

## Correlation of PCDD/F and PCB Concentrations in Soil Samples from the Swiss Soil Monitoring Network (NABO) to Specific Parameters of the Observation Sites

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### Introduction

Soils are natural sinks for persistent organic pollutants (POPs) such as polychlorinated dibenzo-*p*-dioxins (PCDD/F) and polychlorinated biphenyls (PCB). Being lipophilic compounds, these contaminants adsorb to the organic carbon of the soil, and due to the low mobility and high persistence, they accumulate in the soil. Soil therefore represents rather a long-term archive for the atmospheric deposition than an indicator for the actual input of these compounds.

In 1986, on demand of the Swiss ordinance of 9 June 1986 relating to hazardous substances in the soil<sup>1</sup>, a national soil monitoring network (NABO) was set up in Switzerland<sup>2</sup> aiming at monitoring the soil pollution. Sites were selected to reflect typical land use, vegetation, land management, air quality, and soil conditions in Switzerland. 50% of the sites are located on agricultural land, 30% in forests, and 20% on open land with extensive farming (alpine pastures, etc.); two sites are situated in urban parks. The sites are distributed throughout Switzerland including rural/remote areas as well as urban, urban fringe and industrial regions. Soil samples are taken every 5 years and are analysed for eight heavy metals (lead, copper, cadmium, zinc, nickel, chromium, cobalt, and mercury) as well as fluorine. So far, organic pollutants (PAH and PCB) have been determined in isolated samples only<sup>3</sup>, and there is no data on PCDD/F concentrations so far. The present program was set up to fill this knowledge gap. A subset of 23 sites representing locations where contaminant immissions above average were expected was selected for PCDD/F and PCB analysis.

### Methods and Materials

**Sampling:** 23 soil samples were taken between March and July 2002. Each sample consisted of 25 pooled sub-samples taken within an area of 10 m × 10 m at a depth between 0 and 10 cm.

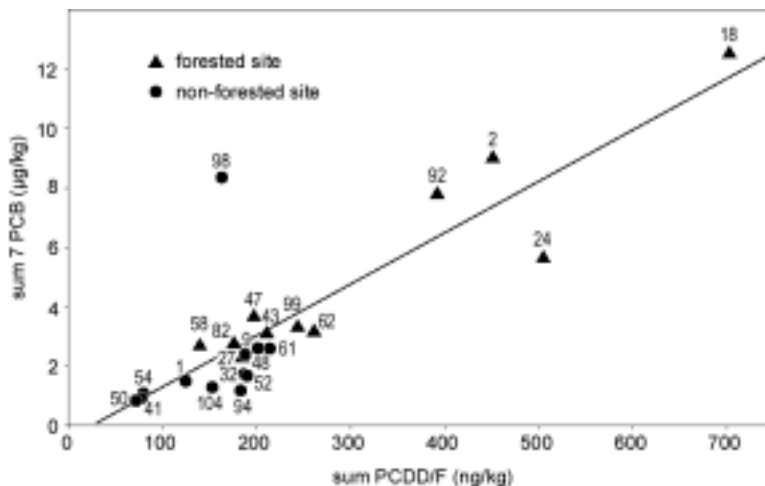
**Sample preparation:** The samples were dried for 1 week at room temperature, stones were removed, and the samples were ground in a mill. Soil was extracted with toluene in a Soxhlet extractor. After adding the internal standard (mixture of  $^{13}\text{C}$ -labeled PCDD/F), the extract was treated with concentrated sulphuric acid and further purified by low pressure liquid chromatography on silica gel, alkaline alumina and active carbon. For determination of PCB, an aliquot of the soil extract was mixed with internal standard (mixture of  $^{13}\text{C}$ -labeled PCB) and purified using a chromatographic glass column packed with silica gel and silica gel containing concentrated sulphuric acid.

**PCDDF and PCB analysis:** Quantitative determination of PCDD/F and PCB was based on gas chromatography / high resolution mass spectrometry and selected ion monitoring. Detection limits are based on a signal-to-noise ratio of 3:1. With exception of heptachlorodibenzo-*p*-dioxin (0.3 ng/kg), octachlorodibenzo-*p*-dioxin (2 ng/kg), and octachlorodibenzofuran (0.3 ng/kg), PCDD/F blank levels were below the detection limits. With exception of PCB 28 (0.05 µg/kg), 52 (0.04 µg/kg), and 101 (0.02 µg/kg), PCB blank levels were below 0.01 µg/kg for single PCB congeners.

## Results and Discussion

PCDD/F levels in the soil samples ranged from 80 to 703 ng/kg, the PCB concentrations (sum of 7 PCB) were between 0.86 and 12 µg/kg (see Table 1). Both PCB and PCDD/F concentrations are in the range of background levels for these compounds as reported in earlier investigations of Swiss soil samples<sup>3-5</sup>. As Figure 1 shows, the total PCDD/F and PCB levels are well correlated and proportional. Most of the concentrations are in a relatively small range: PCDD/F levels are mainly between 80 and 262 ng/kg, and most of the PCB concentrations are between 1.1 and 3.7 µg/kg. The PCDD/F and PCB levels of the remaining 4 samples originating without exception from forested sites (no. 2, 18, 24, and 92) range up to 703 ng/kg and 12 µg/kg, respectively (sample no. 18). The pronounced proportionality of PCDD/F and PCB concentrations suggests that most of the sites are extensively exposed to the same mixture of pollutants.

**Figure 1:** Sum 7 PCB vs. sum PCDD/F concentrations in soil samples (regression equation: sum 7 PCB [µg/kg] =  $0.0173 \times \text{sum PCDD/F [ng/kg]} - 0.424$ ,  $R^2 = 0.720$ ).



**Table 1:** Soil samples from the Swiss soil monitoring network (NABO): Sample description and PCDD/F and PCB concentrations (dry weight basis).

No. County	Region	Characteristics, land utilization	Altitude [m]	Sum PCDD/F [ng/kg]	Sum PCDD/F [ng I-TEQ/kg]	Sum 7 PCB <sup>1)</sup> [µg/kg]
1 Aadorf	Swiss plateau	permanent grassland	537	125	1.6	1.5
2 Zürich	Swiss plateau	coniferous forest	668	451	8.4	9.0
9 Binningen	Swiss plateau	agriculture	324	188	2.4	2.4
18 Langenthal	Swiss plateau	coniferous forest	525	703	11	12
24 Niederlenz	Swiss plateau	deciduous forest	387	505	5.9	5.6
27 Jussy	Swiss plateau	deciduous forest	505	185	2.3	2.3
32 La Brévine	Jurassic	pasture, grassland	1215	187	1.8	1.7
41 Kyburg-Buchegg	Swiss plateau	permanent grassland	464	78	0.95	0.93
43 Orbe	Jurassic	deciduous forest	622	211	2.6	3.1
47 Davos	Alps	coniferous forest	1655	198	2.7	3.7
48 Oberriet	Swiss plateau	agriculture, grassland	409	202	1.8	2.6
50 Realp	Alps	pasture, grassland	2120	72	1.1	0.86
52 Krummenau	Alps	pasture, grassland	1338	191	2.9	1.7
54 Zuzwil	Swiss plateau	agriculture	557	80	1.1	1.1
58 Mels	Alps	young deciduous forest	910	140	2.3	2.7
61 Winterthur	Swiss plateau	city park, lawn	445	215	3.1	2.6
62 Bettlach	Jurassic	deciduous forest	1065	262	4.3	3.2
82 Kappelen	Swiss plateau	deciduous forest	441	176	2.5	2.7
92 Novaggio	South side of alps	deciduous forest	1080	392	6.4	7.8
94 S. Antonino	South side of alps	horticulture	209	183	2.0	1.2
98 Erstfeld	Alps	permanent grassland	455	163	2.5	8.4
99 Visp	Alps	coniferous forest	830	244	4.3	3.3
104 Küsnacht	Swiss plateau	pasture, grassland	1025	153	2.1	1.3

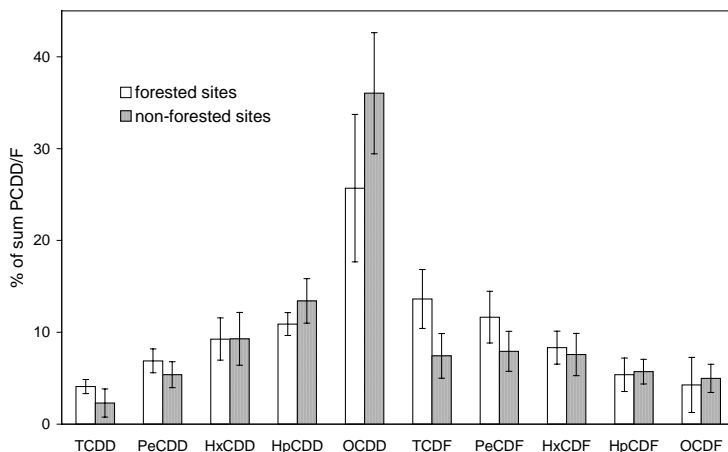
<sup>1)</sup>PCB 28, 52, 101, 118, 138, 153, and 180

Comparison of the contaminant levels and the sample types reveals relatively high exposure of soils from forests. Moreover, the forest soil samples exhibit characteristic differences in the homolog and congener patterns. The PCDD/F pattern of the forest soil samples given in Figure 2 shows a gradient towards higher relative concentrations of the lower chlorinated homologues of both PCDD and PCDF. On the other hand, the PCB congeners in forest soils indicate an opposite trend characterized by a decrease towards the lower chlorinated congeners (see Figure 3). These characteristics have been described in the literature<sup>6,7</sup> and have been investigated and interpreted in detail<sup>8,9</sup>. The canopy of forests is acting as an efficient trap amplifying the transfer of semivolatile organic compounds (SOCs) to the soil. The gaseous fraction of the contaminants is absorbed by diffusion into the cuticular surface of the leaves increasing the input of pollutants to the soil by litter fall. Horstmann and McLachlan<sup>8</sup> have proposed three categories of chemicals differing in their partitioning characteristics: More volatile SOCs as represented by PCB 28 to 118 can achieve a partitioning equilibrium between the gas phase and the leaf leading to a relative decrease in the

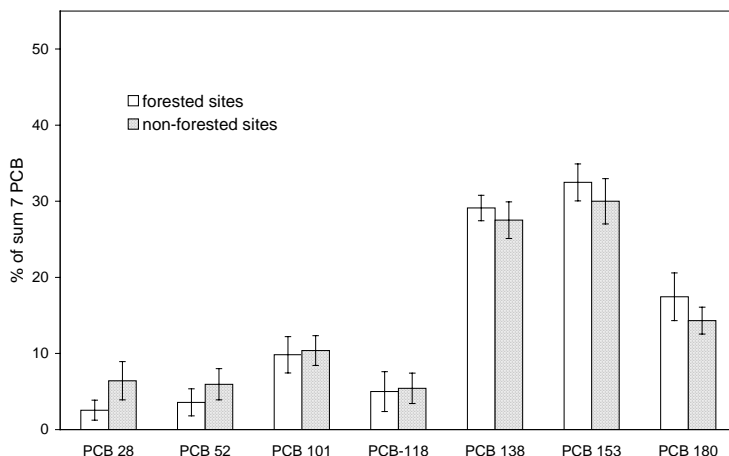
congener pattern (Figure 3). In contrast, the uptake capacity of the leaves for SOC of intermediate volatility is not limited by reaching the partitioning equilibrium which favours the enrichment of the respective compounds and causes high relative concentrations in the congener and homolog patterns (TCDD/F to HxCDD/F in Figure 2, PCB 138 to 180 in Figure 3). For the third category including the relatively involatile SOC gaseous deposition is insignificant in comparison with particle-bound deposition (HpCDD/F and OCDD/F in Figure 2). Hence, the high levels in these forest soils are presumably rather due to higher deposition rates than to higher gaseous or particle-bound air concentrations in the respective locations. Horstmann and McLachlan have shown that in an extreme case deposition of airborne SOC in a forest can be enhanced by a factor of up to 10 compared to a nearby non-forested area exposed to the same aerial gaseous or particle-bound PCDD/F and PCB concentrations<sup>8</sup>.

One of the aims of the present investigation was the elucidation of potential correlations to specific parameters of the observation sites such as geographical location, or altitude above sea level, settlement density, distance, and direction (main wind direction) to local and diffuse emission sources. Unfortunately, the above considerations suggest that any slight differences in the air concentrations of PCDD/F and PCB are likely to be superimposed by the site-specific deposition characteristics. At least, the PCDD/F and PCB levels and the congener/homolog patterns correspond quite well with background levels reported for background soils in central Europe<sup>10</sup>.

**Figure 2:** Average PCDD/F homolog profiles of samples from forested and non-forested sites (error bars indicating standard deviations).



**Figure 3:** Average PCB congener profiles of samples from forested and non-forested sites, respectively (error bars indicating standard deviations).



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### References

- 1 Swiss Confederation Ordinance relating to soil pollutants of 9 July 1986 (OSP); Swiss Confederation: Berne, 1986.
- 2 Swiss Agency for the Environment Forests and Landscape NABO Nationales Bodenbeobachtungsnetz, Messresultate 1985 - 1991; Swiss Agency for the Environment Forests and Landscape: Berne, 1993.
- 3 Berset J. D. and Holzer R. (1995) *Int. J. Environ. Anal. Chem.* 59, 145-165.
- 4 Swiss Agency for the Environment Forests and Landscape NABO Böden der Schweiz, Schadstoffgehalte und Orientierungswerte (1990 - 1996); Swiss Agency for the Environment Forests and Landscape: Berne, 2001.
- 5 Gälli R., Krebs J., Kraft M. and Good M. (1992) *Chemosphere* 24, 1095-1102.
- 6 Hagenmaier H. and Krauss P. (1993) *Organohalogen Compounds* 12, 81-84.
- 7 Horstmann M., Bopp U. and McLachlan M. S. (1997) *Chemosphere* 34, 1245-1254.
- 8 Horstmann M. and McLachlan M. S. (1998) *Atmos. Environ.* 32, 1799-1809.
- 9 Wania F. and McLachlan M. S. (2001) *Environ. Sci. Technol.* 35, 582-590.
- 10 Meijer S. N., Ockenden W. A., Sweetman A., Breivik K., Grimalt J. O. and Jones K. C. (2003) *Environ. Sci. Technol.* 37, 667-672.