Science of the Total Environment 409 (2011) 4891–4898

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Metal/metalloid accumulation/remobilization during aquatic litter decomposition in freshwater: A review

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ARTICLE INFO

Article history:
Received 9 March 2011
Received in revised form 3 August 2011
Accepted 3 August 2011
Available online 9 September 2011

Keywords:
Biosorption
Carbon turnover
Decay
Ecosystem engineers
Fixation
Litter processing

ABSTRACT

The focus of this article is to combine two main areas of research activities in freshwater ecosystems: the effect of inorganic pollutants on freshwater ecosystems and litter decomposition as a fundamental ecological process in streams.

The decomposition of plant litter in aquatic systems as a main energy source in running water ecosystems proceeds in three distinct temporal stages of leaching, conditioning and fragmentation. During these stages metals and metalloids may be fixed by litter, its decay products and the associated organisms. The global-scale problem of contaminated freshwater ecosystems by metals and metalloids has led to many investigations on the acute and chronic toxicity of these elements to plants and animals as well as the impact on animal activity under laboratory conditions. Where sorption properties and accumulation/remobilization potential of metals in sediments and attached microorganisms are quite well understood, the combination of both research areas concerning the impact of higher trophic levels on the modification of sediment sorption conditions and the influence of metal/metalloid pollution on decomposition of plant litter mediated by decomposer community, as well as the effect of high metal load during litter decay on organism health under field conditions, has still to be elucidated. So far it was found that microbes and invertebrate shredder (species of the genera *Gammarus* and *Asellus*) have a significant influence on metal fixation on litter. Not many studies focus on the impact of other functional groups affecting litter decay (e.g. grazer and collectors) or other main processes in freshwater ecosystems like bioturbation (e.g. *Tubifex*, *Chironomus*) on metal fixation/release.

Contents

1. Introduction

High concentrations of metals and metalloids in water and aquatic sediments are a global problem for several types of freshwater ecosystems (Biney et al., 1994; Kouba et al., 2010; Kraak et al., 1991). From ore deposits, enhanced by mining, or industrial waste waters high amounts of metals, metalloids and radionuclides drain into freshwater ecosystems (Dudka and Adriano, 1997; Moiseenko and Kudryavtseva, 2001). This leads to an enhanced risk to the environment and associated ecosystems due to elevated concentrations of metals and metalloids (of which arsenic is the most important) (Nriagu and Pacyna, 1988). Many species and processes in these ecosystems are affected by this (Luoma and Rainbow, 2008). For instance, by the end of

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doi:10.1016/j.scitotenv.2011.08.006

the 1980s, it was estimated that approximately 19,300 km of streams and rivers, and ca. 72,000 ha of lakes and wetlands worldwide were damaged by mining activities (Johnson and Hallberg, 2005). These elements are transported by running water as cations, inorganic complexes and/or organic complexes of humic and fulvic acids being of dissolved organic matter (DOC) (Alberic et al., 2000; Christensen et al., 1999) in addition to that metal associated with suspended particles. Element complexes may adsorb on organic and inorganic particles and lead to a deposit in sediments (Sridhar et al., 2008), particularly in slowly flowing or standing water, like pools of streams, lakes and other wetlands. Therefore, wetlands are known to be a sink for metals and metalloids.

Input of leaf and other plant litter is the most important mechanism for the energy availability of krenal (spring region) and rhitral (stream) as allochthonous ecosystems. Leaf litter, settled on the bottom of the water body, will eventually be decomposed. Leaf litter decomposition proceeds in three distinct temporal stages of leaching, conditioning and fragmentation (Gessner et al., 1999). During the primary decomposition by microorganisms, DOC emerges from the litter and microorganisms and their exudates form a heterotrophic biofilm (Kominkova et al., 2000). Microorganisms of the biofilm like bacteria and fungi are known to accumulate high amounts of metals and metalloids. Furthermore, the accumulation of elements depends on the exudates (Huang et al., 2000), which also influences the survival of the biofilm (Pirog, 1997). While the primary decay proceeds, the leaf litter serves as a main food source for invertebrate shredders (Leroy and Marks, 2006). Shredders cut the leaves into small pieces and consequently accelerate the litter decomposition by increasing surface area which offers a larger space for growth of the periphytic microorganisms and a larger space for biosorption and complexation.

Contaminants accumulate on organic (Sridhar et al., 2008), inorganic (Lin, 1997) sediment particles and their associated microorganism community (D'Souza et al., 2006). Fungi, bacteria, protists, and exudates of microorganisms form the biofilm (Flemming et al., 2007). Several studies have shown that oxygen and nutrient limitation within periphyton are intensified with increasing periphytic biofilms (Mulholland et al., 1994). These findings are generally attributed to reduced advective transport from flowing water to lower layers of cells within the biofilm matrix, hence increasing dependence on diffusive transport. During the feeding activity of invertebrate shredders on leaf litter, the oxygen consumption within the microbial biofilm increases strongly (Hargrave, 1976). In contrast other invertebrates (genus *Chironomus*) enhance the transport of oxygen into sediments by bioturbation overcoming transport limitations (Altmann et al., 2004). The interaction between biofilm properties and metal accumulation is well described (Huang et al., 2000; Schorer and Eisele, 1997). It has been proved that fungi and bacteria exude organic compounds especially exopolysaccharides (EPS) and proteins, which bind high amounts of metals and metalloids (D'Souza et al., 2006; Sridhar et al., 2008; van Leeuwen and Buffle, 2009). The metals and metalloids can be transported in aquatic systems while bound on particles. Transport of particles in running water depends on particle density and surface area (Mulder and Alexander, 2001). Much is known about the physicochemical properties of metal adsorption to organic and inorganic particles, organisms and communities like periphyton, as well as hydrological properties for transport of such particles (Kinniburgh et al., 1999; Pons and Fusté, 1993). The same holds for higher trophic levels of freshwater organisms and the effect of their community on ecological processes such as litter decomposition. But the impact of the other keystone species as ecosystem engineers (e.g. *Gammarus pulex*, *Asellus aquaticus*, *Viviparus viviparus*) in freshwater ecosystems, via top-down regulation, on metal and metalloid accumulation or release has been neglected so far. It was proven that invertebrates (bivalves) influence significantly the metal release by a higher bioturbation rate (Ciutat and Boudou, 2003). In contrast to this, the effect of bioturbation can also enhance the fixation of metals into sediment (Petersen et al., 1998). Furthermore, it was found that crayfish can increase litter decay by bioturbation, and consumption (Usio, 2000), where there is no study on the effect of crayfish on metal fixation/remobilization. In addition, the interaction between litter processing by invertebrates as a main ecosystem function and the resulting changes in sink or source conditions for metals and metalloids in aquatic environments have been the focus in only a few studies. Ecotoxicological tests have shown the impact of metal load on processing rates, but not on mobilization or release of the elements. Schmitt-Jansen et al. (2008) pointed out that aquatic ecology has to be integrated into ecotoxicology. Many species associate with metals and metalloids polluted sediments in aquatic systems (King et al., 2006). For instance invertebrate shredders are associated with streambed sediments and accumulating metals through diet (Geffard et al., 2007). Invertebrates from the genus *Gammarus* are known to be bioaccumulators of a number of metals (Geffard et al., 2010). Nevertheless, the effects of metals on different organisms examined under different environmental conditions reveal big differences (BEAK_International_Incorporated, 1998; Schaller et al., 2009). Furthermore different invertebrates accumulate and respond to various concentrations of metals very differently, even within the same genus (Rainbow, 2002).

Invertebrates show a differential accumulation of metals between the gut system and the remaining tissues of their body (Amyot et al., 1996; Barka, 2007; Neumann et al., 1999; Schaller et al., 2011b; Sola and Prat, 2006). Thereby some invertebrates are able to retain low levels of metals in relation to exposure levels, which may be explained by the ability of gastrointestinal epithelial cells of a number of invertebrates to detoxify heavy metals. Hence the accumulated body concentrations will rise until those gut cells are lost together with their contents (steady state) (Ahearn et al., 1999; Amiard et al., 2006; Burgos and Rainbow, 1998; Nassiri et al., 2000). The process of metal sequestration and detoxification has been found to involve metallothioneins, mitochondria and lysosomes in the gut system of these organisms resulting in this differential accumulation and metal homeostasis including apparent resistance to toxic effects of many metal contaminants (Ahearn et al., 2004; Sokolova et al., 2005). Due to selective pressure, some invertebrates in metal contaminated environments may reduce metal uptake or enact physiological strategies for detoxification (Mouneyrac et al., 2002). But in contrast to this, a lot more studies have shown that some invertebrates accumulate some metals in high amounts and whereas other invertebrates are very sensitive to metal contamination (Borgmann et al., 2005; Casado-Martinez et al., 2010; Croteau et al., 2007).

The main purpose of this article is to critically review the knowledge on interactions between metals as well as metalloids in running water and the decomposer community of leaf litter (Fig. 1). The article deals more specifically with (a) the interaction between dissolved organic carbon release and metal mobilization, (b) the metal/metalloid accumulation during microbial litter decomposition (c) the stoichiometry and interaction of the elements, (d) the influence of animals on metal/metalloid accumulation/remobilization into/from particulate organic matter (POM) during litter decay, and (e) the transfer of metals/metalloids into litter processing invertebrates in contaminated environments resulting in effects on reproduction/survival rates. Furthermore, we discuss the impact of transport pathways and hydrodynamics such as flow velocity on retention of metals and metalloids in ecosystems of running water.

2. Interaction between dissolved organic carbon release and metal mobilization

Leaching of dissolved organic carbon, the first step of litter decomposition in aquatic ecosystems takes place during the first 24 h after immersion (Gessner et al., 1999). Further, DOC content in the water path depends not only on release of organic carbon from litter decomposition in the water body, but also on DOC leaching from catchment area (Hongve, 1999). The composition of DOC depends on the litter