



Dynamics of low-molecular-weight organic acids for the extraction and sequestration of arsenic species and heavy metals using mangrove sediments

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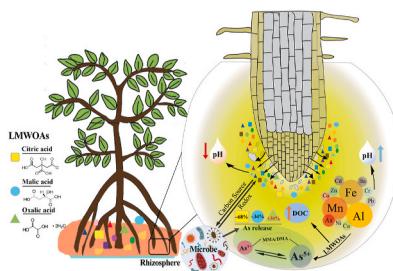
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HIGHLIGHTS

- Microbes facilitated As extraction of citric and malic acid positively under laboratory conditions.
- Under the action of microorganisms, citric acid from root exudates promotes the release of As in mangrove sediments.
- Inorganic As species put a potential exposure risk extracted from sediments via LMWOAs.
- Desorption-absorption dynamics of As synchronized with sedimentation and ageing processes of Fe, Mn, and Al via STEM-EDAX.

GRAPHICAL ABSTRACT



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ABSTRACT

Mangrove wetlands are subjected to pollution due to anthropogenic activities. Mangrove fitness is mainly determined by root exudates and microorganisms activities belowground, but the mechanisms are not yet well known. Rhizospheric interactions among mangrove sediments, microorganisms and root exudates were simulated. In particular, low-molecular-weight organic acids (LMWOA), were examined to explore the metal(loid)s rhizospheric dynamics via batch experiments. Using a combination of comparative sterilised and unsterilised sediments, LMWOA extracts and sediments constituents were examined. Factors such as the solution pH, dissolved organic carbon (DOC), arsenic and iron species and metal(loid)s in the aqueous phase were evaluated. The results show that on an average, the As decreased by 68.3 % and 42.1 % under citric and malic acid treatments, respectively, after sterilisation. In contrast, the As content increased by 29.6 % under oxalic acid treatment. Microorganisms probably facilitate sediment As release in the presence of citric and malic acids but suppress As mobilisation in the presence of oxalic acid. Fe, Mn and Al were significantly ($p < 0.05$) positively correlated with the trace metal(loid)s (Zn, Pb, Ni, Cu, Cr, Co, Ba, Cd and As). The solution pH was negatively correlated with the solution As. Both DOC and pH reach the peaks at the end of all treatments. The As absorption-desorption dynamics are closely linked to proton consumption, Fe-Mn-Al sedimentation of ageing performance and organic ligand complexation. The study provides an insight into the rhizospheric processes of microbial involvement and

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gives an enlightening understanding of the metal(loid)s redeployment for plant adaptation in mangrove wetlands.

Nomenclature

AAC	As adsorption capacity
DOC	Dissolved organic carbon
EDAX	Energy dispersive X-ray
LMWOA	Low-molecular-weight organic acids
MAC	Microbial As contribution
RE	Removal efficiency
STEM	Scanning transmission electron microscopy

1. Introduction

Mangrove ecosystems occur worldwide in coastal saline or brackish water in the tropics and subtropics. They provide several ecological benefits but are subjected to increasing deforestation (Friess et al., 2019; Simard et al., 2019). The overall function of the mangrove wetland is gradually weakening or even degenerating owing to the increasing anthropogenic threats from various sources, including industry, mining, agriculture, and aquaculture (Friess et al., 2019; Hu et al., 2021). Meanwhile, the environmental characteristics of mangrove wetlands, such as high organic matter content, high iron content and presence of reducing states all contributed to the accumulation of heavy metals in mangrove ecosystems (Kulkarni et al., 2018). Heavy metal(lloid) may accumulate in the wetland ecosystem and remain as persistent a polluted and non-degradable pollutant (Mokarram et al., 2020), see Table 1. Mangrove wetlands worldwide have been polluted by heavy metal(lloid)s (e.g. As, Cr, Cu, Pb, and Zn) to varying degrees. Arsenic (As) is a carcinogenic and toxic metalloid that occurs widely and is gradually accumulated in wetland ecosystems (Li et al., 2017; Mei et al., 2021). Long-term exposure to As-contaminated food and water can cause severe health risks (organ disorders and body complications) (Yusof et al., 2020). As pollution is mainly associated with the more toxic inorganic arsenite (As^{3+}) and less toxic arsenate (As^{5+} , the most abundant form).

The two ionised As forms can be methylated into organic forms monomethyl (MMA) and dimethyl (DMA) by microorganisms in a sedimentary environment (Edvantoro et al., 2004; Huang et al., 2012). The aggravating toxicity and phytoremediation of As contamination in mangrove wetlands has become a serious concern. However, the mechanisms and pathways of As phytoextraction in mangroves and their migration behaviour and speciation in rhizospheric microenvironments have not been thoroughly elucidated.

Plants exude a large amount of photosynthesis-derived carbon (11%–40 %) via root exudates, thereby shaping diverse microhabitats (Zhalinina et al., 2018). The processes of root exudation is linked to soil nutrient mobilisation, which is the key to determine the fitness and evolution of plants (Canarini et al., 2019). For instance, low-molecular-weight antimicrobial chemicals may be released into root exudates to repel, inhibit or kill pathogenic microorganisms before biotic stress (Baetz and Martinia, 2014). Meanwhile, plant roots exude compounds such as sugars, amino acids, organic acids and secondary metabolites into the rhizosphere (Bais et al., 2006; Badri and Vivanco, 2009; Baetz and Martinia, 2014). Among these compounds, low-molecular-weight organic acids (LMWOAs) in the rhizosphere are usually in a dissociated mildly acidic state and undergo a dynamic process of continuous synthesis and decomposition (Hees et al., 2003). The concentration of LMWOAs range from a micromole ($10 \mu\text{mol L}^{-1}$) to millimole (5 mmol L^{-1}) in the rhizospheric soil solutions (Strobel, 2001; Jones et al., 2005; Geng et al., 2020; Xiang et al., 2020). The contents and types of LMWOAs in root exudates are affected by soil types, plant species, microbial activity, and nutrient supply etc. (Jones, 1998; Jones et al., 2003). Among the LMWOAs, citric acid was the main component of the root exudates in mangroves *Kandelia obovata* and *Avicennia marina* (Forsk.) Vierh., whereas more acetic and malic acid were the main LMWOAs in the exudates of *Aegiceras corniculatum* (Linn.) Blanco (Lu et al., 2007). Citric acid, oxalic acid, and malic acid were the dominant LMWOAs (84.3%–86.8 %) among 10 acids in the rhizosphere of *A. marina* under arsenite (NaAsO_2) stress (Mei et al., 2021).

The extravasation of organic acids and protons promotes the reproduction of acid-producing bacteria in the rhizosphere. Acid-consuming microorganisms contribute to the decomposition of a large number of LMWOAs in the rhizosphere using the organic matter of root exudates.

Table 1

The content of metals and metalloids in the sediments (mg kg^{-1} DW) of coastal wetlands and mangroves around the world.

Location	Cd	Cu	Cr	Hg	Ni	Pb	Zn	As	Reference
Zhangjiangkou mangrove	0.02–0.2	0.01–22.86	0.03–5.43	–	0.25–4.51	0.04–1.38	5.73–26.09	0.24–16.7	This study
Global mangrove	0.01–87	0.01–4050	0.55–6240	–	0.3–208.4	0.08–1950	0.28–2374	8–40	Bayen (2012)
Danshuei River, Taipei	0.07–0.51	18.4–139	56.3–158	–	21.4–59.3	15.3–56.9	100–401	4.42–20.3	Hong et al. (2021)
Shenzhen Bay mudflat	0.84	65.15	80.91	0.1	39.57	70.74	323.97	152.4	Li et al. (2017)
Shenzhen Bay mangrove	0.94	86.9	109.75	0.13	42.35	76.81	354.86	199.66	Li et al. (2017)
Leizhou Peninsula, China	0.05–0.36	3.37–33.44	8.37–126	3.37–33.44	2.89–96.07	7.26–59.44	26.66–134.56	29.2–52.0	Liu et al. (2015)
Mai Po, Hongkong	2.29–2.9	74.8–82.1	39.2	–	26.5–31.8	76.4–82	233–247	–	Tam et al. (2000)
Nansha Island, China	0.78	113	155	–	48.4	55.3	159	–	Wu et al. (2014)
Daya Bay, Shenzhen	0.19	20	63	0.09	28	223	108	–	Gao et al. (2012)
Beibu Bay, Guangxi	0.08–0.1	68–79	45	0.08–0.09	–	19–34	55–57	18.1–18.7	Xia (2011), Gan (2013)
Jinjiang mangrove, Fujian	0.26–0.30	18.8–20.7	23.4–26.3	–	13.9–15.7	78.1–87.9	109–231	8.75–9.65	Hu et al. (2021)
Xiamen Bay, Fujian	–	37	56	0.12	26	95	194	14	Vane et al. (2009)
Yundang Lagoon, Xiamen	–	67.5	56.0	–	24.73	97.7	228.12	27.52	Chen et al. (2010)
Sundarban, Bangladesh	0.35–0.82	13–30	4382	–	18–38	10–24	46–89	3.4–9.0	Islam et al. (2017)
Dhamara Estuary, India	1.63	29.4	347	–	64.7	31.9	71.4	–	Asa et al. (2013)
Coast of Brazil	1.32	98.6	42.4	1.28	–	161	483	–	Kehrig et al. (2003)
Tanzania	1.05	9.5	22.7	0.09	–	14.6	35.1	–	Mtanga et al. (2008)
Queensland, Australia	0.6	1–12	1–72	–	4–9	4–36	23–56	4–40	Micaela et al. (2002)
Sungei Buloh, Singapore	0.18	7.06	16.61	–	7.44	12.28	51.24	–	Cuong et al. (2005)
Mobile Bay, USA	0.13	10	16	0.15	8	21	25	5.6	Lafabrie et al. (2013)
Fadiouth, Senegal	0.03	3.5	28.8	0.013	2.5	2.4	5.4	–	Bodin et al. (2013)
French Guiana	–	23–27	63–66	0.04	34–42	27–43	123–154	–	Marchand et al. (2006)
Cross River Estuary, Nigeria	–	24.1–32.4	19.9–27.4	–	15.2–30.3	8.8–24.7	140.1–188.9	–	Essien et al. (2008)

The aliphatic low-molecular-weight carboxylic acids are act as a substrate for the growth of a large number of microorganisms (Kusel and Drake, 1999). Furthermore, rhizospheric microorganisms are important media for the production and metabolism of LMWOAs. LMWOAs can act as a substrate to participate in the metabolic processes of microorganisms and even produce and decompose organic acids (Bertilsson and Tranvik, 1998). Plants can promote the growth of microorganisms by adjusting the composition of their rhizosphere, thereby improving their adaptability (Zhalnina et al., 2018). The function of microorganisms reported in mangrove sedimentary wetlands include sulfate-reducing, reduction of nitrate, degradation, and optical activities (Blunt et al., 2014; Zhang et al., 2021a). The rhizosphere microbial constitution depends on plant roots, microorganisms and the physiochemical environment of the soils (Zhalnina et al., 2018). LMWOAs can reduce the redox potential of sediments and improve the activity of anaerobic bacteria, and indirectly accelerate the growth of microorganisms by dissolving and excreting Fe, Al and Mn oxides/hydroxides (Zhao et al., 2002). LMWOAs are also important intermediates in the microbial organic matter metabolism pathway (Hees et al., 2003). Methanogenic bacteria use acetates to produce methane (Kleerebezem et al., 1999). Pyruvate, low-molecular-weight fatty acids and amino acids are precursors for the synthesis of acetyl-CoA and are involved in the metabolism of microorganisms (Xiao and Wu, 2014). A large number of organic acids such as phenolic and fatty acids (linoleic acid, salicylic acid and p-hydroxybenzoic acids) are confirmed as allelochemicals and inhibit the growth of algae (Zheng et al., 2010). The accumulation of organic acids in the rhizosphere of plants leads to toxic effects that affect the diversity of microbial communities (Jr, 1998; Kpomblekou-A and Tabatabai, 2003; Azmi et al., 2015).

Many studies focused on the concentration of organic acids in the soil solution in the rhizosphere, but the functions and mechanisms of organic acids in the rhizosphere are not yet fully understood with regard to the influence of microorganisms on the detoxification of heavy metals and nutrient supply. To address this issue, the study explored the rhizospheric dynamics of simulated root–soil interfaces under the influence of acids in root exudates. In particular, LMWOAs extraction in the case of mangrove sediments with and without microorganisms with regard to element (As/Fe variations etc.) mobilisation, migration, and speciation were examined. The objectives of the present study were as follows: 1) Clarify the influence of the participation of microorganisms on the effects of LMWOAs; 2) interpret the changes and influences of As species in the supernatant of LMWOAs in incubated mangrove sediments; 3) determine the composition and characteristics of mangrove sediments after LMWOA extraction and incubation. The present study has the potential to improve understanding regarding the processes of rhizospheric microbial activity and root exudation to gain an insight into the rhizospheric behaviours of As/Fe and other elements in mangrove wetlands.

2. Materials and methods

2.1. Sediment collection and characteristics

Experimental samples were prepared with mangrove surface sediments (0–30 cm) collected from the Zhangjiangkou Mangrove Forestry National Nature Reserve, People's Republic of China ($24^{\circ} 24'N$, $117^{\circ} 55'E$) in August 2017 (Mei et al., 2020). The characteristics of mangrove sediments are as the following quantification ($n = 3$). The total organic matter content was $12.56\% \pm 0.74$. The pH was 7.64 ± 0.02 (sediment: water = 1: 2.5). The salinity (%) was 16.32 ± 0.24 . The content of total As and total Fe were $14.77 \pm 0.85 \text{ mg kg}^{-1}$ and $4.03 \pm 0.30 \text{ g kg}^{-1}$, respectively. The national standard reference material of soil (GBW-070310, China) was checked for procedural accuracy. The basic properties of the sediments were analyzed using referred standard methods (Yang et al., 2019).

2.2. Comparison of LMWOAs extracts from unsterilised and sterilised sediments

The fresh and homogenised sediments were conducted an activation pretreatment for one month employing NaAsO_2 solution/ultrapure water up to 0 mg kg^{-1} As (N_{As}), the low level of 20 mg kg^{-1} As (L_{As}), and the high level of 40 mg kg^{-1} As (H_{As}) in dry weight (D.W.). The extracted solutions of the three modeling LMWOAs (citric acid, malic acid, and oxalic acid) were selected based on our previous work (Mei et al., 2021), and diluted using 0.01 mol L^{-1} NaCl (prepared with ultrapure water) containing gradient working concentrations (0, 1, 2, 4, 6, and 8 mmol L^{-1} LMWOA). The incubation was placed into a 50 mL polyethylene centrifuge tube with 20 mL LMWOA solution and 0.5 g fresh sediment (sterilised treatment, ST; and unsterilised treatment, NST). All centrifuge tubes were shaken in a rotary shaker (Saifu BHWY-200 Shaker, China) at 200 rpm and 25°C without light for 24 h. Each tube was centrifuged at 8000 rpm for 10 min after incubation. The supernatant of soluble samples was collected to determine variations in As and Fe species (Fe^{2+} , Fe^{3+} and total Fe) as well as the pH after filtration (0.45 μm). The comparative study of the influence of the presence or absence of microorganisms was investigated. As-enriched sediments underwent sterilisation (121°C , 100 kPa for 30 min) using autoclaving pressure steam pot (MJ-54A, STIK Co. Ltd., Shanghai, China). The solid-liquid mixture was centrifuged and separated, variations in the supernatants were determined using the previous procedures mentioned above.

2.3. Assessment of As adsorption–desorption dynamics

To assess As desorption and absorption dynamics, we determined the removal efficiency of LMWOAs and As absorption capacity of incubated sediments in the batch experiment. In the role of microbial part, the index of microbial As contribution to evaluating the response of microorganisms at different LMWOA incubation times ($n = 3$).

The equation to assess the removal efficiency (RE) of LMWOAs regarded extracting the sediment As, the formula of RE (%) is expressed as follows:

$$RE = \frac{\beta}{\alpha} * 100 \quad (1)$$

The equation to calculate the As absorption capacity (AAC) of the sediments after LMWOA extraction (Yusof et al., 2020), the formula of AAC (mg L^{-1}) is expressed as follows:

$$AAC = m * \frac{(\alpha - \beta)}{v} \quad (2)$$

where α is the initial As concentration (mg kg^{-1}) in the sediment while β is the equilibrium concentrations of As in the supernatant solution (mg kg^{-1} DW), v is the volume of As solution in Liter (L), and m is the weight of the freeze-dried sediment (mg).

The equation to assess the rate of microorganism contribution during the processes of LMWOAs extraction from the sediment, the formula of microbial As contribution (MAC%) is expressed as follows:

$$MAC = \frac{(NST_{\text{As}} - ST_{\text{As}})}{\alpha} * 100 \quad (3)$$

where NST_{As} is the As concentration (mg kg^{-1} DW) in the supernatant of unsterilised sediment while ST_{As} is the equilibrium concentrations (mg kg^{-1} DW) of As in the supernatant of the sterilised sediments, α is the initial As concentration in the sediment.

2.4. Effects of LMWOAs to sediment desorption during incubation

To investigate variations in the extracts affected by LMWOAs, citric, malic, and oxalic acid were selected and added to the high-level As sediment (H_{As}) according to the previous incubation conditions for 1, 4,

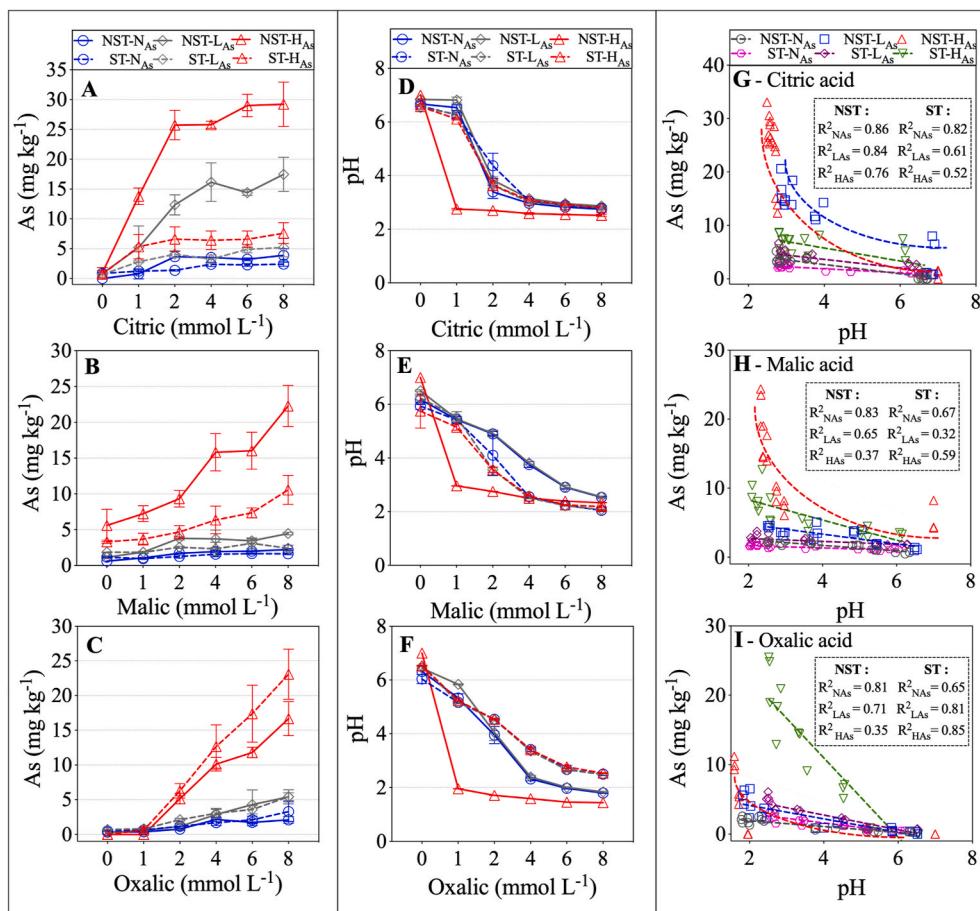


Fig. 1. The As concentration in the supernatant of LMWOA extracts for sterilised treatment (ST, dash line) and unsterilised treatment (NST, solid line) sediments; As content were calculated as the relative concentrations to dry sediment weight (mg kg⁻¹ DW), Mean \pm SE, n = 3. Ultrapure water extraction was used as the control check, but all below the detection limit.

7, and 14 day(s), as described above. A dose of 2 mmol L⁻¹ was applied based on the results of the previous experiment. The effects of LMWOAs on As speciation and elements desorption were assessed in the LMWOAs solution after incubation. In brief, after careful separation of the solid phase and liquid phase, the variations of supernatant As species and elements, and the composition characteristics of freeze-dried sediments (-50°C) were examined. The assessment of As species (inorganic As³⁺, inorganic As⁵⁺, MMA, and DMA) in the supernatants were quantified by adapting the method of high-performance liquid chromatography coupled to a hydride generator with atomic fluorescence spectrometry (HPLC-HG-AFS) (Herrera et al., 2021). Major and trace elements in the supernatant were analyzed after centrifugation (8000 rpm, 10 min) and filtration (0.45 μm). The sediment particle dynamics and elemental composition at the incubation of beginning (1 d) and end (14 d) were characterized by the STEM-EDAX method. The pH and dissolved organic carbon (DOC) were measured to observe the influence of physio-chemical properties in the solution.

2.5. Instrument analysis

The content of total carbon (C), hydrogen (H), and nitrogen (N) in the mangrove sediment was analyzed with an element analyser (Elementar Analyse Systeme GmbH, Hanau, Germany). The total organic matter of sediments was weighted and measured after fully burning at a high temperature (460°C for 6 h) in a muffle furnace. Salinity was measured using a salinometer. The pH of the solution and sediment (sediment: water = 1: 2.5) was measured using a pH meter (Leici PHS-2F, Shanghai, China). The concentration of ferrous ion (Fe²⁺),

trivalent iron (Fe³⁺), and total Fe in the acid supernatant was measured using visible spectrophotometry at 510 nm applied with the 1,10-phenanthroline method as the description in our previous work (Mei et al., 2021). The content of DOC in the solution was determined by a total organic carbon analyser (TOC-VCPh, Shimadzu, Japan). The determination of arsenic species in the supernatant using HPLC-HG-AFS (Tanta technologies). Briefly, the mobile phase of HPLC consisted of 15 mmol L⁻¹ (NH₄)₂HPO₄ (diammonium hydrogen phosphate) buffer pH = 5.8 at a flowrate of 1 mmol L⁻¹. The condition of HG: 5% v/v HCl (chromatographic hydrochloric acid) at a flowrate of 0.25 mL/min, and reducing agent is 0.2% KI - 1% KBH₄ at 0.2% KOH (v/v) at a flowrate of 0.35 mmol L⁻¹. All data were acquired at a detection wavelength of 190 nm via AFS (Tanta D1000). We used the standard addition method for the assessment of arsenic species recovery (85%–115%) due to the lack of reference materials. Elements were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110VDV, USA). The composition characteristics of freeze-dried sediments after LMWOA-extraction were evaluated via STEM-EDAX (FEI Quanta 650 FEG, America).

2.6. Statistical analysis

Data processing and statistical analyses were performed using IBM SPSS, version 23.0 (SPSS Inc., Chicago, IL, USA). All data in triplicate were transformed before testing to reach normal distribution (Shapiro-Wilk), and the homogeneous variance was checked by Levene's test. One-way ANOVA followed by the Post-hoc Duncan's test was performed to assess the significance of the variables. The test was performed to

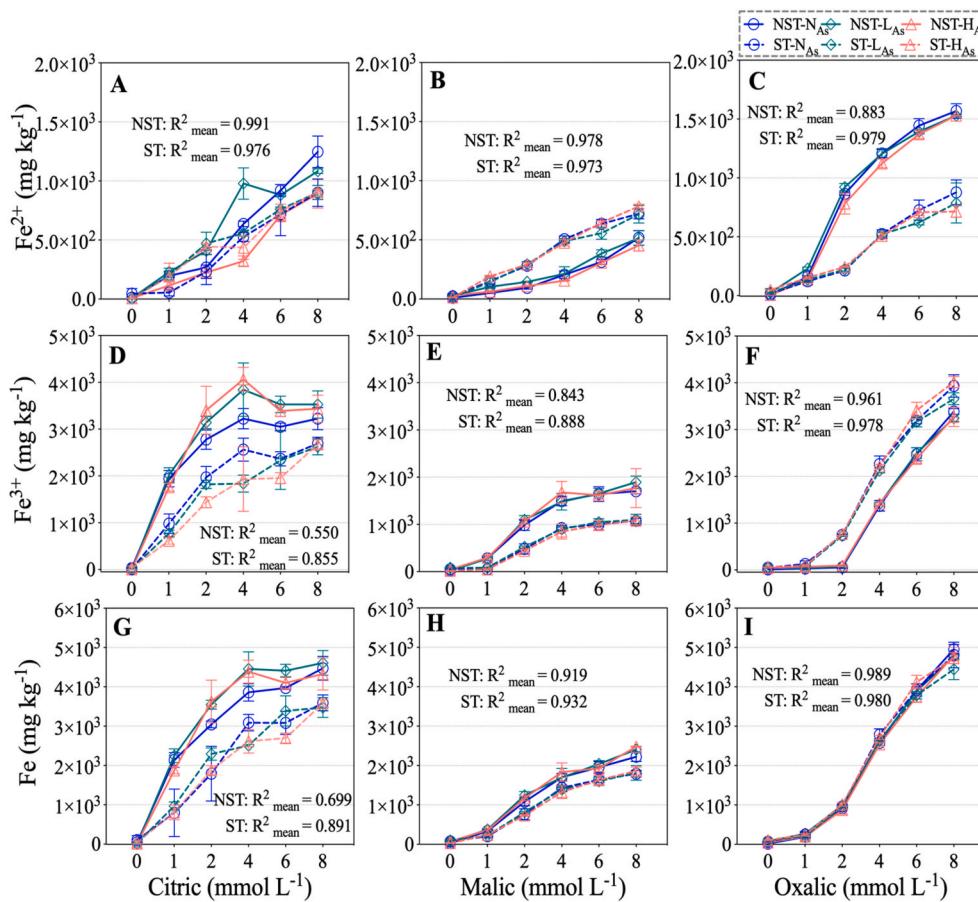


Fig. 2. The concentration of Fe species in the supernatant of LMWOA extracts for sterilised treatment (ST, dash line) and unsterilised treatment (NST, solid line) sediments; All data were calculated as the relative concentrations to dry sediment weight (mg kg^{-1} DW), Mean \pm SE, $n = 3$.

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. Spearman's correlation analysis was employed to determine relationships between the treatments. Graphs in the manuscript are drawn using Origin 9.0 and GraphPad Prism 8.

3. Results and discussion

3.1. Variations in the solution from unsterilised and sterilised sediments

3.1.1. Solution As

A comparative analysis under LMWOA treatments to examine the microbial contribution showed that there are significant differences ($p < 0.001$) between the sterilised and unsterilised sediments in terms of the solution As (Table S1). The results showed that composition of microorganisms probably affects the extraction and behaviour of As in the LMWOAs-sediment mixtures. The preference of rhizospheric bacteria for the consumption of the aromatic organic acids exuded by plants was confirmed in a previous study (Zhalina et al., 2018). The decomposition of LMWOAs was attributed to microbially mediated degradation, not photodegradation in the dark (Shank et al., 2006; Onireti et al., 2017). In this study, differences were observed in the effects of different LMWOAs on As migration (citric acid performs the best extraction). The stronger capacity of citric acid to mobilise As may be attributed to the higher acid strength compared to the other LMWOAs (Onireti et al., 2017). After sterilisation, the As concentration in the supernatant of citric and malic acids decreased, but the As content in the case of oxalic acid treatment increased (Fig. 1A, B and C). The As content in the supernatant under treatment with citric and malic acid decreased on an

average by 68.3 % and 42.1 %, respectively, while that under treatment with oxalic acid increased on an average by 29.6 %. The As content in the supernatant increased with the As content of the sediment ($\text{H}_{\text{As}} > \text{L}_{\text{As}} > \text{N}_{\text{As}}$, Fig. 1). However, the change in As content in the N_{As} and L_{As} treatment groups after sterilisation was not significant (Table S3). The variations in the solution As attributed to the sediments were removed mainly because of the acid strength of LMWOAs and abundance of carboxyl group (Onireti and Lin, 2016; Onireti et al., 2017; Geng et al., 2020). In addition, it is also related to the consumption and decomposition of LMWOAs by microorganism (Jones, 1998).

3.1.2. Solution pH

After incubation, the solution pH in the supernatant decreased as the concentrations of the three acids increased (Fig. 1D, E and F). The pH for low LMWOA doses (0–2 mmol L⁻¹) increased significantly after extraction, while it did not increase under high LMWOA doses (4–8 mmol L⁻¹). The influence of the treatments of the three acids and the addition of As on solution pH was not significant ($p > 0.05$) in the sterilised groups (Fig. 1, Table S2). There was a significant difference in pH ($p < 0.05$) between treatments with citric and malic acids in the control groups (Table S3): the As release in both cases decreased after sterilisation. The supernatant pH values of 1 mmol L⁻¹ for the three acids in the case of the sterilised groups were much higher than those in the case of unsterilised groups (Fig. 1D, E, and F). The solution pH increased after incubation because of the consumption of protons from LMWOAs, acid-neutralising reactions such as H^+ -driven dissolution and cation exchange between soil mineral particles in the LMWOAs-sediment mixture (Onireti and Lin, 2016). Chemical processes may be the dominant factors that enhance pH values after incubation; however, in the presence of microorganisms, the pH was more stable (Fig. 1). The

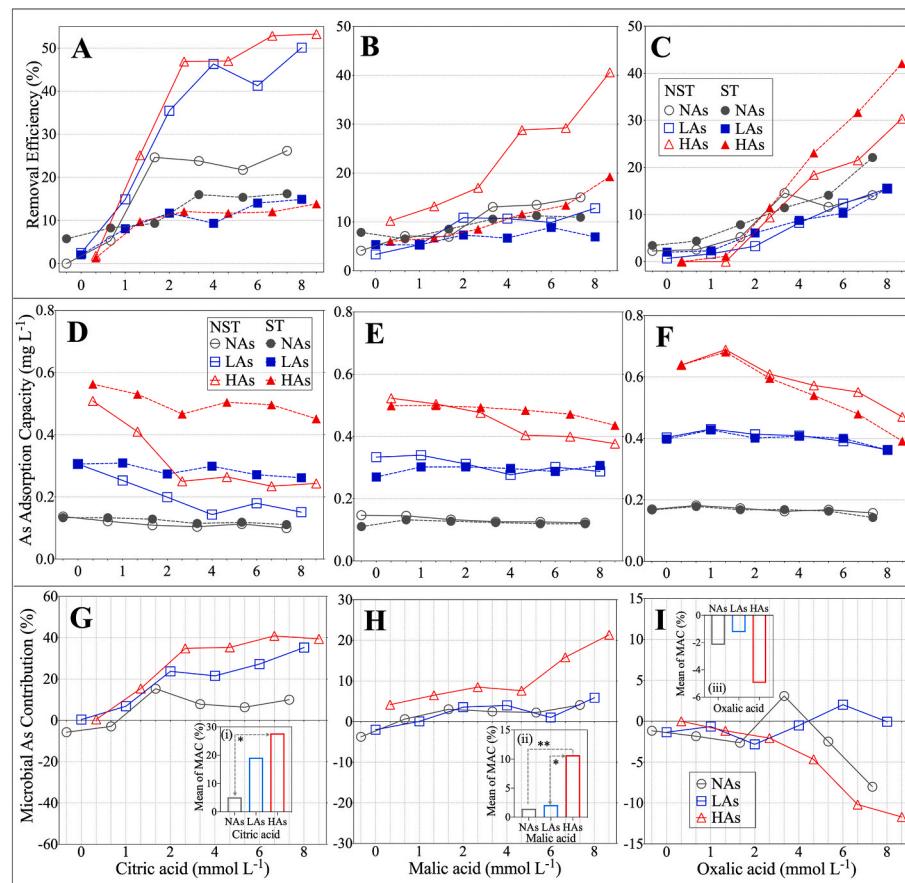


Fig. 3. The assessment of As adsorption–desorption in the LMWOAs–sediment mixture (mean value, $n = 3$). A, B, C for As removal efficiency (RE%) from solid phase to aqueous phase. D, E, F for As adsorption capacity (AAC mg L^{-1}) of mangrove sediment after the LMWOAs extraction. G, H, I for microbial As contribution (MAC%) for sterilised treatment and unsterilised sediment treatment. Nonparametric test (Kruskal–Wallis) was used to evaluate the significance of differences. ‘*’ indicates that the correlation at the 0.05 level is significant; ‘**’ indicates that the correlation at the 0.01 level is significant.

acid-dissociation constants of the three LMWOAs are also associated with changes in the pH values (Mei et al., 2020). The solution pH in all treatments showed a linear correlation ($p < 0.001$) with As. After sterilisation, the linear relationship index changed (mostly decreased) in the absence of microorganisms (Fig. 1G, H, and I). This result indicates that microorganisms may play a crucial role in As release through the consumption and decomposition of LMWOAs, while they have less influence on the variations in the pH values.

3.1.3. Solution Fe species

The variations of Fe species in the solution of the three LMWOAs under gradient dose treatments were measured for the unsterilised and sterilised sediments (Fig. 2). The contents of the three Fe species increased with the LMWOA concentration. After extraction, the average concentrations of Fe and Fe^{3+} in the unsterilised groups were in the following order: citric acid > malic acid > oxalic acid (not significant for the latter two acids). For sterilised groups, the average Fe and Fe^{3+} concentrations followed this order: citric acid > oxalic acid > malic acid (not significant for the former two acids). The Fe^{2+} concentration was in the following order: oxalic acid > malic acid > citric acid ($p < 0.05$). However, there was no significant difference between the three acids after sterilisation (Table S3). Perhaps the Fe reductivity of the Fe(III)-reducing bacteria increased in the presence of oxalic acid (He et al., 2011). Fe compounds were extracted with citric and oxalic acids from contaminated soils mainly via ligand-promoted reactions via non-reductive and reductive pathways, respectively, during As extraction (Joseph et al., 1996; Lee et al., 2017). The fact indicates that the presence of LMWOAs can affect the crystallisation of Fe oxides, resulting in the formation of amorphous or poorly crystallised Fe compounds (Rashid, 1985). There were no significant differences in the Fe species in the case of additional As treatment in all groups ($p > 0.05$). A

comparison of the unsterilised and sterilised groups in terms of the Fe species between showed that the concentrations of the three Fe species under citric acid treatment decreased after sterilisation. The average concentrations of Fe and Fe^{3+} under citric acid treatment reduced by 31.0 % and 37.1 %, respectively. However, the Fe^{2+} concentration increased under malic acid treatment after sterilisation, and the Fe^{3+} and Fe contents decreased by 22.2 % and 44.3 %, respectively. The variation in the Fe content under oxalic acid treatment from the control group was not significant, but the Fe^{2+} content decreased by 21.2 %, while the Fe^{3+} increased by 39.3 %. The solution As was positively correlated with the Fe and the Fe^{3+} contents and negatively correlated with the Fe^{2+} content in the all LMWOAs treatments (Table S4). A similar study reported that the mobilisation of Pb and As is closely associated with the dissolution of soil-borne Fe (Onireti et al., 2017), especially the redox reactions of the Fe species found in the present study.

3.1.4. Assessment of As adsorption–desorption dynamics

As adsorption–desorption dynamic was assessed by considering the removal efficiency (RE), As adsorption capacity (AAC) and microbial As contribution (MAC) for sterilised and unsterilised sediment treatments (Fig. 3). The RE results indicate that citric acid led to significantly higher desorption of As thereby acting as an important determinant of the migration of sediment in the case of the unsterilised group (Fig. 3A).

The AAC results show that the solid phase absorption of As was least affected by oxalic acid (Fig. 3F). The sediments treated with the same LMWOA exhibited higher As adsorption efficiency after sterilisation (except oxalic acid, Fig. 3D, and E). To better understand the role of microorganisms, the MAC was determined. The results revealed that the part of the killed microorganisms in sediments made a positive contribution to facilitate the release of solid phase As under treatment with

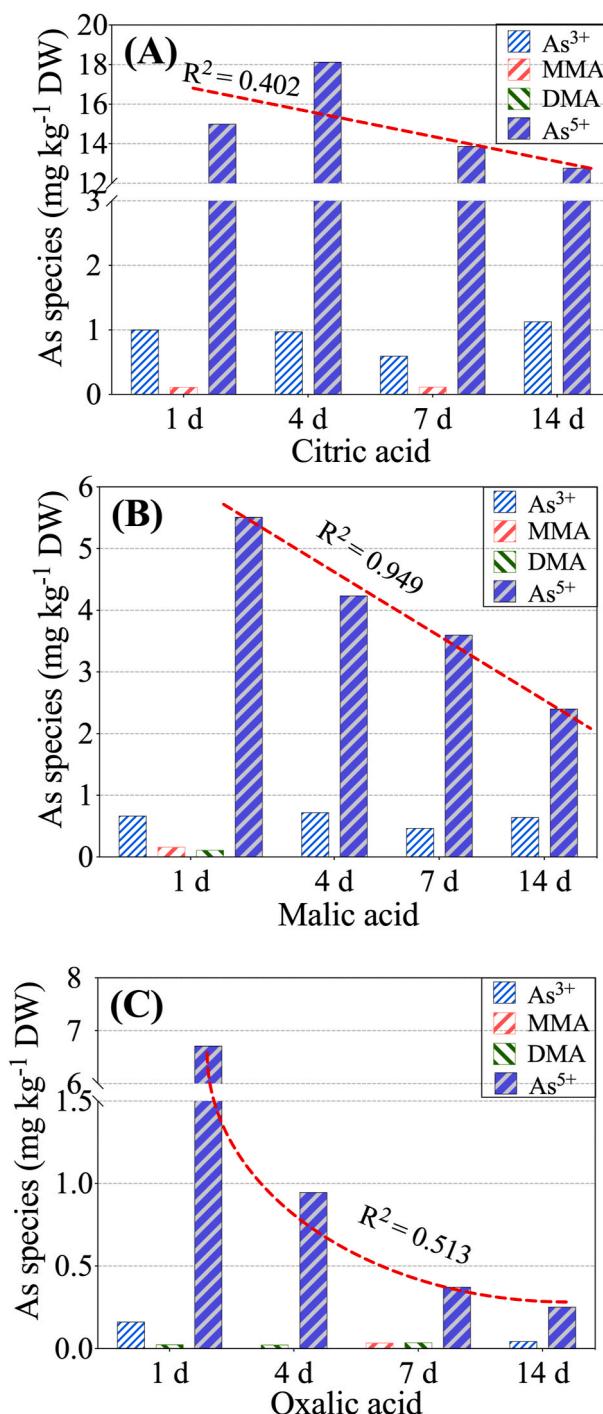


Fig. 4. The four determined As species in the LMWOAs extracts. Inorganic arsenic species: As³⁺ and As⁵⁺; organic arsenic species: monomethylated (MMA) and dimethylated arsenic (DMA). All concentrations were calculated as values extracted from dry sediments (mg/kg DW). Deionized water extraction was used as the control, but all below the detection limit.

citric acid (NAs (5.13 %)–HAs (27.7 %), $p < 0.05$, Fig. 3G (i)) and malic acid (NAs (1.45 %)–HAs (10.7 %), $p < 0.01$; LAs (2.09 %)–HAs (10.7 %), $p < 0.05$, Fig. 3H (ii)). However, the microbial behaviour under oxalic acid treatment was the opposite, with As migration increasing after sterilisation (Fig. 3G). This may indicate that the process (oxalic acid extraction) suppressed the mobilisation of As in the presence of microorganisms (range of MAC: LAs (−4.96 %) to HAs (−1.24 %)).

3.2. Effects of LMWOAs on sediment desorption under incubation

3.2.1. Solution As species variation

Speciation analysis of the supernatant showed that inorganic As⁵⁺ was the dominant species in the three LMWOAs treatments (Fig. 4). The As⁵⁺ concentration in the solution exhibited generally decreasing trends along with increase in incubation time for all the LMWOAs groups, except citric acid on day 1 (Fig. 4). The microbial biodegradation of LMWOAs was a quantitative factor regulating the soluble concentrations in the extracts (van Hees et al., 2005). The average As⁵⁺ concentration extracted from the sediments by the three LMWOAs followed this order: citric acid ($12.8\text{--}18.1\text{ mg kg}^{-1}$) > malic acid ($2.40\text{--}5.51\text{ mg kg}^{-1}$) > oxalic acid ($0.25\text{--}6.72\text{ mg kg}^{-1}$). The values of correlation R^2 of As⁵⁺ with the incubation time of the three LMWOAs treatments was in the following order: malic acid ($R^2 = 0.949$) > oxalic acid ($R^2 = 0.513$) > citric acid ($R^2 = 0.402$). The concentration of inorganic As³⁺ was approximately less than 1 mg kg^{-1} in the citric acid ($0.60\text{--}1.13\text{ mg kg}^{-1}$), malic acid ($0.47\text{--}0.72\text{ mg kg}^{-1}$) and oxalic acid ($0.05\text{--}0.16\text{ mg kg}^{-1}$) treatments. The concentrations of organic As species monomethylarsonic acid (MMA: $0.03\text{--}0.16\text{ mg kg}^{-1}$) and dimethylarsonic acid (DMA: $0.02\text{--}0.11\text{ mg kg}^{-1}$) in the three LMWOA extracts were extremely low or below the detection limits (Fig. 4). LMWOAs promoted soil methylmercury production in the water-level-fluctuating zone (Yin et al., 2018), thereby posing a potential risk in terms of production of organic As compounds as well.

3.2.2. Elemental migration and correlations

The major elements (Na, Fe, Mg, K, Ca, Mn and Al) and trace elements (Zn, Pb, Ni, Cu, Cr, Co, Ba, Cd and As) in the LMWOA extracts from the As-enriched sediments (H_{As} group) after incubation are shown in Fig. 5. The seven major elements exhibited the same trends in the single LMWOA solution, whereas the trends of the different trace elements were different. The chemical mechanisms of heavy metal(lloid)s are attributed to acidification, complexation and reduction by LMWOAs (Jones, 1998; Schwab et al., 2008; Onireti et al., 2017). According to the correlations listed in Table 2, three metals namely Fe, Mn, and Al were significantly ($p < 0.05$) positively correlated with the trace elements, exceptions are As vs. Mn, As vs. Al, and Pb vs. Al. For the Fe oxides and hydroxides, the high abundance and high affinity to As is crucial for controlling the mobilisation of elements (Smedley and Kinniburgh, 2002). The hydrolysis precipitation of Fe ions and their complexation with an organic ligand led to a low concentration of metal(lloid)s in the LMWOA extracts on day 14 of incubation (Geng et al., 2020). The synchronisation effect of Fe, Mn, and Al had a greater influence on the behaviours of trace elements. Zn ($5.73\text{--}37.8\text{ mg kg}^{-1}$), As ($0.42\text{--}16.7\text{ mg kg}^{-1}$), and Cr ($0.69\text{--}5.43\text{ mg kg}^{-1}$) exhibited higher concentrations under the treatment with the three LMWOAs. In addition, oxalic acid promoted the release of Cu (22.9 mg kg^{-1}) and Ni (8.67 mg kg^{-1}) on day 4 of incubation. The variations in Pb and As were both negatively influenced by the solution pH (Table 1).

3.2.3. Solution pH and DOC changes

The solution pH values of all three LMWOA extracts increased (Fig. 6) with the incubation time and were negatively correlated ($p < 0.05$) with the solution As (Table 1). The peak values of pH occurred on day 7 (pH = 7.94) and day 14 (pH = 7.76) in the alkaline solution of oxalic acid; the rest of the LMWOA treatments led to weak acidic states after incubation. The adsorption of ligands onto Fe oxides is favourable at lower pH values, thereby enhancing the dissolution of Fe oxides (Furrer and Stumm, 1986; Lee et al., 2017). The DOC concentrations in all three acid treatments were the highest on day 14, while they were relatively low ($0.02\text{--}0.93\text{ mol kg}^{-1}$) within one week incubation. The degradation and decomposition of oxalic acid likely led to a reduction in the abundance of the oxalate ion in the LMWOA–sediment systems (van Hees et al., 2005; Daniel et al., 2007), resulting in an increase in the DOC and pH. The LMWOAs can also be used to enhance the microbial

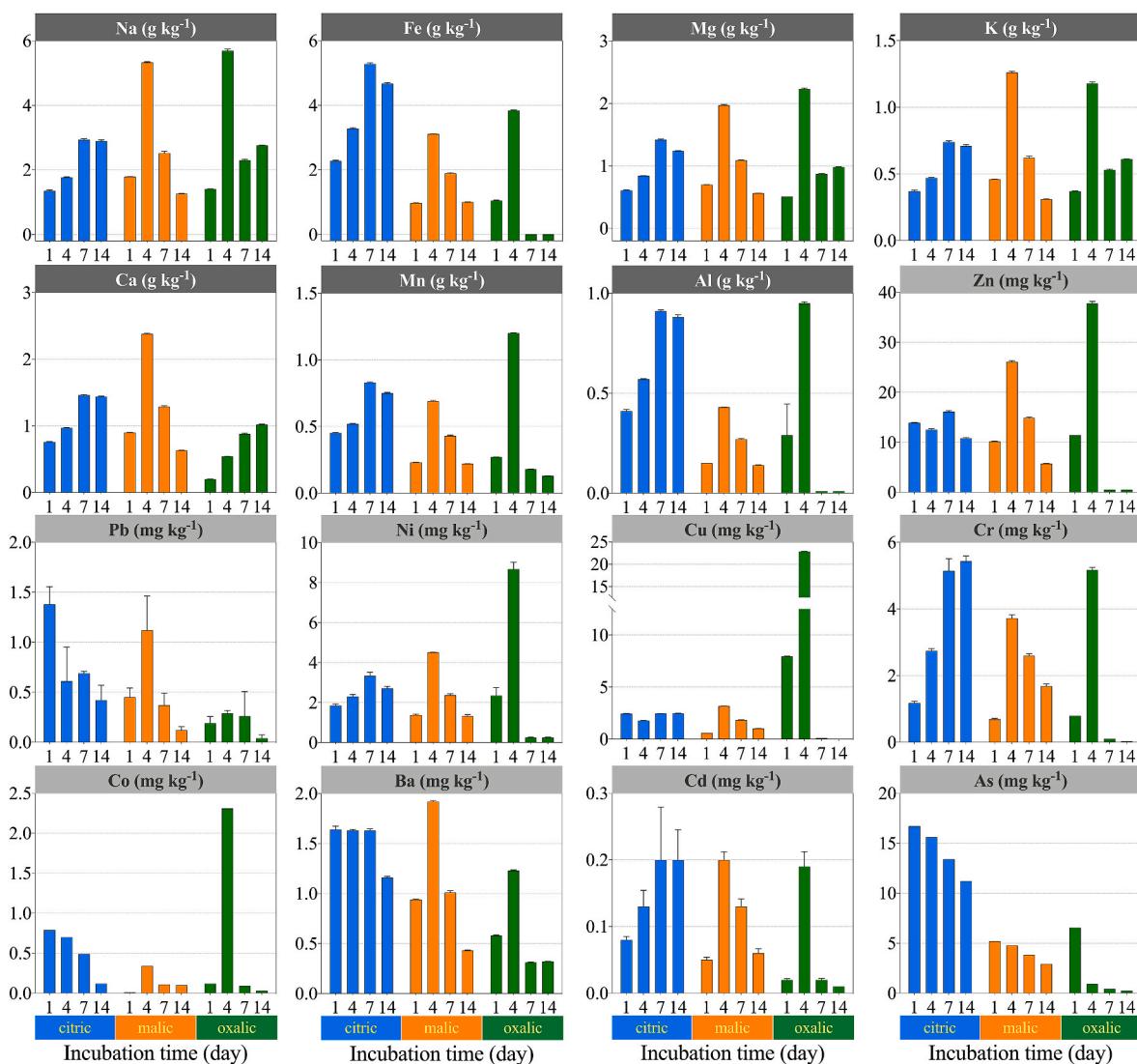


Fig. 5. The general variations of major elements (g kg^{-1} D.W.) and trace elements (mg g^{-1} D.W.) in the supernatant of LMWOA extracts from the As-enrichment sediments after incubation. All data were calculated as the relative concentrations to dry sediment weight (mg kg^{-1} DW).

Table 2

The correlations among the determined parameters in the supernatant during LMWOA incubation with mangrove sediments ($n = 12$). The significant correlations at 0.05 and 0.01 levels are marked in bold.

	DOC	pH	Na	Fe	Mg	K	Ca	Mn	Al	Zn	Pb	Ni	Cu	Cr	Co	Ba	Cd
DOC	1																
pH	0.06	1															
Na	-0.31	0.30	1														
Fe	0.10	-0.23	0.47	1													
Mg	-0.23	0.32	0.97^b	0.55	1												
K	-0.29	0.25	0.98^b	0.54	0.98^b	1											
Ca	0.22	0.10	0.55	0.35	0.59^a	0.64^a	1										
Mn	-0.09	-0.27	0.57	0.96^b	0.64^a	0.62^a	0.28	1									
Al	-0.05	-0.31	0.50	0.97^b	0.55	0.54	0.2	0.98^b	1								
Zn	-0.31	-0.43	0.50	0.75^b	0.57	0.58^a	0.21	0.85^b	0.80^b	1							
Pb	0.03	-0.65^a	0.15	0.59^a	0.25	0.27	0.46	0.60^a	0.56	0.60^a	1						
Ni	-0.26	-0.25	0.66^a	0.85^b	0.68^a	0.71^a	0.30	0.92^b	0.88^b	0.90^b	0.46	1					
Cu	-0.22	-0.34	0.41	0.72^b	0.37	0.42	-0.04	0.79^b	0.80^b	0.78^b	0.29	0.89^b	1				
Cr	0.15	-0.05	0.55	0.94^b	0.64^a	0.61^a	0.37	0.92^b	0.89^b	0.71^b	0.41	0.87^b	0.71^b	1			
Co	-0.09	-0.36	0.23	0.79^b	0.33	0.30	-0.06	0.82^b	0.84^b	0.79^b	0.55	0.68^a	0.72^b	0.67^a	1		
Ba	0.07	-0.59^a	0.30	0.77^b	0.40	0.41	0.39	0.80^b	0.77^b	0.82^b	0.89^b	0.71^a	0.59^a	0.67^a	0.79^b	1	
Cd	0.09	-0.13	0.57	0.91^b	0.69^a	0.67^a	0.57	0.90^b	0.84^b	0.75^b	0.64^a	0.85^b	0.61^a	0.93^b	0.62^a	0.78^b	1
As	0.28	-0.74^b	-0.27	0.59^a	-0.21	-0.18	0.15	0.49	0.54	0.35	0.75^b	0.30	0.34	0.36	0.53	0.68^a	0.43

Note: '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).

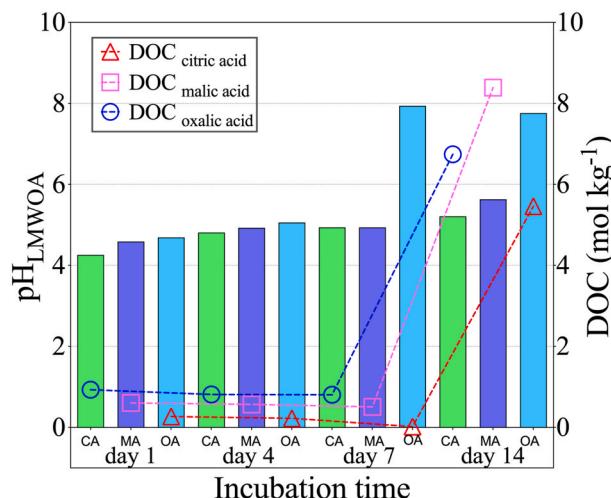


Fig. 6. The pH (bar) and dissolved organic carbon (DOC, dash line) in the supernatant from LMWOA–sediment mixture system of As40 group incubation. pH of citric acid (CA) = green bar; pH of malic acid (MA) = violet bar; pH of oxalic acid (OA) = azure bar. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

degradation of polycyclic aromatic hydrocarbons (Zhang et al., 2021b). In addition, LMWOAs affect the process of soil CO₂ emission (Canarini et al., 2019), which may influence the carbon storage of mangrove wetlands.

3.2.4. Characteristic and composition of sediments

The SEM micrographs of sediments revealed the surface texture and ultrastructure of the freeze-dried samples after LMWOA extraction (Fig. 7). The elemental composition of mangrove sediments from the three LMWOA treatments were characterized by scanning transmission electron microscopy (STEM) coupled with the detector of energy dispersive X-ray analysis (EDAX). After 14 days of incubation, the process improved the agglomerated microstructure and compactness of the sediments (Fig. 7). The particles grew larger because of size aggregation; the precipitation of the solid phase in the solution was associated with ageing performance, particle growth, Fe crystal formation and gel syneresis during two weeks of incubation (Dewhurst et al., 1999; Guo et al., 2010; Rozhkova et al., 2021). The insoluble Ca-LMWOA compounds (excluding the malic compound, Fig. 8) may have formed, in agreement with the results of rhizosphere observation (Rosenstock et al., 2019). The freeze-dried sediments contained many elements, including C, O, Al, Si, P, S, K, Ca, Mn, Fe and As (Fig. 8). The decrease in the proportion of C

weight in the sediments under citric and oxalic acids treatments is consistent with the increase in the DOC content in the solutions (Figs. 6 and 8). Fe and Mn both increased the proportional weight in the sediments after two weeks of incubation, which is in contrast to the trends in the case of supernatant.

4. Conclusion

Interactions between mangrove sediments, microorganisms, and the LMWOAs (citric acid, malic acid and, oxalic acid) exuded by the roots represent the migration and speciation of As/Fe and other elements under laboratory conditions. The release of sediment As was affected by the three modelled LMWOAs. Among the acids, citric acid was the most efficient for the unsterilised groups, while oxalic acid was the most efficient after sterilisation. Microorganisms may facilitate the release of As from sediments to the solution in the presence of citric and malic acids, but they suppress As mobilisation in the presence of oxalic acid. After sterilisation, As extraction from sediments by citric and malic acids decreased, whereas that by oxalic acid increased. This work shows that the mobilised behaviours of Fe, Mn, and Al were synchronized with those of the trace metal(lloid)s i.e. Zn, Pb, Ni, Cu, Cr, Co, Ba, Cd, and As in the LMWOA–sediment mixture. The solution pH was significantly negatively correlated with the solution As. However, the high concentration of DOC at the end of the incubation in contrast with the low contents of supernatant metal(lloid)s. It is worth mentioning that correlation does not necessarily indicate causation. The STEM–EDAX results reveal that particle aggregation leads to the dynamic patterns of the chemical composition of incubated sediments and that this aggregation is associated with the Fe, Mn and Al dynamics. The assumption is likely linked to proton consumption, Fe-Mn-Al sedimentation and ageing performance and organic ligand complexation in the incubated mixture system. The present study proposes that a combination of these LMWOAs and microbial involvement traits contributes to the synchronized migration of As and other metal(lloid)s and provides a potential understanding of the metal(lloid)s dynamics affected by the rhizospheric LMWOAs in mangrove wetlands for the fieldwork.

Credit author statement

Kang Mei: Conceptualization; Data curation, Formal analysis, Investigation, Methodology, Software, Writing - original draft and review & editing. Jiajia Wu and Hualong Hong: Visualization, Investigation, Review & editing. Guirong Wu, Jingchun Liu, Haoliang Lu, and Chongling Yan: Writing - review & editing, Funding acquisition, Project administration, Resources, Supervision, and Validation.

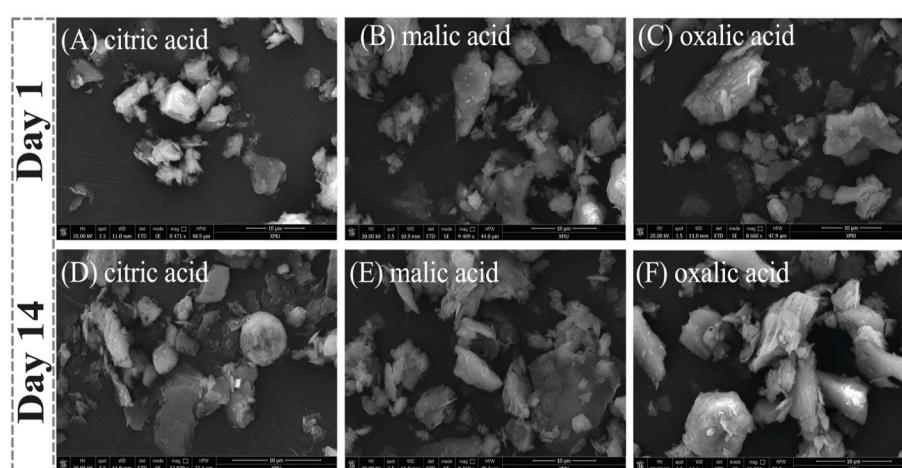


Fig. 7. Ultrastructure image of freeze-dried sediments after LMWOA incubation via scanning transmission electron microscope (STEM) analysis.

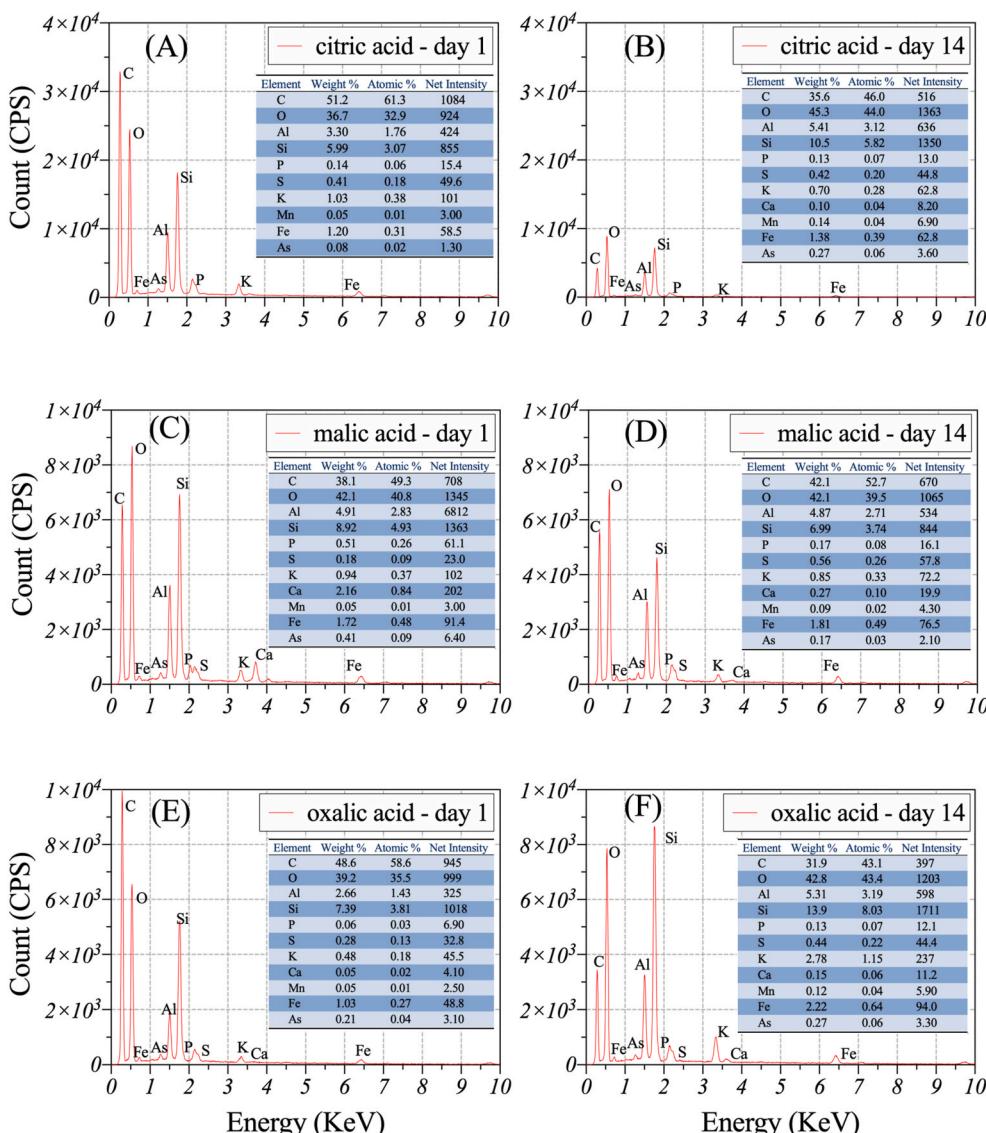


Fig. 8. The energy spectrum and element composition of freeze-dried sediments mapping data after LMWOA incubation via detector of energy dispersive analysis X-ray (EDAX).

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2021.131820>.

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