LEVELS AND FATE OF PERSISTENT ORGANIC POLLUTANTS IN MOUNTAIN SOILS

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Introduction

The Czech Republic is a country, in which industrial development has led to a variety of negative environmental implications in the past forty years. Large amounts of polychlorinated biphenyls (PCBs), technical hexachlorocyclohexane (HCH), lindane (γ-HCH), *p,p'*-DDT and hexachlorobenzene (HCB) were produced between 1950s and 80s. Due to their long-term application, all of these persistent organic pollutants (POPs) are still detectable in abiotic and biotic environmental compartments, especially in soils.

Soil plays an important role in the global fate and distribution of POPs. Detailed soil screening in the Czech Republic as a typical Central European country clearly differentiated between arable, grassland and forest soils [1], and showed that due to the global atmospheric transport, the mountain ecosystems reach higher contamination levels than those found in urban and industrial regions. For example, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) concentrations were 20 times higher in mountain forests than those found in arable and grasslands soils. A high capacity of coniferous needles to scavenge and accumulate atmospheric pollutants from the gas phase, fine particle phase and wet deposition, together with transport to the soil with plant litter is partially responsible for these findings. A high accumulation potential of carbon-rich soils may also be an important factor.

PCDDs/Fs present a problem not only because of their high levels in the mountains, but also due to their immobility (strong sorption to organic matter) and extreme stability (half-lives between 5 and 100 years) in soils [2,3]. Even though there has been a number of regulations and international measures successfully lowering the atmospheric levels of toxic compounds in recent years, we can speculate whether we can also expect to see a decline of POPs in the mountain soils. Here we present a long-term study where PCDDs/Fs were investigated in the range of mountain soils over a 12 years period.

Materials and Methods

Sample collection: Eight mountain soil sampling sites were selected in the Czech border mountains for studies in 1995, 2001 and 2007 (Figure 1). Six sites (mountains Krusne hory, Luzicke Hory, Krkonose) were located in a region that is known as a "black triangle", area historically characterized by large numbers of coal power plants. One sampling site was to the northeast of the country where Beskydy mountains are impacted by antropogenic activities in the Czech and Polish parts of Silesian region, especially by coal mining and iron smelting industries. The sampling site in Sumava mountains in the southern part of the country was chosen as a clean reference region where the low concentration of PCDDs/Fs were confirmed recently [4]. Two inland sampling sites representing forest soils other than mountain ecosytems: a highland rural background station of European Monitoring and Evaluation Programme (EMEP) in Kosetice, and a lowland industrial background site, Mokra near the city of Brno.

Each site was represented by ten sub-samples of the top soil layer (organic horizon) collected from an area of 25×25 m in 1995 and 2001. Both, organic and mineral soil horizons were sampled at all mountain forest sites in 2007. All soil samples were transported to the laboratory, air-dried at laboratory temperature, and sieved through 2-mm mesh. PCDDs/Fs were analyzed in the soil samples from all three campaigns. In addition, the levels of other compounds from major POP groups were determined in the soil profiles in 2007.

Analysis: Toluene extraction was used for PCDDs/Fs analysis. Samples were cleaned-up using a sulfuric acid/silica - sodium hydroxide/silica - activated silica mixed column. A fractionation of PCDD/Fs from PCBs was achieved on an alumina column. Final analysis was performed on a HRGC-HRMS system. Methodology applied in 2007 was the same as used for PCDD/F analysis in the soil, needle and air samples in 1993, 1995 and 2001 and has been described earlier [5-7]. For other POP analyses, all soil samples were extracted with dichloromethane. Fractionation was achieved on a silica gel column; a sulfuric acid modified silica gel column was used for PCBs/OCPs samples. Samples were analyzed using a GC-MS for 16 US EPA polyaromatic hydrocarbons (PAHs), seven indicator congeners of polychlorinated biphenyls (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) as published previously [8, 9]. Recoveries of PCBs and PAHs were determined by spiking all samples with the surrogate standards prior to extraction. Recoveries were higher than 81 % and 76 % for PCBs and PAHs, respectively.
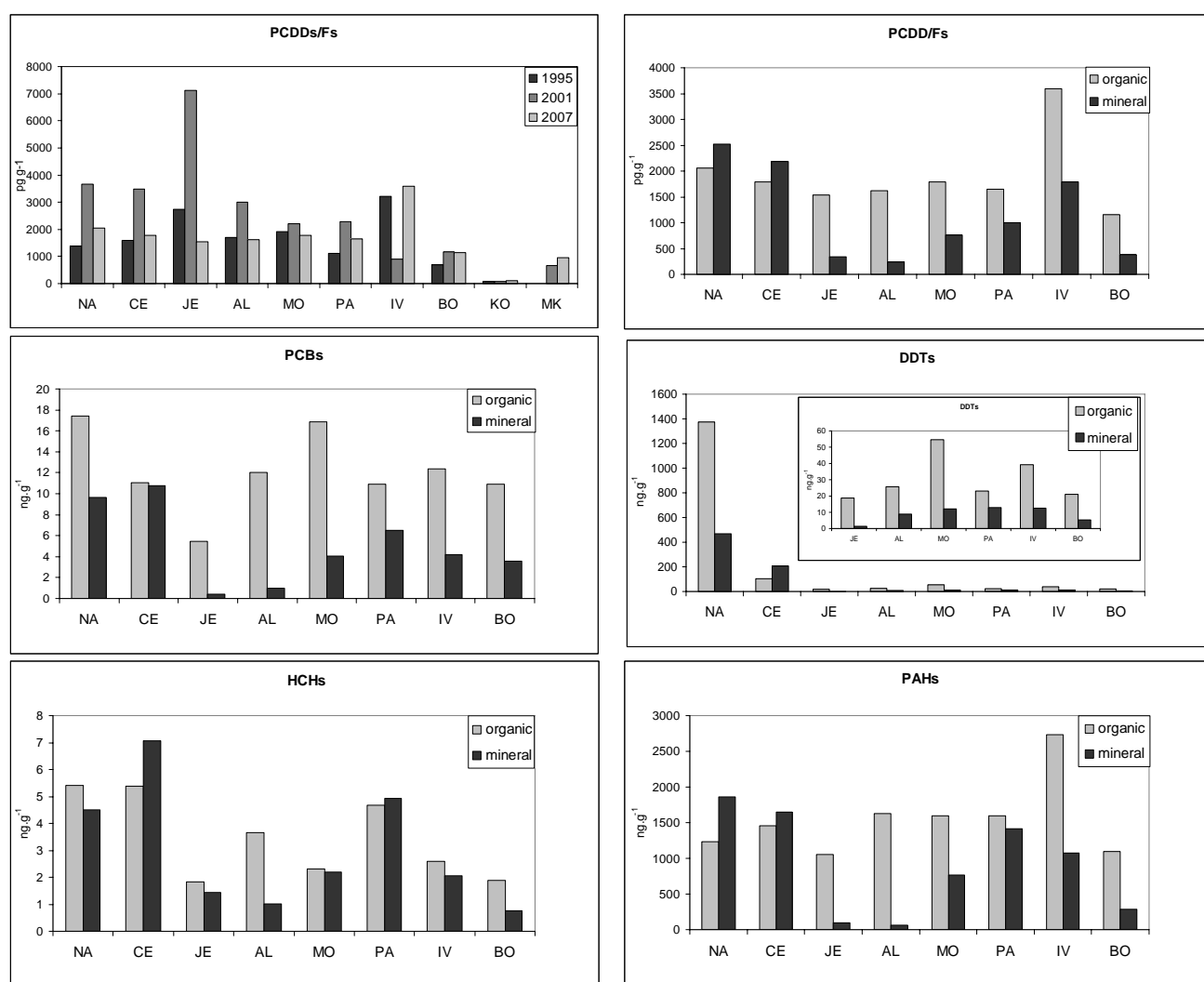
Results and Discussion

Figure 1. POP levels observed in soils. Sites NA – BO represent mountain sites, KO = Kosetice, MK = Mokra. First graph: concentration levels at studied sites in the individual years; following graphs: comparison between organic and mineral horizon for samples from year 2007

PCDDs/Fs levels: The concentrations of PCDDs/Fs in soil samples from 1995 ranged between 694 and 3 220 pg g^{-1} (Boubin and Ivancena, respectively). The concentrations of PCDDs (303–1 104 pg g^{-1}) were significantly lower than the contribution of PCDFs (392–2 482 pg g^{-1}). In 2001, the concentrations of PCDDs/Fs in soils were in the range of 894–7 133 pg g^{-1}. Expressed as toxicity equivalents (TEQs), the total TEQs of PCDDs/Fs were between 19.2 and 141.6 pg TEQ g^{-1}. OCDD and OCDF were the most abundant congeners in both sets of samples. Soils from this campaign were also analyzed for a total organic carbon (TOC) content and the TOC values ranged between 30 and 40% in all samples except for one (8%). In 2007, the levels of PCDDs/Fs in the organic soil horizon ranged between 1 149 and 3 587 pg g^{-1}, expressed in TEQ values between 19.4 and 79.8 pg TEQ g^{-1}. The contents of PCDDs were lower than PCDFs (479–833 pg g^{-1} for PCDDs, 670–2 754 pg g^{-1} for PCDFs), OCDD and OCDF dominated again. An increase of the soil concentrations between 1995 and 2001 followed by a decrease in 2007 is typical for all sampling sites connected to the black triangle. In 2001, the mountain forest soil did not reflect declining atmospheric concentrations of PCDDs/Fs connected to the closure of some power plants in the late 1990s; however, the first signs of this trend were observable in 2007. The PCDD/F concentration was much lower at the reference sites than it was in the mountains for all sampling campaigns, even though a continuous slight increase of PCDDs/Fs levels was observed there between 1995 and 2007. A fact, that all mountain soils manifested higher PCDDs/F concentrations than the rural background site Kosetice, but also than the industrial background site Mokra (see Figure 1), is an interesting finding.

Soil profiles: To further explore whether the temporal trends observed in three soil sampling campaigns can be also identified in the soil profiles, both, organic (upper) and mineral (lower) horizons were sampled in 2007. A set of the sampling sites was identical to the previous studies (1995 and 2001). In addition to PCDDs/Fs, other major groups of POPs (PAHs, PCBs) were analyzed as well. The concentration levels of investigated chemicals in the organic and mineral horizons are shown in Figure 1. The organic carbon content varied from 21 to 42% in the organic and from 6 to 43 % in the mineral horizons. While a decrease in the organic carbon content from the organic to mineral horizons was observed at most of the sites, there were also two sites where upper and lower soils had comparable levels of the organic carbon. This is also reflected in the soil contamination record. The concentrations of PCDDs/Fs in the soil profile manifested a pattern highly similar to the one of PAHs, which indicates similar sources of these compounds. On the other hand, concentration profiles of PCBs or DDTs differed from those of PAHs and PCDDs/Fs.
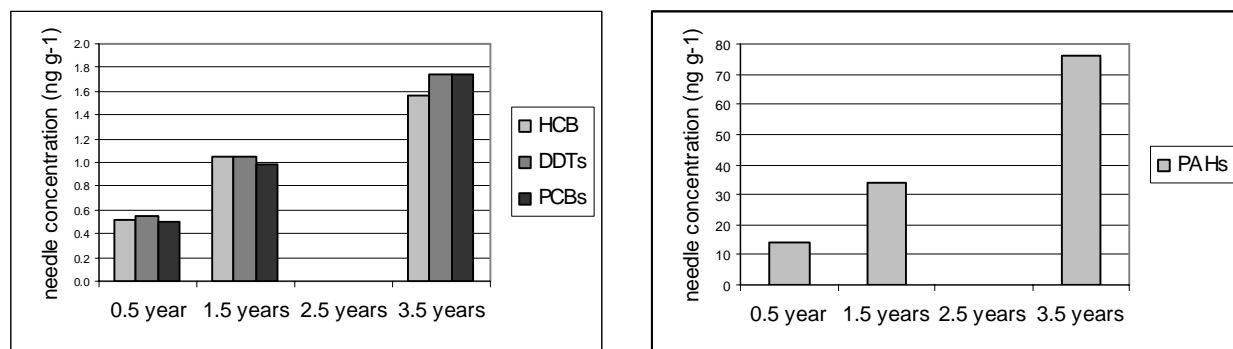

Figure 2. POP concentrations (PCBs, DDTs, HCB, PAHs) determined in pine needles of various ages (0.5, 1.5, 3.5 years)

One has to understand a fate of organic compounds in the forest ecosystems, especially in soils during the humification and mineralization processes in order to decode a record of historical contamination hidden in soil. A forest soil formation process is strongly site specific and cannot be easily generalized. Atmospheric POPs are captured by coniferous needles during their entire life span (3-6 years) and transported to the forest soil with a litter. Figure 2 shows an increase of POP concentrations in needles of various ages [10]. Formation of the F-H horizon strongly depends on the extent of tree defoliation. In a spruce forest, for instance, the annual litter mass has been determined to be about 400 g m^{-2} yr^{-1} [11]. A thickness of this layer is approximately 3 cm given a bulk

litter density of 0.1 g cm^{-3}. The carbon remaining in the forest floor declines abruptly in the first year by about 37% [11]; thereafter, it declines at a rate corresponding to a half decay time of 3.9 years. The humic substance fraction increases during the first year and declines in following years, humic substance in the forest floor decomposes at a somewhat slower rate of 5.1 years [11]. All humification processes depend on temperature, precipitation, humidity, catalytic activity of the soil and other environmental factors. Total carbon is gradually lost from the forest floor by mineralization, leaching of dissolved organic matter, downward movement of fine particles and export by invertebrates. The major pathways were estimated to be mineralization (69.7%) and leaching (22.8%). Moore and Gholz [12, 13] reported that after 3 years about 56 to 60% of the original litter mass was still remained; Qualls [11] determined in the field experiments that 93% of carbon was lost after 13 years. This was a time period during which the organic horizon has turned into the mineral horizon. Results of these experiments prompt that pollutants captured in needles can be found in the litter layer on the forest floor (which is usually not sampled) in about four years. After another four years of litter decomposition they become a part of the F-H horizon. Consequent transformation of the organic horizon to mineral horizon indicated by a decline of the organic carbon content may last at various experimental conditions from 10 to 100 years. This implies difficulties in determination of the age of contamination in forest soils.

Acknowledgements

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