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# Redox-dependent effects of phosphate on arsenic speciation in paddy soils<sup>☆</sup>

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## ABSTRACT

Evaluating speciation of arsenic (As) is essential to assess its risk in paddy soils. In this study, effects of phosphate on speciation of As in six paddy soils differing in redox status were studied over a range of pH (pH 3–9) and different background calcium (Ca) levels by batch adsorption experiments and speciation modeling. Contrasting effects of phosphate on As speciation were observed in suboxic and anoxic soils. Under suboxic conditions, phosphate inhibited Fe and As reduction probably due to stabilization of Fe-(hydr)oxides, but increased soluble As(V) concentration as a result of competitive adsorption between As(V) and phosphate. In anoxic soils, phosphate stimulated Fe and As reduction and caused increases of As(III) in soil solution under both acidic and neutral/alkaline pH. The LCD (Ligand and Charge Distribution) and NOM-CD (Natural Organic Matter-Charge Distribution) model can describe effects of pH, calcium and phosphate on As speciation in these paddy soils. The results suggest that phosphate fertilization may decrease (at low pH) or increase (at neutral/alkaline pH) As mobility in paddy soils under (sub)oxic conditions, but under anoxic conditions and in phosphorus deficient soils phosphate fertilization may strongly mobilize As by promoting microbial activities.

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## 1. Introduction

Potential risk associated with arsenic (As) contamination of soil and water has led to great public concerns in many places over the world (Berg et al., 2001; Nordstrom, 2002; Rodriguez-Lado et al., 2013; Smedley and Kinniburgh, 2002). In paddy soils, which is often under flooded condition, both the solubility and bioavailability of As are high (Kumarathilaka et al., 2018; Takahashi et al., 2004). For this reason, the risk of As in paddy soils is in general higher than in dryland agriculture soils. Good understanding of As behavior in paddy soils is crucial for risk assessment and soil remediation in polluted areas so as to reduce effects of As on food safety and human health.

Reduction-oxidation and adsorption-desorption are two processes important in controlling the speciation of As in soils. Arsenate (As(V)) normally predominates in well oxidized soils (as

H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup>), whereas arsenite (As(III)) becomes more important in slightly reduced soils (as H<sub>3</sub>AsO<sub>3</sub> and H<sub>2</sub>AsO<sub>3</sub>) (Bissen and Frimmel, 2003). Because As(III) adsorbs much weaker to soil minerals than As(V), it is much more soluble and therefore more mobile and more toxic (Campbell and Nordstrom, 2014; Dias et al., 2009). When the soils become reduced, microorganisms affect the fate of As in soils. Dissimilatory As(V)-reducing bacteria can directly reduce As(V) into As(III) resulting in the release of As(III) into aqueous phase (Yamamura et al., 2008). On the other hand, iron (Fe) in soils can act as an important electron acceptor during microbial respiration, leading to the reduction and dissolution of Fe-(hydr)oxides and the release of adsorbed ions (Ohtsuka et al., 2013; Yu et al., 2016). Since Fe-(hydr)oxide is a major sorbent for As in paddy soils, the Fe(III) reduction might reduce the overall As adsorption capacity of soils (Kumarathilaka et al., 2018; Yamaguchi et al., 2011). Both As(V) reduction and Fe-(hydr)oxide dissolution can lead to an increase of As solubility and bioavailability, but the relative contribution of these two mechanisms is difficult to determine.

Paddy soils are commonly fertilized with phosphate fertilizers. The geochemical behavior of phosphate (PO<sub>4</sub><sup>3-</sup>) and arsenate (AsO<sub>4</sub><sup>3-</sup>) is rather similar and both can be adsorbed to Fe- and Al-

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(hydr)oxides, which are important constituents of soils and sediments. The affinity of As(V) for Fe-(hydr)oxides and phyllosilicates rich in Fe is comparable to that of  $\text{PO}_4^{3-}$ , but a higher affinity was found for  $\text{PO}_4^{3-}$  adsorption on Al-(hydr)oxides, allophane and kaolinite (Violante and Pigna, 2002). The presence of phosphate shows multi-folded influences on As speciation. On one hand,  $\text{PO}_4^{3-}$  can greatly suppress the adsorption of As to oxides and to soils (Deng et al., 2018; Rivas-Perez et al., 2015; Smith et al., 2002). On the other hand, phosphorus is an essential nutrient for both crops and microorganisms. In principle, phosphate fertilizers will stimulate microbial activity in phosphorus deficient soils, thus promoting the redox reactions. However, conflicting results have been observed in literatures. Some studies showed that phosphate can increase the reduction of Fe-(hydr)oxides (Fredrickson et al., 1998; Ginn et al., 2017; Kukkadapu et al., 2004; O'Loughlin et al., 2013) and As(V) (Zhang et al., 2017), whereas in other studies it was found that phosphate had insignificant influence on or even inhibited the reduction of Fe-(hydr)oxides (Borch et al., 2007; Zachara et al., 1998) and As(V) (Huang, 2018; Slaughter et al., 2012). In many studies, it has been observed that phosphate can increase the availability of As in paddy soils (Ji et al., 2019; Jiang et al., 2017; Jiang et al., 2014; Lee et al., 2016; Signes-Pastor et al., 2007), but the dominant mechanisms are not really clear.

Complexity of the soil systems and interplay among different factors, e.g. redox potential (Eh), pH, presence of other ions and organic ligands, are obstacles in obtaining clear and quantitative understanding of phosphate effects on As adsorption and reduction. As discussed above, behavior of As is strongly influenced by Eh. In addition, pH is one of the most important soil properties influencing As adsorption as well as reduction in natural soils. It was found that the reduction of As(V) to more mobile As(III) was faster in soils with low pH (Patrick H. Masscheleyn et al., 1991). In a simple electrolyte background (e.g. NaCl), maximum As(III) adsorption to goethite occurs around pH 6–9, whereas maximum As(V) adsorption takes place in the pH range of 4–5 (Deng et al., 2018; Stachowicz et al., 2006). In a more complex system such as in soils, maximum As(V) adsorption moved to pH 6–8 as a result of interaction with  $\text{Ca}^{2+}$  on the surface of minerals (Cui and Weng, 2013). Calcium (Ca) is an important major cation in environmental systems, which can affect the behavior of oxyanions and vice versa (Stumm, 1992). It has been revealed that the presence of Ca increased the adsorption of  $\text{PO}_4^{3-}$  and As(V) by minerals, whereas effects of Ca on the adsorption of As(III) were less significant compared to that of As(V) (Kanematsu et al., 2013; Stachowicz et al., 2008).

In this work, effects of phosphate on the reduction and adsorption of As in six paddy soils under different Eh, pH and Ca levels were studied. The mechanisms of these effects were quantitatively illustrated using sophisticated surface complexation

model, the Ligand and Charge Distribution (LCD) model (Weng et al., 2011) and the Natural Organic Matter-Charge Distribution (NOM-CD) model (Hiemstra et al., 2013). The purposes of this study are: (i) to investigate the effects of phosphate on As speciation in paddy soils under different Eh over a wide range of pH and Ca level; and (ii) using the LCD and NOM-CD model to better understand the mechanisms of changes in As speciation under variations of the above factors.

## 2. Material and methods

### 2.1. Soil samples

Six soil samples were collected from the top soils (0–20 cm) of paddy fields from Liaoning (LN), Jiangsu (JS), Guangdong (GD), and Hunan (HN) (three samples) province of China (Tabl 1). The soil samples were dried at room temperature and sieved over 2 mm. Basic properties of the six soils were characterized (Table 1).

### 2.2. Adsorption experiments

Batch adsorption experiments were conducted. For each soil, subsamples of 2.0 g were put into 50 mL polyethylene bottles. A certain amount of ultrapure water (10 mL) was added firstly to the bottles. Depending on the treatment, stock solutions of As(V) ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ), Ca ( $\text{CaCl}_2$ ) and  $\text{PO}_4^{3-}$  ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ ) were added to the soils. Ultrapure water was added to all samples to obtain a final soil-solution ratio (SSR) of 1:10. For each soil, forty-eight soil suspensions were prepared, which were divided into four series: (i) high concentration of Ca (10 mM), (ii) high concentration of Ca (10 mM) with 0.25 mM  $\text{PO}_4^{3-}$ , (iii) low concentration of Ca (2 mM), and (iv) low concentration of Ca (2 mM) with 0.25 mM  $\text{PO}_4^{3-}$ . The high Ca treatment used 10 mM  $\text{CaCl}_2$  as background electrolyte, which approximately simulated the ionic strength of average field conditions of fertilized top soils (van Erp et al., 1998), while the low Ca treatment (2 mM  $\text{CaCl}_2$ ) has an ionic composition similar to pore water (i.e. 2.5 mM) that has been found in the flood plain soils (Schroder et al., 2005). For all the treatments, the final concentration of As(V) added is 0.25 mM. In each series, pH of the twelve subsamples was adjusted with 0.10 or 0.50 M NaOH or HCl to a pH in the range of 3–9. A blank sample (without addition of soil) was also prepared. The soil suspensions were shaken horizontally (50 rpm) at room temperature for 7 days mostly in darkness. Preliminary kinetic experiments indicated that the system is close to equilibrium after 7 days (Fig. S1). During the first 5 days, pH of the soil suspensions was checked every day and readjusted to the target values if necessary. After 7 days shaking, the end pH of the suspension was measured. In each series, the Eh and Fe(II) concentration were measured in the suspensions of a

**Table 1**  
Properties of the soil samples. pH was measured in 0.01 M  $\text{CaCl}_2$  (soil: solution = 1:2.5); Total amount of Fe- and Al-(hydr)oxides was extracted with dithionite-citrate-bicarbonate (DCB) extraction; Amorphous Al- and Fe-(hydr)oxides were extracted with ammonium oxalate extraction;  $f_{\text{Al}}$  was the contribution of Al to the total reactive surface area; Total reactive surface area of soil (SSA) was calculated from the amount of Fe- and Al- (hydr)oxides; Amount of NOM adsorbed was fitted with the LCD ( $\text{NOM}_{\text{ads}}$ ) and NOM-CD ( $\text{FeNOM}_T$ ) model respectively.

Soil	Location	Soil Type	pH $\text{CaCl}_2$	SOC %	Clay %	Total amount of metal (hydr)oxides $\text{mmol kg}^{-1}$			Amorphous metal (hydr)oxides $\text{mmol kg}^{-1}$			$f_{\text{Al}}$	Reactive P, As $\text{mmol kg}^{-1}$		SSA $\text{m}^2 \text{g}^{-1}$	$\text{NOM}_{\text{ads}}$ , $\text{mg m}^{-2}$	$\text{FeNOM}_T$ , $\text{site nm}^{-2}$
						Fe-DCB	Al-DCB	Mn-DCB	Fe-ox	Al-ox	Mn-ox		P-ox	As-ox			
C1	Shenyang, LN	Fluvo-aquic soil	5.6	1.4	9	220	29.4	4.5	165	45.7	5.0	0.21	25.3	0.01	13.9	0.72	0.75
C2	Yixing, JS	Yellow earths	4.7	1.9	10	247	30.8	2.2	156	52.7	3.3	0.25	12.9	0.02	14.1	1.60	1.85
C3	Zhongshan, GD	Latosolic red earth	6.0	0.6	3	342	81.9	1.1	74	42.5	2.0	0.25	6.1	0.02	10.8	1.79	1.85
C4	Xiangtan, HN	Latosols	7.2	2.7	15	351	42.5	2.0	135	36.6	2.8	0.18	8.8	0.04	13.4	1.91	1.90
C5	Huanggu, HN	Latosols	5.3	2.1	12	348	55.5	2.6	104	33.3	3.0	0.18	3.5	0.03	11.6	2.13	2.09
C6	Zhuzhou, HN	Latosols	4.2	2.4	20	116	34.2	0.0	66	45.9	0.0	0.39	7.1	0.04	7.6	1.29	1.40

subsample around pH 4.3 using a redox potentiometer with a Pt electrode (QX6530, Nanjing, China). Then the suspensions were centrifuged at 9,000 rpm for 20 min and filtered through 0.22  $\mu\text{m}$  filters (PES, Membrana), and the filtrates were stored at  $-4^\circ\text{C}$  till further analysis. Selected soil subsamples were immediately stored at  $-80^\circ\text{C}$  for DNA extraction.

For the filtrates, concentrations of dissolved organic carbon (DOC) were measured with a TOC analyzer (Shimadzu, Japan), concentrations of total soluble As, Fe and Al were determined with ICP-OES (VISTA-MPX, Australia), and concentrations of phosphate were measured with the molybdate blue method. Arsenic speciation was analyzed with HPLC-HG-AFS (High Performance Liquid Chromatography Hydride Generation Atomic Fluorescence Spectrometry; PSA, UK) (Ma et al., 2016) within 4 days. The HPLC-HG-AFS results showed that the speciation of As in soil solutions was dominated by inorganic As, and organic As was not detected for all the samples studied. The presence of relatively large amount of Fe in the filtrates in some of the soils makes the As(V) analyzed on HPLC-HG-AFS unreliable especially after adding phosphate (see Supporting Information). Therefore, concentration of As(V) in these soils was derived from the difference between the total As concentration and the As(III) concentration (HPLC-HG-AFS) (Huang et al., 2013). High-throughput sequencing was used to verify the microbial community differences between soil C1-C3 and soil C4-C6 under various conditions. Details are described in Supporting Information.

### 2.3. LCD and NOM-CD modeling

The LCD modeling approach followed is similar to that of Cui and Weng (2013), and the NOM-CD modeling approach is similar to that of Hiemstra et al. (2013). In both the LCD and NOM-CD model, the Charge Distribution and Multi-Site Complexation (CD-MUSIC) model (Hiemstra and Van Riemsdijk, 1999) was used to describe the reactions of adsorbates with soil mineral surfaces. The CD-MUSIC model parameters were adopted from those obtained for goethite (Table S1), except that the  $\log K$  values for As(V) were adjusted (see Results and discussion). Similar to that of Cui and Weng (2013),  $K$  values for the three As(V) surface species were adjusted with the same scaling factor for each soil (Table S2).

The main difference between the LCD and NOM-CD model is in the way they treat natural organic matter (NOM) adsorbed. The LCD model used the Non-Ideal Competitive Adsorption (NICA) model (Kinniburgh et al., 1999) to calculate the speciation and charge of NOM adsorbed. The NOM adsorbed at the mineral surfaces was simulated with fulvic acid (FA) present in the Stern layer (Weng et al., 2008). The carboxylic groups of NOM in the inner-Stern layer could form inner-sphere complexes ( $\equiv\text{FeOOCR}^{-0.5}$ ) with the singly coordinated surface sites ( $\equiv\text{FeOH}^{-0.5}$ ) on goethite. The other carboxylic and phenolic groups on the adsorbed NOM could bind cations, i.e.  $\text{H}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . The reactions between adsorbed NOM ligands and surface sites of minerals, protons and other cations were calculated with the NICA model, of which the model parameters were assumed as the same as for generic FA (G-FA) in solution (Table S3). The adsorbed NOM was evenly distributed between the inner- and outer-Stern layer. In the NOM-CD model, effects of NOM adsorbed on the adsorption of ions are considered by assuming NOM as a virtual component  $\text{HNOM}^{-1}$ , which is equivalent to a molecule containing two carboxylic groups. As proposed by Hiemstra et al. (2013), three surface complexes are formed between the singly coordinated surface sites on goethite ( $\equiv\text{FeOH}^{-0.5}$ ) and  $\text{HNOM}^{-1}$ , i.e. an inner-sphere ( $\equiv\text{FeNOM}$ ), a protonated inner-sphere ( $\equiv\text{FeNOMH}$ ), and an outer-sphere complex ( $\equiv\text{FeOH}_2\text{NOM}$ ). The model parameters of these species were based on those of Hiemstra et al. (2013). The amount of NOM adsorbed

(i.e.  $\text{NOM}_{\text{ads}}$  in the LCD model and  $\equiv\text{FeNOM}_T$  in the NOM-CD model) was optimized for each soil and was kept constant for different treatments of the same soil. The CD-MUSIC, NICA-Donnan, LCD and NOM-CD model parameters used are shown in Tables S1-S4.

For both the LCD and NOM-CD modeling, the first step was to calculate the activities of free ions (i.e.  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ ) in the aqueous solutions using the measured pH, Ca, Fe, Al, P and DOC concentrations considering solution speciation. Formation of possible inorganic complexes in the solution was considered, including (bi)carbonate species assuming equilibrium with  $\text{CO}_2$  in the atmosphere. Adsorption of  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  to dissolved organic matter (DOM) was calculated with the NICA-Donnan model (Kinniburgh et al., 1999) using parameters of G-FA (Hiemstra and van Riemsdijk, 2006; Milne et al., 2003). Concentration of FA in solution was assumed as two times of DOC. The activities of  $\text{Fe}^{3+}$  in the aqueous solutions were controlled by the solubility of Fe-(hydr)oxides ( $\log K_{\text{so}} = -38.8$ ) (Sommers and Lindsay, 1979). Secondly, the calculated free ion activities and measured pH were used as input for calculating the adsorption of  $\text{PO}_4^{3-}$ , As(V) and As(III) in both the LCD and NOM-CD model. The amount of P measured in the ammonium oxalate extraction was used as input for the total reactively adsorbed  $\text{PO}_4^{3-}$ . The amount of As(V) added to the soil was used as model input for total reactive amount of As, because the initial amount of reactive As (in ammonium oxalate extraction) in these soils (0.01–0.04  $\text{mmol kg}^{-1}$ ; Table 1) is much less than the amount of As added (2.5  $\text{mmol kg}^{-1}$ ), is therefore negligible. The total amount of As was kept constant (2.5  $\text{mmol kg}^{-1}$ ), whereas the ratio between As(V) and As(III) was fitted for each subsample since some of As(V) was reduced into As(III) during the experiment. For each soil, the total reactive surface area of metal oxides was estimated according to Weng et al. (2011), i.e. the amount of Fe and Al in the ammonium oxalate and DCB extraction was transformed into the amount of metal oxides using the molar mass of  $\text{Fe}(\text{OH})_3$  (i.e. 107  $\text{g mol}^{-1}$ ). A specific surface area of 600  $\text{m}^2 \text{g}^{-1}$  was assigned to the amorphous (hydr)oxides (i.e. oxalate extractable fraction), whereas a specific surface area of 100  $\text{m}^2 \text{g}^{-1}$  was assigned to the crystalline (hydr)oxides (i.e. the difference between DCB and oxalate extractable fraction). The total reactive surface area of (hydr)oxides in soils was calculated as the sum of the surface areas in these two fractions (Table 1).

The CD-MUSIC, NICA-Donnan and NOM-CD model calculations were carried out using the software ECOSAT (Keizer and Van Riemsdijk, 1998). The LCD model calculations were performed using the computer program ORCHESTRA (Meeussen, 2003).

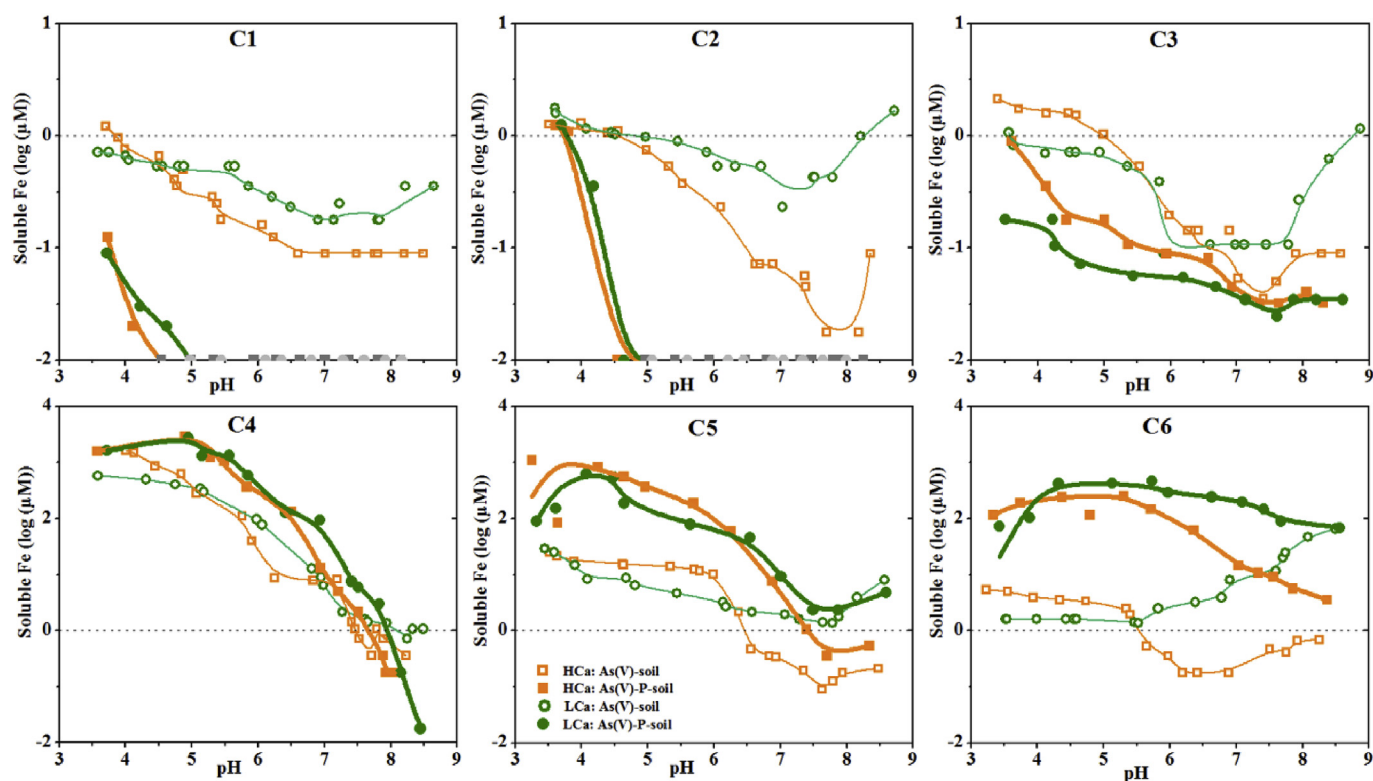
## 3. Results and discussion

### 3.1. Fe

Although all soils were treated in the same way in the batch experiment, different redox potentials were developed. In soil C1-C3, the Eh value measured at  $\sim\text{pH } 4.3$  ranges from 80 to 330 mV, indicating a suboxic environment in these soils during the experiment. The Eh of soil C4-C6 is lower than in soil C1-C3, ranging from  $-200$  to 10 mV at  $\sim\text{pH } 4.3$  (Fig. S2), which indicates a relatively anoxic environment. Because of their differences in Eh as well as in Fe reduction, As speciation and reaction to phosphate addition, the results of soils C1-C3 and C4-C6 were discussed comparatively.

In soil C1-C3, without phosphate added, concentration of Fe in soil solutions ranged from  $<0.01 \mu\text{M}$  to  $2.0 \mu\text{M}$  (Fig. 1). At low pH, the soluble Fe concentrations measured are generally lower than those calculated assuming a solubility of Fe-(hydr)oxides of  $\log K_{\text{so}} = -38.8$  (Fig. S3) (Sommers and Lindsay, 1979). This solubility is at the high end for soil Fe-(hydr)oxides. Therefore, the





**Fig. 1.** Concentration of Fe in solution of soil C1-C3 (above panel) and C4-C6 (below panel). Symbols are measured values; Lines go through most of the data points to guide the eyes. Open symbols: without addition of phosphate; closed symbols: 0.25 mM phosphate was added. Grey colored symbols indicate concentration below the detection limits. HC: 10 mM  $\text{CaCl}_2$ ; LC: 2 mM  $\text{CaCl}_2$ .

results indicate that there was low amount of Fe(II) in the soil solution and Fe-(hydr)oxide reduction was limited. It has been shown that significant Fe-(hydr)oxide reduction takes place at an Eh < 100 mV (Kogel-Knabner et al., 2010). Accordingly, our measurement of soluble Fe speciation at pH ~4.3 showed that in soil C1-C3 soluble Fe was dominated by Fe(III) (Fig. S2). At high pH, the measured soluble Fe concentrations are higher than calculated ones (Fig. S3), which can be caused by underestimation of Fe(III) complexation to DOM in the modeling.

In soil C4-C6, without phosphate addition, the soluble Fe concentrations are in the range of 0.03–1600  $\mu\text{M}$ , higher than in soil C1-C3 (Fig. 1). The soluble Fe concentrations measured are mostly higher or close to those calculated (Fig. S3), indicating presence of large amount of Fe(II). The dominance of Fe(II) in solution was also confirmed by analysis of subsamples (Fig. S2). The Eh of soil C4-C6 are lower than 100 mV, and apparently significant Fe-(hydr)oxide reduction has taken place (Fig. S4). The fact that different Eh was developed in soil C1-C3 and C4-C6 under the same experimental conditions can be attributed to differences in soil properties. Soil Eh is determined by many soil physical, chemical and biological factors. Organic matter is one of the main factors influencing soil Eh. An increase in soil organic matter content generally leads to a lower value of soil Eh (Husson, 2013). In soils rich in easily decomposable organic matter, oxidation processes consume large amounts of  $\text{O}_2$ , leading to a lowering of Eh (Lovley et al., 1998). The organic matter contents in soil C4-C6 are higher than in soil C1-C3 (Table 1), which is in accordance with the lower value of Eh developed in soil C4-C6 (Fig. S2). In addition, the texture in soil C4-C6 is heavier (higher clay content) than in soil C1-C3, which may also contribute to the lower Eh in soil C4-C6. Furthermore, the difference in the microorganism composition in the soil samples used may also have modified the Eh of soils. It has been found that soils undergo more frequent redox

changes would prime a soil for rapid Fe reduction (Yu et al., 2016). However, the shift in Fe-(hydr)oxide reactivity was undetectable by chemical extractions and Mössbauer spectroscopy (Ginn et al., 2017). In this study,  $^{57}\text{Fe}$  Mössbauer spectroscopy results of soil C2 and C4 cannot be used either to explain the difference in the reduction of Fe-(hydr)oxides (Fig. S5).

Apart from the differences in level and speciation of soluble Fe between soil C1-C3 and soil C4-C6 without phosphate addition, striking differences were observed in effects of phosphate. Addition of 0.25 mM phosphate to soil C1-C3 led to a decrease of soluble Fe concentrations (Fig. 1), which cannot be explained by decrease of Fe-(hydr)oxide reduction. In fact when phosphate was added, the Eh even dropped a bit and contribution of Fe(II) to soluble Fe increased (became dominant) (Fig. S2). The decrease of soluble Fe(III) concentration in soil C1-C3 upon phosphate addition can be attributed to a decrease in the solubility of Fe-(hydr)oxides ( $\log K_{\text{so}}$ ) and/or precipitation of iron phosphate. Literature studies have shown that adsorption of ions and organic matter on oxide particles may decrease the surface energy of the particles, leading to a decrease in their solubilities (Majzlan, 2011; O'Loughlin et al., 2010; Shaw et al., 2005). On the other hand, according to our model calculations, strengite ( $\text{FePO}_4 \cdot \text{H}_2\text{O}$ ) minerals can be formed at low pH (Fig. S6). In the presence of these minerals, an increase in soluble  $\text{PO}_4^{3-}$  concentration may lead to a decrease of soluble Fe(III) concentration. Therefore, both the soluble Fe(III) and the soluble Fe(II), which is dependent on concentration of Fe(III) and Eh, decreased. On the contrary, addition of phosphate greatly increased the soluble Fe concentrations in soil C4-C6 (Fig. 1). The extra phosphate added to soil C4-C6 stimulated Fe-(hydr)oxide reduction, which can be explained by increased microbial activity as a result of phosphate addition. Phosphate adsorption trial showed that soil C4-C6 has a strong  $\text{PO}_4^{3-}$  adsorption capacity and thus a

low phosphorus bioavailability (Fig. S7). Addition of phosphate provided phosphorus as a nutrient to soil microbes, and consequently stimulated Fe-(hydr)oxide reduction. Such an effect of phosphorus on microbial activity has been observed in literatures (Fredrickson et al., 1998; Ginn et al., 2017; O'Loughlin et al., 2013). Without addition of phosphate, soluble Fe in soil C4-C6 at pH 4.5–5.0 was equivalent to <0.1–5% of amorphous Fe-(hydr)oxides in the soils. When 0.25 mM phosphate was added, soluble Fe at pH about 4.5 equaled to 4–20% of amorphous Fe-(hydr)oxides.

For all soils (C1–C6) without and with phosphate addition, a high background  $\text{CaCl}_2$  concentration resulted generally in a high soluble Fe concentration at low pH (Fig. 1), which can be explained by firstly changes in activity coefficient (at a higher ionic strength, the concentrations of Fe species are higher at the same ion activity) and secondly increase in  $\text{FeCl}_x$  species at a higher  $\text{CaCl}_2$  concentration. However, at high pH, an increase of  $\text{CaCl}_2$  concentration led to a decrease of soluble Fe concentration. At high pH, Fe complexed with DOM dominates in solution. An increase of ionic strength decreased concentration of DOM (Fig. S8), resulting in a lower concentration of soluble Fe.

### 3.2. LCD and NOM-CD modeling

After optimizing the amount of NOM adsorbed ( $\text{NOM}_{\text{ads}}$  in LCD model and  $\equiv\text{FeNOM}_T$  in NOM-CD model) and the solubility of variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ) (Table S2), both the LCD and NOM-CD model can reasonably explain the changes in soluble  $\text{PO}_4^{3-}$  concentration in these paddy soils under various pH in low and high  $\text{CaCl}_2$  background without and with  $\text{PO}_4^{3-}$  addition (Fig. S6). In the modeling, formation of aluminum and iron phosphate precipitates (i.e. variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ) and strengite ( $\text{FePO}_4 \cdot \text{H}_2\text{O}$ )) were considered, which control  $\text{PO}_4^{3-}$  concentration in solution at low pH (Weng et al., 2011). In most soils, including aluminum and iron phosphate precipitation is necessary for pH below ~5.5, but for soil C4 and C5, it extended up to ~pH 6.5. These two soils have the lowest Eh among the six soils studied. It is possible that during the reductive dissolution of Fe-(hydr)oxides or the re-oxidation of Fe(II), iron phosphate precipitation was more easily formed (Miot et al., 2009; Senn et al., 2017).

There is a close to 1:1 positive linear relationship ( $R^2 = 0.96$ ) between the  $\text{NOM}_{\text{ads}}$  in LCD model and the  $\equiv\text{FeNOM}_T$  in NOM-CD model (Fig. S9a), indicating consistency between these two models, as we observed before (Deng et al., 2019). The optimized values of  $\text{NOM}_{\text{ads}}$  decreased with the increase of native soil phosphate loadings and vice versa (Table 1), demonstrating a competitive relationship between NOM and  $\text{PO}_4^{3-}$  adsorbed on mineral surfaces. The adsorption affinity of As(V) onto Fe-(hydr)oxides ( $K$  values) in soil C1–C6 was reduced by a factor of 5–25 compared to the  $K$  values of As(V) adsorption to goethite. The optimized  $K$  values decreased in general with the increase of Al fraction in Al- and Fe-(hydr)oxides (Fig. S9b). Similar relationship has been found previously in dryland soils (Cui and Weng, 2013). Aluminum substitution in Fe-(hydr)oxides decreases the affinity of As(V) adsorption (Masue et al., 2007).

### 3.3. As in soil C1–C3

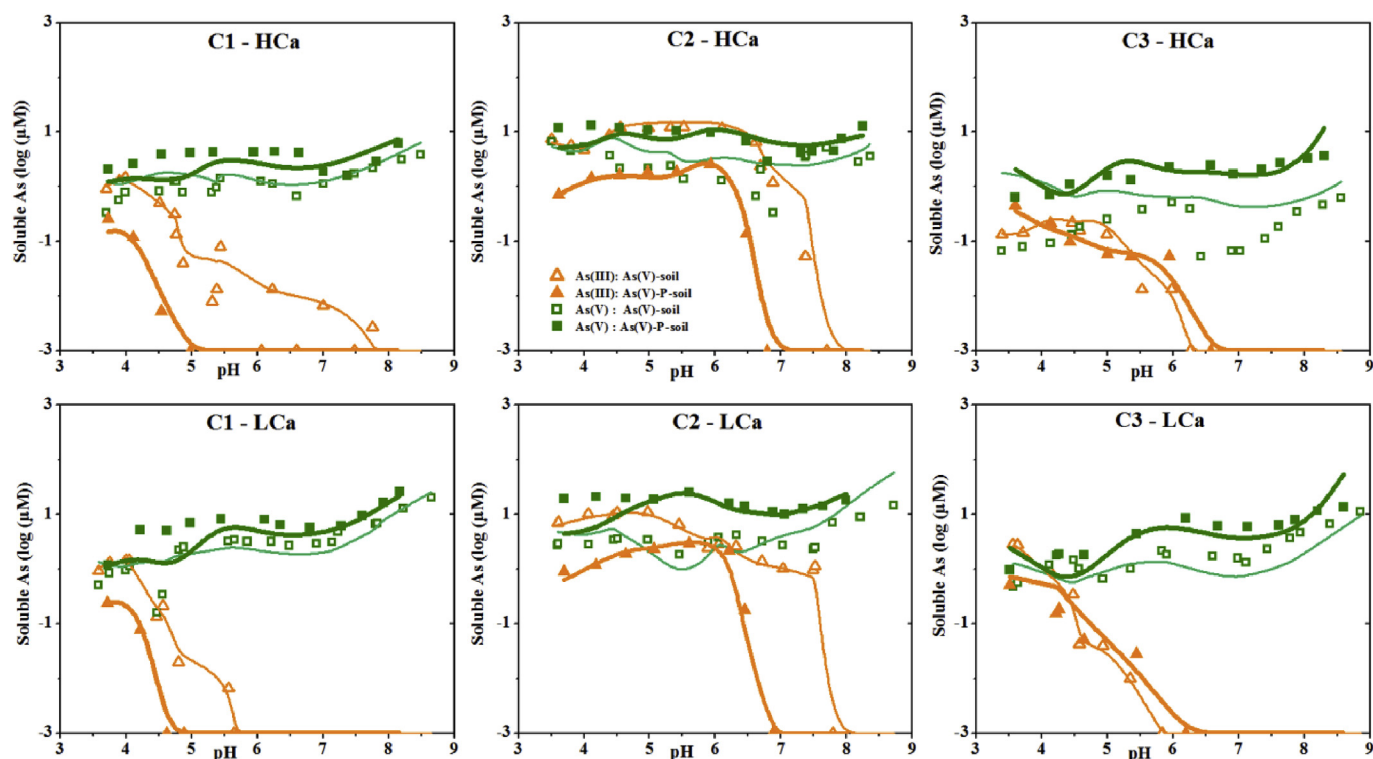
A kinetic trial was conducted before the batch adsorption experiment to investigate the changes of As in soil solution with time. This experiment was carried out without phosphate addition in a 10 mM  $\text{CaCl}_2$  background. The soil pH was not adjusted. The results show that although As was added in the form of As(V), As(III) appeared quickly (within 2 h) in the soil solution (Fig. S1). Both As(V) and As(III) in soil solution decreased with time and in 7 days these concentrations were more or less stable. The results

show that part of As(V) added to these soils were reduced to As(III), and As(III) in solution decreased with time due to adsorption and/or re-oxidation.

Without addition of phosphate, total soluble As concentrations in soil C1–C3 range from 0.2  $\mu\text{M}$  to 20.5  $\mu\text{M}$  in 2 mM  $\text{CaCl}_2$ , 0.05–14.5  $\mu\text{M}$  in 10 mM  $\text{CaCl}_2$  (Fig. 2). As(III) dominates at acidic pH, whereas at high pH As(V) is the major species in solution. Both the dissolution of Fe-(hydr)oxides and the reduction of As(V) consume  $\text{H}^+$ , therefore, higher amount of soluble As(III) was often observed under acidic conditions (Kumarathilaka et al., 2018; Patrick H. Masscheleyn et al., 1991). A relatively higher concentration of soluble As(III) was identified in soil C2, which can be attributed to a larger amount of SOM and DOM in soil C2 than in soil C1 and C3 (Table 1; Fig. S8). It has been proposed that NOM can act as an electron shuttle to promote As(V) reduction (Mladenov et al., 2010). A minimum of soluble As concentration was found around pH 6.0–7.5, similar to that of  $\text{PO}_4^{3-}$  (Fig. S6). The content of soil reactive  $\text{PO}_4^{3-}$  could influence the speciation of As in soils. It was found that the concentrations of both soluble As(V) and As(III) were relatively low in the soils with lower density of reactive  $\text{PO}_4^{3-}$  (such as in soil C3). The decrease of Ca concentration in the background from 10 mM (high Ca) to 2 mM (low Ca) significantly increased the soluble concentration of As(V) especially under alkaline conditions, whereas effect of Ca on soluble concentration of As(III) is small. A higher concentration of Ca facilitates the adsorption of As(V), as well as  $\text{PO}_4^{3-}$ , to metal (hydr)oxides as a result of electrostatic synergy between adsorbed oxyanions and Ca at the mineral-water interface. Similar results have been observed previously in the systems of As–Ca–P–goethite (Deng et al., 2018).

Upon addition of 0.25 mM phosphate, the concentration of soluble As(V) increased especially for intermediate and alkaline pH (Fig. 2). For example, the concentration of soluble As(V) increased from 1.8  $\mu\text{M}$  to 8.7  $\mu\text{M}$  at pH 6.0 with phosphate added in soil C1 in 2 mM  $\text{CaCl}_2$ , and it increased from 0.4  $\mu\text{M}$  to 1.8  $\mu\text{M}$  at the same pH in 10 mM  $\text{CaCl}_2$ . In soil C2, with phosphate addition the concentration of soluble As(V) at pH around 5.5 became four times of that without additional phosphate. These phenomena can be attributed to the competition between As(V) and  $\text{PO}_4^{3-}$  in their adsorption to soil minerals. Dissolution of Fe-(hydr)oxides can be excluded as an explanation for the increases of soluble As(V), because addition of phosphate decreased Fe dissolution in soil C1–C3. Soluble As(III) concentration in soil C1–C3 decreased upon phosphate addition. The LCD and NOM-CD model calculations showed that As(III) in the adsorbed phase decreased as well (Fig. S10), indicating that As(V) reduction was inhibited with phosphate addition in soil C1–C3. This conclusion is in line with the decrease of soluble Fe concentration in these soils when phosphate was added (Fig. 1). Both the reduction of Fe and As(V) was inhibited in soil C1–C3 when phosphate was added, although the Eh dropped slightly (Fig. S2). As discussed above, increase in phosphate loading may have stabilized Fe-(hydr)oxides and decreased Fe reduction and dissimilatory As reduction. In soil C1–C3, with addition of phosphate soluble As is dominated by As(V) and a minimum was found at pH around 6.0–7.5, similar to that in the absence of phosphate. As well, a decrease of Ca concentration led to an increase of soluble As(V) concentration, whereas effects of Ca on As(III) is relatively small. The results show that the effect of phosphate on As distribution in suboxic soils (i.e. C1–C3) is mainly manifested in its competition with As(V), and secondly in the decrease of As(III) as a result of higher stability of Fe-(hydr)oxides with a higher phosphate loading.

After optimization, both the LCD and NOM-CD model can well explain the pH dependency of As concentration and speciation in these paddy soils under various Ca and  $\text{PO}_4^{3-}$  concentrations. With the modeling, speciation of As in the solid phase could be calculated. For soil C1–C3, based on the calculation, 0.8–15% of As(V) was



**Fig. 2.** Concentration and speciation of As in solution of soil C1-C3. The initial concentration of As(V) added was 0.25 mM. In P treatment 0.25 mM phosphate was added. HCa: 10 mM  $\text{CaCl}_2$  (above panel); LCa: 2 mM  $\text{CaCl}_2$  (below panel). Symbols are experimental results, and lines are LCD model calculations. NOM-CD model calculations are similar (Fig. S12).

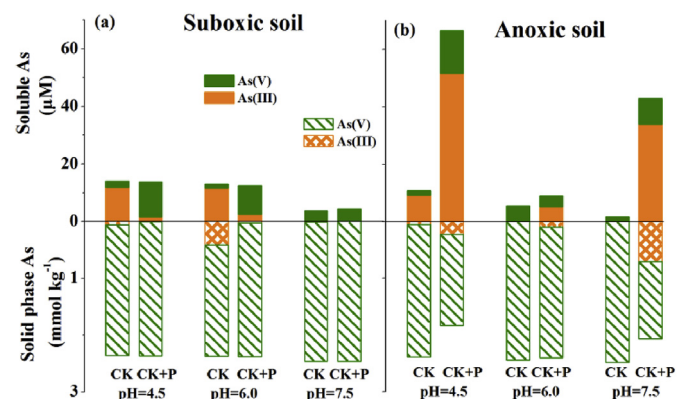
reduced to As(III) without phosphate addition, whereas only 0.1–2% of As(V) was reduced when phosphate was added (Fig. S10). Although the fraction of As(V) reduced is low, As(III) can be dominant in soil solution because of its weak adsorption to soils (Figs. 2 and 3a).

### 3.4. As in soil C4-C6

Without phosphate addition, total concentrations of soluble As in soil C4-C6 range from 1  $\mu\text{M}$  to 60  $\mu\text{M}$  in 2 mM  $\text{CaCl}_2$ , 0.4–40  $\mu\text{M}$  in 10 mM  $\text{CaCl}_2$  (Fig. 4). Mostly, As(III) dominates at low pH,

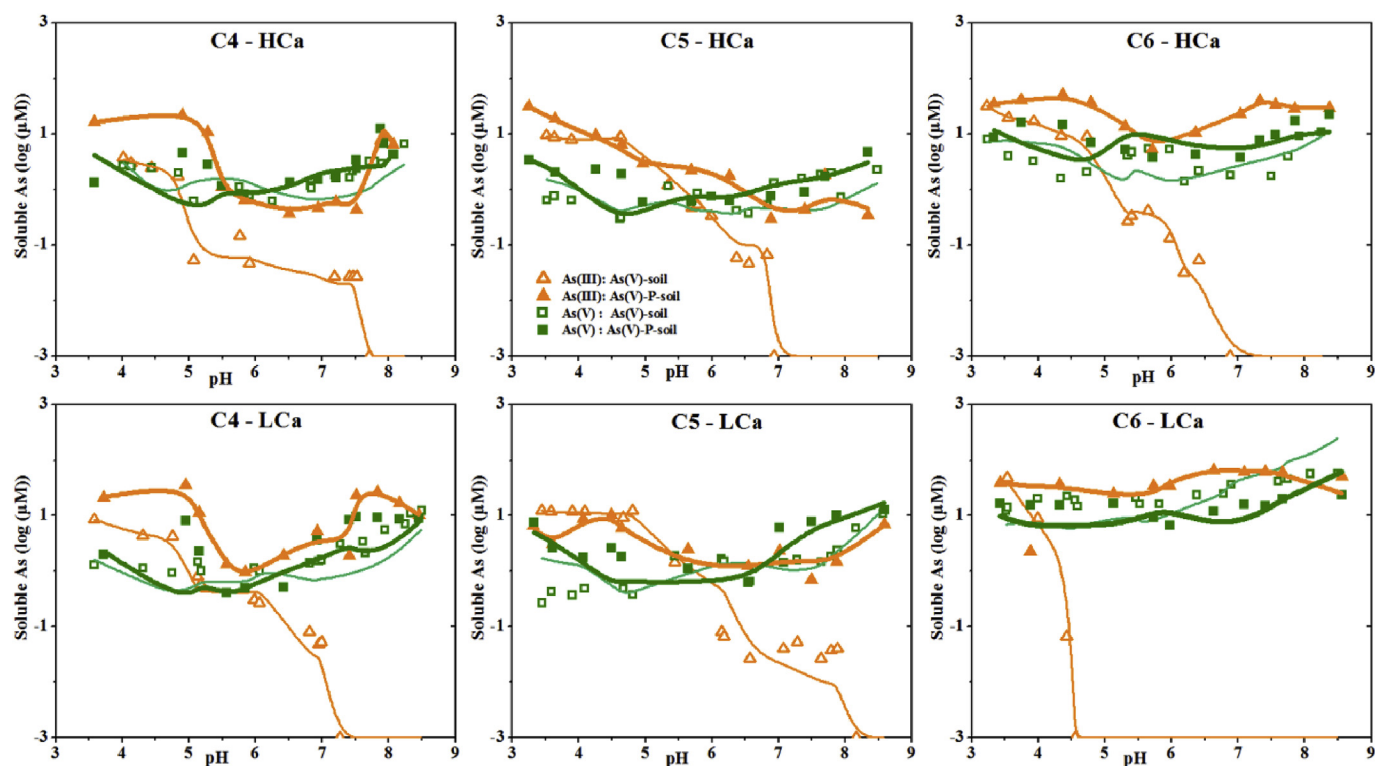
whereas As(V) is more important at high pH in soil solution, which is similar to that in soil C1-C3. However, the relative importance of As(III) is larger compared to soil C1-C3, suggesting a stronger reduction of As(V) into As(III) in soil C4-C6, in accordance with the higher soluble Fe concentration and the lower Eh in soil C4-C6 (especially C4 and C5) than in soil C1-C3. In soils, microorganisms accelerate the reduction-oxidation reactions (such as the reduction of Fe(III) and As(V)). For example, *Clostridium* has been identified as indigenous active bacteria in flooded paddy soils that is capable of reducing As(V) and Fe(III) (Lloyd, 2003; Qiao et al., 2018). *Geobacter* was considered as an important Fe(III) reducer. In the current work, the relative abundance of both *Clostridiales* and *Geobacter* in soil C4 was found higher than that in soil C2 based on 16S rRNA analysis (Fig. S11), confirming a higher activity of microorganisms that can reduce As(V) and Fe(III). Additionally, in soil C4-C6 the lower the reactive  $\text{PO}_4^{3-}$  was, the lower the concentration of soluble As(V) (such as in soil C5). The effect of Ca on soluble concentration of As in soil C4-C6 is similar to that in soil C1-C3, i.e. higher amount of Ca decreased the soluble As(V) under alkaline conditions, especially in soil C5 and C6.

In soil C4-C6, with addition of 0.25 mM phosphate, As(III) became an important As species in solution not only under acidic pH, but also under alkaline pH (Fig. 4). For example, at pH 8.0 the concentrations of soluble As(III) were >70 times higher than that without phosphate addition. According to the LCD and NOM-CD model calculations, with phosphate addition, the fraction of As(V) reduced to As(III) in soil C4 increased from <0.01% to 20% and from <0.01% to 44% at pH around 8.0 in 10 mM and 2 mM  $\text{CaCl}_2$  respectively, and it increased from 1% to 27% and from 4% to 40% at pH about 5.0 (Fig. S10). It can be seen that addition of phosphate led to a strong increase of As(V) reduction, causing a significant increase of soluble As(III) at both acidic and especially alkaline pH.



**Fig. 3.** Effects of phosphate on the solid-solution distribution of As(III) and As(V) in suboxic (C2) and anoxic (C6) soils. CK: 0.25 mM As(V) without additional phosphate; CK + P: 0.25 mM As(V) with 0.25 mM phosphate added. The concentration and speciation of As in solution are based on measured results, whereas the amount and speciation of As in the solid phase are calculated by the LCD and NOM-CD model.





**Fig. 4.** Concentration and speciation of As in solution of soil C4-C6. The initial concentration of As(V) added was 0.25 mM. In P treatment 0.25 mM phosphate was added. HCa: 10 mM  $\text{CaCl}_2$  (above panel); LCa: 2 mM  $\text{CaCl}_2$  (below panel). Symbols are experimental results, and lines are LCD model calculations. NOM-CD model calculations are similar (Fig. S13).

The dissolution of higher amount of Fe-(hydr)oxides also suggested a stronger reduction condition occurred with phosphate additions (Fig. 1).

Although there was more As(V) reduced to As(III) upon phosphate addition, at pH below 6.0, the concentration of soluble As(V) in soil C4-C6 increased when phosphate was added. At pH around 5.0, the increase of As(V) concentration contributed 2–86% of the overall increase of soluble As concentration in soil C4-C6 when phosphate was added. This increase can be resulted from both the competitive adsorption between As(V) and  $\text{PO}_4^{3-}$  and the dissolution of Fe-(hydr)oxides leading to the release of adsorbed As(V). Previous studies showed that the reductive dissolution of Fe-(hydr)oxides had a significant influence on the solubility of As(V) (Bennett et al., 2012; Stroud et al., 2011). In the current study, 0.04–1% and 2.5–14% of Fe-(hydr)oxides was dissolved in the absence and presence of additional phosphate at about pH 5.0, whereas soluble As(V) increased by 2–5.5 times upon phosphate addition around the same pH. Evidently, Fe-(hydr)oxide dissolution contributed to the increase of As(V) in solution, but competition with phosphate is by far more important. At higher pH, either increase, no change or decrease in soluble As(V) concentration was found in soil C4-C6 when phosphate was added, which can be explained by the complementary effects between an increased competition with  $\text{PO}_4^{3-}$  and a decrease of total amount of As(V) as a result of the increase in As reduction. For instance, in soil C5, upon phosphate addition, the significant increase of soluble As(V) at pH > 7.5 is resulted from strong competition with  $\text{PO}_4^{3-}$  and a relatively low fraction of As(V) reductions (<20%; Fig. S10). In soil C6 in 2 mM  $\text{CaCl}_2$  at pH > 6.0, concentration of soluble As(V) decreased upon phosphate addition. According to model calculations, the reason for this counter intuitive change is a drastic decrease of As(V), i.e. more than 50% As(V) added has been reduced into As(III) under this condition (Fig. S10).

In the anoxic soils (i.e. C4-C6) without phosphate addition, As(V) is by far the dominant species in soil solution at pH > 6.0, whereas when phosphate was added, both As(V) and As(III) are important over pH 3–9 (Figs. 3b and 4).

#### 4. Conclusion

Our results revealed that phosphate fertilization may lead to very different impact on As solubility in paddy soils under (sub)oxic and anoxic conditions (Fig. 3). Under (sub)oxic conditions, addition of phosphate results in stabilization of Fe-(hydr)oxides and decreases of As reduction, leading to a decrease of As(III) but an increase of As(V) in solution as a result of competitive adsorption with  $\text{PO}_4^{3-}$ . Depending on the pH and dominance of As(III), phosphate fertilization may cause a decrease (at low pH) or increase (at high pH) of soluble As concentration in (sub)oxic paddy soil. On the contrary, under anoxic conditions phosphate fertilization in phosphorus deficient soils stimulates microbial reduction of Fe-(hydr)oxides and As(V). Consequently, soluble As(III) concentration increases strongly not only at acidic pH, but also at alkaline pH, making As(III) a dominant soluble As species over a wide pH range. Although these soils used in the current work differ in the equilibrium redox potential, the effects of phosphate on the speciation of As in the same group of soils showed the same tendency under two concentration of  $\text{CaCl}_2$  background. Adding phosphate to anoxic soils may increase or decrease soluble As(V) concentrations, depending on the degree of As(V) reduction, degree of Fe-(hydr)oxide dissolution and competition with  $\text{PO}_4^{3-}$ . Please note that although the ratio of P/As added was kept at 1:1 in the current study, the initial contents of phosphate in the soils differ and were higher than the initial As content. If the ratio of P/As added into soils changed, we expect that the major trend of the effects will



remain, but the absolute and relative change may differ, except for the (sub)oxic soils at low pH. For (sub)oxic soils at low pH, on one hand, addition of P may reduce As(V) reduction thus decrease As solubility, but on the other hand addition of P may increase As solubility due to competition for adsorption. Thus the net effect on As solubility depends on which of these two effects dominates. For paddy soils under the period of flooding, the pH of the soil tends to become neutral. In this case, phosphorus fertilization may strongly increase As concentration in soil solution.

The LCD and NOM-CD model can describe these complex interactions by considering: (i) the competitive adsorption and the electrostatic interactions among Ca, As(III, V),  $\text{PO}_4^{3-}$  and NOM adsorbed, (ii) the reduction of As(V) and the dissolution of Fe-(hydr)oxides, and (iii) the precipitation of phosphate minerals in paddy soils. These two advanced surface complexation models (i.e. LCD and NOM-CD) help us to better understand the effects of pH,  $\text{PO}_4^{3-}$  and Ca on the distribution of As between the soil and solution phases. These two models can be further used in assessing the mobility and environmental risks of As in paddy soils or in natural soil/sediment-water systems.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

**Yingxuan Deng:** Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. **Liping Weng:** Conceptualization, Software, Methodology, Validation, Writing - review & editing. **Yongtao Li:** Resources, Writing - review & editing, Supervision. **Yali Chen:** Investigation, Resources. **Jie Ma:** Investigation, Resources.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.114783>.

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