

Fluxes and budgets of Cd, Zn, Cu, Cr and Ni in a remote forested catchment in Germany

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Abstract The input of heavy metals by atmospheric deposition to forested watersheds substantially decreased during the last decades in many areas. The goal of our study was to identify the present sinks and sources of metals and factors influencing metal mobility at the catchment and soil profile scale. We determined concentrations and fluxes of Cd, Zn, Cu, Cr and Ni in precipitation, litterfall, soil solutions (Oi, Oe, Oa horizon percolates, 20 and 90 cm soil depth) and runoff in a forest ecosystem in NE-Bavaria, Germany for 1 year. The metal concentrations in solutions were mostly $<10 \mu\text{g l}^{-1}$ beside Zn ($<1200 \mu\text{g l}^{-1}$). The present total deposition was estimated at 1.0, 560, 30, 1.2 and $10.4 \text{ g ha}^{-1} \text{ year}^{-1}$ for Cd, Zn, Cu, Cr and Ni, respectively. The mass balance (total deposition minus runoff) at the catchment scale indicated actual retention of Zn, Cu and Ni, but an almost balanced budget for Cr and Cd.

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Considering the soil profile scale, the Oi horizon still acted as a sink, whereas the Oe and Oa horizons were presently sources for all metals. The solid–solution partitioning coefficients indicated higher mobility of Cd and Zn than of Cu, Cr and Ni in forest soils. In the mineral soil horizons, K_d values derived from field measurements were substantially larger than those predicted with empirical regression equations from Sauv e et al. (Environ Sci Technol 34:1125–1131, 2000; Environ Sci Technol 37:5191–5196, 2003). The mineral soil acted as a sink for all metals beside Cd. Dissolved organic C and pH influenced the metal mobility, as indicated by significant correlations to metal concentrations in Oa percolates and runoff. The solid–solution partitioning coefficients indicated higher mobility of Cd and Zn than of Cu, Cr and Ni in forest soils. Overall, the decreased deposition rates have obviously induced a source function of the Oe and Oa horizon for metals. Consequently, mobilization of metals from forest floor during heavy rain events and near surface flow conditions may lead to elevated concentrations in runoff.

Keywords Heavy metals · Biogeochemistry · Forest soils · Catchment · Sink and source function

Introduction

Environmental pollution by heavy metals results from many sources including industrial activities, power

generation, transport and agriculture (Tipping et al. 2006). Even remote and rural sites have been contaminated by heavy metals via atmospheric deposition during the last several decades, and in many cases resulted in the build-up of soil metal pools. During the past decades, the emission of heavy metals has diminished in central Europe and consequently, the atmospheric deposition declined (Schulte and Gehrman 1996; Schulte et al. 1996), raising the question of metal behaviour under conditions of decreasing inputs. For example, in Germany the average Cr deposition fell from 8.5 g ha⁻¹ year⁻¹ in 1984 to 3.5 g ha⁻¹ year⁻¹ in 1993 (Schulte and Gehrman 1996). Bulk precipitation was 142 g Pb ha⁻¹ year⁻¹ in 1984 but decreased to 31 g ha⁻¹ year⁻¹ in 1993 (Schulte et al. 1996). In 2002, Pb deposition in a German forest was measured at 7.5 g ha⁻¹ year⁻¹ (Huang and Matzner 2004). Desorption of formally accumulated heavy metals may cause continuing transport of metals within the soil profile and may buffer the response of metal concentrations in runoff to decreasing deposition rates. Input–output budgets for soils and watersheds can be used to describe the mobility, retention and fluxes of heavy metals in the environment. In forested stands and watersheds, positive budgets (net retention) were usually found for Pb, Cu and Cr, including forest floors as well as and mineral soils (Bergkvist et al. 1989). In contrast, negative budgets (net release) have been reported in case of Zn, Cd and Ni. Generally, Pb, Cu and Cr are known to form stable complexes with dissolved organic C (DOC) and are transported through the soil mostly in complexed form (Bergkvist et al. 1989). On the other hand, Zn, Cd and Ni are known to be largely pH sensitive and their mobility is associated with soil acidification. Recent studies have shown a net release of Pb from the forest floor into the mineral soil after reductions of Pb deposition in Germany (Lang and Kaupenjohann 2004; Huang et al. 2008) and North America (Miller and Friedland 1994; Wang et al. 1995; Kaste et al. 2003). Forested catchments represent an important source of drinking water in many regions world wide. Therefore, understanding the mobility of heavy metals in forest soils and forested catchments is essential. Nevertheless, there is lack of data on the mobility of metals other than Pb at the soil profile and catchment scale after reductions in metal deposition.

Solid-solution partition coefficients (K_d) can be used to access metal mobility in soils. The K_d values of metals in natural soils may vary by up to six orders of magnitude 1 kg⁻¹, depending strongly on the nature of metals and on soil properties (Sauvé et al. 1998, 2003). The most important factors affecting metal concentrations in soil solutions are soil total metal concentrations, pH and organic matter content, as suggested by regression analysis in Sauvé et al. (2000). In general, metal affinity for the soil solid phase follows the order Pb > Cu > Zn = Cd > Ni (Adriano 2001). Identification of the processes affecting metal mobility in soil horizons of high C content, like in forest floor horizons, is more difficult than in mineral soils. For example, the effect of a decreasing pH may not only be manifested in the proton competition for metal binding places, but also in the reduction of DOC complexation with metals (Sauvé et al. 2003). Thus, the empirical prediction of metal solid–solution partition in soil horizons of high C content is more difficult than in mineral soils. Furthermore, most K_d values in the literature are based on batch experiments with disturbed soil samples and hence, the validity of such predictions for in disturbed soil conditions is rather questionable.

The aim of this study was (1) to quantify the present sinks and sources of heavy metals in a forest soil and a forested catchment after reduction of atmospheric deposition, (2) to investigate the critical factors for heavy metal mobility at the catchment and soil profile scale, and (3) to test the suitability of empirical predictions of metal solid–solution partitioning coefficients under field conditions.

Materials and methods

Site description

The investigation was carried out in the “Lehstenbach” catchment (4.2 km² 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 1,150 mm. The catchment is dominated by Norway spruce (*Picea abies* [L.] Karst.) stands of different age, and 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). In the past, the Fichtelgebirge has been a region of relative high air pollutant deposition originating from industrial sources in the north and east (Suchara and Sucharová 2002).

Bulk precipitation, throughfall and soil solution sampling

Bulk precipitation, throughfall, and soil solutions were sampled weekly from September 2004 to September 2005. Bulk precipitation and throughfall were sampled with PE collectors (177 cm²) placed 1 m above the ground. A fine sieve made of PE was used between the collector and reservoir against needles. Bulk precipitation and throughfall samples were in situ filtered with 0.45 µm membrane filters (OE 67, Schleicher and Schuell) operating at a suction of about 10 kPa. Bulk precipitation was collected by three samplers at an open site. For throughfall sampling, six samplers were installed in a line and pooled to yield three samples for analysis at each sampling date.

Forest floor percolates were collected by four tension plate lysimeters with a surface area of 176 cm² to which suction of about 10 kPa was 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 the Oi, Oe and Oa horizon. The periodic suction ensured that freely draining water was collected with minimal loss of evaporation. The fairly large pore size of the membranes prevented extraction of capillary water from the forest floor. Soil solutions from 20 cm and 90 cm depth were collected by tension lysimeters operating at a suction of about 10 kPa with four spatial replicates. The lysimeters were made from plastic tubes with a ceramic cup of 1-µm pore-size on top and installed at 20 and 90 cm depth. The lysimeter plates and suction lysimeters had been installed and sampled in the field for more than 3 and 10 years, respectively before the beginning of measurements, and thus potentially Cd, Zn, Cu, Cr and Ni adsorbing surfaces were assumed to be saturated.

Soil sampling

Soil samples were taken in July, 2004. Upland soil samples (ca. 1 kg) were taken according to horizons at the sites “Coulissenhieb” and “Weidenbrunnen”. Each sample was a 1 kg mixture of three samples taken at 2–5 m distance from one another with a corer (Ø 7.5 cm). Forest floor samples and mineral soils were homogenized and sieved to 5 and 2 mm, respectively. Soil samples from two wetland sites (fen and bog) were taken as mixed samples from each three profiles at the site “Schlößnerbrunnen”. Samples were taken at 10 cm intervals to 70 and 60 cm depth and sieved to 5 mm. All soil samples were freeze-dried, grounded and stored at –40°C before further analysis. Soil parameters such as pH, carbon contents and total Al, Fe and Mn contents are shown in Table 1.

Litterfall and runoff sampling

Four PE funnels (35 cm diameter) were installed 1 m above ground. Inside each funnel a polytetrafluorethylene net was installed, to permit water flow through the funnel and to retain the litterfall. Litter was sampled monthly from September 2004 to September 2005. Needle samples were freeze-dried, grounded in a zirconium oxide mill, homogenized and stored at –40°C before analysis. Runoff samples were taken weekly at the weir of the Lehstenbach creek from September 2004 to September 2005.

Calculation of fluxes

Fluxes with throughfall and bulk precipitation were calculated by multiplying the measured volume in the samplers with the concentrations on a weekly basis. Fluxes with soil solutions were calculated by multiplying the weekly concentrations of metals with the estimated weekly water fluxes. Water fluxes with Oa forest floor percolates (703 mm year⁻¹) were calculated from throughfall fluxes (976 mm year⁻¹) on the assumption that percolates amount to 72% of throughfall. This ratio is derived from the measured mean ratios from 1999 to 2001 (Kalbitz et al. 2004), and is also close to the ratio derived from the annual Cl⁻ budget (73%, Schwesig and Matzner 2001). Water fluxes with soil solutions at 20 and 90 cm

Table 1 Carbon contents, pH and total Al, Fe and Mn concentrations of the investigated soils

	Depth (cm)	pH _(H₂O)	C (%)	Al _{total} (mg g ⁻¹)	Fe _{total} (mg g ⁻¹)	Mn _{total} (μg g ⁻¹)
<i>Coulissenhieb</i>						
Oi	8.5–8.0	4.8	47.8	2.72	1.70	374
Oe	8.0–3.0	3.7	37.2	4.80	4.26	83.6
Oa	3.0–0.0	3.6	37.6	11.0	6.30	40.4
E	0.0–10	3.9	3.89	24.1	5.35	45.7
Bh	10–12	3.9	9.05	32.4	16.4	73.2
Bhs	12–30	4.2	5.36	49.4	31.6	246
Bw-C	30–55	4.4	0.84	48.0	22.1	339
<i>Weidenbrunnen</i>						
Oi	7.0–6.0	5.7	49.2	2.60	1.69	276
Oe	6.0–3.5	5.8	34.8	15.6	8.65	134
Oa	3.5–0.0	4.0	20.3	10.0	6.12	45.6
E	0.0–9.0	3.9	5.20	25.4	6.19	55.3
Bh	9.0–20	3.9	5.99	34.1	13.3	103
Bhs	20–30	4.1	4.43	48.0	42.0	238
Bw-C	30–45	4.4	2.93	55.5	23.2	326
<i>Fen</i>						
1	0.0–10	4.9	39.1	11.2	2.94	67.1
2	10–20	5.1	44.3	11.8	2.38	53.3
3	20–30	5.2	42.6	11.0	2.11	36.9
4	30–40	5.1	37.1	13.1	2.55	43.0
5	40–50	5.1	38.9	12.4	2.65	41.4
6	50–60	5.1	39.3	20.2	3.69	61.9
7	60–70	5.1	34.3	35.2	5.11	65.8
<i>Bog</i>						
1	0.0–10	4.4	39.5	17.5	21.4	77.5
2	10–20	4.5	38.9	25.5	6.42	58.3
3	20–30	4.7	31.0	25.3	5.24	46.0
4	30–40	4.7	34.8	40.6	9.37	79.8
5	40–50	4.8	12.4	25.1	6.37	83.7
6	50–60	5.0	1.30	23.5	7.34	102

depth (694 and 554 mm year⁻¹, respectively) were calculated by simulating soil water fluxes with HYDRUS-2D. This calculation is based on soil physical characteristics, daily throughfall amounts and evapotranspiration rates, estimated from meteorological data (Simúnek et al. 1996).

Annual fluxes of metals with litterfall were calculated by multiplying the concentrations with the amount of litterfall on a monthly base. Daily water flux with runoff of the catchment was calculated from the actual level measurements (10 min

resolution) at the weir and the measured concentrations at that day. The annual runoff fluxes were estimated by extrapolating the sum of 52 daily fluxes to 365 days. The annual water flux in runoff estimated in the same way amounted to 410 mm year⁻¹. Alewell et al. (2004), using a similar calculation of runoff fluxes based on biweekly data, estimated the associated error to be up to 25% for time periods less than 1 year. Since we used weekly data to calculate our runoff fluxes, the error of the extrapolation should be less than 25%.

Calculation of interception deposition

The total deposition is calculated as the sum of bulk precipitation and interception deposition, the latter comprising dry deposition of aerosols and gases as well as occult deposition of fog. The interception deposition of metals was calculated using Na as tracer: The annual ratio of interception deposition/bulk precipitation for Na was multiplied with the annual bulk precipitation of the metal in question. The interception deposition for Na was calculated as the difference between throughfall and bulk precipitation. Total inputs to the forest floor were calculated as the sum of throughfall and litterfall fluxes. These inputs include the atmospheric deposition as well as ecosystem internal cycling of metals from the roots to litter (Ukonmaanaho et al. 2001).

Calculation of soil pool

Soil pools of metals up to soil 60 cm depth were calculated by multiplying the measured concentrations in each horizon with horizon depth, soil density and percentage of fine soils material (<2 mm).

Analysis

Soil and litter samples (0.5 g) were digested with 3 ml distilled HNO₃ and 1 ml HCl by High Pressure Accelerated Solvent (HPA-S, Anton Paar, Austria). In the 3-step program, a first heating to 80°C, is followed by heating to 170°C and finally to 270°C, lasting for 90 min. The supernatant was then filtered with membrane filter, diluted to 25 ml with Milli-Q water and measured by ICP-MS (Agilent 7500 Series, Japan). Recovery of Cd, Zn, Cu, Cr and Ni from the certificated pine needle 1575 (NIST) and CRM 7003 and CRM 7004 silty clay were 90–120%. For analysis of Cd, Zn, Cu, Cr and Ni in aqueous samples, 15 ml samples 0.45 µm membrane filtered and directly determined by ICP-MS. Calibration was done by using Rh (10 µg l⁻¹) as internal standard. The pH of solute samples was measured using a combination glass electrode (WTW pH 90, Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). Dissolved organic C was determined after 0.45 µm filtration by infrared detection of CO₂ after high-temperature

combustion (Elementar HighTOC, Elementar Analysensystem GmbH, Hanau, Germany).

Calculation of K_d values

The K_d values for Cd, Zn, Cu, Cr and Ni in the soils were calculated as the ratio of solid phase concentrations determined in a specific horizon to the average concentrations of four spatial replicates in the solutions collected from the corresponding horizon. The variation of the K_d values results from the temporal variation in the soil solution concentrations. In addition, we used the empirical model of Sauvé et al. (2000, 2003) to calculate K_d values for Cd, Zn, Cu and Ni based on pH and contents of soil metal, organic matter and exchangeable cations.

Results

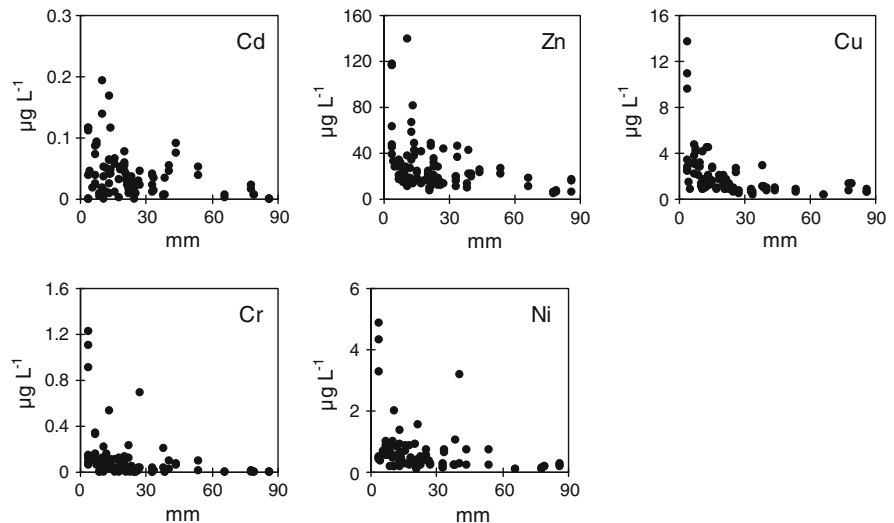
In general, the concentrations of metals in bulk precipitation and throughfall were in the order Zn ≫ Cu > Ni > Cr > Cd (Table 2). This order was also similar in litter, and forest floor percolates (Oi, Oe and Oa), however, different in mineral soil solutions (Zn ≫ Cu = Cr > Ni > Cd at 20 cm and Zn ≫ Ni > Cd > Cu > Cr at 90 cm depth) and in runoff (Zn ≫ Ni > Cu > Cr > Cd). The concentrations in bulk precipitation decreased with increasing amount of bulk precipitation (washout curves) (Fig. 1). The concentrations in throughfall were higher than in bulk precipitation for all metals investigated. The Zn concentrations were up to 409 µg l⁻¹ in throughfall. In comparison, the concentrations of Cd, Cr and Ni in throughfall were mostly <1 µg l⁻¹. For all metals investigated, the concentrations in Oi percolates were lower than in throughfall and the concentrations in percolates increased with depth of the forest floor.

The depth profiles of metal concentrations were metal specific: The Cu concentrations in mineral soil solutions decreased with depth (Table 2) while the concentrations of Zn and Cr in mineral soil solutions peaked at 20 cm depth and then decreased with soil depth. The average Cd concentrations decreased from Oa percolates to 20 cm depth and then increased at 90 cm depth. The depth gradient of Ni concentrations in soil solutions was similar to that of Cd, nevertheless, with highest concentrations in Oa percolates.

Table 2 Concentration of Cd, Zn, Cu, Cr and Ni ($\mu\text{g l}^{-1}$) in bulk precipitation, throughfall, litterfall, forest floor percolates, soil solutions (20 and 90 cm depth) and runoff from September 2004 to September 2005 at the catchment Lehstenbach

	Cd Median, Min–Max	Zn Median, Min–Max	Cu Median, Min–Max	Cr Median, Min–Max	Ni Median, Min–Max
Bulk precipitation	0.03, <DL–0.16	24.3, 5.67–117	1.29, 0.35–11.4	0.05, <DL–1.08	0.48, 0.11–4.16
Throughfall	0.09, < DL–1.03	56.1, 6.94–409	3.07, 1.12–14.4	0.24, 0.03–1.24	1.02, 0.27–11.7
Litterfall ^a	0.10, 0.06–0.15	24.0, 18.0–35.0	4.41, 3.10–5.83	0.62, 0.31–1.13	1.70, 1.36–4.62
Oi percolate	0.07, 0.01–0.31	51.2, 17.4–178	2.08, 0.74–6.35	0.16, 0.02–0.33	0.79, 0.26–1.44
Oe percolate	0.11, 0.06–0.30	44.6, 7.54–290	3.11, 1.64–4.53	0.50, 0.22–1.12	1.19, 0.71–3.04
Oa percolate	0.54, 0.21–1.99	59.8, 15.3–146	3.33, 1.28–7.88	0.96, 0.47–2.57	1.99, 0.93–4.85
Soil solution (20 cm)	0.30, 0.16–0.62	120, 23.8–1,200	2.41, 1.13–9.08	2.41, 1.13–9.07	1.22, 0.40–2.10
Soil solution (90 cm)	0.74, 0.43–1.06	105, 52.4–837	0.44, 0.28–1.17	0.25, 0.20–0.64	1.37, 0.97–3.62
Runoff	0.21, 0.08–0.34	26.3, 6.08–63.9	0.37, 0.14–1.41	0.24, 0.10–0.65	0.77, 0.34–1.16

^a Unit in $\mu\text{g g}^{-1}$

Fig. 1 Concentrations of Cd, Zn, Cu, Cr and Ni in bulk precipitation versus precipitation amounts

The concentrations in runoff were lower than in 90 cm soil solutions for all elements but exceeded those in bulk precipitation in case of Cd, Zn, Cr and Ni.

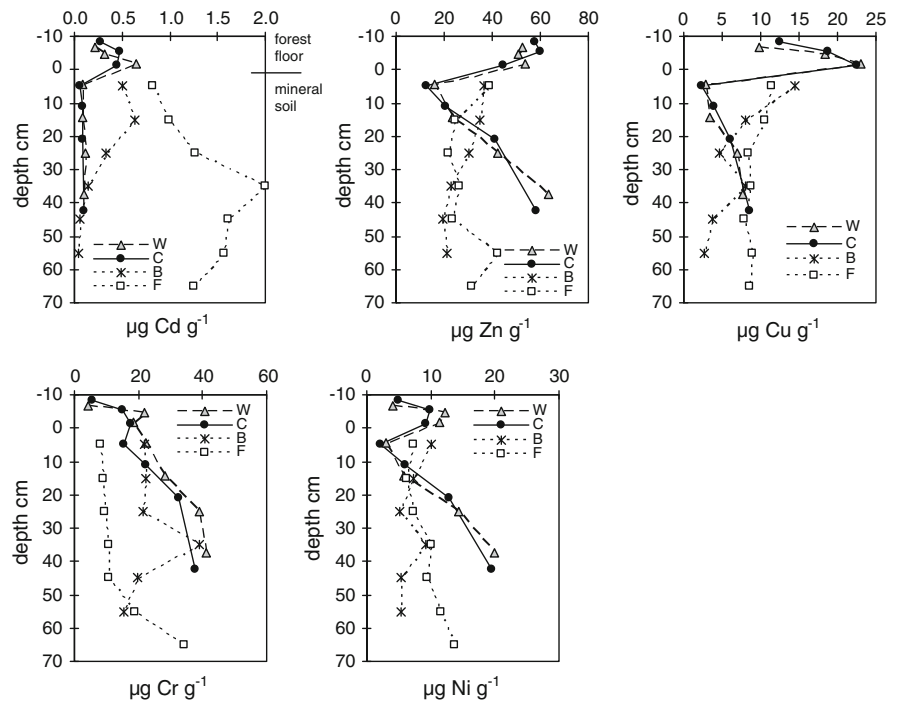
The solid phase concentrations of metals in upland soils were generally in the order $\text{Zn} > \text{Cu} > \text{Cr} > \text{Ni} \gg \text{Cd}$ (Fig. 2). Depth gradients were found metal specific: The concentrations of Cd and Cu peaked in the Oe and Oa horizons whereas those of Cr and Ni had their maximum in the deeper mineral soil horizons. The concentrations of Zn decreased from $60 \mu\text{g g}^{-1}$ in the forest floor to $10 \mu\text{g g}^{-1}$ at 0–10 cm depth and then increased with depth to $60 \mu\text{g g}^{-1}$ at 35–40 cm depth. The pattern of Ni vertical distribution in upland soils was similar to Zn, however, with

concentrations less than $20 \mu\text{g g}^{-1}$. The Cr concentrations increased from $5 \mu\text{g g}^{-1}$ in the Oi horizon to $40 \mu\text{g g}^{-1}$ at 40 cm depth.

In wetland soils, the metal concentrations of metals were in a similar range as in the upland soils in the order $\text{Zn} > \text{Cr} > \text{Cu} \geq \text{Ni} > \text{Cd}$ (Fig. 2). The metal concentrations in the bog soil were generally high at the surface horizon (0–20 cm) and decreased with depth. Additionally, the concentrations of Cu, Cr and Ni peaked at 30–40 cm depth. In comparison, most metals had their maximum concentrations at deeper horizons in the fen soil.

The total deposition of Zn to the catchment was $560 \text{ g ha}^{-1} \text{ year}^{-1}$ (Fig. 3). In comparison, the deposition of Cd, Cu, Cr and Ni was much less with 1.0,

Fig. 2 Concentrations of Cd, Zn, Cu, Cr and Ni in upland and wetland soil profiles of Lehstenbach catchment. C: Coullissenhieb; W: Weidenbrunnen; B: Bog; F: Fen



30, 1.2, and 10 g ha⁻¹ year⁻¹, respectively. Almost half of the total deposition of all metals was by interception deposition. The sum of throughfall and litterfall fluxes largely exceeded total deposition in the case of Cd and Cr, suggesting tree uptake of metals from the soils and translocation to needles. The metal input to the forest floor by throughfall and litterfall largely exceeded the fluxes with Oi percolates. The annual fluxes of Cd were highest in Oa percolates and 90 cm soil solutions (4.6 and 4.2 g ha⁻¹ year⁻¹), whereas the annual fluxes of Zn were highest in 20 cm soil depth (1,484 g ha⁻¹ year⁻¹). The annual fluxes of Cr and Ni peaked at 7.8 and 15.2 g ha⁻¹ year⁻¹ in Oa percolates and then decreased with depth. The mass balance (total deposition minus runoff) at the catchment scale indicated retention of Zn, Cu and Ni, but an almost balanced budget for Cr and Cd (Fig. 3).

The average soil pool of Zn and Cr in the catchment amounted to 144 and 117 kg ha⁻¹ (Table 3). The soil pools of Cu and Ni were less (23.8 and 43.3 kg ha⁻¹, respectively) and the soil pool of Cd was lowest (0.53 kg ha⁻¹). The largest pool of metals was found in upland mineral soils with the exception of Cd. The pools in the forest floor were usually insignificant. The ratios of soil pool in the upland soils to the actual deposition (the budget of total deposition) were 380,

500, 1,030, 160,000 and 5,800 for Zn, Cd, Cu, Cr and Ni, respectively.

Significant positive correlations between water fluxes and metal concentrations in runoff were found for Cd ($r = 0.72$, $p = 0$), Cu ($r = 0.49$, $p = 0$), Zn ($r = 0.61$, $p = 0$), Cr ($r = 0.44$, $p = 0.001$), Ni ($r = 0.65$, $p = 0$) (data not shown) indicating the export of metals under high flow conditions. Negative correlations were found between pH in runoff and concentrations of all metals (Table 4). There were strong and positive correlations between DOC and Cu, Cr and Ni in runoff, Oa percolates and 20 cm soil solutions, whereas the correlation between pH and metal concentrations was most pronounced in Oa percolates (Table 4).

Given the large variation in Cd, Zn, Cu, Cr and Ni concentrations measured over the course of 1 year, the K_d values had a huge range (Table 5). The K_d values of Cd, Zn and Cr were larger in the forest floor than in mineral soils (Table 5). In contrast, K_d values for Ni in mineral soils were larger than in the forest floor. In case of Cu, the K_d values were largest in Bw-C and lowest in Bhs horizons. The K_d values of Cr exceeded those of all other metals by far with values up to 283,000 l kg⁻¹, whereas K_d of Zn were generally less than all other metals. The K_d values predicted by the empirical models of Sauvé et al.

Fig. 3 Annual fluxes of Cd, Zn, Cu, Cr and Ni from September 2004 to September 2005. Total deposition was assumed to be the sum of bulk precipitation (BP) and interception deposition (ID, with *black bars*). Total inputs to the forest floor were calculated as the sum of throughfall (TF) and litterfall (LF, with *black bars*)

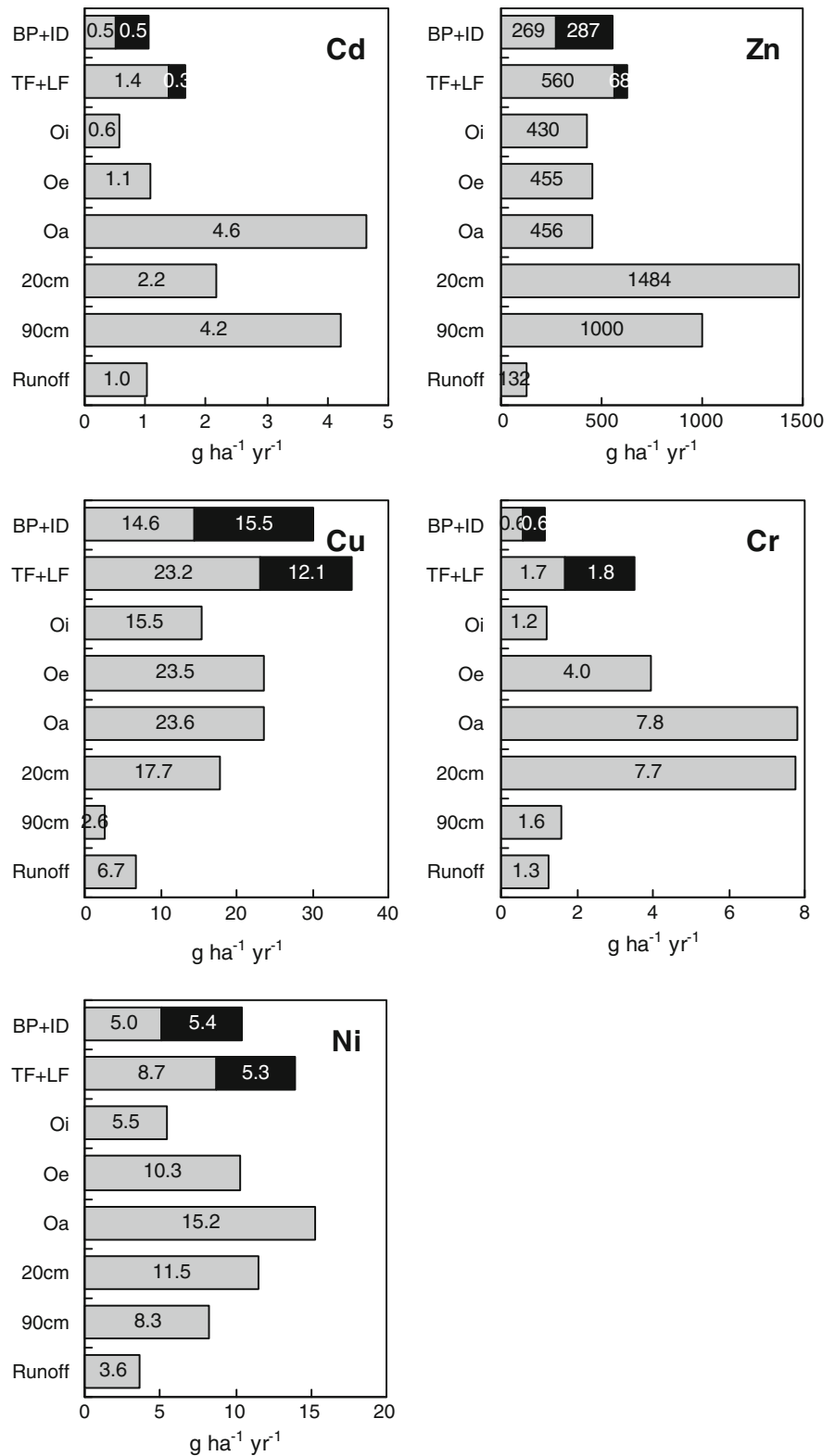


Table 3 Estimated pools of Cd, Zn, Cu, Cr and Ni (kg ha^{-1}) in wetland and upland soils down to 60 cm depth

Total soil pool was estimated as 70% upland soil pool + 30% wetland soil pool according to the area coverage

Species	Cd	Zn	Cu	Cr	Ni
Upland soils	0.53	193	31.1	159	58.2
Forest floor	0.07	8.35	3.16	2.48	1.47
Mineral soils	0.46	184	28.0	157	56.8
Wetland soils	0.53	30.9	6.63	20.4	8.21
Average soil pool at the catchment scale (70% uplands, 30% wetland soils)	0.53	144	23.8	117	43.3
Ratio of soil pool to the actual deposition	380	500	1,030	160,000	5,800

Table 4 Correlations between concentrations of Cd, Zn, Cu, Cr and Ni versus pH and concentrations of dissolved organic carbon (DOC) in different investigated water samples from September 2004 to September 2005

Compartment	Cd	Zn	Cu	Cr	Ni
pH–Bulk precipitation	–0.30**				
pH–Throughfall	–0.50***	–0.31**			
pH–Oi percolate					
pH–Oe percolate	–0.63***				
pH–Oa percolate	–0.77***		–0.43*	–0.64***	–0.78***
pH–20 cm soil solution					
pH–90 cm soil solution					
pH–runoff	–0.83***	–0.49***	–0.45**	–0.71***	–0.62***
DOC–Bulk precipitation		0.66***	0.60***	0.58***	0.57***
DOC–throughfall	0.33*	0.54***	0.51***	0.82***	0.37***
DOC–Oi percolate					0.28*
DOC–Oe percolate			0.82***		
DOC–Oa percolate	0.58**		0.84***	0.92***	0.82***
DOC–20 cm soil solution			0.69***	0.79***	0.44*
DOC–90 cm soil solution					
DOC–runoff			0.51***	0.89***	0.53***

Blanks indicate no significant correlation

*** $p < 0.005$; ** $p < 0.01$; * $p < 0.05$

(2000, 2003) were less than our measured values in most cases and especially in the mineral soil. Only in the forest floor the measured K_d values overlapped partly with those predicted from the empirical model.

Discussion

Sinks and sources and mobility of metals: upland soil profile scale

Considering the fluxes of metals through the upland soil profile, the Oi horizon of the forest floor

presently acted as a sink for all metals, whereas the Oe and Oa horizons were sources for Cd, Cr and Ni. In the past, the forest floor was often shown to be an effective sink for atmospherically deposited pollutants due to the large capacity for cation exchange and the formation of organo-metal complexes (Bergkvist et al. 1989, Räisänen et al. 1997).

The Oi horizon consists mainly of recently fallen litter and the heavy metals pools of the Oi horizon reflect the result of present deposition and of the internal metal cycle rather than reflecting metal deposition of past decades. Thus, the Oi horizon acted as a sink for all metals investigated even under

Table 5 Median and range of solid–solution partition coefficient (K_d) of Cd, Zn, Cu, Cr and Ni (1 kg^{-1}) in upland soils

Partition coefficient (K_d) in 1 kg^{-1}			
Horizon	Field derived		Modelled ^a
	Median	Range	Range
<i>Cd</i>			
Oi	3,830	866–26,800	501–6,350
Oe	4,340	1,590–7,960	506–6,360
Oa	823	223–2,120	505–6,360
Bhs	284	138–533	0.58–14.6
Bw-C	127	88.9–219	0.59–14.7
<i>Zn</i>			
Oi	1,130	325–3,330	<2203
Oe	1,350	207–7,960	<1794
Oa	757	306–2,920	<1755
Bhs	343	34.3–1,730	0.19–4.85
Bw-C	555	69.6–1,110	0.20–4.92
<i>Cu</i>			
Oi	6,040	1,980–17,000	<4070
Oe	6,050	4,150–11,500	<4490
Oa	6,740	2,850–17,500	<4730
Bhs	2,550	676–5,430	7.01–472
Bw-C	19,600	7,370–30,800	11.5–791
<i>Cr</i>			
Oi	35,300	17,100–283,000	–
Oe	30,300	13,500–69,000	–
Oa	18,100	6,780–37,100	–
Bhs	13,400	3,570–28,700	–
Bw-C	15,100	58,900–188,000	–
<i>Ni</i>			
Oi	6,320	3,470–19,200	60.0–3,480
Oe	8,220	3,220–13,800	1,400–4,820
Oa	4,600	1,890–9,840	1,230–4,650
Bhs	10,600	6,140–32,200	0.07–1.73
Bw-C	14,200	5,370–20,000	0.07–1.77

^a Values calculated according to the empirical model of Sauvé et al. (2000, 2003)

–, Empirical models not available

the low present deposition rates. In comparison to the Oi horizon, the Oe and especially the Oa horizon represents much older organic matter in the forest floor and therefore have accumulated metals which were deposited in past decades. Under the present deposition regime the Oe and Oa horizons have become sources for Cd, Ni and Cr but not for Zn and

Cu. Zn and Cu fluxes with forest floor percolates were consistently less than the total deposition confirming ongoing accumulation of these elements in the forest floor. Under conditions of decreasing deposition net release of Pb from the forest floor was already shown for (Wang et al. 1995; Huang et al. 2008), similar to Cd, Ni and Cr in our study.

There may be several reasons for the present net release of Cd, Ni and Cr from the Oe and Oa horizon. Most likely seems desorption of metals from exchangeable pools and from weak complexes caused by the presently lower concentrations of metals in throughfall solutions. The release of heavy metals from forest floors should be mainly controlled by pH or complexation with DOC (Sauvé et al. 1998, 2003). In our site, concentrations of most investigated metals correlated in fact negatively with pH and positively with DOC. Multiple regressions indicated that DOC was more important for Cu and Cr mobility at our site. In contrast, Cd and Ni were mobilized dominantly during episodes of lower pH. DOC concentrations in many surface waters have increased in the past two decades probably as a result of decreasing deposition of sulphur and acidity (Monteith et al. 2007). If DOC concentrations also increased recently in forest floor percolates is unknown. If so, this would have triggered additional release of metals from the forest floor.

The fate of the metals transferred from the forest floor into the mineral soil (up to 90 cm depth) was also found metal specific. In case of Cu, Cr and Ni the mineral soil acted as a sink for metals, in case of Cd, the fluxes at 90 cm depth were almost similar to forest floor percolates and no retention was found. The mineral soil was a source for Zn since fluxes in 90 cm depth exceeded those in forest floor percolates. The low retention of Cd and the release of Zn in the mineral soil coincide with low K_d values for both elements in the mineral soil whereas K_d values for Cu, Cr and Ni were about two orders of magnitude larger, emphasizing the retention of these metals in the mineral soil.

There were large variations of the field derived K_d values, which reflects the disequilibrium of metal solid–solution partitioning (Degryse et al. 2009) and questions their use under field conditions. For the mineral soil horizons, the range of predicted K_d values was orders of magnitude less than the one

obtained from the field measurements, while the ranges overlapped for the forest floor horizons.

Sinks and sources and mobility of metals:
catchment scale

The mass balance (calculated as total deposition minus runoff) of the catchment indicated retention of Zn, Cu and Ni, but an almost balanced budget for Cr and Cd. The concentrations of all metals in runoff from the catchment were largest under conditions of high flow, coinciding with low pH and elevated DOC concentrations in runoff. DOC was more important than pH for Cu and Cr mobility in the forest floor and runoff at our site. In contrast, Cd and Ni concentrations were best correlated to pH. The strong positive correlations between runoff fluxes and concentrations of metals, H⁺ and DOC in runoff emphasize the transport of metals by superficial flow under heavy rain events. These findings emphasize the forest floor as a source of metals in runoff. The general trend of increasing DOC concentrations in surface waters from forested watersheds (Monteith et al. 2007) was also found in the runoff from our site (Strohmeier, unpublished data). Here, average annual DOC concentrations increased almost linearly from 5 to 10 mg l⁻¹ in the time 1988–2009. We assume that this also caused larger metal fluxes in 2005 with runoff as compared to fluxes before the rise.

Since the fluxes of Cd, Zn and Ni with seepage at 90 cm depth in the upland soil were larger than with runoff, the soil deeper than 90 cm or the wetland soils seem rather effective sinks for these metals at the catchment scale (Ukonmaanaho et al. 2001). Fluxes of Cr at 90 cm soil depth were similar to runoff and runoff fluxes exceeded those at 90 cm depth in case of Cu.

The ratio of soil pool of metals in the catchment to the actual deposition was very different for the metals investigated. For Cd, Zn and Cu the historic deposition might explain the soil pools, given the much larger deposition in the past and the long lasting pollution of the region by heavy metals from ore mining and other emissions for several centuries (Michler 1983). In case of Cr and Ni the ratios of soil pools/actual deposition exceed those of the other elements by far, suggesting the contribution of geogenic sources to the soil pools.

Conclusion

The fluxes of metals at the upland soil profile scale indicated a present source function of the forest floor which seems to be the results of recent decrease in deposition. The mineral soil still was a sink for metals released from the forest floor with the exception of Cd. Hence, losses of metals from the watershed by runoff are generally small. The mobilization of heavy metals in forest floor percolates and in runoff seems generally induced by low pH and DOC complexation. Cd and Zn proved to be more mobile than Cu, Cr and Ni. There are mobilizable pools of heavy metals in the Oe and Oa horizon and heavy rain events followed by near surface runoff lead to elevated heavy metal concentrations in runoff. Generally increasing DOC concentrations in runoff will enhance the metal export from the watershed.

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