



Leaching heavy metals from the surface soil of reclaimed tidal flat by alternating seawater inundation and air drying



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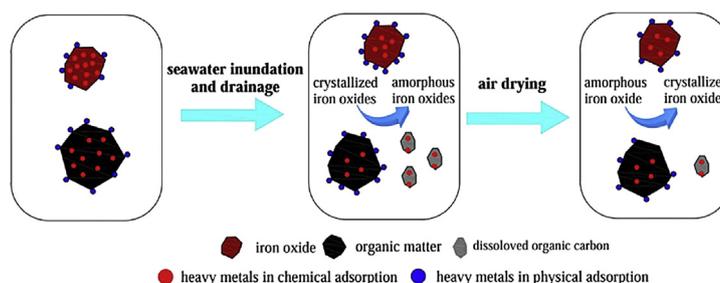
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HIGHLIGHTS

- Leaching by alternating inundation and air drying removed soil heavy metal.
- DGT measurement indicated that seawater inundation dissolved soil heavy metals.
- Newly formed amorphous iron oxides physically re-adsorbed the released heavy metal.
- Seawater inundation increased soil DOC and its complexation with heavy metals.
- Prolonged seawater inundation enhanced the release of soil heavy metals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 January 2016

Received in revised form

2 May 2016

Accepted 9 May 2016

Available online 27 May 2016

Handling Editor: Martine Leermakers

Keywords:

Heavy metals

Reclamation

DGT

Iron transformation

ABSTRACT

Leaching experiments were conducted in a greenhouse to simulate seawater leaching combined with alternating seawater inundation and air drying. We investigated the heavy metal release of soils caused by changes associated with seawater inundation/air drying cycles in the reclaimed soils. After the treatment, the contents of all heavy metals (Cd, Pb, Cr, and Cu), except Zn, in surface soil significantly decreased ($P < 0.05$), with removal rates ranging from 10% to 51%. The amounts of the exchangeable, carbonate, reducible, and oxidizable fractions also significantly decreased ($P < 0.05$). Moreover, prolonged seawater inundation enhanced the release of heavy metals. Measurement of diffusive gradients in thin films indicated that seawater inundation significantly increased the re-mobility of heavy metals. During seawater inundation, iron oxide reduction induced the release of heavy metals in the reducible fraction. Decomposition of organic matter, and complexation with dissolved organic carbon decreased the amount of heavy metals in the oxidizable fraction. Furthermore, complexation of chloride ions and competition of cations during seawater inundation and/or leaching decreased the levels of heavy metals in the exchangeable fraction. By contrast, air drying significantly enhanced the concentration of heavy

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metals in the exchangeable fraction. Therefore, the removal of heavy metals in the exchangeable fraction can be enhanced during subsequent leaching with seawater.

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1. Introduction

Although tidal flat reclamation may result in the loss of natural habitats and water buffering capacity, it has been the main supplement for arable land of coastal countries (Li et al., 2011). With economic growth and urbanization, tidal flat is contaminated with heavy metals caused by fluvial transport, atmospheric deposition, and/or local wastewater discharge (Qiao et al., 2007). Hence, tidal flats may pose potential health risks when crops are grown on reclaimed soil contaminated with heavy metals (Xiao et al., 2015).

Several methods, including bioremediation and physicochemical remediation, are used to remove heavy metals from soil (Ali et al., 2013). To date, bioremediation is considered unsuitable for reclaimed tidal flat because most hyperaccumulators cannot easily adapt to soil with high salinity. The most prevalent physicochemical remediation method is mobilization of heavy metals by adding chemical reagents (acid or chelating agent) and leaching soil by water (Udovic and Lestan, 2012). In this case, chemical reagents may destroy soil property and increase operational cost (Hu et al., 2014). Until now, few studies reported suitable remediation strategies for reclaimed tidal flat soils contaminated with heavy metals.

The mobility of heavy metals in soil is determined by the type of binding forms. All the binding forms of heavy metals, except residual fraction, are easily affected by several factors, such as adsorption/desorption; salinity; contents of organic matter (OM), sulfur, and carbonates; pH; and redox potential (Eh); and plant growth (Du Laing et al., 2009). Furthermore, heavy metals mobility can also be altered by microbes through acidification, Eh change and complexation (Rajkumar et al., 2012). Thus, among them, Eh is a prima important factor in the influence of the mobilization and immobilization of heavy metals in soil (Zhang et al., 2012). Under reducing condition (low Eh), reducible iron and manganese oxides in the solid phase are reduced to soluble Fe^{2+} and Mn^{2+} ; moreover, heavy metals bound to iron and manganese oxides are released (Frohne et al., 2011). However, heavy metal immobilization is induced by the formation of insoluble heavy metal sulfides (Du Laing et al., 2008). Under oxidizing condition, heavy metals coprecipitate with or are adsorbed on metal oxides or soil clay surface. The heavy metals can also be remobilized when S^{2-} is oxidized to soluble SO_4^{2-} (Du Laing et al., 2009). Besides, heavy metals can be mobilized by chloride ions and dissolved organic carbon (DOC) because of the formation of stable and soluble complexes (Karlsson et al., 2006; Pérez-Esteban et al., 2014). In addition to complexation, cations (Na, K, Ca, and Mg^{2+}) are involved in metal extraction through ion exchange in solutions with high ionic strength (Holden et al., 2013). Therefore, we hypothesized that alternating changes in Eh combined with soil washing is an effective strategy to remove metal contaminants from surface soil permanently.

During reclamation of tidal flats, levee systems are built to control seawater from sinking into the reclaimed land. Seawater can flow into the reclaimed land through sluice gate during high tide and drain out of the reclaimed land into the sea again during low tide. In levee systems, soil Eh can be altered by subjecting the reclaimed land soil to seawater inundation, drainage, and air drying. However, speciation transformation of iron oxides, organic matter and sulfur in soil during seawater inundation, drainage, and

air drying and their impact on release of heavy metals binding to soil are not fully understood. The objectives of the research are to (1) examine our hypothesis that alternating seawater inundation and air drying combined with soil washing is an effective strategy used to permanently remove metal contaminants from surface soil; (2) investigate the speciation transformation of iron oxides, organic matter and sulfur in soil during seawater inundation, drainage, and air drying and their impact on release of heavy metals.

2. Materials and methods

2.1. Experimental design

Leaching experiments were conducted in a greenhouse by seawater leaching combined with alternating seawater inundation and air drying. Soils (0–15 cm depth) were collected from a reclaimed tidal farmland in the estuary of Pearl River, which is the largest estuary and a typical region of reclaimed tidal flat in Southern China. The clay minerals of soil samples were mainly composed of illite and kaolin. The chemical compositions are the following major oxides: SiO_2 (43.4%), Al_2O_3 (28.6%), Fe_2O_3 (15.44%), and K_2O (2.6%). The soil samples were fractionated into 39.76% clay (<0.05 mm), 24.84% fine silt (0.1–0.05 mm), 20.15% coarse silt (0.25–0.1 mm), and 15.25% sand (2–0.25 mm). Immediately after collection, all soil samples were air dried and sieved with a 2 mm nylon sieve to remove coarse debris and stones. The samples were then homogenized by thorough mixing until use. Two PVC containers (100 cm width, 200 cm length, and 30 cm depth) with small drainage holes (5 mm diameter) on the bottom and lower lateral sides were prepared. A nylon sieve covered the drainage holes and held the soils. The two PVC containers were separately placed into two other bigger vessels with drain water taps to collect leachate and control water table. Well-mixed soil was placed into the container at a 20 cm depth. Water depth above the soil surface was maintained at 10 cm, and no leaching occurred when the drain water tap was turned off during the inundation. During leaching, flooded water on the soils was leached, and the leachate was drained by turning on the drain water tap. Fresh seawater was also added to the soil to maintain the water depth. The flooded water was then drained before soil air drying. Artificial seawater (33.4‰ salinity and 19‰ chlorinity, Table S1) was used in inundation and leaching.

Two experimental cases were performed through leaching combined with alternating seawater inundation and air drying. A schematic describing the two scenarios was shown in Fig. S1 (supplementary materials). In scenario 1, soil was stored under the seawater inundation condition for 20 d until the Eh value reached about -50 mV. Afterward, the soil was drained and air dried for 10 d, followed by leaching (water percolation) with seawater for 5 d. These steps were repeated, and the seawater inundation period was extended to 30 d. The steps and the corresponding samplings were marked from step 1 to step 6. In scenario 2, the seawater inundation period was extended to 30 d at step 1 and 60 d at step 4. Air drying and seawater leaching was then extended to 30 and 10 d, respectively. The samplings were an average sample on the full depth of the mesocosm and performed in triplicate. Scenarios 1 and 2 lasted for 80 and 170 d, respectively.

Prior to sampling, Eh value of the samples was determined by inserting polished platinum electrodes at depths of 5 cm and 15 cm and allowing them to equilibrate for 15 min before measuring the voltage against a calomel electrode with a pH/mV-meter (PHS-3C).

2.2. Sample analysis

The pH of the samples (including original soil) was measured in a 1/5 soil/distilled water suspension by using a pH/mV meter (PHS-3C) with a combined glass electrode (E-201F). The total heavy metal content of the soil samples was extracted by using an acid mixture of HCl–HF–HNO₃ (3:1:1) (Bettinelli et al., 2000). The detailed information was provided in supplement materials. To distinguish the exchangeable fraction and carbonate fraction of heavy metals, chemical fractionation of heavy metals in the samples was conducted by chemical sequential extraction developed by Tessier et al. (1979). Metal extracted process of samplings from step 1 and 4 were performed in a full N₂-filled glove box. The content of acid volatile sulfides (AVS) in the samples was analyzed according to the method described by Allen et al. (1993) and Fang et al. (2005). The method was based on colorimetric measurement of evolved H₂S after HCl addition. Simultaneously, extractable metals (SEM) were determined after complete H₂S removal through the AVS test. The dissolved sulfide content in the NaOH solution was measured by an ultraviolet spectrophotometer with the methylene blue method at a wavelength of 670 nm (Allen et al., 1993). The contents of Cd, Pb, Zn, Cu, and Cr were determined through flame atomic absorption spectrometry (F-AAS, Shimadzu AA-7000) and graphite furnace atomic absorption spectrometry (GF-AAS, Shimadzu AA-7000). Free iron oxides in the soil sample were extracted using dithionite–citrate–bicarbonate (Taylor and Crowder, 1983), whereas amorphous iron oxides were extracted by ammonium oxalate at pH 3.0 (Borggaard, 1979). The OM content of the soil samples was estimated by loss-on-ignition (Schulte and Hopkins, 1996). DOC was extracted using the method described by Antoniadis and Alloway (2002) using a 0.45 μm membrane filter under vacuum and quantified with a Shimadzu TOC analyzer. Diffusive gradient in thin film (DGT) deployment and soil analysis were analyzed using the methods described by Zhang et al. (1998), detailed information about DGT information was placed in supplementary materials.

Two soil standard reference materials [GBW07401 (GSS-1) and GBW07404 (GSS-4)] and blanks were subjected to digestion and analyzed in compliance with the quality control protocol. The results of the analysis were accepted when the measured concentrations in the reference materials are within one standard deviation of the certified values. The accuracy of the sequential extraction was evaluated by comparing the sum of concentrations determined from five fractions with the total concentration data. The obtained recovery rates were 85.04%–112.03%, 94.85–114.82%, 96.43–102.86%, 91.05–116.36%, and 92.72–95.75% for Cd, Pb, Cu, Cr, and Zn, respectively.

2.3. Data analysis

The removal rate of heavy metals in terms of percent removal efficiency is defined as Equation (1). Data were analyzed by Duncan's multiple range test at a probability level of 5% by using SPSS 18.0 statistical package. All figures were drawn using the PC-based origin 9.0.

$$\text{Removal rate (\%)} = \frac{100(C_0 - C)}{C_0} \% \quad (1)$$

where C_0 and C are the contents of Cd, Pb, Cu, Zn, or Cr in control (original soil) and treated soils, respectively.

3. Results

3.1. Occurrence and speciation of heavy metals in original soil

The concentrations and speciation of heavy metals in the original soil are listed in Table S2. The concentrations of Zn, Pb, Cu, Cr and Cd are: 461.72, 132.97, 63.93, 34.64 and 2.94 mg kg⁻¹, respectively. Heavy metal speciation in original soil indicated that the residual fraction (42%–87%) was the dominant binding form. Among the other four fractions, heavy metals were mainly in the reducible and/or oxidizable fractions. The proportion of the reducible fraction of Cd was the highest at 23%, followed by the exchangeable fraction (14%), carbonate fraction (11%), and oxidizable fraction (10%). The dominant binding form of Pb was the oxidizable (11%) and reducible fractions (10%), and the proportion of the exchangeable and carbonate fraction was lower than 2%. Similar to Pb, Cr was dominated by the reducible (25%) and oxidizable fractions (20%), and the carbonate and exchange fractions were lower than 1%. Cu had the highest proportion of the oxidizable fraction (45%), followed by the reducible fraction (15%). Moreover, the oxidizable fraction in Zn was 8%.

3.2. Occurrence and speciation of heavy metals in treated soils

After the treatment, the contents of all heavy metals, except Zn, significantly decreased ($P < 0.05$, Table 1). Scenario 2 exhibited higher removal rate than scenario 1. In the former, the amount of Cd reduced was 51%, which is the highest among all heavy metals, followed by Cr (39%). The removal rate of Pb and Cu were 19% and 15%, respectively. The removal rates of Cd, Cr, Pb, Cu, and Zn in scenario 2 were 36%, 36%, 15%, 10%, and 2%, respectively.

Supplementary materials (Tables S3 and S4) present the distribution of chemical speciation of heavy metals in scenarios 1 and 2 during the treatment. The concentrations in most of the speciation decreased after the treatment, except for the residual fraction of all heavy metals and the exchangeable and carbonate fractions of Cu. The removal rates of the chemical speciation of heavy metals in scenario 2 were higher than those in scenario 1. In the former, the reducible fraction of heavy metals, except Zn, significantly decreased after seawater inundation and drainage (step 1). Moreover, the oxidizable, exchangeable, and carbonate fractions of Cd, Pb, and Cr significantly decreased at step 1. After air drying (step 2), the carbonate, reducible, and oxidizable fractions of heavy metals decreased, whereas all exchangeable fractions, except Pb, increased. All exchangeable fractions, except for Pb, significantly decreased at step 3 after the soil leaching. From step 4 to step 6, although the contents of most heavy metals decreased, the downward trend was slower compared with those at the first three steps. Aforementioned, compared with other heavy metals, Zn was lightly leached after the treatment both in scenarios 1 and scenarios 2. However, the concentrations of the most metal speciation except residual fraction decreased significantly. Thus, a lower removal efficiency of Zn might be attributed to a high proportion of residual fraction (87%).

Table 1
Concentration of total metals in different steps for each scenario (mg/kg, dry weight soil).

Property		Cd	Pb	Cr	Cu	Zn
S1	CK	2.94 ± 0.10a	132.97 ± 1.01a	34.64 ± 0.94a	63.93 ± 1.55a	461.72 ± 10.77a
	Step1	2.54 ± 0.04b	131.44 ± 7.78ab	31.65 ± 2.80b	61.61 ± 0.93ab	459.78 ± 18.45a
	Step2	2.46 ± 0.09b	127.74 ± 8.48abc	30.35 ± 0.74b	61.57 ± 0.33ab	460.35 ± 8.35a
	Step3	2.38 ± 0.12b	123.11 ± 4.38abc	29.93 ± 0.39b	59.22 ± 5.24ab	457.91 ± 14.30a
	Step4	2.14 ± 0.12c	122.11 ± 9.79abc	26.66 ± 1.92c	57.42 ± 4.16b	456.25 ± 16.71a
	Step5	2.02 ± 0.09cd	118.42 ± 1.04bc	23.40 ± 2.34d	57.58 ± 1.03b	452.01 ± 9.30a
	Step6	1.87 ± 0.09d	113.6 ± 11.39c	22.31 ± 0.82d	57.43 ± 2.64b	452.84 ± 10.23a
Removal rate		36%	15%	36%	10%	2%
S2	CK	2.94 ± 0.10a	132.97 ± 1.01a	34.64 ± 0.94a	63.93 ± 1.55a	461.72 ± 10.77a
	Step1	2.03 ± 0.09b	121.76 ± 6.78b	27.04 ± 2.59b	59.40 ± 1.70b	455.39 ± 31.76a
	Step2	1.98 ± 0.13b	117.55 ± 5.37bc	25.96 ± 1.46b	58.31 ± 1.57bc	458.00 ± 17.97a
	Step3	1.83 ± 0.16b	113.85 ± 2.18cd	24.46 ± 0.93bc	57.06 ± 1.16bcd	455.48 ± 22.25a
	Step4	1.58 ± 0.14c	109.26 ± 0.95d	22.56 ± 0.41cd	55.35 ± 2.89cd	451.50 ± 18.64a
	Step5	1.55 ± 0.09c	107.34 ± 3.31d	21.25 ± 1.84d	54.44 ± 0.63cd	450.31 ± 12.16a
	Step6	1.45 ± 0.06c	107.46 ± 5.06d	20.96 ± 1.58d	54.14 ± 3.56d	450.33 ± 34.88a
Removal rate		51%	19%	39%	15%	2%

S1 represents scenario 1, S2 represents scenario 2.

CK: control, step 1: seawater inundation and drainage, step 2: air drying, step 3: seawater leaching, step 4: seawater inundation and drainage, step 5: air drying, and step 6: seawater leaching.

Letters "a," "b," "c," and "d" indicate significant differences at $p < 0.05$ within each column.

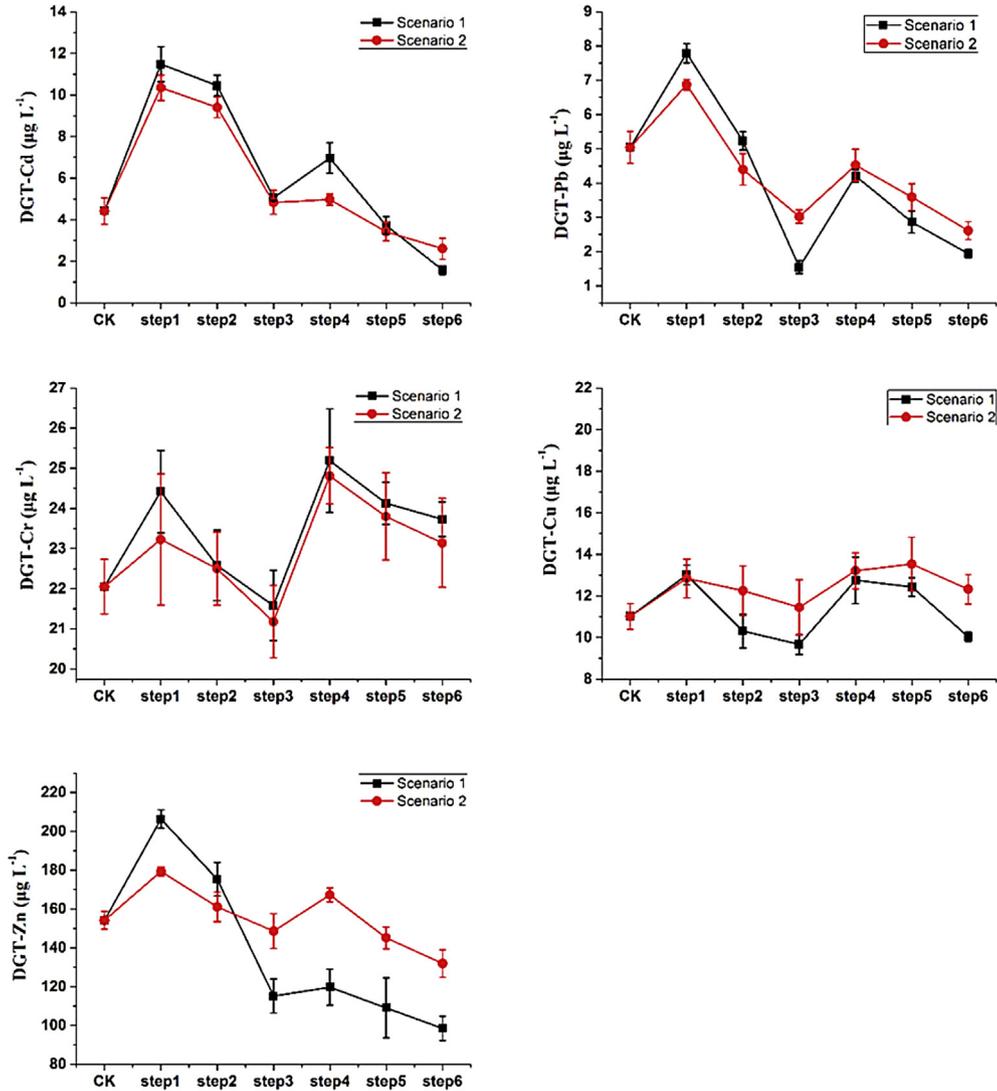


Fig. 1. C_{DGT} of heavy metals in soils in different treatment steps (CK: control, step 1: seawater inundation and drainage, step 2: air drying, step 3: seawater leaching, step 4: seawater inundation and drainage, step 5: air drying, and step 6: seawater leaching).

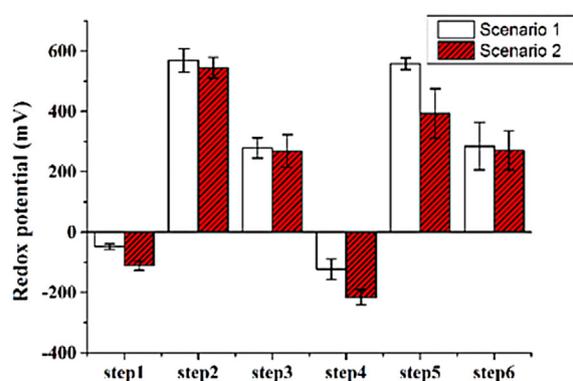
3.3. Concentrations of soil heavy metals measured by DGT

The C_{DGT} values of heavy metals in soils at each step are presented in Fig. 1. All C_{DGT} values increased after seawater inundation and drainage (steps 1 and 4). By contrast, C_{DGT} significantly decreased after air drying and leaching (steps 2, 3, 5, and 6). In the original soil, the sequence of C_{DGT} values is as showed: $C_{DGT-Zn} > C_{DGT-Cr} > C_{DGT-Cu} > C_{DGT-Pb} > C_{DGT-Cd}$. In most steps, C_{DGT} of Cd, Pb, and Zn between scenarios 1 and 2 significantly differed. However, C_{DGT} of Cr and Cu between scenario 1 and scenario 2 did not significantly differ. The DGT concentration of Cd, Pb, and Zn significantly decreased after step 6 in both scenarios compared with the control, but Cu and Cr did not significantly change after step 6 in both scenarios. The C_{DGT} of heavy metals monitored their remobilization and desorption from the solid phase.

3.4. Changes in Eh, pH, $\sum SEM/AVS$, and concentrations of amorphous iron oxides, free iron oxides, OM, DOC, AVS after the treatment

The Eh and pH values of soil in the two scenarios are presented in Fig. 2. After seawater inundation and drainage (steps 1 and 4), the soil was under the reducing condition, with Eh values ranging from -50 mV to -216 mV. After air drying for a few days, the soil was transformed to the oxidation condition, with Eh value ranging from $+269$ mV to $+569$ mV. Scenario 2 was under the stronger reducing condition than scenario 1 at each step because of prolonged seawater inundation. Soil pH decreased after the first treatment (step 1, seawater inundation and drainage) and gradually increased in the following treatments.

The contents of amorphous iron oxide, free iron oxides and crystallized iron oxides in different treatment steps are presented in Fig. 3. Ferric is reduced into the aqueous ferrous state under the reducing condition and subsequent formation of secondary Fe-bearing minerals or oxidized again to surface oxidic layer (Borch et al., 2009; Zhang et al., 2012). The amount of crystallized iron oxides decreased, whereas that of amorphous iron oxides increased after seawater inundation and drainage. This finding indicates that crystallized iron oxides were transformed into amorphous iron oxides. Conversely, air drying induces the transformation from amorphous iron oxides to crystallized iron oxides by promoting dehydrate (Tack et al., 2006). Thus, the amount of crystallized iron oxides increased, whereas that of amorphous iron oxides decreased after air drying. Moreover, the amount of amorphous and free iron oxides decreased after the subsequent seawater leaching compared with that after air drying.



The contents of OM and DOC are shown in Fig. 4. OM may be decomposed by anaerobic microbes under the inundation condition (Croué et al., 2003) and oxidized to CO_2 during weathering after air drying (Wengel et al., 2006). Therefore, the amount of OM decreased after all the treatment. The levels of DOC increased after seawater inundation and drainage, as well as after leaching, but significantly decreased after air drying.

AVS concentration and $\sum SEM/AVS$ ratio are presented in Fig. 5. Sulfate concentration in soil was relatively low (<30 mg kg^{-1}). AVS content and $\sum SEM/AVS$ ratio increased after seawater inundation and drainage and then decreased after air drying. $\sum SEM/AVS$ ratio was higher than 1 at each step, whereas AVS concentration was higher in scenario 2 than that in scenario 1. Meanwhile, $\sum SEM/AVS$ ratio was higher in scenario 2 than that in scenario 1 at each step.

4. Discussion

4.1. Speciation transformation and release of heavy metals during seawater inundation

After the seawater inundation and drainage treatment, the amount of all heavy metals (Cd, Pb, Cr, and Cu), except Zn, significantly decreased in scenario 2 ($P < 0.05$, Table 1). The C_{DGT} of soil heavy metals increased after seawater inundation and drainage. The concentrations in most of the speciation significantly decreased ($P < 0.05$), except for the residual fraction of all heavy metals and the exchangeable and carbonate fractions of Cu. The decrease in the reducible and oxidizable fractions was higher than that in the other fractions (Tables S3 and S4). These results indicated that the chemical speciation of heavy metals was transformed during soil seawater inundation.

An increase in C_{DGT} under seawater inundation implied that more heavy metals were bonded by DGT device from soil solution during the deployment time (Zhang et al., 1998); this phenomenon might result from an increase in free metal ions released from solid phase dissolution and/or desorption from solid phase. In contrast to our results, previous finding revealed that flooding promotes metal adsorption as an increase of hydrous Fe oxides, as a consequent, lower C_{DGT} (Li et al., 2015). Thus, an increase in C_{DGT} in our experiment might be attributed to the strong exchange ability of salinity to heavy metals adsorbed by soil under seawater inundation. Some of the increased dissolved heavy metals were drained during drainage treatment, resulting in a significant decrease of heavy metals in soil.

Oxygen depletion under seawater inundation resulted in the occurrence of a reducing condition, with low Eh values ranging

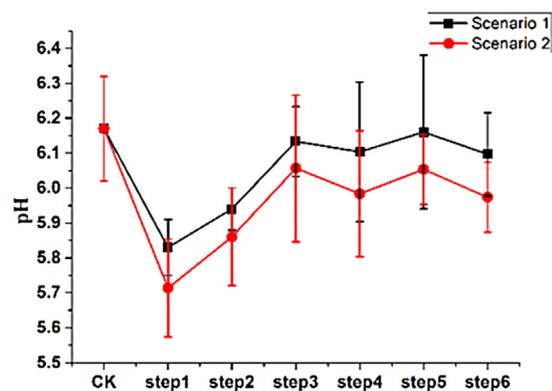


Fig. 2. Redox potential and pH in soils in different treatment steps (CK: control, step 1: seawater inundation and drainage, step 2: air drying, step 3: seawater leaching, step 4: seawater inundation and drainage, step 5: air drying, and step 6: seawater leaching).

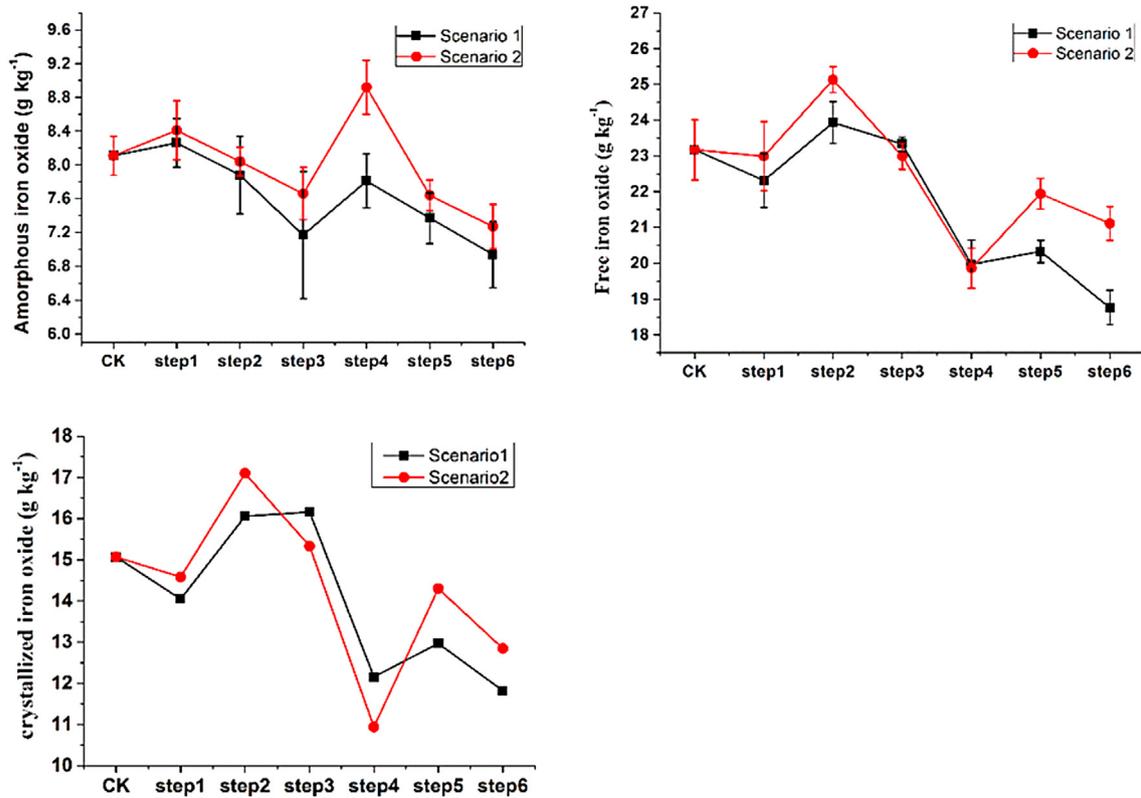


Fig. 3. Content of amorphous iron oxide, free iron oxides and crystallized iron oxides in soils in different treatment steps (CK: control, step 1: seawater inundation and drainage, step 2: air drying, step 3: seawater leaching, step 4: seawater inundation and drainage, step 5: air drying, and step 6: seawater leaching).

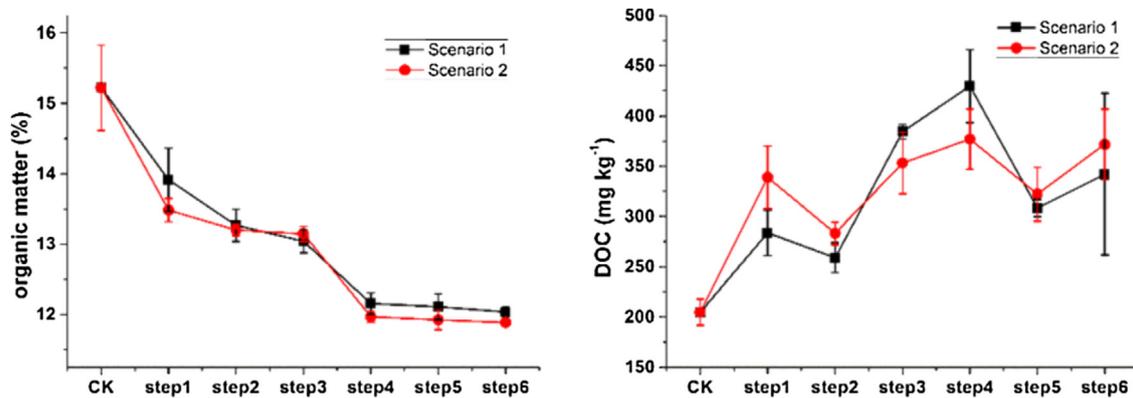


Fig. 4. Content of organic matter (OM) and DOC in soils in different treatment steps (CK: control, step 1: seawater inundation and drainage, step 2: air drying, step 3: seawater leaching, step 4: seawater inundation and drainage, step 5: air drying, and step 6: seawater leaching).

from -50 mV to -216 mV (Fig. 2), thereby facilitating the concomitant release of Fe^{2+} and reducible heavy metals from sediments because of the reduction of iron (III) hydroxides (Zak et al., 2004). However, the released Fe^{2+} would be easily re-oxidized to amorphous iron oxides in the surface oxic layer (Fan et al., 2014), whereas the increased amounts of amorphous iron oxides would co-precipitate with and re-adsorb more soluble heavy metal ion than crystallized iron oxides because of their larger surface area (Zhang et al., 2016). After seawater inundation and drainage, the reducible fraction decreased, specifically at step 1 (Tables S3 and S4). This suggests that heavy metals were re-adsorbed onto the newly formed amorphous iron oxides mainly through physical adsorption (belongs to the exchangeable fraction),

rather than chemical adsorption. Thus, the reduction of iron oxides significantly decreased the reducible fraction.

OM may be anaerobically degraded through microbial activity, thereby supplying electrons, protons, DOC, and chelating agents and releasing heavy metals in the flooded soil (Zhang et al., 2012). DOC exhibits a high potential to form a complex with heavy metals (Li et al., 2013); as such, DOC is an important carrier for heavy metals from refractory OM in surface water and into the sediment (Croué et al., 2003; Bolan et al., 2014). In the present experiment, the amount of OM decreased, whereas that of DOC increased after seawater inundation and drainage, as well as after leaching. High molecular weight OM, that complexes metals was degraded by bacteria and transformed into low molecular weight DOC that also

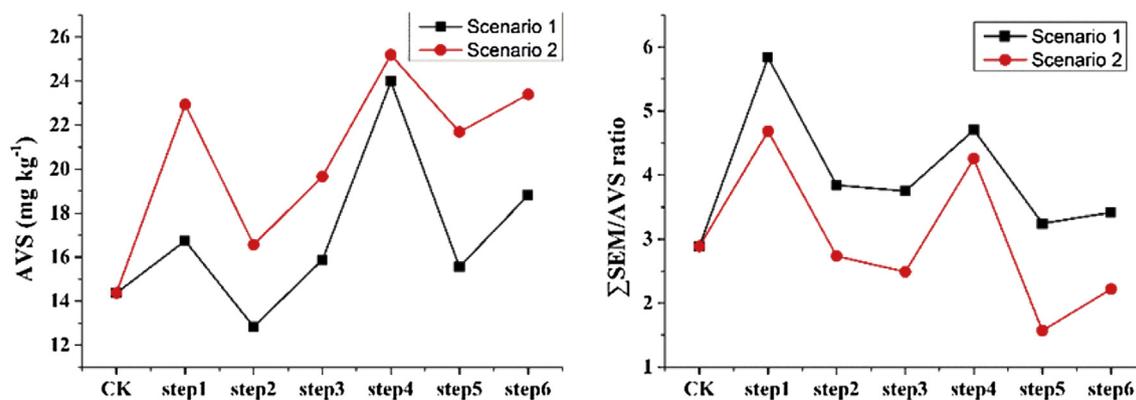


Fig. 5. Content of AVS and $\Sigma\text{SEM}/\text{AVS}$ ratio in soils in different treatment steps (CK: control, step 1: seawater inundation and drainage, step 2: air drying, step 3: seawater leaching, step 4: seawater inundation and drainage, step 5: air drying, and step 6: seawater leaching).

complexes metals. Thus, the concentration of heavy metals complex with DOC increased. A part of the DOC complex with heavy metals was drained or leached, resulting in decreased oxidizable fractions of heavy metals. Furthermore, the reduction from sulfate to S^{2-} may increase the oxidizable fraction because of the formation of sparingly soluble metal–sulfide complexes and/or (co)precipitation of sulfide minerals under reducing soil condition (Zhang et al., 2012). Although AVS concentration increased after seawater inundation and drainage (Fig. 5), the sum of heavy metal concentration (ΣSEM) increased much more than the AVS concentration and was significantly higher than the AVS concentration in the soils. Therefore, SO_4^{2-} reduction did not generate sufficient amount of S (–II) (aq) to bind to heavy metal ion. The increased DOC complex contributed to the decreased oxidizable fraction of heavy metal.

Carbonate fraction is activated by H^+ attack and partially transformed into loosely adsorbed or exchangeable species (Zhao et al., 2013). Under seawater inundation condition, CO_2 (soil respiration) and some organic acids produced by anaerobic microorganisms may accelerate carbonate dissolution (Janssen et al., 2009). Compared with the control, soil pH significantly decreased after step 1 and then gradually increased in the subsequent steps, resulting in relatively higher removal rate of the carbonate fraction at step 1 (Tables S3 and S4). In the subsequent steps, most of the microbes were killed by air drying step and/or the nutrients for microbes might be exhausted or leached. These phenomena resulted in a decrease in microbial activity, a decrease in the amount of released organic acid, and an increase in soil pH (Qiu and McComb, 1995).

Iron oxide reduction, OM decomposition, and carbonate fraction dissolution contributed to the release of heavy metals. Some heavy metals released were dissolved in the soil solution, whereas the other heavy metals may be re-adsorbed into the soil particles and exist in the exchangeable fraction. Under chloride ion complexation and cation competition (Na, K, Ca, and Mg) (Zhao et al., 2013), these exchangeable heavy metals are released again and drained or leached. Therefore, the exchangeable fraction significantly decreased after seawater inundation and drainage and/or leaching compared with that in the control. Similar results were reported by Speelmans et al. (2007).

4.2. Speciation transformation and release of heavy metals during air drying

Physical and chemical changes occur after air drying. These changes include sediment compaction, sediment particle aggregation, iron transformation, and OM mineralization (Blackwell

et al., 2010). Heavy metal ions adsorbed on the iron oxide surface in solutions will be occluded during the precipitation of re-oxidized Fe after soil drainage (Contin et al., 2007). Heavy metals would be immobilized when they occluded in crystal crystalline Fe oxides because of the strong chemical bond between the ion and the oxide surface (Nico et al., 2009). On the other hand, heavy metals adsorbed onto amorphous iron oxides were in the equilibrium state with the exchangeable fraction and the complex with heavy metal (Contin et al., 2007). Thus, amorphous iron oxides can slowly release the adsorbed heavy metals during air drying. In our experiment, the amorphous iron oxides were transformed to crystallized iron oxides after air drying, whereas the reducible fraction did not significantly change. This is because the amount of heavy metals released from amorphous iron oxides could be a possible offset by occlusion in the crystal crystalline Fe. Although some of microbial biomass would be killed and microbial activity would be reduced after soil air drying (Meisner et al., 2015), the amount of OM still slightly decreased. OM mineralization will accompany the release of associated heavy metals. The slight decrease in the amount of OM resulted in slight decrease in the oxidizable fraction. Since the concentration of oxidizable fraction was much higher than that of the exchangeable fraction, even a slight release of the oxidizable fraction may significantly increase the amount of the exchangeable fraction after air drying. Fan et al. (2014) confirmed that the cation exchange capacity of air drying soil is only half of the capacity of the flooded soil because of sediment particle aggregation. Similarly, Tack et al. (2006) also reported that the amount of soluble heavy metals in soil increased after drying. Their findings imply the loss of the adsorption sites after soil air drying. Thus, the increased heavy metals in exchangeable fraction in our experiment could be easily leached in the subsequent seawater leaching step.

Although heavy metals could be efficiently removed from surface soil by this treatment, secondary environmental risk caused by the release of polluted seawater after drainage and/or leaching steps should be remarkably considered. It would be pose high environmental risk if the leachate from surface soil is drained directly into seawater. The composition of the enriched water was also not analyzed to verify a transfer of heavy metal from soil to leachate and to evaluate its risk. In the field of real reclaimed tidal flats, leachate from surface soil may continue to penetrate the soil downward (30–70 cm deep); in deep soil, heavy metals leached from the surface soil are adsorbed. The leachate from deep soil is then drained through deep ditch. Our previous study demonstrated that heavy metals released from topsoil (0–20 cm) accumulate in deep soil, and leachate from deep soil can satisfy environmental

quality requirements by regulation during leaching in column experiment (Tong, 2010; Yang et al., 2016). Furthermore, our experiment was in mesocosms, as such, our results might not fully represent real systems. Many factors, such as soil Eh, soil conductivity, and water salinity, may differ between mesocosms and real field because of differences in soil texture, rainfall and drainage. However, more detailed information in real field should be further investigated.

5. Conclusions

Seawater inundation and air drying significantly influenced the mobilization of heavy metals in most binding forms, except for residual fraction. The contents of heavy metals (Cd, Pb, Cu, and Cr), except Zn, in surface soil significantly decreased after the treatment. Prolonged seawater inundation and air drying enhanced the release of heavy metals. Iron oxide reduction and OM degradation into DOC were the main causes of decreased reducible and oxidizable fractions, respectively. We believe that leaching combined with alternating seawater inundation and air drying is an effective method for removing heavy metals from the surface of the reclaimed flat soil during flat reclamation.

Acknowledgments

The present study was financially supported by the Ministry of Science and Technology of China (2012BAC07B05), National Natural Science Foundation of China (41371321) and the project of the Integration of Industry, Education and Research of Guangdong Province (2015B090903070).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2016.05.019>.

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