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Spring Snowmelt and Mercury Export from a Forested Catchment in the Czech Republic, Central Europe

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Abstract The annual output of filtered mercury (Hg) from Lesni potok catchment, a forested ecosystem in central Europe, was estimated at 0.87 μg m^{-2}. More than 70% of the annual mercury output flux occurred during the spring snowmelt period. The snowmelt period is the most important part of the hydrological year in central European forested ecosystems. Average filtered concentrations of mercury (17.8 ng L^{-1}) and DOC (10.5 mg L^{-1}) in the stream water during snowmelt were greater than average values for the rest of the hydrological year. Omitting frequent daily or bi-daily filtered mercury analysis during the snowmelt caused underestimation of the annual mercury output flux (0.79 μg m^{-2}) and decreased the accuracy of flux calculations.

Keywords Mercury · DOC · Snowmelt · Acidified catchment · Czech Republic

Mercury (Hg) contamination in the environment poses a serious threat to human and wildlife health (Wiener et al. 2003). Hg is a potent neurotoxin that biomagnifies in the food chain. The main exposure pathway of Hg to humans is through the consumption of fish (Leermakers et al. 2005). To date there are no advisories to limit fish consumption in the Czech Republic probably due to lack of data and information on environmental contamination with Hg. But in countries like USA and Nordic European states with extensive research in the field of environmental Hg, advisories are common. Populations that consume large quantities of fish such as subsistence fishermen have shown neurological disorders linked to Hg (Harper and Harris 2008).

Mercury enters the atmosphere from both natural and anthropogenic sources. Natural emissions of Hg originate primarily as emanations from minerals, releases during volcanic activity, sea spray and forest wildfires. Most of the atmospheric Hg is likely to be a result of anthropogenic emissions (Wängberg et al. 2007). The main anthropogenic sources of mercury to the atmosphere have been coal and oil combustion, waste combustion, production of cement and lime, production of iron or steel and chemical industry processes, e.g. chlor-alkali plants (Brandão et al. 2005).

Atmospheric deposition of Hg in Europe has declined in the past three decades (Pacyna et al. 2009) but few measurements have been made in the Czech Republic. However, the sulfur (S) emission history from coal burning in the Czech Republic has been an exceptional example by European or world standards (Kopáček and Veselý 2005). The annual emission of S reached up to 1.2×10^6 tons in the 1980s, but has since declined sharply (Kopáček and Veselý 2005). A few studies indicated a relationship between S and Hg in deposition by cluster analyses of element concentrations in mosses across the whole Czech Republic and also by principal component analysis of the same sample set (Suchara and Sucharová 2004). Moreover the area of the central Czech Republic has been exposed to historical pollution with Hg deposition originating from mining and smelting in the Příbram district (Ettler et al. 2007, 2008).

Once deposited into forested ecosystems Hg accumulates primarily in surface soil horizons and its concentration sharply decreases with depth in the mineral soil (Schwesig and Matzner 2000; Adriano 2001). The behavior of Hg in soil profiles is largely influenced by organic matter

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(Grigal 2003), and to a much lesser extent by clay content, mineralogy and by oxides of Al, Fe and Mn (Nater and Grigal 1992). Soils can also be a direct source of Hg to associated surface waters (Swain et al. 1992; Lorey and Driscoll 1999).

Previous studies emphasizing the important role of forested landscapes with respect to Hg cycling in the environment were carried out in remote areas with relatively low anthropogenic Hg emission and deposition rates (i.e. Scandinavia and North America). Very little is known about the forested watersheds in Central Europe, especially in the Czech Republic, which were exposed to higher rates of air pollutant deposition. Previous studies indicated Hg contamination of soils and ecosystems in the Czech Republic (e.g. Suchara and Sucharová 2004; Ettler et al. 2007) but provided no information concerning Hg dynamics in ecosystems.

Furthermore, Hg mobility in the environment is fundamentally tied to that of organic carbon. Hg export is linearly related to DOC export, and the Hg-DOC relation has been shown to be co-linear across multiple catchments in the USA (Shanley et al. 2002; Dittman et al. 2009).

The understanding of Hg export from forested ecosystems is essential to estimate the potential for Hg transformation processes and to evaluate the environmental risks. To our knowledge, this paper represents the first attempt to measure stream Hg export within the historically impacted area in the central Czech Republic.

Materials and Methods

Export of Hg was studied in the small (0.765 km^2) Lesní Potok (LP) catchment approximately 30 km ESE from Prague in the Czech Republic (Fig. 1). The LP catchment is in a rural setting on the northern slope of the Nature State Reserve "Voděradské bučiny" (Voděrady Beech-stands). Elevation ranges from 406 to 505 m. The catchment is 99% forested; 46% coniferous (mainly Norway spruce; Picea abies) and 53% deciduous (mainly European beech; Fagus sylvatica) typically in discrete single-species stands.

For the period 1994–2009, average annual precipitation was 681 mm and the measured annual average stream runoff was 90 mm, indicating >85% evapotranspiration (Navrátil et al. 2007). The annual average air temperature at the LP catchment is +9°C.

The catchment is underlain by two types of granite: monzogranitic Říčany type and syenogranitic Jevany type. The coarser Říčany monzogranite surrounds the circular-shaped body of the Jevany syenogranite. The mineralogical composition of both types is almost identical: ~27% quartz, ~29% orthoclase, ~35% plagioclase and ~6% biotite (Navrátil 2003). The typical soil type at the LP catchment is Cambisols with an average thickness of ~1 m. The LP catchment is drained by acidic streamwater (mean pH ~ 5.0) dominated by Ca^{2+} and SO_4^{2-}. The LP stream drains to a pond used for fish farming.

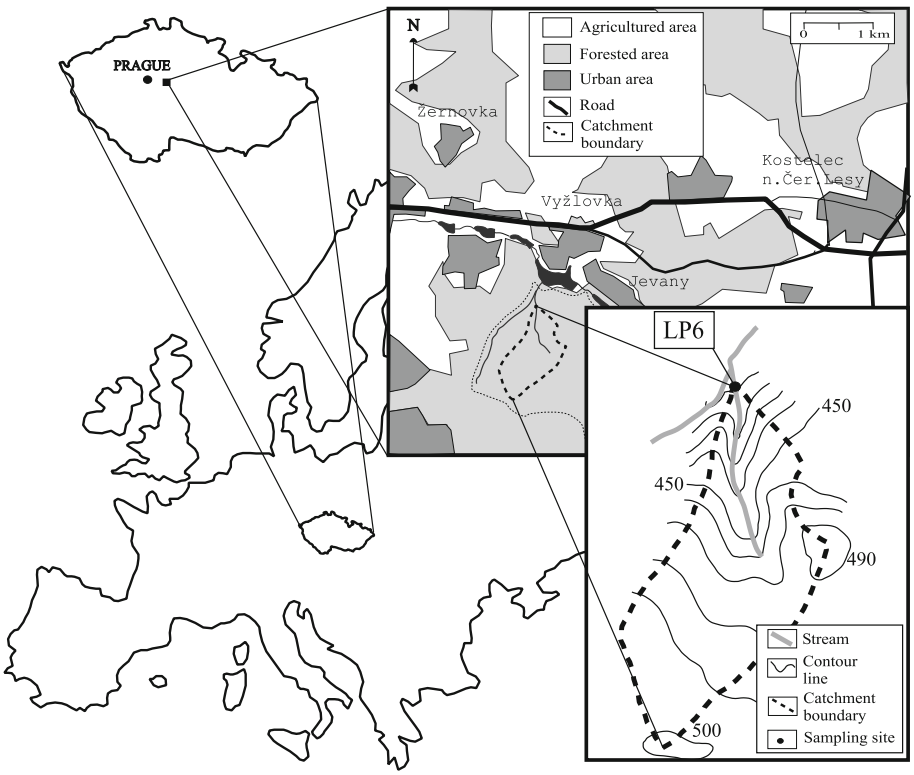

Fig. 1 Location and map of the Lesni Potok (LP) catchment and the sampling sites

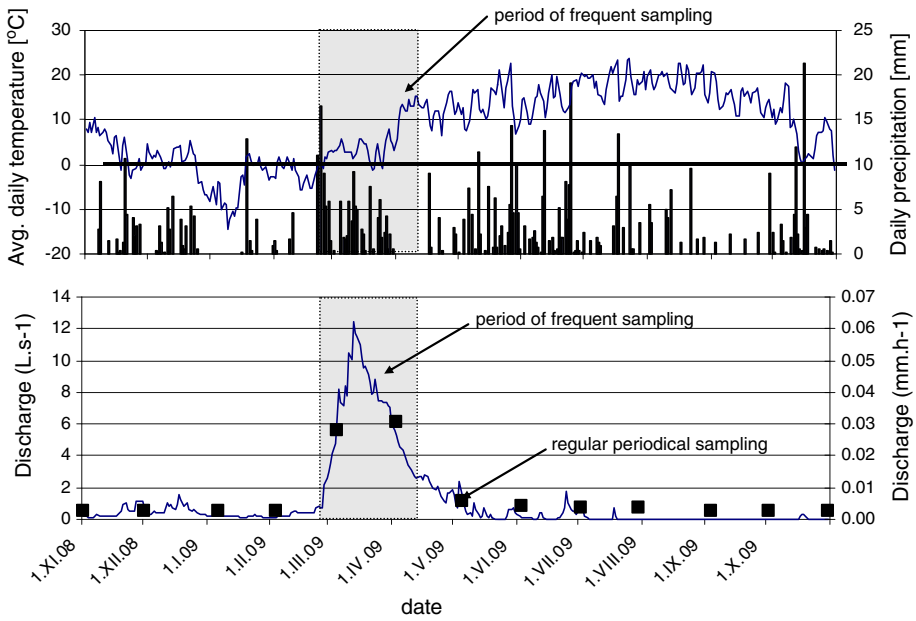

Fig. 2 *Upper panel*—Average daily temperature in °C (*solid line—left axis*) and daily precipitation in mm (*columns—right axis*) at LP catchment. *Lower panel*—Discharge in L s^{-1} (*left axis*) and mm h^{-1} (*right axis*) with snowmelt period from 27 February to 13 April 2009 denoted by *rectangle*. *Squares* denote the dates of regular periodic sampling

Catchment Lesni potok (LP) is a part of the GEOMON monitoring network administered by the Czech Geological Survey (Fottová 1995). The stream is sampled monthly in accordance with GEOMON protocols. Exclusively for the aims of this study, a period of frequent sampling (1–6 days apart) was conducted during snowmelt (27th February to 13th April 2009).

Samples were collected in dark glass bottles and transported to the laboratory. All samples were then filtered through a 0.4-μm glass fiber filter. A filtered aliquot of 150 mL was stabilized with mixture of HCl, $KBrO_3$ and KBr for Hg analysis and passed through the UV cracker (PSA 10.570, flow ~2.5 mL min^{-1}) prior to analysis by CV-AFS (PS Analytical Millenium Merlin). The QA/QC of the Hg analysis was checked against standard material ORMS-4 by the National Research Council Canada of certified value 22 ± 1 ng L^{-1} with the result 24.6 ± 1.2 ng L^{-1}.

Stream stage was measured with a float recorder at a 90-degree V-notch weir and recorded at 30-min intervals. Stage was converted to discharge using the theoretical rating verified by measurements. The regular samples of streamwater were collected just below the V-notch at site LP6 (Fig. 1).

DOC (dissolved organic carbon) was determined using a Tekmar–Dohrmann DOC analyzer at the laboratories of Czech Geological Survey, Prague. Isotopic composition of oxygen were determined on a Mat Finnigan spectrometer at the laboratories of Czech Geological Survey, Prague.

Calculation of Hg flux was calculated as:

$$\text{Hg flux} = [\text{Hg}] \times Q \quad (1)$$

Where Hg is the concentration of Hg (ng L^{-1}) and Q is the average daily watershed discharge (l day^{-1}). For days not sampled, Hg concentration was assigned from the sample closest in time. Monthly fluxes represent summed daily fluxes and annual flux is a sum of monthly fluxes. Hg yield was calculated by dividing Hg flux by catchment area (765 000 m^2).

Results and Discussion

The hydrological year at Lesni potok catchment usually has highest discharges during the snowmelt period, which typically occurs in the period from February to April (Fig. 2). The period from May to September typically has episodic increases in discharge caused by rainstorm events. The

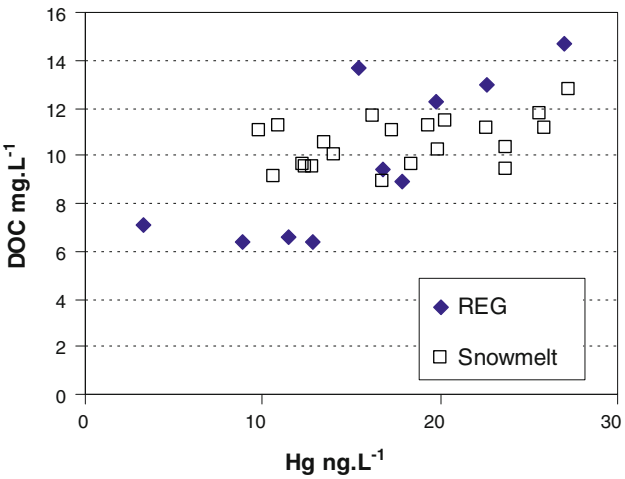

Fig. 3 Relationship of Hg and DOC concentrations in LP stream water during year 2009. *REG* regular monthly samples, *Snowmelt* period of frequent sampling

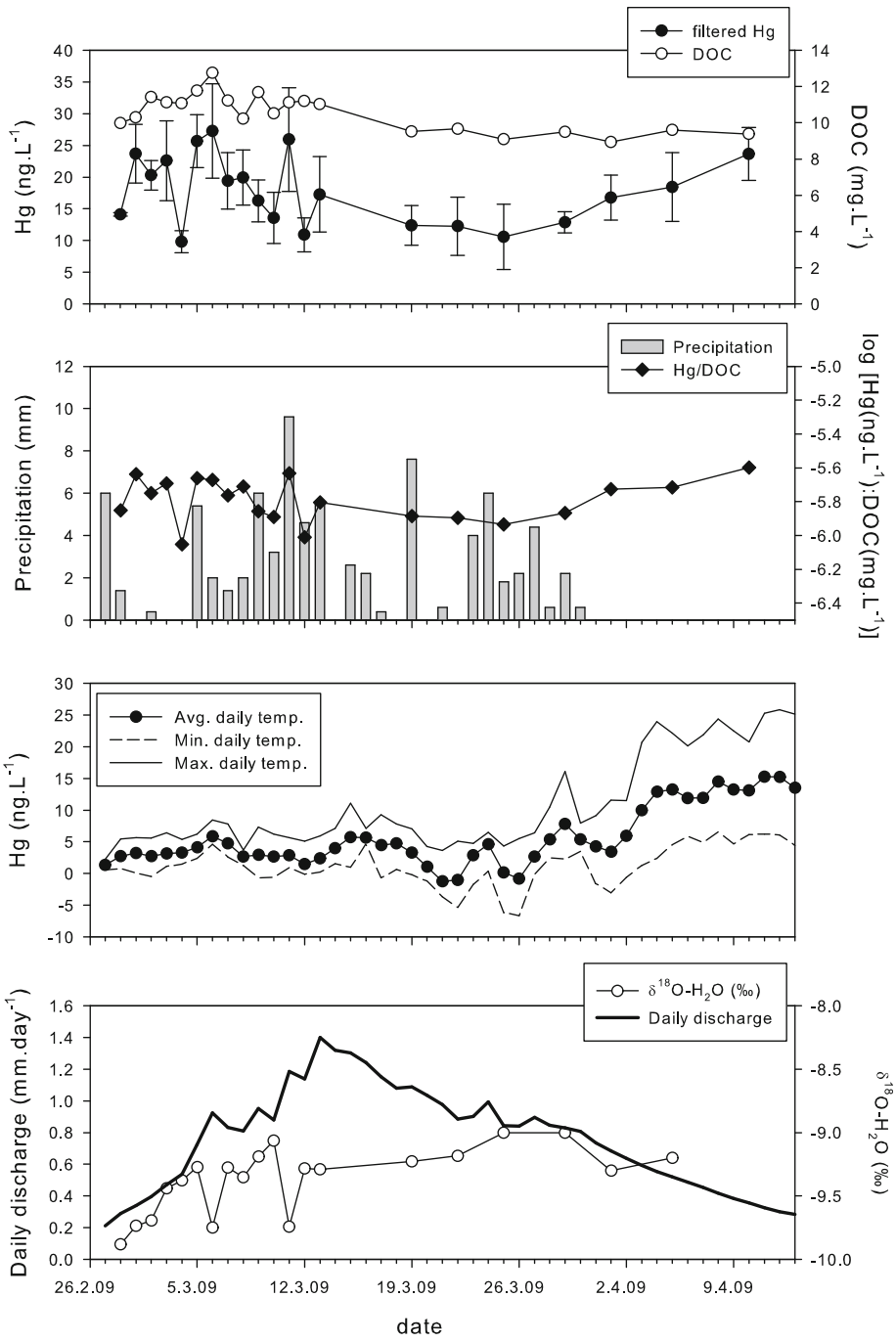

Fig. 4 Changes of selected parameters during the frequently sampled period of snowmelt at LP. *Top panel*—(*left axis*) filtered Hg concentrations, (*right axis*) DOC concentrations; *Upper middle panel*—(*left axis*) daily precipitation, (*right axis*) log of ratio Hg/DOC (both in mg L^{-1}); *Lower middle panel*—(*left axis*) average, maximal and minimal daily temperature in °C; *Bottom panel*—(*left axis*) daily discharge, (*right axis*) isotopic signatures of $\delta^{18}O\text{-}H_2O$ (‰)

lowest discharges usually occur during the period of higher temperature, which correlate with the growing season (Fig. 2). Root systems of the vegetation are able to take up most of the water due to its slow movement through the catchment. The distribution of the monthly samples according to the GEOMON protocol is shown in Fig. 2.

The concentrations of filtered Hg in the stream water of LP catchment ranged from 3.2 to 27.0 ng L^{-1} in hydrological year 2009 (November 2008 through October 2009). Hg concentrations were relatively low for the winter period (October–February) with lower DOC concentrations. During the spring snowmelt, concentrations of Hg and DOC increased due to changes in hydrology (Fig. 3). The increased concentration of DOC in the summer period (May–July) results from increased bacterial activity in the upper soil layers decomposing the forest litter and from an increased level of evapotranspiration.

Hg concentrations increased during the spring snowmelt period, especially during its initial stages (Fig. 4). Snowmelt was accompanied by rainfall, which led to

runoff increases. Isotopic signatures δ^{18}O-H_2O (‰) of individual stream samples suggested 2 days (6th and 11th March, indicated by arrows in Fig. 4—bottom panel) had the most significant contribution of atmospheric water in the stream. Hg concentrations on the 6th and 11th March were the highest of the snowmelt period. The maximum Hg concentration on the 6th of March (Fig. 4) was coincident with the first snowmelt flood crest. The subsequent decrease in discharge was due to a decrease in mean daily temperature from 4.8°C to 2.4°C on 12th of March (Fig. 4). Although the mean daily temperature of 2.4°C is above freezing, subfreezing nighttime temperatures slowed the melt. The mean daily temperature recovered back to 5.6°C on the 15th of March (Fig. 4). This increase in mean daily temperature was accompanied by periods of rainfall, increasing discharge to its snowmelt maximum values during the period from 13th to 15th of March.

From the water output point of view, 80% of the total annual runoff occurs in March and April, thus the increased concentrations of Hg and DOC concentrations magnify the Hg flux (Table 1). On the other hand, increased Hg and DOC concentrations in the period from May to July are less important for the annual total Hg and DOC export flux due to low levels of water output during these months (Table 1).

Seasonal differences in watershed hydrology represent the major driving force in terms of Hg export from forested ecosystems such as LP catchment. We calculated the annual flux of Hg using the GEOMON network protocol of 12 samples per year (Table 1). The annual output of Hg from LP catchment during the hydrological year 2009 totaled 0.610 g for a yield of 0.798 μg m^{-2}. By including data from the frequently sampled snowmelt period the annual Hg output increased to 0.668 g, yielding 0.873 μg m^{-2} (Table 1). The annual output flux of Hg from the LP catchment calculated when including data from the frequent sampling during the period of the highest annual discharge was almost 10% higher than the flux calculated using the monthly GEOMON samples only.

The relatively small difference between the two annual Hg output fluxes has been due to inclusion of two regular GEOMON sampling dates (3rd March and 1st April) within the frequently sampled period. Had the snowmelt period occurred between the regular samples, the difference between the two annual fluxes would be even greater. High-flow events at other times of the year, such as summer and fall storms, are also under-represented by the sampling protocol; accounting for these may increase the Hg flux estimate even more.

The snowmelt period during the 2009 hydrological year represented over 70% of the annual runoff. Thus the inclusion of frequent sampling during high flow periods, especially on streams with similar hydrological characteristics

Table 1 Overview of pH, Hg and DOC concentrations, discharge at time of sampling, calculated water and Hg output from the LP catchment[a]

Sampling date	Actual discharge (mm h^{-1})	pH	fil. Hg (ng L^{-1})	DOC (mg L^{-1})	Month	Water output (10^3 m^3)	Fil. Hg output (g)	Fil. Hg output (ug m^{-2})
1.12.2008	0.002	5.41	3.2	7.1	Nov-2009	1.1	0.004	0.005
6.1.2009	0.001	5.68	12.8	6.3	Dec-2009	1.7	0.021	0.028
3.2.2009	0.001	5.67	11.5	6.6	Jan-2010	0.5	0.005	0.007
3.3.2009	0.027	5.23	22.6	12.9	Feb-2010	1.3	0.029	0.038
1.4.2009	0.038	5.25	16.8	9.4	Mar-2010	21.7	0.364	0.476
5.5.2009	0.005	5.45	17.8	9.0	Apr-2010	7.6	0.135	0.176
3.6.2009	0.004	5.60	19.7	12.2	May-2010	1.4	0.027	0.035
2.7.2009	0.003	5.74	27.0	14.7	Jun-2010	0.7	0.020	0.026
30.7.2009	0.000	5.98	15.4	13.7	Jul-2010	0.3	0.004	0.006
27.8.2009	No disch.				Aug-2010	0.0	0.000	0.000
30.9.2009	No disch.				Sept-2010	0.0	0.000	0.000
4.11.2009	0.002	5.42	8.8	6.4	Oct-2010	0.1	0.001	0.001
AVG. reg. sampling	–	5.49	15.6	9.8	SUM regular sampling	36.2	0.610	0.798
AVG. reg. + frequent sampling	–	5.37	18.0	10.3	SUM regular+frequent sampling	36.2	0.668	0.873
Snowmelt—frequent sampling period	–	5.32	17.8	10.5	SUM snowmelt	25.8	0.408	0.533

[a] Bottom lines contain average values calculated from regular samples and from the frequent sampling period with appropriate outputs and fluxes

such as LP stream, will be extremely important for future projects monitoring the Hg output from forested ecosystems.

In context of filtered Hg concentrations reported by studies from uncontaminated forest ecosystems of the United States (US) averaging uniformly at 1–2 ng L^{-1} (Shanley et al. 2008) the average filtered Hg concentration reported by this paper 18 ng L^{-1} was significantly higher but the annual output fluxes of filtered Hg from US catchments ranging from 0.17 to 1.19 μg m^{-2} were comparable to the annual output flux of 0.87 μg m^{-2} (Table 1) from LP catchment. This was due to the low annual water runoff from LP catchment. Annual bulk water flux to the LP catchment ~680 mm coupled with high level of evapotranspiration ~85% causes relatively high concentrations of conservative stream solutes such as Cl^- at LP catchment (Navrátil et al. 2003).

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