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Seasonal differences in trace element concentrations and distribution in *Spartina alterniflora* root tissue

Huan Feng [a, *], Yu Qian [b], J. Kirk Cochran [c], Qingzhi Zhu [c], Christina Heilbrun [c], Li Li [d], Wen Hu [d], Hanfei Yan [d], Xiaojing Huang [d], Mingyuan Ge [d], Evgeny Nazareski [d], Yong S. Chu [d], Shinjae Yoo [e], Xuebin Zhang [f], Chang-Jun Liu [f]

[a] Department of Earth and Environmental Studies, Montclair State University, Montclair, NJ 07043, USA
[b] School of Ecology and Environmental Sciences, Yunnan University, Kunming, Yunnan 650091, PR China
[c] School of Marine and Atmospheric Science, State University of New York, Stony Brook, NY 11794, USA
[d] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA
[e] Computational Science Initiative, Brookhaven National Laboratory, Upton, NY 11973, USA
[f] Biological Sciences Department, Brookhaven National Laboratory, Upton, NY 11973, USA

HIGHLIGHTS

- Synchrotron XRF nanometer-scale investigation for elemental distributions.
- Iron (Fe) may scavenge As and Cr and impact their distribution in the root system.
- Seasonal variations in S, P and Fe were found in porewater and root epidermis.
- Plant nutrient needs determine element transport and accumulation in the root.

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ABSTRACT

The present study uses nanometer-scale synchrotron X-ray nanofluorescence to investigate season differences in concentrations and distributions of major (Ca, K, S and P) and trace elements (As, Cr, Cu, Fe and Zn) in the root system of *Spartina alterniflora* collected from Jamaica Bay, New York, in April and September 2015. The root samples were cross-sectioned at a thickness of 10 μm. Selected areas in the root epidermis and endodermis were mapped with a sampling resolution of 100 and 200 nm, varying with the mapping areas. The results indicate that trace element concentrations in the epidermis and endodermis vary among the elements measured, possibly because of their different chemical properties or their ability to act as micronutrients for the plants. Elemental concentrations (As, Ca, Cr, Cu, Fe, K, P, S and Zn) within each individual root sample and between the root samples collected during two different seasons are both significantly different ($p < 0.01$). Furthermore, this study indicates that the nonessential elements (As and Cr) are significantly correlated ($p < 0.01$) with Fe, with high concentrations in the root epidermis, while others are not, implying that Fe may be a barrier to nonessential element transport in the root system. Hierarchy cluster analysis shows two distinct groups, one including As, Cr and Fe and the other the rest of the elements measured. Factor analysis also indicates that the processes and mechanisms controlling element transport in the root system can be different between the nutrient and nonessential elements.

1. Introduction

Although human activities have caused the loss of large areas of salt marshes worldwide, these wetlands play an important ecosystem role as habitats and nurseries for marine life (e.g., fish, invertebrates and birds), and as filters removing contaminants from

* Corresponding author.
E-mail address: fengh@montclair.edu (H. Feng).

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coastal waters. Wetland plants acquire metals and other trace elements from the rhizosphere (Williams et al., 1994; CaCador and Catarino, 1998; Weis and Weis, 2004; Gallagher et al., 2008; Qian et al., 2012, 2014). During plant growth, a number of transporter proteins and/or membrane channel proteins are involved in taking up from environment and transporting nutrients within the tissue, which can cause the accumulations of the microelements within the plant tissue such as root (Morrissey and Guerinot, 2009; Smith et al., 2003). Many trace elements are micronutrients required by plants for their growth. Investigation of the mechanisms that control the mobility and storage of such elements in the roots is important. With seasonal variations, many wetland plant species have developed survival strategies during the dormancy and growing seasons, which are controlled by their biological clock that tells them how to adjust their activities, including nutrient uptake and storage through the root system. Therefore, the concentration and distribution of trace elements in the plant root in spring and fall seasons provide an opportunity to investigate the effect of seasonal variations on trace and major element transport and storage and the relationships among various elements.

Traditional wet chemistry analytical methods have limitations in the measurement of elemental concentrations because they can only provide bulk concentrations in the plant roots. For example, the dithionite–citrate–bicarbonate (DCB) method for extraction of Fe plaque can only easily extract Fe plaque on the root surface (Taylor and Crowder, 1983; Liu et al., 2004, 2008; Hu et al., 2014; Huang et al., 2015a). The method cannot extract Fe from the entire root tissues nor can it map the element distribution in a root cross-section. Synchrotron X-ray microfluorescence (μXRF) technique has an advantage in studying metal concentration and distribution in plants because it provides detailed information of the element distribution on the surface and within the plants with micrometer or nanometer scale resolution (Martin et al., 2001; Hansel et al., 2002; Martin et al., 2006; Zimmer et al., 2011; Al-Sid-Cheikh et al., 2015; Feng et al., 2013, 2015, 2016). Therefore, synchrotron X-ray nanoprobe measurement can provide new insights into the mechanisms taking place in plants during the course of metal uptake and transport at levels where interactions can be understood. The salt marsh cord grass, *Spartina alterniflora,* is native to the Atlantic coast of the United States and the predominant wetland species in Jamaica Bay, New York. In this study, we apply synchrotron X-ray nanofluorescence technique to investigate the distribution of As, Ca, Cr, Cu, Fe, K, P, S and Zn, which are essential nutrients for plant growth, in the root tissue of *S. alterniflora* from Jamaica Bay. The purpose of this study is to improve our current knowledge of transport and accumulation of trace elements in the root system in order to better understand the ecological function of the salt marsh ecosystem.

2. Materials and methods

2.1. Sample collection and preparation

Jamaica Bay in New York is a coastal lagoon characterized by numerous salt marsh islands and an urban lagoon that has lost extensive acreage of these salt marsh islands, ~70% over the period 1951 to 2003, and studies are ongoing to ascertain the cause of the loss (Hartig et al., 2002; Gateway National Recreation Area (GATE) and Jamaica Bay Watershed Protection Plan Advisory Committee (JBWPPAC, 2007). Elders Point East in north Jamaica Bay was a degraded marsh vegetation that was restored during 2006–2007 by emplacing sand on the mudflat surface to build it up and subsequently planting *S. alterniflora* (Campbell et al., 2017). Field study was conducted in April and September 2015 at a sampling site in Elders Point East marsh, located in the northwestern part of Jamaica Bay (40° 38′ 10.208″N, 73° 50′ 44.59″W). Single ~50 ml samples of porewater were taken using porewater "sippers" at each of four depths - 5, 10, 15, and 25 cm- in the marsh peat. The sippers were made of hollow acrylic rods that ended in a small opening (Cochran et al., 2013). Each sipper was connected to Tygon tubing which could be connected to a 50 ml plastic syringe. A valve connected to the Tygon tubing between the syringe and the sipper facilitated purging of the syringe. The first draw of porewater was discarded. Porewater samples were then drawn into the syringe through the sipper. The samples were immediately filtered in the field through 0.45 μm filters. Aliquots for dissolved sulfide, nutrients and trace elements were collected. The sulfide aliquots were fixed in the field by adding 0.5 ml of 0.05M $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ to each sample. The samples were then stored in a cooler, covered with ice, shipped to Stony Brook University in the same day, and measured in the laboratory.

During each sampling event in April and September 2015, one sample of whole *S. alterniflora* was collected with the associated peat on site using stainless steel spades, placed into large plastic containers and then transported to Stony Brook University for further treatment. Soils were carefully removed from the roots by hand and the trace residual soil on the roots was carefully rinsed off with small amounts (<20 ml) of deionized water. The sample was further treated at Brookhaven National Laboratory in preparation for synchrotron nanofluorescence (nano-XRF) measurement. In brief, a piece of fresh root sample, which had a diameter of ~1 mm, was selected and a section of the root was suspended in an optimal cutting temperature (OCT) compound (FSC 22™ Frozen Section Compound, Surgipath Medical Industries, Surgipath, Canada). This OCT compound was used to embed tissue samples prior to frozen sectioning on a microtome-cryostat and did not infiltrate the specimen. It was then rapidly cooled to −20 °C in the cooling chamber of a cryotome (Cryostat CM1950, Leica Microsystems). Once OCT solidified, the cryotome was used to cut a 10 μm thin section. The thin section of the root samples was mounted on a silicon nitride membrane window (Norcada Inc., Edmonton, Canada), which has a window area of 1 mm × 0.5 mm for sample placement, and then fixed on an aluminum holder ready for synchrotron nano-XRF analysis (Fig. 1 a and b). Between the time of preparing the thin section and its analysis by synchrotron nano-XRF, the sample was kept in a desiccator at the Hard X-ray Nanoprobe (HXN) Beamline at the National Synchrotron Light Source II (NSLS-II) of the Brookhaven National Laboratory (Upton, NY).

2.2. Porewater analysis

Total dissolved sulfide (as $\sum H_2S = [H_2S] + [HS^-] + [S^{2-}]$) was measured on the porewater samples using techniques described by Kolker (2005) and Cochran et al. (2013). Briefly, porewater sulfide was measured colorimetrically (Cline, 1969; Reese et al., 2011). Absorbances were measured at 670 nm using a BMG Labtech spectrophotometer, and were compared with those determined for reference materials of different sulfide concentrations. Standard curves had precisions of better than ±5%. Total dissolved phosphate (as $\sum PO_4^{3-} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$) was measured using a Lachat Nutrient Autoanalyzer. Analytical precision was ±5%. Total dissolved iron (as $\sum Fe = Fe^{3+} + Fe^{2+}$) was measured colorimetrically using the ferrozine method (Stookey,