PCNs, PCDDs, PCDFs and coplanar PCBs in agricultural soil of Central Europe – an example of Poland: pattern and sources

Barbara Wyrzykowska[1], Nobuyasu Hanari[1], Anna Orlikowska[2], Ilona Bochentin[2], Jerzy Falandysz[1], Nobuyoshi Yamashita[1]

[1]1 National Institute of Advanced Industrial Science and Technology (AIST)
[2]2 Department of Environmental Chemistry & Ecotoxicology, University of Gdańsk

Introduction

The sources and environmental levels of the dioxin-like compounds are generally broadly described; nevertheless for some regions *i.e.* Central and Eastern Europe, there is insufficient number of data regarding these classes of contaminants, mostly due to limited access to state-of-the-art analytical techniques in the past. Most of the countries in the region (*e.g.* Poland, Germany, former Czechoslovakia, and former USRR) produced and used organochlorines for many applications. The special attention must be given to fact that CEE countries still face problems of safe storage of chemicals classified as toxic (*e.g.* PCBs, pesticides). Sometimes lack of facilities and technologies for destruction of these chemicals predestinates disposal on landfills as main route of toxic waste management in CEE region.[1] Limited national surveys seem to emphasize the scale of the problem *e.g.* in Poland the total amount of dielectric oil with PCBs contained in capacitors, transformers and other electromagnetic equipment was assessed as 8000 to 9500 tons.[2] A knowledge of detailed composition and characteristics of pattern and profile of dioxin-like compounds in the environmental matrices is essential for identification of the "hot spots". In this study soil was considered as a typical organochlorines accumulating environmental matrix with long-memory – which makes it suitable for identification of pollution sources. Additionally, since hard coal but sometimes also household waste combustion and other uncontrolled combustion processes are of special importance as a possible source of dioxin-like compounds in the countries with minor participation of incineration to methods of solid waste disposal, furnace bottom ash from wood/coal heating muffle stove for domestic use was analyzed to investigate concentrations and compositions of POPs.

Materials and methods

Agricultural soil samples were collected at several locations in Poland in October 2002, including areas at some distance to the past manufacture facilities of the Polish technical PCB. Soil samples were homogenized and deep-frozen at –20ºC. Prior to analysis samples were freeze-dried and sieved (1mm mesh). Extraction was performed in two step procedure with mixture of acetone and hexane (1:1, v/v) and subsequently with toluene in accelerated solvent extraction (ASE) system. Additionally 5 types of ashes obtained from household combustion of different fossil fuels and materials - as hard coals, coke, wood, solid domestic waste mixture - performed in wood/coal heating muffle stove for domestic use were analyzed to investigate concentrations and compositions of dioxin-like compounds. Ash samples were homogenized and sieved (1mm mesh). After acidification and filtration, samples were extracted in two step procedure of liquid-liquid extraction (liquid phase) followed by Soxhlet extraction of solid phase with dichloromethane and subsequently with toluene. The concentrated extracts of soil and ash were cleaned using a multi-layer silica gel column chromatography and subsequently fractionated by using activated basic alumina column chromatography, Hypercarb-HPLC and PYE-HPLC. The analysis of PCDDs, PCDFs, PCBs and PCNswas performed by high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS). Details of the analytical procedure are given elsewhere.[3]

Results and discussion

2,3,7,8 substituted PCDDs and PCDFs

Total 2,3,7,8 substituted PCDDs concentration in soils ranged from 5.2 to 41 pg/g and PCDFs from 5.1 to 19 pg/g d.w. respectively.Concentration of PCDDs/Fs at agricultural areas away from the urbanized sites (*e.g* 7c) are on

average much lower if compared to that of cropland a somehow closer to industrialised and urbanized areas (*e.g.* 2b, 4b, 8a, 11a, 12a, 13a). The contaminants fingerprint obtained seem to reflect many possible sources of dioxins and furans *e.g.* exhaust gases from vehicles, landfills leakages, manufacture and use of PCB, possible use of pentachlorophenol in the past as well as trans-boundary deposition from the west as dominating wind direction. Importantly I-TEQ of agrciultural soils from rural areas can be considered among the lowest concentrations internationally.[4]

Table 1. Concentrations (pg/g d.w.) and I-TEQs (pg TEQ/g d.w.) of 2,3,7,8 – substituted PCDDs and PCDFs in Polish agricultural soil

	1a	**1b**	**2a**	**2b**	**4b**	**5b**	**7a**	**7c**	**8a**	**11a**	**12a**	**13a**
2,3,7,8 PCDDs	41	9.0	5.2	17.5	32.0	13.0	6.8	16.4	20.6	10.9	13.7	13.8
∑TEQsPCDDs	0.053	0.016	0.0058	0.027	3.42	0.021	0.014	0.036	3.54	0.018	0.029	0.024
2,3,7,8 PCDFs	11.2	5.44	3.89	18.1	17.8	8.23	5.31	5.10	18.2	16.1	11.7	19.2
∑TEQsPCDFs	0.051	0.021	0.017	0.89	0.83	0.035	0.032	0.024	2.35	0.98	0.055	1.48

The profile of PCDDs/Fs of agriculture soil under suspected to some degree influence of urbanized/industrialized agglomerations resembled profile obtained for ash after burning of coal and coke – fossil fuels used into the greatest extend also in industry.

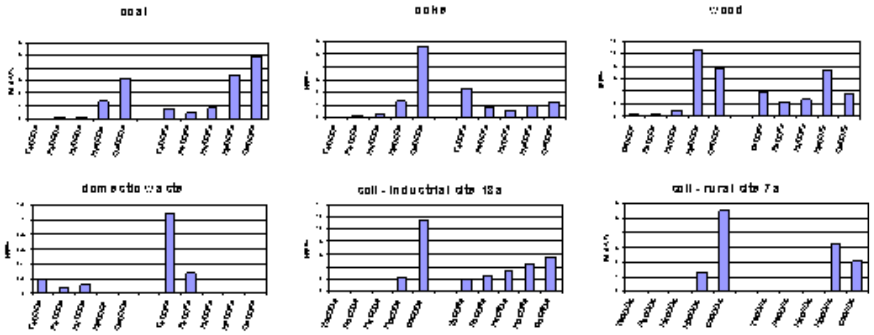

Figure 1. Profile of 2,3,7,8 – substituted homologues of PCDDs and PCDFs in furnace bottom ash and Polish agricultural soil from industrial and rural areas.

The pattern of homologue groups of PCDDs/Fs of "typical"agricultural soil resembles profile similar for samples where PCP was used.[5] Interestingly profile of PCDDs/PCDFs from ash obtained from burning mixture of domestic wastes (including mostly plastic and paper) has demonstrated higher concentrations of lowly chlorinated dioxins, which were less abundant or even not detected in other ash samples. In soil samples 2,3,7,8-TeCDD was actually below LOD (<0.17 pg/g d.w) in all investigated samples, 1,2,3,7,8-PeCDD was detected in two samples from urbanized areas (4b and 8a), while 2,3,7,8-TeCDF was detected only in three samples – 4b collected in the vicinity of Włocławek city, with prominent chemical industry and in two samples from industrialized Silesia region (11a and 13a). Thus role of furnace bottom ash as a source of most toxic PCDDs/Fs should not be overestimated, but it can be considered as a possible source of highly chlorinated dioxins and furans (Fig. 1).

Non-*ortho* and mono-*ortho* PCBs

In soil samples total concentration of coplanar PCBs ranged from 29 to 200 pg/g d. (0.077 – 0.42 pgTEQ/g d.w.), with highest abundance found for congeners IUPAC # 77, 105 and 118 (Fig. 2a). Similarly to the total PCBs [6], highest concentrationswere found in soils from urbanized and industrialized areas of Poland, including areas neighboring former production sites of technical PCB formulations. On the other hand samples from rural and typically agricultural areas of the country showed lowest concentrations of coplanar PCBs. PCBs concentrations were in the range similar to those reported for agricultural soils or from rural areas of the globe. [4] Based on

fingerprints of coplanar PCBs in ash (data not shown) there are no clear implication for considering it as a source of dioxin-like biphenyls for agricultural soil.

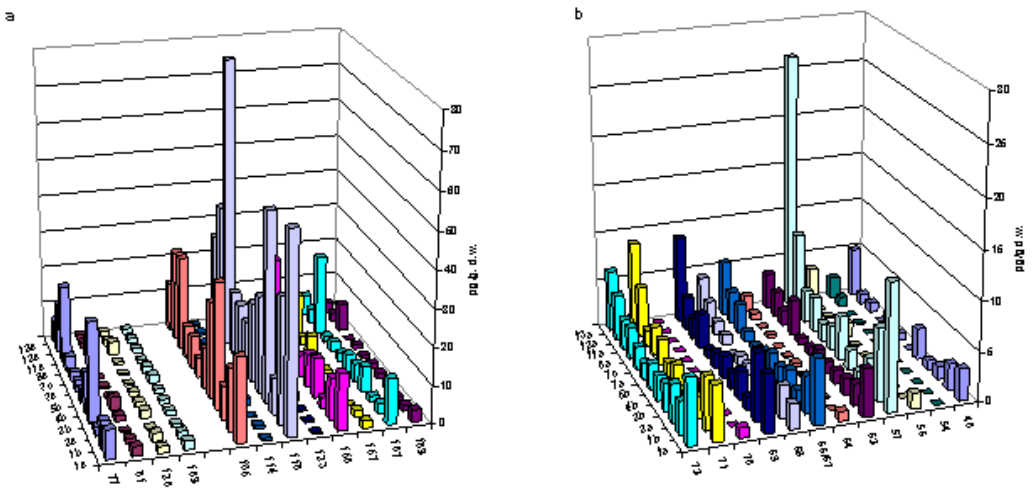

Figure 2. Dioxin-like PCBs (a) and PCNs (b) in soils from Poland (pg/g dry weight).

PCNs

In soil total PCNs concentration was as from 350 to 1100 pg/g d.w. with dioxin-like PCNs concentration ranged from 11 to 77 pg/g d.w. (0.023 – 0.15 pgTEQ/g d.w. tentatively). Within dioxin-like PCNs congeners IUPAC # 57, 66/67, 69, 71 and 73 were predominant in all investigated samples (Fig. 2b). Interestingly while examining profile of total PCNs homologue group's higher proportion of low chlorinated members was found in soil from rural areas. Further – if compared with pine needles [6] – soil was in general enriched in triCNs and tetraCNs. Analysis of CN homologue groups in furnace bottom ash showed that low chlorinated members are predominant in all types of analyzed ashes (Fig. 3). Similar pattern of PCNs was recently found in the laboratory scale incineration of PCN containing wastes (FB belts) with the highest concentrations of triCNs and tetraCNs. [7] Interestingly in the case of soil collected at the site somehow neighboring the former production site of the highly chlorinated Polish PCB formulation – Chlorofen (12a), the proportion of low volatile and of higher particle bound affinity heptaCNs and octaCNs was higher in soil then in pine needles. Based on published data on PCNs recognized as impurities of PCBs technical preparation [8] it can be concluded that Chlorofen could have played role as a source of highly chlorinated naphthalenes to the local environment. Additionally improperly disposed ash from household combustion, as well fly ash from combustion processes should be considered as a potential source of lowly chlorinated naphthalenes.

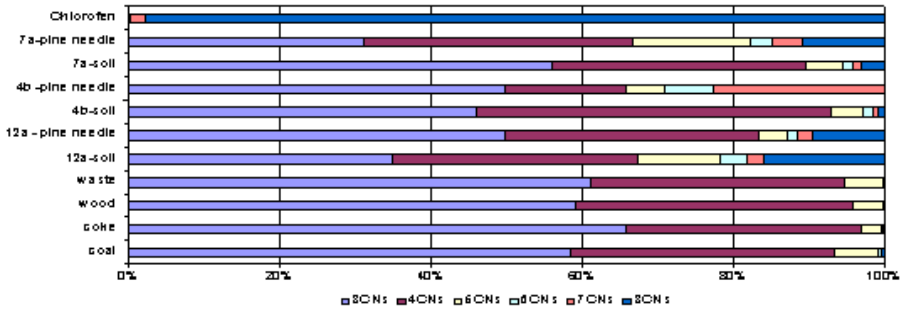

Figure 3. Composition of PCN homologue groups in samples of Polish agricultural soil, pine needles compared to profile of Chlorofen[8] and different types of furnace bottom ash.

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