Importance of dioxin-like PCBs and PCNs for TEQs of agricultural soils with low level of 2,3,7,8-TeCDDs and its analogues

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Introduction

The guidelines for level of PCDD/Fs and PCBs are based on dioxin-TEQs in many countries. In developing thresholds for soil based on health risk assessment dose additivity is the default assumption while estimating total toxicological potential. Experimental studies with combinations of dioxin and furan congeners have helped to validate the additivity principle of the TEQ approach. Nonetheless it is suggested that use of additive effect in the TEF concept is unlikely to result in large errors of TEQ concentration prediction.[1] In this study, in addition to 2,3,7,8 substituted PCDDs/Fs and non-*ortho* and mono-*ortho* PCBs, PCNs with reported dioxin-like toxicity[2] were considered as important contributors to total TEQs of Polish agricultural soil, since in many investigated cases environmental level of 2,3,7,8-TeCDDs and its analogues with the highest TEFs assigned were often below the limit of quantification.

Materials and methods

Agricultural soil samples were collected in Poland in October 2002. Most of the samples originated from typical rural sites away from cities and industry, but for some indirect long-range impacts could be possible (Fig.1). Soil samples were homogenized and deep-frozen at –20ºC. Prior to analysis samples were freeze-dried and sieved (1mm mesh). Extraction was performed by means of accelerated solvent extraction (ASE) in two step procedure (1^{st} step – acetone and hexane (1:1, v/v), 2^{nd} step – toluene). The concentrated extracts were cleaned up using a multi-layer silica gel column chromatography and fractionated by using activated basic alumina column chromatography and two-dimensional HPLC. The analysis of PCDDs, PCDFs, PCBs and PCNs was 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

In this study TEF values (for PCDDs, PCDFs, non-*ortho* and mono-*ortho* PCBs) and TEF adjusted REP values* (for PCNs with reported dioxin-like toxicity) were combined with agricultural soil chemical residue data to calculate cumulative Toxic Equivalent (TEQ) concentrations according to the equation:

$$TEQ = \Sigma n1[PCDDi \times TEFi] + \Sigma n2[PCDFi \times TEFi] + \Sigma n3[PCBi \times TEFi] + \Sigma n4[PCNi \times TEF^{REP*}i]$$

This concept was adopted from work of Fitzgerald (2003) based on use of additive TEQs of dioxins, furans and coplanar PCBs to establish health-based soil criteria for dioxins used for risk assessment of soils contaminated with these chemicals.[1]As there is no Polish or universal EU legislation for concentrations of dioxin-like chemicals in agricultural soils, a comparision of obtained data was made against guidelines based on protection of human health criteria which incorporates the WHO tolerable daily intake for PCDDs/Fs of 10 pg/kg body wt/day giving appropriate threshold in soil reported as 10 pg I-TEQ /g, which actually corresponds to the most restrictive soil thresholds in Europe set for Sweden (<10 pg I-TEQ g^{-1} d.w.).[5,6] Additionally data were compared to reference values for land-use and remediation of contaminated soil in Germany for dioxin-like chemicals, which assumes that for preventive reasons and as a long-term objective, the dioxin concentrations of soil used for agricultural purposes should be reduced to below 5 pg TEQ/g d.w.[1]Absolute TEQs concentrations of Polish agricultural soil are summarized in Table 1, while relative contribution of PCDDs, PCDFs, PCBs and PCNs is demonstrated on Figure 1.

Table 1. Concentrations (pg TEQs/g d.w.) of dioxin-like compounds in Polish soil

	1a	1b	2a	2b	4b	5b	7a	7c	8a	11a	12a	13a
dioxin-likePCNs	0.14	0.098	0.042	0.056	0.040	0.048	0.030	0.023	0.064	0.057	0.084	0.15
coPCBs	0.21	0.25	0.054	0.26	0.18	0.14	0.081	0.077	0.10	0.42	0.20	0.17
PCDDs	0.053	0.016	0.0058	0.027	3.42	0.021	0.014	0.036	3.54	0.018	0.029	0.024
PCDFs	0.051	0.021	0.017	0.89	0.83	0.035	0.032	0.024	2.35	0.98	0.055	1.48
S TEQ	**0.46**	**0.39**	**0.12**	**1.2**	**4.5**	**0.24**	**0.16**	**0.16**	**6.1**	**1.5**	**0.36**	**1.8**

Only 40% of the Polish agricultural soil samples (2b, 4b, 8a, 11a, 13a - all collected from urban or industrial locations from central and southern Poland) demonstrated predominant contribution (from 68 to 97%) of 2,3,7,8 substitued PCDDs/Fs to total TEQs. In remaining 60% of samples – with low concentrations/not detectable 2,3,7,8 substituted lowly chlorinated PCDDs/Fs – the data indicated that combined contribution of coplanar PCBs and PCNs to the toxic equivalency across soils was from 62 to 91%. In those samples PCNs contributed from 19 of 31% to the toxic equivalency across soil samples, while coplanar PCBs from 45 to 65% respectively. Noteworthy the realtive contribution of coplanar PCBs and PCNs to total TEQs was rather regardless of the characteristic of the sampling locations – soils from industrial, urban and rural areas showed similar pattern. This situation is a consequence that 2,3,7,8-chlorine substituted PCDD/PCDF homologue and congener profiles for soils sampled in this study are strongly dominated by highly chlorinated hepta- and octachlorinated congeners, while 2,3,7,8-TeCDD was below the limit of detection (<0.17 pg/g d.w.) in all samples and 1,2,3,7,8,-PeCDD was detected only in sample 4b and 8a. Similarly the tetra- and penta-2,3,7,8-chlorine substituted furans were only detected in few samples (4b, 11a, 13a). The congener profile of coplanar PCBs is dominated by mono-*ortho* PCB – #118 (approximately 32 to 46%) followed by PCB #105 (13 to 32 %) with no apparent differences in profiles observable between different locations. Also in the case of dioxin-like PCNs profile of congeners was similar with PCN #57, 66/67, 69, 71 and 73 dominating in all investigated samples.

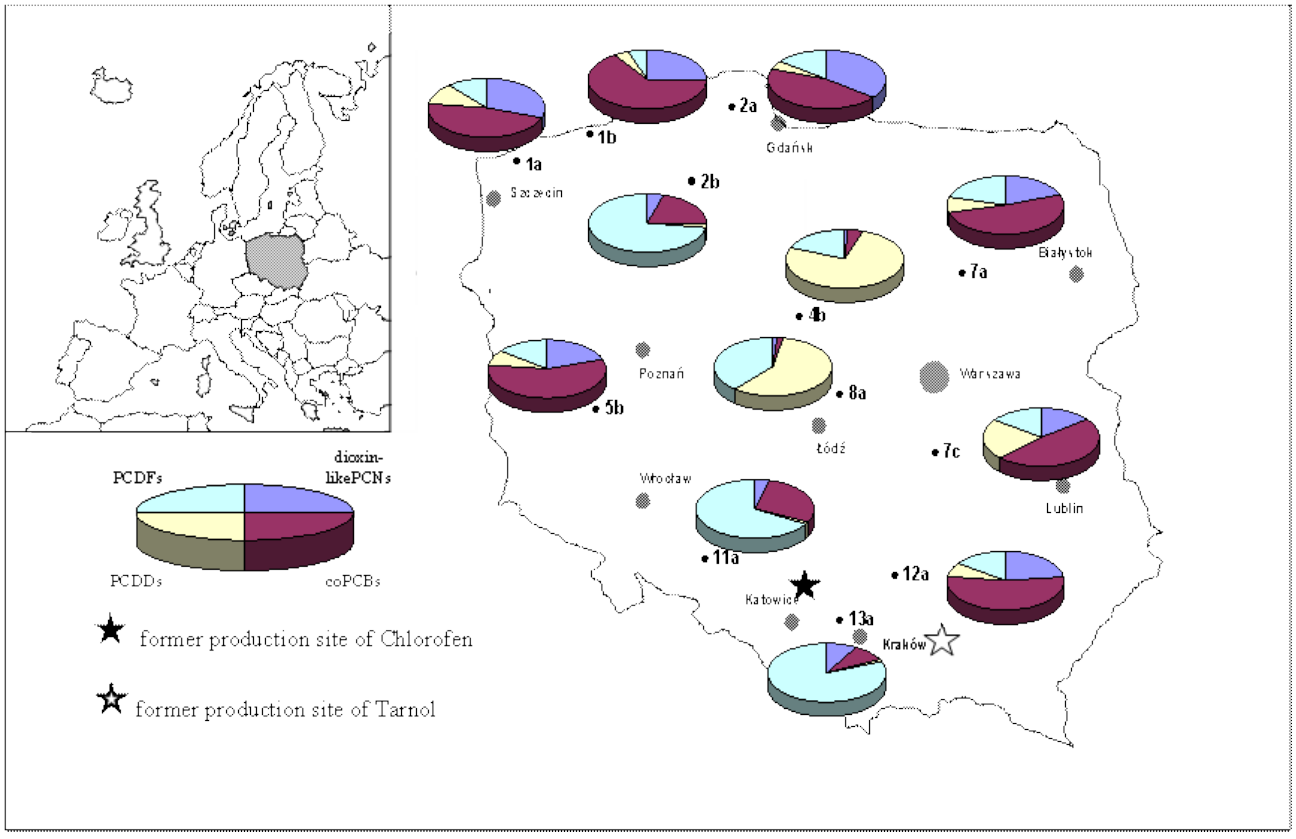

Figure 1. The relative (%) contribution of PCDDs/Fs, dioxin-like PCBs and PCNs to cumulative TEQs of Polish agricultural soils.

Total TEQ profiles are mostly determined by the presence, or rather absence, of the certain sources of lowly chlorinated PCDDs/Fs

to environment. Since in Poland the MSW incineration processes can not be considered as an important source of PCDDs/Fs multiple anthropogenic sources should be thought out *e.g.* exhaust gases from vehicles, paper bleaching and other chemical processes, leakages from landfills and possibly – to some extent – uncontrolled combustion processes or household combustion, former manufacturing and use of PCB technical formulations, which can contain furans as impurities, as well as former use of PCP.[7]

In general the concentrations of dioxin-like chemicals in samples from urban and industrial locations were in typical range measured for only PCDDs/Fs (I-TEQs) in soils of EU (<1-100 pg I-TEQ/g d.w.).[6] Importantly, none of the samples exceeded the threshold of 10 pg I-TEQ /g d.w.[5]In one case (8a) I-TEQ of 5.9 pg I-TEQ/g d.w. slightly exceeded the value of <5 pg I-TEQ/g d.w. set for Germany as a target protective concentration for agricultural soils and the total TEQ of all dioxin-like compounds in this sample was as 6.1 pg TEQ/g d.w. In conlusions it has to be said that for areas with low environmental levels of 2,3,7,8 substituted PCDDs/Fs, dioxin-like PCBs and PCNs should be considered as important contributors to the toxic equivalency of soils, especially in the rural areas and areas with smaller urbanization and industralization ratio.

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* *For dioxin like PCNs REPs were rounded to value of either 1 or 5 according to approach used to deriving TEFs by WHO[4]*