Persistent Organochlorine Pesticides and Polychlorinated Biphenyls in Soils in Poland

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Abstract
Surface (0-10 cm) soil samples were collected from various sites in Poland in 1990-1994 to understand concentrations, spatial distribution and possible sources of pollution with organochlorine pesticides (HCBz, HCHs, DDTs and CHLs) and PCBs. Measurement was made using a two step clean-up of soil extract, with concentrated sulphuric acid and Florisil gel, followed by capillary gas chromatography (HRGC) with electron capture detection or mass spectrometry (HRGC/LRMS). PCBs were detected in all samples; HCBz, HCHs and DDTs were absent (<0.01 ng/g dry wt) in one sample and CHLs in a few of the 60 samples examined. Residues of DDTs dominated in agricultural and forest soils, PCBs in urban soils. The urban soils and especially those from industrialised areas were much more polluted with HCBz than agricultural and forest soils, and for HCHs and CHLs the concentrations did not show any clear trend.

Key words: HCBz, HCHs, Lindane (γ-HCH), Chlordanes (CHLs), DDTs, PCBs, Organochlorine, Pesticide, Soil, Poland.

Introduction
The terrestrial environment of Poland has, until recently, been poorly characterised with respect to man-made persistent compounds such as polychlorinated biphenyls (PCBs), chlordanes (CHLs), hexachlorobenzene (HCBz) and isomers of hexachlorocyclohexane (HCHs). Due to relatively high application rates the mean concentration of DDTs in agricultural soils in Poland in the 1960s was 900 ng/g dry weight and in single samples up to 3500 ng/g were recorded (1). Until recently technical DDT was also used in the former East Germany, and due to long-range transport from neighbour countries by air masses, some was deposited on the surface matrices in Poland (2). In the case of PCBs, military activity of the former Soviet army troops could be a source of environmental pollution in Poland (3). The revolatilisation from soil has been suggested as a main source of

atmospheric PCBs and HCBz in the area of the city of Gdańsk in Northern Poland (4). PCBs, DDTs, HCHs, HCBz and CHLs are organochlorine compounds usually found in varying concentrations in soils in Poland; however, a large part of the extractable organic chlorine (EOCl) present in soils in Northern Poland is made up of unidentified persistent compounds other than chlorobiphenyls and pesticides (5).

In this paper the concentrations and spatial distribution of organochlorine pesticides and PCBs in soils in Poland are discussed with reference to local sources and long range atmospheric transport.

Materials and Methods

The samples of soil of different type and use were collected at many sites in Poland 1990-1994 (Table 1). The surface layer (0-10 cm) was collected with a vertical corer. All soil samples were packed in chemically clean polyethylene bags and stored until analysis under temperature controlled conditions. The soil samples were sieved using a 32 mesh size sieve (500 μm). A soil sample (20 g) was mixed with 20 ml *n*-hexane-prewashed water in a 250 ml glass stoppered Erlenmayer flask and allowed to soak for 30 minutes. The sample was extracted with 150 ml of acetone for an hour. The acetone extraction was repeated twice for each sample. The combined supernatant was decanted into a 3 litre separatory funnel containing 200 ml of *n*-hexane in 1300 ml of *n*-hexane prewashed water, and the funnel was shaken for 10 minutes. The *n*-hexane extract was washed three times with 200 ml of *n*-hexane prewashed water, dried by passing it through a layer of anhydrous sodium sulphate, and then concentrated to 5 ml by using a Kuderna-Danish (KD) concentrator. The extracts were cleanedup with concentrated sulphuric acid and subjected to column chromatography fractionation with activated Florisil gel (130°C, 12h). The first fraction eluted with *n*-hexane contained HCB, *p,p'*- DDE, PCBs and *trans*-nonachlor. The second fraction eluted with 20% dichloromethane in *n*-hexane contained chlordane compounds and metabolite (*trans*-chlordane, *cis*-chlordane and *cis*-nonachlor and oxychlordane), *p,p'*- DDT, *p,p'*- DDD, *o,p'*- DDT and HCH isomers (α, β and γ). Each elute was concentrated in a KD concentrator down to 5 ml and washed with 2 ml of concentrated sulphuric acid. Sulphur eluted in the first fraction was removed by treatment with copper chips. The identification and quantification of organochlorines were made using a capillary column gas chromatograph with a ^{63}Ni electron capture detector (HRGC-ECD; Hewlett Packard 5890 Series II). The GC system was equipped with a moving-needle-type injection system (splitless and solvent-cut mode). The capillary column of 0.25 mm i.d. and 30-m length (J & W Scientific Co. USA; 10% dimethyl polysiloxane, 0.25 μm bonded phase) for HCB and PCBs, and DB-1701 (J & W Scientific Co., USA; 14% cyanopropyl phenyl polysiloxane, 0.25 μm bonded phase) for organochlorine pesticides were used. The temperature of the column oven was programmed from 160°C (4 min hold) to 240°C at a rate of 2°C/min, with a final holding of 20 min. Helium and nitrogen were used as carrier (2 ml/min) and make-up (60 ml/min) gases, respectively. The injector temperature was kept at 250°C and detector temperature was maintained at 300°C. DDTs were the sum of *p,p'*- DDT, *o,p'*- DDT, *p,p'*- DDE and*p,p'*- DDD, HCHs were the sum of the α, β and γ, and CHLs were the sum of *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, *cis*-nonachlor and

oxychlordane. The PCB concentrations in the samples were calculated by totaling the concentrations of the individually resolved peaks of different PCB isomers and congeners, while an equivalent mixture of the technical Kanechlor formulations (KC 300:400:500:600) of known chlorobiphenyl composition and content (CB%) was used as an analytical standard. The detection limit of the method was 0.1 ng/g for pesticides and 1.0 ng/g for PCBs, and recovery rates of these compounds were between 95 and 105%. The analytical procedure used is described in detail in another paper (6). Some of the extracts were examined using a capillary column gas chromatograph and a low resolution mass spectrometer (HRGC/LRMS) (4).

Results and Discussion

The concentrations of HCBz, HCHs (α, β and γ isomers), DDTs (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE), CHLs (*cis-* and *trans*-chlordane, *cis- and trans*-nonachlor, and oxychlordane) and PCBs in agricultural, forest and urban soils are summarized in Table 1.

HCBz in Polish agricultural and forest soils and also in urban soils in the northern part of the country revealed uniform distribution and relatively small concentrations, *i.e.* 0.26 ng/g dry weight (arithmetic mean weighted). In urban soils from the highly industrialized sites in southern part of Poland the concentrations of HCBz were much higher, *i.e.* ranging from 0.86 to 9.9 ng/g in Kraków area and from 0.46 to 30 ng/g in Katowice (Table 1). Hexachlorobenzene in relatively small quantities (187.6 tones) was used as a fungicide in Poland in 1962-1973 (7). Apparently elevated concentrations of HCBz in urban soils in the southern part of Poland, when compared to the northern regions of the country - 0.20 to 0.33 ng/g in the city of Gdańsk, suggest industry and thermal processes as plausible explanations.

In the case of HCHs, the concentrations did not show any clear trend dependent on the soil type, and the arithmetic mean weighted concentration was 6.7 ng/g dry weight. Lindane (γ-HCH was widely applied in agriculture in Poland in 1956-1982, and in total 7510.3 tonnes were used (7). Technical BHC (benzenehexachloride), which consists of the mixture of α, β, γ, δ and ε isomers of HCH, was registered in Poland as a soil fumigant and applied mainly in forestry, but no records are available on the total quantity used or the period of application.

DDT is an organochlorine insecticide with the longest history of application in Poland, and in 1947-1980 78947.5 tonnes of technical DDT were produced 48151.7 tonnes were used and 30795.8 tonnes was exported abroad (7). Because of relatively high application rates of DDT for agricultural purposes and in forestry in Poland,the residues of DDTs quantified in various environmental matrices and in humans were temporarily rather high (1, 9, 10). Technical DDT was used in forestry in the former East Germany up to 1989, and in 1984, ~500 tonnes were applied (11). In this study agricultural and forest soils contained DDTs in concentration up to 1400 ng/g dry weight, while up to 2600 and 4300 ng/g was recorded in urban soils and in soils at the specific sites, respectively (Table 1). *p,p'*-DDT, on the average, was a main (>50%) constituent of DDTs quantified in the soils examined.

Table 1. Organochlorine pesticides and PCBs in soil in Poland (ng/g dry weight)

Soil type & site	HCB	γ-HCH	HCHs	DDTs	CHLs	PCBs
Agricultural soils						
Gdańsk (8)*	0.20±0.10	0.51±0.24	1.3±1.2[a]	93±160	1.0±1.3[a]	8.5±9.8[b]
	(0.10-0.41)	(0.23-1.0)	(0.31-2.9)	(0.95-510)	(0.05-2.8)	(1.6-28)
Borsk	0.096	1.2	NA	16	NA	1.0
Orneta	0.23	0.88	NA	11	NA	NA
Warszawa	0.31	1.4	NA	17	2.6	9.5
Sandomierz	NA	0.23	NA	13	NA	NA
Poganice	0.04	-	0.16	2.2	ND	2.3
Bolesławowice	0.08	-	0.31	30	0.30	5.9
Płoty	0.38	-	27	1400	2.8	5.1
Warnowo (2)	0.04	-	0.71	340	0.46	5.8
	(0.03-0.04)		(0.67-0.75)	(270-400)	(0.41-0.51)	(2.8-8.9)
Forest soils						
Toruń	NA	-	NA	110	NA	NA
Kętrzyn	0.32	1.7	NA	33	NA	18
Grudziądz	0.30	0.92	NA	8.5	NA	1.5
Grodno I	0.94	-	7.6	660	1.2	38
Karnocice	0.08	-	0.94	11	0.14	2.8
Urban soils						
Jurata	<0.01	-	0.57	11	1.1	15
Gdańsk (4)	0.29±0.05	-	0.98±0.36	22±19	0.38±0.09	21±7
	(0.20-0.33)	-	(0.41-1.4)	(2.3-53)	(0.23-0.46)	(11-530[c])
Poganice	0.54	-	1.3	53	0.31	15
Świnoujście	0.74	-	2.1	150	1.6	230
Świnoujście (7)[d]	0.40±0.30	-	15±22	670±1500	4.0±5.8	900±1100
	(0.11-1.0)		(1.1-64)	(13-4300)	(ND-18)	(32-3400)
Katowice (9)	6.4±9.0	-	5.9±3.0	110±85	2.7±1.3	380±280
	(0.46-30)		(1.1-11)	(22-2600)	(1.0-5.8)	(67-870)
Kraków (9)	2.1±3.2	-	15±34	410±740	0.22±0.19	48±36
	(0.19-9.9)		(ND-110)	(12-2400)	(ND-0.64)	(4.6-110)
Nowa Huta (3)	1.1±0.8	-	3.1±3.4	33±5	0.76±0.80	64±33
	(0.49-2.2)		(0.63-8.0)	(27-40)	(0.18-1.9)	(34-110)
Kraków (3)[f]	1.3±0.5	-	2.3±1.3	27±18	0.48[e]	54±4
	(0.86-2.0)		(1.2-4.2)	(4.3-48)		(51-58)

*Number of the samples; [a] three samples; [b]five samples; 530[c] ng/g in a sample collected close to the marine paints factory in Oliwa; [d]military ground; [e]detected in one sample; [f] close to chloro-alkali plant; ND (not detected; <0.01 ng/g); NA (not analysed)

DDTs in concentrations up to 1400 ng/g dry weight, while up to 2600 and 4300 ng/g were recorded in urban soils and in soils at specific sites, respectively (Table 1). *p,p'*-DDT, on the average, was a main (>50%) constituent of DDTs quantified in the soils examined. Both the relatively high concentrations of DDTs recorded in agricultural, garden and forest

soils at several sites as well as the high proportion of *p,p'*-DDT in most of the samples seem to reflect the past history of application of technical DDT in Poland.

Chlordanes are minor compounds among pesticide residues quantified in soils examined (Table 1). Chlordane was not used in Poland, and small concentrations noted earlier in farm and game animals and human adipose fat (9, 10), as in the soil samples in this study, indicate long range atmospheric transport from distant sources and subsequent deposition.

The arithmetic mean weighted concentration of PCBs in agricultural and forest soils was 8.6 ng/g dry weight, what is apparently less than was found in urban soils, which contained 170 ng/g (n = 31), on the average, while 900 ng/g was quantified at the military area (Table 1). There is an apparent spatial gradient of PCBs in urban soils in Poland, with concentrations increasing from the north (21±7 ng/g in the city of Gdańsk) towards highly populated and industrialised regions in southern part of Poland such as the city of Kraków (48±36 -64±33 ng/g) or Silesia (380±280 ng/g in Katowice) (Table 1).

It is to concluded that relatively high concentrations of HCBz, HCHs, DDTs and PCBs were found in the soils from southern Poland, which resulting from heavy application on agricultural land and for hygenic purposes and usage in industrial activities. In addition, it is necessary to monitor the contamination by PCBs in the former Soviet military sites in Poland.

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References

1. Korczyński J; *Biul. I.O.R.* **1968**, 41, 75.
2. Eriksson G, Jensen S, Kylin H, Strachan W; *Nature*, **1989**, 341, 42.
3. Falandysz J, Kawano M, Wakimoto T; *Organohalogen Compd.* **1997**, 32, 172.
4. Falandysz J, Brudnowska B, Iwata H, Tanabe S; *Organohalogen Compd.* **1998**, submitted.
5. Kawano M, Falandysz J, Tsuji S, Kitamura S, Wakimoto T; *J. Environ. Chem.* **1997**, 7, 7.
6. Thao VD, Kawano M, Tatsukawa R; *Environ. Pollut.* **1993**, 81, 61.
7. Dąbrowski J, Siłowiecki A, Heinish E, Wenzel-Klein S; Anwendung chloroorganisher Pesticide in Polen und hieraus entstehende ökologisch - chemische und ökotoxicologische Folgen. p. 19-24, in *Schadstoffatlas Oteuropa - Ökologisch-chemische und ökotoxi-kologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost-Mitteleuropa.* Eds. E. Heinisch, A. Kettrup, S. Wenzel-Klein, Ecomed, Landsberg am Lech, **1994**, ISBN 3-609-69540-4.
8. Kawano M, Ramesh A, Thao VD, Tatsukawa R, Subramanian AN; *Intern. J. Environ. Anal. Chem.* **1992**, 48, 163.
9. Falandysz J, Kannan K; *Z. Lebensm. Unters. Forsch.* **1992**, 195, 17.

10. Tanabe S, Falandysz J, Higaki T, Kannan K, Tatsukawa R; *Environ. Pollut.* **1993**, 79, 45.
11. Heinish E, Wenzel-Klein S; p. 4-7. in *Schadstoffatlas Oteuropa - Ökologisch-chemische und ökotoxi-kologische Fallstudien über organische Spurenstoffe und Schwermetalle in Ost-Mitteleuropa.* Eds. E. Heinisch, A. Kettrup, S. Wenzel-Klein, Ecomed, Landsberg am Lech, **1994**, ISBN 3-609-69540-4.