Science of the Total Environment 775 (2021) 145685

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Low-level arsenite boosts rhizospheric exudation of low-molecular-weight organic acids from mangrove seedlings (*Avicennia marina*): Arsenic phytoextraction, removal, and detoxification

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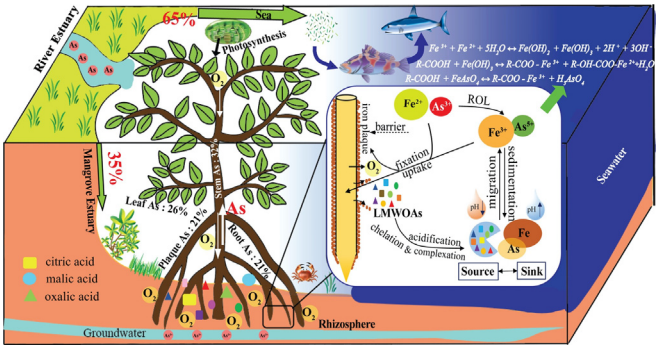
HIGHLIGHTS

- Low-level trivalent arsenite boosts LMWOAs exudation of mangroves to reduce arsenic toxicity.
- Citric, oxalic and malic acid were the three main components (84.3%–86.8%) of root exudates.
- The As tolerance mechanisms include lowering ROL, translocating As, releasing LMWOAs, and facilitating As fixation.
- *A. marina* seedlings are potentially propitious to As phytoextraction, removal and detoxification.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 October 2020
Received in revised form 2 February 2021
Accepted 3 February 2021
Available online 6 February 2021

Editor: Charlotte Poschenrieder

Keywords:
Root exudates
Fe species
Radial oxygen loss
Arsenic translocation
Migration and speciation
Mangrove wetland

ABSTRACT

Arsenic (As) contamination in mangrove wetlands has become a major concern. However, the impact of As on mangroves and the rhizospheric mechanism remains unclarified. In this study, various properties and responses of mangrove seedlings were investigated after exposure to arsenite (As^{3+}). The results indicate that low-level As promoted the secretion of Low-molecular-weight organic acids (LMWOA, 4.5–6.59 mg/kg root in dry weight) and Fe plaque formation in their rhizospheres. Citric, oxalic, and malic acid were the three main components (84.3%–86.8%). Low-level As (5 and 10 μmol/L) also inhibited the rate of radial oxygen loss (ROL) but increased the accumulation of plant As (stem > leaf > root) and plaque As (0.23–1.13 mg/kg root in dry weight). We selected model LMWOAs to further examine As migration and speciation over time in As-enriched sediments (0, 20 and 40 mg/kg). The results reveal that LMWOAs promoted sediment As mobilisation and followed the order of citric acid > malic acid > oxalic acid. The hydrolysis and precipitation of Fe^{3+} and the complexation with organic ligand led to aqueous As and Fe sedimentation and, conversely, increased solution pH and re-translocated free As. The tolerance mechanisms include lowering ROL, translocating As and releasing LMWOAs to reduce its toxicity, and facilitating the fixation in sediment of oxidised As. The present study highlights the fact that mangroves are potentially favourable for As phytoextraction, removal and detoxification.

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https://doi.org/10.1016/j.scitotenv.2021.145685
0048-9697/

1. Introduction

Arsenic (As) is a ubiquitous, highly carcinogenic, and redox-active element apt to become enriched in wetland ecosystems based on cumulative trends (highest records = 152.4–199.7 mg/kg) (Huang et al., 2012; Li et al., 2017). Arsenic occurs abundantly in reducing sediments in the form of an inorganic oxyanion as arsenite (As^{3+}) and as arsenate (As^{5+}) in natural aerobic environments (Mestrot et al., 2011; Mandalk et al., 2019). However, conversion between the more toxic As^{3+} and the less toxic As^{5+} via redox is unable to remove As from sediments (Huang et al., 2012), but phytoextraction can effect favourable remediation. As species could enhance (As^{3+}, As^{5+}) or inhibit (dimethylarsinic acid, DMA) the release of low-molecular-weight organic acids (LMWOAs) in several tree species (Mleczek et al., 2018; Drzewiecka et al., 2019; Gąsecka et al., 2021), and promote As accumulation in the rhizosphere to activate phytoextraction and detoxification mechanisms (Johansson et al., 2008; Magdziak et al., 2020). To date, little information has been published concerning the pathways for As phytoextraction, translocation, migration behaviour and speciation in mangrove habitats. Consequently, the mechanisms involved in mangrove plant tolerance to As and their influence on the removal of As pollutants may have been overlooked.

LMWOAs derived from root exudates as dissolved organic matter (DOM; <10%) in soil and are actively or passively released into the mangrove rhizosphere (Lu et al., 2007; Borggaard et al., 2019; Sun et al., 2019). LMWOAs are involved in various rhizospheric processes, such as supplying plant nutrients (K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, PO_4^{3-}, and SO_4^{2-}) (Liu et al., 2017), facilitating the biodegradation of toxic pollutants (PAHs) (Jiang et al., 2017; Sivaram et al., 2019), altering the bioavailability of heavy metals (HMs) and metalloids (Xie et al., 2013; Chen et al., 2018), and modifying rhizospheric pH (Lu et al., 2007; Huang et al., 2020). Cd (13%) and Ni (28%) uptake by plant roots (*Thlaspi caerulescens* L. and *Alyssum bertolonii* (Desv)) are closely related to LMWOAs (Boominathan and Doran, 2003). LMWOAs have been found to form complexes with metal cations (Cd^{2+} and Fe^{2+}) resulting in the mobilisation of metal(loid)s in mangrove sediments (Xie et al., 2013; Jian et al., 2019). Furthermore, the exudation of phytosiderophores (complexes of low-molecular-weight amino acids) could promote Fe uptake at a lower cost in terms of carbon and energy (Oburger et al., 2014).

In tree physiology exposure to the As forms As^{3+}, As^{5+}, and DMA induce the elevated production of phenolic acids in photosynthetic tissue and roots in *Ulmus laevis* Pall, where phenolic acid levels correlate with the accumulation of organic As in roots and As^{3+} in leaves (Drzewiecka et al., 2018). Additionally, mutual interactions between As forms affect As phytoextraction. Gąsecka et al. (2021) reported that DMA causes the intense accumulation of As^{3+} and As^{5+} in common oak (*Quercus robur* L.). Similarly, in the case of plants (*Salix viminalis* L.) growing in (un)polluted mine sludges, the superbioconcentration of As, B, K, and Mg has been observed (Mleczek et al., 2018). However, the effects of root exudates (especially LMWOAs) on the biogeochemical behaviour of metal(loid) pollutants (such as As forms) in mangrove ecosystems have been received little attention.

Mangroves are located in the coastal intertidal wetlands of tropical and subtropical regions, and are well known to intercept substantial contaminants in maintaining ecological balance (Li et al., 2016; Lu et al., 2017). Mangrove wetlands are susceptible to HMs and metalloids pollution (retaining 35% of As) due to their high content of Fe and organic matter and low oxygen (O_2) content in muddy areas (Ferreira et al., 2010; Mandalk et al., 2019). A crucial adaptive strategy for mangrove roots is to release excessive O_2 into the surroundings to oxidise the rhizosphere (Mei et al., 2014) in a process referred to as radial oxygen loss (ROL). It has been reported that the tolerance of wetland plants to metal(loid)s such as As is related to their ROL (Mei et al., 2009). ROL oxidises rhizospheric Mn and Fe, inducing Fe plaque formation on root surfaces which serve as a physical barrier to prevent the absorption of metal(loid)s (As, Cd, and Pb) and even nutrients (N, P) (Liu et al., 2008; Mei et al., 2014; Nguyen et al., 2019). Therefore, the secretion of organic acids from mangrove roots is another vital complementary function in enhancing adaptation.

LMWOAs are the main components of root exudates and exhibit a comprehensive influence on mangrove plants and sediments based on complex mechanisms during As contamination. In the present study, the mangrove pioneer *Avicennia marina* (Forssk.) Vierh. was selected as a model wetland plant. The study aimed to: (1) elucidate the relationships among LMOWA exudation, As translocation in plants, ROL and Fe plaque formation; (2) investigate the effects of the most reactive LMWOAs on the mobilisation and desorption of As from the sediments; and (3) explore the influence of LMWOAs on As speciation from mangrove sediments under batch experimental conditions. Our study has the potential to improve understanding regarding phytoextraction and mangrove tolerance to As toxicity, and the rhizospheric behaviour of metalloid As-contaminated sediments in mangrove ecosystems.

2. Materials and methods

2.1. Pot cultivation

2.1.1. Mangrove growth

Young seedlings of *Avicennia marina* (Forssk.) Vierh. within breeding rhizoboxes were grown for three-months in pots cultivated with Hoagland solution containing inorganic As^{3+} ($NaAsO_2$). Each seed was germinated and grown in a cylindrical rhizobox (caliber * height = 10 cm * 9.5 cm) filled with acid-cleaned sea sand in greenhouse conditions of photosynthetically active radiation (PAR) = 800–1000 μmol/m^2/s, T = 25 °C, and light/dark = 12 h/12 h. Three rhizoboxes were placed in one pot (upper caliber * lower caliber * height = 29 cm * 20 cm * 18 cm) and immersed in 25% Hoagland's nutrient solution (2 L, prepared with deionized water) for the first week, and the concentration was increased by 25% once per week until 100% had been reached after one month. Then, different amounts of arsenite were added using $NaAsO_2$ (0, 5, 10, 20, and 30 μmol/L), with each amount being applied in three replicates, and the plants were cultured for three months. The volume of nutrient solution was kept the same by homogenisation and the addition of deionized water every week.

2.1.2. Root exudates

The method used for the collection and processing of root exudates from *A. marina* was adopted from previous work (Lu et al., 2007; Oburger et al., 2014). Briefly, all impurities adsorbed on the root surface were removed as much as possible after the seedlings were first harvested, and the visible and clean roots of the seedlings were then immersed twice in an opaque beaker containing 200 mL of deionized water. The beaker was wrapped entirely in foil to ensure that the roots were in darkness and kept in a greenhouse illumination incubator for 6 h. The sample liquids containing root exudates were then filtered (0.45 μm) and frozen at −20 °C, before being concentrated to 1.5 mL in a freeze dryer (FE-1-50, Boyikang Co. Ltd., Beijing, China). The 0.2-μm samples were then filtered and stored in Agilent liquid vials (2 mL) at −80 °C until LMWOA analysis using high-performance liquid chromatography (Agilent 1200 series HPLC system, California, USA).

2.1.3. ROL

The rate of ROL of the mangrove seedlings was measured using the modified titanium (Ti^{3+})-citrate method (Mei et al., 2014), in which 200 mL of Hoagland's nutrient solution (deoxygenated by nitrogen blowing for 1 h) was poured into a 250 mL beaker. The bases of the clean roots were coated with paraffin oil to insulate against atmospheric O_2. The roots were then immersed in the nutrient solution, which had a 2-cm upper layer of paraffin oil, and 30 mL of titanium citrate was injected into the solution with a syringe. The control treatment involved no plants. All beakers were wrapped with foil to protect the roots from

light. After 6 h of light culture, the beakers were gently shaken, and solution samples were collected via syringes. The absorbance value of oxidised titanium (Ti^{3+}) was measured at 527 nm (UV–Vis Spectrometer; Beijing Ruili Co. Ltd., China), and then all roots were dried at 70 °C to measure their dry weight (DW, Heating and Drying Oven, Jinhong Co. Ltd., Shanghai, China). The amount of O_2 secretion of the entire root system was calculated according to a working curve made up of several known Ti^{3+} concentrations. The calculation formula was as follows:

$$\text{ROL } rate\left(\mu mol\ O_2\ g^{-1}\ \text{root DW}\ day^{-1}\right) = \alpha^* \frac{(\beta-\gamma)}{4^* m} \quad (1)$$

where, α is the initial volume (L) of Ti^{3+}-citrate; β is the concentration (μmol/L) of Ti^{3+} in the blank (without plants), γ is the concentration (μmol/L) of Ti^{3+} after 6 h of incubation with plants, and m (g) is the root DW.

2.1.4. Fe plaque formation

Fresh roots were used for Fe plaque extraction using the citrate–bicarbonate–dithionite (CBD) method on the root surface of each mangrove seedling (Taylor and Crowder, 1983; Mei et al., 2014). The total As (plaque As) and total Fe (plaque Fe) in the Fe plaque were assessed by shaking with 0.03 mol/L tri-sodium citrate, 0.125-mol/L sodium bicarbonate and 1 g of sodium dithionite for 2 h (dithionite was added to keep the solution anaerobic). After extraction, the solutions were centrifuged at 8000 rpm for 5 min (Hetich Universal 320R Centrifuge, Germany) and then filtered (0.45 μm) before analysis. The root samples were dried and weighed as before.

2.1.5. As translocation in plants

Mangrove plants were used to separate the gathering of roots, stems, and leaves after the collection of root exudates and Fe plaque. Intact roots were carefully cut off from the aerial portion of the plants, and leaves were removed from the stems. Subsamples (~0.2 g) of three plant parts were weighed, freeze-dried (−50 °C), ground and then digested separately with HNO_3/H_2O_2 (120 °C for 6 h; High-Pressure Asher, Zhenghong Co. Ltd., Nanjing, China) (Poykio et al., 2000). The national standard reference material of bush plant (GBW-07603, China) was checked for procedural accuracy (recovery: 85%–115%). The digestion solution was made up to 50 mL with 5% HCl (V/V) and stored at −20 °C prior to analysis.

2.2. Effect of LMWOAs on sediment As mobilisation

2.2.1. Characteristics and preparation

Experimental sediments were collected from surface layers (within 30 cm) of the mangrove forest located in the Jiulong River estuary, Fujian, China (24° 24′ N, 117° 55′ E) on August 2017. The characteristics of these sediments have been described thoroughly elsewhere (Mei et al., 2020). The national standard reference material of soil (GBW-070310, China) was checked for procedural accuracy. The mixed and homogenised sediments (As background value = 14.8 ± 0.85 mg/kg) were added by means of an inorganic trivalent arsenite solution ($NaAsO_2$) up to 0 mg/kg (DW) As (As0; control), 20 mg/kg As (As20) and 40 mg/kg As (As40).

2.2.2. Extraction of As from sediments with LMWOAs

The maximum amounts of secreted LMWOAs (citric, malic, and oxalic acid) in the root exudates of seedlings were used as a measure to study As migration behaviour and species changes. The above three acids were selected as model LMWOAs for the batch experiments to examine the temporal migration behaviour of As in the sediment–liquid system. All treatments were carried out in 50-mL polyethylene centrifuge tubes containing 20 mL of 2-mmol/L LMWOA which acted as reactors. Fresh sediment samples of 0.5 g were placed in the tubes, after which each was shaken by a vortex oscillator for 30 s to blend the mixture. A sediment/LMWOA ratio which achieved complete desorption and extraction at equilibrium was aimed for based on the results of preliminary experiments (liquid/solid = 40/1).

2.2.3. Incubation conditions

All tubes were incubated in a rotary shaker (Saifu BHWY-200 Shaker) at 200 rpm and 25 °C in the dark for 6 h and 12 h and 1, 2, 4, 7 and 14 days. Each tube was centrifuged at 8000 rpm for 10 min after incubation. The supernatant was further passed through a 0.45-μm filter before analysis. Triplicated samples were collected to determine variations in As and Fe species (Fe^{2+}, Fe^{3+} and total Fe) as well as the pH of the supernatants.

2.2.4. Enrichment factor and extraction recovery

To better assess the extraction efficiency and migration effects of sediment As in the rhizosphere, calculations of the enrichment factor (EF) and extraction recovery (ER) were applied to evaluate the response dynamics at different LMWOA incubation times ($n = 3$) (Li et al., 2020). The higher the EF value, the greater the exposure risk. Conversely, the higher the ER value, the greater the accumulation coefficient of As in the sediments, and the lower the risk.

$$EF\ (\%) = \frac{aqueous\ As}{solid\ As} * 100 \quad (2)$$

where, *aqueous As* (mg/kg DW) is the As concentration in the LMWOAs solutions, and *solid As* (mg/kg DW) is the As concentration in the sediments.

$$ER\ (\%) = \frac{maximum\ As - aqueous\ As}{maximum\ As} * 100 \quad (3)$$

where, *aqueous As* is the same as above, and *maximum As* (mg/kg DW) is the maximum concentration of As in the LMWOAs solution.

2.3. Effects of LMWOAs on As speciation

2.3.1. Sediment treated with LMWOAs

To examine variations in As in the sediments and extracts affected by LMWOAs, citric, malic, and oxalic acid were selected and added to the high-level As sediment (As40) according to the previous incubation conditions for 6 h and 1, 4, and 14 days, as described above. After careful separation of the solid and liquid phases, variations in the supernatants were quantified using the same method as before.

2.3.2. As species assessment

The treatment procedure of sediment As species as been previously described (Giral et al., 2010; Huang et al., 2012) was used to calculate amounts of inorganic As^{3+} and As^{5+} in centrifugal sediments. In particular, 0.2 g fresh sediment samples were weighed with a microwave tube and a composite solution of 30 mL consisting of 1-mol/L orthophosphoric acid and 0.5-mol/L ascorbic acid was added to the tube under nitrogen-gas conditions. The mixtures were then subjected to microwave digestion, as in the previously described procedure. We used the standard addition method for the assessment of sediment arsenic speciation due to the lack of reference materials. Recovery levels (85%–115%) were acceptable for all the elements determined. The digested solutions were filtered (0.45 μm) and stored at −20 °C after centrifugation (8000 rpm; 5 min) until analysis.

2.4. Instrument analysis

LMWOAs concentration in root exudates was analyzed by HPLC using a modified method based on the description given in previous work (Lu et al., 2007). In summary, an Agilent 1200 Reverse phase-HPLC system was applied to analyze LMWOAs, equipped with an Agilent HC-C18(2) analytical column (4.6 * 250 mm, 5 μm) for sample

separation. The mobile phase consisted of A: 25 mmol/L KH_2PO_4 (pH = 2.4) and B: chromatographic methanol at a ratio of A: B = 98%: 2%. All LMWOA data were acquired at a flow-rate of 0.7 mL/min and detection wavelength of 210 nm. Ten commonly reported organic acids from root exudates were selected. Mixed standard solutions contain oxalic, tartaric, citric, succinic, malic, maleic, fumaric, formic, acetic, and lactic acids (see Fig. S1). The rate of ROL was determined at 527 nm with a UV–vis Spectrometer (Beijing Ruili Co. Ltd., China). Fe and As in iron plaque were measured using atomic absorption spectroscopy (AAS Vario 6, Thermo Fisher Scientific, USA) and atomic fluorescence spectrometry (AFS-930, Beijing Jitian Co. Ltd., China) respectively. The As concentration was diluted in 5% hydrochloric acid (V/V), reduced by thiourea for half an hour and measured by AFS with mobile phases consisting of NaOH and KBH_4. The concentration of ferrous ion (Fe^{2+}) in the acid solution was measured using 1,10-phenanthroline spectrophotometry at 510 nm. Total Fe in the solution was reduced to Fe^{2+} with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) and sulphuric acid. The content of trivalent iron (Fe^{3+}) was calculated by subtracting the Fe(II) from the total Fe. The pH of the sample solution was measured using a pH meter (Leici PHS-2F, Shanghai, China). Inorganic As species were analyzed by HPLC (Agilent 7500 HPLC System, California, USA) with simultaneous ICP-MS and electrospray ionization mass spectrometry (ESIMS, Agilent 6460 Triple Quadrupole LC/MS, California, USA). All chemical reagents applied in this study were of chromatographic grade.

2.5. Statistical analysis

Data processing and statistical analysis were performed using IBM SPSS Version 23.0 (SPSS Inc., Chicago, IL, USA). All data were transformed before testing to reach normal distribution (Shapiro-Wilk, $p > 0.05$) and the variances could be considered homogeneous (Levene's test, $p > 0.05$). One-way ANOVA followed by the *post-hoc* Duncan's test was performed to assess the significance of the parameters determined for objects investigated at $\alpha = 95\%$. To establish the significance of effects, the test was performed to investigate differences between mean values and standard error (S.E.) in triplicate. For the data that does not conform to a normal distribution, we used a nonparametric test (Kruskal-Wallis) to evaluate the significance of differences, e. g., As distribution in the plant. Spearman's correlation analysis was employed to determine relationships between variables. Graphs in the paper are drawn using Origin 9.0 and GraphPad Prism 8.

3. Results

3.1. Seedling response to As stresses in pot cultivation

3.1.1. LMWOAs exudation

The addition of As significantly enhanced the total LMWOAs secreted from the *A. marina* roots, except at the maximum concentration (Fig. 1A; $p < 0.05$). Citric acid, malic acid and oxalic acid were the

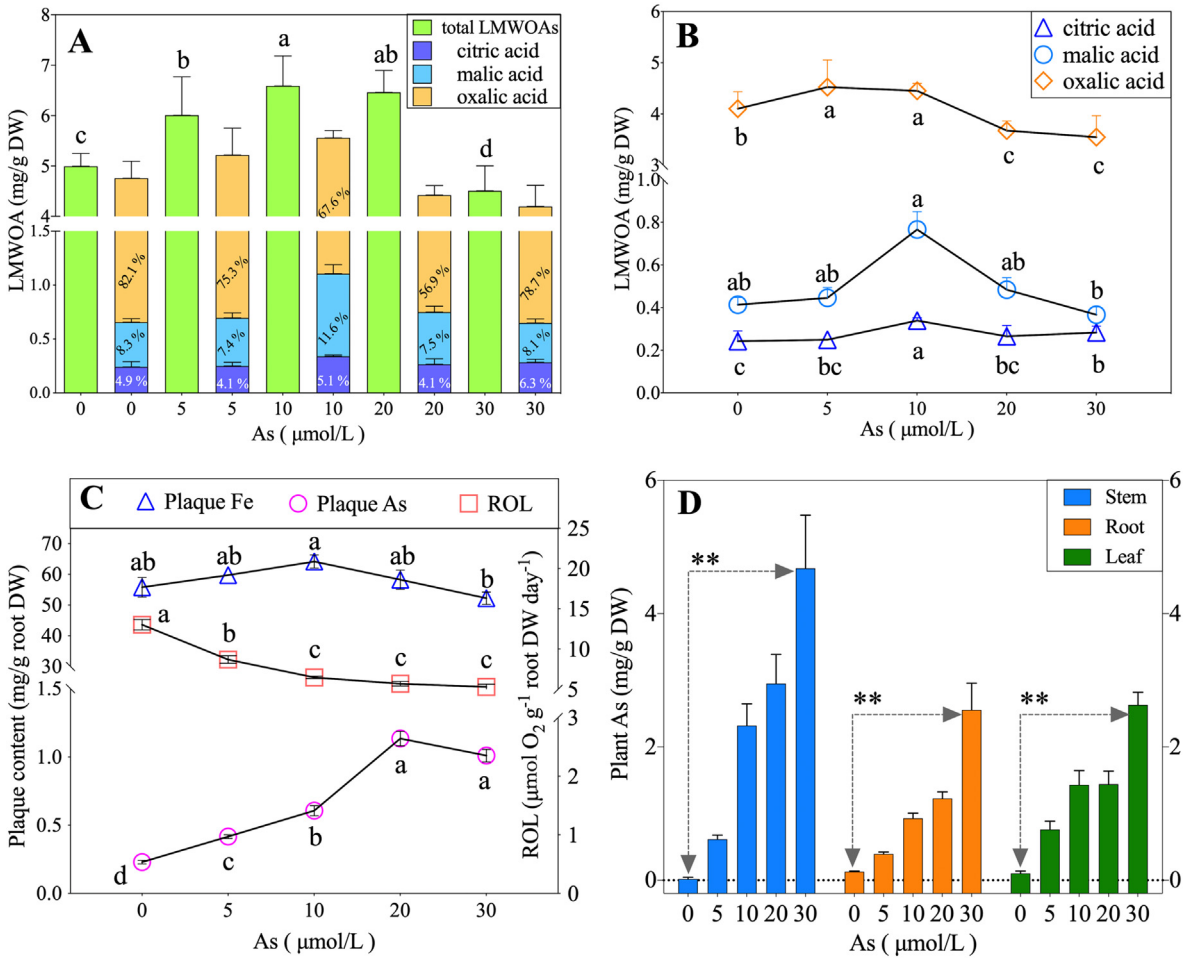

Fig. 1. The root exudation responses of mangrove seedlings under arsenite treatment in pot cultivation. **A**. the secretion of low molecular weight organic acids (LMWOA), LMWOAs were calculated as the relative concentrations to dry root weight (mg/g DW). **B**. variations of the most three abundant LMWOAs (oxalic acid > malic acid > citric acid); **C**. As and Fe concentration in iron plaque of root surface, rates of radial oxygen loss (ROL); **D**. As translocation in the plant parts of *Avicennia marina* seedlings. All data were transferred as concentrations in dry weight of plant (DW), Mean ± SE, n = 3; different letters in each treatment indicate significant differences among As doses at the level of $p < 0.05$. ** indicates that the significance at the 0.01 level is significant (two-tailed).

Table 1
The correlations among the determined parameters in pot experiment ($n = 15$). The significant correlations at 0.05 and 0.01 levels are marked in bold.

	Total acids	Citric acid	Malic acid	Oxalic acids	Other acid	Stem As	Root As	Leaf As	Plaque Fe	Plaque As
Total acids	1									
Citric acid	0.378	1								
Malic acid	**0.787**[b]	**0.738**[b]	1							
Oxalic acid	**0.536**[a]	0.235	**0.569**[a]	1						
Other acids	**0.873**[b]	0.386	**0.566**[a]	0.214	1					
Stem As	0.265	**0.580**[a]	0.248	−0.285	**0.563**[a]	1				
Root As	0.008	**0.519**[a]	0.068	**−0.518**[a]	0.338	**0.945**[b]	1			
Leaf As	0.186	**0.562**[a]	0.194	−0.304	0.472	**0.991**[b]	**0.961**[b]	1		
Plaque Fe	**0.758**[b]	**0.612**[a]	**0.737**[b]	**0.712**[b]	**0.636**[a]	0.150	−0.079	0.085	1	
Plaque As	0.112	0.324	0.028	**−0.628**[a]	0.452	**0.895**[b]	**0.936**[b]	**0.889**[b]	−0.175	1
ROL	−0.205	**−0.605**[a]	−0.194	0.385	**−0.528**[a]	**−0.958**[b]	**−0.965**[b]	**−0.954**[b]	−0.144	**−0.908**[b]

[a] Indicates that the correlation at the 0.05 level is significant (two-tailed).
[b] Indicates that the correlation at the 0.01 level is significant (two-tailed).

three major LMWOA components, constituting over 70% of the total LMWOAs (Fig. 1A). The two lowest concentrations of As (especially 10 μmol/L) acted to promote the release of the three acids, while the highest concentration (30 μmol/L) did not (Fig. 1B).

3.1.2. Rates of ROL

The As treatment significantly reduced the rate of ROL compared with the control (Fig. 1C; $p < 0.01$). In particular, the maximum ROL value of the mangrove seedlings in the control was double the minimum ROL value in the highest As treatment (30 μmol/L). Negative relationships were found among rates of ROL, root As, stem As, leaf As, and As in Fe plaque (Table 1; $p < 0.05$). However, Fe concentration in the Fe plaque showed no significant correlation with ROL (Table 1).

3.1.3. As and Fe in Fe plaque

The As and Fe concentrations in the Fe plaque demonstrated a different trend, with the Fe concentration increasing insignificantly ($p > 0.05$) and then decreasing gradually after the highest value (10 μmol/L). At the same time, a continuous upward trend was found in plaque As concentration (Fig. 1C). The exudation of LMWOAs was positively correlated with plaque Fe (Table 1). However, there was no evidence of correlation between plaque Fe and plaque As ($p > 0.05$).

3.1.4. As translocation in the plants

The total As concentrations in the plants were detected from various gradient As treatments (Fig. 1D). In comparison with the control groups, As levels in plants significant increased ($p < 0.01$) after As treatment at the highest concentration (30 μmol/L, Fig. 1D). An ascending trend was found, reflecting increases in As content in the stems, roots, and leaves with increasing concentration of As (Fig. 1D). The accumulation and distribution of As in the plants decreased in the order of stem > leaf > root (mean values).

3.2. Variations in LMWOAs extracts after sediment incubation

3.2.1. Solution As

Under LMWOA and As treatments, the As concentration in acid solution exhibited a general decreasing trend (Fig. 2). The As concentration extracted from mangrove sediments by the three LMWOAs revealed the following order: citric acid > malic acid > oxalic acid (Table S3). The As concentration significantly increased through As addition ($p < 0.01$) to the LMWOAs extracts and showed the following decreasing trend: As40 > As20 > As0. The total As levels in the citric acid extracts were 2.88 and 4.16 times those in the malic and oxalic acids respectively (Table S3). At day 14 of the citric acid group, there were no significant differences in solution As among the three As treatments (Fig. 2A), while malic acid and oxalic acid showed the same behaviour at day 7 (Fig. 2B) and day 2 (Fig. 2C), respectively. The As content was always below the detection limit in the extracts after 14 days irrespective of the nature of the LMWOA extraction (data not shown). The maximum peak values of As in the three LMWOA groups all occurred at 6 h for the As40 group and 12 h for the As20 group (Fig. 2).

3.2.2. Solution pH

After incubation, the solution pH of the three acids clearly increased (Fig. 4A, B, and C) and was negatively correlated ($p < 0.01$) with As concentration (Fig. 4D, E, and F). It is apparent that the higher the As addition, the greater the correlation coefficient (As40 > As20 > As0; Fig. 3). However, no significant differences were found among the As0, As20, and As40 groups ($p > 0.05$). The mean R^2 values regarding the correlation with pH variation of the three LMWOAs ranged from 0.84 to 0.86. The As in the solution of citric (R^2: 0.67–0.85) and malic acids (R^2: 0.45–0.62) showed a linear correlation with pH (except for As20 in the malic acid), while the As in oxalic acid showed a nonlinear correlation with pH (R^2: 0.39–0.94). The higher the As content, the stronger the correlation (Figs. 4D, E, and F).

3.2.3. Solution Fe species

The concentrations of Fe species in response to the LMWOAs were also determined in the extracts (Fig. S2). Under LMWOA treatment, the order regarding Fe and Fe^{3+} concentrations were as follows for both: citric acid > malic acid > oxalic acid (not significant between the latter two regarding extracted Fe levels). The concentration of Fe^{2+} followed the order of oxalic acid > malic acid > citric acid (Table S3, $p < 0.05$). However, there were no significant differences in Fe species concentrations under As treatment ($p > 0.05$). In general, the concentration of Fe species decreased gradually after reaching a peak within one day, with the exception of the Fe^{2+} extracted by malic acid which increased for seven days (Fig. S2A). It is worth mentioning that at the 7th and 14th days after exposure, either only a scarce amount of Fe in the extracts could be detected or the Fe level was below the detection limit. Results for the ratio of Fe^{3+} to Fe^{2+} revealed that significantly more Fe^{3+} was dissolved in the citric acid compared with the other two acids (Fig. S3). Reductive Fe^{2+} was a major part of the oxalic (12 h–14 d) and malic acid treatments (2–14 d; Figs. S2; S3).

3.2.4. Enrichment factor and extraction recovery

The EF decreased with increments of incubation time, and ER increased with time for all the LMWOAs treatments (Fig. 5). Thus, the results indicate that citric acid had a significantly higher proportional contribution to the transfer of sediment As. The ER results also revealed that after two weeks of incubation, the extracted As in the supernatants (aqueous phase) all returned to the sediments (solid phase; Fig. 5).

3.3. As speciation in sediments and changes in LWMOA solutions

3.3.1. Changes in LWMOA solutions

Variations in the LMWOA extracts and As speciation in the sediment under LMWOA treatment after incubation are presented in Table 2. The changes in As in the supernatant are consistent with the results

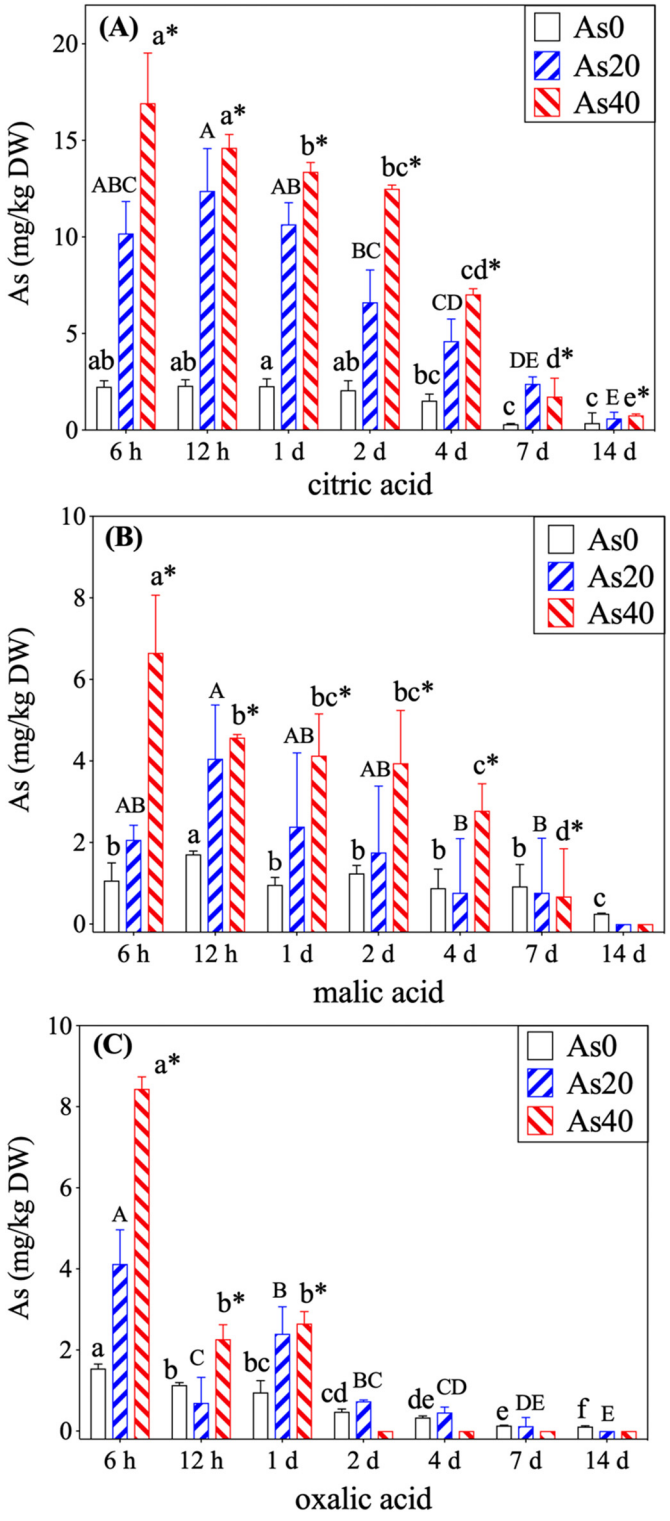

Fig. 2. As concentration in the LMWOAs extracts. As concentration was calculated as values extracted from dry sediments (mg/kg DW). Deionized water extraction was used as the control, but all below the detection limit. Mean ± SE, $n = 3$; different letters in each As-group denote significant differences ($p < 0.05$).

described above. The results collected from all the LMWOA solutions after incubation revealed that Fe^{3+} was the main Fe species at the beginning of exposure (6 h; Table 2). However, Fe^{2+} then increased and exceeded Fe^{3+} to become the main Fe species after four days of incubation for malic acid and after one day of incubation for oxalic acid (Table 2). The total Fe and total As both reached peak values after one day of incubation in all treatments. The solution pH in the extracts increased over incubation time, and the final stage (14 d) was close to neutral (Table 2).

3.3.2. As speciation in sediments

Speciation analysis of the sediments revealed that inorganic As^{3+} and As^{5+} were the dominant species in most of the incubation treatments. No organic species such as monomethylarsonic acid (MMA) or dimethylarsonic acid (DMA) were detected. The three LMWOAs all slightly (but not significantly) altered the concentration of As^{3+} in the sediment. The percentage of As^{5+} in the sediment after LMWOA extraction was in all cases much higher than that of As^{3+}, except after exposure to citric or malic acid after one day of incubation (Fig. 6). The As concentrations decreased in the aqueous phase, while inorganic As^{5+} concentrations increased in the sediments. At the same time, levels of inorganic As^{3+} were not significantly altered (Table 2, Fig. 6). It is unclear why there was no significant difference in the unknown part of the As species in the sediments irrespective of incubation of time ($p > 0.05$; Table 2).

4. Discussion

4.1. Plant response during pot cultivation

The present study has found that inorganic As^{3+} treatment associated with the exudation of LMWOAs and low-level As (5 or 10 μmol/L) increased LMWOA secretion in the roots of *A. marina*. This indicates that low-level As could probably alleviate the toxicity of As during the early growth stages of mangrove seedlings. The results show that, under As treatment, citric acid (4.1%–6.3%), malic acid (7.4%–11.6%) and oxalic acid (56.9%–82.1%) were predominantly released. Similar results have been reported suggesting that the stress of both sufficiency (Pb, Cd, and As) and deficiency (Zn and P) of metal(loid)s significantly promote the exudation of oxalates (Hoffland et al., 2006; Johansson et al., 2008). LMWOAs facilitated the detoxification mechanisms of toxic metal(loid)s, including ligand binding and sequestration as well as adaptation and survival strategies (Yamaguchi et al., 2019; Magdziak et al., 2020). However, results for tree species and different forms of arsenic vary. A previous study reported that treatments of As species (As(III), As(V) and DMA) applied to *Acer platanoides* L. seedlings may have caused elevated exudation of LMWOAs and phenolic compounds in the rhizospheres (Magdziak et al., 2020). DMA inhibited LMWOAs biosynthesis in *Acer pseudoplatanus* L. and *Betula pendula* Roth roots and their rhizospheric exudation (Gąsecka et al., 2021). As treatment (As^{3+}, As^{5+}, and DMA) also caused increased production of phenolic acids in *Ulmus laevis* Pall (Drzewiecka et al., 2018). The high concentration of As enhanced phenolic acid in *Acer platanoides* L. and *Tilia cordata* Mill, while LMWOAs and glutathione were suppressed in the former tree species (Drzewiecka et al., 2019).

Furthermore, the occurrence and exudation of LMWOAs are related to the habitat characteristics of mangroves, such as Fe plaque formation on root surfaces and ROL due to a lack of O_2 (Cheng et al., 2015; Dai et al., 2017; Lin et al., 2018). Since a positive correlation was found between Fe plaque and total LMWOAs, our study indicates that Fe plaque may increase LMWOA exudation in response to nutrient intake. Although ROL plays a critical role in Fe plaque formation by oxidizing Fe^{2+}, we found that Fe content in the plaque was not significant (52.2 ± 2.01–64.2 ± 2.13 mg/kg root DW; Fig. 1D). This may be attributed to deficiencies in ferrous iron in the nutrient solutions. In addition, ROL has been shown to influence rhizosphere oxidation, enhancing the tolerance to unfavourable environmental stresses such as metal(loid)s pollution and mangrove waterlogging (Li et al., 2019; Cheng et al., 2020). Higher ROL has also been shown to lead to high oxidation and strong tolerance (McDonald et al., 2001; Mei et al., 2014). In the present study, As (III) exposure had adverse effects on the rate of ROL, and the tolerance of wetland rice plants to As is significantly inhibited by ROL (Mei et al.,

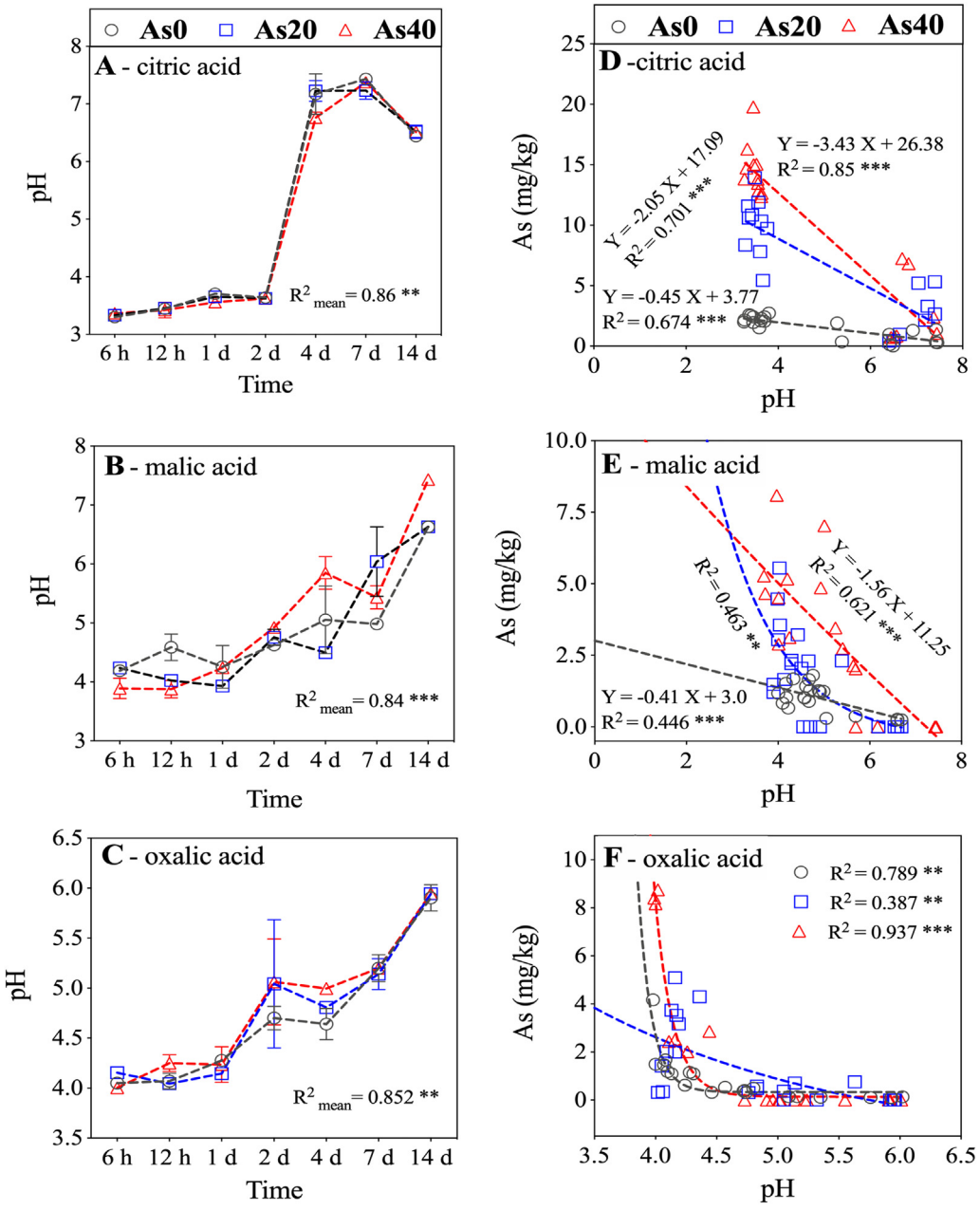

Fig. 3. pH values (A, B, and C) in the extracts after sediment incubation under LMWOAs treatment (Mean ± SE, $n_1 = 3$;), and the correlation of As and pH (D, E, and F) in LMWOAs solution after sediments incubation ($n_2 = 21$). Grey dot = As0 group, blue square = As20 group, and red triangle = As40 group. "**" indicates that the correlation at the 0.01 level is significant; "***" indicates that the correlation at the 0.001 level is significant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2009). Previous studies have shown that, in response to metal(loid) stress, wetland plants reduce their root porosity (Armstrong and Armstrong, 2001) and alter the anatomy of their root structures (Cheng et al., 2010), thereby inhibiting the rate of ROL. Furthermore, metal(loids) inhibit mangrove photosynthesis so as to enhance adaptive strategies for tolerance (of Cd and Zn) at the expense of chlorophyll synthesis and structural changes (Cheng et al., 2010; Jian et al., 2019).

In this study, a single period of exposure to arsenite had adverse effects (decline in biomass and ROL) on the growth of *A. marina* during pot cultivation. Our data reveal that As translocation in Fe plaque and plant organs exhibited the same ascending trends under As treatment. ROL tends to have greater effects on As fractionation and mobility, while higher ROL inhibits As translocation, which is closely related to As oxidation and fixation (Mei et al., 2012; Wagner et al., 2020). The present findings indicate that, on average, the plant As (root: 21%, stem: 32%, and leaf: 26%; graph abstract) and plaque As (21%) increased and were negatively correlated with the rate of ROL. Moreover, close negative relationships were found between oxalic acid levels and each of stem As, root As, leaf As, and plaque As. These results indicate that the mangrove seedlings invoke coping mechanisms to tolerate toxic As^{3+} by reducing ROL and releasing LMWOAs.

4.2. Variations in LMWOA extracts

Under individual LMWOA and As treatments, solution As decreased over time and increased in relation to the content in the sediments (As40 > As20 > As0). Similar results were found in a study of leaching behaviour for HMs (Fe, Cd, Cr, and Cu) from iron tailings (Geng et al., 2020) and the mobilisation of As and Fe (Onireti et al., 2017), both under single LMWOA treatment. The concentrations of As and Fe species decreased steadily after two days, and that of As dropped to extremely low levels after seven days (citric acid: 0–2.39 mg/kg; malic

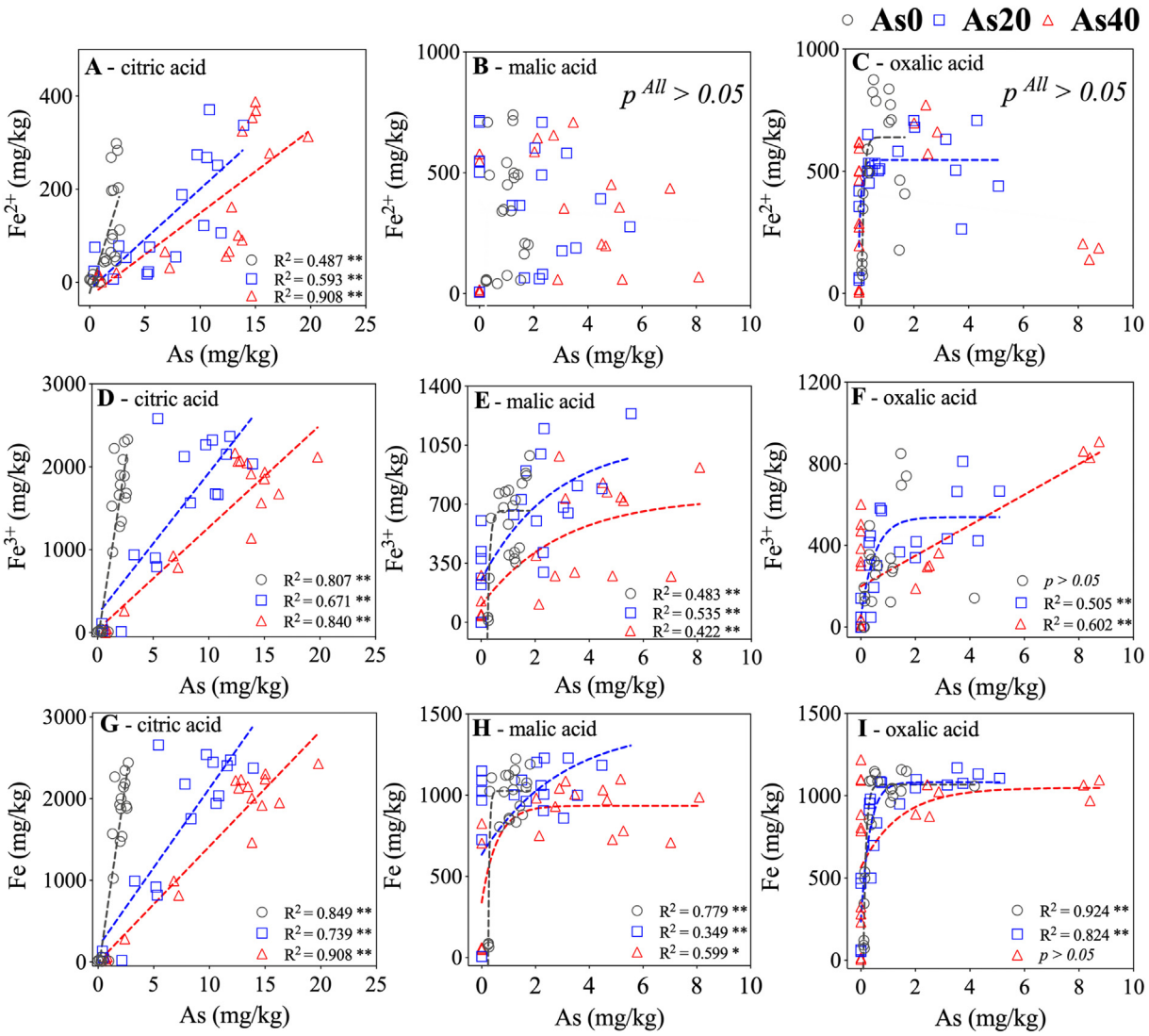

Fig. 4. The correlation of arsenic and Fe species in the aqueous phase under As treatment after incubation ($n = 21$). Grey dot = As0 group, blue square = As20 group, and red triangle = As40 group. "*" indicates that the correlation at the 0.05 level is significant; "**" indicates that the correlation at the 0.01 level is significant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

acid: 0–0.77 mg/kg; oxalic acid: 0–0.73 mg/kg; Fig. 2). At the same time, the pH values increased significantly (4.81–7.12). After incubation for 14 days, As content was below the detection limit, which may be due to the hydrolysis precipitation of Fe species (Jiang et al., 2019) and complexation/chelation with organic ligands in the sediments (Wang et al., 2019). In addition, the deprotonation of hydroxyl and carboxyl groups led to the adsorption of positive metal ions to form insoluble complexes (Ash et al., 2016; Geng et al., 2020), causing the pH values to increase. An interpretation of these finding might be that the concentrations of As, Fe^{3+} and Fe (excluding Fe^{2+}) negatively influenced values of pH (Fig. 3). The increases in pH may be due to the formation of hydroxides via mineral hydration (Hu et al., 2016), iron dissolution (Onireti et al., 2017), ageing performance of solution (Mei et al., 2020) and the processes of H^+ consumption (Wang et al., 2018).

The capability of citric, malic and oxalic acids to extract As, Fe^{3+} and Fe from sediments revealed the following order: citric acid> malic acid > oxalic acid (for the same incubation time, Tables S3 and S4). Interestingly, the performance with regard to Fe^{2+} was just the opposite, with the order being: oxalic acid > malic acid > citric acid (Table S3). A previous report indicated that the leaching of Cd and Fe followed the order of citric acid > malic acid > oxalic acid (Geng et al., 2020). In addition, the synchronization effect between Fe species and As under citric acid treatment, as well as between As and pH, was greater than with the other two acids (Table S5). These results indicate that citric acid mobilises As and Fe more effectively than the other two acids. The results of mapping data (EF and ER) have also demonstrated these phenomena (Fig. 5). Evidence has also been found that citric acid can form stronger complexes via the dissolution of amorphous Fe oxides (Schwab et al., 2008) and lower the reduction potential of Fe^{3+}/Fe^{2+} (Zhang et al., 2020). The number of carboxyl groups (-COOHs) in malic acid and oxalic acid (both containing two) is lower than that in citric acid (three), with the latter providing more functional groups and H^+ at the same concentration as the former two (Geng et al., 2020). These results indicate that acid strength (oxalic acid > citric acid > malic acid) was not a vital factor affecting the migration of As and Fe (Onireti et al., 2017).

The ratio of Fe^{3+}/Fe^{2+} had significant effects on the release of As extracted by the LMWOAs (Fig. S3). It has been previously reported that metal(loid)s species present in mangrove sediments mainly consist of ferromanganese oxides (Lu et al., 2007). Our findings reveal that the concentration of Fe^{3+} accounted for the majority of the total Fe in the LMWOAs, with Fe^{3+} also exhibiting good assistance to the release of As (such as by citric acid). However, the ratio of Fe^{3+}/Fe^{2+} decreased to less than 1 after two days in the malic acid and after 6 h in the oxalic

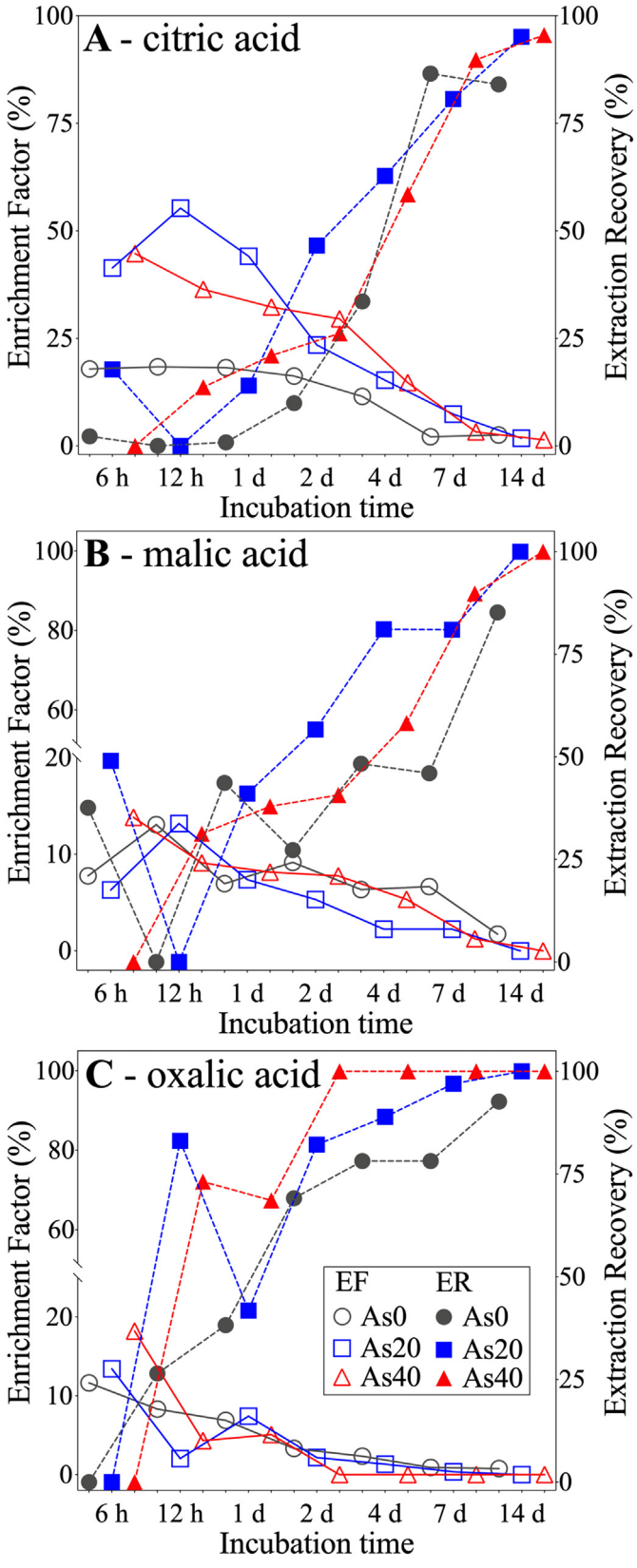

Fig. 5. The migration effects of adsorbed and desorbed As affected by LMWOAs in the present study (Mean value, n = 3). (EF: Enrichment Factor; ER: Extraction Recovery).

acid, indicating that the amount of Fe^{2+} exceeded that of Fe^{3+}. This could be due to the following factors: 1) hydrolysis precipitation, with Fe^{3+} readily precipitated by hydrolysis; 2) ferric malate complexation, as the strong affinity of malic acid could determine the reduction potential of Fe^{3+}/Fe^{2+}; and 3) reducibility, since oxalic acid possesses strong complexing properties and reducibility, reducing dissolved Fe^{3+} to Fe^{2+} and enhancing the formation of highly soluble iron oxalate complexes (Du et al., 2011; Onireti and Lin, 2016; Jiang et al., 2019; Zhang et al., 2020). In this case, the correlation between Fe species and As (R^2 of Fe: 0.739–0.908; Fe^{3+}: 0.671–0.84; Fe^{2+}: 0.487–0.908) was more favourable in citric acid than in the other two acids (Fig. 4). Hence, the results strongly indicate that the ratios of dissolved Fe^{3+} and Fe^{3+}/Fe^{2+} play key roles in As release from sediments under LMWOA treatment, especially regarding the mobilisation of citric acid. However, it is worth mentioning that correlation does not necessarily indicate causation.

4.3. Sediment As speciation and solution changes

The addition of LMWOAs profoundly altered the sediment As speciation and biogeochemical behaviour. The conversion from the more toxic As^{3+} to the less toxic As^{5+} in sediment was mainly based on insoluble As complexes, and the migration of dissolved As in the extracts was more active in the early stages of incubation (Table 2). It has been convincingly shown in a previous study that the release of As^{3+} and As^{5+} in soil solids (mainly amorphous Al and Fe oxides) occurs via dissolution of the sorbents (oxides) (Borggaard et al., 2019). In the present study, the As^{5+} in the sediment was mobilised and transferred to the solution after one day, while the aqueous As was transferred to the solid phase once again, and the species occurred in the form of As^{5+} (34.68%–45.12%, Fig. 6). As described earlier, the Fe (mainly Fe^{3+}) and As levels in solution decreased dramatically after four days due to hydrolysis precipitation, the formation of Fe oxides (hydroxides) and complexation, significantly influencing pH. As^{5+} is generally less stable than As^{3+} in most sediments and soils (Huang et al., 2012), and this was confirmed in the present study. The concentrations of As^{3+} ranged from 4.94 to 10.1 mg/kg (citric acid), 8.24 to 11.7 mg/kg (malic acid), and 5.34 to 8.71 mg/kg (oxalic acid), as shown in Table 2. This may indicate that the reduction of As^{5+} to As^{3+} after four days was the rate-limiting step affecting the transformation of As species (Kenyon et al., 2005) and inhibiting the activity of As^{5+}.

The unknown As species also constituted a significant proportion of the total As after incubation (26.14%–47.29%). The explanation for this might be the conversion of inorganic As into organic MAA (Kenyon et al., 2005) along with the As volatilisation of indigenous microbial activity (Edvantoro et al., 2004; Huang et al., 2012). We deduce that the destiny of As in sediment is significantly affected by LMWOAs, as incubation in ultrapure water was barely enough to mobilise sediment As (not detected in the solutions; data not shown). The more As extracted from the sediment pool by the LMWOAs (citric acid > malic acid/oxalic acid), the lower the occurrence of As^{5+} and As^{3+}. These results indicate that the abundant concentrations of diverse root exudates in treatments with As-contaminated sediments may have enhanced As bioavailability. In addition, the LMWOA of different root exudates could serve as adjuvants for the phytoextraction of various metal(loid) pollutions, including As in mangrove wetlands (Xie et al., 2013). Based on the above discussion, we can conclude that the root exudates of LMWOAs in rhizospheres may represent an important pathway to influence the biogeochemical behaviour of As, including solid–liquid migration and species conversion.

5. Conclusions

In conclusion, the results of the present study reveal that low-level As^{3+} predominantly promoted the exudation of LMWOAs (mainly citric acid, malic acid, and oxalic acid) while decreasing O_2 release. The extraction of sediment As varied significantly among three model LMWOAs, with citric acid being much more efficient than the other two acids. However, the limitations of the present

Table 2
Changes in the LMWOAs extracts and arsenic speciation in the As-enrichment sediments after incubation.

Treatment	Time	Variations in LMWOA extract					Arsenic species in sediment (mg/kg, DW)		
		pH	Fe^{2+} (g/kg)	Fe^{3+} (g/kg)	Fe (g/kg)	As (mg/kg)	As^{3+}	As^{5+}	Unknown
Citric acid	6 h	3.37 ± 0.08b	0.315 ± 0.04a	1.79 ± 0.29a	2.10 ± 0.28a	16.9 ± 2.59b	7.73 ± 0.14ab	16.9 ± 2.80c	17.3 ± 5.07a
	1 d	3.56 ± 0.01b	0.118 ± 0.04b	2.01 ± 0.09a	2.13 ± 0.12a	29.2 ± 3.70a	4.94 ± 1.42b	4.76 ± 0.59d	21.1 ± 2.64a
	4 d	6.48 ± 0.50a	0.056 ± 0.02c	0.570 ± 0.10b	0.603 ± 0.13b	9.30 ± 3.95c	10.1 ± 3.06a	24.9 ± 5.31b	15.7 ± 4.86a
	14 d	6.51 ± 0.06a	0.016 ± 0.00c	0.030 ± 0.01c	0.041 ± 0.03c	0.760 ± 0.07d	7.78 ± 0.94ab	30.7 ± 5.63a	20.8 ± 4.78a
Malic acid	6 h	3.89 ± 0.17c	0.062 ± 0.01c	0.875 ± 0.14a	0.937 ± 0.14a	5.42 ± 2.60b	9.04 ± 0.59a	17.2 ± 3.29b	28.4 ± 5.64a
	1 d	4.24 ± 0.04c	0.351 ± 0.01b	0.716 ± 0.04a	1.07 ± 0.05a	22.3 ± 2.88a	9.29 ± 2.73a	7.87 ± 2.83c	20.6 ± 7.66a
	4 d	5.85 ± 0.28b	0.571 ± 0.02a	0.267 ± 0.14b	0.838 ± 0.14a	2.78 ± 0.66b	11.65 ± 2.41a	24.2 ± 1.17a	21.4 ± 2.05a
	14 d	7.43 ± 0.02a	0.011 ± 0.01d	0.045 ± 0.01c	0.056 ± 0.01b	ND	8.24 ± 0.99a	24.7 ± 8.16a	27.1 ± 7.20a
Oxalic acid	6 h	4.00 ± 0.02d	0.176 ± 0.03c	0.867 ± 0.04a	1.04 ± 0.07a	8.44 ± 0.29b	8.71 ± 0.30a	20.3 ± 6.29c	22.4 ± 6.46a
	1 d	4.24 ± 0.18c	0.704 ± 0.06a	0.350 ± 0.05b	1.05 ± 0.03a	16.7 ± 2.45a	5.35 ± 0.29b	18.0 ± 1.13c	19.5 ± 3.31a
	4 d	5.00 ± 0.03b	0.489 ± 0.02b	0.337 ± 0.04b	0.826 ± 0.05b	ND	8.37 ± 1.48a	31.9 ± 4.27a	19.7 ± 3.17a
	14 d	5.95 ± 0.06a	0.012 ± 0.01d	ND	0.012 ± 0.01c	ND	6.53 ± 0.40b	26.7 ± 2.04ab	26.8 ± 2.30a

Data are shown as mean ± SE ($n = 3$). Different letters in each sub-column denote significant differences ($p < 0.05$). ND means not detected. Unknown: arsenic species excluded As^{3+} and As^{5+}.

study including that these findings may be restrict to pot experiments. In addition, the exploration of As speciation in sediments has revealed that the conversion from the more toxic As^{3+} to the less toxic As^{5+} may have been boosted by the LMWOAs after incubation. These results indicate that the As in sediments, considered as a 'sink', may turn into a 'source' under the influence of rhizospheric LMWOAs. Besides being associated with ROL, Fe species and pH variations, all of the mentioned factors combine to influence As mobilisation, migration, translocation, and speciation.

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 acquisition, Project administration, Resources, Supervision, Validation. **Jin Fan:** Visualization, Investigation. **Xin Guo:** Writing – original draft, Writing – review & editing, Investigation. **Jiajia Wu:** Writing – original draft, Writing – review & editing, Investigation. **Yi Zhou:** 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.

Acknowledgements

This research was kindly supported and funded by the major program (31535008) of National Natural Science Foundation of China and National Important Scientific Research Programme of China

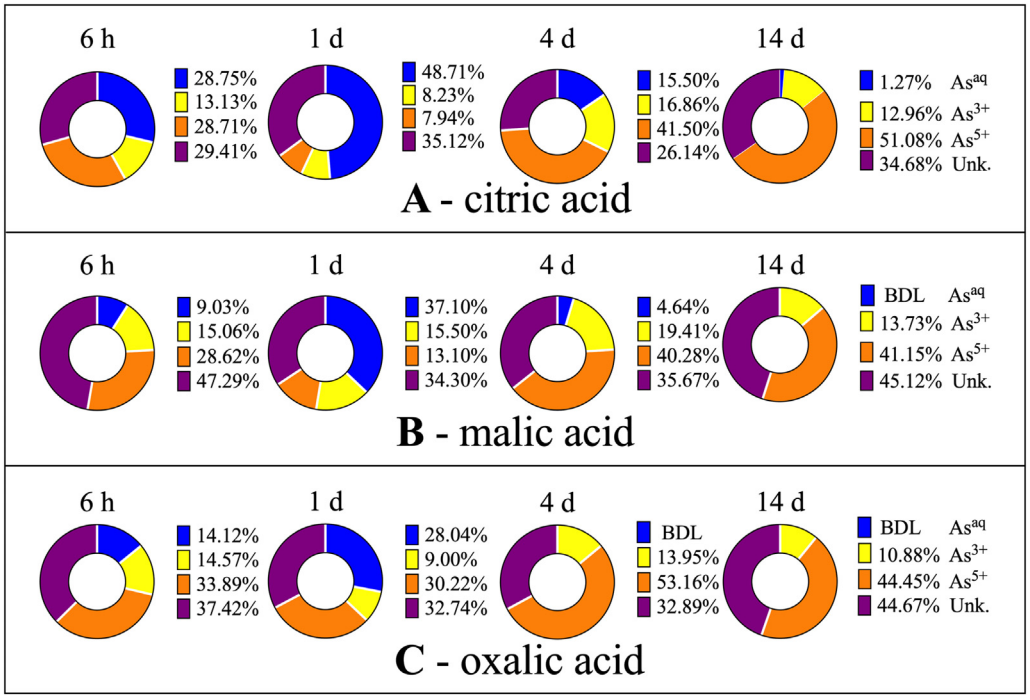

Fig. 6. The ratio of As variation and speciation in LMWOA-sediment mixture system after As40 group incubation. Asaq (blue) indicates total arsenic in the solution; As^{3+} (yellow) and As^{5+} (orange) are inorganic arsenic species in the sediments. Unknown (Unk., violet) presents not extracted and detected part of arsenic in sediments. BDL means below detection limit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(2018YFC1406603). We would like to thank Professor Deli Wang for his help and advice. Special thanks to Tao Ding of Newcastle University, UK for assistance in preparing the manuscript. The authors are also grateful to the anonymous referees for their constructive comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145685.

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