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Dynamics of mercury and methylmercury in forest floor and runoff of a forested watershed in Central Europe

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Abstract. Forested watersheds are an important part of the terrestrial mercury and methylmercury cycle, and a link between the atmospheric and aquatic environment. This study was conducted to determine the contribution of the forest floor to the pools and fluxes of total Hg (Hg_{total}) and methylmercury (MeHg) in a forested catchment, and to identify factors influencing the mobility of both compounds. Throughfall deposition, litterfall, runoff and fluxes with forest floor percolate of Hg_{total} and MeHg were sampled during one year in a coniferous catchment in Germany. Total deposition of Hg_{total} was 552 mg ha^{-1} a^{-1} with litterfall contributing one third. Nearly 60% of the total input of Hg_{total} reached the mineral soil with the forest floor percolate, but less than half of this fraction was found in the runoff of the catchment. Total deposition of MeHg was 2.6 mg ha^{-1} a^{-1}, with litterfall as the dominating pathway. Only 19% of the MeHg deposition was discharged from the forest floor, but the flux of MeHg with runoff was nearly twice as high. Only few correlations with other solution parameters were found. Fluxes of both compounds with forest floor percolates depended mainly on water fluxes, which was not true for the runoff. The forest floor of the upland soil is an effective sink for MeHg, but not for Hg_{total}. Differences in the mobility of both compounds in the forest floor disappeared at the catchment scale, probably because other processes (i.e. Hg_{total} immobilization and MeHg formation) dominated.

Introduction

Mercury (Hg) is released into the environment by both, natural sources and human activities. Due to its physicochemical properties, Hg is a widespread element on the global scale and has to be considered as a ubiquitous pollutant today. Human activities like combustion of fossil fuels, artisanal gold-mining (Nriagu & Wong 1998) and several industrial, chemical and pharmaceutical applications of Hg have significantly increased atmospheric Hg emissions, especially in the northern hemisphere (Slemr 1996) and in highly industrialized regions of Central Europe (Pacyna 1996). As a consequence, elevated input fluxes and pools of Hg have been found in several environments (Lindqvist et al. 1991; St. Louis et al. 1995; Vasiliev et al. 1998; Lucotte et al. 1995; Allan 1999). Especially high amounts of the highly-toxic species methylmercury (MeHg) in predatory organisms of limnic/aquatic foodwebs have been reported even in remote areas (Hånkanson et al. 1988; Watras et al. 1994; Rolfhus & Fitzgerald 1995; Mason et al. 1995; Wagemann et al. 1998). Several attempts have been made to elucidate the pathway of Hg compounds from atmospheric deposition into the biota of aquatic systems. Studies in remote areas of Scandinavia and North America emphasized the role of forested catchments as filters between atmosphere and hydrosphere (Hultberg et al. 1995; Rudd 1995; Bishop & Lee 1998; Lindberg 1996; Watras et al. 1996). Hultberg et al. (1994) postulated a higher mobility of MeHg as compared to total Hg (Hg_{total}) in forested catchments, based on higher MeHg/Hg_{total} ratios in the annual runoff fluxes of forested catchments as compared to the input by deposition. Differences in mobility have been attributed to hydrological factors, including water flow pathways and soil temperature effects (Munthe et al. 1998), and wetland soils have been found to influence significantly the MeHg export of boreal catchments (Lee et al. 1995, 1998; St. Louis et al. 1996; Branfireun et al. 1998). Other findings in Central Europe did not reveal any difference in the mobility of Hg_{total} and MeHg on the scale of an annual input/output budget, but found opposite depth gradients of MeHg and Hg_{total} in the forest floor, indicating differences in release and mobility of these compounds on a smaller scale (Schwesig & Matzner 2000). It has been shown that litterfall is an important pathway for Hg_{total} and MeHg deposition into terrestrial soils of forested catchments (Munthe et al. 1995; Lindberg 1996). In terrestrial soils, highest contents of both compounds are usually found in the organic material of the forest floor (Lee et al. 1994; Lindqvist et al. 1991; Padberg 1991; Lamersdorf 1988; Schwesig et al. 1999), and large stores of Hg compounds in the mineral soils emphasize the importance of transport processes from the forest floor into the mineral soil (Lee et al. 1994; Schwesig & Matzner 2000). Thus the release of Hg compounds from the organic layer of the forest floor can be considered as an initial step of Hg mobilization in forested catchments, and seems to be of high importance for the discharge of Hg compounds, and especially MeHg, into aquatic systems. The role of dissolved organic carbon (DOC) for the transport of several organic and inorganic pollutants in soils has been stated earlier (Haitzer et al. 1999; Kalbitz & Wennrich 1998; Temminghoff et al. 1997; Marschner 1999), and several studies have found Hg_{total} and MeHg in surface waters associated with dissolved organic carbon (Pettersson et al. 1995; Driscoll et al. 1995). The forest floor is a source of DOC and an important link in the cycling of Hg in forest ecosystems, and usually also has the highest MeHg and Hg_{total} contents of terrestrial soils. Thus, it is an important task to elucidate whether the release of Hg_{total} and MeHg from the forest floor contributes substantially to the export of both compounds into the aquatic environment, and whether this transport is linked to the dynamic of DOC. To our knowledge, different mobilities of Hg_{total} and MeHg during the process of litter decomposition in the forest floor have not been shown by direct measurement in the field yet. Attempts to measure or estimate fluxes of these compounds in soils were restricted to the mineral soil (Lee et al. 1994), to estimation by use of soil solution gained by centrifugation (Bishop et al. 1995a), or to column experiments using samples of highly contaminated sites (Hempel et al. 1995).

The aim of this study was thus to determine pools and fluxes of Hg_{total} and MeHg in the forest floor of an upland soil in a forested watershed and their contributions to the catchment budget. A further aim was to investigate whether differences in the behavior of MeHg and Hg_{total} among the layers of the forest floor support the hypothesis of a different mobility of MeHg as compared to Hg_{total}.

Materials and methods

Site

The coniferous ‘Lehstenbach’ catchment (420 ha), dominated by Norway spruce (*Picea abies* [L.] Karst.) stands of different age is located in the Fichtelgebirge mountains, NE Bavaria, Germany (11°52′10″ E; 50°08′35″ N). The elevation ranges from 700 to 880 m a.s.l., and the annual precipitation is approx. 1100 mm, and the mean annual temperature is about 5 °C. Soils derived from deeply weathered granite form a mosaic of dystric cambisols and podzols (FAO-classification) with loamy to sandy texture. Approximately 30% of the catchment area are covered by wetlands of both bog and fen type.

Our study was carried out at the ‘Coulissenhieb’ site at the edge of the catchment, which represents a 2.5 ha Norway spruce stand (approx. 140 years old). The ground vegetation is composed of patches of mainly two grasses *Calamagrostis villosa* and *Deschampsia flexuosa*, and of *Vaccinium myrtillus*. The forest floor is a well stratified mor type of approximately 9 cm depth and consists of a litter (Oi), a fermented (Oe) and a humified (Oa) organic layer with an average thickness of 1.0, 4.0, and 3.5 cm, respectively. Maximum rooting of the spruce and ground vegetation occurs in the Oa and Ah horizon. The pH (H_2O) of the forest floor ranges from 4.04 in the Oi to 3.39 in the Oa, which represents the lowest pH throughout the whole soil profile. The

Table 1. Contents and storage of Hg_{total} and MeHg in the forest floor (modified from Schwesig et al. 1999).

	Hg_{total}		MeHg	
	ng g^{-1}	g ha^{-1}	ng g^{-1}	g ha^{-1}
Oi	123	2.5	0.94	0.019
Oe	377	45	0.55	0.066
Oa	495	121	0.24	0.059
Sum of all layers		169		0.144

mineral soil is highly acidic as indicated by low pH and low base saturation of the cation exchange capacity.

Rates of atmospheric deposition of sulphate and protons in the Fichtelgebirge region have decreased significantly during the last decade (Klemm & Lange 1999; Alewell et al. 2000). Total atmospheric deposition (calculated as sum of throughfall and litterfall deposition) of Hg_{total} and MeHg in 1998/1999 were 541 and 3.5 mg g ha^{-1} a^{-1}, respectively (Schwesig & Matzner 2000). Contents and storage of Hg_{total} and MeHg in the soils of the watershed have been determined in an earlier study (Schwesig et al. 1999, Table 1).

Sampling and flux measurements

Sampling of throughfall and forest floor percolates was performed biweekly on three subplots of the Coulissenhieb site. Each subplot consisted of three amber borosilicate collectors of 177 cm^2 installed 1 m above ground in dark polyethylene tubes to avoid any impact of sunlight. Sampling bottles (1000 mL, Schott) were preacidified with 2 mL of HCl (suprapur) to stabilize Hg compounds during the sampling period. Throughfall samples for other analytical procedures were collected by 5 polyethylene samplers of 326 cm^2 at each plot.

For litterfall sampling, six polyethylene funnels (35 cm diameter) were installed 1 m above ground. Inside each funnel a polytetrafluorethylene (PTFE) net was installed, to permit water flow through the funnel and to retain the litterfall. Litterfall was sampled every other month. Total input to the soil was calculated as the sum of litterfall and throughfall (LF + TF), since the root uptake of Hg is assumed to be neglectable (Bishop et al. 1998). Thus, Hg compounds in litterfall stem from atmospheric deposition and have to be considered as an input to the system.

Percolates from the forest floor were collected by plate lysimeters of 180 cm^2 installed close to the throughfall collectors. The lysimeters were made of plastic material with a polyethylene plate of 50 μm pore size and a total thickness of 1.5 cm. Lysimeter plates had been installed in the field more than two years before the beginning of Hg measurements, and thus potentially adsorbing surfaces were assumed to be saturated. For maintenance and repair purposes lysimeters were deinstalled before our experiment. Prior to reinstallation in the field, the lysimeters were percolated in the laboratory with standard and soil solutions of known DOC, MeHg and Hg_{total} concentrations, and no memory effects or contamination could be observed. In the field the lysimeters were subjected to a suction of 300 hPa for 1 minute every 3 minutes, and the solution was transferred through a tygon tube with inner teflon coating into borosilicate glass bottles placed in the mineral soil protected from sunlight. At each of the three plots 9 plate lysimeters were installed (three replicates underneath the Oi, the Oe and the Oa layer of the forest floor, respectively). To minimize effects of disruption due to installation, no suction was applied during the first week after installation, and samples of the first two months after installation were rejected.

All samples were taken fortnightly from September 1998 to September 1999, and analysed for major ions, and dissolved organic C and N for each sampler separately. For Hg and MeHg analysis, the solution of the three replicates per layer were pooled (volume weighted) at each plot, to obtain a sample volume sufficient for the speciation of Hg-compounds.

The fluxes of elements through the humus layer and with throughfall were calculated by multiplying the measured volume in the samplers by the determined concentration on a biweekly basis. Due to the limitations of the lysimeter plates (e.g. bypass flow) water and element fluxes in the organic layer were underestimated when using only the measured water volumes for flux calculations. Thus, the water fluxes were adjusted such that the annual Cl^- bugdet of the forest floor was balanced, using the annual sum of biweekly measured Cl^- fluxes with throughfall (obtained as mean value from 5 throughfall samplers at each of the three subplots). The correction factor ranged from 1.37 to 1.51, and the corrected water fluxes were in plausible relation to water fluxes by throughfall and runoff (Table 2). During snow-melt the water fluxes in the forest floor had to be estimated, since the collection bottles overflowed. Soil temperature was measured in 5 cm depth in 10 minute intervals.

Biweekly water flux with runoff of the catchment was calculated from level measurements (10 min. time resolution) at the weir. The cumulative water flux was multiplied by the biweekly measured concentrations to obtain biweekly Hg-fluxes with runoff.

Table 2. Water fluxes during the sampling period September 1998 to September 1999 – uncorrected and after correction using the annual Cl^- budget.

Compartment	Measured water flux (mm)	Corrected water flux (mm)
Throughfall	1079	
Oi layer	561	814
Oe layer	573	866
Oa layer	574	786
Runoff	823	

Analytical methods

Samples were filtered through a 0.45 μm membrane using cellulose acetate filters. Samples for analysis of Hg compounds were filtered with pre-washed 1 μm fiberglass filters, which had been tested in preliminary experiments to be suitable for the trace analysis of Hg compounds. Analysis included pH (glass electrode, WTW pH 90), concentration of Ca^{2+}, Mg^{2+}, Na^+, K^+, Si, Fe^{3+}, Mn^{2+}, Al^{n+} and total sulfur (Plasma Emission Spectroscopy, ICP-AES, Integra XMP, GBC, Australia), NH_4^+, Cl^-, NO_3^-, and SO_4^{2-} (ion chromatography, Dionex 2000i- SP). Dissolved organic carbon (DOC) was determined as CO_2 after persulphate-UV-oxidation (Foss Heraeus LiquiTOC) and total N in solution as NO_x after combustion at 700 °C (Abimed Total N Analyzer TN-50). Dissolved organic nitrogen (DON) was calculated as difference between total N and mineral N, dissolved organic sulfur (DOS) was calculated as difference between total sulfur and sulfate. Percolate samples for Hg analysis were stabilized by addition of 500 μL HCl (Merck, suprapur) per 250 mL, and stored in 250 mL borosilicate vessels in the dark at a temperature of 2 °C until further analysis. Analysis of Hg_{total} was performed by FIA-Amalgam-CVAFS (flow injection – amalgamation – cold vapor atomic fluorescence spectroscopy) after UV digestion with HNO_3 and H_2O_2. Speciation of MeHg in solid and liquid samples was performed by a HPLC-CVAFS (high pressure liquid chromatography – cold vapor atomic fluorescence spectroscopy) coupling (Falter & Ilgen 1997) after distillation (according to Horvat et al. 1993) and preconcentration as pyrrolidinedithiocarbamate-complexes on a RP C-18 column.

Detection limit was 2 ng/L for Hg_{total} and 10 pg/L for MeHg. For samples below detection limit a concentration of half the detection limit was assumed.

Table 3. Median and range of Hg_{total}, MeHg and DOC concentrations in throughfall, litterfall, runoff, and forest floor percolates during the sampling period September 1998 to September 1999.

Compartment		Hg_{total}		MeHg		DOC	
		Median	Range	Median	Range	Median	Range
Litterfall	ng g^{-1}	70	38–88	0.57	0.23–1.49	–	–
Throughfall	ng L^{-1}	27	11–230	0.08	0.01–0.46	10	1.7–242
Oi percolate	ng L^{-1}	42	8–115	0.10	0.01–0.56	37	9–156
Oe percolate	ng L^{-1}	43	11–144	0.07	0.01–0.64	32	8–119
Oa percolate	ng L^{-1}	58	13–101	0.06	0.01–0.35	31	6–91
Runoff	ng L^{-1}	13	5–129	0.12	0.01–0.40	8	3–48

Results

Maximum concentrations of Hg_{total} were found in throughfall, whereas the median concentration was higher in forest floor percolates (Table 3). The median MeHg concentration in percolates of the uppermost forest floor (Oi layer) was slightly higher than in throughfall, but in contrast to Hg_{total} decreased in the deeper layers. Concentrations in runoff as compared to the solution leaving the forest floor (Oa percolate) were lower for Hg_{total}, but higher for MeHg. Some data on DOC are also given in Table 3, for details see Michalzik and Matzner (1999).

Only few correlations were found of MeHg or Hg_{total} concentrations with other measured chemical parameters of the forest floor percolate (concentrations of H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, Si, Fe^{3+}, Mn^{2+}, Al^{n+}, total S, total N, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}, DOC, DON and DOS).

For the data set of all plots and layers a weak but highly significant correlation of Hg_{total} and H^+ concentrations in forest floor percolates ($r = 0.28$, $p = 0.002$) was found. Layer specific weak ($r < 0.5$) correlations were found for Hg_{total} concentrations in the Oa layer percolates ($n = 38$) with DOC ($p = 0.04$), with MeHg ($p = 0.024$) and with H^+ ($p < 0.01$), and in the Oe layer percolates ($n = 33$) for MeHg concentration with water flux ($p = 0.012$) and soil temperature (mean values of the biweekly sampling intervals) at 5 cm depth ($p < 0.05$). Despite the positive correlation to temperature for MeHg, concentrations of MeHg and Hg_{total} in the forest floor did not show a distinct seasonality.

Biweekly runoff concentrations and fluxes of Hg_{total} and MeHg are given in Figure 1. Highest concentrations of MeHg ($>$0.15 ng/L) occurred mainly from June to August, whereas Hg_{total} concentrations were also elevated ($>$20

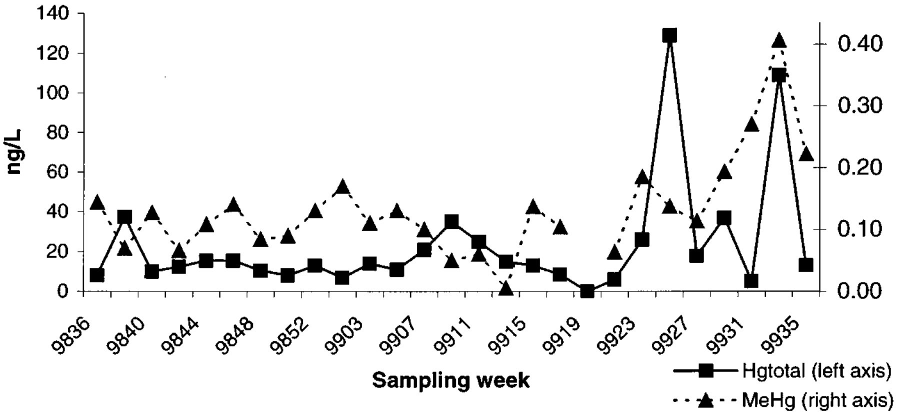

Figure 1(a). Biweekly concentrations of Hg_{total} and MeHg in the runoff of the Lehstenbach catchment.

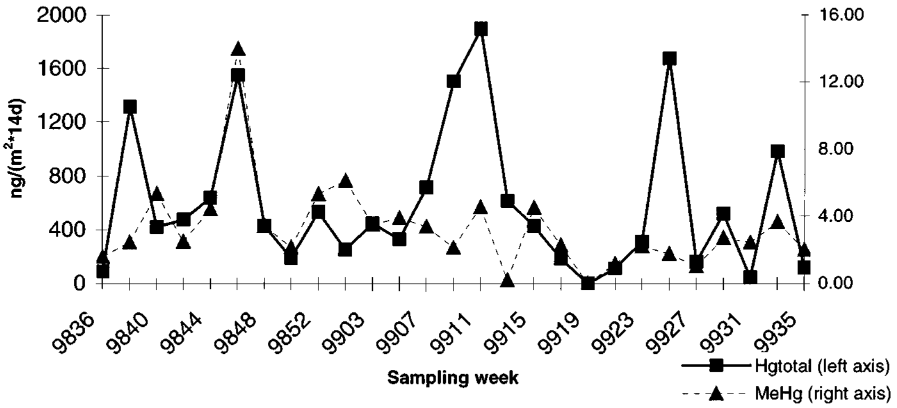

Figure 1(b). Biweekly fluxes of Hg_{total} and MeHg in the runoff of the Lehstenbach catchment.

ng/L) during snowmelt. However, high fluxes of both compounds occurred at episodic events throughout the whole year. High runoff fluxes of Hg_{total} during the cooler seasons (autumn, winter and spring) coincided with events of high water fluxes (heavy rain or snowmelt events), whereas high runoff fluxes of Hg_{total} in summer occurred at low water fluxes and were thus due to elevated concentrations. MeHg fluxes with runoff were not linked with Hg_{total} fluxes in runoff, except one single event in autumn 1998 (Figure 1(b), sampling week 9846), where high water fluxes in runoff due to a strong rain period resulted in high catchment output of both compounds. The increase in MeHg concentrations in the runoff during the summer months was not as pronounced as for Hg_{total} and thus did not result in elevated flux of MeHg with the runoff. There were no significant correlations either of Hg_{total} with

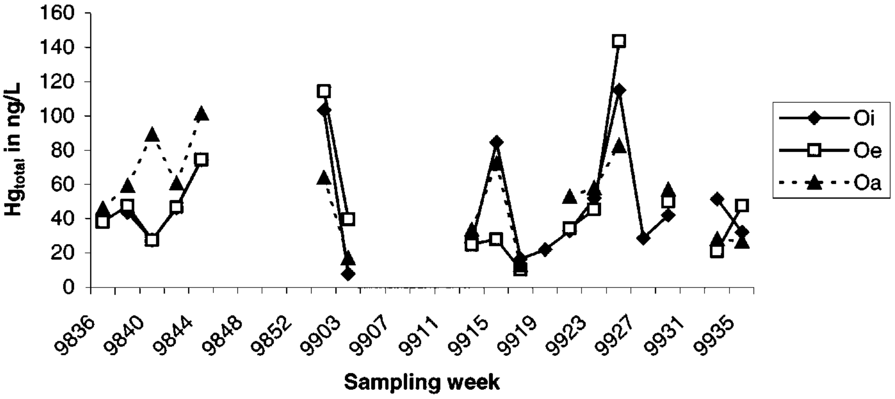

Figure 2(a). Biweekly concentrations of Hg$_{total}$ in the forest floor percolates.

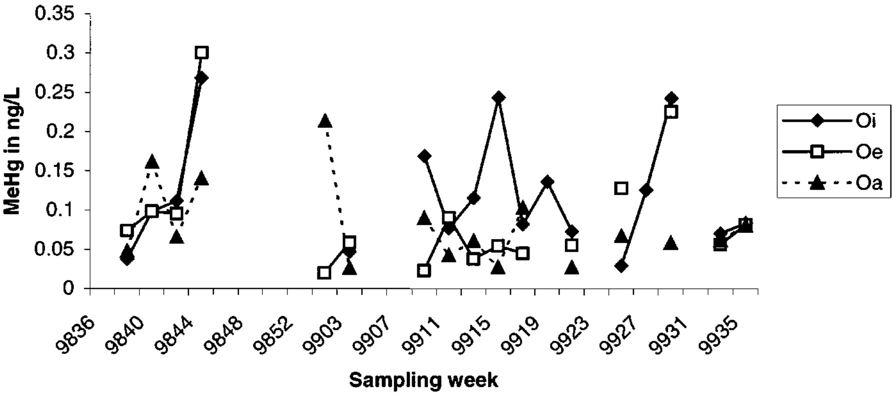

Figure 2(b). Biweekly concentrations of MeHg in the forest floor percolates.

MeHg concentrations or of water fluxes with concentrations or fluxes of both compounds in the runoff. Correlations with other chemical parameters were found between concentrations of Hg$_{total}$ and DOC ($r = 0.57$, $p < 0.01$), and Ca, Mg, Na, and Cl (all approx. −0.5, $p < 0.05$). In case of MeHg correlations with electric conductivity (−0.52, $p < 0.01$), aluminum (−0.43, $p < 0.05$) and sulfate (−0.44, $p < 0.05$) were found, but not with DOC.

Biweekly concentrations and fluxes of Hg$_{total}$ and MeHg with forest floor percolates are given in Figures 2 and 3. From December to March, fluxes of both compounds were almost zero, due to frozen lysimeters and the snow cover of the soil. During the remaining time of the year, Hg$_{total}$ concentrations and fluxes of the three forest floor layers often paralleled. MeHg fluxes with forest floor percolate (Figure 3(b)) were very different for each layer and did not correspond well with Hg$_{total}$ fluxes.

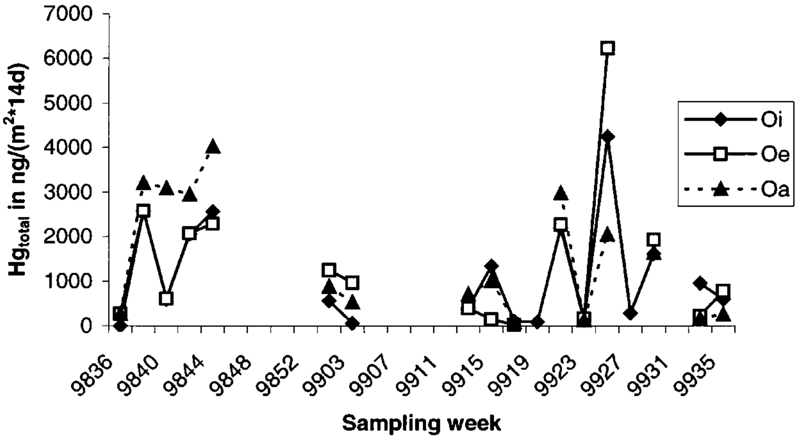

Figure 3(a). Biweekly fluxes of $\mathrm{Hg_{total}}$ with forest floor percolates.

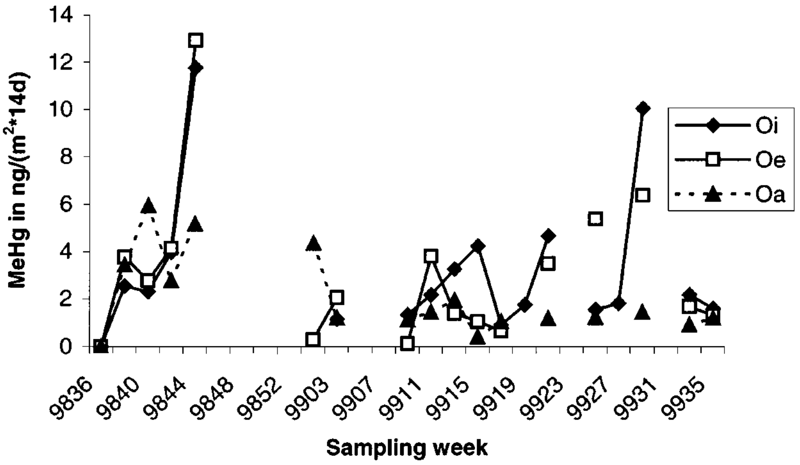

Figure 3(b). Biweekly fluxes of MeHg with forest floor percolates.

Fluxes of $\mathrm{Hg_{total}}$ and MeHg correlated well with water fluxes in throughfall as well as in all layers of the forest floor (Table 4), with slightly stronger correlations for fluxes of $\mathrm{Hg_{total}}$. Strong and highly significant correlations between the different layers were found for concentrations as well as for fluxes of $\mathrm{Hg_{total}}$. For MeHg these correlations could only be found for Oi and Oe layers, and disappeared in the Oa layer. Concentrations and fluxes of both compounds in throughfall did not correlate with concentrations and fluxes in forest floor percolates, except for $\mathrm{Hg_{total}}$ fluxes in Oi percolates (Table 5).

Based on the biweekly sampling for one year, annual fluxes of MeHg and $\mathrm{Hg_{total}}$ with deposition, forest floor percolate and runoff were calculated. Total

Table 4. Correlation coefficients r (Spearman) between fluxes of water and Hg compounds in several compartments.

Compartment	Hg_{total}	MeHg
Throughfall	0.723**	0.519**
Oi	0.735**	0.585**
Oe	0.810**	0.750**
Oa	0.731**	0.458**
Runoff	n.s.	n.s.

*: significant with $p < 0.05$.
**: significant with $p < 0.01$.
n.s.: no significant correlation.

Table 5. Correlation coefficients r (Spearman) for concentrations and fluxes of Hg compounds between different compartments.

	Hg_{total}		MeHg	
Compartments	Fluxes	Concentrations	Fluxes	Concentrations
Throughfall/Oi	0.600*	n.s.	n.s.	n.s.
Oi/Oe	0.908**	0.802**	0.821**	0.564*
Oe/Oa	0.544*	0.626*	n.s.	n.s.
Oi/Oa	0.692**	0.503*	n.s.	n.s.

*: significant with $p < 0.05$.
**: significant with $p < 0.01$.
n.s.: no significant correlation.

deposition of Hg_{total} during the measuring period was 552 mg ha^{-1} a^{-1}, with litterfall contributing approximately one fourth to the total amount (Figure 4). Approximately 54% of the total annual deposition (296 mg ha^{-1} a^{-1}) were discharged from the Oi layer during the same period. The subjacent layers contributed only small amounts of Hg_{total}, increasing the flux of Hg_{total} leaving the forest floor to 330 mg ha^{-1} a^{-1}, which was nearly 60% the total input of Hg_{total} into the forest floor. Only a part (approximately 48%) of the Hg_{total} mobilized from the forest floor was found in the runoff of the catchment. This means that only 29% of the total deposition of Hg_{total} was discharged via the catchment's runoff.

Annual total deposition of MeHg was 2.57 mg ha^{-1} a^{-1}, with litterfall as the dominating pathway, contributing two third (Figure 5). Approximately one third (0.83 mg ha^{-1} a^{-1}) of the total deposition was discharged from the Oi layer. This flux decreased during the percolation through the subjacent layers, and the flux of MeHg leaving the lower boundary of the forest floor

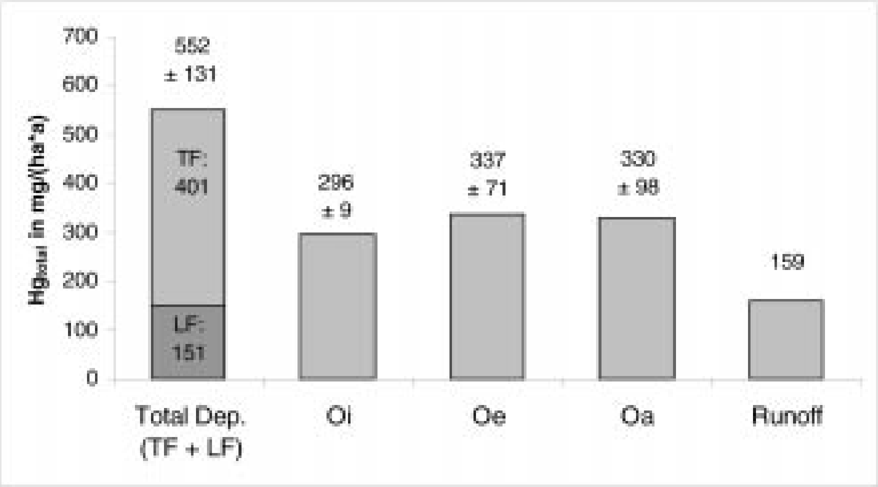

Figure 4. Annual fluxes of $\mathrm{Hg}_{\mathrm{total}}$ (± standard deviation indicating the spatial variability of the three subplots) from September 1998 to September 1999. Total Deposition was assumed to be the sum of litterfall (LF) and throughfall (TF).

and entering the mineral soil was only 0.48 mg ha^{-1} a^{-1}, which represents 19% of the annual total deposition. The annual flux of MeHg with the runoff was nearly twice the MeHg flux leaving the forest floor. The flux of MeHg discharged from the catchment via runoff was 0.89 mg ha^{-1} a^{-1}, which is approximately 35% of the total deposition, resulting in a similar input/output ratio on an annual catchment scale as for $\mathrm{Hg}_{\mathrm{total}}$.

Discussion

Forest floor

The forest floor is an effective sink for MeHg, but $\mathrm{Hg}_{\mathrm{total}}$ is less effectively retained. This can be seen from concentrations as well as from the fluxes of both compounds.

Substantial amounts of $\mathrm{Hg}_{\mathrm{total}}$ were transported into the mineral soil (60% of the total deposition), whereas only 19% of the MeHg deposition reached the mineral soil (Figures 4 and 5).

Sorption and desorption processes of $\mathrm{Hg}_{\mathrm{total}}$ may occur in the uppermost forest floor (Oi), as indicated by the lack of correlations between $\mathrm{Hg}_{\mathrm{total}}$ concentrations in throughfall and forest floor percolate, and the damping of the concentration range. But the strong correlations of $\mathrm{Hg}_{\mathrm{total}}$ concentrations and fluxes between the different forest floor layers (Table 5) suggest only

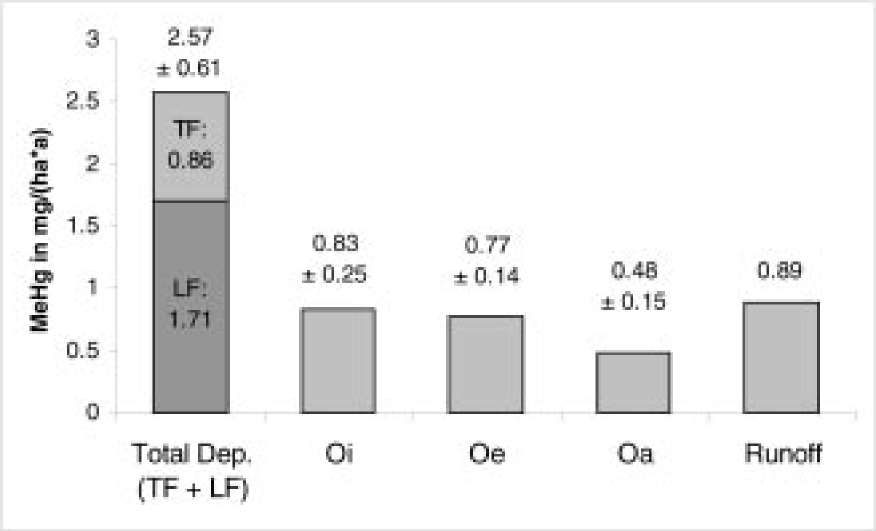

Figure 5. Annual fluxes of MeHg (± standard deviation indicating the spatial variability of the three subplots) from September 1998 to September 1999. Total Deposition was assumed to be the sum of litterfall (LF) and throughfall (TF).

a weak interaction with the solid phase of the deeper layers. For MeHg these correlations disappeared in the deeper layers, emphasizing the different behavior of MeHg, and the role of solid phase interactions with the forest floor or transformation to other species for MeHg. Transport of MeHg within the forest floor is also decoupled from throughfall, as indicated by the lack of correlations of both MeHg fluxes and concentrations in the forest floor with MeHg in throughfall. This is another hint to the importance of immobilisation or transformation processes for MeHg in the forest floor.

In spite of the highest Hg_{total} content, the Oa layer was almost inert with respect to the current Hg_{total} fluxes and concentrations in solution (Figure 4). Inorganic Hg(II) is strongly sorbed to humic substances, and can not easily be removed (Kerndorff & Schnitzer 1980), but the sorption process itself is rather slow and can take up to several weeks (Thanabalasingam & Pickering 1985). Thus, effective immobilization of the current Hg_{total} deposition may be hampered by fast percolation through the forest floor, and release of formerly accumulated Hg_{total} hindered by a hysteresis effect.

The current fluxes do not explain why Hg_{total} increases with depth and MeHg decreases with depth in the solid phase of the forest floor (Table 1). Instead they indicate either transformation processes of MeHg like demethylation or an ongoing accumulation of MeHg also in the deeper layers of the forest floor, and a Hg_{total} accumulation only in the Oi layer. The latter seems to be dominated by the input with litterfall, since the fluxes out of the Oi layer were in the same order of magnitude as the throughfall deposition. In contrast to the fluxes, the depth gradient and storage indicated a strong (historical) accumulation of Hg_{total} in the Oa layer. These discrepancies may be due to changes in the atmospheric deposition in the catchment, which decreased significantly during the last decade for several air pollutants (Alewell et al. 2000; Klemm & Lange 1999). Thus, a hysteresis of the Hg_{total} adsorption seems to be the most probable explanation for the inert behavior of the Oa layer. This means that the reversibility of Hg_{total} accumulation is low, and Hg_{total} pollution of the forest floor a long-term environmental challenge even under decreasing deposition. The current annual fluxes of both Hg_{total} and MeHg out of the forest floor represent only a fractional amount (2 and 3‰) of the stores in the forest floor (Table 1). Consequently, special attention ought to be paid to factors and processes influencing the stability or mobility of the remaining pools of these compounds in the forest floor.

The lack of a distinct seasonality in Hg_{total} concentrations suggests that temperature effects were only of minor importance for the release of Hg_{total} from the forest floor. This was confirmed by the lack of correlations between Hg_{total} concentrations and soil temperature. The H^+ and DOC concentrations seemed to have some influence on the release of Hg_{total} from the Oa layer. However, the influence of DOC on Hg_{total} transport turned out to be less important than expected from findings in the aquatic environment (Driscoll et al. 1995). Biweekly fluxes of Hg_{total} in forest floor percolates seemed to depend mainly on water flux (Table 4), indicating that the release of Hg_{total} is strongly affected by hydrological conditions. Elevated transport of Hg_{total} bound to suspended particles or replenishment by desorption in the Oi layer are the most probable explanations for the linkage of Hg_{total} fluxes with water fluxes. However, this can only be confirmed by further experiments e.g. by isotope labelling.

The MeHg concentrations of the Oe percolate are at least partly dependent on water fluxes and soil temperature as shown by correlations. This might be a hint to methylation processes. The potential of flooded humus to form MeHg has been shown by Porvari and Verta (1995), and might also be of importance at water-saturated conditions in anaerobic microzones of the forest floor. The occurence of anaerobic microzones in forest floors was shown by van der Lee et al. (1999). The relevance of DOC for the MeHg concentrations was low, contradicting findings from the aquatic environment (e.g. Lee & Iverfeldt 1991).

Fluxes of MeHg in the forest floor were influenced by water fluxes to some extent, as shown by the correlations (Table 4) but less than in case of Hg_{total}. Despite the effects on MeHg concentrations, the influence of hydrological conditions on the fluxes of MeHg thus was not as pronounced as for Hg_{total}. For MeHg fluxes processes like transformation to other species or interaction with the solid phase were of major importance, as also detectable by the lack of correlations between the MeHg fluxes of the deeper forest floor layers (Table 5).

Catchment scale

Runoff concentrations of both compounds seemed to be influenced by the seasonal temperature variation, since maximum concentrations mainly occurred during the summer months. This may be due to decomposition of Hg containing organic substances at higher temperature or biological methylation processes, probably in the wetlands of the catchment, in case of MeHg. Although the increasing MeHg concentrations in runoff did not coincide with increasing fluxes, the elevated concentrations may be highly relevant for aquatic biota.

Hg_{total} concentrations in runoff showed a stronger and more significant correlation with DOC than in the forest floor percolate, emphasizing the relevance of DOC for Hg_{total} export from forested catchments. This may be due to the lower concentrations of DOC in runoff as compared to the forest floor percolates (Table 3). Continuously high DOC concentrations in the percolates may conceal effects of DOC on Hg_{total} concentrations and fluxes. MeHg concentrations in runoff were not dependent on DOC. This suggests different factors influencing the transport of Hg_{total} and MeHg in the catchment.

Elevated Hg_{total} concentrations during snowmelt also indicated the existence of Hg_{total} pools in the catchment, which can be mobilized by events of high water flux. Single events of high Hg_{total} discharge occurred during heavy rain events and snowmelt in autumn and winter (Figure 1(b)). This may be explained by mainly superficial water flow pathways passing through upper soil horizons with high content of Hg_{total}, which was confirmed by previous findings of similar episodic patterns of Hg_{total} in runoff (Bishop et al. 1995b; Lee et al. 1998). In contrast to Hg_{total}, the MeHg concentrations and fluxes in runoff did not increase during snowmelt.

The high runoff fluxes of both compounds during autumn rainfalls in 1998 (Figure 1(b), sampling weeks 9842–9844) coincided with high fluxes in the forest floor (Figures 3(a) and (b)), emphasizing the relevance of superficial water flow pathways at heavy rain events. But for the complete sampling period, there was no significant correlation between fluxes of water and of either Hg_{total} or MeHg with runoff. The lack of correlations between concentrations (and fluxes) of both compounds in the runoff suggests different factors controlling the release of Hg_{total} and MeHg, respectively. Although single events of high water fluxes are relevant for the discharge of both compounds with the runoff, during the main time of the year other factors were of importance, which still have to be identified.

Based on annual fluxes, the output/input ratio of the watershed (runoff vs. total deposition) was similar for both species with 29% for Hg_{total} and 35% for MeHg, and thus a higher mobility of MeHg at the catchment scale was not confirmed. But comparison of deposition and lysimeter fluxes with runoff fluxes has to be interpreted with respect to mobility with caution, since methylation or demethylation can occur and strongly influence the input/output ratio. The differences in mobility of MeHg and Hg_{total} in the forest floor disappeared at the watershed scale, possibly because other processes dominated in other compartments of the catchment. Only a part of the Hg_{total} transported into the mineral soil reached the runoff. This is a strong indication of other sinks for Hg_{total} in the watershed, e.g. immobilization in the mineral soil, as also indicated by the large pools of Hg_{total} in the mineral horizons (Schwesig et al. 1999). Furthermore volatilization due to reductive processes in the aquifer or immobilization in the river sediment might be feasible sinks for Hg_{total} in the catchment. At the catchment scale the retention of MeHg in the forest floor was compensated by other sources in the ecosystem, as can be shown by the fluxes with runoff, which were nearly two times higher than the fluxes out of the forest floor. This confirms earlier results of Bishop et al. (1995a), who found that MeHg in soil solution of podzols was insufficient to sustain the MeHg level in runoff. Main MeHg sources are probably the wetlands in the catchment, where MeHg contents were exceeding those in the forest floor of terrestrial soils up to hundredfold (Schwesig et al. 1999), and are probably due to in-situ methylation of inorganic Hg.

Conclusions

The forest floor plays an important role for the cycling of Hg_{total} and MeHg in forested catchments. It can be considered as an effective sink for MeHg, as only a small fraction of the MeHg deposition is transported into the mineral soil, but Hg_{total} is less effectively retained.

There are indications that the recovery of the forest floor from historical Hg_{total} accumulation is delayed by a hysteresis effect of the Hg_{total} adsorption.

Storages of both compounds in the forest floor exceeded the annual fluxes by several orders of magnitude. Thus, any changes in the forest floor like enhancement of either mineralization or accumulation may affect strongly the Hg budget of the watershed.

In spite of different mobilities of Hg_{total} and MeHg in the forest floor, and different factors controlling their release with runoff, these differences are not recognizable in an input/output budget for the whole catchment on an annual scale. There are indications for other sources of MeHg in the catchment like methylation in the wetland soils, which should be quantified in further investigations.

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