Environ Sci Pollut Res (2012) 19:3942–3949
DOI 10.1007/s11356-012-0975-0

RESEARCH ARTICLE

Invertebrates control metal/metalloid sequestration and the quality of DOC/DON released during litter decay in slightly acidic environments

Jörg Schaller · Susanne Machill

Received: 5 December 2011 / Accepted: 8 May 2012 / Published online: 29 May 2012

Abstract Plant litter and organic sediments are a main sink for metals and metalloids in aquatic ecosystems. The effect of invertebrate shredder (a key species in litter decay) on metal/metalloid fixation by organic matter is described only under alkaline water conditions whereas for slightly acidic waters nothing can be found. Furthermore, less is known about the effect of invertebrate shredders on the quality of dissolved organic carbon (DOC) and nitrogen (DON) released during litter decay. We conducted an experiment to investigate the impact of invertebrate shredder (*Gammarus pulex)* on metal/metalloid fixation/remobilization and on the quality of DOC/DON released under slightly acidic water conditions. During decomposition of leaf litter, invertebrate shredder facilitated significantly the emergence of smaller particle sizes of organic matter. The capacity of metal fixation was significantly higher in smaller particles (POM 2,000–63 μm) compared to original leaf litter and litter residues. Thus, *G. pulex* enhanced metal fixation by organic partition of sediments by increasing the amount of smaller particle of organic matter in aquatic ecosystems. In contrast, the capacity of metal/metalloid fixation in the smallest fraction of POM (<63 μm) was lower compared with leaf residues in treatment without invertebrates. Remobilization of metals and metalloids was very low for all measured elements. A significant effect of invertebrates on quantitative formation of DOC/DON was confirmed. The quality of released DOC/DON, which may affect metal/metalloid remobilization, was also significantly affected by invertebrate shredders (e.g., more carboxylates). Hence, invertebrate shredder enhanced significantly the fixation of metals/metalloids into POM in slightly acidic environments.

Keywords Adsorption · Carbon quality · Ecosystem processes · FT-IR · Metalloids

Responsible editor: Elena Maestri

J. Schaller (✉)
Institute of General Ecology and Environmental Protection,
Technische Universität Dresden,
PF 1117,
01737 Tharandt, Germany
e-mail: Schaller@forst.tu-dresden.de

S. Machill
Bioanalytical Chemistry, Technische Universität Dresden,
Bergstrasse 66,
01069 Dresden, Germany

Introduction

High concentrations of metals, metalloids and radionuclides are of global concern in freshwater ecosystems and environmental health where concentration levels are mainly affected by element release from ores and contaminated soils (Baborowski and Bozau 2006; Dinelli et al. 2001). Metals and metalloids dissolve at low pH (predominantly as cations), low Eh and within a neutral to alkaline aerobic milieu (e.g., as carbonate complexes) (Burton et al. 2008). They readily form organic complexes with humic and fulvic acids as part of dissolved organic carbon (DOC) (Zhao et al. 2009), are fixed to colloids, and consequently remain mobile. The dissolved elements may also adsorb on organic and inorganic compounds in the water body, for instance, inorganic particles and leaf litter, which settle forming water sediment (Dienemann et al. 2006; Karbassi et al. 2008). Small streams as allochthonous ecosystems depend on external input of energy by organic matter entry including leaf litter. During the first step of litter decomposition (e.g., in small streams), DOC emerges (Wallace et al. 2008) with microorganisms (e.g., hyphomycetes and bacteria) being the first colonizers and decomposers of, for example, leaves. These microorganisms establish a biofilm on the decomposing litter and at the same time produce exudates, in particular exo-polysaccharides (EPS) (Flemming et al. 2007) with a large surface area and hence more functional groups resulting in higher adsorption capacity for metals/metalloids. In the second step of litter decay, invertebrate shredders facilitate the decomposition processes (Hieber and Gessner 2002). An invertebrate shredder of high importance because of its abundance is *Gammarus pulex* L. (Schaller et al. 2008). The genus *Gammarus* is dominant in most fresh water ecosystems in Europe and Central Asia. *G. pulex* is a Crustacean that is able to survive in weak alkaline to weak acidic water until a pH of around 5 (Meijering 1991), whereas the mortality increases with decreasing pH (Felten et al. 2008). *G. pulex*, feeding on litter, substantially influences the formation of small particle sizes within particulate organic matter (POM) (Benfield 2007; Camilleri 1992). The impact of *G. pulex* on heavy metal, metalloid and radionuclide fixation during litter decomposition is described for a variety of metals/metalloids in both laboratory and field experiments under neutral to low alkaline pH conditions (Schaller et al. 2008, 2010a, b). For lower pH values, nothing is known, to our best knowledge (Schaller et al. 2011). At lower pH the speciation and complexation of the metals/metalloids is different, resulting in more mobile metals and/or less mobile metalloids (Tipping et al. 2003), which in turn may result in lower/higher fixation of these elements by litter during decay. Furthermore, nothing is known about the effect of invertebrate shredder on the quality of DOC released from organic matter. Effects of DOC (as quantitative not qualitative parameter) on metal/metalloid remobilization are quite well understood, whereas less is known about the composition of this DOC (from sugar to humic acids and other forms of higher polymeric compounds). Different DOC compounds may have different effects on remobilization, complexation, and transport of metals/metalloids. A first approach to describe this complex system of interactions would be a detailed characterization of DOC and the resulting effect on metal/metalloid remobilization. An understanding of these processes is particularly important in estimating the potential of these ecosystem processes to enhance metal/metalloid sequestration. This in turn is of special interest in view of high costs (up to \$10 m^3) and low efficiency of conventional water treatment plants (Gatzweiler et al. 2004).

The aim of our study was to investigate the impact of invertebrate shredders on element accumulation during litter decay and the removal potential of these elements in low acidic waters. Furthermore, the impact of invertebrate shredder on the quality and quantity of DOC released from the litter was investigated.

Material and methods

The test organisms

The specimens of *G. pulex* L. were collected from a stream in Dresden (Germany) called Prießnitz. To adapt the animals to experimental conditions, the specimens of *G. pulex* were acclimated for 5 days in the laboratory (in 40 l tap water, 12–15°C, ~100 lx of light intensity for 14 h/day) until the start of the experiment. During the acclimation period, the animals were supplied with degrading leaves of alder (*Alnus glutinosa* L.), the same used in the experiment.

Litter collection and treatment

Leaf litter used in the experiment was from fresh fallen leaf (*Alnus glutinosa)*, collected from uncontaminated plants at a trial plot at Moritzburg near Dresden (Germany). Leaf litter was placed into mesh bags (nylon mesh, 250 μm pore size) and exposed to heavy metal contaminated water (pH 5.3) for 14 days at a former uranium mining site in Lengenfeld (Saxony, Germany), to allow colonization of leaf litter with microbes adapted to heavy metals as well as to allow the organic matter to accumulate heavy metals. An exposure time of the leaf litter of 14 days was used for comparability with other experiments (Schaller et al. 2008, 2010a). The metal/metalloid concentration in this water (in $\mu g\ l^{-1}$) were 45 (manganese), 108 (iron), 49 (arsenic), 23 (gallium), 1.4 (lead) and 74 (uranium).

Experimental conditions and design

The experiments were conducted in batch culture modified from Canhoto et al. (2005). pH was stabilized to 5.3 by adding HCl and Eh were stabilized by aeration (0.5 l filtered air/min). Each test vessel contained 3 l of tap water at a temperature of 17°C, 3.9 g DM^{-1} of leaf litter, and it was set up with 100 individuals of *G. pulex* (G+) or without *G. pulex* (G−). The chosen density of individuals of *G. pulex* was in naturally existing range (Welton 1979) and was used previously (Schaller et al. 2008). The experiments were replicated five times with a duration of 7 weeks. The experiments were set with 14 h/day light.

Sampling, sample preparation and analysis

During the experiment water samples were taken for metal and DOC analysis at an interval of 1 week during the 7-week experiment (four replicates per date) using PE (polyethylene) bottles. For element analysis, 20-ml water samples were acidified with HNO_3 (analytical grade, Carl Roth Germany) immediately after collection. For DOC determination, 20-ml water samples were filtered using a 0.45-μm cellulose-acetate filter membrane (Whatman GmbH, Germany) and immediately frozen at −20°C. Fourier transform infrared spectroscopy (FT-IR) analysis was done to determine the effect of invertebrate shredders on the quality of remobilized DOC using a FT-IR spectrometer (Nicolet 210). The inspissated samples were introduced directly by a golden gate ATR facility and measured each with 500 scans. The range of measurements is 4,000 to 650 cm^{-1} with a resolution of 2 cm^{-1}. For evaluation, a baseline correction was carried out using the points at 3,700 and 1,800 cm^{-1}.

At the end of the experiment, the solid samples were partitioned into different sizes by sieving through 2,000-, 250- and 63-μm polyethylene sieves to separate the different fractions of POM. The *G. pulex* were separated from the material collected on the sieves using a tweezer. The leaf litter and the POM samples were digested in a closed vessel microwave system (MARS5 CEM Corp., Mattews, USA) according to DIN-EN-13805 (2002) using nitric acid and hydrogen peroxide. All water samples were acidified and kept at room temperature before metal analysis with inductively coupled plasma mass spectrometry (ICP-MS; Plasma Quad PQ2+, VG Elementar, Winsford, UK) according to DIN-EN-ISO-17294-2 (2004). The ICP-MS was calibrated using standards prepared from single-element and multi-element solutions (Bernd Kraft, Duisburg, Germany). Calibration validity was confirmed with standard reference material GBW7604, poplar leaves (Office of CRM's, China), digested in the same manner as the litter samples. Limit of detection (LOD) was calculated as the 3-fold standard deviation of instrument blank (acidified water). DOC in the water samples was determined using a TOC Analyzer 5000 (Shimadzu, Japan) according to DIN-EN-1484 (1997). Carbon and nitrogen contents in the solid samples were measured with Elementar vario el III (Hanau, Germany) in accordance with DIN-ISO-10694 (1995). All chemicals used in the experiment were of analytical grade.

Statistical analysis

Analysis of variance (ANOVA) was used to compare the elemental (including DOC and DON) data between all different treatments during the experiment, whereas for the comparison of the data between start and end of experiment the *t*-test was used. Data of the element content of the different fractions in the different treatments were statistically analyzed with the *t*-test using SPSS version 11.5.

Results and discussion

Impact of invertebrate shredder on POM and DOC formation

The decomposition of litter is evident by a significant weight loss and formation of smaller particles which in turn is enhanced by invertebrates (Levinton 1995). The formation of smaller particles of organic matter (particles sizes: 250–2,000 and 63–250 μm) in this experiment was significantly higher in treatments with *G. pulex* (G+) compared to treatments without invertebrate shredders (G−) (Fig. 1; $p<0.01$), whereas no significant differences between the two treatments were found for a particle size <63 μm. As was expected, less leaf litter at the end of the experiment ($p<0.01$) was found in the treatment with invertebrates (G+) compared to the treatment without invertebrates (G−). It has long been described that the shredder cuts the leaf litter into smaller parts, partially ingests and excretes them or distributes undigested litter as POM of smaller particle sizes (Graça 2001). Furthermore, shredder may influence the release of soluble polymeric organic carbon and nitrogen in the course of decomposition and, in later stages, even the formation of humic substances (Berg and McClaugherty 2003). Considering Fig. 2, DOC and DON increased significantly in both treatments during the experiment is revealed (ANOVA, $p<0.01$). At the end of the experiment significant higher concentrations were found for DOC and DON ($p<0.01$, *t*-test) in the treatment with (G+) compared to the treatment without invertebrates (G−). The enhanced DON concentration in the treatment with invertebrate shredders (G+) can be explained by the excretion of nitrogen compounds by the invertebrates (Horne 1968; Rosas et al. 2001).

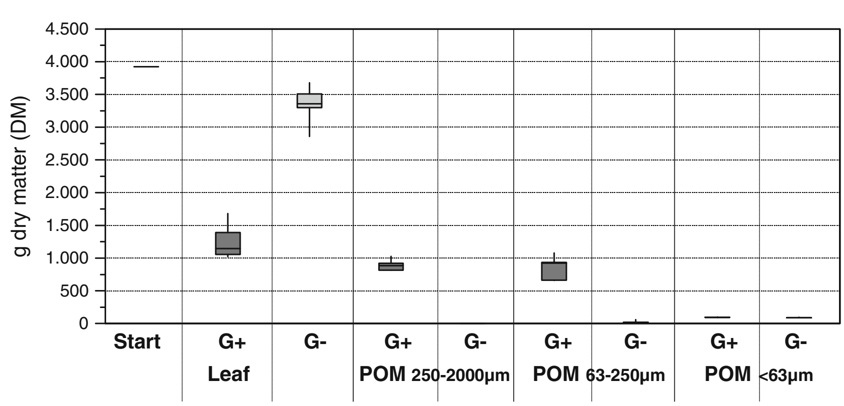

Fig. 1 POM with different sizes in treatments with (G+) and without the invertebrate shredder *Gammarus pulex* (G−) at start and end of the experiment. Significant differences were found between treatments with (G+) and without invertebrates (G−) for leaf, POM (250–2,000 μm) and POM (63–250 μm) ($p<0.01$), tested with *t*-test

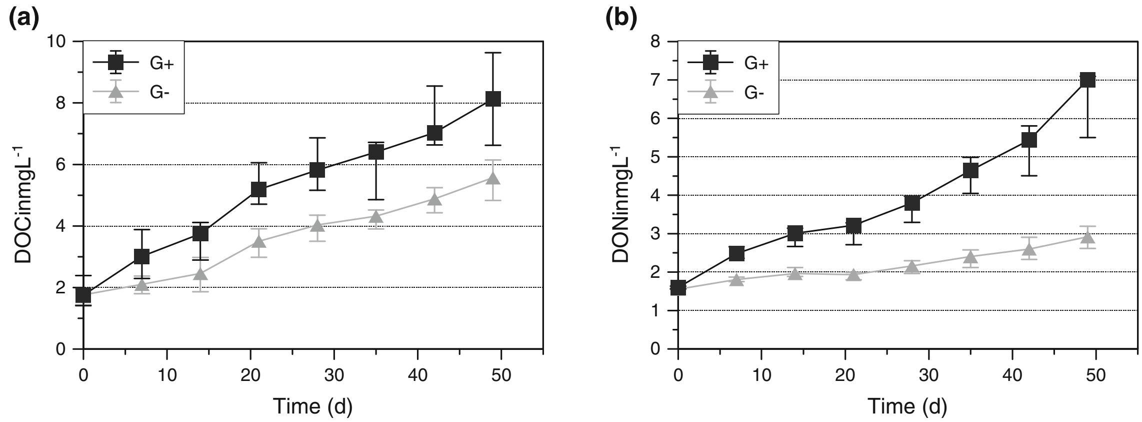

Fig. 2 Remobilization of **a** dissolved organic carbon (DOC) and **b** dissolved organic nitrogen (DON) during the 7 weeks of experiment (Median, Min Max). Significant differences were found between treatment with (G+) and without invertebrates (G−) at the end of experiment ($p<0.01$ for DOC and DON, tested with *t*-test)

The results of an enhanced DOC/DON release in the treatment with invertebrates (G+) shown in Fig. 2 were supported by findings of FT-IR measurements (Fig. 3). The FT-IR spectra of the different treatments are dominated in the upper wavenumber region by a broad absorption band at about 3,377 cm^{-1}, which is caused by O–H and N–H stretching (Abdulla et al. 2010). This is overlaid by the C–H stretching of sp^2 hybridised (3,051 cm^{-1}) and sp^3 (2,829 cm^{-1}) carbon. The strong band at 1,633 cm^{-1} in the upper wavenumber region contributes a lot of vibrations, e.g., O–H and N–H deformation, amid bands of proteins (Abdulla et al. 2010), C = C stretching and the antisymmetric stretching of carboxylates. The band at 1,409 cm^{-1} should be mainly caused by C–H deformation and the symmetric stretching of carboxylates (Mao et al. 2000), whereas the absorption at 1109 cm^{-1} is due to C–O–C and C–OH stretching (Brandenburg and Seydel 2002). Sulfate stretching also contributes to this band which is confirmed by a small band at 1,008 cm^{-1} in the FT–Raman spectra (data not shown due to intensive fluorescence and the absence of other bands). The most obvious difference between spectra of the treatment with (G+) and without invertebrates (G−) (see Fig. 3) is the presence of C–H stretching bands in spectra G+ which are missed in spectra of G−. This indicates the absence (or only small amount) of C–H groups in the latter samples. This statement is spectroscopically confirmed in the upper wavenumber region (see Fig. 3) by the smaller intensity of the band at 1,409 cm^{-1} in these spectra. Other differences in spectra reflect natural inhomogeneity between samples. In summary, invertebrate shredders significantly enhance the formation of smaller particles and influence the amount and quality of DOC. Since the quality effects of DOC on metal/metalloid remobilization is a largely neglected part in this research area at the moment (Schaller et al. 2011), we initiate here a first impulse by measuring DOC quality in our experiment. Comparing the few existing results of specific DOC quality on metal/metalloid remobilization (Kolokassidou et al. 2009) with our data, no DOC compound can be found explaining the enhanced/reduced metal/metalloid remobilization. Further research on the effect of specific DOC quality on metal/metalloid remobilization is needed to explain the remobilization potential of specific DOC compounds.

Amount of metals/metalloids accumulated by organic particles under litter decay affected by *G. pulex*

At the end of the experiment, we found that the enrichment of metals/metalloids in smaller particles from organic matter for both treatments (with [G+] and without invertebrates [G−]) depends on the particle size (Table 1). Comparing remaining leaf parts and different POM fractions (250–2,000 and 63–250 μm), significant differences were found for all measured elements ($p<0.01$), except for manganese in the treatment with invertebrates (G+). At the same time, significant differences between both treatments (G+ and G−) were revealed in leaves and POM (fraction 63–250 μm) for all elements ($p<0.01$) except for manganese in leaves. Hence, the presence of invertebrates is essential for the metals/metalloids fixation capacity of litter, by increasing the amount of smaller particles, which can accumulate higher amounts of metals/metalloids. The enrichment into lower particle sizes can be explained by both increasing surface area of the litter as the volume decreases and higher adsorption capacity of a larger amount of growing biofilm enhancing the surface even more (heterotrophic microorganisms). It is well established that the growing biofilm (periphyton) with its larger surface area and hence more functional groups results in higher metal and metalloid fixation (Flemming et al. 1996; Schorer and Eisele 1997). Furthermore, EPS are described to fix high amounts of metals/metalloids. The microorganisms are able to protect themselves against high metal concentrations by producing

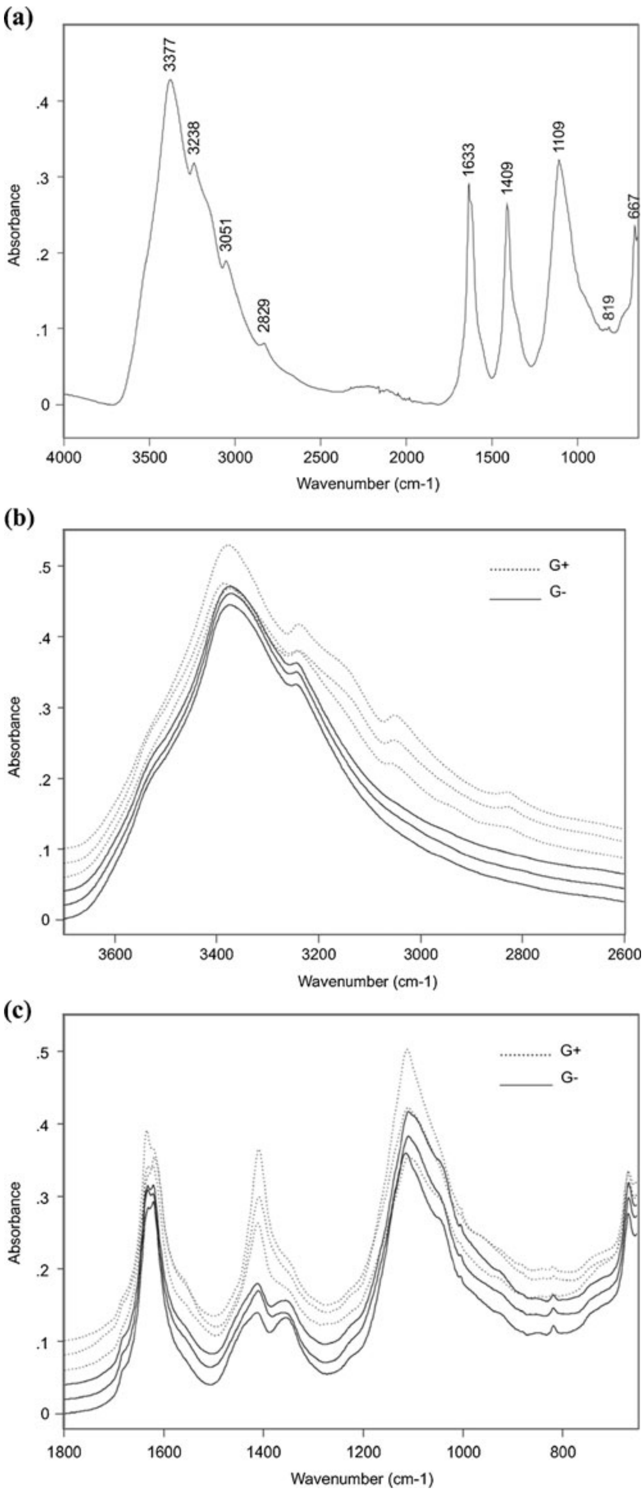

Fig. 3 FT-IR-ATR spectra of the inspissated water samples of treatments with (G+) and without invertebrate feeding (G−) in different wavenumber regions, absorbance offset 0.02

excess EPS, which is probably their most important survival mechanism (Pirog 1997). The microorganisms are capable of controlling the amount of EPS in their environment (Zhang and Bishop 2003).

A formation of POM (250–2,000 μm) could not be detected in the treatment without invertebrates. Hence, it was only in the treatment with invertebrates (G+) that a significant metal/metalloid enrichment from leaf litter to POM (250–2,000 μm) was found. In contrast, significant ($p<0.05$) higher concentrations of all measured elements were found for treatment G− compared to G+ for POM (63–250 μm). However, there is a significant difference in the amount of POM produced in the different treatments (G+, G−) with G+ producing the highest amount of POM. Considering the quantity of the different particle sizes (Fig. 1) we conclude that in treatments with the invertebrate shredder *G. pulex* more metal and metalloid can be fixed.

In addition, significantly less metals/metalloids ($p<0.05$) were found for both treatments between leaves and POM (<63 μm) (Mn, Ga, Pb, U and As, Fe only in treatment without invertebrates). A possible explanation for the low metal/metalloid content in POM (<63 μm) would be the composition of these particles consisting mainly of hardly degradable (e.g., lignin) carbon compounds. This in turn results in less attached biofilm (Ardon and Pringle 2007), or may pass the alimentary canal of the invertebrates, which may also result in less attached biofilm (Franken et al. 2005; Kulesza and Holomuzki 2006).

Furthermore, the results of our slightly acidic experiment show the same effect of invertebrate shredder on metal/metalloid fixation by organic sediments (in the fractions between 2,000 and 63 μm) as described for neutral to slightly alkaline conditions (Schaller et al. 2008, 2010a, b), but are contrary for POM <63 μm. Consequently, it could be concluded that the process of metal/metalloid accumulation into organic sediments (POM <63 μm) by invertebrate shredders occur as long as the invertebrates could survive.

Remobilization of metals/metalloids during litter decomposition

No clear effect of invertebrate shredders on metal/metalloid remobilization was revealed due to large error bars at low concentrations (Fig. 4), whereas the overall remobilization of metals/metalloids was very low. The clearest effects were revealed for gallium, which increased with increasing DOC/DON (Fig. 5), as previously shown for molybdenum (Schaller et al. 2010a). A high correlation between gallium and DOC as well as DON was proven only in the treatment with invertebrates (G+) (Fig. 5). Significantly higher concentrations of manganese, gallium and arsenic were found at the end comparing with the start of the experiment in treatments with invertebrates (G+) ($p<0.01$, *t*-test). In contrast no clear differences were found for manganese, gallium and arsenic between both treatments (G+ and G−) at any time.

Table 1 Influence of invertebrate feeding (G+ with and G− without invertebrates) on metal/metalloid enrichment/depletion into the different organic fractions of decomposing leaf litter (units for all values are mg kg^{-1} DW^{-1}, n=5)

Fraction	Treatment	Value	Manganese	Iron	Arsenic	Gallium	Lead	Uranium
Leaf start	G+/−	Median	321	8,011	6.8	57.3	7.2	80.5
		Min	258	6,755	5.7	41.9	4.0	77.7
		Max	375	13,318	11.8	81.2	7.6	94.0
Leaf end >2,000 µm	G+	Median	183	1,490	1.2	9.6	4.8	49.6
		Min	136	1,356	1.0	8.5	4.0	46.3
		Max	215	2,542	2.7	15.2	6.4	78.3
	G−	Median	182	3,797	3.0	27.0	6.4	59.6
		Min	162	2,380	1.8	20.4	5.6	55.6
		Max	202	5,214	4.3	45.9	7.2	64.7
POM 250–2,000 µm	G+	Median	157	12,800	10.4	60.7	12.6	171.2
		Min	122	11,881	9.7	54.7	12.3	166.3
		Max	201	14,155	11.8	66.1	16.9	190.5
POM 63–250 µm	G+	Median	219	12,809	10.6	76.5	12.9	170.4
		Min	128	12,528	10.3	56.0	11.7	160.4
		Max	356	14,870	13.2	83.9	13.6	183.8
	G−	Median	762	28,070	30.2	320	25.3	234.1
		Min	524	23,859	26.3	237	19.4	176.8
		Max	884	57,726	60.6	566	57.5	321.8
POM <63 µm	G+	Median	32	1,222	1.3	5.18	1.7	11.3
		Min	22	697	1.0	1.66	1.1	6.6
		Max	52	2,909	3.2	10.2	2.2	16.4
	G−	Median	16	970	1.2	5.59	1.8	10.0
		Min	13	427	0.7	4.37	0.9	1.7
		Max	45	2,641	3.0	8.74	2.9	11.2

Furthermore, in treatment G+ a significant decrease ($p<0.05$) of iron water concentration and in treatment G− a significant decrease ($p<0.05$) in lead water concentration was found in the course of the experiment (*t*-test). In contrast, the uranium concentration increased slightly in treatment G− ($p<0.05$). The low effects of DOC on metal/metalloid remobilization are in accordance with the results of Schaller et al. (2010a), but contrasting others (Sachs et al. 2007). As noted earlier, further research on the impact of specific DOC quality on metal/metalloid remobilization is needed to explain the specific remobilization pattern. Nevertheless, it could be concluded that 8 mg l^{-1} DOC dominated by O–H–, N–H–, C–H–, C = C–, C–O–C– and C–OH groups do not remobilize high amounts of metals/metalloids in the presence of POM of different sizes, except of gallium.

Conclusion

During the decay of leaf litter, *G. pulex* facilitated significantly the formation of smaller particle sizes of organic matter. The capacity of metal/metalloid fixation was significantly higher for smaller particles (POM 2,000–63 µm) compared to the original leaf litter and litter residues. Hence, *G. pulex* enhanced metal/metalloid fixation into the organic partition of sediments by increasing the amount of smaller particle sizes of organic matter. In contrast to this, in the smallest fraction of POM (<63 µm) the capacity of metal/metalloid fixation was lower compared with the leaf residues in the treatment without invertebrates. The remobilization of the metals and metalloids was very low for all measured elements. Thus, invertebrate shredder enhanced significantly the fixation of metals/metalloids in weak acidic environments. In addition, a significant effect of invertebrates on the quantitative formation of DOC/DON was proven. Furthermore, the quality of released DOC/DON, revealed by FT-IR measurements, was also significantly affected by invertebrate shredders. However, specific metal/metalloid remobilization experiments are still needed to estimate the impact of specific DOC quality (compounds) on metal/metalloid release. In conclusion, invertebrate shredders significantly enhance the binding capacity for metals/metalloids in organic sediments under weak acidic water conditions. Hence, allochthonous aquatic ecosystems with an existing functional animal group of shredders are a sink for metals and metalloids.

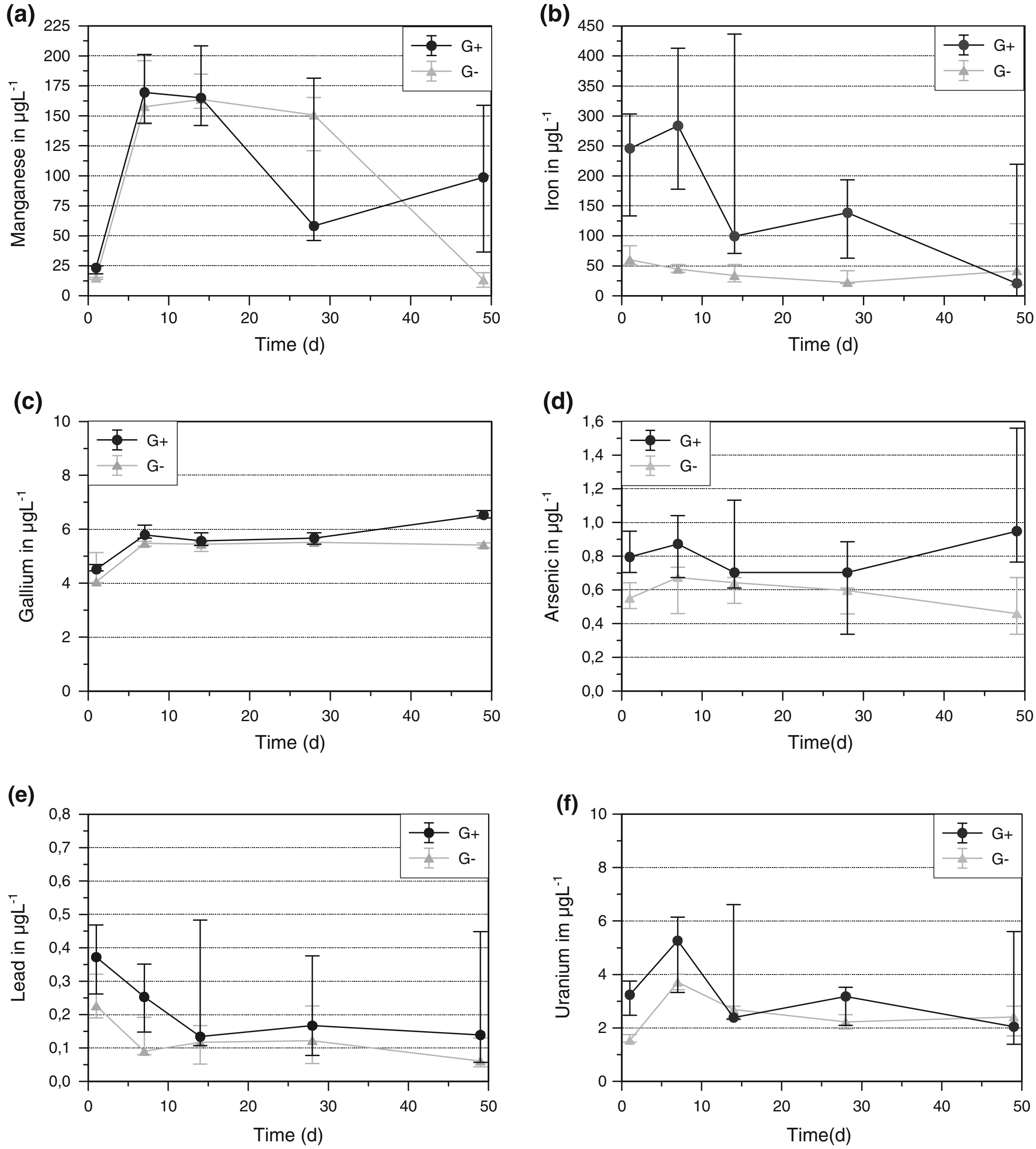

Fig. 4 Mobilization of metals and metalloids during the experiment for treatments with (G+) and without invertebrate shredders (G−). Significant differences were found between the different treatments (G+/G−) for manganese, gallium and arsenic ($p<0.01$) tested with *t*-test. Furthermore, significant differences between start and end of experiment were found for treatment with invertebrates (G+) for manganese, gallium and iron ($p<0.05$) and for treatment without invertebrates (G−) for gallium, lead and uranium ($p<0.05$), tested with *t*-test

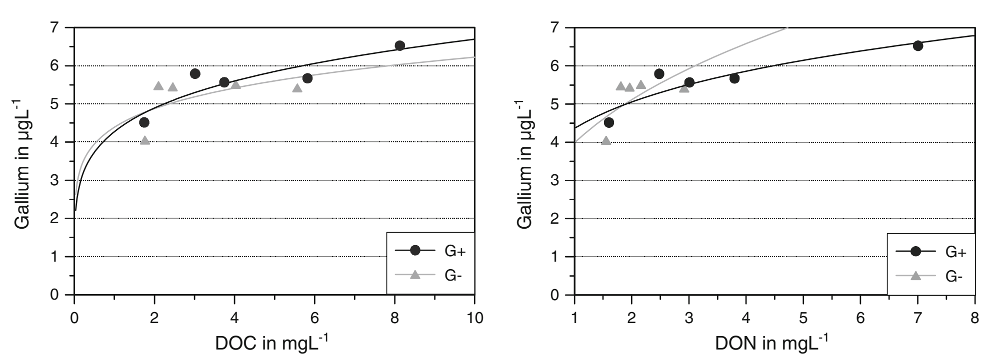

Fig. 5 Correlation of gallium in water with DOC for treatments with invertebrates (G+) (R^2=0.89, $p<0.05$) and without invertebrates (G−) (not significant), and correlation of gallium in water with DON for treatments with invertebrates (G+) (R^2=0.91, $p<0.05$) and without invertebrates (G−) (not significant)

References

Abdulla HAN, Minor EC, Dias RF, Hatcher PG (2010) Changes in the compound classes of dissolved organic matter along an estuarine transect: a study using FTIR and (13)C NMR. Geochim Cosmochim Acta 74:3815–3838

Ardon M, Pringle CM (2007) The quality of organic matter mediates the response of heterotrophic biofilms to phosphorus enrichment of the water column and substratum. Freshw Biol 52:1762–1772

Baborowski M, Bozau E (2006) Impact of former mining activities on the uranium distribution in the River Saale (Germany). Appl Geochem 21:1073–1082

Benfield EF (2007) Decomposition of leaf material. In: Hauer FR, Lamberti GA (eds) Methods in stream ecology. Elsevier, San Diego, pp 711–720

Berg B, McClaugherty C (2003) Plant litter. Springer, Berlin, 286 pp

Brandenburg K, Seydel U (2002) Vibrational spectroscopy of carbohydrates and glycoconjugates. In: Chalmers JM, Griffiths PR (eds) Handbook of vibrational spectroscopy, applications in life, pharmaceutical and natural sciences, vol. 5. Wiley, Chichester, UK, pp 3481–3507

Burton ED, Bush RT, Sullivan LA, Johnston SG, Hocking RK (2008) Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. Chem Geol 253:64–73

Camilleri JC (1992) Leaf-litter processing by invertebrates in a mangrove forest in Queensland. Mar Biol 114:139–145

Canhoto C, Graca M, Bärlocher F (2005) Feeding preferences of shredders. In: Graca M, Bärlocher F, Gessner MO (eds) Methods in study litter decomposition. Springer, Dordrecht, pp 297–302

Dienemann H, Dienemann C, Dudel EG (2006) Influence of allochthonous plant litter on fixiation of uranium in sediments. In: Merkel B, Hasche-Berger A (eds) Uranium in the environment. Springer, Berlin, pp 149–157

Dinelli E, Lucchini F, Fabbri M, Cortecci G (2001) Metal distribution and environmental problems related to sulfide oxidation in the Libiola copper mine area (Ligurian Apennines, Italy). J Geochem Explor 74:141–152

DIN-EN-13805 (2002) Lebensmittel - Bestimmung von Elementspuren – Druckaufschluss, Deutsche Fassung, Deutsches Institut für Normung, Berlin

DIN-EN-1484 (1997) Anleitung zur Bestimmung des gesamten organischen Kohlenstoffs (TOC) und des gelösten organischen Kohlenstoffs. Deutsches Institut für Normung, Berlin

DIN-EN-ISO-17294-2 (2004) Wasserbeschaffenheit - Anwendung der induktiv gekoppelten Plasma-Massenspektrometrie (ICP-MS) — Teil 2: Bestimmung von 62 Elementen (ISO 17294-2:2003). Deutsche Fassung EN ISO 17294-2:2004, Deutsches Institut für Normung, Berlin

DIN-ISO-10694 (1995) Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis) (ISO 10694:1995). Deutsches Institut für Normung, Berlin

Felten V, Charmantier G, Mons R, Geffard A, Rousselle P, Coquery M, Garric J, Geffard O (2008) Physiological and behavioural responses of *Gammarus pulex* (Crustacea: Amphipoda) exposed to cadmium. Aquat Toxicol 86:413–425

Flemming H-C, Schmitt J, Marshall KC (1996) Sorption properties of biofilms. In: Calmano W, Förstner U (eds) Sediments and toxic substances. Springer, Berlin, pp 115–147

Flemming H-C, Neu TR, Wozniak DJ (2007) The EPS matrix: the "House of Biofilm Cells". J Bacteriol 189:7945–7947

Franken RJM, Waluto B, Peeters E, Gardeniers JJP, Beijer JAJ, Scheffer M (2005) Growth of shredders on leaf litter biofilms: the effect of light intensity. Freshw Biol 50:459–466

Gatzweiler AT, Jakubick AT, Kiessig G (2004) Remediation options and the significance of water treatment at former uranium production sites in Eastern Germany. In: (IAEA) IAEA (ed) Treatment of liquid effluent from uranium mines and mills. IAEA, Vienna, pp 127–144

Graça MAS (2001) The role of invertebrates on leaf litter decomposition in streams — a review. Int Rev Hydrobiol 86:383–393

Hieber M, Gessner MO (2002) Contribution of stream detrivores, fungi, and bacteria to leaf breakdown based on biomass estimates. Ecology 83:1026–1038

Horne FR (1968) Nitrogen excretion in crustacea: I. Herbivorous land crab *Cardisoma guanhumi* Latreille. Comp Biochem Physiol 26:687

Karbassi AR, Monavari SM, Bidhendi GRN, Nouri J, Nematpour K (2008) Metal pollution assessment of sediment and water in the Shur River. Environ Monit Assess 147:107–116

Kolokassidou K, Szymczak W, Wolf M, Obermeier C, Buckau G, Pashalidis I (2009) Hydrophilic olive cake extracts: characterization by physicochemical properties and Cu(II) complexation. J Hazard Mater 164:442–447

Kulesza AE, Holomuzki JR (2006) Amphipod performance responses to decaying leaf litter of *Phragmites australi*s and *Typha angustifolia* from a Lake Erie coastal marsh. Wetlands 26:1079–1088

Levinton J (1995) Bioturbators as ecosystem engineers: control of the sediment fabric, Inter-individual interactions and material fluxes. In: Jones CG (ed) Linking species and ecosystems. Chapman & Hall, New York, pp 29–36

Mao JD, Hu WG, Schmidt-Rohr K, Davies G, Ghabbour EA, Xing BS (2000) Quantitative characterization of humic substances by solid-state carbon-13 nuclear magnetic resonance. Soil Sci Soc Am J 64:873–884

Meijering MPD (1991) Lack of oxygen and low pH as limiting factors for *Gammarus* in Hessian brooks and rivers. Hydrobiologia 223:159–169

Pirog TP (1997) Role of *Acinetobacter* sp. exopolysaccharides in protection against heavy metal ions. Microbiology 66:284–288

Rosas C, Cuzon G, Taboada G, Pascual C, Gaxiola G, Van Wormhoudt A (2001) Effect of dietary protein and energy levels on growth, oxygen consumption, haemolymph and digestive gland carbohydrates, nitrogen excretion and osmotic pressure of *Litopenaeus vannamei* (Boone) and *L-setiferus* (Linne) juveniles (Crustacea, Decapoda; Penaeidae). Aquac Res 32:531–547

Sachs S, Brendler V, Geipel G (2007) Uranium(VI) complexation by humic acid under neutral pH conditions studied by laser-induced fluorescence spectroscopy. Radiochim Acta 95:103–110

Schaller J, Weiske A, Mkandawire M, Dudel EG (2008) Enrichment of uranium in particulate matter during litter decomposition affected by *Gammarus pulex* L. Environ Sci Technol 42:8721–8726

Schaller J, Mkandawire M, Dudel EG (2010a) Heavy metals and arsenic fixation into freshwater organic matter under *Gammarus pulex* L. influence. Environ Pollut 158:2454–2458

Schaller J, Weiske A, Mkandawire M, Dudel EG (2010b) Invertebrates control metals and arsenic sequestration as ecosystem engineers. Chemosphere 79:169–173

Schaller J, Brackhage C, Mkandawire M, Dudel EG (2011) Metal/metalloid accumulation/remobilization during aquatic litter decomposition in freshwater: a review. Sci Total Environ 409:4891–4898

Schorer M, Eisele M (1997) Accumulation of inorganic and organic pollutants by biofilms in the aquatic environment. Water Air Soil Pollut 99:651–659

Tipping E, Smith EJ, Lawlor AJ, Hughes S, Stevens PA (2003) Predicting the release of metals from ombrotrophic peat due to drought-induced acidification. Environ Pollut 123, 239v253

Wallace TA, Ganf GG, Brookes JD (2008) A comparison of phosphorus and DOC leachates from different types of leaf litter in an urban environment. Freshw Biol 53:1902–1913

Welton JS (1979) Life-history and production of the amphipod *Gammarus pulex* in a Dorset chalk stream. Freshw Biol 9:263–275

Zhang XQ, Bishop PL (2003) Biodegradability of biofilm extracellular polymeric substances. Chemosphere 50:63–69

Zhao LYL, Schulin R, Nowack B (2009) Cu and Zn mobilization in soil columns percolated by different irrigation solutions. Environ Pollut 157:823–833