow River has already begun to increase (Figure 5).

Table 1. Parameters of Freundlich crossover-type equations calculated by a non-linear fit for the P adsorption isotherms of the Yellow River sediments and the calculated role of each sediment as a sink or source of phosphate calculated by δ.

Sampling site	K (L/μmol)	β	EPC_0 (μmol/L)	R^2	δ	SINK/ SOURCE
H1	0.623	0.440	0.2936	0.9975	-0.03	EQUILIBRIUM
H2	1.095	0.316	0.3161	0.9977	-0.02	EQUILIBRIUM
H3	0.119	0.683	0.2419	0.9994	0.05	EQUILIBRIUM
H4	0.066	0.924	0.9290	0.9975	-0.55	SOURCE
H5	0.101	0.822	2.3129	0.9924	-0.76	SOURCE
H6	0.476	0.455	0.2290	0.9954	-0.16	SOURCE
H7	0.271	0.531	0.0774	0.9989	0.29	SINK
H8	0.416	0.461	0.0742	0.9981	0.13	SINK
H9	0.184	0.662	0.0323	0.9851	0.11	SINK
H10	0.367	0.369	0.0194	0.9905	0.42	SINK
H11	0.220	0.654	0.0161	0.9820	0.20	SINK
H12	0.118	0.663	0.0936	0.9921	0.17	SINK
H13	0.160	0.534	0.0516	0.9980	0.40	SINK
H14	0.272	0.500	0.0032	0.9953	0.34	SINK
H15	0.189	0.548	0.1903	0.9936	1.04	SINK
H16	0.212	0.590	0.0839	0.9879	0.31	SINK
H17	0.804	0.364	0.0968	0.9963	0.12	SINK
H18	0.941	0.366	0.4194	0.9993	0.15	SINK
H19	0.109	0.703	0.2323	0.9910	0.21	SINK
H20	0.211	0.518	0.0452	0.9956	0.60	SINK

H21	0.469	0.507	0.0194	0.9857	0.37	SINK

Comparison to other major world rivers. The Yellow River is impacted by considerable nutrient pollution (both N and P).[22, 35] Previous studies have used the increase in fluxes of nitrate as a measure of the degree of nutrient pollution in this and other river catchments.[36] Using nitrate and ammonium data collected from a similar transect down the river in 1989-2000 [36] compared with the phosphate values obtained in this study collected during 2007, a Nitrate:Phosphate molar ratio of 760:1 was calculated. This value of 760:1 was similar in magnitude to the values we obtained from the three stations sampled in the lower reaches in 2011 (720-1510) and to previous measurements in the river (167-368).[4, 5, 22, 37] These ratios are very much higher than those determined for other major rivers globally which are generally between 10 and 100.[5, 28] They are also much higher than the molar N:P ratios in typical sewage , industrial or atmospheric inputs to Yellow River.[8] The very high Nitrate:Phosphate ratio means that the Yellow River is an extreme P limited ecosystem: there is very little available P for biological uptake and photosynthesis because of the high inorganic particulate load. In addition to having a high Nitrate:Phosphate ratio (700-1480), the Yellow River also has a high Nitrate:Ammonium ratio (29-194).[5, 36, 37] This ratio is a factor of 4 higher than that of the Yangtze River and is higher than other major rivers worldwide (Figure 4).[27] Both phosphate [2] and to a lesser extent ammonium are particle reactive chemical species. Ammonium, like phosphate, tends to be adsorbed onto inorganic particulate matter, especially clays.[38] In addition it is known that bacterial nitrification is encouraged by the presence of particulate matter.[39] This results in ammonium being converted into nitrate which then remains in solution because nitrate is not particle reactive. Thus we suggest that the quasi-linear general relationship between Nitrate: Phosphate ratio and Nitrate: Ammonium ratio in major rivers (Figure 4) represents the general effect of inorganic particles on river nutrient chemistry, with particle reactive chemical species (phosphate and ammonium) being removed from the water column while nitrate accumulates. The Yellow River represents the highest ratios because of its relative high suspended sediment load.

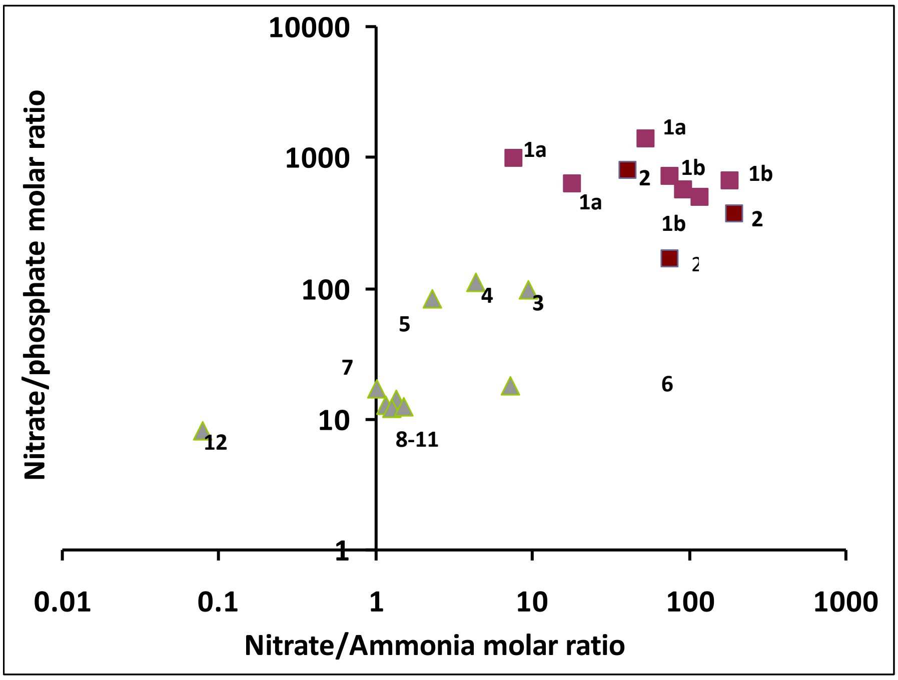


Figure 4. The molar ratio of nitrate/phosphate vs nitrate/ammonium for a selection of major rivers (squares represent the values from the Yellow River while triangles are that of other major rivers in the world). Specifically the data presented is (1a) Yellow River (this study -2011 data), (1b) Yellow River (2008-2009)[22], (2) Yellow River (this study -2007 data with Chen et al. N data, Meybeck & Turner et al.) [5, 36, 37], (3) Danube [5], (4) Zhuijiang [4], (5) Changjiang [4], (6) Niger [28], (7) Negro [28], (8) Ganges [5], (9) Amazon [28], (10) Solimoes [28], (11) Mississippi [28], (12) Zaire [28].

Effect of TPM reduction on P cycling. Sediment loads in the Yellow River prior to 1980 were in the range of 22-65 g/L.[3-5, 40] At Zhengzhou in the lower reaches of the river, the average value for TPM was 23.9 g/L between 1952 and 2010 but decreased to 5.4 g/L in 2006, to 2.2 g/L in 2009 and to 6.1 g/L in 2010.[22] Intensive river basin management has been implemented and more than 3100 reservoirs have been built in the entire catchment to provide freshwater for more than 100 million people.[22] Consequently, TPM in the Yellow River has been reduced by over an order of magnitude over recent decades, leading to a significant biogeochemical and ecological impact.

There is significant nutrient pollution within the river catchment, with increasing inputs from both point source and non-point source, particularly fertilizers applied to support agriculture.[36, 41] The TP input in the Yellow River is reported to be high compare to other world major rivers (e.g. 182 μmol/L (1985-1989) [7], 16 μmol/L (2002)[26]). Such a high TP input does not result in a high DIP in the river in pre-1980 (~ 0.3 μmol/L) because much of it was adsorbed by the very high TPM. As the TPM is reduced to 0.76±0.45 g/L in the mid-lower riches of the Yellow River (Figure 2A), the average phosphate concentration increases to 0.43 μmol/L (Figure 5). However, the current DIP level is still lower than the world average level (0.48 μmol/L, inserted figure in Figure 5).

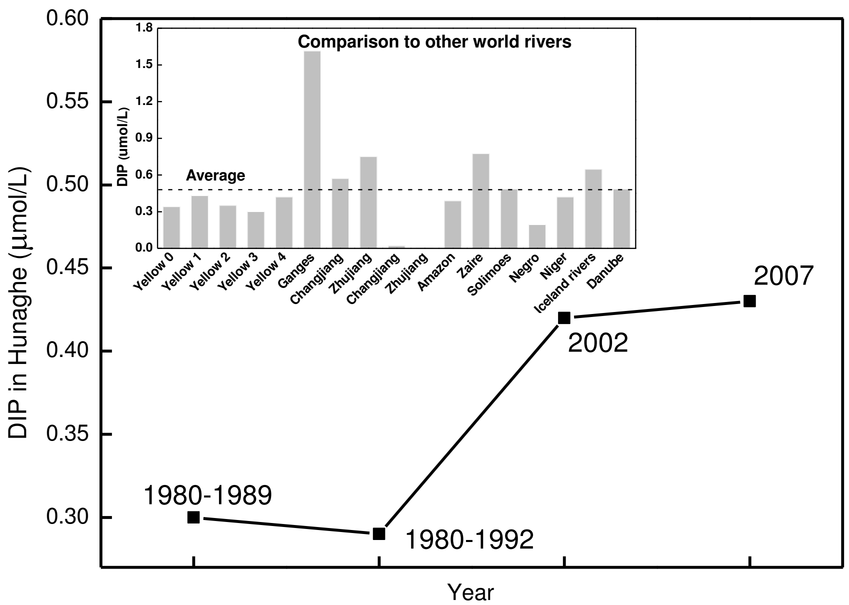


Figure 5. The average DIP level in Yellow River from 1980s to 2007 and comparison to that of other world rivers. Inserted chart: Yellow River 1,[5] Yellow River 2,[7, 8] Yellow River 3,[26] Yellow River 4 (this study), Ganges,[5] Changjiang,[4] Zhujiang,[4] Changjiang,[37] Zhujiang,[37] Amazon,[28] Zaire,[28] Solimoes,[28] Negro,[28] Niger,[28] Iceland rivers,[28] Danube[28]

Results from laboratory simulations (Figure 6) show that over the range of TPM measured in the Yellow River (0-50 g/L), reducing the TPM will cause an increase in the amount of phosphate remaining in solution. For the sample from the H19 station, at the highest TPM concentration tested (50 g/L), nearly all of the added P was removed by adsorption when $C_0 \leq 6.4$ μmol/L (Figure 6). As TPM decreased, more of the added P remained in solution. The relationship between C_{eq} and C_0 approached to linear with a slope of 1 as TPM reduced to zero (dotted line in Figure 6). The extent that this slope deviates from 1 can be used to measure the impact of TPM changes on DIP levels in solution. At the conditions of C_0 6.4 μmol/L and 13 μmol/L, the slope increased from below 0.4 at TPM 50 g/L to about 0.8 at TPM 5 g/L, and then markedly from 0.94 to 1 at below 1 g/L (inserted chart of Figure 6). This result suggests that, for site H19, when TPM is reduced below 1 g/L, the ability to remove added P is dramatically reduced.

Using the equilibrium adsorption constants in Table 1 and the isotherms in Figure S1, the P removal ability and residual P in the water were predicted and modeled for all 21 stations (Figure 7). The amount of DIP that can be removed by different samples of Yellow River suspended sediment under the equilibrium concentration of 0.4 μmol/L is shown in Figure 7A. Suppose the TP input of Yellow River is 16 μmol/L[25] and DIP counts for 5% of TP,[7] so that the total DIP input is 0.8 μmol/L. Under these conditions, the remaining DIP was predicted in Figure 7B. The DIP was maintained at an average of 0.28 μmol/L at TPM of 1 g/L and 0.70 μmol/L at TPM of 0.2 g/L (Figure 7B). The latter is higher than class V surface water quality in China[42] which is known to cause eutrophication. We therefore propose a TPM value of 0.2~1 g/L as a critical threshold for the Yellow River, below which most phosphate input to the river cannot be removed by the particles.

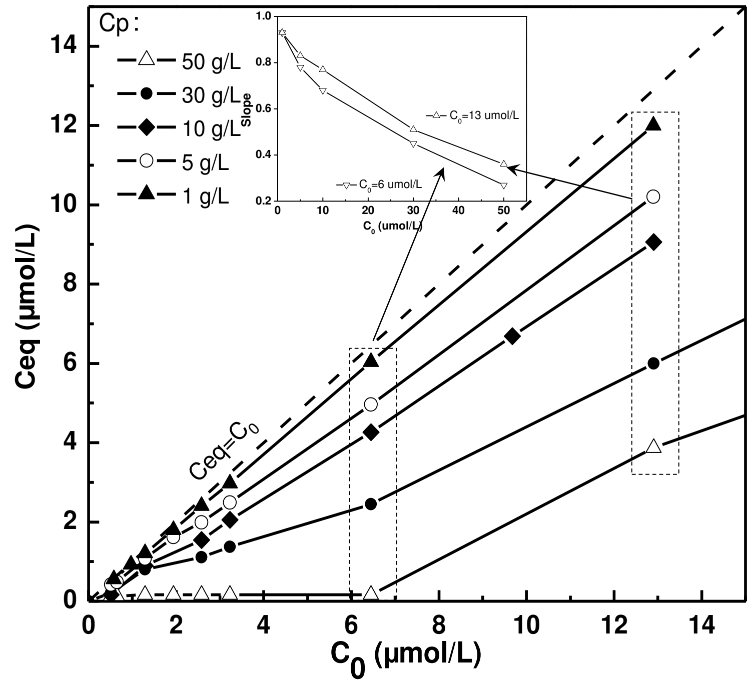


Figure 6. The relationship between the initial phosphate concentration (C_0) and the final equilibrium concentration (C_{eq}) under different sediment concentrations (1, 5, 10, 30 and 50 g/L). The sediment sample came from Jinan station (H19). Dotted line represents a 1:1 slope between the C_0 and Ceq, meaning no adsorption occurs. The inserted chart describes the influence of TPM on the conservative behavior between the C_{eq} and C_0.

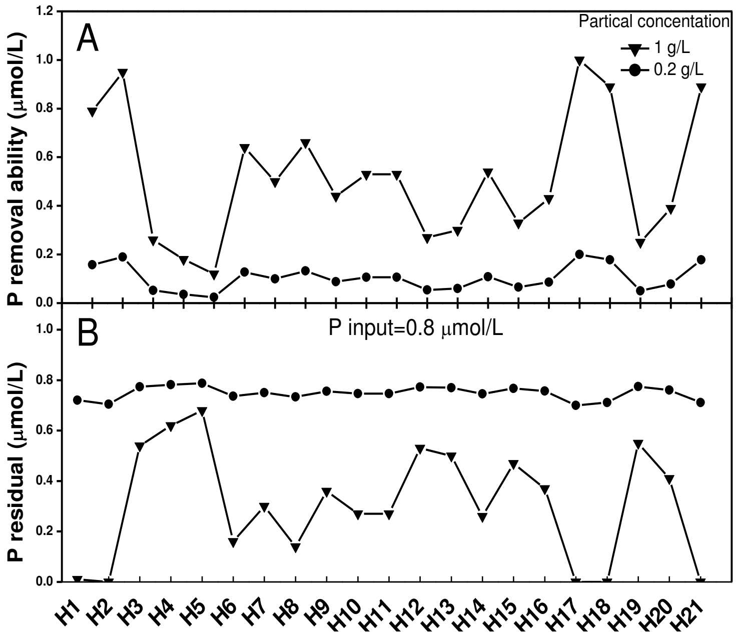


Figure 7. P removal ability for sediment samples of all 21 stations of Yellow River (A); and the residual P left in water when DIP input is 0.8 μmol/L (B).

Two factors are responsible for the above mentioned P buffer effect (Figures 6 and 7): one is the surface reactivity of the solids to P and the other is the TPM. The Yellow River TPM has a rather low reactivity to P and the Freundlich adsorption constant (k) ranged between 0.07-1.1 L/μmol (Table 1). This adsorption coefficient for particles of the Yellow River, which is dominated by the Loess, is similar to that of Saharan dust (k = 2 L/μmol)[10] which is shown to be relatively unreactive to phosphate, and is much smaller than that of Nile TPM (k =40 L/μmol) that is known to have much higher P affinity.[10] In the Yellow River system, where the k values are low, the reduction of the DIP in the water dominantly depends on TPM concentration changes. The average TPM of Yellow River at the time of sampling was 0.66±0.41 g/L (middle reach) and 1.01 ±0.48 g/L (lower reach) where most P input is received, which has already reached the upper limit of the threshold that we predicted (0.2 – 1 g/L). Accordingly, a significant increase in DIP has already been observed over recent decades (Figure 5). If the TPM is to be further reduced below the lower limit of the threshold (e.g. 0.2 g/L), we predict that the DIP in Yellow River will be further increased. It is important to note that the Yellow River TPM differs greatly in different seasons and under different hydraulic conditions. The modeling results suggest that the natural flow of suspended particles in Yellow River should not be further reduced by anthropogenic activities, or else, water quality problems (e.g. eutrophication) may irreversibly occur in this large ecological system. For other rivers (e.g. Nile) where suspended matter is highly reactive to P (high k values), the threshold can be lower than the 0.2~1 g/L.

Global environmental change is altering the flux and nature of TPM in rivers in various ways, which will alter the terrestrial input of P to the ocean and the modeling of global P cycle. Soil erosion increases the flux of chemically weathered particles into rivers while climate change can alter the chemical and physical weathering rates. Within many rivers dams are removing particles from the water column. All these processes together alter the ability of particles in the river to buffer the concentration of bioavailable P. The modeling of P carried out in this study represents a method to study this important biogeochemical cycle elsewhere.

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Supporting Information

Water quality parameters (Table S1), Phosphorus speciation in sediment samples (Table S2), and Freundlich crossover-type adsorption isotherms and sediment EPC_0 (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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