



The migrated behavior and bioavailability of arsenic in mangrove sediments affected by pH and organic acids

Kang Mei^{a,b}, Jingchun Liu^{a,*}, Rongrong Shi^a, Xin Guo^a, Haoliang Lu^a, Chongling Yan^{a,b}

^a Key Laboratory of Ministry of Education for Coastal and Wetland Ecosystems, Xiamen University, Xiamen 361102, China

^b State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, China

ARTICLE INFO

Keywords:

Low molecular weight organic acids (LMWOAs)
Arsenic
Mobilization and migration
Fe species
Solution pH

ABSTRACT

Batch experiments were conducted to study the migration behavior of arsenic (As) and iron (bivalent, trivalent, and total Fe) of the presence of the low molecular weight organic acids (LMWOAs) citric acid, malic acid, and oxalic acid in As-enriched mangrove sediments. The results for supernatant As/Fe species were significant according to each LMWOA treatment. Significant non-linear correlations were found among As level, pH, and acid dose based on our predictive model. The capacity of LMWOAs to mobilize As/Fe species followed the order of citric acid > malic acid/oxalic acid. The supernatant As correlated positively with the LMWOAs dose and negatively correlated with the pH. As migration was affected by acid strength, the number of carboxyl groups, the pH and levels of Fe compounds in the sediments. The results indicate that LMWOAs can potentially attenuate As contamination from mangrove sediment, allowing for a better understanding of As/Fe behavior in the rhizosphere.

1. Introduction

Root exudates are primarily botanical photosynthetic products which are actively or passively released into the rhizosphere (Sun et al., 2012; Agnello et al., 2014; Lu et al., 2017). Many studies have shown that root exudates accelerate organic pollutant degradation and modify the bioavailability of metal pollutants in various ways, including as nutrient sources for rhizosphere microorganisms (Phillips et al., 2012; Y.Y. Wang et al., 2014), changing rhizosphere pH (Lu et al., 2007; Niu et al., 2013) or forming dissolved metal-organic complexes with metal pollutants (Lu et al., 2007; Agnello et al., 2014; Montiel-Rozas et al., 2016; J. Li et al., 2019). Low molecular weight organic acids (LMWOAs) play a key role in modifying the bioavailability of metal pollutants (Sun et al., 2012; Lu et al., 2017). However, few studies have evaluated the specific mechanisms involving individual LMWOA components in rhizoremediation. Several studies have reported an association between LMWOAs, such as tartaric acid (X.C. Li et al., 2019), succinic acid (Wang and Mulligan, 2013), and oxalic acid (Kim and Baek, 2019) and the mobility of modified metals, but the functional mechanism for this remains unclear.

Mangroves act as an important link between terrestrial and marine ecosystems and are commonly regarded as a potential sink and source of heavy metal(loid)s due to characteristics such as the high organic carbon and sulfur content of muddy anaerobic sediments and relatively

low current speeds (Lin et al., 2018). Arsenic (As) is a metal pollutant that has previously been detected at high levels in some mangrove sediments. The highest As level recorded was up to 320 mg kg⁻¹ in the surface sediment of the Bothnian Bay, Finland (Leivuori and Niemistö, 1993), while an As level of 199.66 mg kg⁻¹ has been reported in mangrove wetlands by Li et al. (2017). In light of the carcinogenicity and non-biodegradability of As, its accumulation in mangroves has received considerable attention.

The biogeochemistry of As accumulation in mangroves is influenced by many factors such as plant accumulation (Lin et al., 2018), the amount of oxygen that is released by plant roots (Lin et al., 2018), and the presence of Fe oxides/hydroxides and sulfur in the sediment (Ma and Lin, 2012). High NaCl salinity also impedes the adsorption of arsenic into sediments as a result of competition from Cl⁻ ions or a reduction in interparticle attraction by Na⁺ (Chakraborty et al., 2012b). Root exudates are one of the most important factors in controlling the mobility of As in the rhizosphere of mangrove plants. The effect of LMWOAs on As mobility has been widely studied. Nworie et al. (2017) reported that oxalic acid treatment could remove between 10%–30% of the total As from the soil but found no clear relationship between total As and total Fe released by the treatment. On the other hand, treatment with citric, malic, and tartaric acids removed less than 10% of the total soil As, and a close relationship was observed between the levels of As and Fe extracted. Lee et al. (2017) found that the concurrent release of

* Corresponding author.

E-mail address: liujingchun@xmu.edu.cn (J. Liu).

As and Fe occurred through oxalate extraction. The hyperaccumulator *Pteris vittata* has been widely reported to secrete phytic acid to promote the dissolution of As from As-bearing minerals (Liu et al., 2016; Tu et al., 2011). However, while Das et al. (2017) did not detect phytic acid in the root exudates of *P. vittata*, they did find that the addition of various levels of As enhanced malic acid, oxalic acid, and succinic acid secretion by the roots. The different results found by different researches could be due to variations in experimental conditions, such as soil type, pollutant content, and plant species, among others. Further studies are needed to clarify the relationship between As mobility and LMWOAs.

Variations in the LMWOAs secreted by mangrove roots have been reported under polluted conditions (Lu et al., 2007; W.Y. Wang et al., 2014; X.C. Li et al., 2019). However, the vital role of LMWOA release in heavy metal mobilization and the related mechanisms involved in the mangrove rhizosphere remain unclear. For this reason, our study mainly focused on the mobilization and migration of As that interact with LMWOAs in order to explore the response mechanisms in the water-sediment interface of the rhizosphere.

The composition of LMWOAs secreted by roots varies according to plant species (Y.Y. Wang et al., 2014). However, citric acid, malic acid, and oxalic acid are the most common and dominant LMWOAs detected in mangrove sediments (Lu et al., 2007; Johansson et al., 2008; J. Li et al., 2019). We hypothesized that LMWOAs may promote the mobilization of As and improve its bioavailability in the mangrove rhizosphere. Citric, malic, and oxalic acids were selected to examine the effects of LMWOAs on the adsorption of As in an LMWOA solution-sediment mixture. The objectives of this study were: 1) to determine the relationship between As and Fe released under varying dosages of organic acids; and 2) to explore the migration patterns of As in the water-sediment system of the sedimentary mangrove environment based on the statistical analysis of influential parameters.

2. Materials and methods

2.1. Sampling and characteristics

Sediment samples were collected from sediment layers within 30 cm from the surface from a pure *Kandelia obovata* forest site in the Jiulong River estuary in Fujian, China (24° 24' N, 117° 55' E). After collection, debris was removed and homogenized for later use. The mangrove sediments were added to an arsenite solution (NaAsO₂) containing up to 40 mg kg⁻¹ As in dry weight (no background value) for further analysis. Fresh sediments were stored in a greenhouse at 25 °C for 30 days and were mixed and activated every 12 h to reach a homogeneous state prior to use. The characteristics of the sediments are shown in Table 1. The general properties of the pretreated sediment were then analyzed using standard methods described by Bodin et al. (2013) and Yang et al. (2019).

Table 1
Chemical characteristics of mangrove sediments (n = 3).

| Parameter | Mean values |
|---------------------------------|--------------|
| Total organic matter (%) | 12.56 ± 0.74 |
| Moisture content (%) | 53.65 ± 0.02 |
| C (%) | 1.30 |
| H (%) | 1.12 |
| N (%) | 0.12 |
| pH (sediment: water = 1:2.5) | 7.64 ± 0.02 |
| Salinity (‰) | 16.32 ± 0.24 |
| Total As (mg kg ⁻¹) | 14.77 ± 0.85 |
| Total Fe (g kg ⁻¹) | 4.03 ± 0.30 |

2.2. Desorption experiments

Citric acid, malic acid, and oxalic acid were selected as typical LMWOAs to examine the influence of their dose and pH on the desorption and extraction of As in the water-sediment system. All treatments were carried out in 50 mL polyethylene centrifuge tubes with 20 mL LMWOA and 0.5 g fresh sediments. Each tube was shaken by a vortex oscillator for 30 s to blend the mixture. The ratio of sediment to LMWOA was calculated with the aim of achieving complete desorption and extraction at equilibrium. The background solution contained 0.01 mol L⁻¹ sodium chloride as an electrolyte solution to maintain ionic equilibrium (Chakraborty et al., 2012b; J.Q. Li et al., 2019) and three sets of experiments were conducted.

In **Experiment 1 (E1)**, working solutions of the three LMWOAs were diluted using ultrapure water (18.2 Ω) containing different acid concentrations (0, 1, 2, 4, 6, and 8 mmol L⁻¹). In **Experiment 2 (E2)**, a suitable concentration of LMWOAs was selected based on the results of E1 to adjust the working solutions to different gradient pH levels (2, 3, 4, 5, 6, and 7; all LMWOAs = 2 mmol L⁻¹) in order to examine the influence of the same dose of LMWOAs in different pH conditions. In **Experiment 3 (E3)**, the concentrations of working solutions were the same as in E1, but their pH levels were maintained at 5 (LMWOAs: 0, 1, 2, 4, 6, and 8 mmol L⁻¹; for all, pH = 5). Sodium hydroxide and hydrochloric acid were used to regulate the pH of the LMWOA solutions. All tubes were incubated in a rotary shaker (Saifu BHWY-200 Shaker) at 200 rpm and 25 °C in the dark for 24 h. Each tube was centrifuged at 8000 rpm for 10 min after incubation. The supernatant was further passed through a 0.45 μm filter membrane prior to analysis. A triplicate experiment was conducted to determine variations in As and Fe species and the pH of the supernatants. Blanks with no additional As were used as controls. All chemical reagents were of analytical grade.

2.3. Instrumental analysis

The supernatant pH was measured using a pH meter (Leici PHS-2F, Shanghai, China). Total As concentration was determined using an atomic fluorescence spectroscopy photometer (AFS-930, Beijing Jitian Co. Ltd., China). The determination of ferrous iron, Fe (II), and total iron (Fe) was accomplished using the 1,10-phenanthroline spectrophotometric method at a wavelength of 510 nm (UV-vis Spectrometer, Beijing Ruili Co. Ltd., China), as described elsewhere (Sun et al., 2019). The Fe was reduced to Fe (II) with hydroxylamine hydrochloride (NH₂OH·HCl) and sulfuric acid. The content of trivalent iron, Fe (III), was calculated by subtracting data for Fe (II) from Fe.

2.4. Desorption kinetics

The Freundlich isotherm was used to represent the adsorption equilibrium (kinetic reaction) of the liquid onto the surface of a solid material such as contaminated sediments (or microplastics) in batch experiments (Tor et al., 2009; Gouda et al., 2019; Wang et al., 2019). The desorption and migration of heavy metals from solid-phase sediments to liquid-phase sediments were evaluated using the Freundlich isotherm equation as a reverse process:

$$C_{DM} = \alpha * C_{SM}^{\beta} \quad (1)$$

The form of logarithmic variation (all base 10) is as follows:

$$\log C_{DM} = \alpha * \log C_{SM} + \log \beta \quad (2)$$

where C_{DM} (mg kg⁻¹) indicates the concentration of dissolved metal in the liquid phase, C_{SM} (mg kg⁻¹) represents the content of sediment metal, and α and β are the Freundlich coefficients.

This process is affected by environmental conditions such as the pH of the sediment and its microenvironment, the content of organic matter, and the total metal content of the sediment. Based on the above,

the following semi-empirical equation was proposed to describe the desorption of heavy metals (Cu, Zn, Cd, Pb, etc.) in contaminated soil solutions. For more detailed information, see McBride et al. (1997) and Sauve et al. (2000).

$$\log DM = \alpha + \beta * pH + \gamma * \log\left(\frac{TM}{OM}\right) \quad (3)$$

where DM (mg kg⁻¹), pH, TM (mg kg⁻¹), and OM (g kg⁻¹) indicate the dissolved metal in the liquid phase, the pH of the soil solutions, and the total metal and organic matter content of the soil samples respectively, while α , β , and γ are constants.

In our batch experiments, we studied the effects of various factors such as the dosage, pH, and the type of organic acid involved. We used the following predictive equation to describe the migration of As in the mangrove sediment mixture and LMWOAs solution:

$$\log As = \alpha + \beta * pH + \gamma * \log\left(\frac{TAs}{LMWOA}\right) \quad (4)$$

Here, As (mg kg⁻¹) indicates the As content in the liquid phase, pH represents the pH value of the solution, TAs (mg kg⁻¹) is the total As in the sediment, and LMWOA (g kg⁻¹) is the concentration of organic acid. α , β , and γ are constants.

2.5. Statistical analysis

Data processing and statistical analyses were performed using IBM SPSS, version 23.0 (SPSS Inc., Chicago, IL, USA). One-way ANOVA and multiple comparisons (LSD, Duncan's multiple range tests) were performed in order to test for significant differences between the variables. Spearman's correlation analysis was performed to determine the relationship between the treatments. Graphs were drawn using Origin 9.0 and GraphPad Prism 6 software.

3. Results

3.1. Variations of supernatant As

The concentrations of As in the supernatant in different As and LMWOA treatments are shown in Fig. 1. Significant increases ($p < 0.01$) were observed in all supernatant As concentrations after the LMWOAs were added compared with the supernatants that received no LMWOAs. The As content showed a tendency to increase with increasing concentrations of LMWOAs in E1 (Fig. 1a, b, and c). More As was extracted by LMWOAs from sediments with high As content (As₄₀) than from those with low As content (As₀) sediment (Table 2).

At the same LMWOA concentration level, the three LMWOAs showed a capacity to extract As in the following order: citric acid ($p < 0.05$) > malic acid > oxalic acid ($p > 0.05$). The average concentration of As in the supernatant of citric acid was greater than those in malic acid and oxalic acid by factors of 1.47 and 2.42 respectively.

For As treatments at the same molar levels, the As concentrations were in the following order: As₄₀ > As₀. For As concentration in the control group (As₀), no significant difference ($p > 0.05$) was observed between the low LMWOA dose (0–2 mmol L⁻¹) and the high LMWOA dose (4–8 mmol L⁻¹). However, there was a significant difference ($p < 0.01$) in the As₄₀ group between the low (0–2 mmol L⁻¹) and the high (4–8 mmol L⁻¹) concentrations (except for oxalic acid, see Fig. 1c). This indicates that 2 mmol L⁻¹ LMWOA was the critical and optimal concentration to mobilize As and was subsequently applied in E2 in this study.

The results of E2 showed that, in general, As content decreased as pH increased (Fig. 1d, e, and f; except for citric acid at pH = 2). Unlike in E1, the extraction of sediment-borne As by LMWOAs was in the following order: citric acid > oxalic acid > malic acid ($p < 0.01$). The results showed that the supernatant content of As in citric acid was 5.45

times and 4.09 times those of malic acid and oxalic acid respectively, indicating that malic acid and oxalic acid were more susceptible to increasing pH than citric acid.

There was an ascending trend under the same pH for As concentration in the supernatant for both citric acid and malic acid (but not for oxalic acid, see Fig. 1 E3). The capability of LMWOAs to extract As sediment was in the following order: citric acid > malic acid > oxalic acid ($p < 0.05$). The greater the LMWOA concentration, the higher the amount of As extracted (Fig. 1g). In general, As concentration in the supernatant increased significantly ($p < 0.05$) as the dosage of citric acid increased for both the As₀ and As₄₀ groups. As with the malic acid treatment in E1, there was no significant difference ($p > 0.05$) between the high and low LMWOA doses in the As₄₀ group (Fig. 1h). Moreover, no significant change was observed in the As content extracted by oxalic acid at the same pH (Fig. 1i).

3.2. Variations of supernatant pH

The initial pH of several LMWOAs before treatment decreased as the concentrations increased (1, 2, 4, 6, and 8 mmol L⁻¹). The pH ranges of malic acid (2.69–3.07) and citric acid (2.53–2.87) were higher than that of oxalic acid (1.32–1.44). Changes in the supernatant pH in this study are shown in Fig. 2. A significant increase in pH ($p < 0.05$) was observed following treatment with mangrove sediments and extraction. The influence of the addition of As on pH was not significant ($p > 0.05$) in the As₀ and As₄₀ groups (Table 2).

The supernatant pH in both E1 (range of R²: 0.992–0.997) and E2 (range of R²: 0.979–0.994) showed a nonlinear correlation ($p < 0.001$). There was no significant difference in supernatant pH among the three LMWOAs in E1, while pH in E2 and E3 showed the following trends of oxalic acid > malic acid > citric acid and oxalic acid > malic acid/citric acid respectively (Table 2). Under the condition of the same pH (Fig. 2, E3), the supernatant pH in oxalic acid showed an increasing trend, but the pH in the citric acid supernatant showed a decreasing trend. The supernatant pH in both citric acid (R² = 0.635) and oxalic acid (R² = 0.871) showed a linear correlation with the concentration of LMWOA, but the supernatant pH in malic acid presented the same pH level (Fig. 2, E3).

3.3. Variations of Fe species

The content of the three Fe species according to the concentration or pH of LMWOA is illustrated by nonlinear regression fitting curves with exponential or logarithmic equations, except for Fe (III) in oxalic acid in E3 (Fig. 3, $p < 0.05$). As in As extraction, the concentrations of Fe species increased as the concentration increased in E1 and E3 (Fig. 3). The multiple comparisons showed significant differences ($p < 0.05$) in the contents of Fe (II) and Fe in the supernatant among the LMWOAs (Table 2). The three LMWOAs showed a capacity to extract both Fe and Fe (III) in the following order: citric acid > oxalic acid > malic acid, while the content of Fe (II) in the LMWOA supernatant followed the order of oxalic acid > citric acid > malic acid (Table 2, E1). The content of Fe (III) and Fe for citric acid and malic acid were observed to increase initially, and then reached a plateau at 4–8 mmol L⁻¹ (except Fe for malic acid), while Fe (II) content increased gradually for the three acids (Fig. 3, E1). However, no significant difference ($p < 0.05$) in Fe species was observed between the As₄₀ group and the As₀ group in any treatments (data not shown).

t-Test results showed that the Fe species content in E2 (after pH adjustment) was significantly different ($p < 0.01$) compared with the dose of 2 mmol L⁻¹ LMWOAs in E1. Compared with the dose effects in E1, the contents of Fe species in E3 were higher at pH = 2, but far lower at pH > 3 than at 2 mmol L⁻¹ of each corresponding LMWOA (Fig. 3, E1, E3). The content of Fe species showed a tendency to decrease with pH, indicating that Fe content was negatively correlated with pH ($p < 0.01$).

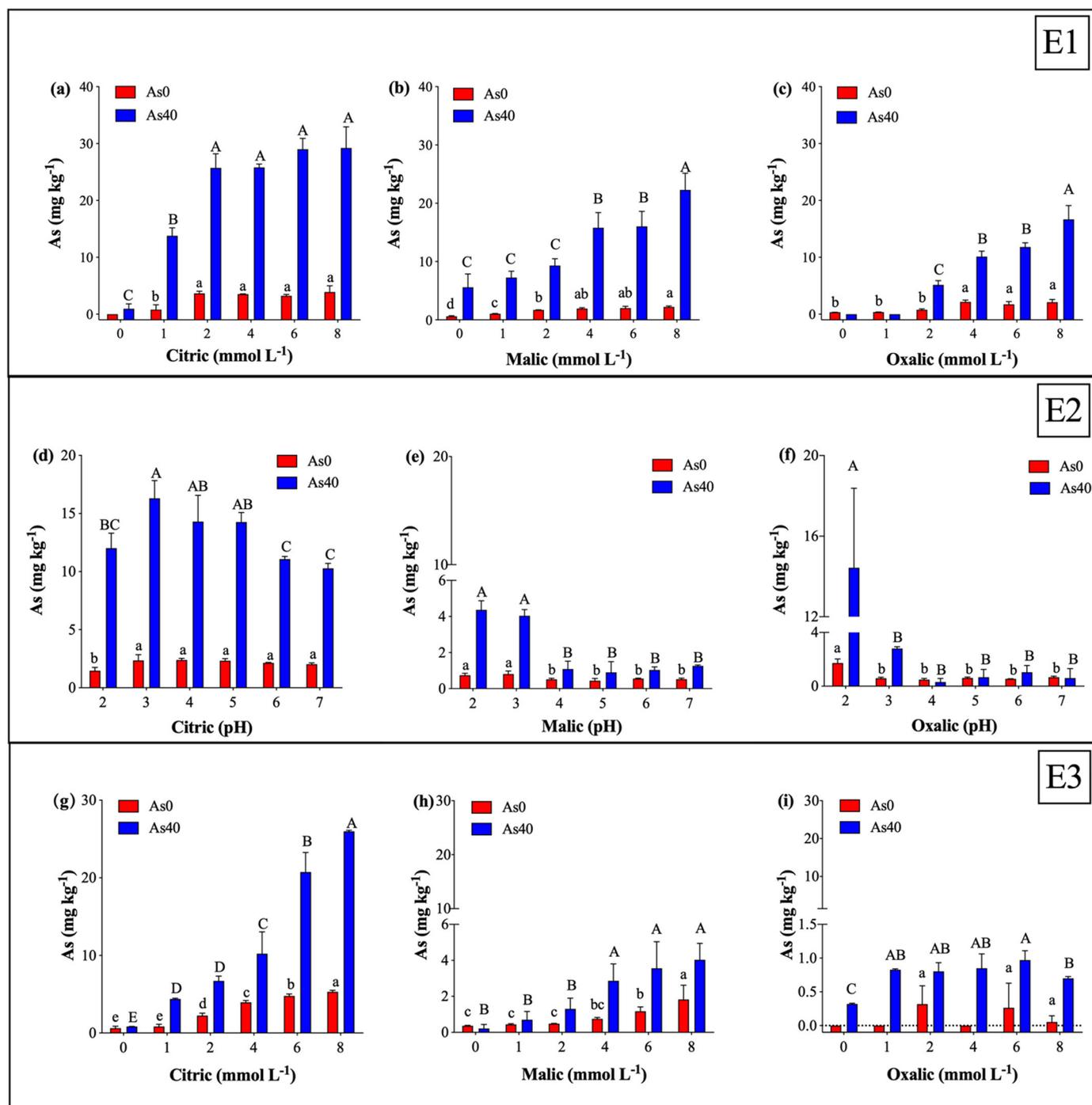


Fig. 1. As content in the LMWAO supernatants. A, B, C for Experiment 1 (E1): dose effects of the three LMWAOs; D, E, F for Experiment 2 (E2): adjusted the three LMWAOs of the same concentration (2 mmol L⁻¹) to different pH gradients; G, H, I for Experiment 3 (E3): adjusted all three LMWAOs of different concentrations to the same solution pH = 5. As0 = control group and As40 = As-enriched group. Different letters were indicated significant differences ($p < 0.05$).

The content of Fe species in the supernatant in E3 is shown in Fig. 3g, h, and i. The LSD-t-test results show that the Fe species content was significantly different ($p < 0.01$) from that in E1. This suggests that the extraction of Fe species was inhibited after the adjustment of the pH of LMWAO (E3). A similar trend was observed for As extraction in E1, although the pH levels of all the solutions were the same.

4. Discussion

Most studies indicate that root exudates such as LMWAOs can potentially be used to reduce heavy metal pollution in the soil through

acidification, complexation, and reduction-dissolution (McBride et al., 1997; Onireti et al., 2017; J.Q. Li et al., 2019). The capacity of LMWAOs along with pH and acid dose to mobilize As and Fe in mangrove sediments has been fully explored in our work. In our study, individual LMWAOs significantly differed in their capacity to mobilize As and Fe species, and this finding has also been noted in previous research (Jia et al., 2016). The highest value of As supernatant among the three experiments was found for citric acid extraction at 11.36 mg kg⁻¹ in E1, 7.69 mg kg⁻¹ in E2, and 6.76 mg kg⁻¹ in E3 (Table 2). These results are consistent with the findings for As and Pb extraction by organic acids (Onireti et al., 2017). On the one hand, LMWAOs are

Table 2

Values of the determined indexes in this study. Fe (II)/Fe (III)/Fe: g kg⁻¹; As: mg kg⁻¹. Significant differences ($p < 0.05$) were indicated by different letters.

| | | Fe (II) | Fe (III) | Fe | As | pH |
|-------------------|--------|---------|----------|-------|--------|-------|
| LMWOAs extraction | | | | | | |
| E1 | Citric | 0.49b | 2.56a | 3.05a | 11.36a | 4.29a |
| | Malic | 0.21c | 1.06b | 1.26c | 5.60b | 3.69a |
| | Oxalic | 0.86a | 1.22b | 2.08b | 3.65b | 4.31a |
| E2 | Citric | 0.38a | 1.17a | 1.56a | 7.69a | 5.71c |
| | Malic | 0.13b | 0.27b | 0.4c | 1.41c | 5.94b |
| | Oxalic | 0.35a | 0.31b | 0.66b | 1.88b | 6.26a |
| E3 | Citric | 0.56a | 0.79a | 1.33a | 6.76a | 6.65b |
| | Malic | 0.08b | 0.16b | 0.25b | 1.45b | 6.70b |
| | Oxalic | 0.05b | 0.16b | 0.23b | 0.53c | 7.49a |
| As addition | | | | | | |
| As0 | | 0.46a | 1.54a | 2.08a | 1.79b | 4.03a |
| As40 | | 0.48a | 1.65a | 2.18a | 11.54a | 4.18a |
| As0 | | 0.22b | 0.57a | 0.79b | 1.16b | 5.90b |
| As40 | | 0.33a | 0.59a | 0.92a | 6.15a | 6.09a |
| As0 | | 0.21b | 0.42a | 0.63a | 1.3b | 6.77b |
| As40 | | 0.25a | 0.36b | 0.60a | 4.38a | 7.13a |

associated with changes in As behavior in soil and soil solutions in the rhizospheric microenvironment (Wang and Mulligan, 2013; Onireti et al., 2017), and these effects of LMWOAs may be attributable to their ability to continuously produce conjugated ions (Wang and Mulligan, 2013; Onireti and Lin, 2016). In addition to the ionic effects, the ability of the tricarboxylic citric acid to extract As was greater than that of

either of the dicarboxylic acid (malic acid and oxalic acid). The stronger desorption behavior of citric acid may be related to its number of carboxylic substituents and higher acid strength compared with malic acid and oxalic acid at the same molar concentrations.

4.1. pH dependence of the solution-sediment mixture

The dissociation equilibrium constant (pKa) of organic acids has been found to have a significant influence on the mobilization of heavy metals as well (Onireti et al., 2017; Xing et al., 2018). Here, the pH of the supernatant was significantly negatively correlated with As content (Fig. 4; except for malic acid and oxalic acid in E3). The strong linear correlations between As and pH in both E1 and E2 indicate that the release of sediment As was greatly affected by pH. The acidification effects of LMWOAs can change the pH of the soil solution (Tu et al., 2004). However, the higher content of As supernatant observed in citric acid extraction in this study appeared to be attributable to the strong complexation that was induced by the LMWOA ligands.

Upon the addition of LMWOAs to the mangrove sediments, pH variations among the three LMWOAs supernatants were consistent in both E1 and E2 (Fig. 2). Ageing processes caused LMWOA protons to be continuously consumed in the mixture, leading to an increase in pH and drastic changes in the Fe species (Lu et al., 2007; Marschner, 2013). The mechanism involved may be attributable to the following processes: 1) the H⁺-driven dissolution of soil mineral and proton consumption caused by the cation exchanges in neutralization reactions; 2) differences in the types and structures of LMWOAs and the different values of

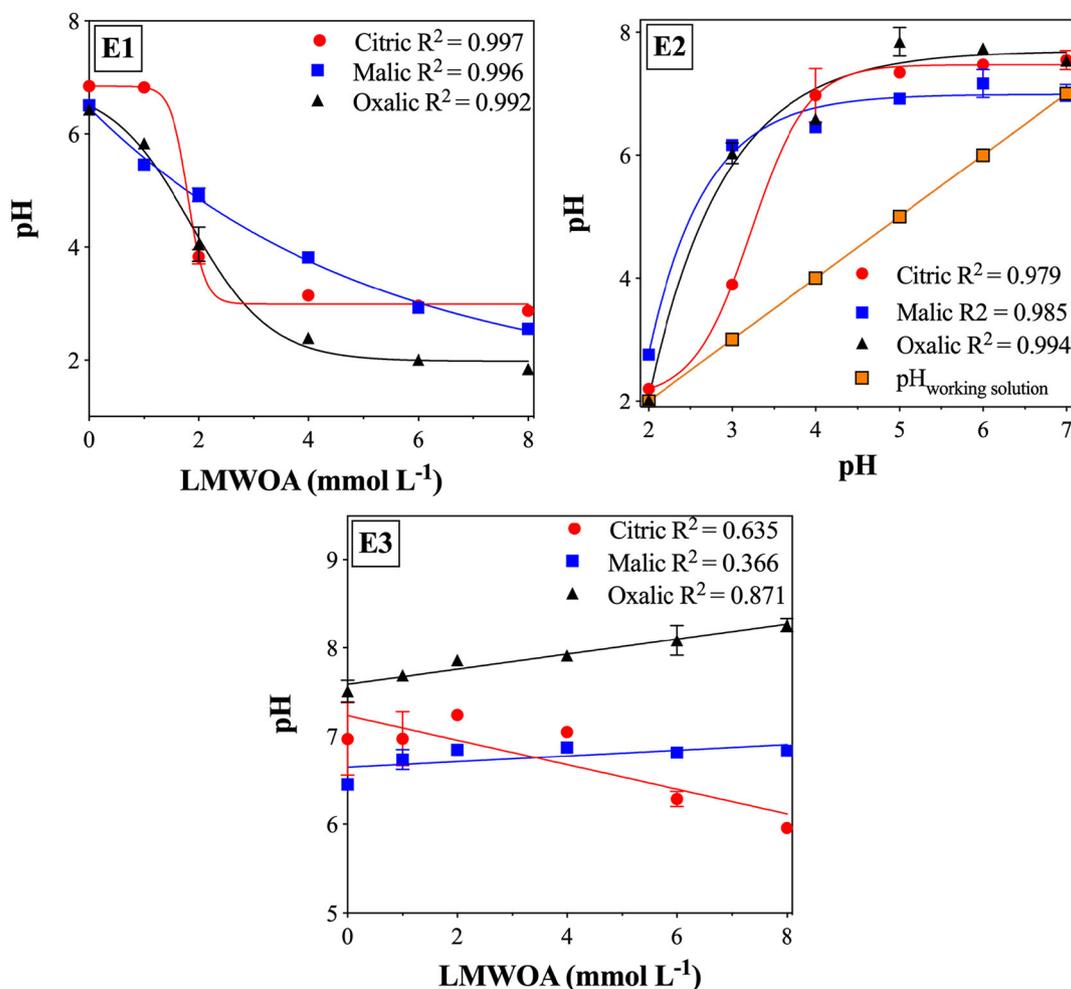


Fig. 2. The variation of pH in the LMWOAs supernatants in the As-enriched group of this study (no significant difference was found in the pH between the As40 group and the As0 group, data of As0 group not shown).

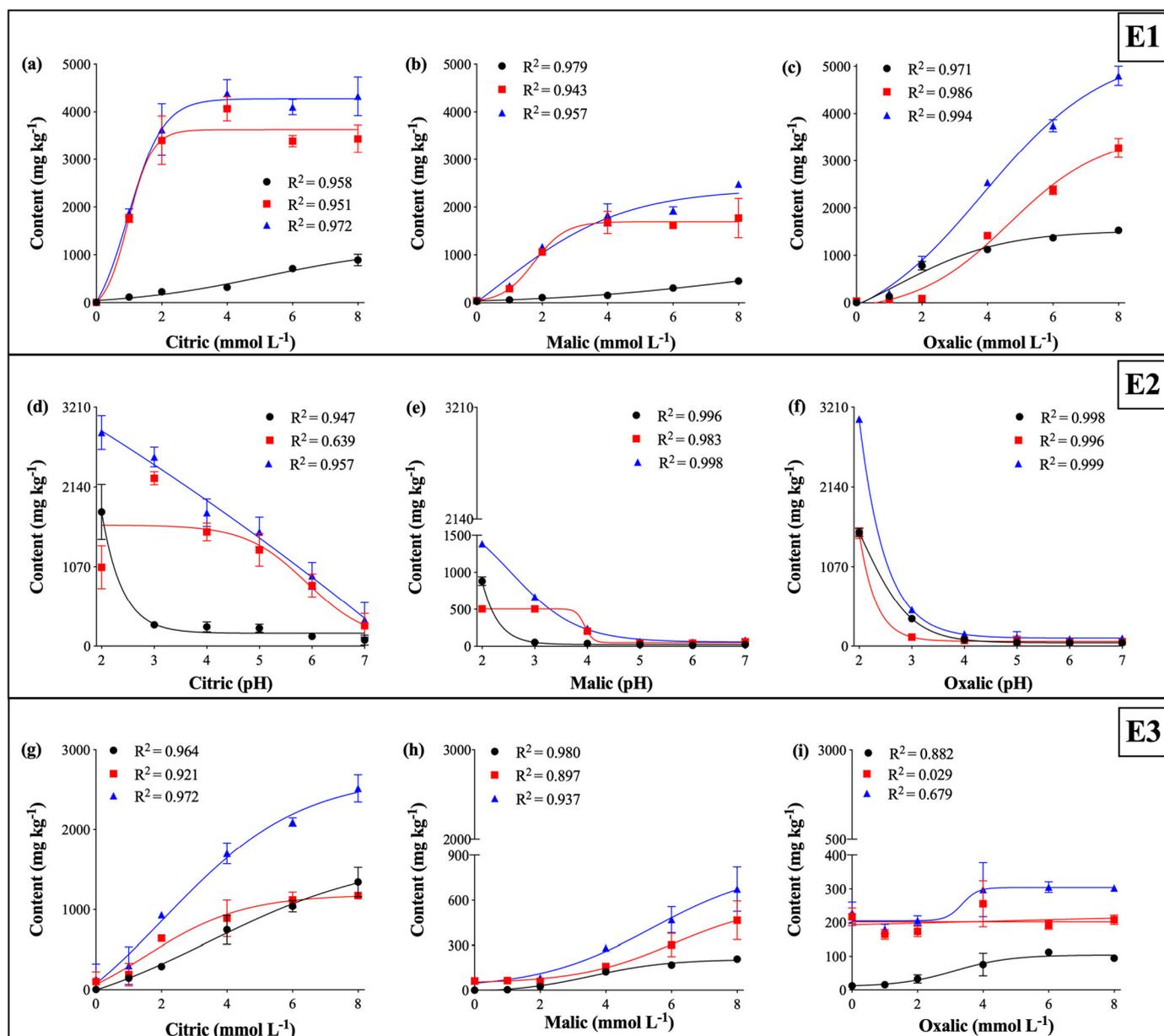


Fig. 3. The content of Fe species supernatant in the As-enriched group; A, B, C for E1; D, E, F for E2; G, H, I for E3. Fe (II) = black circle; Fe (III) = red square; total Fe = blue triangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

pKa (acid dissociation constant) of citric acid (3.13, 4.76, 6.40), malic acid (3.46, 5.11), and oxalic acid (1.23, 4.19); and 3) the physicochemical properties of the sediments such as the content of Fe/Al minerals (Onireti et al., 2017).

4.2. Cooperation with Fe species and its influences

The substantial Fe content ($4.03 \pm 0.30 \text{ g kg}^{-1}$, Table 1) present in mangrove sediments (Fe oxide, Fe hydroxide, and Fe minerals, etc.) is closely related to the behavior of As, including in the neutralization reactions of the (co-)precipitation of secondary Fe/Mn/Al oxyhydroxides (Vitkova et al., 2015). There was a positive correlation between the As and Fe species in the supernatant (Fig. 5, except for oxalic acid in E3). Values of R^2 (Pearson correlation) for Fe and As ranged from 0.770–0.973; Fe (II) vs. As: 0.515–0.931 and Fe (III) vs. As: 0.700–0.987 (Fig. 5i is not included, $p > 0.05$). It may suggest that LMWOAs extracted As and Fe species from the sediments through the dissolution of Fe compounds (Lu et al., 2007). Fe complexes play an

essential role as adsorbents in soil adsorption, such as when dissolved soil-borne Fe binds arsenate and heavy metals (Onireti et al., 2017). This mechanism may involve two pathways: 1) the interaction of As with exchangeable Fe to form As-Fe compounds directly; and 2) the coupling adsorption and co-precipitation of Fe compounds (oxide/hydroxide, amorphous Fe, etc.) with sediment-borne As (Onireti et al., 2017).

Amorphous Fe and poorly-crystallized Fe have a strong affinity for heavy metal(oid)s (Tu et al., 2004). As has been demonstrated associate with amorphous and poorly-crystalline Fe and Al hydrous oxides (Wu et al., 2016). For instance, Pb and As in the soil extracted by organic acids were significantly affected by Fe content (Feng et al., 2013). Our results also showed higher pHs weaken Fe species extraction (Fig. 3, E2). These processes were also closely associated with Fe compounds, such as in the chemical co-precipitation between As (III) and FeS at pH = 5, while surface adsorption replaced it at pH > 6 (Onireti and Lin, 2016).

The amounts of Fe species and As in the supernatant extracted by

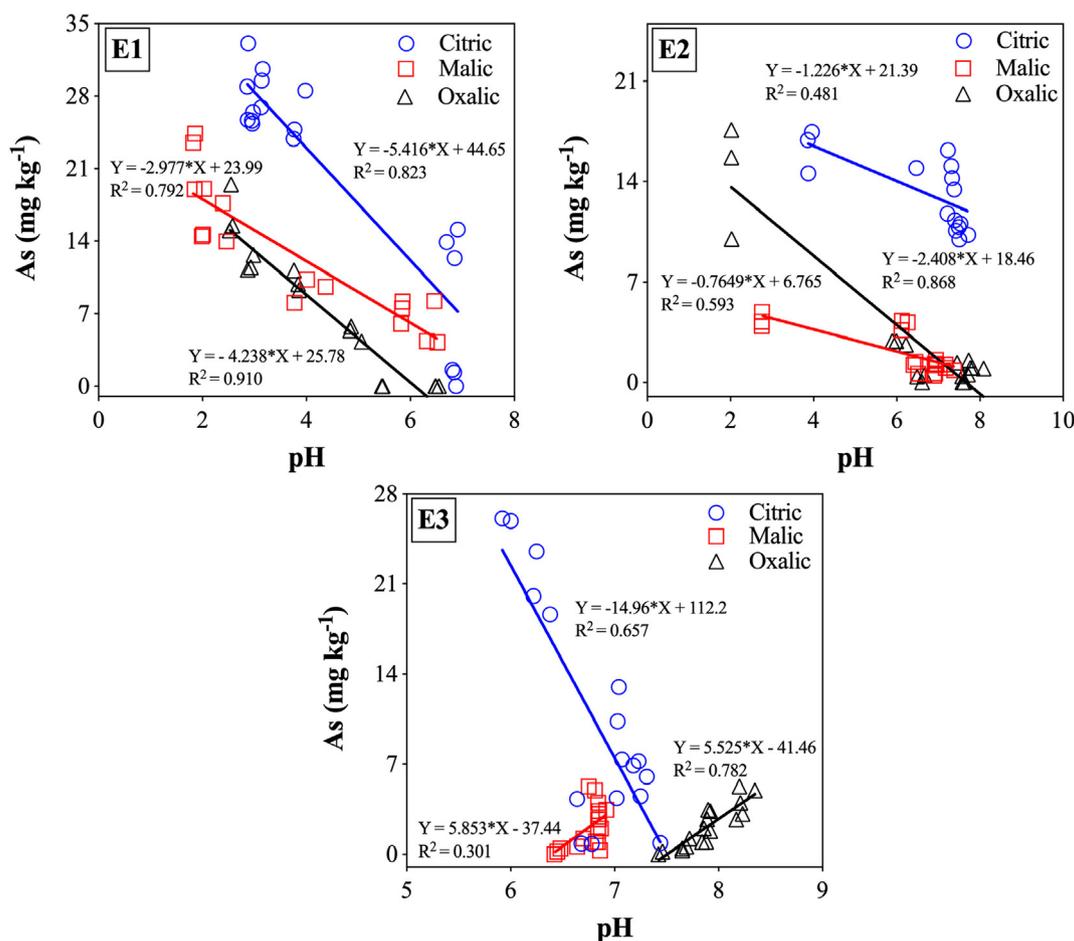


Fig. 4. The plots of the supernatant pH vs. As in the As-enriched group.

oxalic acid at the same pH value of 5 were extremely low (Fig. 5i), indicating that insoluble Fe oxalates and oxalate surface complexes were probably formed when the oxalate concentration was insufficient (Vitkova et al., 2015). In comparison to E1, in E3 the solubility of Fe oxalate decreased as pH increased (Fig. 3c, i). The low concentration of oxalic acid meant that Fe-oxalate co-precipitates formed, while soluble Fe oxalate was generated at higher concentrations (Tu et al., 2004; Onireti and Lin, 2016). This may be due to the direct generation of HO[•] induced by dissolved ferric ion (Wang et al., 2013). The marked drop in As supernatant in malic acid and oxalic acid in E2 indicates that the concentration of 2 mmol L⁻¹ was too low to effectively extract sediment As or mobilize Fe species (Fig. 3e, f). The dissolution of Fe oxides could be facilitated by the formation of soluble Fe-ligand complexes when abundant concentrations of LMWOAs are present (Onireti et al., 2017). However, unstable chelates of carboxyl groups and heavy metals affect the adsorption of sediments (Panias et al., 1996), due to factors such as space size and the number of carboxyl (-COOH) and phenolic (-OH) functional groups. The formation of soluble complexes affects the bioavailability of heavy metals and alters their toxicity in the rhizosphere (Jones, 1998).

4.3. Other possible influential factors

Apart from the mechanisms mentioned above, LMWOA acidification is another major factor affecting the rhizosphere. LMWOAs can acidify and decrease the pH of the rhizosphere through nutrient uptake and coupling protons near roots as a result of ion imbalances (Mench et al., 2010). This study found a significant negative correlation between pH and As ($p < 0.001$). However, no significant difference ($p > 0.05$) in

supernatant pH was observed among the three LMWOAs in E1, although there were differences in the As and Fe species (Table 2). These results indicate that the pH effects of LMWOAs themselves may not be the most important factor in regulating the mobilization and migration of As and heavy metals. Another noteworthy finding is that the number of carboxyl groups and protons on the organic ligand increased the surface area of the binding sites in contact with the sediments and led to the migration of As and Fe into the solution. Total organic matter ($12.56 \pm 0.74\%$, in this study) in the sediments plays a vital role in controlling As bioavailability (Chakraborty et al., 2012a).

A positive correlation between the supernatant As content and the pH of malic acid and oxalic acid was found in E3, whereas the opposite was found for citric acid ($p < 0.05$, Fig. 4, E3). These results were consistent with the correlation between supernatant pH and LMWOA concentration (Fig. 2, E3). This means that the acid-neutralizing capacity of both malic and oxalic acids was attenuated at the given pH (=5) and the protons introduced by the LMWOAs were mostly consumed by the sediments. The reductive and non-reductive dissolution of Fe is crucial to the release of As (Han et al., 2011). Plus, the dissolved organic matter contained in mangrove sediments can also interact with Fe/Al colloids, and their binding influence may indirectly increase the mobilization of metals in a soil solution (Onireti et al., 2017).

4.4. Predictive desorption model

Details of the mechanisms involved in the relationship between pH, As, and LMWOAs are as yet unknown. However, as shown in Fig. 6, from the semi-empirical kinetic reaction model (Eq. (4)) proposed in this study, it was found that E1 (R^2 ranging from 0.88 to 0.92) and E3

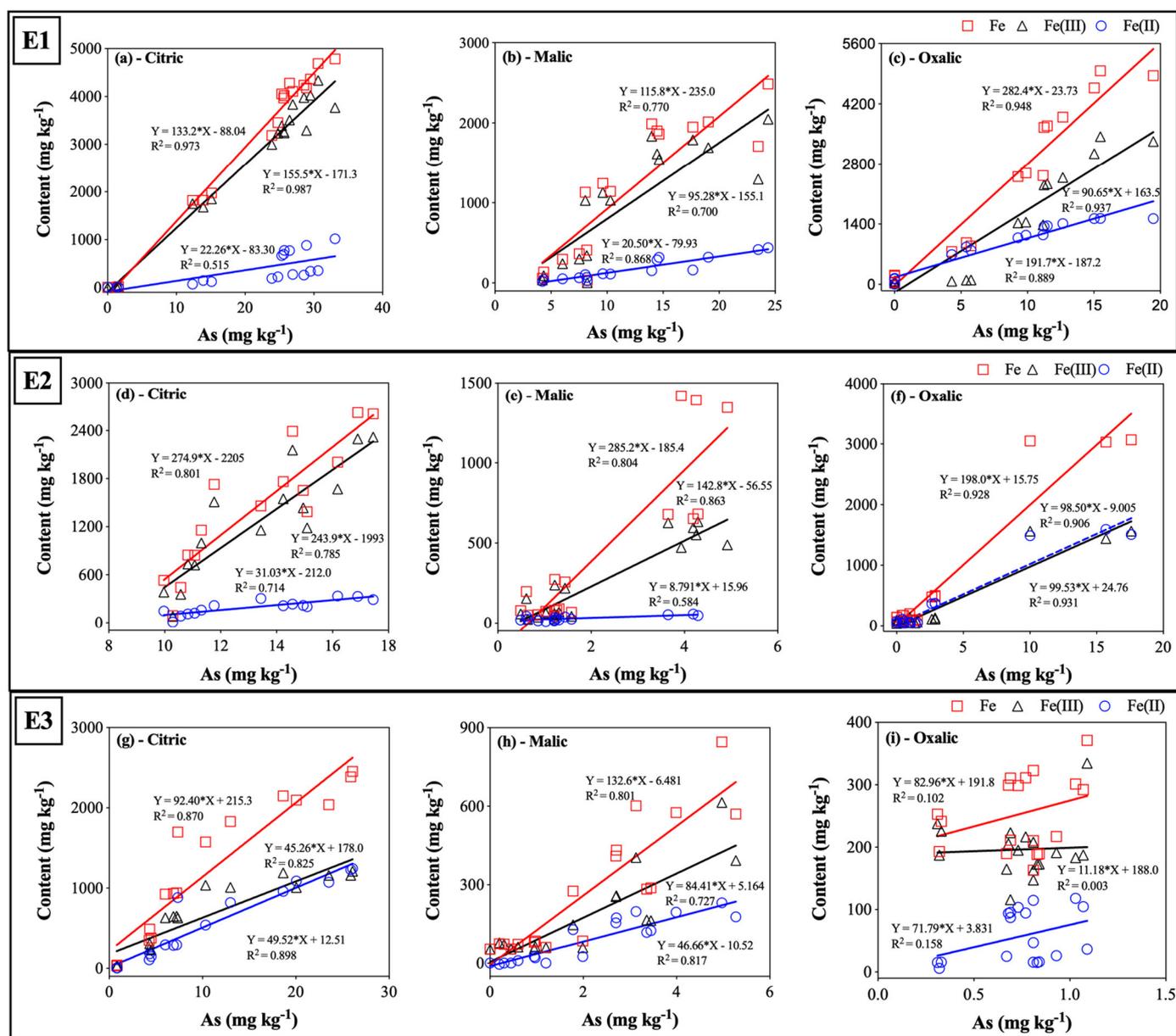


Fig. 5. The plots of As vs. Fe species in the supernatants for A, B, C of E1; D, E, F of E2; G, H, I of E3 in the As-enriched group. Fe (II) = blue circle; Fe (III) = cyan triangle; Fe = red square. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(R^2 ranging from 0.64 to 0.95) both displayed good correlations ($p < 0.001$) using multiple regression analysis. The poor relationship in E2 (range of R^2 : 0.08–0.43) may be attributable to the same and low concentration of LMWOs. No statistical significance was observed for citric acid extraction in E2, and malic acid ($R^2 = 0.4301$, $p = 0.006$) and oxalic acid ($R^2 = 0.2904$, $p = 0.03$) both showed obvious effects affected with the same concentration of LMWOs (Fig. 6, E2), indicating that the desorption of As was tightly connected with all three regulatory factors of pH value along with the type and concentration of the LMWOs.

5. Conclusion

The results of this study indicate that the bioavailability of As and Fe species significantly increased ($p < 0.001$) with the addition of root exudates. The As levels in supernatants extracted by the three LMWOs at the same concentration were in the following order: citric acid > malic acid/oxalic acid. At the same pH, As extraction exhibited the

trend: citric acid > malic acid > oxalic acid. The As supernatant concentration was significantly positively correlated with LMWOA concentration and negatively correlated with supernatant pH. The mobilization and migration of As were closely related to the dissolution of Fe species. The results suggest that the promotion by LMWOAs of the release of As sediment may occur via the dissolution of Fe compounds. Increasing the pH boosted the capacity of the dissolved Fe compounds to co-precipitate with As and be transferred from the LMWOA solution to the solid phase. These results suggest that the use of organic acids as activating and chelating agents for heavy metals such as As deserves more attention in the remediation and treatment of heavy metal pollution in mangrove wetlands.

CRedit authorship contribution statement

Kang Mei: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Writing - original draft, Writing - review & editing. **Jingchun Liu:** Writing - review & editing, Funding

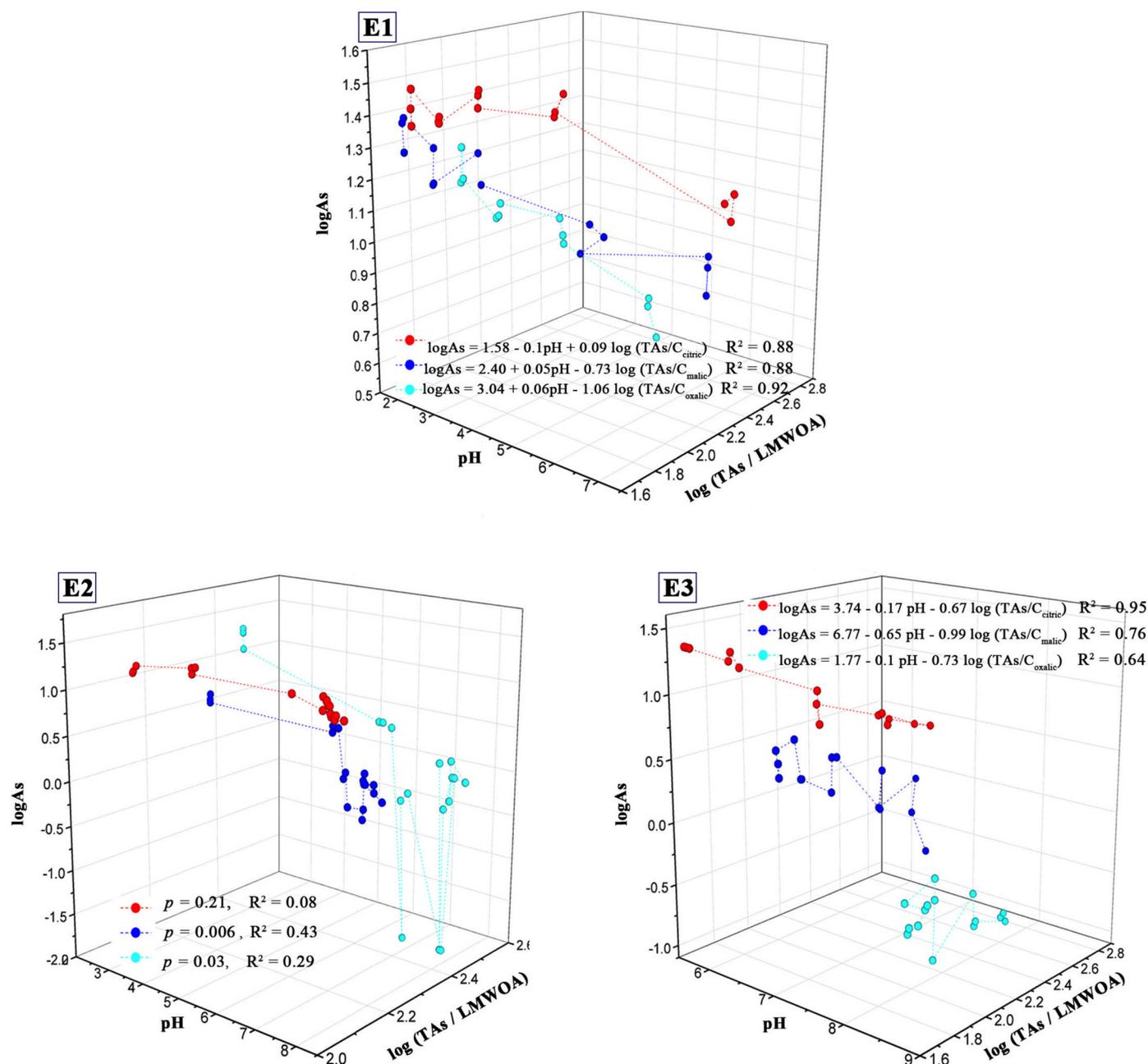


Fig. 6. The 3D plots of the predictive equation were shown among supernatant As, supernatant pH, and concentration of LMWOA in this study (n = 18), red = citric acid; blue = malic acid; cyan = oxalic acid. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

acquisition, Project administration, Resources, Supervision, Validation. **Rongrong Shi:** Visualization, Investigation. **Xin Guo:** Writing - original draft, Writing - review & editing, Investigation. **Haoliang Lu:** Writing - review & editing, Funding acquisition, Project administration, Resources, Supervision, Validation. **Chongling Yan:** Writing - review & editing, Funding acquisition, Project administration, Resources, Supervision, Validation.

Declaration of competing interest

No conflict of interest exists in the submission of this manuscript, and the manuscript is approved by all authors for publication.

Acknowledgments

This research was funded by the major program of National Natural

Science Foundation of China (31535008) and National Important Scientific Research Program of China (2018YFC1406603). We wish to thank the anonymous reviewers for their constructive comments to improve the manuscript.

References

- Agnello, A.C., Huguenot, D., Van Hullebusch, E.D., Esposito, G., 2014. Enhanced phytoremediation: a review of low molecular weight organic acids and surfactants used as amendments. *Crit. Rev. Environ. Sci. Technol.* 44, 2531–2576.
- Bodin, N., N'Gom-Ka, R., Ka, S., Thiaw, O.T., de Morais, L.T., Le Loch, F., Rozuel-Chartier, E., Auger, D., Chiffolleau, J.F., 2013. Assessment of trace metal contamination in mangrove ecosystems from Senegal, West Africa. *Chemosphere* 90, 150–157.
- Chakraborty, P., Babu, P.V.R., Sarma, V.V., 2012a. A new spectrofluorometric method for the determination of total arsenic in sediments and its application to kinetic speciation. *Int. J. Environ. Anal. Chem.* 92, 133–147.
- Chakraborty, P., Jayachandran, S., Babu, P.V.R., Karri, S., Tyadi, P., Yao, K.M., Sharma, B.M., 2012b. Intra-annual variations of arsenic totals and species in tropical estuary

- surface sediments. *Chem. Geol.* 322, 172–180.
- Das, S., Chou, M.L., Jean, J.S., Yang, H.J., Kim, P.J., 2017. Arsenic-enrichment enhanced root exudates and altered rhizosphere microbial communities and activities in hyperaccumulator *Pteris vittata*. *J. Hazard. Mater.* 325, 279–287.
- Feng, Q., Zhang, Z., Chen, Y., Liu, L., Zhang, Z., Chen, C., 2013. Adsorption and desorption characteristics of arsenic on soils: kinetics, equilibrium, and effect of Fe(OH)₃ colloid, H₂SiO₃ colloid and phosphate. *Procedia Environ. Sci.* 18, 26–36.
- Gouda, M.M., Dawood, Y.H., Zaki, A.A., Ibrahim, H.A.S., El-Naggar, M.R., Gad, A., 2019. Adsorption characteristic of Cs⁺ and Co²⁺ ions from aqueous solutions onto geological sediments of radioactive waste disposal site. *J. Geochem. Explor.* 206.
- Han, Y.S., Jeong, H.Y., Demond, A.H., Hayes, K.F., 2011. X-ray absorption and photoelectron spectroscopic study of the association of As (III) with nanoparticulate FeS and FeS-coated sand. *Water Res.* 45, 5727–5735.
- Jia, H., Lu, H.L., Liu, J.C., Li, J., Dai, M.Y., Yan, C.L., 2016. Effects of root exudates on the leachability, distribution, and bioavailability of phenanthrene and pyrene from mangrove sediments. *Environ. Sci. Pollut. Res.* 23, 5566–5576.
- Johansson, E.M., Fransson, P.M.A., Finlay, R.D., van Hees, P.A.W., 2008. Quantitative analysis of root and ectomycorrhizal exudates as a response to Pb, Cd and As stress. *Plant Soil* 313, 39–54.
- Jones, D.L., 1998. Organic acids in the rhizosphere - a critical review. *Plant Soil* 205, 25–44.
- Kim, E.J., Baek, K., 2019. Selective recovery of ferrous oxalate and removal of arsenic and other metals from soil-washing wastewater using a reduction reaction. *J. Clean. Prod.* 221, 635–643.
- Lee, J.C., Kim, E.J., Baek, K., 2017. Synergistic effects of the combination of oxalate and ascorbate on arsenic extraction from contaminated soils. *Chemosphere* 168, 1439–1446.
- Leivuori, M., Niemistö, L., 1993. Trace metals in the sediments of the Gulf of Bothnia. *Aqua. Fennica.* 23.
- Li, R., Chai, M., Li, R., Xu, H., He, B., Qiu, G.Y., 2017. Influence of introduced *Sonneratia apetala* on nutrients and heavy metals in intertidal sediments, South China. *Environ. Sci. Pollut. Res. Int.* 24, 2914–2927.
- Li, J., Liu, J.C., Yan, C.L., Du, D.L., Lu, H.L., 2019a. The alleviation effect of iron on cadmium phytotoxicity in mangrove *A. marina*. Alleviation effect of iron on cadmium phytotoxicity in for mangrove *Avicennia marina* (Forsk.) Vierh. *Chemosphere* 226, 413–420.
- Li, J.Q., Chen, J.Y., Lu, T.T., Wang, Y., Zhang, H.J., Shang, Z.B., Li, D.L., Zhou, Y.M., Qi, Z.C., 2019b. Effects of low-molecular weight organic acids on the transport of graphene oxide nanoparticles in saturated sand columns. *Sci. Total Environ.* 666, 94–102.
- Li, X.C., Reich, T., Kersten, M., Jing, C.Y., 2019c. Low-molecular-weight organic acid complexation affects antimony (III) adsorption by granular ferric hydroxide. *Environ. Sci. Technol.* 53, 5221–5229.
- Lin, Y.S., Fan, J., Yu, J.F., Jiang, S., Yan, C.L., Liu, J.C., 2018. Root activities and arsenic translocation of *Avicennia marina* (Forsk.) Vierh seedlings influenced by sulfur and iron amendments. *Mar. Pollut. Bull.* 135, 1174–1182.
- Liu, X., Fu, J.W., Guan, D.X., Cao, Y., Luo, J., Rathinasabapathi, B., Chen, Y.S., Ma, L.Q., 2016. Arsenic induced phytate exudation, and promoted FeAsO₄ dissolution and plant growth in As-hyperaccumulator *Pteris vittata*. *Environ. Sci. Technol.* 50, 9070–9077.
- Lu, H.L., Yan, C.L., Liu, J.C., 2007. Low-molecular-weight organic acids exuded by Mangrove (*Kandelia candel* (L.) Druce) roots and their effect on cadmium species change in the rhizosphere. *Environ. Exp. Bot.* 61, 159–166.
- Lu, H.N., Sun, J.T., Zhu, L.Z., 2017. The role of artificial root exudate components in facilitating the degradation of pyrene in soil. *Sci. Rep.* 7, 7130.
- Ma, Y., Lin, C., 2012. Arsenate immobilization associated with microbial oxidation of ferrous ion in complex acid sulfate water. *J. Hazard. Mater.* 217–218, 238–245.
- Marschner, P., 2013. *Marschner's Mineral Nutrition of Higher Plants*, Second edition. Science Press.
- McBride, M., Sauve, S., Hendershot, W., 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *Eur. J. Soil Sci.* 48, 337–346.
- Mench, M., Morel, J.L., Guckert, A., Guillet, B., 2010. Metal binding with root exudates of low molecular weight. *Eur. J. Soil Sci.* 39, 521–527.
- Montiel-Rozas, M.M., Madejon, E., Madejon, P., 2016. Effect of heavy metals and organic matter on root exudates (low molecular weight organic acids) of herbaceous species: an assessment in sand and soil conditions under different levels of contamination. *Environ. Pollut.* 216, 273–281.
- Niu, Z.X., Li, X.D., Sun, L.N., Sun, T.H., 2013. Dynamics of three organic acids (malic, acetic and succinic acid) in sunflower exposed to cadmium and lead. *Int. J. Phytoremediat.* 15, 690–702.
- Nworie, O.E., Qin, J., Lin, C., 2017. Differential effects of low-molecular-weight organic acids on the mobilization of soil-borne arsenic and trace metals. *Toxics* 5, 18.
- Onireti, O.O., Lin, C.X., 2016. Mobilization of soil-borne arsenic by three common organic acids: dosage and time effects. *Chemosphere* 147, 352–360.
- Onireti, O.O., Lin, C.X., Qin, J.H., 2017. Combined effects of low-molecular-weight organic acids on mobilization of arsenic and lead from multi-contaminated soils. *Chemosphere* 170, 161–168.
- Panias, D., Taxiarchou, M., Paspaliaris, I., Kontopoulos, A., 1996. Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. *Hydrometallurgy* 42, 257–265.
- Phillips, L.A., Greer, C.W., Farrell, R.E., Germida, J.J., 2012. Plant root exudates impact the hydrocarbon degradation potential of a weathered-hydrocarbon contaminated soil. *Appl. Soil Ecol.* 52, 56–64.
- Sauve, S., Hendershot, W., Allen, H.E., 2000. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environ. Sci. Technol.* 34, 1125–1131.
- Sun, B.Q., Gao, Y.Z., Liu, J., Sun, Y.D., 2012. The impact of different root exudate components on phenanthrene availability in soil. *Soil Sci. Soc. Am. J.* 76, 2041–2050.
- Sun, H.F., Ma, R.Y., Nan, Y.L., Feng, R.J., 2019. Insight into effects of citric acid on adsorption of phthalic acid esters (PAEs) in mangrove sediments. *Ecotoxicol. Environ. Saf.* 169, 353–360.
- Tor, A., Danaoglu, N., Arslan, G., Cengeloglu, Y., 2009. Removal of fluoride from water by using granular red mud: batch and column studies. *J. Hazard. Mater.* 164, 271–278.
- Tu, S.X., Ma, L., Luongo, T., 2004. Root exudates and arsenic accumulation in arsenic hyperaccumulating *Pteris vittata* and non-hyperaccumulating *Nephrolepis exaltata*. *Plant Soil* 258, 9–19.
- Tu, S., Ma, L., Rathinasabapathi, B., 2011. Characterization of phytase from three ferns with differing arsenic tolerance. *Plant Physiol. Biochem.* 49, 146–150.
- Vitkova, M., Komarek, M., Tejnecky, V., Sillerova, H., 2015. Interactions of nano-oxides with low-molecular-weight organic acids in a contaminated soil. *J. Hazard. Mater.* 293, 7–14.
- Wang, S., Mulligan, C.N., 2013. Effects of three low-molecular-weight organic acids (LMWOAs) and pH on the mobilization of arsenic and heavy metals (Cu, Pb, and Zn) from mine tailings. *Environ. Geochem. Health* 35, 111–118.
- Wang, Y.J., Xu, J., Li, J.J., Wu, F., 2013. Natural montmorillonite induced photooxidation of As (III) in aqueous suspensions: roles and sources of hydroxyl and hydroperoxyl/superoxide radicals. *J. Hazard. Mater.* 260, 255–262.
- Wang, W.Y., Zhang, X.F., Huang, J., Yan, C.L., Zhang, Q., Lu, H.L., Liu, J.C., 2014a. Interactive effects of cadmium and pyrene on contaminant removal from co-contaminated sediment planted with mangrove *Kandelia obovata* (S., L.) Yong seedlings. *Mar. Pollut. Bull.* 84, 306–313.
- Wang, Y.Y., Fang, L., Lin, L., Luan, T.G., Tam, N.F.Y., 2014b. Effects of low molecular-weight organic acids and dehydrogenase activity in rhizosphere sediments of mangrove plants on phytoremediation of polycyclic aromatic hydrocarbons. *Chemosphere* 99, 152–159.
- Wang, F.Y., Yang, W.W., Cheng, P., Zhang, S.Q., Zhang, S.W., Jiao, W.T., Sun, Y.H., 2019. Adsorption characteristics of cadmium onto microplastics from aqueous solutions. *Chemosphere* 235, 1073–1080.
- Wu, C., Zou, Q., Xue, S.G., Pan, W.S., Yue, X., Hartley, W., Huang, L., Mo, J.Y., 2016. Effect of silicate on arsenic fractionation in soils and its accumulation in rice plants. *Chemosphere* 165, 478–486.
- Xing, X.G., Ding, S.M., Liu, L., Chen, M.S., Yan, W.M., Zhao, L.P., Zhang, C.S., 2018. Direct evidence for the enhanced acquisition of phosphorus in the rhizosphere of aquatic plants: a case study on *Vallisneria spiralis*. *Sci. Total Environ.* 616, 386–396.
- Yang, D., Liu, J.C., Wang, Q., Hong, H.L., Zhao, W.W., Chen, S., Yan, C.L., Lu, H.L., 2019. Geochemical and probabilistic human health risk of chromium in mangrove sediments: a case study in Fujian, China. *Chemosphere* 233, 503–511.