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# A barrier to metal movement: Synchrotron study of iron plaque on roots of wetland plants

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A wetland with attractive plants hosting birds and other wildlife is an esthetically pleasing prospect that is gaining popularity as a way of stabilizing or remediating metal-contaminated soils and sediment (Weber and Gagnon, 2014; Weis and Weis, 2004). In such a wetland it is important to understand the processes taking place — for example, if stabilization is indeed occurring, or if instead, metals are in a soluble form that can migrate and contaminate soils and sediment elsewhere. Metals in a soluble form may also be taken up by the wetland plants, thereby entering the ecosystem and possibly contaminating food that animals eat.

A synchrotron study of wetland plants from an urban brownfield site by Feng et al. (2016) offers information about a wetland scenario similar to that described above. In this study, multiple metals in plants from wetlands were studied to see if the metals were being sequestered inside or outside the plants. The study looked at the roots of two plant species from two locations at a brownfield formerly used as a railway

yard. One location had standing water, referred to here as the "wetter" location, and the other was assumed to be the "drier" location. Cu, Pb and Zn were present at elevated concentrations in the soil and sediment along with high concentrations of Fe and Mn. The two studied plants were *Phragmites australis* (common reed), obtained from both locations, and Typha latifolia (cattail) (Fig. 1), available only from the drier location.

Synchrotron-based techniques were used, which allowed for minimal sample manipulation to visualize the root structure and the distribution of metals in the roots of the plants. The sample manipulation consisted of simply cleaning the roots with deionized water, and then placing the samples in holders appropriate for the synchrotron-based method used

One synchrotron-based method was X-ray computed microtomography (µCMT), carried out with dried root samples in a holding tube, to produce high resolution three dimensional tomographic images of the root systems (Fig. 2). This method showed high X-ray attenuation in the epidermis (outermost cell layer) of the root tissue. The high X-ray attenuation was attributed to Fe plaque, whose formation on the surface of wetland plant roots is well known (Tripathi et al., 2014; Liu et al., 2010; Pan et al., 2014).

The other synchrotron-based method used in the study was X-ray microfluorescence ( $\mu$ XRF) at the micro-meter scale, with fresh samples that had been frozen and sliced in optimal cutting temperature (OCT) compound (a commercially available formulation of water-soluble glycols and resins) (Feng et al., 2013; Sakura, 2016).  $\mu$ XRF was used to map, or visualize, the distribution of metals in the epidermis and vascular tissues of the root structures. This analysis confirmed the presence of Fe in the epidermis. Pb, Cu, Mn, and Zn were enriched in the same area as the Fe (on the epidermis) in Typha and Phragmites from the drier location. This was seen for Pb, Mn and Zn in Phragmites from the wetter location but not as markedly for Cu. Instead, Cu was also enriched in some of the inner structures of the root.

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Fig. 1 – Photo showing Typha latifolia L at a sampling site in Liberty State Park, New Jersey, USA.

This picture is courtesy of Dr. Yu Qian, Montclair State University.

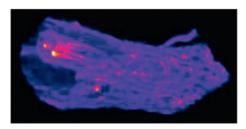


Fig. 2 – Three-dimensional image of Typha latifolia L. root with root hair showing from Synchrotron X-ray computed microtomography ( $\mu$ CMT) measurement. High attenuation substances showing in red are seen in the epidermis. Although the chemical composition of the high-attenuation substance cannot be identified using the current synchrotron  $\mu$ CMT measurement, synchrotron X-ray microfluorescence ( $\mu$ XRF) measurement has confirmed that Fe plaque is concentrated within these substances (Feng et al., 2016). This fig. is courtesy of Dr. Feng, Montclair State University.

The  $\mu XRF$  results were used to quantify the metals in the roots by comparison to standard reference materials (NIST 1832 and 1833, thin glass film on polycarbonate). This type of quantification is highly uncertain and not commonly carried out, but no attempt was made to quantify the uncertainty. The authors found statistically significant differences between the concentrations in the epidermis and those inside the plant. Metals were correlated with each other on the epidermis, but for the most part not inside the plant.

Although the authors did not compare results for the different plant species, or for plants from different wetland locations (drier vs. wetter), an examination of the data reveals that Mn and Pb concentrations were substantially lower in the plant epidermis and vascular tissue from the wetter location compared with the same plant species from the drier location, even though the soil/sediment concentrations were similar. At the same time, the differences between the epidermis and vascular metal concentrations were much less dramatic in the plant from the wetter location compared with the same plant from the drier location. Thus the plaque sequestration and scavenging of metals appears to be occurring to a lesser degree in the wetter conditions compared with drier conditions. This is rather counter-intuitive, considering that Fe plaque formation tends to be greater in wetter and more anaerobic conditions compared with drier conditions (Tripathi et al., 2014). Differences in plant metal uptake in different types of wetlands have been seen in other studies (Zhang et al., 2011; Hansel et al., 2001).

The Cu inside the plant from the wetter location was even higher than on the epidermis, a finding that entirely contradicts the idea of metal scavenging by epidermal Fe plaque to prevent infiltration by contaminants. Plant nutritional needs must factor largely into how the Cu is taken up under the study conditions, and indeed, the authors conclude that metal transport and accumulation are element specific.

Overall the study shows that metals are associated with Fe plaque on the outside of the roots of two very common wetland plants, which is a good confirmation that stabilization by the plants is probably taking place. Interesting future studies could look at non-essential toxic elements additional to the Pb examined in the study (e.g., Cd, As, Sb, U, Tl) as these may be of concern in contaminated site scenarios. For example, differences in Cd and As uptake by different rice cultivars were thought to be related to the amount of Fe plaque formed on the roots: more Fe plaque was associated with less Cd and As uptake (Liu et al., 2010; Pan et al., 2014). At the same time, a closer look at the essential elements that are common at contaminated sites - Cu and Zn - would be warranted to gain a better understanding of how these elements are stabilized; the present study indicates that there are probably powerful plant controls at work to ensure nutritional needs are met.

To comprehensively assess wetland stabilization as a remediation technique, future research scenarios should include the presence and absence of plants, to determine the overall ability of the plants to phytostabilize metals in a wetland. However, even a low phytostabilization contribution might be a useful part of a low cost remediation method for brownfields and other contaminated sites that have a combination of metal contaminants present.

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