Influence of allochthonous plant litter on the fixation of Uranium in sediments

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Abstract. Plant litter of *Alnus glutinosa* (L.) GAERTNER (alder) and *Quercus spec*. (oak) was investigated downstream an abandoned uranium mine tailing. Uranium concentrations in unwashed samples varied between 20 – 2000 $\mu g*g^{-1}*DM^{-1}$ with differences between plant compartments: wood (app. 50 $\mu g*g^{-1}*DM^{-1}$), leaves (app. 200 – 400 $\mu g*g^{-1}*DM^{-1}$) and alder cones (app. 700 $\mu g*g^{-1}*DM^{-1}$). Compared to leaves from oak alder leaves contain significantly more uranium. Washing partially removes attached particles from the leaf surface. Uranium concentrations in unwashed alder leaves were usually smaller than in washed samples (<2000$\mu g*g^{-.1}*DM^{-1}$).

Introduction

After World War II various dumps and tailings were formed in Saxony and Thuringia as a result of uranium mining activities. Contaminated mining- and seepage-wateremerge up until today (Merkel et al., 1998) from many of those. In some cases this leads to the development of natural wetlands (in East Germany e.g. in Schneckenstein, Lengenfeld, Johanngeorgenstadt, Neuensalz).

It is known that uranium may precipitate in the course ofreduction processes e.g. mediated by sulfur reducing bacteria (Dybeck, 1962). But it has to be considered that the decay of organic matter releases carbon dioxide.Especially in the form of carbonate in a neutral to alkaline milieu this is able to form complexes with uranium and thus transfer it into solution. In the past numerous experimentson biosorption of uranium onto various materials like yeast etc. were carried out (Golab et al., 1991; Bustard et al., 1997). However, in natural wetlands permanent decay causes continuous change of surfaces, hencelab results are not applicable.

Therefore the question of uranium fixation on plant litter in natural systems still remains.

Material and methods

Sampling sites in Saxony (Neuensalz Tailing Mechelgrün/Vogtland) were chosen based on the German “Altlastenkataster (A.LAS.KA; Altlastenkataster = Register of old neglected deposits of toxic waste)” as well as on hydrological and geological maps. The selected sites have local activity concentrations higher than 1 $Bq*g^{-1} *DM^{-1}$ in sediments and uranium concentrations in seepage-water higher than 20 $\mu g\ L^{-1}$.

Two sampling points are located in a pond called “Forellenteich” (app. 1000m²), the more western point being a sediment trap (size 750x250x100mm, exposition time: June-August 2003). By the trap mainly leaves of alder s.a. were collected along with some few oak leaves.

Leaves and cones or acorns respectively of oak and alder were gathered at the sampling points. Unwashed leaf samples were carefully removed from the trap using plastic tweezers. Some samples had to be cleared of invertebrates, snails and algae.

Leaf-surfaces of washed samples were thoroughly rinsed 5 times with aqua dest. Acorns (were cut in halves, one half being the unwashed part. The other half was cleaned carefully with a toothbrush.

All samples were air-dried to constant weight (dry matter). Litter samples were mineralised using HNO3/H2O2, sediment samples using HNO3/HCl in a pressure- and temperature-controlled microwave system (Mars 5, CEM, U.S.A.).

PH-values were measured directly in the field (TM 39, Meinsberg). All water

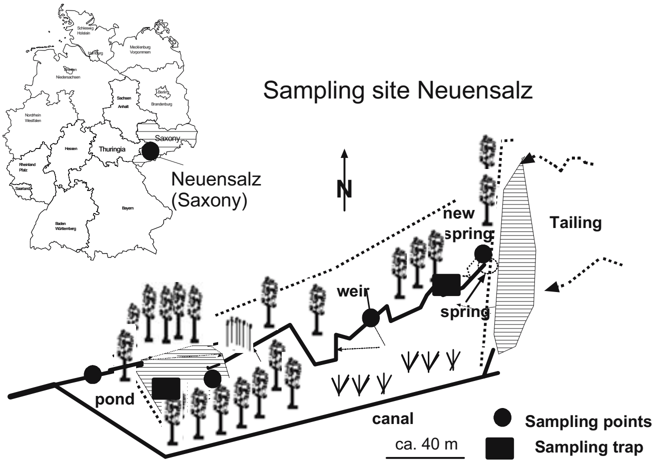

Fig. 1. Sampling site Neuensalz (schematic) with sampling points (weir: gauge station)

samples were filtered within 24 hours through 0.45 µm membrane filters (cellulose nitrate, Sartorius, Göttingen) and acidified with HNO3. Uranium, lead and arsenic were analysed by ICP-MS (PQ2+, TJA, U.K). Anions were measured ursing ion-chromatography (DX-500, AS 14).

Results

Based on pH-values water within the sampling site can be classified as neutral to slightly alkaline (pH 7.5-8.5) with a conductivity of about 1000 µS*cm^{-2}. Nitrate concentrations in the pond range between 15 – 30 mgL^{-1}, uranium concentrations below the tailing between 150-250 µg L^{-1}.

A temperature gradient between (sampling points) “new spring” (11.5 °C) and “weir” (6,9 °C) can be seen in December 2003. This is caused by mine waters leaving the ground at a relatively constant temperature of app. 12 °C cooling down as it flows.

Uranium in litter from different plant species and plant compartments

Uranium concentrations in the litter differ nearly one order of magnitude between different plant compartiments selected form the sediment (see Fig 2) where at the same time variation within each compartment is high. The concentration between leaf from oak and alder is not very, but the median of all alder leaf samples is a little higher than the median of oak leaves.

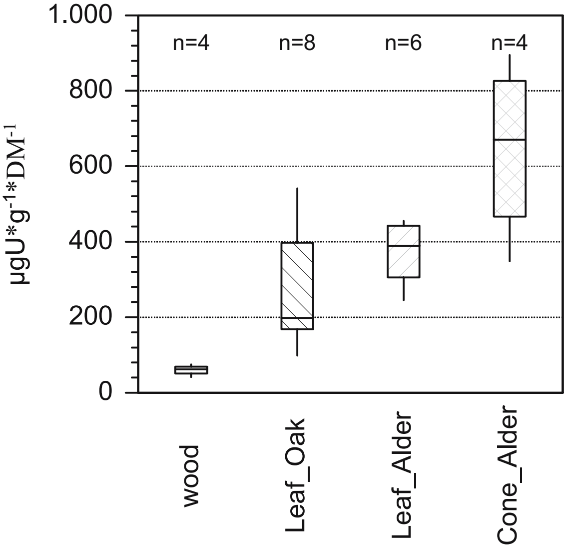

Fig. 2. Uranium content in unwashed plant samples the Forellenteich (July 2003).

A comparison between cones (alder) and acorn shells is difficult, because they both fall at different times. Unwashed acorn shells in April (after an exposition time of 5 ½ months, similar to the alder cones) contain less uranium (Acorns: median 100 µg*g^{-1} *DW^{-1}).

Distribution of uranium in the sampling aera

Geochemistry uses catena for proving emissions of uranium from dumps or along seepage-water paths as well as the elimination potential for e.g. nitrate. Uranium concentration in leaves from alder and oak of different sampling points are shown in Fig. 3. The distance between the point in the stream and the pond is app. 160 m, (a) between new spring and weir app. 150 m (b).

Fig. 3 suggests a otherwise: there seems to be a coherence/connection between between the distance from the source and the uranium concentration in the plant litter. This correlation seems stronger for oak leaves (Fig.3b) from spring and weir than for alder leaves from stream and pond.

Distribution of uranium in and on plant litter

Uranium and arsenic both can be precipitated by HFO (HydroFerricOxide). Hydrochemically arsenic and uranium often react antagonistically. Due to high iron content with great variations in leaves it is difficult to find a reference for this micro nutrient. In opposition to iron lead is only scarcely transported into wood and leaves by the investigated plants. Lead is known to have a high affinity to organic

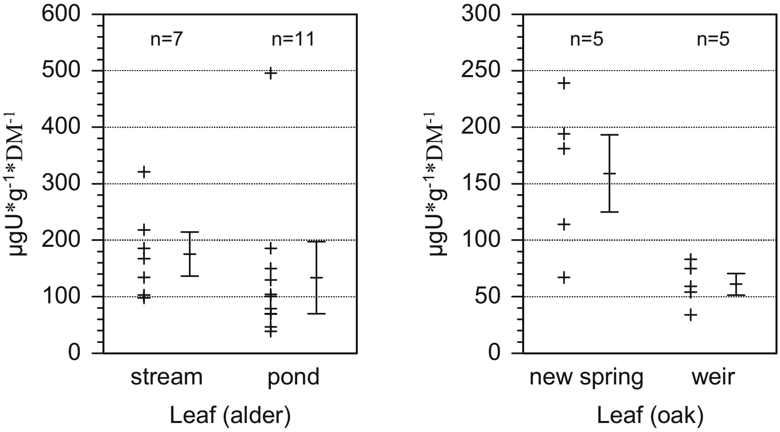

Fig. 3. a) Uranium concentrations in unwashed alder leaves from traps in the stream and in the pond “Forellenteich”, exposition time tree months: June – August 2003) and b) in unwashed oak leaves from new spring and weir (December 2003).

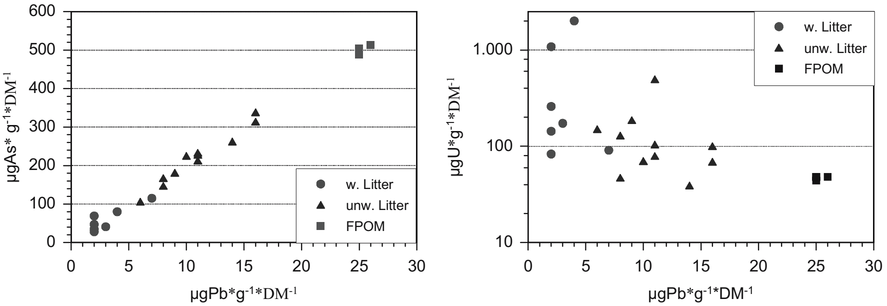

Fig. 4. Contents of uranium and arsenic in unwashed and washed alder leaves (dry matter) and in FPOM (fine particular organic material) (trap in “Forellenteich”, summer 2003).

substance, hence it is enriched in organic layers. So a removal of lead by washing processes would hint the existence of attached particles and. biofilms. Fig. 4 shows the concentrations of As and Pb as well as Pb and U for washed and unwashed samples as well as in the FPOM (fine particular organic matter). Arsenic and lead display a clear correlation.

Uranium shows a different behaviour. Highest uranium concentrations were found in washed leaves (2000 µgU*g^{-1}) and there is no positive correlation between lead and uranium. Uranium contents in FPOM are even smaller than in the leaves.

A comparison of washed and unwashed acorns is shown in Fig. 5. In difference to leaves acorns have a “closed “ surface, their structure can rather be compared with wood (see Fig. 2).

Acorn shells displayed in Fig. 5 contain significantly more uranium than wood. The uranium concentration in washed (cleaned) samples is distinctly lower than in unwashed samples.

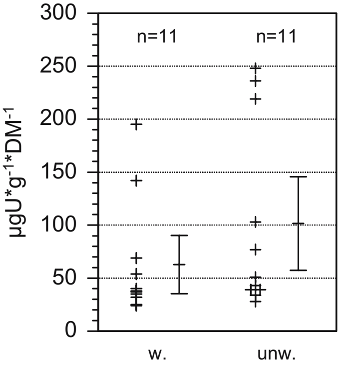

Fig. 5. Uranium concentrations in washed and unwashed acorn shells (April 2004).

Discussion

Aboveground parts of trees scarcely take up uranium (Stoklasa 1932, Thomas 2000, Brackhage and Dudel 2002). For alder this was confirmed by Brackhage et al. (2004) in the same site. Compared to plant litter on dumps (Schlema; Dienemann et al. 2002) the here found plant litter samples had a 10power higher uranium content, which leads to the conclusion that uranium contamination is based on contact with water or sediment.

Selected processes which may lead to an enrichment of uranium in plant litter are discussed in the following:

(1) If contact with sediment and thus the sorption of ore particles were the main process washed samples should generally contain less uranium than unwashed samples. This is definitely not true for the trap-samples from the pond. In opposition to uranium lead and arsenic show a distribution as expected. However, this might be caused by an loosely attached biofilm which was removed by the washing process.

(2) Arsenic and uranium both could be bound onto iron hydroxides by co-precipitation. Here arsenic shows a higher affinity to HFO. However, since arsenic concentrations in alder leaves could obviously be reduced by washing processes (Fig. 4) while uranium concentrations were not influenced, this fixation can be excluded.

(3) On the surface of a biofilm there might be an oxidative milieu which could arsenic cause to be fixed. Within the biofilm conditions are reducing (Smith 2001). Thus U(VI) might be reduced to U(IV), which might precipitate (Brooks et al. 2003, Bender et al. 2000). But even this does not provide a satisfying explanation for the differences between washed and unwashed samples.

(4) Possibly all results could be caused by sorption (see Kalin et al., 2005). However, during decay surfaces constantly change so the sorption conditions undergo a constant change and it seems unlikely for uranium to stay attached all the time under changing conditions. Maximum uranium concentrations of almost 2 mgU*g^{-1} and extremely high standard deviation in the washed as well as in the unwashed samples from the trap in the pond supports the assumption of uranium precipitation.

(5) The reducing effects of tannic acids have been used for centuries in leather treatment. According to the Japanese patent JP2001235593 uranium compounds may be reduced by tannic acid. According to another Japanese patent (JP2038316) uranium can be won using acorns (in neutral to alkaline milieu).

    Unwashed acorn contain more uranium than washed acorns (in opposition to alder leaves) Since oak leaves contain more tannic acid than alder leaves, the influence of tannic acid cannot be the main process responsible for uranium fixation in neutral to basic milieu. Uranium concentrations in oak leaves were significantly smaller than in alder leaves just as acorn shells contained less uranium than alder leaf litter.

(6) An explanation for higher uranium contents in alder leaves compared to oak leaves could be the different surface. Another distinction between the leaves is the decay rate. Several scientists show alder leaves to decompose relatively fast (Gessner 1991, Sridhar et al. 2001). One possible explanation could be the C/N-ratio as discussed in Schönbrunn (1992). Among others, temperature has a major impact on the decay rate. Measurements showed temperature at the spring to be always distinctly higher than at the weir. This may accelerate microbial turnover processes. Hence the smaller uranium concentrations in oak leaves found at the weir could be caused by differing microbial community. Altogether this process offers the opportunity to discuss the order of uranium concentrations between unwashed samples like wood, oak leaves and alder leaves.

(7) This order could also be explained by direct microbial reduction of uranium in plant litter. For this process, different surfaces of leaves and wood are important. But then, the inhibition of microbial decay of oak litter and pine litter by organic substances is known for years.

Different authors prove a massive uranium enrichment by *Pseudomonades* - (Tawfik et al. 2005; Fritsche 1985). Their appearance in plant litter as well as in sediment has been described by Fritsche (1985). Other bacteria like *Geobacter metallireducens, Desulfovibrio desulfuricans, Shewanella putrefaciens* and *Clostridium sp.* are known for the ability to reduce and precipitate uranium(VI)compounds (Lovley et al., 1991, 1992, 1993a, 1993b; Francis et al. 1991, 1994; Payne et al., 2004). Suzuki and Banfield (1999) show many fungi to contain even more uranium than bacteria. This might also be applicable for aquatic hyphomycetes. Gessner and Chauvet (1993) and Schönborn (1992) proved aquatic hyphomycetes to play a key role at decomposition processes.

(8) Alder cones consist of a relatively nutrient rich seed and a relatively stable cone. It is possible that the seed itself is faster decayed in permanent ponds or streams. There is an obvious pH-gradient due to decay. (Furthermore, decay sets free fulvic and humic acids, which precipitate with uranium to fulvates and humates. Borstel (1984) assumes this may be a way of enriching uranium in coals.

Conclusion

It is essential for radiological measurements of subhydric humus layers to investigate them separated from the sediment below, where extremely high activities (> 10 Bqg^{-1}) may occur.

Besides restrictions for use and access of concerned water-bodies it is necessary to create rules for sediment clearing regarding the radiological aspects. An application of these results could lead to more effective passive water treatment facilities.

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