The occurrence of PCDDs/Fs in high-mountain ecosystems of the Czech Republic*

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Introduction

Many organic air pollutants including of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/Fs) with long half-life times are distributed between different environmental compartments to reach equilibria governed by physical properties of the individual compounds. Many of the organic compounds in the environment, are persistent, bioaccumulative and posses toxic (so called PBTs). Bioaccumulation can lead to the lipid rich tissue of biota, and subsequent biomagnification in the food chain. Atmospheric transport and wet and dry deposition are important pathways for these substances into terrestrial and aquatic ecosystems [1-3]. The predominant part of the long-range transport takes place in the atmosphere. After deposition, in the case of wet deposition, vapour-phase and dissolved-phase PCDDs/Fs movement into soils is controlled by the equilibrium sorption/desorption process between the soil compartments (air, water, mineral, and organic matter) [4]. Soil contamination is one of the long-term environmental problems generated by many anthropogenic activities of the last decades [5]. For non-polar organic pollutants, the equilibrium favours sorption to the organic carbon in the soil.

Persistent organic pollutants (POPs) could effect forest trees either directly by diffusion into interior leave parts or indirectly through a change in soil properties and soil biota. They can enter forest trees by a root uptake from the contaminated soil followed by translocation in the plant by the xylem and by gas-phase and/or particle-phase deposition onto the waxy cuticle of needles or by uptake through the stomata. The phloem translocation then follows. These pathways are a function of the physical and chemical properties of the pollutants, environmental conditions (ambient temperature, organic content of the soil, the plant species determines the surface area and lipids available for accumulation [6-8]. The green parts of higher plants, such as pines, are covered with a lipophilic epicuticular wax. This lipophilic surface is an excellent sorbent for semi-volatile POPs, which consequently are found in plants wherever collected [9]. Conifer needles may serve as passive biomonitors for airborne pollutants by reflecting the average contamination profiles in the air [10].

Sampling sites, methods

We have investigated the effects of some anthropogenic organic pollutants, e.g. polycyclic aromatic hydrocarbons, chlorinated pesticides, polychlorinated biphenyls, dibenzo-p-dioxins and dibenzofurans on high-mountain spruce ecosystem of Czech Republic. Sampling sites were located in czech boundary high-mountain ecosystems (Krkonoše, Krušné hory, Lužické hory, Šumava, Beskydy) [11]. The main goal of this study was the description of this model ecosystem (air, needles, soil) from the point of view of POPs content in selected ecosystem compartments and their bioavailability for the spruce trees. The analysis was focused to ambient air, humus soil horizons and two compartments of the spruce needles (cuticular wax and the rest of needles). The six permanent research plots with Norway spruce in the Krkonoše Mts. were used in the first sampling campaign in 1994 (only soil samples were collected and analysed) [2]. Three sampling sites in the Krkonoše Mts., one in the Šumava Mts., two in the Krušné hory Mts., one in the Lužické hory Mts., and one in the Beskydy Mts. were selected for the second sampling campaign in autumn 1995 [11]. During this second campaign, the ambient air, soils and needles samples were collected and analysed.

In addition, air samples were collected by using of mobile high-volume samplers TOCOEN Ltd. with polyurethane foam. Samples were collected at eight open air places, as such as possible neighbouring to the permanent plots, according to the source of electric power. The content of POPs in selected organic soil horizons and Norway spruce needles were analysed in eight Montana Norway spruce (Picea abies /L./ Karst) in these sites. Samples were taken in adjacent places of the permanent research plots, where the response of forest stands to multiple stress impacts have been followed for several years. Soil samples were collected from humus horizons F and H, from the depth about 3 - 8 cm, under grass stand formed by dominant species Calamagrostis villosa. Soil samples were air dried and sieved through 2 mm mesh steel screen. Spruce needles were sampled from the windward branch of the seventh whorls (or in the case of broken or dwarf tops from the whorls in similar position - the border of upper fifth of the crown). All three-year-old needle sets were cut and air dried.

The main goal of these experiments were recognising the contribution of long-range transport of persistent organic compounds to the critical loading of the environment. The advantage of this high-mountains plots was fact, that the long-range atmospheric transport was dominated source of these pollutants in these experimental sites (they are more than 700 and half of them 1,000 m over the see). Norway spruce is dominating forest tree types in czech forests, from this reason the spruce needles were selected as model bioaccumulating system. The use of spruce needle concentration does not take into consideration that there are different conditions of uptake for lipophilic organic pollutants between different tree-species [12]. The basic description of research plots used in the second campaign is in Table 1.

The chemical analysis was done by the isotope-dilution-method with ^{13}C surrogates for all 17 2,3,7,8-substituted congeners. Samples after soxhlet extraction and clean-up procedure were analysed for contents of PCDDs/Fs the measuring with HRGC/HRMS methods. The clean-up procedure and PCDDs/Fs analysis were carried out according to Schramm *et al.* [13, 14].

Table 1: Basic characteristic of studied areas and forest stands

Number of site	Mountains	Plot	Altitude [m a.s.l.]	Exposure decline [°]	Bedrock	Soil type	Age of growth [y]
1	Šumava	Boubín	1,300	NNW/5	Migmatite	Cambisol Podsolic	145
2	Krušné hory	Načetín	760	NW/3	Granite	Cambisol Podsolic	65
3		Červená jáma	870	SE/3	Granite	Cambisol Podsolic	63
4	Lužické hory	Jedlová	710	NW/24	Granite	Podsol	40
5	Krkonoše	Mumlava	1,190	SW/5	Granite	Podsol	80
6		Pudlava	1,140	S/12	Granite	Podsol	102
7		Pašerácký chodníček	1,310	SW/12	Mica Schist	Cambisol Cryptopodsol	145
8	Beskydy	Kykulka	900	NW/22.5	Sandstone	Cambisol	105

Results and discussion

We have studied pathways of high-mountain forest ecosystems contamination by POPs in boundary czech mountains. Our previous results have described the potential combined inputs of organochlorines and other POPs to forest soils. The first is probably long-range transport from the sources inside and outside of this region and the second can be from the forest composting processes [3, 12]. The first part of results from the second campaing is shown in Tables 2-4. Table 2 describes observed values of groups of PCDDs/Fs homologous concentrations in ambient air, pine needles and soils, Tables 3 and 4 describe the contents of 2,3,7,8-substituted congeners of PCDDs/Fs in the same types of environmental matrixes from the whole sampling network.

PCDDs/PCDFs are present in ambient air (24 hrs sampling time) on all sampling sites. The values are comparable to the values measured at the Košetice station (mean value in 1994 - 1995 0.384 $pg.m^{-3}$ with the slightly decreasing tendency in the recent years). The highest value has been found again on the locality Lužické hory mountains (0.816 $pg.m^{-3}$), second highest is the Krkonoše mountains (0.323 $pg.m^{-3}$) and the third highest has been found in the Krušné hory mountains (0.264 $pg.m^{-3}$). Although we have expected certain increased values in Krkonoše and Krušné hory mountains, the high pollution of Lužické hory mountains was surprising. PCDDs dominate in all ambient air samples. Concentrations were in the range with lowest and highest values of 0.033 and 0.816 pg Σ $TEQ.m^{-3}$, respectively. We can compare this data with data for example from UK where the concentrations of PCDDs/Fs were in the range with lowest and highest values of 0.025 and 1.410 pg Σ $TEQ.m^{-3}$, respectively [14].

The concentrations of PCDDs/PCDFs in the spruce needles are more interesting. The highest value has Beskydy mountains (14.30 $pg.g^{-1}$) followed by Lužické hory mountains again (10.14 $pg.g^{-1}$) and Krušné hory mountains (9.62 $pg.g^{-1}$). The PCDDs/PCDFs ratios are in the range from 20:1 to 1.6-1.1:1. Only one exception is Beskydy mountains, where the ratio is

quite opposite (1:4.5), which reflects most probably mining and smelting activity in Ostrava region. The similar ratio PCDDs/PCDFs 1:3.4 we have observed in the soils from this locality.

Due to long-time accumulation of PCDDs/PCDFs in the soils, their concentration is much higher compare to the "background value" (5 $pg.g^{-1}$ TEQ). The highest concentration is in Beskydy mountains (3 220.13 $pg.g^{-1}$, 49.24 $pg.g^{-1}$ TEQ) followed by Lužické hory mountains (2 727.13 $pg.g^{-1}$, 44.01 $pg.g^{-1}$ TEQ), but the highest toxicity has Krkonoše mountains (53.51 $pg.g^{-1}$). We will get the value which should be monitored at least, from the point of view of the future development of the whole high mountain ecosystem.

Conclusions

The high mountain spruce forest ecosystem is heavily polluted by POPs, especially mountains in north part of Czech Republic, mainly Lužické hory Krušné hory, and Krkonoše mountains. These boundary mountains represent the southern part of the "Black triangle". The content of POPs in high-mountain spruce ecosystem is about one order of magnitude higher compare to the lowlands. The measured concentration have reached the values which should be monitored in order to forecast the future development of the whole high mountains ecosystem and biological effects of the POPs.

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Table 2: Concentrations of PCDDs/Fs in ambient air, spruce needles and soils
czech boundary high mountains ecosystems

	Σ Ds/Fs	Σ Fs	Σ T-Fs	Σ Pe-Fs	Σ He-Fs	Σ Hp-Fs	OCDF	Σ Ds	Σ T-Ds	Σ Pe-Ds	Σ He-Ds	Σ Hp-Ds	OCDD
Concentration of PCDDs/Fs in ambient air (pg/m3)													
Churáňov (S)	0.1182	0.0322	0.0313	< 0.0003	< 0.0003	< 0.0003	0.0009	0.086	< 0.0003	< 0.0003	< 0.0003	0.0083	0.0777
Načetín (KH)	0.1028	0.0016	< 0.0003	< 0.0003	< 0.0003	0.0006	0.001	0.1012	< 0.0003	< 0.0003	0.0009	0.0058	0.0945
Hotel Lesná (KH)	0.2643	0.003	< 0.0003	< 0.0003	0.0007	0.0009	0.0014	0.2613	0.0029	< 0.0003	0.0012	0.0088	0.2484
Jedlová (LH)	0.8163	0.1478	0.0723	0.0163	0.0215	0.0141	0.0237	0.6685	0.0144	0.0069	0.0149	0.0782	0.5542
Růžová hora (K)	0.0573	0.0025	< 0.0003	< 0.0003	0.0007	0.0004	0.0015	0.0547	< 0.0003	< 0.0003	0.001	0.0032	0.0505
Labská bouda (K)	0.3231	0.0022	< 0.0003	< 0.0003	< 0.0003	0.0011	0.0011	0.3209	< 0.0003	< 0.0003	0.0008	0.0069	0.3132
Výrovka (K)	0.0566	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	< 0.0003	0.0566	< 0.0003	< 0.0003	< 0.0003	0.0034	0.0532
Bílý kříž (B)	*0.0381*	*0.0016*	*< 0.0003*	*< 0.0003*	*0.0004*	*0.0004*	*0.0008*	*0.0365*	*< 0.0003*	*< 0.0003*	*0.0007*	*0.0029*	*0.033*
Concentration of PCDDs/Fs in spruce needles (pg/g)													
Boubín (S)	2.75	1.08	0.62	0.23	0.17	0.06	< 0.01	1.67	0.01	0.01	0.16	0.17	1.31
Načetín (KH)	4.69	2.22	1.55	0.42	0.21	0.04	< 0.01	2.47	0.01	0.04	0.26	0.39	1.77
Červená jáma (KH)	9.62	0.46	0.24	0.1	0.09	0.03	< 0.01	9.16	< 0.01	0.03	0.6	0.42	8.11
Jedlová (LH)	10.14	2.72	1.03	0.73	0.53	0.43	< 0.01	7.42	0.01	0.04	0.76	1.48	5.13
Pudlava g (K)	0.86	0.12	0.09	0.01	< 0.01	0.02	< 0.01	0.74	< 0.01	< 0.01	< 0.01	0.13	0.61
Mumlavská hora (K)	6.73	0.79	0.32	0.18	0.19	0.09	0.01	5.94	< 0.01	< 0.01	0.07	0.36	5.5
Pašerácký chodníček g (K)	0.93	0.2	0.16	0.02	0.01	0.01	< 0.01	0.73	< 0.01	< 0.01	0.03	0.09	0.61
Bílý Kříž (B)	14.3	11.7	6.25	3.65	1.4	0.41	< 0.01	2.6	0.01	0.07	0.52	0.57	1.42
Concentration of PCDDs/Fs in soils (pg/g)													
Boubín g (S)	624.51	391.97	96.66	70.94	83.82	35.33	35.23	302.53	5.8	12.24	28.29	62.33	193.87
Načetín g (KH)	1386.5	824.94	286.13	221.2	166.64	71.15	79.82	561.56	50.65	53.38	59.77	97.44	300.32
Červená jáma g (KH)	1584.88	922.95	371.17	233.04	173.92	75.17	69.65	661.93	69.92	62.34	65.55	118.34	345.78
Jedlová g (LH)	2727.13	1623.59	510.3	406.39	305.42	179.71	221.76	1103.54	88.82	91.5	122.27	185.56	615.39
Pudlava g (K)	2468.51	1448.54	383.2	333.03	372.05	173.39	186.86	1019.97	56.13	73.18	106.12	187.21	597.34
Mumlavská hora (K)	1836.05	1037.62	328.03	274.95	208.61	109.16	116.87	798.43	42.12	62.59	86.25	150.35	457.12
Pašerácký chodníček g (K)	1107.61	645.7	208.2	162.29	137.86	63.12	74.22	461.91	26.81	42.53	47.79	86.15	258.64
Pašerácký chodníček x (K)	1741.4	943.3	342.31	277.94	179.71	73.9	69.45	798.1	45.67	58.18	80.79	144.99	468.46
Ivančena g (B)	3220.13	2481.86	432.71	407.13	446.11	344.07	851.84	738.27	47.24	66.66	72.01	130.01	422.34

S = Šumava, KH = Krušné hory, LH = Lužické hory, K = Krkonoše, B = Beskydy
g = soil overgrown by grass, x = soil without grass

Table 3: Concentration of 2378-substituted PCDDs in ambient air, spruce needles and soils, czech boundary high mountains ecosystems

	2378-T	12378-Pe	123478-He	123678-He	123789-He	1234678 Hp
Concentration of 2378-substituted PCDDs in ambient air (pg/m3)						
Churáňov (S)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0061
Načetín (KH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,026
Hotel Lesná (KH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,006
Jedlová (LH)	< 0.01	< 0.01	< 0.01	0,0025	< 0.01	0,0485
Růžová hora (K)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0022
Labská bouda (K)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0036
Výrovka (K)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0019
Bílý kříž (B)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0019
Concentration of 2378-substituted PCDDs in spruce needles (pg/g)						
Boubín (S)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,05
Načetín (KH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,14
Červená jáma (KH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,11
Jedlová (LH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,4
Pudlava g (K)	0.07	< 0.01	0.01	< 0.01	< 0.01	< 0.01
Mumlavská hora (K)	0.14	0.01	0.05	0.01	0.01	< 0.01
Pašerácký chodníček g (K)	0.07	< 0.01	0.01	< 0.01	< 0.01	< 0.01
Bílý Kříž (B)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,17
Concentration of 2378-substituted PCDDs in soils (pg/g)						
Boubín g (S)	0,01	1,3	1,27	2,84	2,13	30,32
Načetín g (KH)	0,21	2,49	3,35	4,78	3,78	47,68
Červená jáma g (KH)	1,93	3,49	3,62	6,09	4,37	57,69
Jedlová g (LH)	2,11	5,85	6,13	9,9	8,76	93,56
Pudlava g (K)	8,43	5,5	6,01	9,71	6,52	98,32
Mumlavská hora (K)	0,22	4,18	4,72	7,3	7,07	76,32
Pašerácký chodníček g (K)	< 0.01	2,14	2,05	4,28	3,48	44,02
Pašerácký chodníček x (K)	0,21	3,76	3,99	7,24	5,83	72,14
Ivančena g (B)	0,62	4,43	5,19	6,68	5,46	65,39

S = Šumava, KH = Krušné hory, LH = Lužické hory, K = Krkonoše, B = Beskydy
g = soil overgrown by grass, x = soil without grass

Table 4: Concentration of 2378-substituted PCDFs in ambient air, spruce needles and soils, *czech boundary high mountains ecosystem*

	2378-T	12378/48-Pe	23478-Pe	123478/9-He	123678-He	123789-He	234678-He	1234678-Hp	1234789-Hp
Concentration of 2378-substituted PCDFs in ambient air (pg/m3)									
Churáňov (S)	0,001	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Načetín (KH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0006	< 0.01
Hotel Lesná (KH)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0007	0,0009	< 0.01
Jedlová (LH)	0,0033	0,0018	0,0016	0,002	0,001	ND	0,005	0,0128	< 0.01
Růžová hora (K)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0007	0,0004	< 0.01
Labská bouda (K)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0011	< 0.01
Výrovka (K)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Bílý kříž (B)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,0004	0,0004	< 0.01
Concentration of 2378-substituted PCDFs in spruce needles (pg/g)									
Boubín (S)	0,3	0,03	0,04	0,01	0,01	< 0.01	0,03	0,06	< 0.01
Načetín (KH)	0,75	0,05	0,1	0,01	0,01	< 0.01	0,03	0,04	< 0.01
Červená jáma (KH)	0,06	0,01	0,01	0,01	0,01	< 0.01	0,01	0,03	< 0.01
Jedlová (LH)	0,57	0,14	0,17	0,04	0,07	< 0.01	0,07	0,43	< 0.01
Pudlava g (K)	< 0.01	0,02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,06
Mumlavská hora (K)	0,04	0,09	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,13
Pašerácký chodníček g (K)	0,01	0,01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0,04
Bílý Kříž (B)	1,64	0,56	0,75	0,13	0,18	< 0.01	0,16	0,41	< 0.01
Concentration of 2378-substituted PCDFs in soils (pg/g)									
Boubín g (S)	12,13	9,59	10,24	11,65	8,9	0,73	8,71	25,04	3,69
Načetín g (KH)	10,5	21,99	15,43	21,39	16,63	2,56	14,01	48,46	8,36
Červená jáma g (KH)	20,42	23,7	17,88	22,74	17,69	2,03	15,89	52,06	8,41
Jedlová g (LH)	27,42	44,17	32,4	51,11	36,82	3,93	29,59	126,56	16,79
Pudlava g (K)	36,26	42,18	37,32	50,79	37,6	5,48	31,9	119,8	16,55
Mumlavská hora (K)	16,8	27,79	21,94	31,77	22,92	2,21	20,07	74,46	11,48
Pašerácký chodníček g (K)	12,98	16,11	13,38	18,38	13,82	2,22	12,31	42,37	7,89
Pašerácký chodníček x (K)	19,27	24,07	19,27	24,11	19,09	1,23	17,09	52,21	7,02
Ivančena g (B)	31,89	46,85	36,14	69,3	46,01	10,74	37,14	247,43	35,11

S = Šumava, KH = Krušné hory, LH = Lužické hory, K = Krkonoše, B = Beskydy

g = soil overgrown by grass, x = soil without grass