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Effect of Fire on Pools of Mercury in Forest Soil, Central Europe

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Abstract In year 2006, 17.9 ha of forest was burned during a forest fire at the Bohemian Switzerland National Park found in northern part of Czech Republic (CR), central Europe. Complete combustion of organic soil (4,039 t) on the burned area caused volatilization of 1.34 ± 0.07 kg of Hg. Thus Hg emissions due to fire amounted to 75.1 g ha^{-1}. The average burned forested areas in CR for the period 2000–2006 were reported at 356 ha with estimated Hg emissions at 26.7 kg year^{-1}, while the average anthropogenic emissions in the same period amounted to 3 t year^{-1}. Thus estimated mean emissions of Hg from burned forest soil in the period 2000–2006 reached 1% of the annual anthropogenic Hg emissions.

Keywords Hg distribution in soil · Natural Hg emissions · Hg soil pools · Czech Republic

Mercury is today considered as a global pollutant that has been released into the atmosphere by both natural and anthropogenic sources. Anthropogenic Hg emissions have been fairly well quantified (e.g. Pacyna and Pacyna 2002; Pacyna et al. 2001, 2003). On the contrary, natural emissions have not been as well characterized. Natural Hg emissions originating from forest fires have been accounted as one of the important Hg non-point sources (Wiedinmyer and Friedli 2007).

Mercury enters terrestrial ecosystems via litterfall, throughfall and dry deposition. In several studies litterfall was shown to be the most important flux of Hg in forest ecosystems (Munthe et al. 1999; Rea et al. 1996; Sheehan et al. 2006). Terrestrial soils retain more than 90% of Hg currently deposited on terrestrial landscapes (Fitzgerald 1995) and represent a very large pool of Hg. In organic horizons Hg is strongly sorbed to organic matter (Yin et al. 1996; Mierle and Ingram 1991) and Hg concentrations are usually higher than in mineral soil horizons (Schwesig and Matzner 2000; Ettler et al. 2007). Nevertheless the mineral soil Hg pool is generally larger than that in the organic one (Krabbenhoft et al. 2005). Sorption, mobilization and transport mechanisms in these two pools is very different, leading to different participation in the Hg biogeochemical cycle that likely places much higher degree of importance on Hg in organic horizons (Krabbenhoft et al. 2005).

Natural mechanism redistributing Hg and affecting Hg cycling in forest ecosystems are the forest fires. During fires Hg^0 is released to the atmosphere from soils as well as from living and dead vegetation (Artaxo et al. 2000; Friedli et al. 2001). Relatively large Hg losses during forest fires result from the low volatilization temperatures (100–300°C) of Hg species (Biswas et al. 2007). The amount of Hg released during wildfire is limited by Hg accumulation prior to burning. Recent studies documented importance of forest fires in the United States (Sigler et al. 2003; Friedli et al. 2003; Engle et al. 2006; Biswas et al. 2007, 2008), contributing ∼30% to the US EPA National Emission Inventory (Wiedinmyer and Friedli 2007).

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In the Czech Republic (CR) significant anthropogenic sources of Hg to the atmosphere are reported annually (i.e., Anonymous 2007), but information on natural Hg emissions from biomass volatilized during forest fires has been estimated only once (Cinirella and Pirrone 2006). This study assesses Hg distribution in forest soils at Bohemian Switzerland National Park (BSNP) and it quantifies Hg release from soils during a single forest fire event in year 2006.

Materials and Methods

The Bohemian Switzerland National Park was established on 1st January, 2000 in northern tip of the Czech Republic (Fig. 1). It stretches on area of 79 km^2 and belongs to the unit of Bohemian Cretaceous Basin. The bedrock is formed predominantly by quartz sandstones of Turonian age. The long-term mean annual temperature is about 7°C and mean annual precipitation height is 800 mm. Forest fire due to unknown reasons begun on 22nd July 2006 and lasted for 1 week. Area impacted by the forest fire covers 17.9 ha and is found in hardly accessible terrains in altitudes from 300 to 430 m.a.s.l. The soils at BSNP were described as Albic Podzols and Podzols (WRB classification) and vegetation composed of coniferous forests with prevailing Norway spruce (*Picea abies*) and Scots Pine (*Pinus sylvestris*).

Soils were sampled at four sites in an unburned and four sites in a burned area with similar vegetation and geological substrate. Soils were sampled from 0.5 to 1.2 m deep dig pits according to the individual morphological horizons. The soil bulk density of organic horizons was determined by means of a 15 × 15 cm frame, and for mineral horizons we used core cutter method with 100 cm^3 steel rings. Underlying bedrocks were sampled at the bottom of each soil profile. Soils were freeze–dried, sieved through 2-mm polyethylene sieve and homogenized.

Soil pH was determined using a 1:2.5 (v/v) ratio of soil and deionised water suspension (Pansu and Gautheyrou 2006). Soil total organic carbon (TOC) and total sulphur (S_{tot}) were determined using a Eltra Metalyt CS1000S elemental analyser. Cation exchange capacity (CEC) was determined as the sum of basic cations and Al extracted with 0.1 M $\mathrm{BaCl_2}$ solution. Basic cations and Al were determined by flame atomic absorption spectrometry (FAAS; Varian SpectrAA 200 HT). Soil acidity was measured by back titration with 0.05 M NaOH. Oxalate-extractable Fe, Al and Mn were determined in 0.2 M ammonium oxalate/oxalic acid solution at pH 3 (Pansu and Gautheyrou 2006). The contents of oxalate-extractable Fe ($\mathrm{Fe_o}$), oxalate-extractable Al ($\mathrm{Al_o}$) and oxalate-extractable Mn ($\mathrm{Mn_o}$) in extracts were determined by ICP-OES (Thermo Elemental Intrepid II).

Analysis of total Hg was performed by cold-vapour atomic absorption spectrometry (CV-AAS) using Altec

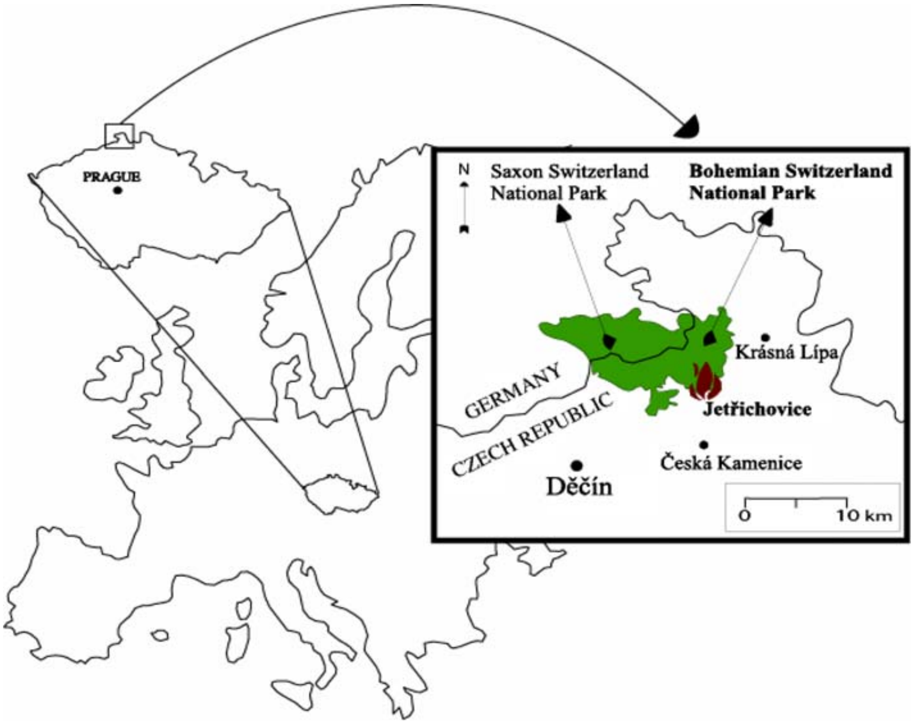

Fig. 1 The Location of Bohemian Switzerland National Park in the Czech Republic and Europe

AMA 254 Hg analyzer. The determinations were performed in triplicate (relative standard deviation (RSD) was <5%).

Quality control of Hg measurements was ensured by the analysis of standard reference material 'Soil Orthic Luvisols S-MS' produced by PB analytical (Slovakia). Each of the 42 samples was considered to be a vector with 14 variables (sample pH, CEC, total acidity, exchangeable fraction of Na, Ca, K, Mg and Al, TOC, S_{tot}, oxalate-extractable Fe, Mn and Al, concentration of total Hg). As a result, a data matrix with dimensions of 42 × 14 was used for calculation of Pearson correlation coefficients. The values lower than detection limit (DL) were removed from the dataset.

Results and Discussion

Typical soil profile of Podzols at BSNP consisted of Oi, Oe and Oa organic horizons, eluvial E, sesquioxidic Bs and C horizons. Selected physicochemical properties of studied soils are given in Table 1. All soils had acidic pH ranging from 3.2 to 4.0. Organic horizons contained >40% organic carbon, and higher concentrations of exchangeable cations than the mineral soil horizons. Grain size distribution in mineral horizons indicated a relatively constant clay fraction throughout the whole soil profile. Silt fraction increased downwards as the sand fraction decreased.

Concentrations of TOC in mineral horizons were low with slightly elevated value in the sesquioxidic Bs horizon. Increased concentrations of exchangeable Al and H^+, oxalate-extractable Fe and Al were observed in the Bs horizon (Table 1). Accumulation of Fe, Al and TOC in the Bs horizon is typically observed in Podzols.

Figure 2 shows the vertical Hg distribution in eight profiles sampled in this study and related concentrations of Hg in the bedrock (sandstone). Mercury was significantly enriched in the organic horizons (up to 633 μg kg^{-1}), whereas the maximum Hg concentration in mineral horizons E, B and C was almost ten times lower, i.e., up to 76 μg kg^{-1} (Fig. 2). Such distribution of Hg in soil profile represents typical distribution of Hg at non-contaminated sites (Navarro et al. 2005). Concentrations of Hg at BSNP in organic and mineral horizons correspond with ranges reported for central Europe by Schwesig et al. (1999) and Grigal (2003).

The correlation coefficients between total Hg concentrations and physicochemical properties of soils are given in Table 2. Due to very different matrix of organic and mineral soils we divided the dataset of all soil samples further into two groups of organic (Oi, Oe, Oa horizons) and mineral soils (E, Bs and C horizons).

Table 1 Mean physicochemical properties and Hg concentrations of individual soil horizons from eight sampled soil profiles

Horizon	Oi	Oe	Oa	E	Bs	C
Hg (μg kg^{-1})	123	364	511	16	41	8
pH	3.3	3.2	4.0	3.4	3.4	3.9
CEC (meq kg^{-1})	635	1,040	1,148	232	175	68
TN (%)	1.73	1.77	1.28	0.16	0.12	<0.05
TOC (%)	44.6	45.2	41.3	2.2	3.5	0.5
S_{tot} (%)	0.14	0.21	0.18	0.03	0.03	<0.02
Soil bulk density (g cm^{-3})		0.19^a		1.45	1.11	1.15
Grain fraction clay (%)	–	–	–	9	9	10
Grain fraction silt (%)	–	–	–	20	27	41
Grain fraction sand (%)	–	–	–	72	64	50
Exchangeable H (meq kg^{-1})	618	1,180	1,340	94	227	69
Exchangeable Na (meq kg^{-1})	6	8	9	4	4	4
Exchangeable Ca (meq kg^{-1})	123	87	52	6	9	5
Exchangeable Mg (meq kg^{-1})	18	10	7	4	3	3
Exchangeable K (meq kg^{-1})	8	7	5	3	2	2
Exchangeable Al (meq kg^{-1})	27	22	40	5	410	7
Al_o (mg kg^{-1})	1,054	3,103	7,131	4,535	6,645	4,294
Fe_o (mg kg^{-1})	1,463	4,876	7,232	3,245	9,224	2,635
Mn_o (mg kg^{-1})	139	36	13	4	5	11

CEC cation exchange capacity; *TN* total nitrogen; *TOC* total organic carbon; S_{tot} total sulfur; Al_o, Fe_o, Mn_o oxalate-extractable Al, Fe and Mn

[a] Summary value for all O horizons

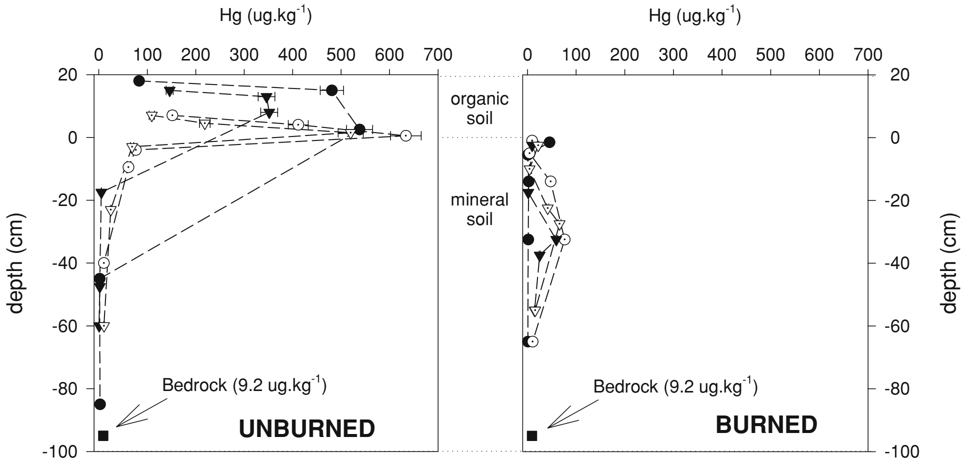

Fig. 2 Vertical Hg distribution in four unburned and four burned plots. *Error bars* indicate standard deviations

Table 2 Pearson correlation coefficients between total Hg concentration and physicochemical parameters for all soil samples (All, n = 42), organic soil samples (Organic, n = 12) and mineral soil samples (Mineral, n = 30)

	All Hg	Organic Hg	Mineral Hg
pH	−0.606	−0.899**	0.063
CEC (cation exchange capacity)	0.899**	0.762*	0.851**
TN (total nitrogen)	0.657**	−0.410	0.493
TOC (total organic carbon)	0.805**	−0.223	0.795**
S_{tot} (total sulfur)	0.824**	0.631	−0.168
Exchangeable H^+	0.942**	0.861**	0.802**
Exchangeable Na	0.237	−0.169	0.000
Exchangeable Ca	0.386	−0.728**	0.296
Exchangeable Mg	0.355	−0.568	0.275
Exchangeable K	0.272	−0.487	0.012
Exchangeable Al	0.537**	−0.028	0.517*
Al_o (oxalate-extractable Al)	0.091	0.839*	0.337
Fe_o (oxalate-extractable Fe)	0.195	0.813*	0.548**
Mn_o (oxalate-extractable Mn)	0.056	−0.602	0.007

* Statistically significant at $p < 0.1$

** Statistically significant at $p < 0.001$

In the dataset of all samples, Hg concentrations in soil correlated positively with exchangeable H^+, CEC, S_{tot}, TOC, TN and exchangeable Al. These correlations follow from significant difference between organic and mineral horizons. Increased exchangeable H^+, CEC, S_{tot}, TOC, TN and exchangeable Al result from the accumulation of organic material in the O horizons as has been reported by others (Yin et al. 1996; Ettler et al. 2007). Therefore, data were split into two groups on the basis of organic matter content (organic = Oi, Oe, Oa horizons, mineral = E, B and C horizons; see Table 2). It is noteworthy that significant correlation between Hg and oxalate-extractable Fe ($p < 0.001$) was observed for organic and mineral dataset but was absent in the whole dataset. This indicates that relationship between Hg and oxalate-extractable Fe exists but is different in organic and mineral soils. We suggest that significant correlation between Hg concentrations and TOC in mineral horizons results from transport of Hg in complexes with DOC downwards in the soil profile. Presence of organic matter may increase the CEC in mineral horizons especially in soils with a low clay content (Table 1). Correlations of Hg with TOC, CEC and oxalate-extractable Fe suggest that organic matter and amorphous Fe oxides were important traps for Hg binding at BSNP.

The Hg soil pools were calculated from soil thickness, soil bulk density and Hg concentration. Total soil Hg pools calculated at the unburned area varied from 126 to 208 g ha^{-1}. This variability may be attributed to the variability in the soil profile thickness. Thickness of the organic horizons varied from 7 to 18 cm with a mean of 12 cm (n = 20). Thickness of the mineral soil horizons ranged from 40 to 118 cm with mean value of 63 cm (n = 8). Mean Hg pools in the organic and mineral horizons calculated from data on the excavated soil profiles were comparable ranging between 83.3 and 85.5 g ha^{-1}.

Area of 17.9 ha in hardly accessible part of BSNP was burned during 1-week long forest fire in 2006 (Fig. 1). Severity of the forest fire was extreme due to the previous long period of drought. Total burnout of the organic soil horizons was reported from the burned area (Votapek and Drozd 2006). No data were available concerning the volume of standing and burned biomass on this area. Therefore, we will not include standing biomass into calculation of Hg emissions. Forest fire caused volatilization of Hg from 4,039 t of organic soil (O horizons) from an area of 17.9 ha. Using mean Hg concentration in all O horizons (Table 1) we estimated Hg emissions from the burned organic soil to be 1.34 ± 0.07 kg. Thus Hg emissions due to fire amounted to 75.1 g ha^{-1}, which is comparable to the 50–100 g ha^{-1} range reported from forest fires in Alaska (Woodruff et al. 2001). Uncertainties associated with our estimates are related especially to the variability in thickness of soil horizons of the burned area.

Mean Hg concentrations and soil bulk density of the Oa horizons at BSNP were comparable to the reported values for other forests in CR (Suchara and Sucharova 2002). Therefore, we assume that the Hg emission (75.1 $g.ha^{-1}$) from forest fire at BSNP is representative of the entire country. Using the total area (53 ha) of burned forests in CR during year 2006 (Barbosa et al. 2006), we may estimate annual emissions from this natural Hg emission source for the entire CR. The calculation yields total annual emissions of Hg from soils during forest fires in CR to be 3.98 kg in 2006. Total anthropogenic emissions in CR reported for year 2006 reached 3.7 t (Anonymous 2007). Therefore natural Hg emissions from soils burned during forest fires in CR in year 2006 were only 0.1% of the annual anthropogenic emissions.

It should be noted that in 2006 in CR, less forested areas were burned than any other year since 2000. The average burned forested areas in CR for the period 2000–2006 are estimated at 356 ha with Hg emissions at 26.7 kg, while the average anthropogenic emissions in the same period amounted to 3 t $year^{-1}$ (Anonymous 2007). Estimated mean emissions of Hg from burned soil in the period 2000–2006 reached 1% of the annual anthropogenic Hg emissions.

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