Polychlorinated biphenyls and polychlorinated naphthalens in pine needles and soil from Poland – concentrations and patterns in the view of the long-term monitoring of ambient air pollution

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Introduction

Polychlorinated naphthalenes (PCNs) and polychlorinated biphenyls (PCBs) are widespread environmental pollutants that originate mainly from technical formulations formely used for many industrial applications. Manufacture of PCNs dates from the beginning of twentieth century and its highest rate of used was during 1930-1950 and total global production of those compounds was estimated as 150 000 tonnes[1,2]. Manufacture of PCBs started in 1929, as the beginning of their commercial use, and continued until 1990s with above 1,5 million metric tons produced[3].
In Poland the production of PCBs did not bring a major contribution to the world market, the amount of total Polish PCB formulations – Chlorofen and Tarnol – was estimated as 1,700 metric tons. Nevertheless not identified quantities of PCB formulations from Soviet Union (Sovol) and Czechoslovakia (Delor) were imported to Poland before 1971. The presence of commercial PCB mixtures made in Germany (Clophen), France (Pyralen), and Italy (Phenaclor) in Polish installations cannot be excluded[2]. Morover both PCBs and PCNs are continuously formed and released to the environment during many antrophogenic processes[1,3]. It has been reported that PCN are impurities of technical preparations of PCBs[4].
Even though highly hydrophobic, semi-volatile, thermally stabile, with low flammability and with 15 congeners reportedly eliciting Ah receptor-mediated mechanism of toxicity, polychlorinated naphthalenes are still relatively less studied than other dioxin-like compounds. Recently published data on historical profiles of PCNs in dated sediments cores showed that concentrations of those compounds decreased since middle 1980s[5,6], hence very few data on their long term distribution in the lower troposphere exist. In the case of PCBs, this study has given special attention to trace analysis of nona- and decachlorinated congeners. Despite of routinely analysed di- to octa

homologue groups, nona- and decachlorinated isomers could be considered as a tool for source determination based on specific fingenprint of PCBs homologue groups in environmental samples and technical formulations. The very little studied before isomer-specific pattern of nona- and decaCBs varied in technical mixtures investigated[7], consequently this fingerprint could be considered as one of the tools to identify highly chlorinated Chlorofen technical formulation formerly produced and used in Poland, as a potential source of pollution with PCBs.
Since preliminary investigations have revealed that pine needles can absorb organohalogens from the ambient air[8], in this study they were selected as a cost effective and easy collectable environmental matrix suitable for long-term monitoring of the lower troposphere pollution with PCNs, PCBs and other dioxin-like compounds. Simultaneously to pine needles soils samples were investigated to determine intercorrelations between concentrations and patterns of polychlorinated naphthalenes and polychlorinated biphenyls in pine needles and soil. Consequently sustainability of pine needles as a passive sampler for monitoring of ambient air pollution with PCNs and PCBs with regards to the concentrations of those compounds in soil/air media was evaluated.

Materials and Methods

The one year old pine (*Pinus sylvestris* L.) needles and soil samples were collected at several locations in Poland in October 2002, both with regards to rural areas as well as those with heavy industrialisation ratio and heavily populated, including areas of former production of Polish technical PCBs formulations (Figure 1). Additionally Chlorofen technical mixture was analysed to determine fingerprint of PCBs in this formulation. The pine needle samples were homogenized and stored at –20 ºC until analysis. Soil samples were deep-frozen at –20 ºC and prior to analysis were freeze-dried.
The pine needles samples were Soxhlet extracted using toluene and 50 % methyl alcohol in methylene chloride (1:1, v/v). Soil samples were extracted in two step procedure with mixture of acetone and hexane (1:1, v/v) and subsequently with toluene in accelerated solvent extraction (ASE) system. The concentrated extract was cleaned using a multi-layer silica gel column chromatography and subsequent steps of fractionation were performed using activated basic alumina column chromatography, Hypercarb-HPLC and PYE-HPLC. Identification and quantification of PCNs and PCBs were done using high-resolution gas chromatograph (HRGC) coupled to a high-resolution mass spectrometer (HRMS). Detailed analytical procedures are given elsewhere[8].

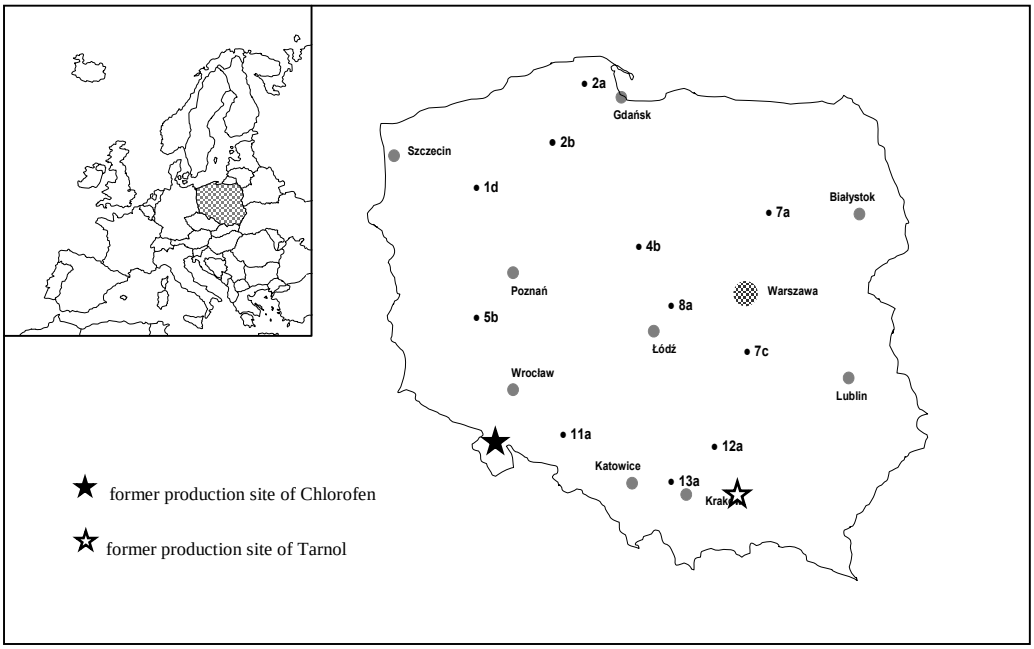


Figure 1. Location of the sampling sites and former production sites of technical PCBs formulations.

Results and Discussion

PCBs

Total PCBs concentration in pine needles were in the range from 2.8 to 50 ng/g wet weight (Table 1, Figure 2a). Samples from the heavily industrialized areas of southern part of the country as well as densely populated central Poland have showed highest PCBs concentrations. It should be noted that in samples collected form areas neighboring the former production sites of technical PCBs formulations the elevated total PCBs concentrations corresponded to highest abundances of highly chlorinated homologue groups of hexa-, hepta- and octachlorinated biphenyls (Figure 2b), which were find to be predominant in Chlorofen, both in the present study results as well as in the data already published[4,7].

Table 1. Total PCBs concentration of pine needles from Poland (ng/g wet weight)

	1d	2a	2b	4b	5b	7a	7c	8a	11a	12a	13a

	ng/g wet weight										
2CB	0.13	0,011	0,095	0,12	0,084	0,12	0,12	0,15	0,26	0,067	0,048
3CB	0,94	0,41	3,74	3,73	0,65	1,14	1,06	2,55	3,84	0,78	0,78
4CB	1,23	1,97	12,6	12,4	0,70	1,83	1,94	8,77	13,0	3,18	3,15
5CB	1,81	1,16	5,35	4,92	0,77	1,43	1,42	4,97	7,46	2,04	2,04
6CB	1,16	1,91	7,75	7,79	0,43	0,97	0,96	10,8	15,91	4,51	4,59
7CB	0,34	1,20	3,62	3,58	0,14	0,33	0,37	5,68	8,53	1,79	2,39
8CB	0,063	0,17	0,36	0,39	0,013	0,040	0,046	0,68	1,06	0,27	0,34
9CB	0,006	0,0029	0,0073	0,0055	0,0018	0,0011	0,0020	0,013	0,019	0,013	0,013
10CB	0,0012	0,0018	0,0039	0,0037	0,00098	0,0011	0,0012	0,0020	0,0032	0,0055	0,0061
total	**5,68**	**6,83**	**33,5**	**32,9**	**2,78**	**5,87**	**5,92**	**33,6**	**50,1**	**12,7**	**13,4**

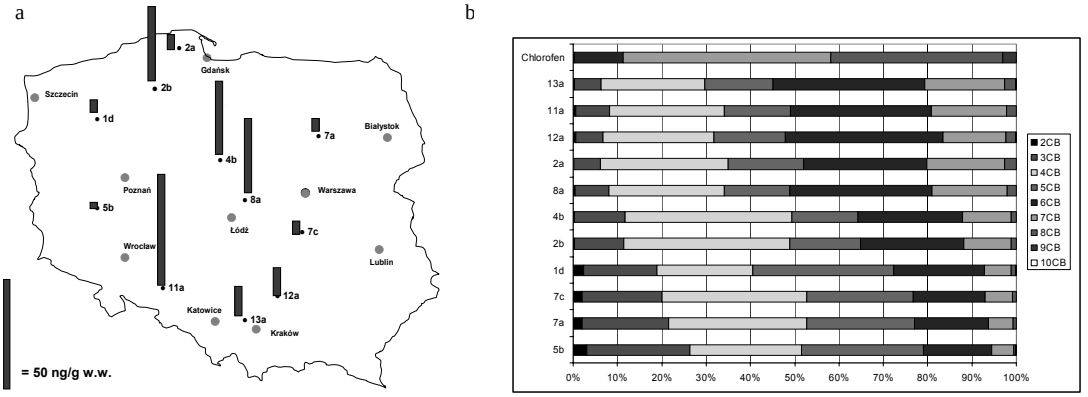


Figure 2. Total PCBs concentrations in pine needles from Poland (ng/g wet weight) (a) and homologue groups pattern in pine needles and Chlorofen (b).

In this study nona- and decachlorinated congeners were considered as an important tool to determine the potential impact of technical formulation formerly used as a source of pollution with those compounds. Nonachlorinated biphenyls (IUPAC # 206, 207, 208) were identified in eleven among thirteen formulations recently analyzed by authors[7], with the highest abundance found for highly chlorinated ones (Aroclor 1268 and 1260, Chlorofen, Sovol, Kanechlor 600 and 500, Delor 106, Clophen A60). Decachlorinated congener (# 209) was identified only in four formulations examined *i.e.* Aroclor1268, ClophenA60, Aroclor1260 and Chlorofen, comprising respectively

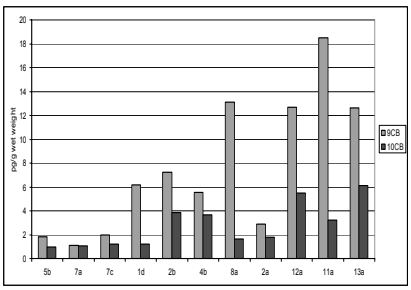


Figure 3. 9CB and 10CB pattern in pine needles from Poland (pg/g wet weight).

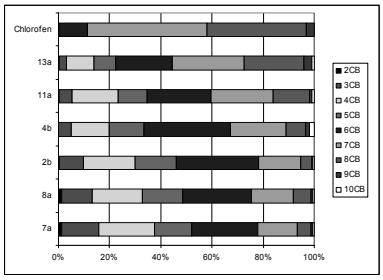
8.9, 2.8, 1.3 and 0.82% of the total bulk of 9CB and 10CB detected.

In pine needles from Poland the highest abundances of 9CB and 10CB were found in pine needles from the sites 11a, 12a and 13a (Figure 3), which are somehow related to the Chlorofen and Tarnol production sites (Figure 1) and furthermore – neighboring the areas of extensive mining industry, when Chlorofen was used as a lubricant in hydraulic systems[9]. High concentrations were also found in samples of the rather heavily populated and industrialized areas of central and northern Poland. In contrary – in sample from vicinity of Olsztyn (7a), neighboring poorly developed areas of Poland, the concentrations of nona- and decabiphenyls were lowest, and ratio between those two homologue groups was approximately 1:1 in opposite to the tendency of much more abundant 9CBs homologue group - if compared with 10CB - observed in other samples.

In soil samples concentrations of PCBs ranged from 0.61 to 8.6 ng/g dry weight (Table 2) and though noticeably lower than concentrations observed for pine needles, they represented similar tendency both in concentrations, homologue group patterns and nona- and decachlorinated biphenyls fingerprint (Figure 4).

Table 2. Polychlorinated biphenyls in soil from Poland (ng/g dry weight)

	7a	8a	2b	4b	11a	13a
	ng/g dry weight					
2CB	0,0072	0,012	0,0075	0,0022	0,026	0,0077
3CB	0,089	0,11	0,18	0,11	0,436	0,15
4CB	0,13	0,17	0,39	0,32	1,55	0,52
5CB	0,088	0,14	0,31	0,28	0,985	0,41
6CB	0,16	0,24	0,62	0,71	2,14	1,06
7CB	0,094	0,15	0,31	0,47	2,10	1,36
8CB	0,032	0,062	0,083	0,16	1,22	1,13
9CB	0,0046	0,0071	0,011	0,034	0,096	0,15
10CB	0,0033	0,0049	0,010	0,043	0,070	0,048
total	**0,61**	**0,90**	**1,93**	**2,12**	**8,63**	**4,83**



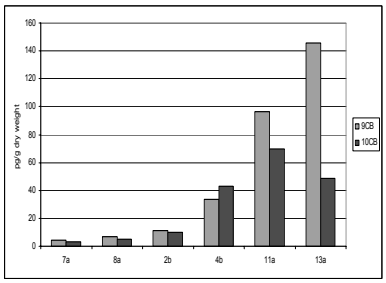


Figure 4. PCBs homologue groups pattern in soil and Chlorofen (a) with 9CB and 10CB concentrations in soil from Poland (pg/g wet weight) (b)

PCNs

Concentration of PCNs ranged from 165 to 925 pg/g wet weight (Table 3). As for PCBs the highest concentrations were found in samples from industrial and heavily populated areas of Poland, with the highest concentration observed for samples nearest to the areas of production and intense use of technical PCBs preparations (mining industry in Silesia region).

Table 3. Polychlorinated naphthalenes in pine needles from Poland (pg/g wet weight)

	1d	2a	2b	4b	5b	7a	7c	8a	11a	12a	13a
	pg/g wet weight										
3CN	44,4	71,9	125,9	117,3	168,6	68,9	106,1	167,8	234,0	460,8	168,2
4CN	45,2	84,3	93,9	129,9	110,0	78,7	80,0	163,9	241,0	309,2	164,8
5CN	23,9	42,1	38,0	41,6	41,8	34,7	47,1	62,9	37,7	34,6	42,3
6CN	5,96	17,3	12,9	13,0	7,68	6,38	6,78	17,5	9,7	11,6	17,2
7CN	11,2	26,40	19,3	17,1	6,98	8,45	8,83	29,5	17,7	19,1	22,1
8CN	33,8	128,41	95,7	59,0	27,7	24,3	23,2	135,1	72,76	88,5	101,3
total	**164,6**	**370,4**	**385,7**	**378,0**	**362,8**	**221,3**	**272,0**	**576,8**	**613,0**	**923,9**	**515,8**

PCNs concentration were more uniform if compared with PCBs in pine needles (Figure 5a) and in the homologue pattern no clear tendency was observed (Figure 5b). Based on published data on PCNs recognized as impurities of PCBs technical preparation[4] it can be concluded that Chlorofen has played role as a source of polychlorinated naphthalenes to the local environment. Isomer specific pattern of penta- and hexachlorinated naphthalens in pine needles and Chlorofen (data not shown) demonstrated noticeable resemblance. Nevertheless other sources – as an incineration processes or leakages from landfills – should not be forgotten.

Figure 5. Total PCNs concentrations (pg/g wet weight) (a) and homologue group pattern in pine needles from Poland (b).

In soil PCNs concentrations ranged from 452 to 609 pg/g dry weight (Table 4) and were even more uniformly distributed than in pine needles, what can suggest some balance existing between soil/air media and furthermore it could be assumed that even though homologue pattern of polychlorinated naphthalenes in soil - if compared with Chlorofen (Figure 6) - seems to reflect role of technical formulation formerly used as possible source of pollution with PCNs, this role should not be overestimated. The more variable concentrations of pine needles seem to reflect also the other sources of pollution with those compounds.

Table 4. Polychlorinated naphthalenes in soil
from Poland (