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Iron plaque formation and heavy metal uptake in *Spartina alterniflora* at different tidal levels and waterlogging conditions

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ABSTRACT

Tidal flat elevation in the estuarine wetland determines the tidal flooding time and flooding frequency, which will inevitably affect the formation of iron plaque and accumulations of heavy metals (HMs) in wetland plants. The present study investigated the formation of iron plaque and HM's (copper, zinc, lead, and chromium) accumulation in *S. alterniflora*, a typical estuarine wetland species, at different tidal flat elevations (low, middle and high) in filed and at different time (3, 6, 9, 12 h per day) of waterlogging treatment in greenhouse conditions. Results showed that the accumulation of copper, zinc, lead, and chromium in *S. alterniflora* was proportional to the exchangeable fraction of these metals in the sediments, which generally increased with the increase of waterlogging time, whereas the formations of iron plaque in roots decreased with the increase of waterlogging time. Under field conditions, the uptake of copper and zinc in the different parts of the plants generally increased with the tidal levels despite the decrease in the metals' exchangeable fraction with increasing tidal levels. The formation of iron plaque was found to be highest in the middle tidal positions and significantly lower in low and high tidal positions. Longer waterlogging time increased the metals' accumulation but decreased the formation of iron plaque in *S. alterniflora*. The binding of metal ions on iron plaque helped impede the uptake and accumulation of copper and chromium in *S. alterniflora*.

1. Introduction

Spartina alterniflora L., a perennial salt marsh plant native to Eastern North America, has been introduced to China in the 1990s to stabilize eroding coastal banks (Li et al., 2009; Smith and Lee, 2015). *S. alterniflora* (Alberts et al., 1990; Windham et al., 2001; Weis and Weis, 2004; Quan et al., 2007; Salla et al., 2011) and many other salt marsh plants, such as *Phragmites australias* Trin. (Windham et al., 2001; Quan et al., 2007; Weis and Weis, 2004; Altaisan, 2009), *S. maritima* (Reboreda and Caçador, 2008; Padinha et al., 2000), *S. densiflora* (Mateos-Naranjo et al., 2008, 2011; Idaszkin et al., 2015), and *S. argentinensis* (Redondo-Gómez et al., 2011), can accumulate large quantities of heavy metals (HMs), including copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), manganese (Mn), nickel (Ni), cadmium (Cd), and arsenic (As), to the root with small amounts being transported to the aerial parts of the plants. Metals accumulated in the plants might also be released to the ambient environment due to the decomposition of plant litters or through the leaf salt excretion process of some species (Windham et al., 2001; Weis and Weis, 2004), and some of the HMs may enter the food web of the estuarine ecosystems (Dorgelo et al., 1995). Therefore, marsh plants can either be sources or sinks for HMs, which play important functions in biogeochemical cycling of HMs in estuarine wetlands (Weis and Weis, 2004; Chen et al., 2017).

The distribution and survival of salt marsh plants in coastal wetlands are determined mainly by the tidal inundation, and the frequency as well as duration of the tidal inundation vary greatly in the tidal flat (Huckle et al., 2000; Winkel et al., 2011; Brownstein et al., 2013; Duarte et al., 2014). The variation of the frequency and duration of the tidal flooding have profound influence on the adsorption and desorption behaviors of HMs in sediment through the modification of the redox potential (Eh), pH, dissolved organic carbon, redox chemistry of iron (Fe), Mn, and sulfur (S) (Zhu et al., 2012; Shaheen et al., 2014; Calvo-Cubero et al., 2016), and hence influence the accumulation and uptake of HMs in marsh plants (Thakur et al., 2016; Yan et al., 2017). Under waterlogging conditions, the Eh of the sediment usually decreases with increasing water inundation time, during which the insoluble Fe^{3+} and $Mn^{3+/4+}$ (hydr)oxides are reduced to soluble Fe^{2+} and Mn^{2+}, respectively, and the HMs that fixed to Fe^{3+} and $Mn^{3+/4+}$ (hydr)oxides are transformed into more mobile forms and released to soil pore water. Longer water inundation time may further decrease the Eh, and the sulfate in the sediment will be reduced to its metal-complexing form, sulfide (Reddy and DeLaune, 2008). With draining water,

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the sediments turned oxic, in which the co-precipitation or adsorption and subsequent immobilization of these metals occur. The extractable HMs in the sediments exert major influences on plants' growth and metal accumulation, and the fractionation of HMs in the sediments is closely correlated with the alternating hydrological regime of the sediment (Zhao et al., 2016).

To adapt to anaerobic conditions, wetland plants can produce aerenchyma, which allows the conduction of oxygen (O_2) from above ground plant parts to roots to maintain regular root respiration (Armstrong et al., 1992; Mainiero and Kazda, 2005). Iron (Fe) plaque is a common concomitant of radical oxygen loss (ROL) in the roots of wetland plants, which is induced by oxidation of Fe^{2+} to Fe oxides that are precipitated as plaque on the root surface (Armstrong, 1992; St-Cyr and Crowder, 1989). The effects of Fe plaque on metal uptake is controversial; conflicting results were reported as to whether the presence of the plaque reduces or increases the metal uptake of the plants (Ye et al., 1997; Batty et al., 2000; Tripathi et al., 2014). Most of the studies suggested that Fe plaque can bind with some toxic HMs and co-precipitate outside the root tissues, affecting the metal uptake in aquatic plants (Ye et al., 1997; Batty et al., 2000). Fe plaque was found to decrease the mobility of As, Mn, Cu, Pb, and Zn in some wetland plants, such as *Phragmites australis* (Batty et al., 2000), *Typha latifolia* (Blute et al., 2004) and *S. densiflora* (Cambrollé et al., 2008). Similar effects were also observed on Mn, Zn, Ni, Pb, Cr, and Cd in mangrove species, including *Bruguiera gymnorrhiza*, *Excoecaria agallocha, Acanthus ilicifolius*, and *Kandelia obovata* (Pi et al., 2011; Du et al., 2013).

The formation of Fe plaque in wetland plants are species-specific and are generally affected by various biotic and abiotic factors, such as oxidizing capacity of plant roots, texture, organic matter, and pH of the sediments (St-Cyr and Crowder, 1989; Armstrong et al., 1992; Tripathi et al., 2014). In China, hydrological regime (waterlogging or draining) of the coastal wetland sediments suffered great effects from reclamation activities (Ma et al., 2014) and extreme climate events (Duarte et al., 2015), which are both becoming more frequent because of the rapid economic development and climate change. To our knowledge, however, still very little is known about the Fe plaque formation in *S. alterniflora* and its roles in the HM accumulation and translocation in this plant under the influences from the periodic tidal inundation. The present study therefore aimed to investigate the effects of the periodic flooding and the variation of the physiochemical properties of the tidal flat on the uptake of HMs and formation of Fe plaque in *S. alterniflora*.

2. Materials and methods

2.1. Experimental setup

2.1.1. Field sampling

The frequency and duration of tidal inundation usually decrease as the elevation of the marsh increases (Huckle et al., 2000). In field conditions, *S. alterniflora* occupies a wide range of tidal levels with varied tidal elevations. Plants that grow in low tidal positions usually receive more waterlogging compared with those grown in high tidal positions. To investigate the variation of Fe plaque formation and HM accumulation in *S. alterniflora* at different waterlogging regimes under field conditions, we collected samples of the different plant parts of *S. alterniflora* and the ambient sediment in North Chongming Island on October 14, 2016 (Fig. S1 in the Supplementary Material). Three tidal positions (low, middle and high) were set along a transect with different distances from the tidal creek, in which the low tidal position was spaced 100 m apart from the tidal creek, the middle tidal creek spaced 200 m apart from the low tidal positions, and the high tidal position spaced 160 m apart from the high tidal positions. Triplicate samples (leaf, stem, and root) of *S. alterniflora* were collected at each tidal position, and the collected samples were placed into an ice chest and brought to the laboratory for HMs and Fe plaque measurements. During the sampling of plant samples, the Eh values of the rhizosphere sediments were measured in situ with an Oxidation Reduction Potential (ORP) meter (Spectrum IQ150, Spectrum Technologies Inc., USA), and the ambient sediment samples were also collected and brought to the laboratory for future measurement of soil texture, salinity, and total organic matter content.

2.1.2. Greenhouse-controlled experiment

To investigate the effects of different waterlogging times on the formation of Fe plaque and metal uptake in *S. alterniflora*, we designed automatic waterlogging systems to mimic the different tidal inundation times in real habitats. The waterlogging system was composed of an upper water tank [75 cm (L) × 60 cm (W) × 75 cm (H)], a polypropylene (PP) pot [50 cm (L) × 20 cm (W) × 40 cm (H)], and a lower water tank (with size the same as that of the upper water tank). PP pots were used for the cultivation of the seedlings, and holes with a diameter of 2 cm were punched evenly on the side walls of the pots for convenient water drainage. The PP pots sown with the seedlings of *S. alterniflora* were placed in the upper water tank. During the experiment, the treatment solutions in the lower water tank were pumped into the upper water tank that is automatically controlled by a time switch and kept in the upper water tank for a given period. Then, the solution in the upper tank was drained to the lower water tank through a time-controlled electric valve to complete a water cycle.

Seedlings of *S. alterniflora* with comparable size (approximately 40 cm in height) were collected in Nanhui, Shanghai. A total of 15 PP pots were prepared for the experiment. The collected *S. alterniflora* seedlings were carefully transplanted into the PP pots with the sediments collected from the ambient habitats. Each pot had six seedlings and contained approximately 6 kg of sediments. The physiochemical parameters of the sediments are summarized in Table S1 (Supplementary Material). The texture of the sediment was silt loam with TOM content of 8.8% ± 2.3%, and the background concentrations of Cu, Zn, Pb, and Cr are 12.5 ± 1.6, 62.2 ± 4.9, 5.8 ± 0.8, and 18.6 ± 1.0 mg Kg^{-1}, respectively. The pots were placed in greenhouse with a daily temperature of 20–30 °C, a relative humidity of 59–80%, and a light intensity of 800–1400 μmol photons $m^{-2}\ s^{-1}$. The seedlings were irrigated with tap water once daily until the start of the treatments. After 14 days of rejuvenation, seedlings were also randomly divided into five groups, and each group was set in triplicates. Four groups were placed into water tanks that received different waterlogging times (3, 6, 9, and 12 h) with treatment solution containing HMs, namely, 3 h + HMs, 6 h + HMs, 9 h + HMs, and 12 h + HMs. The pots were waterlogged twice a day to simulate the semidiurnal tide in Yangtze River estuarine. The treatment solution was prepared by dissolving appropriate amounts of $CuCl_2$, $ZnCl_2$, $PbCl_2$, and $CrCl_3$ into salt water (10‰ NaCl) to make the final concentrations of 23.4, 60.8, 18, and 11.2 mg L^{-1} for Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cr^{3+}, respectively. The selection of metals and metal concentrations were based on a previous investigation on total bioavailable sediment HMs in Yangtze River estuarine (Chen et al., 2001).

Plant samples were collected 60 days after the treatment. One seedling in each pot was carefully pulled from the sediment and sufficiently washed with deionized water. Fresh lateral roots of the plants were collected and kept at 4 °C for the analysis of Fe plaque. The leaves, stems, and roots of the other plants were separated and dried in an oven at 70 °C for 48 h for the analyses of HMs. The sediments in the pots were also collected at the end of the experiments for the measurement of HMs. The collected sediment samples were air dried, grained in mortar, and then passed through a 1-mm sieve. The samples were stored in a desiccator for future analyses.

2.2. Determinations

2.2.1. Total and acid fraction HMs in sediments

For the measurement of total HMs in the sediments, 0.5 g of sediment sample was digested in a 50-mL polytetrafluoroethylene beaker