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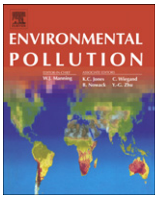

Review

Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: A review

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A new index, the relative treatment efficiency index (RTEI), to quantify treatment impacts on metal and metalloid removal in constructed wetlands.

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ABSTRACT

This review integrates knowledge on the removal of metals and metalloids from contaminated waters in constructed wetlands and offers insight into future R&D priorities. Metal removal processes in wetlands are described. Based on 21 papers, the roles and impacts on efficiency of plants in constructed wetlands are discussed. The effects of plant ecotypes and class (monocots, dicots) and of system size on metal removal are addressed. Metal removal rates in wetlands depend on the type of element ($Hg > Mn > Fe = Cd > Pb = Cr > Zn = Cu > Al > Ni > As$), their ionic forms, substrate conditions, season, and plant species. Standardized procedures and data are lacking for efficiently comparing properties of plants and substrates. We propose a new index, the *relative treatment efficiency index* (RTEI), to quantify treatment impacts on metal removal in constructed wetlands. Further research is needed on key components, such as effects of differences in plant ecotypes and microbial communities, in order to enhance metal removal efficiency.

1. Rationale for using constructed wetlands for improvement of water quality

Aquatic ecosystems are used directly or indirectly as recipients of potentially toxic liquids and solids from domestic, agricultural and industrial wastes (Demirezen et al., 2007; Peng et al., 2008). Pollutants may accumulate in surface waters, groundwater, substrates and plants (Aksoy et al., 2005), and can be divided into four classes: nutrients (P, N), organic contaminants (e.g. polycyclic aromatic hydrocarbons, polychlorinated biphenyls and pesticides), xenobiotics derived from the pharmaceutical industry (personal care products, hormones, etc.) and metals and metalloids (e.g. Cu, Zn, Fe, Cd, Ni, Pb, Hg, Cr, Sr, Al, Ba, Se, and As). For convenience, we will refer to both metal and metalloids as 'metals' throughout the paper. Constructed wetlands have been used to successfully improve the quality of contaminated waters and wastewaters for at least two decades (Murray-Gulde et al., 2005a; Maine et al., 2009; Zhang et al., 2010) while natural 'volunteer' wetlands have been improving water quality over millions of years. Of special interest in this respect are volunteer wetlands associated with mining activities (Beining and Otte, 1996, 1997). The functions of macrophytes include production of organic matter, pollutant uptake and bioengineering of the rhizosphere, e.g. maintenance of habitats for micro-organisms.

Some macrophytes have accumulator phenotypes for one or several metals (Kamal et al., 2004). These plants can accumulate metals in concentrations 100,000 times greater than in the associated water (Mishra and Tripathi, 2008), and therefore have been used for metal removal from a variety of sources (Mishra and Tripathi, 2008). Hyperaccumulators can tolerate, take up and translocate high levels of certain metals that would be toxic to most organisms. They are defined as plants that complete their life cycle with foliar metal concentrations exceeding (mg kg^{-1} dry weight, DW) $Cd > 100$, Ni and $Cu > 1000$, and Zn and $Mn > 10{,}000$ (Zavoda et al., 2001). However, most of works on metal (hyper) accumulators has been done on dryland plants. To date no emergent wetland plants have been identified as hyperaccumulators. Metal removal through uptake by macrophytes in wetlands is therefore relatively minor compared to other processes. The main functions of these plants are to provide organic matter needed to perpetuate the biogeochemical processes in the substrate through die-back, and to provide organic compounds via exudation from the roots (Jenssen et al., 1993). These characteristics make them essential in

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constructed wetlands, which are considered effective, cost-efficient and environmentally friendly bio-processes for quality improvement of polluted water (Brix, 1997; Stottmeister et al., 2003).

Constructed wetlands can be classified into types based on their characteristics. One system defines four types based on the dominant plant species (Arias and Brix, 2003): (1) floating macrophytes (e.g. *Eichhornia crassipes*, *Lemna minor*), (2) floating-leaf macrophytes (e.g. *Nymphea alba*, *Potamogeton gramineus*), (3) submersed macrophytes (e.g. *Littorella uniflora*, *Potamogeton crispus*), and (4) emerged rooted macrophytes (e.g. *Phragmites australis*, *Typha latifolia*). Another common classification divides wetlands according to their hydrology: (1) surface flow wetlands, (2) horizontal subsurface flow wetlands, (3) vertical subsurface flow wetlands, and (4) hybrid systems (Arias and Brix, 2003).

2. Metal removal processes in wetlands

Four mechanisms affect metal removal in wetlands (Lesage et al., 2007a): (1) adsorption to fine textured sediments and organic matter (Gambrell, 1994), (2) precipitation as insoluble salts (mainly sulphides and oxyhydroxides), (3) absorption and induced changes in biogeochemical cycles by plants and bacteria (Kadlec and Knight, 1996), and (4) deposition of suspended solids due to low flow rates. All these reactions lead to accumulation of metals in the substrate of wetlands. The efficiency of systems depends strongly on (i) inlet metal concentrations and (ii) hydraulic loading (Kadlec and Knight, 1996).

2.1. Adsorption

Sorption, the transfer of ions from a soluble phase to a solid phase, is an important mechanism for removal of metals in wetlands. It may result in short-term retention or long-term stabilization. Sorption describes a group of processes which includes adsorption (physisorption, i.e., physical processes with weak bindings, chemisorption, i.e., chemical processes with strong bindings), absorption (e.g. with biochemical processes when a compound from the external media is entering into a living organism) and precipitation reactions. Metals are adsorbed to particles by either ion exchange depending upon factors such as the type of element and the presence of other elements competing for adsorption sites (Seo et al., 2008) or chemisorption. Retention of Pb, Cu, and Cr by adsorption is greater than Zn, Ni, and Cd (Sheoran and Sheoran, 2006).

Freundlich and Langmuir models (Bohn et al., 1979) may be used to determine maximum metal immobilization and their retention capacity over time (Lesage et al., 2007b; Seo et al., 2008), as follows:

Freundlich, $q = K\mathrm{Ce}^{(1/n)}$, to describe adsorption onto a heterogeneous surface, where q = adsorption capacity (metal concentration on adsorbing material, mg kg^{-1}), K = constant linked to adsorption capacity, Ce = concentration (mg L^{-1}), and n = empiric parameter linked to sorption intensity.

Langmuir, $q = ab\mathrm{Ce}/(1 + b\mathrm{Ce})$, for monolayer adsorption on a homogeneous surface with a finite number of identical sorption sites, where q = mass of metal adsorbed to the substrate (mg kg^{-1}), Ce = concentration at the equilibrium (mg L^{-1}), a = adsorption capacity maximum to the substrate (mg kg^{-1}), and b = a constant linked to the metal fixation force.

Another useful parameter to quantify adsorption capacity of a material for an ion is the distribution coefficient Kd (Alloway, 1995).

$$\mathrm{Kd} = \frac{\text{Equilibrium metal concentration adsorbed}}{\text{Equilibrium metal concentration in solution}}$$

To quantify the retention capacity of substrates over time, column experiments may be used. In this case, the Thomas model is relevant (Seo et al., 2008): $C/\mathrm{Co} = 1/(1 + \exp((K\mathrm{th}/Q)(\mathrm{qo}M - \mathrm{Co}V)))$, where Co = metal concentration at the influent (mg L^{-1}), C = metal concentration at the effluent (mg L^{-1}), Kth = Thomas constant (L D^{-1} mg^{-1}), Q = flow rate (L D^{-1}), qo = maximum adsorption capacity (mg g^{-1}), M = total mass of sorbing (g), and V = Total volume of solution passed through the column (L).

2.2. Co-precipitation and redox reactions

Some metals, e.g. Fe, Al, and Mn, can form insoluble compounds through hydrolysis and/or oxidation. This leads to formation of a range of oxides, oxyhydroxides and hydroxides (Sheoran and Sheoran, 2006). Fe removal depends on pH, redox potential and the presence of anions (ITRC, 2003). The amounts and forms of Fe in solution strongly affect metal removal. Fe(II) is soluble and represents an important bioavailable fraction. It can be oxidized to Fe(III) in conjunction with H^{+} ion consumption under aerobic conditions (Jönsson et al., 2006). Fe(III) can deposit onto root surfaces of aquatic macrophytes (Weiss et al., 2003), forming plaques with a large capacity to adsorb metals (Doyle and Otte, 1997; Cambrolle et al., 2008), aided also by the action of Fe(II)-oxidizing bacteria (Emerson et al., 1999). Fe(III) can precipitate to produce oxides, hydroxides and oxyhydroxides with which other metals may co-precipitate. Fe(II) can also precipitate as oxides (Jönsson et al., 2006) or co-precipitate with other metals such as Zn, Cd, Cu or Ni (Matagi et al., 1998). Iron oxides have a particularly strong affinity for cations with a similar size compared to Fe(III) and Fe(II), e.g. Zn, Cd, Cu, and Ni (Dorman et al., 2009). Therefore, those TE may combine with Fe forming metal-oxide complexes (Benjamin and Leckie, 1981). This co-precipitation is limited when Fe(II) forms complexes with for example $\mathrm{SO_4^{2-}}$ (Sung and Morgan, 1980), thus reducing the potential of metal removal. Arsenic may also be removed from the water column by adsorbing onto amorphous iron hydroxides or by co-precipitating with iron oxyhydroxides (Manning et al., 1998).

Metals can also form insoluble compounds through reduction. Under chemically reducing conditions ($\mathrm{Eh} < 50$ mV) sulfates can be reduced to sulfides. These can combine with various elements, i.e., As, Hg, Se, and Zn, to co-precipitate in relatively insoluble forms (Murray-Gulde et al., 2005b). Some macrophytes, e.g. *Schoenoplectus californicus*, contribute to reductive conditions into the substrate (Dorman et al., 2009).

A constructed wetland based on a matrix with exclusively reducing conditions, however, cannot be efficient. These conditions promote massive ion release, particularly of Fe and Mn, into the water by reduction of the oxides and oxyhydroxides trapped in the substrate (Goulet and Pick, 2001). Most metals in the porewater precipitate as metal oxides or adsorb onto organic matter at redox potentials higher than 100 mV. Between 100 mV to −100 mV, metal oxides are reduced resulting in a release of dissolved metals. These metals can still adsorb onto organic matter if adsorption sites are available. Below −100 mV metals may be mainly associated with sulfides (Goulet and Pick, 2001). Most macrophytes play a role in maintaining oxidizing conditions by shoot-to-root oxygen transport (Armstrong, 1978). Such conditions promote formation of iron oxides, hydroxides and oxyhydroxides, such as the iron-plaques, and consequently result in metal removal by adsorption and co-precipitation. Considering the processes essential in metal removal it may be useful to design a system with two separate compartments, i.e., a first compartment to promote sulphate reduction and induce their combination with As, Hg, Se, and Zn ions, and a second, oxidizing compartment to enhance metal co-precipitation with