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Original Research

Evaluation of the Status of Contamination of Arable Soils in Poland with DDT and HCH Residues; National and Regional Scales

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Abstract

The aim of our study was to evaluate the content of organochlorine pesticides (DDTs and HCHs) in the upper layer of arable soils in Poland. 214 soil samples were analyzed for the content of three HCH congeners (α-HCH, β-HCH, and γ-HCH) and three DDT compounds (pp'DDT, pp'DDE, and pp'DDD). The median soil concentration of Σ3DDT was 24.39 $\mu g \cdot kg^{-1}$, while for Σ3HCH it was 2.85 $\mu g \cdot kg^{-1}$ with the highest contribution of γ-HCH isomer. Polish criteria for agricultural soils not polluted with DDTs are met by half of the samples. In the case of γ-HCH the Polish limit value of 0.5 $\mu g \cdot kg^{-1}$ was met in 6.5% of the samples. However, according to the less restrictive systems applied in other countries (Canada, Romania) none of the soil samples create a hazard due to contamination with DDTs, and only 6-11% exhibit too high concentrations of γ-HCH (residues of Lindane). The mean contents of DDTs and γ-HCH in soils from different provinces varied widely with the reverse interdependence of both groups of pesticides. The districts with the highest concentrations of DDT (Podlaskie, Wielkopolskie, and Mazowieckie) were characterized by the lowest mean residues of Lindane. This suggests the long-term effects of the prescriptive state system of distribution of pesticides used in Poland more than 40 years ago.

Keywords: arable soil quality, soil contamination, organochloride pesticides, DDTs, HCHs, Lindane

Introduction

Organochlorine pesticides (OCP) were for many years applied widely in agriculture. They enter soils mainly through direct application (local pesticide usage), but on a global scale all soils are exposed to the inputs of OCPs from atmospheric depositions, which contribute substantially to the loads of those substances in the terrestrial environment [1, 2]. The very important groups of OCPs are hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs), which were used worldwide as pesticides before their application was restricted in the 1970s because of high persistence and toxicity [3-5].

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The most popular isomer from the HCH group is γ-HCH; the main component (98%) of pesticide Lindane was applied widely in the past in Poland and other countries as an insecticide and fumigant for a wide range of soil-dwelling and plant-eating (phytophagous) insects (7, 9). It was commonly used on a wide variety of crops, in warehouses, in public health to control insect-borne diseases, and (with fungicides) as a seed treatment [6 - 8]. Besides application as a pesticide, γ-HCH was applied in the pharmaceutical industry, by veterinarians and as an impregnating agent [1, 7, 9]. Lindane is persistent in most soils, with a field half-life of 1-2 years and is classified as a moderately toxic compound in EPA toxicity class II [10]. In accordance with the decision of the European Commission, the utilization of Lindane for plant protection on EU territory has been banned since August 2002 [11]. In Poland Lindane was produced in Zakłady Chemiczne "Organika-Azot" in Jaworzno; the production (over 300 $t \cdot year^{-1}$) contributed to about 50% of overall use of this pesticide in the country and was halted in 1982 [4, 12]. A recent EMEP (the European Monitoring and Evaluation Program) report indicates a significant decrease of environmental levels of γ-HCH due to the reduction of Lindane application, but the passive air sampling campaign organized in 2006 with participation of the Institute of Soil Science and Plant Cultivation in Puławy suggested these values to be underestimated [13]. The other HCH isomers, α-HCH and β-HCH, are by-products during Lindane production; α-HCH was also the main constituent of pesticide BHC (benzenehexachloride) of more specific applications [5, 14] and the main component of complex HCH pesticide "technical Lindane" [9, 15].

The term DDT is commonly applied to 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (pp`-DDT). Technical grade DDT is made up of 77.1% pp`-DDT, 14.9% op`DDT, 4% pp`DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene, 0.1% op`DDE, 0.3% pp`-DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane), 0.1% op`DDD and a number (3.5%) of unidentified compounds [16]. DDT is highly persistent in soils with reported half-lives of 2-15 years [9, 17]. Under aerobic conditions dehydrochlorination is the dominant reaction that facilitates the degradation of DDT primarily to DDE, while under anaerobic conditions more rapid dechlorination results primarily in the formation of DDD characterized by extremely high (reaching 190 years) persistence in soils [9, 17]. DDT was extensively applied as an insecticide after World War II and is still used in some equatorial countries [3, 7, 18, 19]. DDT has been produced in Poland since 1947 in Zakłady Chemiczne "Organika-Azot" in Jaworzno, but for a short time and on a small scale [1]. The most popular DDT technical product in Poland was Azotox, followed by Ditox and Tritox; it is estimated that the annual rate of DDT use in years 1974-80 in the country was 3,880 Mg [12].

DDTs and HCHs constitute a large part of obsolete pesticides stockpiled in many CEE countries, including Poland; leakage from these places may spread contamination to surrounding soil, groundwater, and water courses [4, 7, 14, 20]. Organochlorine pesticides released to the environment were often transported with river sediments and suspended particulate matter to the sea creating, the possibility for aquatic environment degradation (7, 20). It is evaluated that the total number of reclaimed pesticide tombs in 1998-2010 was 180 with about 16,367 Mg of toxic products; the OCPs were responsible for about 38% of total volume. At the same time, the number of pesticide burial grounds to be reclaimed was estimated as 62, with about 3,750 Mg pesticide waste products [21].

High concentrations of DDTs and HCHs are often found in human tissues, blood, and excretions such as adipose tissue and milk [9, 22]. It has been estimated that more than 90% of organochlorine body burden in the general population occurs via diet [1]. Thus, information on the concentrations of those substances in the soils where most of the food of plant origin is produced is of utmost importance. This is particularly important for Poland, where arable lands cover 46% of total area [23] and local products prevail in the Polish food market.

The aim of our work was to evaluate the concentrations and distributions of DDTs and HCHs in agricultural soils in Poland with particular reference to the regional variations.

Fig. 1. Sampling point map of the area. The main cities of the administrative provinces are marked: Wrocław – Dolnośląskie (Lower Silesia Province), Bydgoszcz – Kujawsko-Pomorskie (Kujawy-Pomerania Province), Lublin – Lubelskie (Lublin Province), Zielona Góra – Lubuskie (Lubuskie Province), Łódź – Łódzkie (Łódź Province), Kraków – Małopolskie (Małopolska Province), Warszawa – Mazowieckie (Mazovia Province), Opole – Opolskie (Opole Province), Rzeszów – Podkarpackie (Podkarpacie Province), Białystok – Podlaskie (Podlasie Province), Gdańsk – Pomorskie (Pomerania Province), Katowice – Śląskie (Silesia Province), Kielce – Świętokrzyskie (Świętokrzyskie Province), Olsztyn – Warmińsko-Mazurskie (Warmia-Mazuria Province), Poznań – Wielkopolskie (Wielkopolska Province), and Szczecin – Zachodniopomorskie (West Pomerania Province).

Materials and Methods

Description of the Studied Area and Soil Sampling

The sampling area covered the entire country. Localization (confirmed by the GPS method) of sampling points (n=214) reflected dissemination of arable lands across Poland and covered 16 administrative districts (provinces) (Fig. 1). The districts vary in industrialization/urbanization as well as agricultural production conditions and profiles. Provinces Wielkopolskie, Mazowieckie, and Lubelskie have the greatest areas for the production of cereals, while cultivation of rapeseed covers the largest territories in Zachodnio-Pomorskie, Dolnośląskie, and Wielkopolskie regions [23]. The highest land contributions for production of potatoes correspond to Opolskie, Mazowieckie, and Łódzkie Provinces [23]. The relatively high use of pesticides for the 4 crops' protection is recorded mainly in the western regions (Zachodnio-Pomorskie, Dolnośląskie, Lubuskie), but also in Pomorskie and Podkarpackie Provinces [24]. Simultaneously, Zachodnio-Pomorskie and Wielkopolskie Provinces were characterized by the greatest amounts of obsolete pesticides (6,366 Mg) stored in various types of tombs [14, 21].

The sampling campaign (year 2005) was carried out within the framework of the Monitoring of Arable Soils Chemistry program [25, 26]. All soil samples were taken from the surface layer (0-20 cm) of arable fields. Each sample was a composite of about 10 subsamples collected from an area of 100 m^2. Soil materials were air-dried for 48 hours at about 20ºC, mixed until homogenous, sieved through a 2 mm sieve, and stored in the dark at 16-18ºC before further characterization.

Analysis

Soil physicochemical characteristics include particle size distribution, soil organic matter content, and pH. The distribution of soil particle size was established by an aerometric method [27]. Organic carbon (C_{org}) content was determined by sulfochromic oxidation of organic carbon [28], followed by titration of the excess $K_2Cr_2O_7$ with $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$. Organic matter content (OM) was calculated and based on the relationship: OM=1.724*C_{org}. pH was measured potentiometrically in 1:2.5 (m/V) suspension of soil in 1 mol·L^{-1} KCl solution [29].

OCP analysis comprises three HCH congeners (α-HCH, β-HCH, and γ-HCH) and three DDT compounds (pp'DDT, pp'DDE, and pp'DDD). The analytical procedure followed the ISO 10382 [30] standard with some modifications. Soil samples (10 g) were mixed with 2 g of diatomaceous earth, spiked with 10 µL of a recovery standard (PCB-155, Dr. Ehrenstorfer GmbH), and subjected to pressurized fluid extraction in the Dionex ASE200 apparatus with a mixture of hexane and acetone (70:30 v/v). Soil extracts were concentrated and the solvent was exchanged to hexane. The concentrated extracts were passed through a glass column packed with glass wool, 2 g of deactivated alumina oxide (15% in MilliQ water), 1 g of powdered mercury, and 1 cm of anhydrous sodium sulfate. The eluates were transferred to a dry packed adsorption column and eluted with 20 mL of petroleum ether. The solvent was exchanged to hexane following vacuum evaporation; the extracts were concentrated to 1 mL. Determinations of DDT and HCHs were performed in a single run using gas chromatography (Agilent 6890) with microelectron capture detector (^{63}Ni) and confirmed for select samples by gas chromatography-mass spectrometry in selected ion monitoring mode. The fused silica capillary column (DB-5, 30 m × 0.32 mm I.D, 0.32 µm film thickness, Agilent Technologies) was applied. Quality control included calculations of method detection limits (MDLs) from the procedural blanks (n=6) according to the equation MDL=100*LOD, where LOD is the limit of detection in µg·mL^{-1}. The MDL for pp'DDT, pp'DDD and pp'DDE was within limits of 0.17-0.03 µg·kg^{-1}. For α-HCH, β-HCH and γ-HCH, the MDLs were 0.03 µg·kg^{-1}, 0.06 µg·kg^{-1}, and 0.05 µg·kg^{-1}, respectively. In cases where the contaminant concentration was below the method quantification limits (MQL=3MDL), the MDL was used for the calculations. The recoveries, calculated from spiked sand samples, were between 71-82% for the DDTs and 59-67% for the HCHs. More detailed analysis methodology was described elsewhere [31].

Statistic

Statgraphics Centurion (version XV, Statpoint Technologies, Inc. Warrenton, VA) was used for statistical analyses. All data were tested to meet assumptions for parametric statistical analysis and were log transformed when necessary (normal distribution checked based on standardized skewness and standardized kurtosis). For basic evaluations a standard set of summary statistics was applied. The median values were considered best for the description of the overall mean data. One-way analysis of variance (ANOVA) was used for the evaluation of the differences between the parameters with application of LSD procedure to discriminate among the means (at $p \leq 0.05$ level). Pearson's product-limit correlation was used as a measurement of association among the chemical and soil parameters. Values of $p \leq 0.05$ were considered statistically significant.

Results and Discussion

Soil Characteristics

Generally, the basic physicochemical characteristics of the soils were relatively uniform (CoV of 16-62%). The medians (M) for the content of the clay fraction φ<20 µm and organic matter (OM) were 21% and 1.67%, respectively, while median for pH was 5.25 (Table 1). These correspond to the coarse texture, low organic matter, and acidic soils – typical not only for Poland, but also for other neigh-

Table 1. Statistical evaluation of soil properties and OCP concentrations (n=214).

Parameter	Average (A)	Median (M)	Range (R)	Lower quartile (LQ)	Upper quartile (UQ)	Standard deviation (SD)	Coeff. of variation (CoV)
Soil properties							
fr<0.02 mm (%)	25.30	21	4-83	14	36	16	62%
OM (%)	1.89	1.67	0.12-5.46	1.4	2.06	0.84	44%
pH_{KCl}	5.24	5.25	3.50-6.90	4.60	5.90	0.84	16%
OCP concentrations (μg·kg^{-1})							
α-HCH	0.29	0.18	0.02-1.52	0.12	0.35	0.28	95%
β-HCH	0.09	0.06	0.02-1.33	0.06	0.06	0.11	129%
γ-HCH	5.87	2.55	0.05-151.44	1.47	5.06	12.96	221%
Σ3HCH	6.25	2.85	0.11-152.08	1.8	5.55	13.01	208%
pp`DDT	26.80	11.28	0.17-325.57	4.18	29.72	41.49	155%
pp`DDE	2.20	9.44	0.04-212.45	3.04	22.06	31.95	150%
pp`DDD	21.35	0.80	0.03-141.25	0.28	1.91	9.78	444%
Σ3DDT	50.35	24.39	0.24-450.09	8.11	60.13	70.43	140%
Total OCP	56.60	29.67	0.35-453.20	13.03	65.97	72.44	128%

boring countries like the Czech Republic [3]. Complete characteristics of the soil samples was supplied by Terelak et al. [26].

The regional variability of soil properties was less pronounced; the mean OM content for 16 provinces was within limits of 1.3-2.4% and pH_{KCl} in the range of 4.3-5.3 (data not shown).

Concentrations and Composition of DDTs and HCHs in Soils

Statistical evaluations of the concentrations of OCPs, DDTs, and HCHs in the soils are given in Table 1. The total content of OCPs ranged widely from 0.35 to 453.2 μg·kg^{-1}, but the interquartile range was narrow (13.03-65.97 μg·kg^{-1}). Comparable values were reported in China (4.80-219.10 μg·kg^{-1}) [8], while higher range (6-12,644 μg·kg^{-1}) was observed in soils in Romania [15]. The dominant contaminants were DDTs (over 83% of total OCP content). This is justified by the greater popularity of DDTs and its wider use in Poland in relation to Lindane [21], as well as by its greater persistence [5, 10, 33]. Similar DDT prevalence in the OCP group was reported in other studies [3, 8, 10, 33].

The concentrations of Σ3DDTs exhibited higher variability (CoV of 140%) than total OCPs (Table 1) with the interquartile range of 8.11-60.13 μg·kg^{-1}. The median contents of individual isomers decreased in the order pp'DDT>pp'DDE>pp'DDD with the concentration of pp'DDD one order lower than the two other isomers. High prevalence of pp'DDE, the product of dehydrochlorination, confirms predominance of transformation processes typical for aerobic environments such as the plough layer of arable soils [5, 7]. The concentrations of DDTs in the soils are comparable with the results of other studies presented in Table 2. The median content of Σ3DDTs (24.39 μg·kg^{-1}) is on the same level as data of Kawano et al. [10] and Szpyrka et al. [12] for Poland, Holoubek et al. [3] for the Czech Republic (34.2 μg·kg^{-1}), Ene et al. [15] for Romania (23.3 μg·kg^{-1}), and Li et al [19] for Yangtze River Delta in China (15.71 μg·kg^{-1}). Higher DDT contents were found by Witczak et al. [34] in the forest soils in Szczecin region in Poland (Table 2). The last observation can be explained by the fact that DDTs form strong associations with soil organic substances, and forest soils are usually more reachable in organic matter than arable soils [3, 8, 15]. This may lead to stronger sorption and lower degradation rates of DDT residues.

The concentrations of total HCHs were one order of magnitude lower than DDTs with median value of ΣHCHs of 2.85 μg·kg^{-1} and interquartile range of 1.80-5.55 μg·kg^{-1} (Table 1). There was no statistically significant relationship (at $p \leq 0.05$ level) between the content of HCHs and DDTs (data not shown). The dominant compound was γ-HCH, which contributed 90% to the Σ3HCHs, followed by α-HCH (median contribution 7%) and β-HCH (2%). These results are in agreement with the fact that γ-HCH was the main component (99 %) of pure Lindane, which was widely used in the past in Poland [6, 10]. The same tendency (predominance of γ-HCH) was observed by Falandysz et al. [5] for soils from southern Poland. Low contributions of α-HCH in total HCH residues in soils do not exclude limited use of technical HCH (60-70% α-HCH, 5-12% β-HCH, and 10-12% γ-HCH) or even specific applications (e.g. forest fumigations) of BHC with α-HCH as the main constituent [5].

Table 2. Concentrations of DDTs and HCHs in select soils around the world.

Location (n)	Concentration of pesticides (μg·kg^{-1})			References
	Mean	Median	Range	
ΣDDT				
China, Yangtze River Delta – agricultural soils (39)	36.49	15.71	0.57- 302.73	Li et al. [19]
China, Beijing – alluvial soils (131)	77	-	1.4-5910.8	Zhang et al. [32]
East China – upland field (22)	16.58	-	ND – 73.55	Gao et al. [8]
Romania SE, various sites (17)	108	23.3	ND – 5826	Ene et al. [15]
Romania SE, background soils (7)	27	10.5	ND – 93	Ene et al. [15]
Romania, South – rural (17)*	214.7	-	64.6-466.9	Covaci et al. [35]
Mexico, Tabasco – surface soils	-	11-46**	2-123	Torres-Dosal et al. [38]
Czech Republic – arable soils (39)	113.7	34.2	4.0-1018.3	Holoubek et al. [3]
Germany – central area agricultural soils (11)	63.87	-	23.7-173	Manz et al. [9]
Poland, Katowice – urban soils (9)	110	-	23-260	Falandysz et al. [5]
Poland – forests in Szczecin region (7)	81.67	83.8	50.2-120.2	Witczak et al. [34]
Poland – agricultural soils (16)	210	25.5	1.1-1700	Kawano et al. [10]
Poland SW – agricultural soils (50)	41	14	0.1-29.6	Szpyrka et al. [12]
Poland – Lublin region, agricultural soils (34)	-	25.18	3.32-385.20	Maliszewska-Kordybach et al. [31]
Poland – agricultural soils (214)	50.35	24.39	0.24-450.09	This study
pp`DDT				
East China – upland field (22)	4.44	-	ND – 18.55	Gao et al. [8]
China, Beijing – alluvial soils (131)	19.06	-	ND – 1778.70	Zhang et al. [33]
Czech Republic – arable soils (39)	58.36	20.30	1.88-516.40	Holoubek et al. [3]
Germany – central area agricultural soils (11)	-	-	14.7-87.1	Manz et al. [9]
Poland – Lublin region, agricultural soils (34)	-	11.31	1.29-385.20	Maliszewska-Kordybach et al. [31]
Poland – forests in Szczecin region (7)	34.56	36.12	23.7-48.9	Witczak et al. [34]
Poland – agricultural soils (214)	26.80	11.28	0.17-325.57	This study
ΣHCH				
Czech Republic – arable soils (39)	3.54	4.00	0.65-4.00	Holoubek et al. [3]
Romania SE, various sites (17)	65	24.5	ND – 6818	Ene et al. [15]
Romania SE, background soils (7)	15	3	ND – 61	Ene et al. [15]
Romania, South – rural (17) a	193.5	-	150.7-236.3	Covaci et al. [35]
China, Hong Kong, surface soils	6.2	-	5.7-7.6	Zhang et al. [32]
Germany – central area agricultural soils (11)	-	-	4.60-11.50	Manz et al. [9]
China, Beijing – alluvial soils (131)	1.47	-	0.64-32.32	Zhang et al. [33]
Poland, Katowice – urban soils (9)	5.9	-	1.1-11	Falandysz et al. [5]
Poland – agricultural soils (16)	5.06	0.66	ND – 27	Kawano et al. [10]
Poland – Lublin region, agricultural soils (34)	-	0.22	0.04-0.48	Maliszewska-Kordybach et al. [31]
Poland – forests in Szczecin region (7)	5.78	6.55	2.22-8.23	Witczak et al. [34]
Poland – agricultural soils (214)	6.25	2.85	0.11-152.08	This study

Table 2. Continued.

Location (n)	Concentration of pesticides (μg·kg⁻¹)			References
	Mean	Median	Range	
γHCH				
China, Beijing – alluvial soils (131)	0.28	-	ND – 2.63	Zhang et al. [32]
East China – uppland field (22)	0.84	-	ND – 5.05	Gao et al. [8]
Czech Republic – arable soils (39)	0.91	1.00	0.18-1.00	Holoubek et al. [3]
Germany – central area agricultural soils (11)	-	-	1.54-5.60	Manz et al. [9]
Poland – Lublin region, agricultural soils (34)	-	0.06	0.05-0.45	Maliszewska-Kordybach et al. [31]
Poland – forests in Szczecin region (7)	5.37	5.40	2.22-8.23	Witczak et al. [34]
Poland – agricultural soils (214)	5.87	2.55	0.05-151.44	This study

*0-5 cm layer, **geometric mean

α-HCH is the most volatile isomer, thus its persistence in soils is relatively low [5, 22, 33]. Simultaneously, high volatility increases the possibility of long-range transport of α-HCH and its inputs to soils with atmospheric depositions transported from treated regions [2, 15]. Our data are in contrast to information from southeastern Romania [15, 35], where α-HCH had highest shares (>63%) in ΣHCH burden in soils. The authors concluded that this was technical HCH, which was used in agricultural practices in the majority of locations in Romania instead of pure Lindane [15]. The very low contribution of γ-HCH (about 15%) in total HCH burden was observed by Gao et al. [8] in soils from Hongze Lake region in China; the dominant isomer was β-HCH – the most stable and the least degradable among other HCH isomers.

Assessment of the Level of Pollution of Soils with DDTs and γ-HCH

Systems of evaluations of soils contaminated with OCPs varied widely in different countries. One of the reasons is insufficient amount and quality of data on the effects of those substances on humans and biological components of terrestrial ecosystems [22]. Polish regulations [36] include only one guide value for soils of specific use, allowing for classification into two arbitrary groups (polluted-unpolluted), while in many systems diverse limit values related to the degree of hazard for humans and ecosystem (e.g. normal, precautionary, alert, trigger, intervention, target, etc.) are applied [22].

The level of pollution of soils with ΣDDTs and HCH isomers was evaluated on the basis of the Polish limit values (PLV) for upper layers of soils for agricultural use [36] (Figs. 2 and 3). For comparison, two other systems having clear criteria for agricultural soils were applied: one system (from Romania) as an example of a Central European country [35] and another from Canada [17].

Half of the soil samples exhibited too high level of DDT residues as compared to PLV (Σ3DDTs of 25 μg·kg⁻¹), 27 % of the samples had content of Σ3DDTs more than two times higher, and in 14.5% the concentrations of Σ3DDTs exceeded the PLV four times (Fig. 2). This corresponds well with the data (48% of contaminated samples) for agricultural soils in Lublin region [31, 37] and the level of contamination of river sediments in Poland (45% of samples

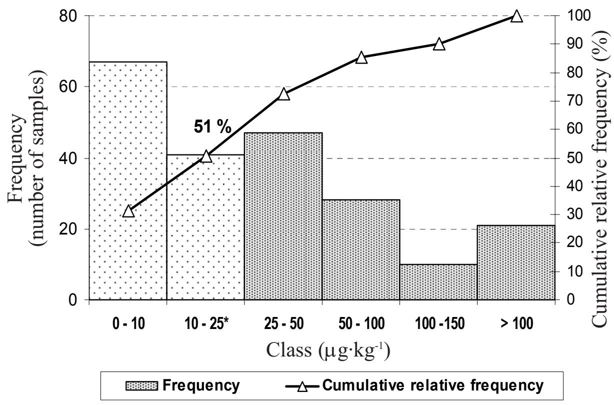

Fig. 2. Histogram of Σ3DDT concentrations in arable soils in Poland.*) limit value for the upper layer of soils of agricultural use according to Polish regulations [36]; bars with lighter shading denote classes below limit value.

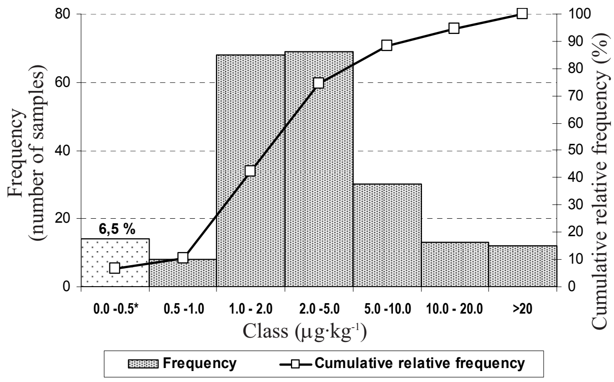

Fig. 3. Histogram of γ-HCH concentrations in arable soils in Poland.*) limit value for the upper layer of soils of agricultural use according to Polish regulations [36]; bar with lighter shading denotes class below limit value.

exceeded the limit) that received OCPs from agricultural fields [6]. Romanian regulations [35] specify the threshold value for "normal content" of DDTs in agricultural soils as 150 $\mu g \cdot kg^{-1}$ – this criterion is met by 90% of the samples from arable fields in Poland (Fig. 2). The same regulations set "alert value" (requirement of monitoring and reduction) for an agricultural soil as 500 $\mu g \cdot kg^{-1}$ [35]; similar limit value is specified in Chinese regulations (class II) as ensuring the safety of agricultural products [33]. Canadian Soil Quality Guidelines for the Protection of Environment and Human Health give an even higher limit (700 $\mu g \cdot kg^{-1}$) for the acceptable concentration of total DDT in soils of agricultural use [17]. According to all these systems the soils from the arable land in Poland do not create a hazard for human health or biotic elements of the environment and do not need any actions.

Relatively high DDT residues in part of the agricultural soils are a consequence of intensive application of this pesticide in the past periods in Poland and other European countries [3, 5, 6, 20, 38]. The extensive use of DDT resulted both from its efficacy as an insecticide and from the low costs of manufacturing. It is estimated that approximately 0.7-0.8 million Mg were produced in Europe in 1945-83 [17]. However, in spite of many restrictions and bans, DDT is still being produced and used in many equatorial countries, [3, 7, 14]; from these areas they can be transported with atmospheric particles to temperate regions, i.e. to most European countries, including Poland [1].

Evaluations of γ-HCH residues indicate on higher level of contamination than in the case of DDT – Fig. 3. The relevant PLV (0.5 $\mu g \cdot kg^{-1}$) has been met in no more than 6.5% of the samples (Fig. 3). 58% of the total data set exhibited content at least four times higher than the guideline and in almost 12% of the soils the limit was exceeded 20 times. Romanian "normal level" of 1 $\mu g \cdot kg^{-1}$ [35] was met in 10.3% of samples, while the guide value of 20 $\mu g \cdot kg^{-1}$ for "alert level" was exceeded in 6% of soils (Fig. 3). Three sampling points (1.5%) had the content of γ-HCH higher than the Romanian "intervention value" of 50 $\mu g \cdot kg^{-1}$ [35]; their diversified locations suggest accidental pollution (data not shown). Canadian limit value [17] for Lindane in agricultural soils (10 $\mu g \cdot kg^{-1}$) was not met in 11.7% of the samples (Fig. 3). Compared to DDT, the use of Lindane in the past years in Poland was lower (7519 Mg versus 48,152 Mg of DDTs) [10] and its concentrations in soils are 10 times lower than DDTs (Table 1). However, Lindane had a very broad scope of applications; besides direct use as a pesticide it was utilized widely for veterinary purposes and the protection of seed corn [9, 10]. It has been applied longer after the withdrawal of the use of DDTs and even after the official ban time [10]. Atmospheric depositions also contribute substantially to HCH inputs to soils; Poland is estimated as the country with moderate annual net deposition fluxes of γ-HCH; however, those assessments are considered to be underestimated [13]. Disadvantageous results of the assessment of the state of pollution of the soils with γ-HCH are mainly a consequence of low threshold values for γ-HCH, resulting from chemical and biological properties creating higher risk of leaching and negative ecotoxic effects [5, 7]. One limit value specified by Polish regulation [36] does not allow for the evaluation of different levels of risk. More differentiated Canadian [17] and Romanian [35] systems lead to more positive and realistic evaluations. High level of contamination of the soils with γ-HCH (many times higher than recommended values) was also observed in central Germany [9].

In none of the samples did the concentrations of β-HCH or α-HCH exceed the limits set in Polish regulations, which are 10 $\mu g \cdot kg^{-1}$ and 25 $\mu g \cdot kg^{-1}$, respectively [36]. This indicates that those residues in the studied soils are not problematic.

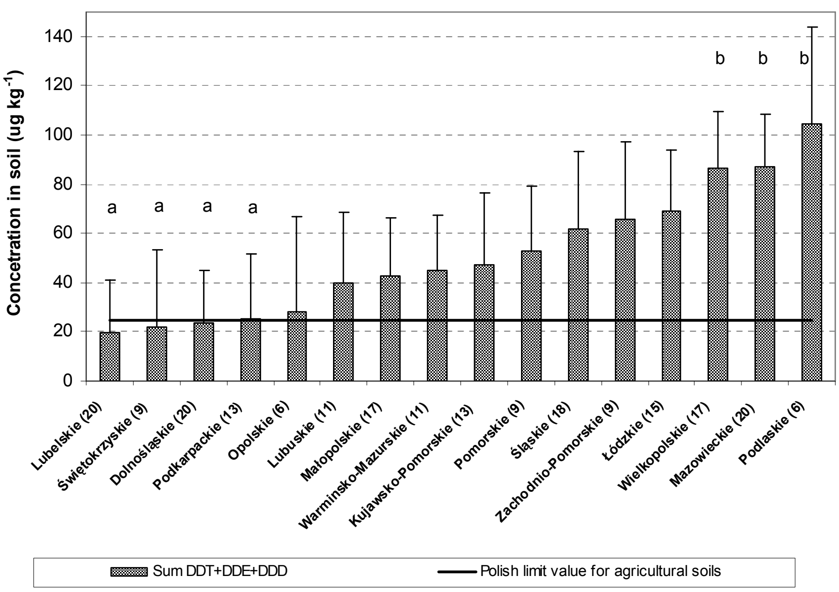

Fig. 4. Mean concentrations of Σ3DDTs in arable soils in the main administrative districts (provinces) in Poland. X axis; in parentheses are the number of sampling points in the district. The bars represent 95% LSD limits (+). The values with the same letter do not differ significantly at p≤0.05 level.

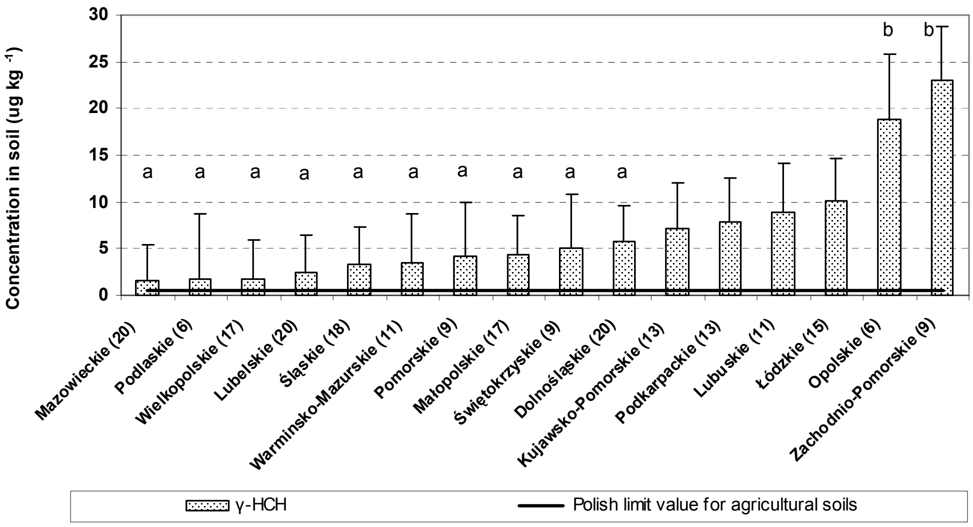

Fig. 5. Mean concentrations of γ-HCH in arable soils in the main administrative districts (provinces) in Poland. X axis; in parentheses are the number of sampling points in the district. The bars represent 95% LSD limits (+). The values with the same letter do not differ significantly at p≤0.05 level.

Regional Variability in OCP Concentrations

The concentrations of ΣDDT and γ-HCH in the main Polish provinces are presented in Figs. 4 and 5. In both cases the data varied widely. Two groups of regions with statistically different (p≤0.05) mean contents of DDTs can be distinguished. The territories exhibiting highest residues of Σ3DDTs include Podlaskie, Mazowieckie and Wielkopolskie, while a less contaminated group covers Lubelskie, Świętokrzyskie, Dolnośląskie, and Podkarpackie provinces (Fig. 4). The most uniform (CoV of 45-95 %) results were obtained in Lubuskie, Podlaskie, and Śląskie provinces, while the highest differences (CoV of 143-150%) were observed in Świętokrzyskie, Opolskie, Warmińsko-Mazurskie, and Dolnośląskie provinces. This may indicate local pollution sources or incidental contamination at some points. Data on the residues of DDTs in soils were not related (data not shown) to the actual profiles of agricultural production [23] or the regional use of pesticides [24].

Assessments of the regional variability of γ-HCH residues (Fig. 5) varied from those for of DDTs. The most contaminated group covers two Provinces: Zachodnio-Pomorskie and Opolskie, characterized even presently by the highest usage of pesticides for four main crops production [24]. A statistically different (p≤0.05) group with the lowest γ-HCH concentrations includes 10 provinces: Mazowieckie, Podlaskie, Wielkopolskie, Lubelskie, Śląskie, Warmińsko-Mazurskie, Pomorskie, Małopolskie, Świętokrzyskie, and Dolnośląskie. Variability of inter-regional results was also different than for DDT data. The concentrations of γ-HCH in all provinces from the less contaminated group were relatively uniform (CoV of 43-95%). The highest variability (CoV of 210%) was in Zachodnio-Pomorskie Province with the highest mean γ-HCH residues followed by Lubuskie and Kujawsko-Pomorskie provinces (data not shown).

High levels of DDTs and HCHs in northwestern Poland were reported in other publications [10, 34], while the low content of HCHs in the agricultural soils from Lublin region was confirmed in our earlier studies [31, 37].

For both pesticide residues it was difficult to establish geographical relationships, but the results exhibit an interesting regularity: provinces with the highest DDT content in soils (Podlaskie, Wielkopolskie, and Mazowieckie) are characterized by the lowest residues of Lindane and vice versa (Figs. 4 and 5). Data on the regional use of those two groups of pesticides in the past times are not available; however, the observed inverse relationship between their residues in soils from the different administrative regions seems to reflect clearly central prescriptive system of distribution of pesticides in Poland before 1980.

Conclusions

The concentrations of DDTs and HCHs in arable soils in Poland are on similar levels to other European countries (Romania, Czech Republic, Germany) and some regions of China (Table 2). DDTs are the main components of the OCPs. Interquartil range (IR) for Σ3DDT is 8.11-60.13 $\mu g \cdot kg^{-1}$ with the median of 24.39 $\mu g \cdot kg^{-1}$. The concentrations of HCHs are one order of magnitude lower with the IR for Σ3HCH of 1.8-5.55 $\mu g \cdot kg^{-1}$ and the median value of 2.85 $\mu g \cdot kg^{-1}$. Assessment of the level of pollution of the soils based on Polish regulations [36] indicates that only half of the samples met the criterion for the content of Σ3DDT in the upper layer of unpolluted agricultural soils (Fig. 2). The same criterion for γ-HCH is met in 6.5% of the soil samples (Fig. 3). In contrast to Polish arbitrary regulations [36], the systems applied in other countries allows for the assessment of the degree of risk. According to Canadian [17] and Romanian [35] regulations, all arable soils in Poland are safe as regards pollution with DDTs, but up to

11.7% of them may create risk due to contamination with γ-HCH. There are significant differences in mean regional concentrations of DDTs and HCHs in Polish arable soils with reverse interdependence of the contents of both groups of pesticides. The Podlaskie, Wielkopolskie, and Mazowieckie Provinces are characterised by the highest mean concentrations of DDTs and the lowest residues of Lindane (γ-HCH). This is likely due to the prescriptive system of distribution of pesticides applied in Poland before the ban on the use of DDT and HCH about 40 years ago.

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