Dioxin-like compounds (PCDDs, PCDFs and coplanar PCBs) in pine needles from Poland

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), -furans (PCDFs) and -biphenyls (PCBs) have been recognized as ubiquitous pollutants of great concern due to their characteristics of environmental persistence, tendency to bioaccumulate in the living organisms and high toxicity[1,2]. PCDDs and PCDFs have never been intentionally produced by human, and are micro-contaminants formed during different thermal processes[3]. However, PCBs present the group of industrial chemicals till now used or contained in various industrial materials and goods, first of all in electromagnetic equipment including capacitors and transformers[4].

Recently, many countries have undertaken monitoring of the aforesaid semi-volatile compounds in the ambient air to quantify their emitted amounts, determine regional transport processes, as well as estimate specific sources[1,4]. It is possible by using as a biomonitors, needles of pine trees which are widespread distributed in whole Europe and Asia. The surface wax layer of the needles poses an ability to absorb the lipophilic compounds from the surrounding air[5].

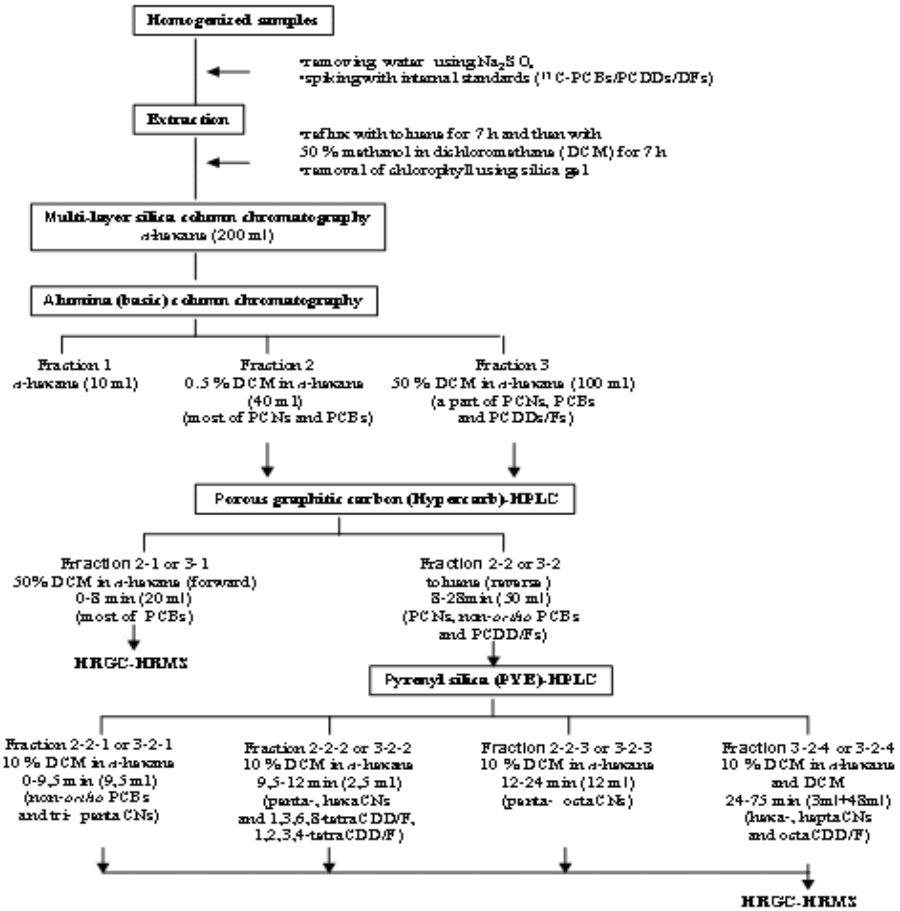
In the present study pine needles were employed as biomonitors of PCDD/DFs and planar PCBs concentrations in Poland. This country with its division on the industrial, agricultural and forestry sites gives opportunity to identify different kind of sources and their patterns in the environment. Also location in the centre of Europe makes Poland interesting region to observe an impact of those pollutants from surrounding countries and this way to trace their transport.

Materials and Methods

The one year old pine needle samples were collected during October 2002 at eleven sites in Poland (Figure 1). At each sampling point needles were taken from several *Pinus silvestris* trees at height of 1,5-2 m above the ground in distant at least 200 m from the nearest road. The samples immediately after collection were packed in aluminium foil and put in plastic bags. They were frozen and stored at -20°C until analysis.

Figure 1. Location of the sampling sites of pine needles in Poland and former production sites of PCBs technical preparations (★) .

The samples were Soxhlet extracted using toluene and 50% methanol in dichloromethane. The concentrated extract was cleaned using a multi-layer silica gel column chromatography. Alumina column chromatography, Hypercarb-HPLC and PYE-HPLC separation were performed to fractionate various analytes. Identification and quantification of PCDDs and other investigated dioxin-like compounds were done using high-resolution gas chromatograph (HRGC) coupled to a high-resolution mass spectrometer (HRMS). Details of analytical procedure are given in Scheme 1 and elsewhere[6].



Scheme 1. Outline of the analytical procedure used.

Results and Discussion

In this study a quality of ambient air in Poland was surveyed for dioxin-like compounds (PCDDs, PCDFs and coPCBs) using pine needles as passive sampler. Table 1 presents the analytical results of the eleven samples from various parts of the country.

Table 1. Concentrations of PCDDs, PCDFs, total PCBs and coPCBs with details of sampling

Sample	Tree species	Sample weight	Place of collection	PCDDs	PCDFs	total PCBs	coPCBs
		g		pg/g w.w.		ng/g w.w.	pgTEQ/g w.w.
1d	*Pinus sylvestris* L.	10,25	Tuczno	26,7	29,8	5,68	0,14
5b	*Pinus sylvestris* L.	10,61	Sława Śląska	25,0	37,0	2,78	0,30
7a	*Pinus sylvestris* L.	10,10	Parciaki	24,4	45,1	5,87	0,28
7c	*Pinus sylvestris* L.	10,10	Radom	13,4	23,5	5,92	0,21
2a	*Pinus sylvestris* L.	15,07	Choczewo	22,7	26,4	6,83	1,19
2b	*Pinus sylvestris* L.	15,20	Człuchów	28,3	34,2	33,48	0,7
4b	*Pinus sylvestris* L.	15,30	Włocławek	21,1	25,5	32,91	1,07
8a	*Pinus sylvestris* L.	15,26	Kutno	26,9	32,3	33,59	1,53
11a	*Pinus sylvestris* L.	10,17	Opole	27,3	61,9	50,08	1,11
12a	*Pinus sylvestris* L.	15,24	Jędrzejów	17,1	20,8	12,66	1,13
13a	*Pinus sylvestris* L.	15,15	Olkusz	47,6	77,1	13,36	1,54

Total PCDDs concentration ranged from 13 to 48 pg/g wet weight and for PCDFs from 21 to 77 pg/g w.w. (Table 1, Figure 3). A somewhat elevated concentrations of PCDDs and PCDFs were at the south of Poland at highly industrialised region known due to mining industry of hard coal and metallurgy as well as of high rates of urbanisation (samples 11a and 13a) (Figure 3). Nevertheless, if consider homologue specific pattern of PCDDs and PCDFs no major differences were noted between spatially scattered sampling sites (Figure 2).

In all samples highly chlorinated PCDDs/DFs dominated (Figure 2). Their similar pattern can suggest that formation of these chemicals occur in similar conditions. Energy production and fossil fuel co-fired power boilers are probably the main sources in industrial regions, however heating of houses by small stoves and hard coal with added household wastes plays important role at rural sites.

The coplanar PCBs concentration ranged from 0.14 to 1.54 pgTEQ/g wet weight. The highest concentrations of coplanar PCBs were found in the samples from industrialized and heavily populated areas of Poland (samples 11a, 12a, 13a). Interestingly in the sample collected near Kutno city (sample 8a) the concentration of coPCBs were higher than for samples collected near the Tricity agglomeration (2a, 2b) or near the Warsaw agglomeration (7c) (Figure 4). The possible explanation is the vicinity of landfill with PCBs containing wastes. According to the latest inventory about PCBs in Poland the number of equipment containing unidentified amounts of PCBs (*i.e.* capacitors, transformers) was estimated as above 11 200 pieces[7]. On the other hand the lowest concentrations of coplanar PCBs were found in samples from eastern and western parts of the country - up to ten times in magnitude smaller if compared with central and southern areas – what can suggest that former production of technical PCBs preparation, mining and other industries as well as PCBs containing waste disposal are the major sources of those compounds to environment.

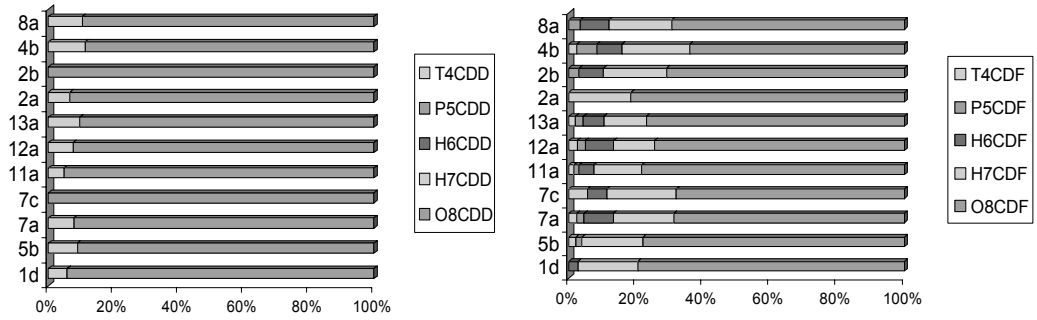


Figure 2. PCDDs and PCDFs homologue groups composition of pine needles from Poland.

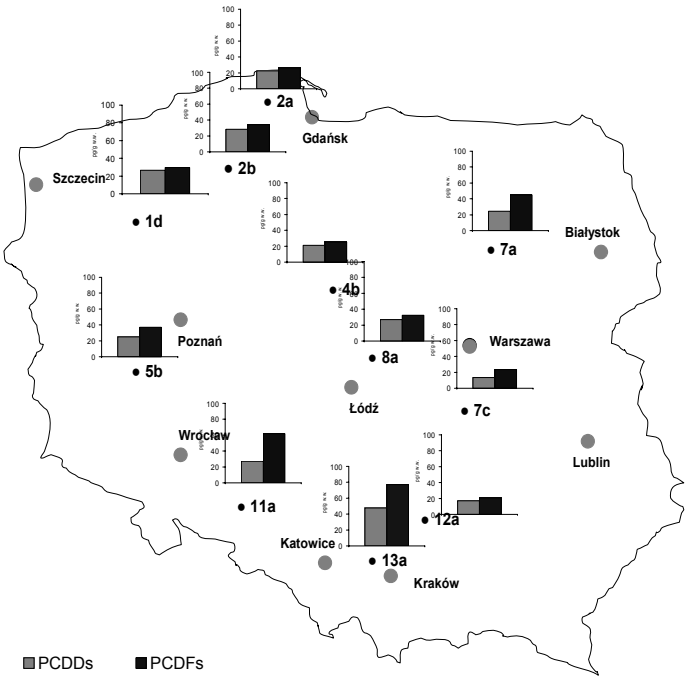


Figure 3. Total PCDDs and PCDFs concentration in pine needles from Poland (pg/g wet weight).

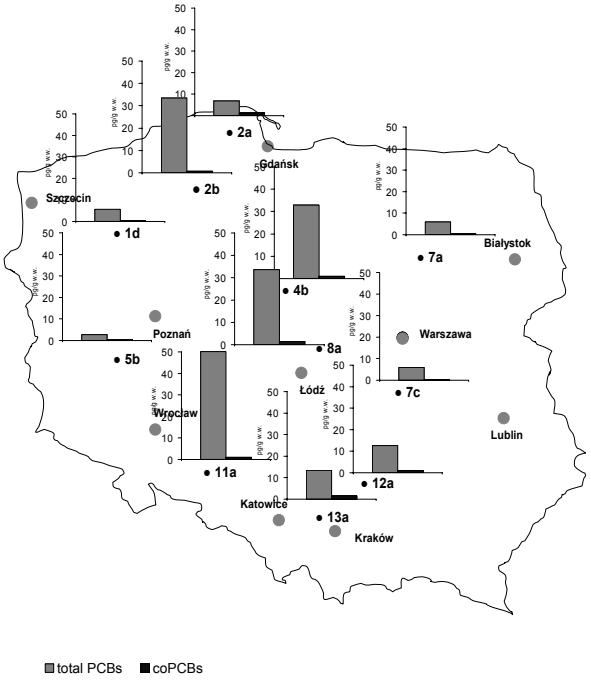


Figure 4. Total PCBs (ng/g wet weight) and coplanar PCBs (pgTEQ/g wet weight) concentration in pine needles from Poland.

The total PCBs concentrations ranged from 2.8 to 50 ng/g wet weight (Table 1, Figure 4). The pine-needle samples at the sites in southern Poland, and which were collected at the areas neighboring to former production sites of the Polish PCBs formulations (Chlorofen, Tarnol) showed greatest PCBs load (Figure 1 and 4). Production and use of Chlorofen in the past still seems to be an important source of these compounds in southern Poland. The compositional pattern of PCBs homologue groups observed in pine needles (Figure 5) shows that pine needles at the sites somehow related to production and use of Chlorofen (lubricant in hydraulic and other systems used in mining) showed the highest abundance of highly chlorinated groups of 6CB, 7CB and 8CB. Those highly chlorinated homologue groups were reported to be predominant in Chlorofen composition (Figure 5). Elevated concentrations of PCBs were also found in the pine-needles from other industrial and heavily populated areas (2b, 4b, 8a). The levels of PCBs in pine-needles from rural sites of Poland (1d, 5b, 7a) were almost ten times lower than from other regions. Despite of former production and use of technical PCBs formulations, landfill disposal of items containing technical formulations of these compounds and leakages from those places, could be considered as an important sources of PCBs in Poland. Higher concentrations of electrical equipment in industrial

area could be on of the reason of so significant differences between concentration of PCBs and in urbanized and rural sites in Poland.

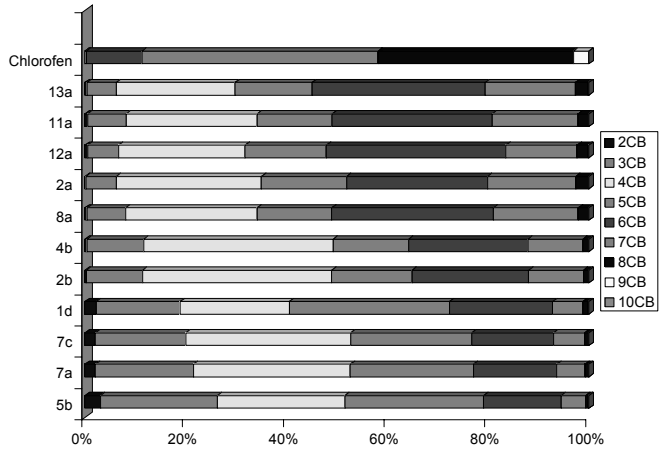


Figure 5. Total PCBs homologue groups composition in pine needles from Poland compared with Chlorofen.

Acknowledgments

The authors are grateful to Dyrekcja Generalna Lasow Panstwowych, Warsaw, Poland and to Dyrekcje Regionalne Lasow Panstwowych for kind cooperation.

References

1. Martinez M., Díaz-Ferrero J., Martí R., Broto-Puig F., Comellas L., Rodríguez-Larena M. C. (2000) Chemosphere 41, 1927.
2. Nakao T., Aozasa O., Ohta S., Miyata H. (1998) Organohalogen Compounds 39, 347.
3. Falandysz, J., Szymczyk, K. (2001) Polish Journal of Environmental Studies, 10, 189.
4. Safe S., Brown K. W., Donnelly K. C., Anderson C. S., Markiewicz K. V., McLachlan M. S., Reischl A., Hutzinger O. (1992) Environ. Sci. Technol. 26, 394.
5. Sinkkonen S., Kämäräinen N., Paasivirta J., Lammi R. (1997) Chemosphere 35, 2193.
6. Hanari N., Horii Y., Okazawa T., Falandysz J., Bochentin I., Orlikowska A., Puzyn T., Wyrzykowska B., Yamashita N. (2004) J. Environ. Monit. 06, 305.
7. Bogutyn W. (2003) Persistent Organic Polutants in Poland. The results of PCBs inventory. Stockolm Convention – GEF Report. GF/POL/INV/R.23, Warsaw 2003