



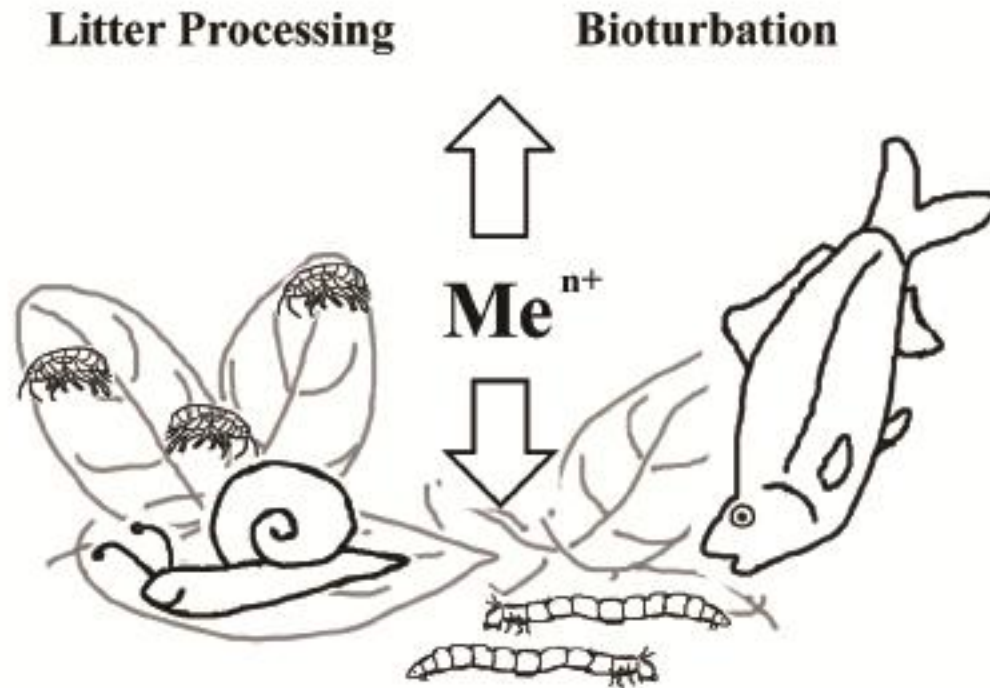
# **Metal/metalloid accumulation/remobilization during aquatic litter decomposition in freshwater**

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## Key-processes during litter decay



Schaller et al. 2011, *Sci. Total Environ.*, 409: 4891-4898

## Aquatic ecosystems affected by former mining



pH 7.5

eH 400 mV

discharge 5-10 L s<sup>-1</sup>

Leaf litter input

Population of

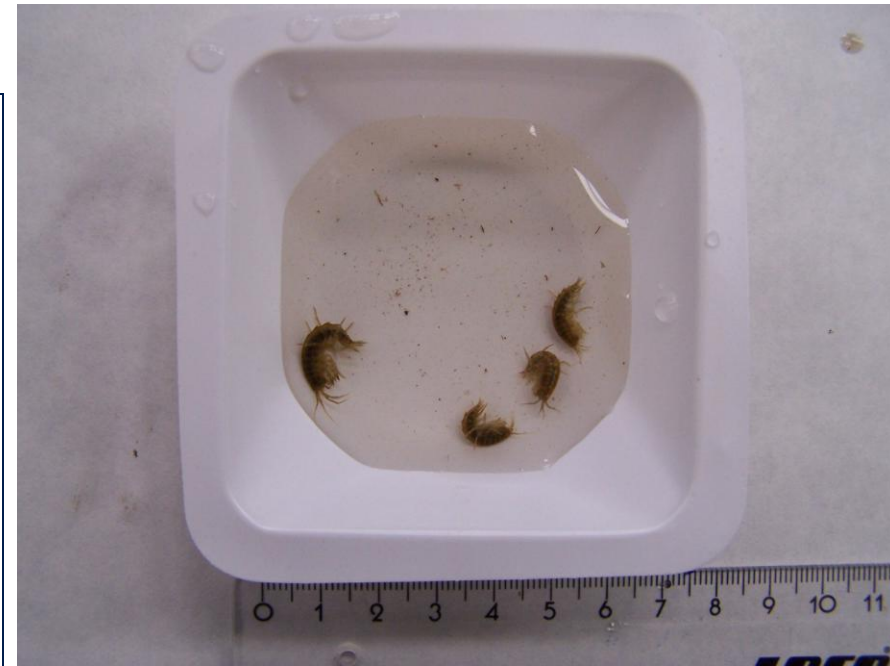
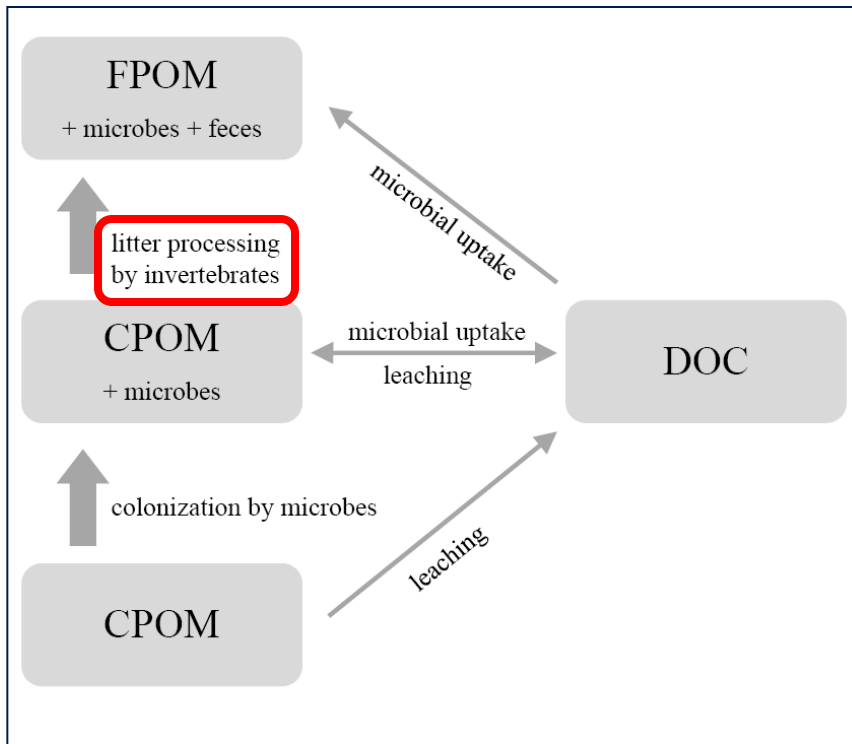
invertebrate shredder

(key-species of litter  
decomposition)

## Background: metal/ metalloid content in water of polluted streams

	Content in water <b><math>\mu\text{g} \cdot \text{L}^{-1}</math></b>	Content in sediments <b><math>\text{mg} \cdot \text{kg}^{-1} \cdot \text{DM}^{-1}</math></b> (organic rich)
Mn	375	50.000
Co	1.6	130
Cu	4.6	350
Zn	5.8	350
As	30	400
Cd	0.3	8
Pb	0.4	20
U	150	350

## Background: Main processes of litter decay in aquatic systems



*Gammarus pulex* is a main litter processing invertebrate in Europe

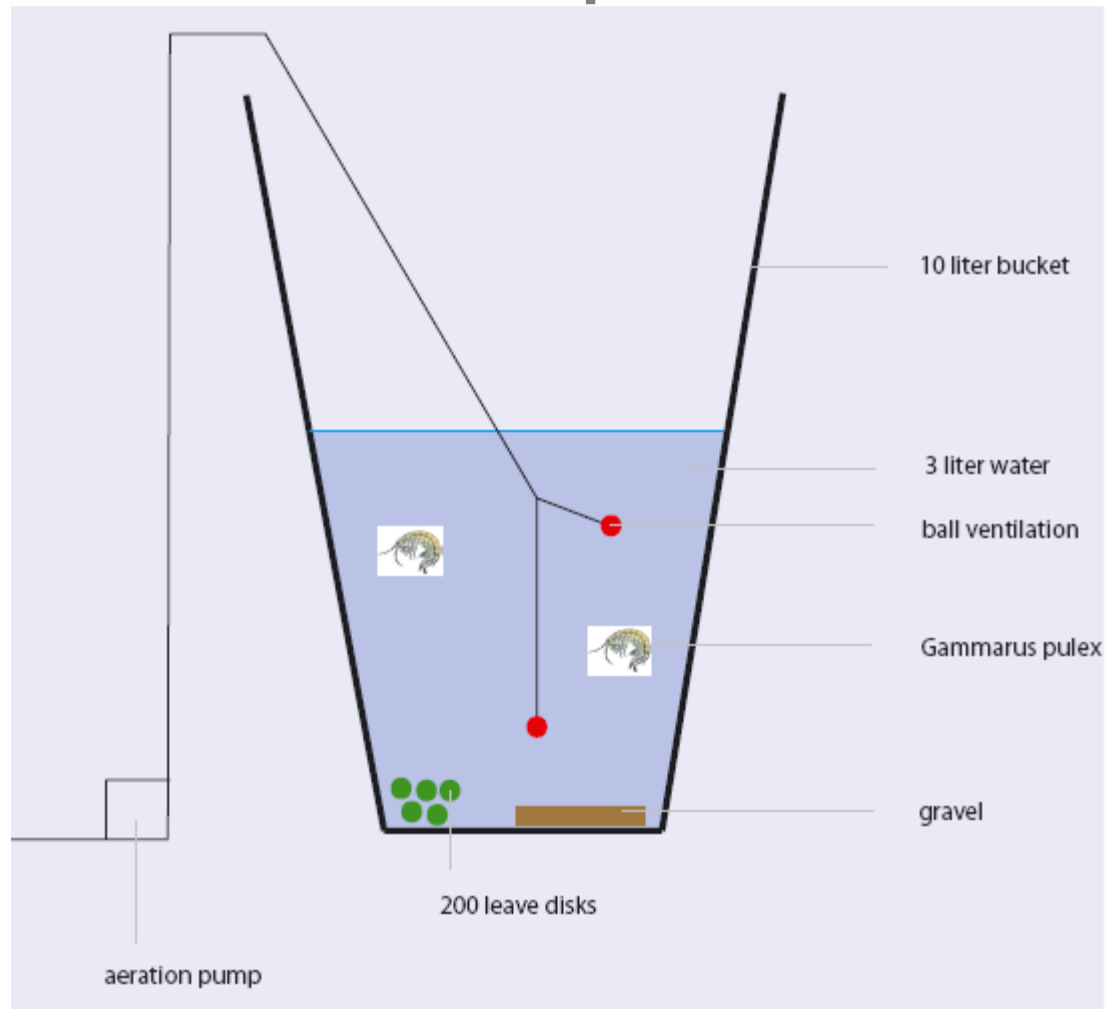
Schaller et al. 2011, Sci. Total Environ., 409: 4891-4898

Resulting questions:

**Which influences do invertebrate shredders have on metal/ metalloid fixation?**

**Which influence do invertebrate shredders have on DOC – release and consequently on metal remobilization?**

## Batch experiment

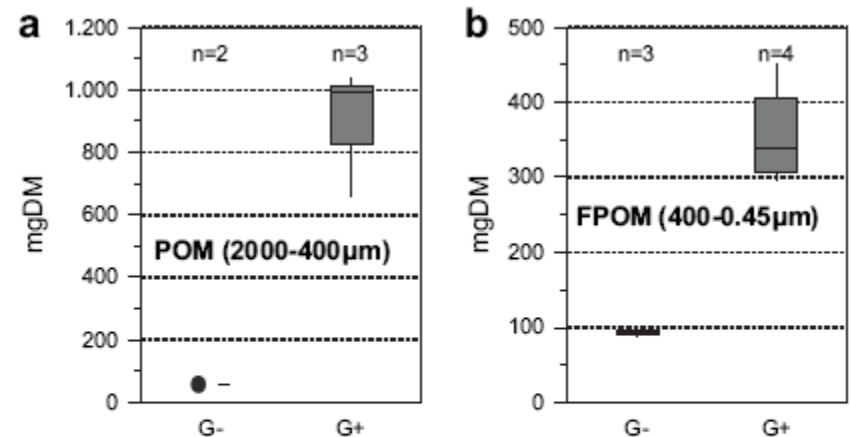


## What are the effects of invertebrate shredder on litter properties?

- litter processing
- formation of smaller particles
- increasing of the surface area

G+ with invertebrates  
 G- without invertebrates

- higher surface area → more biofilm
- biofilm has very good sorption properties



**Fig. 1.** Accumulation of fine particulate organic matter (0.45–400 µm particle size FPOM) (a) and particulate organic matter (400–2000 µm particle size POM) (b) for treatment with (G+) and without (G–) *G. pulex*. The values are median with maximum and minimum. Between treatments with (G+) and without (G–) *G. pulex* are significant differences ( $p < 0.05$ ) on formation of smaller particle sizes.

Schaller et al. 2010, Environmental Pollution 158:2454-2458



# In which fraction of the sediments the highest metal and metalloid content is found?

→ **below 2000  $\mu\text{m}$**

data in  $\text{mg kg}^{-1} \text{DW}^{-1}$

**Table 2**

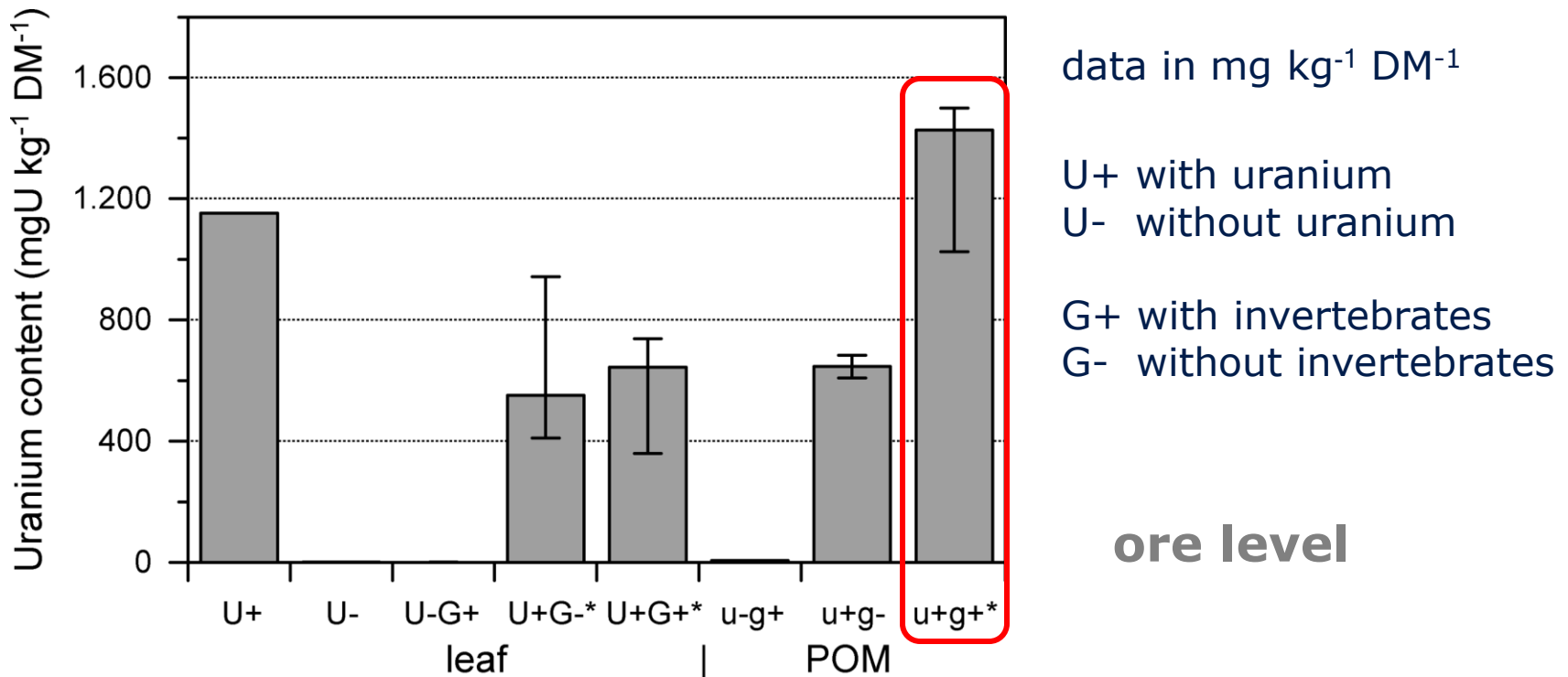
Influence of invertebrate shredding treatments on heavy metal enrichment into the different organic fractions of decomposing leaf litter (units for all values are  $\text{mg kg}^{-1} \text{DW}^{-1}$ ;  $n = 4$ ; and, the values are median indicated in bold, minimum and maximum). Above thick line: Element content in original preconditioned leaf litter at the beginning and solid resting parts of leaf litter at the end of experiment; below thick line: elements content in decay products of litter processing with and without invertebrate shredders.

Fraction	Ca	Mn	Fe	Co	Cu	Zn	As	Mo	Cs	Pb
Conditioned leaf litter at start (mixed sample from 8 leaf disks, one disks per leaf) $t = 0$	<b>34,821</b>	<b>3730.2</b>	<b>1440.1</b>	<b>10.02</b>	<b>33.94</b>	<b>262.8</b>	<b>9.33</b>	<b>9.75</b>	<b>0.62</b>	<b>4.54</b>
Leaf litter without invertebrate Feeding at the end of experiment $t = 14$ days	<b>31,966</b> 23,653 31,967	<b>1115.0</b> 1034.5 1443.3	<b>1348.7</b> 1282.6 1363.2	<b>4,65</b> 4.38 6.13	<b>26.39</b> 20.99 27.57	<b>225.0</b> 149.5 229.6	<b>8.29</b> 7.42 8.73	<b>2.85</b> 2.29 4.37	<b>0.58</b> 0.50 0.52	<b>3.71</b> 3.45 3.85
Leaf litter with invertebrate feeding at the end of experiment $t = 14$ days	<b>28,707</b> 21,469 32,530	<b>513.9</b> 292.9 539.3	<b>471.3</b> 421.7 529.4	<b>2,75</b> 2.58 3.53	<b>21.64</b> 21.31 22.98	<b>193.6</b> 142.9 212.2	<b>3.13</b> 2.02 3.24	<b>4.84</b> 2.28 6.49	<b>0.09</b> 0.06 0.13	<b>2.33</b> 1.63 2.99
POM (400–2000 $\mu\text{m}$ ) without invertebrate feeding after experiment $t = 14$ days	<b>22,180</b> 18,206 26,154	<b>6066.3</b> 4945.1 7187.5	<b>11,491</b> 10,993 11,989	<b>21.11</b> 17.89 24.33	<b>88.31</b> 87.14 89.49	<b>1558.5</b> 800.5 2316.4	<b>58.6</b> 48.7 67.4	<b>5.12</b> 4.22 6.02	<b>4.14</b> 3.32 4.95	<b>21.60</b> 15.53 27.67
POM (400–2000 $\mu\text{m}$ ) with invertebrate feeding after experiment $t = 14$ days	<b>31,097</b> 27,871 33,255	<b>3979.7</b> 3086.6 4551.5	<b>5395.7</b> 4398.3 6568.5	<b>15.13</b> 14.46 17.19	<b>80.01</b> 70.84 105.39	<b>1712.4</b> 1528.3 1896.5	<b>34.8</b> 32.0 37.6	<b>5.09</b> 3.83 5.48	<b>2.59</b> 2.40 2.79	<b>15.96</b> 14.44 18.49
FPOM (0.45–400 $\mu\text{m}$ ) without invertebrate feeding after experiment $t = 14$ days	<b>32,447</b> 29,771 50,663	<b>5249.3</b> 5069.9 5429.8	<b>14,239</b> 5744 16,590	<b>25.89</b> 24.24 39.68	<b>176.89</b> 151.57 214.35	<b>1170.5</b> 909.7 1304.9	<b>69.3</b> 64.5 74.1	<b>8.05</b> 3.65 12.11	<b>5.44</b> 5.41 6.76	<b>35.66</b> 15.25 47.44
FPOM (0.45–400 $\mu\text{m}$ ) without invertebrate feeding after experiment $t = 14$ days	<b>38,435</b> 31,911 45,633	<b>4432.6</b> 3655.1 5813.5	<b>6056.0</b> 5514.5 8342.4	<b>17.34</b> 14.95 24.91	<b>109.25</b> 105.59 112.18	<b>965.0</b> 562.3 2036.9	<b>43.5</b> 41.4 59.6	<b>5.54</b> 3.93 6.88	<b>2.54</b> 1.97 4.03	<b>17.68</b> 14.16 20.71

Schaller et al. 2010, Chemosphere 79: 169-173

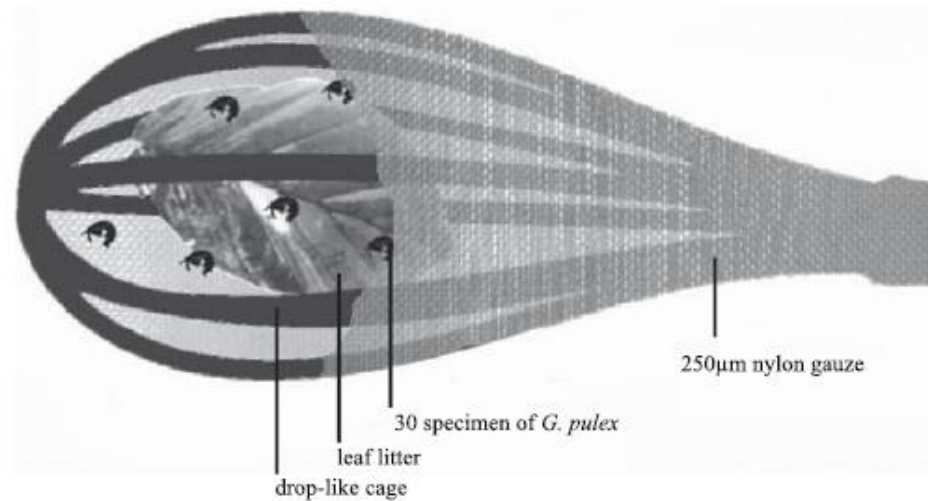
In which fraction of the sediments the highest metal and metalloid content is found?

→ below 2000 µm



Schaller et al. 2008, Environmental Science & Technology 42:8721-8726

## Field experiment



**Fig. 1.** Experimental setup including 30 specimens of invertebrate shredders, pre-treated leaf litter (4 weeks exposed in stream at study site) and support medium (drop-like cage) sewed into nylon gauze (with polyethylen yarn). Length 18 cm. Diameter 7.0 cm.

## Confirmation of laboratory data in the field

**Table 3**

Metal and metalloid content in the in leaf litter after 4 weeks without invertebrate feeding (L4 – G), leaf litter after 4 weeks without and 2 weeks with invertebrate feeding (L6+G) and particulate organic matter (250–2000 µm) after 2 weeks of invertebrate feeding (POM + G) in mg kg<sup>-1</sup> ash free dry mass. *n* = 15. (median – bold, minimum and maximum). Significant difference: \*\*(*p* < 0.005), \*(*p* < 0.05), – no significant difference and + (*p* < 0.01; significant more uranium in the leaf litter).

	L4 – G	L6 + G	POM + G
Mg	<b>2850</b> (2720–3130)	<b>3180</b> (3020–3440)	<b>11 800**</b> (7090–21 700)
P	<b>2530</b> (2300–3400)	<b>2040</b> (715–4330)	n.d.
Ca	<b>25 100</b> (23 100–29 900)	<b>20 500</b> (18 400–28 000)	<b>39 000<sup>-</sup></b> (25 000–72 400)
Mn	<b>5810</b> (5540–18 200)	<b>4240</b> (2730–9640)	<b>57 900**</b> (18 400–129 000)
Co	<b>29.2</b> (14.9–60.7)	<b>7.9</b> (4.9–19.3)	<b>139**</b> (47–209)
Cu	<b>69</b> (53–161)	<b>82</b> (66–113)	<b>371*</b> (196–493)
Zn	<b>201</b> (138–229)	<b>152</b> (114–197)	<b>356*</b> (232–647)
As	<b>36</b> (25–83)	<b>22</b> (8–53)	<b>415**</b> (167–845)
Cd	<b>3.6</b> (2.6–4.6)	<b>1.9</b> (1.2–4.6)	<b>10*</b> (4.6–20)
Pb	<b>1.6</b> (1.2–2.6)	<b>0.8</b> (0.2–2.4)	<b>28.8*</b> (5.0–47.5)
U	<b>523</b> (483–875)	<b>664</b> (494–1000)	<b>335*</b> (207–807)

data in mg kg<sup>-1</sup> DM<sup>-1</sup>

L6+G = leaf litter after 6 weeks of with invertebrate feeding  
 POM+G = particulate organic matter after 2 weeks of invertebrate feeding

ph = 7.5  
 eH = 400 mV

→ **exception uranium**

Schaller et al. 2010, Chemosphere 79: 169-173

## In which fraction of the sediments the highest metal and metalloid content is found?

**Table 2**

Metal and metalloid content in the initial leaf litter (ILL), leaf litter after 6 weeks without invertebrate feeding (L6 – G) and removed biofilm from the 6 weeks exposed leaf litter (BL6 – G) in mg kg<sup>-1</sup> ash free dry matter (*n* = 10). (median – bold, minimum and maximum).

	ILL	L6 – G	BL6 – G
Mg	<b>3790</b> (3680–4030)	<b>3370</b> (3320–3620)	<b>8830</b> (5800–28400)
P	3770 (2820–3960)	<b>2040</b> (2010–2750)	n.d.
Ca	<b>17 600</b> (16 500–19 500)	<b>31 200</b> (29 800–36 600)	<b>31 400</b> (15 000–85 500)
Mn	<b>1120</b> (986–1150)	<b>8790</b> (4840–12 400)	<b>34 800</b> (17 300–62 600)
Co	<b>2.1</b> (1.9–2.3)	<b>33.6</b> (16.6–47.8)	<b>110</b> (62–208)
Cu	<b>12</b> (11–17)	<b>122</b> (92–172)	<b>331</b> (198–941)
Zn	<b>109</b> (105–126)	<b>249</b> (156–287)	<b>629</b> (290–2056)
As	<b>1.2</b> (1.0–2.8)	<b>54</b> (29–77)	<b>354</b> (181–656)
Cd	<b>0.12</b> (0.07–0.15)	<b>4.8</b> (2.2–5.3)	<b>7.2</b> (4.9–18.1)
Pb	<b>1.8</b> (1.5–2.0)	<b>2.0</b> (1.6–4.2)	<b>56</b> (28–131)
U	<LOD	<b>794</b> (689–841)	<b>355</b> (128–1220)

→ in the biofilm

data in mg kg<sup>-1</sup> DM<sup>-1</sup>

ILL = initial leaf litter (unpolluted)

L6-G = leaf litter after 6 weeks of without invertebrate feeding

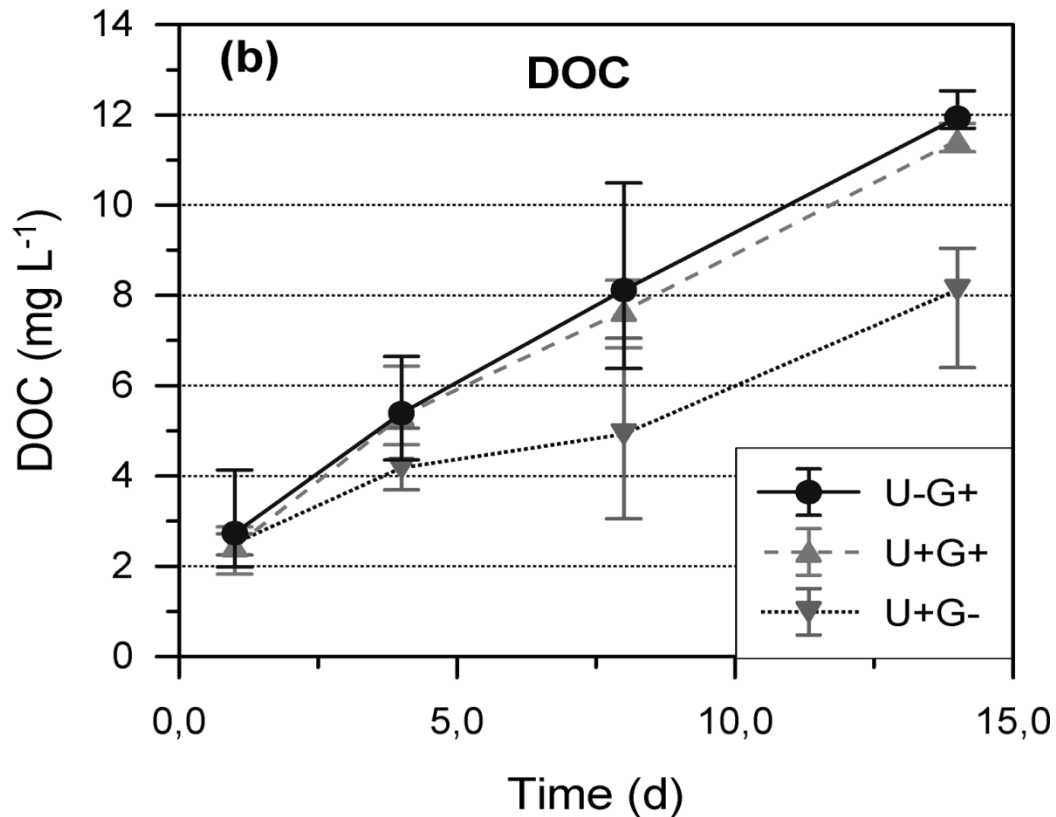
BL6-G = removed biofilm from the 6 weeks exposed leaf litter

ph = 7.5

eH = 400 mV

Schaller et al. 2010, Chemosphere 79: 169-173

## Which influence do invertebrate shredders have on DOC – release?



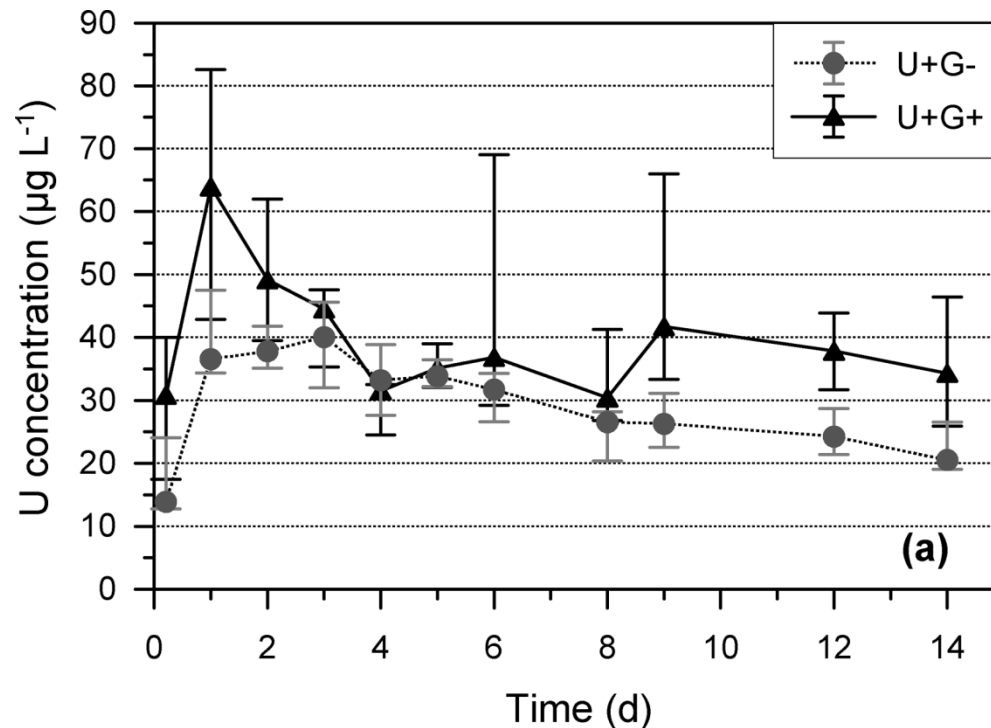
U+ with uranium  
 U- without uranium

G+ with invertebrates  
 G- without invertebrates

Schaller et al. 2008, Environmental Science & Technology 42:8721-8726

Which influence does increase of DOC have on the metal/  
metalloid remobilization?

→ **very low influence!**



U+ with uranium

U- without uranium

G+ with invertebrates

G- without invertebrates

Schaller et al. 2008, Environmental Science & Technology 42:8721-8726

Which influence does increase of DOC have on the metal/metalloid remobilization?

→ very low influence!

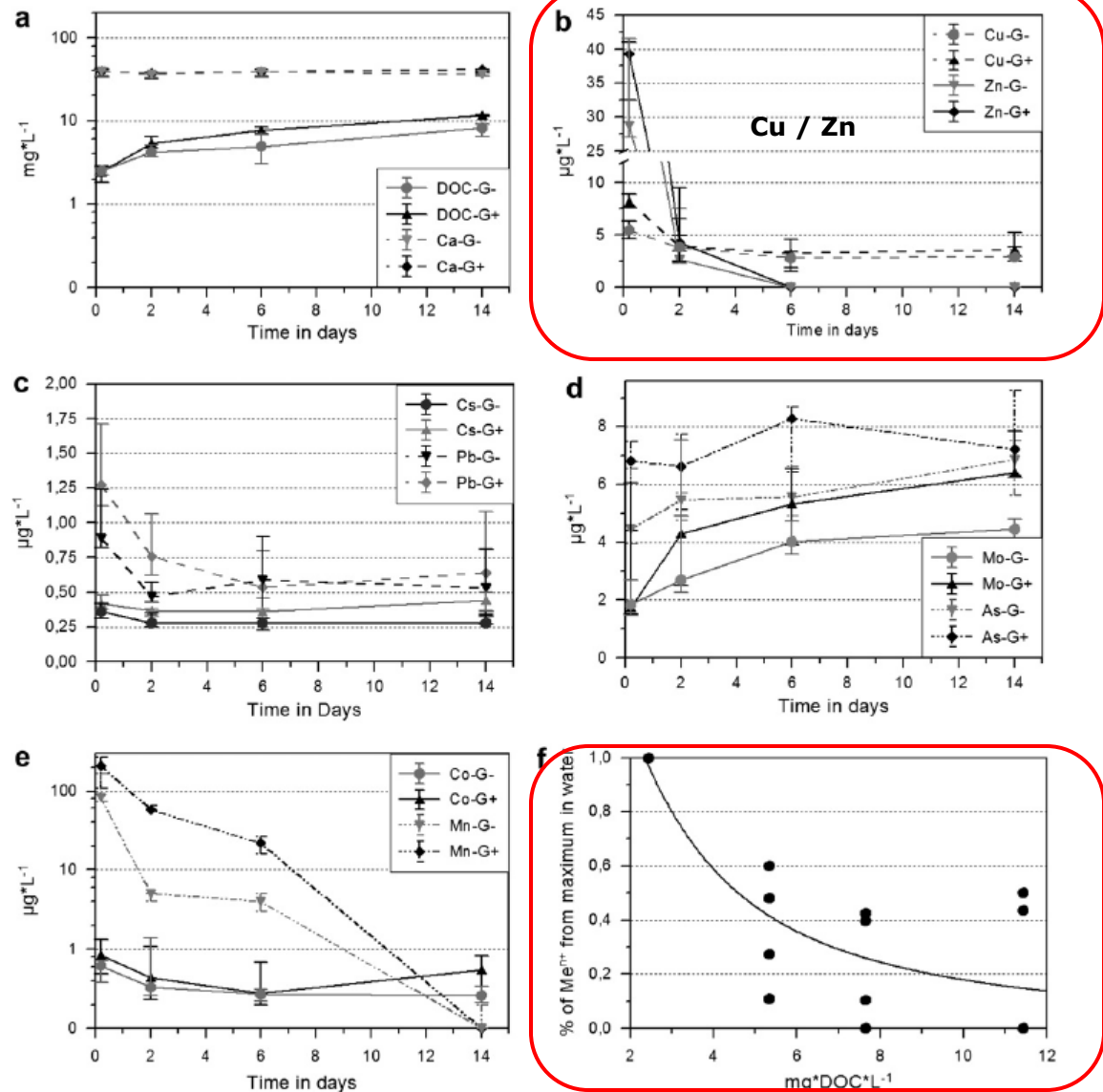


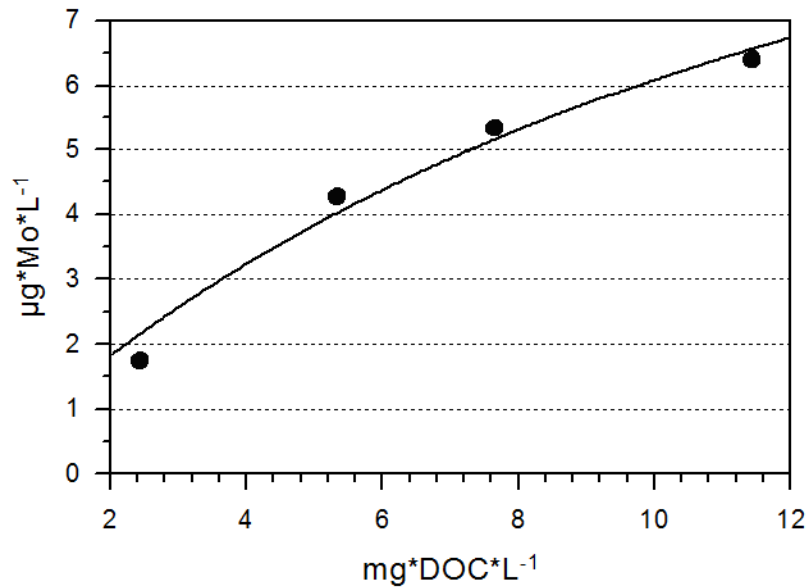
Fig. 2. (a–e) Mobilization of heavy metals and dissolved organic carbon (DOC) during 14 day of experiment for treatments with (G+) and without (G–) *G. pulex*. The values are median with maximum and minimum,  $n = 4$ . (f): Correlation of metals in water (manganese, copper, zinc, calcium and lead) with DOC. Normalized data;  $n = 5$ ,  $R^2 = 0.86$ ,  $p < 0.005$ .

Schaller et al. 2010, Environmental Pollution 158:2454-2458



Which influence does increase of DOC have on the metal/  
metalloid remobilization?

**Any exceptions?**  
**→ molybdenum**



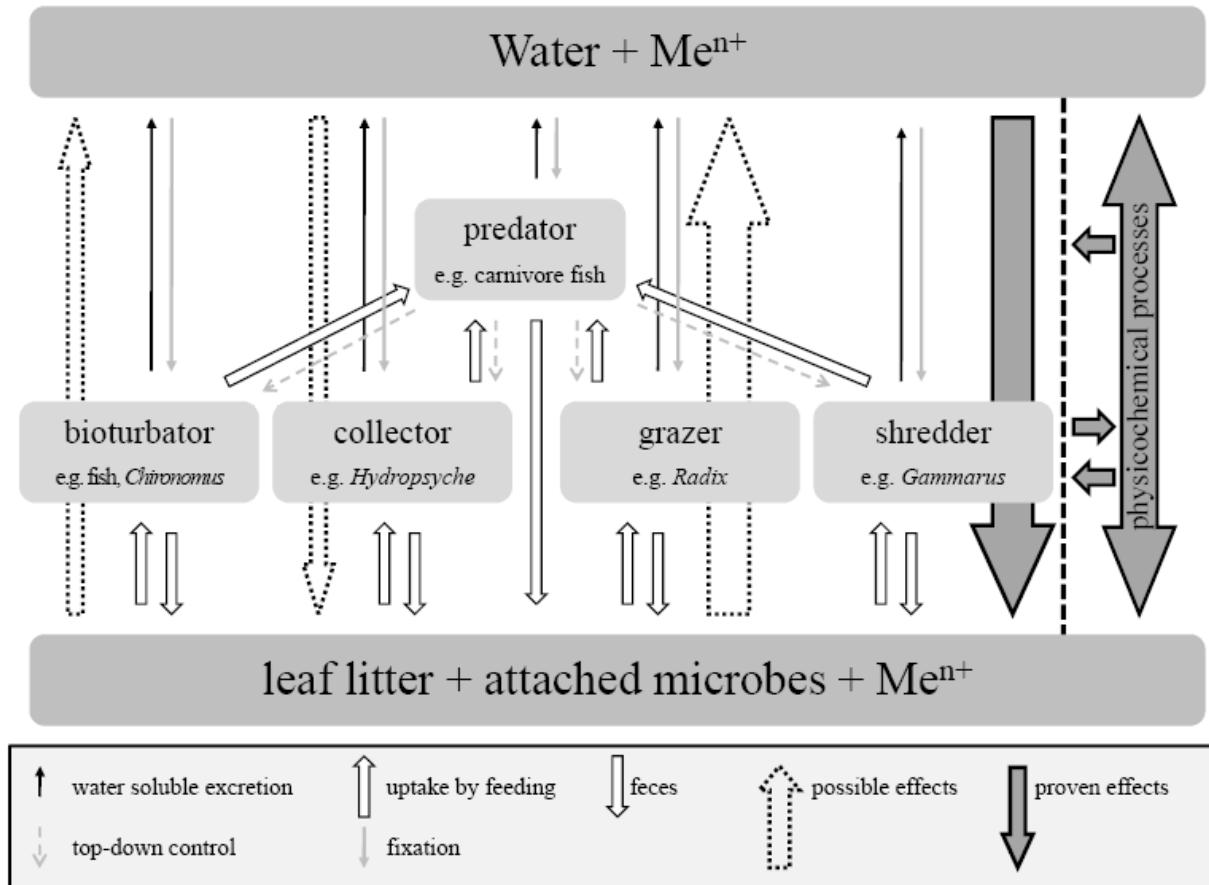
Correlation between dissolved molybdenum and dissolved organic carbon (DOC). R2 0.988,  
p < 0.01.

Schaller et al. 2010, Environmental Pollution 158:2454-2458

## Conclusion

- Invertebrate shredder affect significantly the accumulation of metals and metalloids into organic sediments
- Concentrations of ore level can be reached
- These effects also take place at a low metal / metalloid concentrations in the water
- Increased DOC levels do not weaken this effect (exception: molybdenum)

# Outlook:



Schaller et al. 2011, *Sci. Total Environ.*, 409: 4891-4898

# Thank you for your attention!

- Schaller, J., A. Weiske, M. Mkandawire, and E. G. Dudel. 2008. Enrichment of Uranium in Particulate Matter during Litter Decomposition Affected by *Gammarus pulex* L. **Environmental Science & Technology** 42:8721-8726.
- Schaller, J., A. Weiske, M. Mkandawire, and E. G. Dudel. 2010. Invertebrates control metals and arsenic sequestration as ecosystem engineers. **Chemosphere** 79:169-173.
- Schaller, J., M. Mkandawire, and E. G. Dudel. 2010. Heavy metals and arsenic fixation into freshwater organic matter under *Gammarus pulex* L. influence. **Environmental Pollution** 158:2454-2458.
- Schaller, J., C. Brackhage, M. Mkandawire and E.G. Dudel, 2011. Metal/metalloid accumulation/remobilization during aquatic litter decomposition in freshwater: A review. **Sci. Total Environ.**, 409: 4891-4898.