

## Effects of titania nanoparticles on phosphorus fractions and its release in resuspended sediments under UV irradiation

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### ABSTRACT

Little is known about the effects of nano-TiO<sub>2</sub> on the transformation and transport of phosphorus (P) in resuspended sediments. Chemical sequential extraction was used to investigate P fractions and its release in resuspended sediments under the influence of nano-TiO<sub>2</sub> and UV irradiation. The results showed that the contents of sediment P in all fractions decreased with increasing nano-TiO<sub>2</sub> concentration in UV irradiation, while increased in the dark controls. Furthermore, P release from all fractions was greater in UV irradiation than in the controls. Elevated concentrations (10–50 mg L<sup>-1</sup>) of nano-TiO<sub>2</sub> in UV irradiation significantly facilitated the release of P from organic and Fe oxide fractions, possibly resulting from the partial photo-degradation of organic matter and photochemical transformation of Fe oxides. Apparently, nano-TiO<sub>2</sub> in UV irradiation did not immobilize the loosely sorbed P and reductant soluble P release from the resuspended sediments, possible because (1) some of P released from those fractions were refurbished by the P released from OM; (2) photocatalysis of nano-TiO<sub>2</sub> reduced binding capacity of the resuspended sediments. Our results suggest that the photocatalysis of nano-TiO<sub>2</sub> may offer the potential to regulate the transformation and transport of sediment P in the aquatic environment.

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### 1. Introduction

Titania nanoparticles (nano-TiO<sub>2</sub>) are widely used for applications such as pigments, coatings, sunscreen cosmetic additives, and increasingly for the photocatalytic degradation of various pollutants in water, air and soil media [1–5]. It is generally assumed that the extensive usage of nano-TiO<sub>2</sub> around the world introduces increasing amount of nano-TiO<sub>2</sub> into the environment, and this will consequently pose potential risk to the ecosystem [6–8]. Recent studies [8,9] demonstrated that some nanoparticles including nano-TiO<sub>2</sub> actually end up in the aquatic environment with significant quantity, suggesting the potential threat of nano-TiO<sub>2</sub> to such environment. Therefore, it is crucial to understand the behavior and effects of nano-TiO<sub>2</sub> in the aquatic environment.

Luckily, the knowledge on the ecotoxicology of nano-TiO<sub>2</sub> in aquatic environment has been increasing almost exponentially [1,7,10,11]. For example, Lovern and Klaper [12] first reported the effect of nano-TiO<sub>2</sub> on an environmental sentinel organism, and claimed that the lethal concentration of nano-TiO<sub>2</sub> was only 10 ppm for *Daphnia magna* following 48-h aqueous exposure. Sun et al. [13,14] showed that when exposed to As(V)-contaminated water in the presence of nano-TiO<sub>2</sub>, carp accumulated consid-

erably more As than in the absence of nano-TiO<sub>2</sub>, and more importantly most of aqueous As(III) was oxidized to As(V) in the presence of nano-TiO<sub>2</sub> under sunlight. Admas et al. [15] found that nano-TiO<sub>2</sub> had a toxic effect on bacteria, and light was a significant factor for the increasing toxicity of nano-TiO<sub>2</sub>. Furthermore, nanoparticles have a large surface area, crystalline structure and great reactivity [16,17] and they may affect the mobilization of toxic and/or harmful chemicals in the environment. To date, most researches focused on ecotoxicology of nanoparticles in the aquatic environment. It is still unclear how nano-TiO<sub>2</sub> influences on the transformation, transport and fate of concurrent contaminants.

Sediment phosphorus (P) release is one of the greatest concerns because it can contribute significantly to the pool of bioavailable P in lake, which must be controlled to avoid eutrophication [18–21]. The transformation, fate and transport of sediment phosphorus are significantly influenced by sediment organic matter (OM) [22–24]. Photo-induced degradation of sediment OM during resuspension can occur under newly exposed to light irradiation [25,26]. Nano-TiO<sub>2</sub> are photosensitive, and produce reactive oxygen species (ROS) in the presence of light [27,28]. They can efficiently suspend in soil solution [4]. Therefore, nano-TiO<sub>2</sub> may facilitate the photolysis of OM under light irradiation once they enter the aquatic environment, and interact with resuspended sediments. Evidently, photo-degradation of sediment OM can significantly impact the behavior of sediment phosphorus, whereas the high adsorption capacity of nano-TiO<sub>2</sub> [29–31] may possibly retard the release of

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sediment phosphorus during resuspension. Little is known about the effects of nano-TiO<sub>2</sub> on the transformation and transport of phosphorus in resuspended sediments. Therefore, it is important to determine how and to what extent the emerging nano-TiO<sub>2</sub> may influence the transformation, fate and transport of sediment phosphorus.

The objectives of this study were to explore the effects of nano-TiO<sub>2</sub> on: (1) sediment P fractions, (2) P release and its release fractions, and (3) potential mechanisms of P release in resuspended sediment in the presence and absence of UV irradiation. The information from this study would better clarify the potential of nano-TiO<sub>2</sub> and UV irradiation on the behavior of phosphorus of resuspended sediments.

## 2. Materials and methods

### 2.1. Materials

Nano-TiO<sub>2</sub> was purchased from Gaosida Nanomaterial Company (Jilin Province, China) with an anatase phase purity of 99.9%, a specific surface area of 32.5 m<sup>2</sup> g<sup>-1</sup> and an average particle size of 35 nm. Ultrapure water was used throughout the experiment. All other chemical reagents were of analytical-reagent grade. Laboratory equipments and containers were dipped in 25% (v/v) HNO<sub>3</sub> solution for at least 12 h, and rinsed with ultrapure water prior to each use. All equipment used in the experiments was sterilized at 121 °C for 0.5 h.

Other instruments and equipment used in this study included UV-vis spectrophotometer (Shimadzu, Japan), TOC analyzer (Shimadzu, Japan), atomic absorption spectrophotometer (AAS, Thermo, U.S.A.), 320-S pH meter (Mettler-Toledo Delta), high-pressure mercury lamp (160 W, Philips), orbital shaker with constant temperature (Zhicheng, China) and Milli-Q Advantage A10 (Millipore, U.S.A.) ultrapure water purification system.

### 2.2. Sediment sampling and analysis

Sediments were collected in December 2008 from the estuarine of Jiulongjiang River in Fujian province, Southern China (24°27'57.13"N, 117°48'31.70"E) using grabs. Sediment samples were taken to the laboratory in sealed plastic bags in iceboxes, freeze-dried, sieved through 100-mesh sieve, and stored for further experiments. Triplicate sediment sample were used to analyze selected physicochemical properties, including pH, total phosphorus (TP), total Fe and organic carbon (OC). Sediment pH was measured in soil-water suspension (soil:water = 1:5, w/v). TP was determined by the vanadomolybdo-phosphoric acid colorimetric method after acid digestion [32]. Total Fe was determined by AAS after HF-HNO<sub>3</sub>-HClO<sub>4</sub> digestion, and organic carbon was determined using the potassium dichromate method [33].

### 2.3. Nano-TiO<sub>2</sub> experiments with UV irradiation

A nano-TiO<sub>2</sub> stock solution (50 mg L<sup>-1</sup>) was prepared in a Erlenmeyer flask using ultrapure water, and sonicated in a Sonicleaner bath (Lucas Dawe Ultrasonics) for 5 h. Dispersion in stock solution was verified using UV-vis methods [34]. Recent life cycle predictions and investigations on nano-TiO<sub>2</sub> in the environment indicated that the concentrations of nano-TiO<sub>2</sub> were 0.7–16 μg L<sup>-1</sup> in the effluent of wastewater treatment plants [9,35], 0.6 mg L<sup>-1</sup> in the runoff of the new façade [8], and 0.1–3 mg Ti L<sup>-1</sup> in raw sewage [35]. The concentration of nano-TiO<sub>2</sub> in the environment may increase over the time because nano-TiO<sub>2</sub> has been used for decades and would be widely used in the future [5]. Therefore, five nano-TiO<sub>2</sub> concentrations (0, 5, 10, 20, and 50 mg L<sup>-1</sup>) were selected to further experiments, which were diluted from the stock solution of

nano-TiO<sub>2</sub>. These nano-TiO<sub>2</sub> concentrations are either similar to or higher than its possible concentrations in the environment.

To eliminate the influence of microorganisms, sieved sediments were first sterilized at 121 °C and 117 kPa for 1.5 h. Then 5 g sterilized sediments were added into series of 1000-ml Pyrex reagent bottles. Nano-TiO<sub>2</sub> solutions (1000 ml each) of different concentrations were carefully added into the bottles with little disturbance of the sediment samples. The concentration of sediment suspensions was 5 g L<sup>-1</sup>, which was relevant to disturbed environments [25].

Similar to Suntest CPS<sup>+</sup> or XLS<sup>+</sup> [26], an orbital shaker was used to carry out the UV irradiation experiment, in which a 160 W high-pressure mercury lamp (>300 nm of emission spectrum, 2850 lm of luminous flux) was positioned at the level of the bottles. The bottles were placed cylindrically around the lamp. All the bottles underwent UV irradiation for 2 d at a rate of 12 h d<sup>-1</sup>, while shaking at 100 rpm in an orbital shaker at 20 ± 1 °C. The control bottles were sealed using Al foil, and kept in the dark (without light irradiation). The control bottles were labeled as Dk-0, Dk-5, Dk-10, Dk-20 and Dk-50 to represent the various nano-TiO<sub>2</sub> concentrations, while the bottles with UV irradiation were labeled as UV-0, UV-5, UV-10, UV-20, and UV-50, respectively. All treatments were done in triplicate.

At the end of the irradiation, the light-exposed suspensions and their controls were filtered separately through 0.45 μm GF/C filter membranes, and the filtrates were used for the analyses of dissolved organic carbon (DOC) [25], total dissolved Fe (TDF), and ferrous iron [Fe(II)] [36]. The content of Fe(III) was calculated by subtracting Fe(II) from total dissolved Fe. The differences of contents of DOC, TDF, and Fe(III) in the suspensions before and after the resuspension were attributed to the release from the sediments during resuspension. Sediment samples were also freeze-dried to determine P fractions in the sediments and the P release from the sediments. The differences of P concentration in various fractions in the sediments before and after UV irradiation were also considered to be P released from the sediments due to the irradiation.

### 2.4. Sediment P fractions

The concentrations of P in various inorganic fractions (IP) were determined using a sequential extraction scheme for lake sediments [37], which used 1 M NH<sub>4</sub>Cl, 0.11 M NaHCO<sub>3</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, 1 M NaOH, and 0.5 M HCl to respectively extract loosely sorbed P (NH<sub>4</sub>Cl-P), reductant soluble P (BD-P), metal oxide bound P (NaOH-P), and calcium bound P (HCl-P) fractions from sediments. The extracts were first centrifuged, and the supernatants were filtered through a 0.45 μm GF/C filter membrane. The P concentrations in the solutions were determined by molybdenum-blue/ascorbic acid method [36]. TP was determined by the vanadomolybdo-phosphoric acid colorimetric method after acid digestion [32]. The organic P (Org-P) was calculated by subtracting IP from TP.

### 2.5. Statistical analysis

The data reported were the means of triplicates, of which the standard error deviation was within 6%. The normality assumption of Pearson correlation analysis was performed using one sample Kolmogorov-Smirnov test. Duncan's post hoc test was employed to determine the differences observed of sediment P fractions, the released amounts of P fractions, TP. The comparison was also made for DOC and total dissolved Fe and Fe(III) from resuspended sediments among different treatments. All statistical analyses were conducted at a significance level of 0.05.

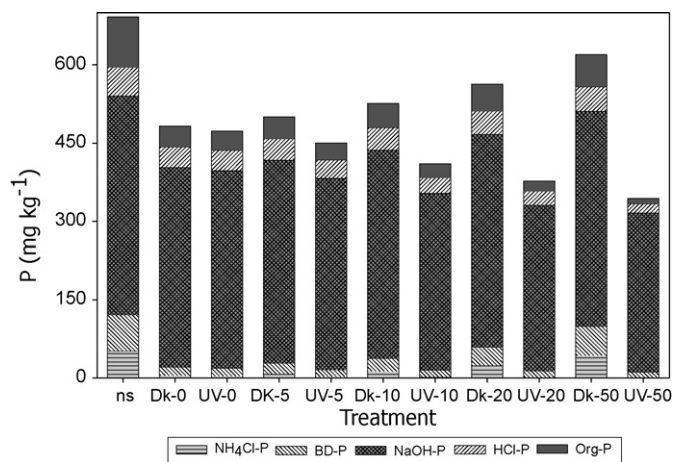


Fig. 1. P fractions in sediments with different treatments (ns: native sediment).

### 3. Results

#### 3.1. Sediment characteristics

The pH, OC, Total Fe and TP of the native sediments were 6.46, 33.25 g kg<sup>-1</sup>, 66.42 g kg<sup>-1</sup>, 691.95 mg kg<sup>-1</sup>, respectively. The contents of NaOH-P, Org-P, BD-P, HCl-P and NH<sub>4</sub>Cl-P were 419.04, 97.29, 69.50, 54.99, 51.93 mg kg<sup>-1</sup>, respectively (Fig. 1), indicating a decreasing order of NaOH-P > Org-P > BD-P > HCl-P > NH<sub>4</sub>Cl-P among the P fractions. It can be concluded that P in the native sediment was primarily bound to Fe and Al oxides minerals and bound to OM [38].

#### 3.2. Sediment P fractions in different treatments

Significant differences of sediment P fractions were observed between the UV irradiation and their companion controls (dark). In the dark controls, the contents of different P fractions increased significantly with increasing nano-TiO<sub>2</sub> concentrations, whereas the contents in UV irradiation decreased significantly with increasing nano-TiO<sub>2</sub> concentration (Fig. 1). Noticeably, the different among sediment P fractions were significantly greater in dark controls than in UV irradiation (Fig. 1). Generally, the relative contributions of NH<sub>4</sub>Cl-P, BD-P, HCl-P and Org-P were significantly greater in dark controls than in UV irradiation, while that of NaOH-P was lower

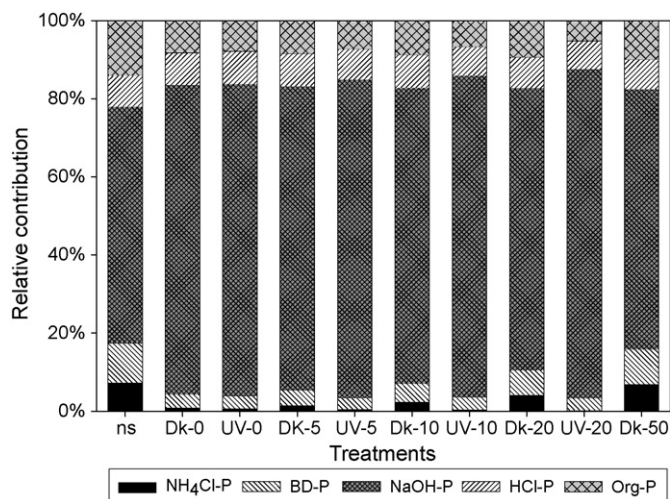


Fig. 2. The relative contribution of different P fractions to sediment TP with different treatments (ns: native sediment).

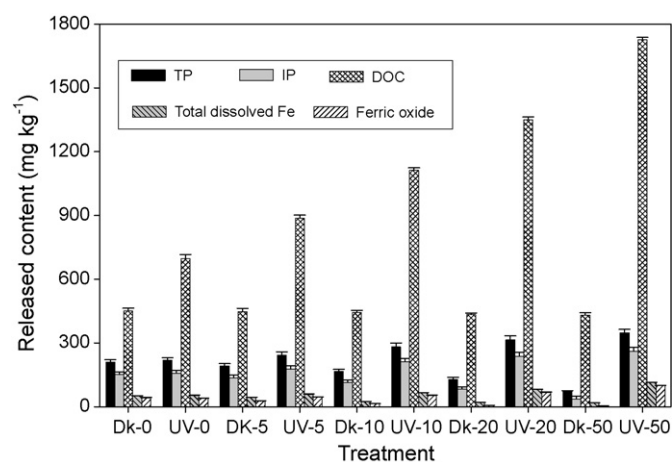


Fig. 3. Release of TP, IP, DOC, total dissolved Fe and Fe(III) from resuspended sediments with different treatments.

in dark controls than in UV irradiation (Fig. 2). The order of the P fractions was: NaOH-P > Org-P > HCl-P > BD-P > NH<sub>4</sub>Cl-P for dark controls, as compared to the order of NaOH-P > HCl-P > Org-P > BD-P > NH<sub>4</sub>Cl-P for UV irradiation. Interestingly, the sediment P in dark controls was primarily bound to Fe and Al oxides minerals and OM, while that in UV irradiation primarily bound to Fe and Al oxides minerals and carbonates.

#### 3.3. P release related to sediment properties

##### 3.3.1. DOC, Fe and P release

There were significantly greater contents of TP, IP, DOC, and TDF and Fe(III) released from sediments that were treated with UV irradiation than dark controls (Fig. 3). In dark controls, the released amounts of TP (71.96–209.27 mg kg<sup>-1</sup>), IP (36.39–151.83 mg kg<sup>-1</sup>), DOC (431.58–451.35 mg kg<sup>-1</sup>), TDF (18.21–50.69 mg kg<sup>-1</sup>) and Fe(III) (4.51–42.09 mg kg<sup>-1</sup>) decreased with increasing nano-TiO<sub>2</sub> concentrations, while the contents of TP (218.25–347.25 mg kg<sup>-1</sup>), IP (158.22–261.05 mg kg<sup>-1</sup>), DOC (697.00–1725.70 mg kg<sup>-1</sup>), TDF (52.47–113.61 mg kg<sup>-1</sup>) and Fe(III) (39.17–99.15 mg kg<sup>-1</sup>) in UV irradiation increased with increasing nano-TiO<sub>2</sub> concentrations. Among the sediments studied, the release percentage ranged from 49.76–89.60% for TP, 50.57–75.35% for IP, 1.30–5.19% for DOC,

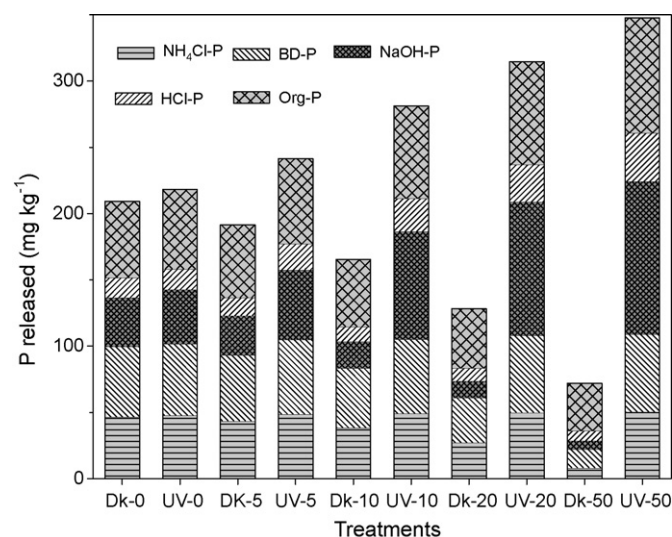


Fig. 4. P released from different P fractions of resuspended sediments with different treatments.

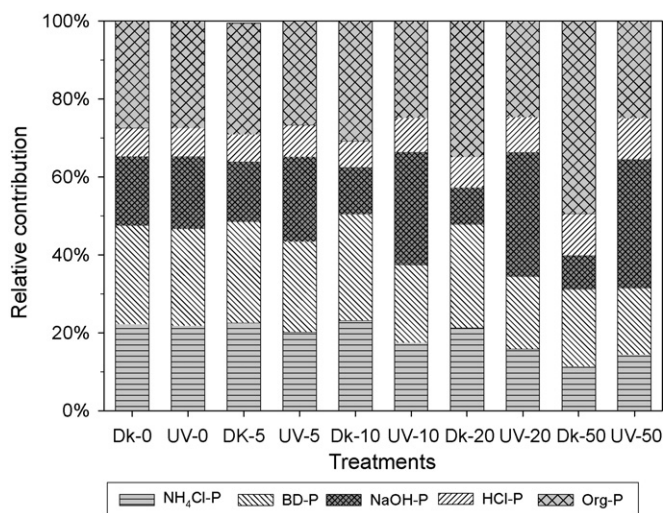


Fig. 5. Percentages of the P released from different fractions to its TP release in different treated sediments.

Table 1

Correlation between released P and released amount of DOC, total dissolved Fe, and Fe(III) in sediments with different treatments ( $\text{mg kg}^{-1}$ ,  $n = 10$ ).

	NH <sub>4</sub> Cl-P	BD-P	NaOH-P	HCl-P	Org-P	TP
DOC	0.871**	0.839**	0.962**	0.967**	0.996**	0.987**
Total dissolved Fe	0.587	0.607	0.749*	0.63	0.761*	0.751*
Fe(III)	0.604	0.622	0.732*	0.542	0.749*	0.744*

\* Indicates  $P$  values < 0.05.

\*\* Indicates  $P$  values < 0.01.

and 0.03–0.17% for total dissolved Fe. This indicated that IP was the greatest contributor to TP release from resuspended sediment regardless of UV irradiation treatment.

For dark controls, the order of P release was Org-P > BD-P > NH<sub>4</sub>Cl-P > NaOH > HCl-P (Fig. 4), and fractions Org-P, BD-P, NH<sub>4</sub>Cl-P and NaOH-P demonstrated relative greater percentages in P release to its TP release (Fig. 5), although the P release in all fractions was significantly decreased with increasing nano-TiO<sub>2</sub> concentrations (Fig. 4). For UV irradiation, the P releases from all the fractions were notably greater than those of dark controls (Figs. 4 and 5). Fractions Org-P and NaOH-P showed significantly increases with increasing nano-TiO<sub>2</sub> concentrations, while NH<sub>4</sub>Cl-P, BD-P and HCl-P did not (Figs. 4 and 5). Interestingly, NaOH-P and Org-P accelerated the P release as nano-TiO<sub>2</sub> concentration was elevated to 10–50 mg L<sup>-1</sup> (Figs. 4 and 5) due to Org-P and NaOH-P remained as the major contributors to TP release. This phenomenon can also be confirmed from the results in Fig. 6.

### 3.3.2. P release related to sediment properties

The released P of all fractions was positively correlated to DOC release (Table 1). In addition, both TDF and Fe(III) were positively correlated to P release from NaOH-P and Org-P as well as TP release, but there was no significant correlation to NH<sub>4</sub>Cl-P, BD-P, and HCl-P fractions (Table 1).

## 4. Discussion

### 4.1. Changes of P fractions and release from resuspended sediments

No significant change in pH, TDF, and DOC was observed in the dark controls in this study. Phosphorus fractions in the sediments largely depended on pH [39], Eh, OM [40], and the amounts of Fe, Al

and carbonates [41,42]. This could explain why there was no significant difference in the dominant fractions between the native sediments and the sediments in dark controls. Our results showed that the sediment P in dark controls was primarily bound to Fe and Al oxides minerals and OM, suggesting that nano-TiO<sub>2</sub> could not facilitate the solubilization of P fractions in the resuspended sediments in dark controls. Nano-TiO<sub>2</sub> was reported to possess high adsorption capacity due to its ultra-fine particle size and high surface area [30,31]. It is possible that P released from the fractions was re-adsorbed by nano-TiO<sub>2</sub>. This might be the reason why significant decrease in P was observed in the fractions along with increasing nano-TiO<sub>2</sub> concentrations in dark controls. Based on the explanation, it could be concluded that nano-TiO<sub>2</sub> could retard P release by redistributing P from sediment fractions to the surfaces of nano-TiO<sub>2</sub> in the absence of light irradiation.

The sediment P in the UV irradiation, however, was primarily bound to Fe and Al oxides minerals and carbonates. That is, HCl-P, instead of Org-P, was one of the dominant P fractions of sediments in UV irradiation. This might be because nano-TiO<sub>2</sub> could facilitate the transformation of sediment Org-P during resuspension in UV irradiation, and this explanation was supported by the positive correlations between Org-P release and the release of DOC, TDF and Fe(III).

In the dark controls, Org-P appeared to be the greatest contributor to the TP release, followed by BD-P and NH<sub>4</sub>Cl-P. The possible reasons were: (1) resuspended sediments directly released dissolved Org-P and BD-P and NH<sub>4</sub>Cl-P into water; (2) indirectly oxidative released Org-P when exposed oxygen and BD-P release once oxygen was depleted [40,41,43]. In a similar study, Kalnejais [44] concluded that sediment resuspension enhanced contaminants release not only due to the exposure to oxygen in bottom water, but also because dissolved species were released directly to water.

Noticeably, the P release from all fractions of resuspended sediments was significantly greater in UV irradiation than the dark controls, indicating that UV irradiation significantly enhanced P release from resuspended sediments. Both Org-P and NaOH-P were the major contributors of the released P in UV irradiation at elevated nano-TiO<sub>2</sub> concentrations (10–50 mg L<sup>-1</sup>), indicating that the transformation of NaOH-P and Org-P could effectively enhanced by nano-TiO<sub>2</sub> at an elevated nano-TiO<sub>2</sub> concentration (>10 mg L<sup>-1</sup>), but not readily without light assistance or at the low nano-TiO<sub>2</sub> concentration (0 and 5 mg L<sup>-1</sup>). These conclusions were supported by the positive correlation between DOC, total dissolved Fe and Fe(III) release and NaOH-P and Org-P release.

In UV irradiation, the P release from Org-P and NaOH-P significantly increased with increasing nano-TiO<sub>2</sub> concentration, while NH<sub>4</sub>Cl-P, BD-P and HCl-P remained relatively stable, indicating that nano-TiO<sub>2</sub> with UV irradiation could only effectively affect the mobility for Org-P and NaOH-P in the sediment resuspension. Furthermore, NH<sub>4</sub>Cl-P and BD-P release demonstrated a gentle increase with increasing nano-TiO<sub>2</sub> concentrations in UV irradiation. However, the same fractions in the dark controls demonstrated a decrease trend with increasing nano-TiO<sub>2</sub> concentration. This means that nano-TiO<sub>2</sub> in UV irradiation did not immobilize the loosely sorbed P and reductant soluble P release from the resuspended sediments. One of the possible reasons might be that some P released from Org-P due to UV irradiation had refurnished the loss of P due to the influence of nano-TiO<sub>2</sub>. Another possible reason might be that the photocatalysis of nano-TiO<sub>2</sub> resulted in decreasing binding capacity of sediments during resuspension due to the losses of Fe and OM [19,45,46].

The native sediments with TP of 691.95 mg kg<sup>-1</sup> could be classified as moderate pollution ( $500 \text{ mg kg}^{-1} < \text{TP} < 1300 \text{ mg kg}^{-1}$ ) [40]. The results from this study indicated that the transformation and transport of sediment P might be facilitated by the photocatalysis

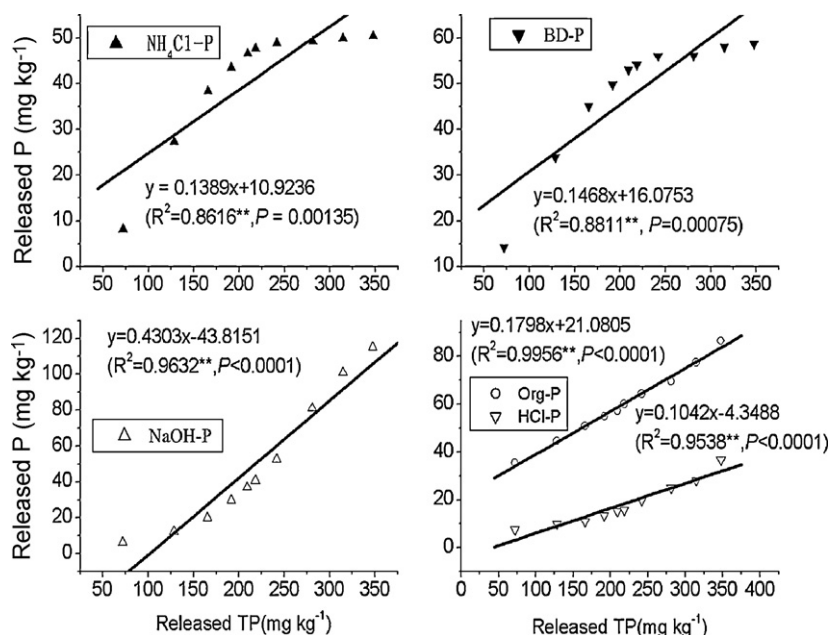


Fig. 6. Correlation between P released from different P fractions and TP concentrations in different treated sediments ( $n = 10$ ).

of nano-TiO<sub>2</sub>, resulting in potential risks of eutrophication to the aquatic environment when the native sediments were suspended.

#### 4.2. Potential mechanisms of P fractions transformation and release

The release of DOC from the resuspended sediments in this study was over the range of 18.02–900.75 mg kg<sup>-1</sup> which was investigated in previous study [25]. The differences of DOC release between the dark controls and UV irradiation were at the range of 245.65–1294.12 mg kg<sup>-1</sup>, which significantly increased with increasing nano-TiO<sub>2</sub> concentration. This indicated that OM degradation was significantly enhanced by high amount of nano-TiO<sub>2</sub> in the aquatic environment [31]. Nano-TiO<sub>2</sub> was photosensitive, and could produce reactive oxygen species (ROS) in the presence of light [27,28]. The ROS could efficiently suspend in soil suspensions [4,47], making OM more accessible for oxidation [48–50]. Most importantly, ROS were oxidant that could directly oxidize OM in resuspended sediments. Therefore, OM degradation was enhanced effectively, resulting in elevated transformation and transport of sediment P [22,23]. This hypothesis was partially supported by the positive correlation between P fractions and DOC release (Table 1).

Photochemical oxidation and reduction of Fe often accompanies with oxidative degradation of organic complexes, including OM with low-molecular-weight and humic substances [45,46,51]. Therefore, organically bound Fe can be photochemically liberated by solar radiation including UV irradiation [42,52]. Again, Fe(III)-hydroxy complexes can undergo photochemical reduction to Fe(II) under UV irradiation in aqueous solutions [53]. Considering that Ferguson et al. [54] and Sun et al. [14] reported the oxidation of As (III) to As (V) by nano-TiO<sub>2</sub> photocatalysis, nano-TiO<sub>2</sub> might also be capable of facilitating the oxidation of Fe(II) to Fe(III). As a result, the rapid circles of Fe oxidation and reduction may strongly affect the aggregation and sedimentation of Fe oxides, oxyhydroxides, and hydroxides [55]. Consequently, the photochemical transformation of Fe and photo-degradation of OM may enhance the release of NaOH-P and Org-P from the resuspended sediments through liberating P adsorbed to iron oxides, oxyhydroxides, hydroxides,

and OM [19,41]. This hypothesis can be supported by the positive correlation between P released from NaOH-P, Org-P, TP and the concentrations of DOC, TDF, Fe(III) release (Table 1).

There is no doubt that the results on the chemical mechanism of P release and P fractions transformation in resuspended sediments were very preliminary. Other mechanisms, such as changes in molecular conformation or functionality of OM, the distribution of nano-TiO<sub>2</sub> in sediments, and P sorption on nano-TiO<sub>2</sub>, may fundamentally affect the fate of P in the sediments. In addition, organisms (e.g. algae, bacterial, virus) in sediment–water interface may also play critical roles in the P fraction transformation and P release [40,50,55]. It is also unclear that how and to what extent the emerging nano-TiO<sub>2</sub> interacts with organisms and influences the transfer, fate and transport of sediment P or any other components. Further investigations are necessary in the future.

#### 5. Conclusions

Nano-TiO<sub>2</sub> in dark controls retarded the release of different P fractions possibly due to its high adsorption capacity. Organic P was the greatest contributor to TP release in the resuspended sediments in the dark controls, followed by BD-P and NH<sub>4</sub>Cl-P, probably because of direct dissolution of Org-P, BD-P and NH<sub>4</sub>Cl-P and the indirect release of BD-P under oxygen depletion.

Nano-TiO<sub>2</sub> with UV irradiation could effectively enhance the transport of P from sediment fractions into water probably due to the photocatalysis of nano-TiO<sub>2</sub>. Both Org-P and NaOH-P were the major contributors to the TP release from the resuspended sediments under UV irradiation and at elevated nano-TiO<sub>2</sub> concentrations (10, 20 and 50 mg L<sup>-1</sup>), resulting from the partial photo-degradation of OM and photochemical transformation of Fe. The transformation of NaOH-P and Org-P of the sediments during resuspension was significantly facilitated by high concentration of nano-TiO<sub>2</sub>, but not readily without light or at a low concentration of nano-TiO<sub>2</sub>. Nano-TiO<sub>2</sub> in UV irradiation did not immobilize NH<sub>4</sub>Cl-P and BD-P release from the resuspended sediments, possible because (1) some of P released from those fractions were refurbished by the P released from OM; (2) photocatalysis of nano-TiO<sub>2</sub> reduced binding capacity of the resuspended sediments. These

results suggest that the photocatalysis of nano-TiO<sub>2</sub> may offer the potential to regulate the transformation and transport of sediment P in the aquatic environment, and thereby to influence the process of eutrophication.

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