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Chapter 6

Biogeochemistry of Metals in the Rhizosphere of Wetland Plants — An Explanation for "Innate" Metal Tolerance?

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Abstract. Wetland plant rhizospheres are often aerobic and oxidized, while the bulk soils are anaerobic and chemically reduced. As a result metals tend to be immobile in the bulk soil, but are mobilized by plant-induced changes in the rhizosphere. This leads to enrichment of metals near the roots and enhanced availability for uptake by plants. It is proposed here that the apparent metal tolerance of wetland plants compared with dryland plants, without the development of separate metal-tolerant ecotypes, is due to the relatively high exposure of plant roots to metals under the soil conditions prevailing in wetlands.

6.1. General Biogeochemistry of Wetland Soils

One of the characteristics defining wetlands is the presence of hydric soils (Keddy, 2000; Mitsch & Gosselink, 2000). These soils tend to be less developed than dryland (as opposed to wetland) soils — they often lack a clear stratification into various horizons and are homogenous in texture — and are usually anaerobic and chemically reduced (Gambrell & Patrick, 1978). As a consequence, the dominant form of iron is the divalent ferrous iron, Fe^{2+}, while the prevailing form of sulfur is sulfide, S^{2-}. Pyrite and other iron–sulfur compounds may be formed, and metals such as zinc, cadmium and lead tend to precipitate as highly insoluble metal sulfides (Gambrell, 1994). The mobility of metals under such conditions is therefore low and this partly explains the successful application of wetlands for removal of metals from wastewater (Odum et al., 2000).

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6.2. The Rhizosphere of Wetland Plants

In order to live in the anaerobic soil conditions, wetland plants have developed a root morphology different from that of dryland plants. Many species have porous roots for the supply of oxygen for root respiration, often forming a specialized tissue known as aerenchyma or air tissue. This supply of oxygen is thought to be more than sufficient for root respiration and excess oxygen may leak into the rhizosphere. This is known as radial oxygen loss (ROL) (Armstrong & Armstrong, 1990).

The rhizosphere of wetland plants, therefore, can be aerobic, and the generally chemically reduced conditions of the bulk soil are reversed. Sulfur and iron are oxidized to form sulfate and the trivalent ferric iron, Fe^{3+}. As a consequence many wetland plants form a layer of ferric (oxy-) hydroxides on the root surface, also known as iron plaque (Mendelssohn et al., 1995).

6.3. Metal Mobility in the Rhizosphere of Wetland Plants

The presence of aerobic, oxidized conditions in the rhizosphere and the formation of iron plaque on wetland plant roots in an otherwise anaerobic, chemically reduced bulk soil has important consequences for the mobility of metals (Jacob & Otte, 2003). While bound to sulfides under the conditions prevailing in the bulk soil, metals such as zinc are highly immobile, because metal sulfides are generally insoluble. But, when these sulfides become oxidized to form soluble sulfates, the metals are mobilized. Consequently, wetland plants have been found to enhance porewater concentrations of metals (Fig. 1) (Wright & Otte, 1999). Rhizosphere oxidation may also lead to a decrease in pH, which could explain mobilization of metals independent from changes in redox status of the soil (Jacob & Otte, 2003), and Wright & Otte (1999) indeed found a reduction in pH coinciding with the mobilization of zinc due to the presence of plants.

Metals like zinc have a high affinity for adsorption and co-precipitation with iron (oxy-) hydroxides, and thus, metals mobilized in the rhizosphere diffuse towards iron plaque on wetland plant roots and are immobilized on or immediately adjacent to the root surface. The bulk soil thus acts as a source of metal while the iron plaque acts as a sink, creating a diffusion gradient driven by the oxidation processes in the rhizosphere. Compared to the bulk soil, iron plaque may be enriched in metals (Otte et al., 1989; Caçador and Vale, 2001), as may be the rhizosphere soil immediately surrounding the roots (Fig. 2) (Doyle & Otte, 1997).

Whether the iron plaque and rhizosphere are enriched depends on the metals and plant species involved (Crowder et al., 1987; Otte et al., 1989; Doyle & Otte,

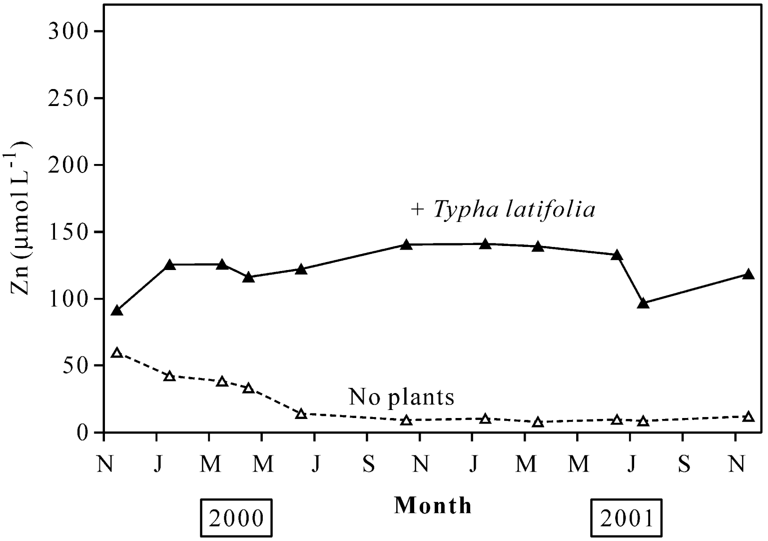

Figure 1: Concentrations of zinc in porewater of lead-zinc mine tailings from Tara Mines, Ireland, without (no plants) or planted with *Typha latifolia* during a 2-year period. For further details see Wright & Otte (1999).

1997; Ye et al., 1997a, 1998a; Caçador & Vale, 2001). However, metals adsorbed (as opposed to chemically bound) to iron plaque are probably still available for uptake by the plants, because plants can mobilize metals from adsorption sites directly or indirectly by exudation of protons or chelators (Marshner, 1988; Zhang, 1991). It is also likely that the exposure of plant roots to metals in solution at the root surface is higher if iron plaque is present than when it is not, because iron plaque accumulates metals relative to the bulk soil (Otte et al., 1989). This may be an important difference between wetland plants and dryland plants, as it may explain why wetland plants appear to be generally more tolerant to metals than dryland plants.

6.4. An Explanation for the Development of Innate Metal Tolerance in Wetland Plants?

Most studies on metal tolerance in plants have focused on dryland plants (Ernst, 1974; Verkleij & Schat, 1990), while metal tolerance in wetland plants has had very little attention. This recently changed with the increasing interest in using wetland cover for rehabilitation of mine wastes (Willianen et al., 1998; McCabe & Otte, 2000). Surprisingly, the few investigations into metal tolerance of wetland

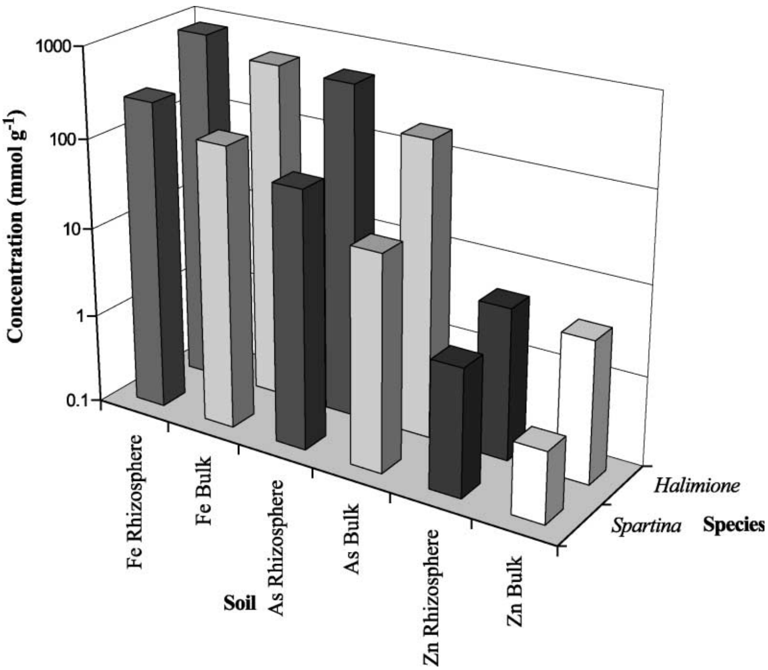

Figure 2: Concentrations of Fe, As and Zn in bulk soil and rhizospheres of *Spartina anglica* and *Halimione portulacoides* (after Doyle & Otte, 1997).

plants have been unable to identify differences in sensitivity between populations that had been exposed to various levels of metal concentrations in their respective habitats, as is normally found for dryland plants (Ernst, 1974; Verkleij & Schat, 1990). Populations from non-polluted and metal-enriched habitats showed similar growth performance in the presence of high concentrations of metals, suggesting that innate tolerance to metals is a common trait of wetland plants (McCabe et al., 2001). McNaughton et al. (1974) were the first to report on tolerance to zinc, cadmium and lead in *T. latifolia* and observed that this trait existed in this species without the development of specific metal-tolerant populations. Ten years later, Taylor & Crowder (1984) confirmed tolerance to copper and nickel in the same species. More recently, Ye et al. (1997b) confirmed the findings for *T. latifolia* and the same research team made similar observations in *Phragmites australis* (Ye et al., 1997c, 1998b). Then McCabe & Otte (2000) reported that populations of floating sweetgrass *Glyceria fluitans* that had not previously been exposed to zinc were capable of growing well in zinc-lead mine tailings containing highly elevated levels of metals. McCabe et al. (2001) and Moran & Otte (2004) found no differences in tolerance of *G. fluitans* to zinc when comparing a population from

Table 1: Tolerance index when exposed to 1000 μmol l^{-1} Zn (% response relative to control plants exposed to 2 μmol l^{-1}) for leaf length (ll), leaf number (ln), root length (rl) and survival rate (sr) of populations of four species of wetland plants, *Juncus articulatus*, *Juncus effusus*, *Eriophorum angustifolium* and *Glyceria fluitans* from non-contaminated (NC) and contaminated (C) locations in Europe.

Species	Population	NC/C	Origin	ll	ln	rl	sr
J. articulatus	Kippure	NC	Ireland	14	18	5	0
	Navan	C	Ireland	12	10	14	0
J. effusus	Cavan	NC	Ireland	23	33	31	40
	Glendalough	C	Ireland	22	34	4	10
E. angustifolium	Kippure	NC	Ireland	51	78	17	70
	Glendalough	C	Ireland	53	39	7	60
G. fluitans	Navan	C	Ireland	58	60	40	100
	Glendalough	C	Ireland	30	51	44	100
	Camborne	C	Cornwall	103	94	82	113
	Thisted	NC	Denmark	71	58	13	70
	Radostowo	NC	Poland	47	70	24	111

Plants were grown under the same conditions in a greenhouse in hydroponic culture ($n = 10$).

a zinc-lead tailings pond with one that had not been exposed to various elevated levels of zinc.

We have recent observations (Table 1) to suggest that there are wetland plant species, such as *Juncus articulatus*, that are less tolerant to zinc than the species mentioned above, but the evidence so far suggests that in contrast to dryland plants, metal tolerance in wetland plants is the rule rather than the exception. This cannot be explained by reduced uptake of metals — wetland plants do take up higher amounts of metals when exposed to elevated concentrations (Fig. 3).

The metal tolerance mechanisms in wetland plants, therefore, must be physiological and may have evolved in response to the biogeochemical conditions prevailing in the rhizosphere. It may be that over evolutionary periods of time wetland plants under natural, unpolluted conditions have consistently been exposed to higher concentrations of metals at the root surface than dryland plants.

This is supported by the following observations.

- Wetlands, particularly sedimentary systems such as salt marshes and estuarine floodplains, tend to act as sinks for metals and as a result the sediments of such wetlands tend to have higher metal concentrations than surrounding dryland habitats (Salomons & Förstner, 1984).

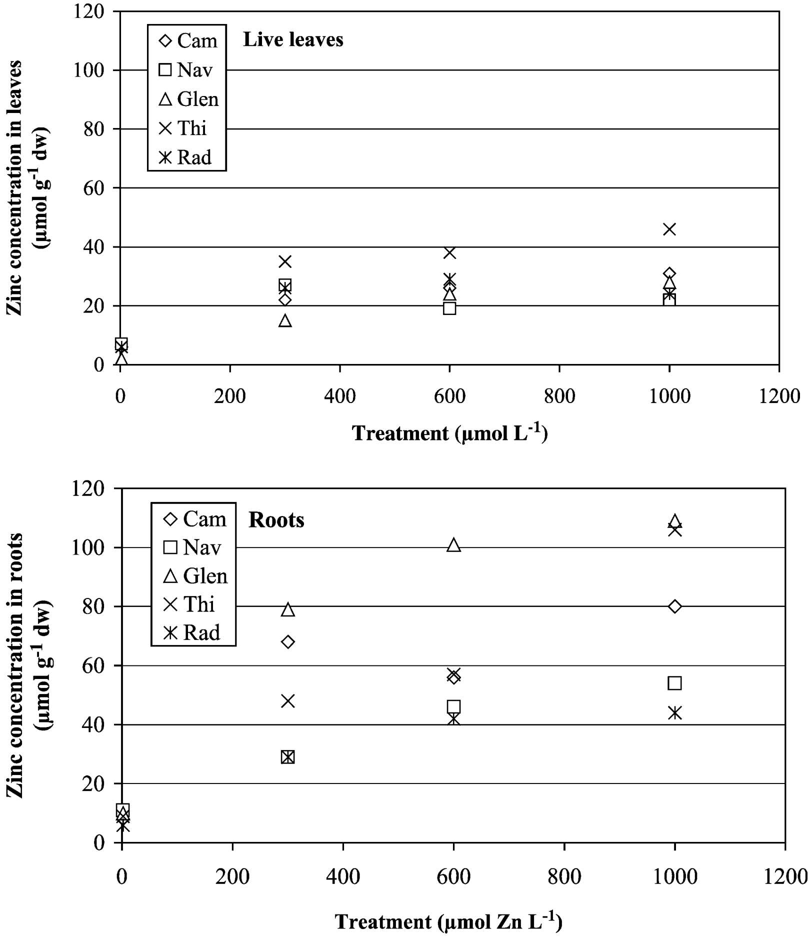

Figure 3: Mean zinc concentrations (µmol Zn g^{-1} dry weight) in live leaves (top) and roots (bottom) of four populations of *G. fluitans* from four populations: Camborne, Cornwall, UK (Cam), Glendalough, Ireland (Glen), Thisted, Denmark (Thi) and Radostowo, Poland (Rad), grown at 2, 300, 600 or 1000 µmol Zn l^{-1} for 84 days. Plants were grown under the same conditions in a greenhouse in hydroponic culture ($n = 10$).

- While the concentrations in the rhizospheres of dryland plants tend to have similar or lower metal concentrations than the bulk (or non-rhizosphere) soils (Youssef & Chino, 1989; Lorenz et al., 1997; McGrath et al., 1997; Luo et al., 2000; Wang et al., 2002), the situation tends to be the opposite in wetlands, as explained above (Fig. 2). In addition, wetland plants mobilize metals in the rhizosphere, even in mine tailings in which availability of zinc to plants is more than sufficient for growth (Fig. 1) (Wright & Otte, 1999).

We suggest here that this has led to higher uptake of metals by wetland plants compared to dryland plants and that this through evolution has led to the subsequent development of innate tolerance to metals in wetland plants. This hypothesis as well as the physiology and genetics underlying innate metal tolerance in wetland plants clearly need further investigation.

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