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Fluxes of inorganic and organic arsenic species in a Norway spruce forest floor

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The forest floor layers are generally a source for inorganic arsenic species but a sink for most organic arsenic species under the present deposition rate.

Abstract

To identify the role of the forest floor in arsenic (As) biogeochemistry, concentrations and fluxes of inorganic and organic As in throughfall, litterfall and forest floor percolates at different layers were investigated. Nearly 40% of total As_{total} input (5.3 g As ha^{-1} yr^{-1}) was retained in Oi layer, whereas As_{total} fluxes from Oe and Oa layers exceeded the input by far (10.8 and 20 g As ha^{-1} yr^{-1}, respectively). Except dimethylarsinic acid (DMA), fluxes of organic As decreased with depth of forest floor so that <10% of total deposition (all <0.3 g As ha^{-1} yr^{-1}) reached the mineral soil. All forest floor layers are sinks for most organic As. Conversely, Oe and Oa layers are sources of As_{total}, arsenite, arsenate and DMA. Significant correlations ($r \geq 0.43$) between fluxes of As_{total}, arsenite, arsenate or DMA and water indicate hydrological conditions and adsorption–desorption as factors influencing their release from the forest floor. The higher net release of arsenite from Oe and Oa and of DMA from Oa layer in the growing than dormant season also suggests microbial influences on the release of arsenite and DMA.

Keywords: Arsenic speciation; Throughfall; Litterfall; Forest floor percolate

1. Introduction

Arsenic (As) creates adverse effects on the environment and human health due to its toxicity and bioaccumulation. The major cause of human As uptake is through contamination of drinking water from either natural geological sources or from anthropogenic activities like mining and agricultural sources (Adriano, 2002). Since the toxicity of As depends on its chemical form, speciation of As is necessary in order to access the environmental risk more precisely.

The forest floor may act as a natural biogeochemical barrier that suppresses the percolation of As and thus strongly accumulates deposited As (Matschullat, 2000). The forest floor is also the most biologically active part of the soil profile and has a distinguishable vertical stratigraphy. The uppermost layer (Oi) consists of the largely undecomposed litter. The fermentation of older litter occurs in the middle layer (Oe) of the forest floor and takes about 2–5 years, depending upon temperature and moisture conditions. The product of litter decomposition (humification) is a microbiologically stable organic matter (Oa) at the bottom of the forest floor. An investigation of 192 Czech forest sites showed that the As concentrations in the forest floor ranged from 5.5 to 167 μg g^{-1} with a median of 19.2 μg g^{-1} (Suchara and Sucharová, 2002). Wenzel et al. (2002) investigated soil solutions collected with suction cups from the forest floor at different polluted sites in Austria. The As concentrations in soil solution from the unpolluted forest floors ranged from 1.5 to 6.9 μg L^{-1} with a median of 4.3 μg L^{-1}. Much higher concentrations of As in soil solutions were observed from the highly polluted forest floors (12–110 μg L^{-1}). The As concentrations in the forest floor reflect well atmospherically deposited As. The closer the sites to

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the pollution sources are, the higher As concentrations in the forest floor (Gustafsson and Jacks, 1995; Suchara and Sucharová, 2002). In unpolluted soils, the As concentrations of the forest floor were always much lower than in the mineral soil. In contrast, the As concentrations in the forest floor may be higher than in the mineral soil in polluted soils (Gustafsson and Jacks, 1995). However, As retention of the forest floor is assumed to be not effective in a long-term perspective. Huang and Matzner (2007) showed the mobilization of As from the forest floor and its migration downward to the mineral soil. The forest floor at their site has become a source of As under the present As deposition rates. The depositional fluxes of As in Scottish rural areas were highest in the period 1940–1950 (40 g ha^{-1} yr^{-1}) and declined to 5.0 g ha^{-1} yr^{-1} in the 1990s (MacKenzie et al., 1998). The As deposition in rural areas of Germany decreased from 11 g As ha^{-1} yr^{-1} in 1984 to 3.0 g As ha^{-1} yr^{-1} in 1993 (Schulte and Gehrmann, 1996).

Forested catchments serve as sources of drinking water in many regions worldwide. Past studies showed that the forest floor is an important link in the cycling of As in forest ecosystems (Matschullat, 2000; Wenzel et al., 2002). There may be transfer of As from the forest floor into surface waters by superficial flow during heavy rain events, as indicated by strong and significant correlation between As concentrations in runoff and runoff fluxes (Huang and Matzner, 2007). However, the limited knowledge about As mobilization makes the assessment of As pollution in waters from forested catchments difficult. Different properties of the individual forest floor layers (e.g. C content, pH, cation exchange capacity, chemical compositions and aggregates) may lead to different behaviour of As. Thus, the aim of this study was to determine fluxes and establish budgets of inorganic and organic As species in individual forest floor layers of an upland soil in a forested catchment, in order to gain better understandings of the role of the forest floor in the As biogeochemistry.

2. Experimental

2.1. Site description

The investigation was carried out in the "Lehstenbach" catchment (4.2 km^2 size) in the German Fichtelgebirge Mountains, located at an elevation of 700–880 m a.s.l. at 50°08' N, 11°52' E. Mean annual air temperature is 5 °C, and mean annual precipitation is approximately 1150 mm. The catchment is dominated by Norway spruce (*Picea abies* [L.] Karst.) stands of different age. A 30% of the area is covered with wetland soils of bog and fen type. Upland soils are mainly Dystric Cambisols and Haplic Podzols (FAO classification) of sandy to loamy texture, developed from deeply weathered granitic bedrock. The forest floor is a well-stratified mor type of approximately 9 cm depth (Gerstberger et al., 2004). The Fichtelgebirge is a region of relatively high air pollutant deposition originating from large industrial sources to the north and east (Czech Republic) (Suchara and Sucharová, 2002).

2.2. Reagents and standards

Arsenate (As(V)), arsenite (As(III)) and dimethylarsinic acid (DMA) were purchased from Merck. Arsenobetaine (AsB) was obtained from Fluka, and monomethylarsonic acid (MMA), arsenocholine (AsC), trimethylarsine oxide (TAMO) and tetramethylarsonium iodide (TETRA) from Argus Chemicals, Italy. De-ionized water used throughout the work was purified in a Milli-Q system (Millipore, Milford, MA). Individual stock solutions (50 mg As L^{-1}) of As(III), As(V), MMA, DMA, TMAO, TETRA, AsB and AsC were prepared in Milli-Q water and stored at 4 °C in the dark. A multi-compound working solution with a total concentration of 40 μg As L^{-1} was prepared before each use by dilution of the stock solutions with Milli-Q water.

2.3. Sample collection and preparation

Throughfall and forest floor percolates were sampled weekly from June 2004 to June 2005. Throughfall was sampled with PE collectors (177 cm^2) placed 1 m above the ground. A fine sieve made of PE was used between the collector and reservoir against needles. Throughfall were then immediately *in situ* filtered to 0.45 μm with membrane filter (OE 67, Schleicher & Schuell) operating at a suction of about 10 kPa. Six samplers were installed in a line and pooled to yield three samples at each sampling date.

Forest floor (Oi, Oe and Oa) percolates were collected by each four tension plate lysimeters per depth with a surface area of 176 cm^2 operating at a suction of about 10 kPa applied for 1 min every 3 min. The lysimeters were made from plastic bowls with a polyethylene 50-μm pore-size membrane on top and installed underneath Oi, Oe and Oa layers. The periodic suction ensured that freely draining water was collected with minimal risk of water saturation. The lysimeter plates had been installed and sampled in the field more than 3 years (since August 2001) before the beginning of measurements, and thus potentially As adsorbing surfaces were assumed to be saturated.

To prevent the transformation of As species, the PE sampling bottles for throughfall and forest floor percolates were placed in the mineral soil and covered with 20 cm thick Styrofoam chips to protect from sunlight and keep the solutions at low temperatures (4–8 °C). The As speciation was tested with <7% variation during 1 week storage under such condition. Furthermore, As speciation of all aqueous samples was conducted directly by after sampling and finished within 12 h. Addition of acids or ethylenediaminetetraacetic acid for stabilization is not recommended here due to potential alert of species distribution (e.g. As oxidation; Palacios et al., 1997; Hall et al., 1999), interference of the chromatography and change of chemical compositions of the solutions (e.g. dissolved organic C (DOC)).

Litterfall was collected by four polyethylene funnels (35 cm diameter) installed 1 m above ground. Inside each funnel a polytetrafluorothylene (PTFE) net was installed, to permit water flow through the funnel and to retain the litterfall. Litterfall was sampled every month from June 2004 to June 2005, freeze-dried, grounded, homogenized and stored at −20 °C. For As speciation, litter (0.3 g) was four times extracted with 4 ml methanol–water (20%, v/v) in a 10 ml polyethylene tube. After ultrasonic treatment for 10 min, the samples were centrifuged (8800 *g*) and the supernatant was then analysed with HPLC–ICP-MS.

2.4. Speciation of arsenic species

A high performance liquid chromatograph (HPLC) instrument (BIOTEK Instruments, USA), consisting of a gradient pump (System 525), capillary PEEK tubing (0.25 mm i.d.) and a 200-μl injection loop (Stainless Steel), and an HPLC autosampler 465 (Kontron Instruments, Germany) was connected to an anion-exchange column (IonPak AG7 and AS7, both Dionex) and coupled to a ICP-MS (Agilent 7500c, Japan), equipped with a concentric nebulizer (Glass Expansion, Australia) and a Scott-type glass spray chamber.

The separation was performed at a flow rate of 1 ml min^{-1}, using a nitric acid gradient between pH 3.4 and 1.8. Dipotassium salt of benzene-1,2-disulfonic acid (0.05 mM) was added to the eluent as an ion-pairing reagent. At the outlet of the separation column, an internal standard (10 μg Ge L^{-1} in 0.01 M nitric acid) was added by means of a Y-connector.

Identification of As species was confirmed by spiking real litterfall extracts and throughfall with a mixture of standards (Fig. 1). Additionally, peak identification was conducted with a second chromatographic method in the spiked samples (Francesconi et al., 2002) (data not shown). Shortly, analysis was performed on a PRP-X100 column with a mobile phase of 20 mM $NH_4H_2PO_4$ pH 5.6 (for As(III), DMA, MMA and As(V)) or on a Zorbax 300-SCX column with a mobile phase of 20 mM pyridine pH 2.6 adjusted with HCOOH (for AsB, TMAO, AsC and TETRA). We have tried to identify As species in