Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.996008

57 (2016) 1310–1321
January

Taylor & Francis
Taylor & Francis Group

Evaluation of organochlorine pesticide residues in soil and plants from East Europe and Central Asia

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Received 9 July 2014; Accepted 19 November 2014

ABSTRACT

Agriculture products such as cereals, fruit, and vegetables are often found to be contaminated with residues of persistent pesticides and other toxic substances. The major source of entry of these compounds to food chain is the contaminated soil. Therefore, the status of the residue level of most persistent organochlorinated pesticides (OCP) in soil and agricultural crops should be monitored regularly. The frequency of occurrence and contamination levels of OCP residues in samples of soils, cereals, fruit and vegetables from different geographical regions such as Central Asia and East Europe were determined. The samples of soil, fruit (black currant), vegetables (beans, carrots, celery, cucumbers, lupine, parsley, and tomatoes) and cereals collected from Kazakhstan and Poland contained residues of different OCPs like aldrine, dieldrine, hexachlorocyclohexane isomers and dichlorodiphenyltrichloroethane (DDT) complex. Endosulfan and dicofol were also found in some samples in the concentration ranging from 0.008 to 0.8 mg/kg, particularly in samples of tomatoes from Kazakhstan. In the samples of the soil taken from Polish and Kazakhs farms, DDT and metabolites were detected. In the case of DDT complex, i.e. DDD, DDE, and DDT, the concentration ranged between 0.005 and 0.542 mg/kg and the pp´ isomers were more frequently encountered than their op´ counterparts.

Keywords: Organochlorinated pesticides; Soil; Fruit; Vegetables; Kazakhstan; Poland

1. Introduction

The Republic of Kazakhstan is a country of the former Soviet Union. All pesticides which were used in the Soviet Union must have also been used in Kazakhstan. The Republic of Kazakhstan has 35 million ha, out of which 20 million ha are fertilized. Previously, the pesticides used in Kazakhstan covered a land area of about 18–20 million ha. Beforehand, the volume of used pesticides was approximately

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Presented at the 12th Scientific Conference on Microcontaminants in Human Environment 25–27 September 2014, Czestochowa, Poland

35 thousand tons of 200 different kinds of pesticides. Over the past few years that land area has been reduced to 10 million ha, and 80% of which make up organochlorine pesticides. The average annual rate of pesticide use almost doubled in the period of 10 years from 1962 to 1972 and was it was supposed to double again before 1994. By 1995 it reached 13.6 thousand tons. This was one of the reasons why Kazakhstan had so many cases of hazardous effects on the health of the population during that time [1,2]. In 1986, the Ministry of Health of Kazakhstan announced publicly about citizens that had been poisoned by organochlorine pesticides. Until 1980 organochlorine pesticides like DDT and HCH and others, had been widely used in Kazakhstan. The use and dispersion of organochlorine pesticides such as DDT, HCH and others over a long period of time polluted from 10 to 20% of soil in Kazakhstan. Unfortunately, the monitoring has not covered the recent years. HCH became banned in 1986, but HCH was included on a special list of pesticides which were permitted to be used as a part of a mix of several pesticides. These are the reasons why lindane occurs widely in a range of living organisms, including humans as it keeps circulating in the environment. Fortunately, endrin, aldrin and dieldrin have never been used in Kazakhstan in agriculture [3], however, endosulfan and dicofol have been used as insecticides for a long time in Kazakhstan [4]. Now these pesticides are also banned. In 1996, the Government of Kazakhstan decided to limit using any banned or spoiled pesticides; 150 out of approximately 574 tons were banned and restricted since they were regarded as highly toxic chemicals [5]. A difficult economic situation has led to the use of banned and spoiled pesticides illegally. In several interviews, plant protection officers and agro-technicians mentioned that pesticides (such as DDT and HCH) that had been banned in the 1970s in the USSR were still widely used in Kazakhstan [6,7]. These banned pesticides are believed to have been retrieved from abandoned pesticide storehouses within Kazakhstan [8] or smuggled in from neighbouring countries and distributed via black market channels. The annual imports of pesticides into Kazakhstan increased from 2076 tons in 1999 to 16,600 tons in 2006, however, these figures refer only to pesticides imported and sold through official channels. There are also many illegal dealers selling generic and surrogate pesticides of unknown provenance (e.g. from China as mentioned above) at cheaper prices. The approximate volume of pesticides smuggled into the country is not known [9].

Polish agriculture differs from both the one in European Union and from other post-communist countries. Due to numerous historical circumstances it is also diversified from the West to the East and from the South to the North of Poland. There are prosperous regions with fertile soils and a high level of intensive agricultural production. Those regions will be able to compete against EU markets. However, there are also regions where the soil quality is poor. Apart from that basic and climatic conditions are adverse for farming and farmers run mostly small-scale farms.

Agriculture still plays an important role in Polish economy. Arable lands account for 59% (18.4 million ha) of the total area of the country with a rate of 0.48 ha of arable lands *per capita*. The numbers show the importance of farming from an economical and social point of view. Compared with agriculture systems in other European countries, Polish agriculture seems to be a lot closer to environmental solutions and improvements. Almost 50 years of communist efforts to collectivise this sector of economy did not bring any spectacular success. Most farmland is still in private hands, farms are small, multifunctional and land management is extensive. The last decade has brought great economic changes effecting Polish farmers more than any other social group. Nowadays Polish agriculture is extensive and sustainable in environmental sense more by the default than by farmers will. The crop yield of extensive farming is relatively low due to low usage of pesticides and fertilizers. The new and stricter monitoring method for production and trade of plant protection products (PPP) came into force in Poland in 2002. Moreover, in 2002 the new system of monitoring regarding the use of pesticides came into force. It is a four-year cycle of monitoring 10 of the most important Polish crops such as: potatoes, cereals, legumes, sugar beets, oil plants, fibre plants, corn, vegetables, strawberries, and orchards [10]. The average use was 3.5 kg/ha (of an active ingredient). The research also showed to what extent Poland is divided in terms of pesticide use—a very high amount of PPP in the western part of Poland with about 6 kg/ha and a very low in the eastern part with about 1.5 kg/ha. It is very important to have an efficient control system of plant PPP in Poland. The harmonization with EU legislation should help to improve this plan. The Stockholm Convention aims at the elimination of persistent organic pollutants (POPs), some of the most unwanted chemicals in the world. POPs are toxic, bioaccumulative, and highly persistent and pose a global threat to all living beings. Nine of the chemicals initially targeted by the POPs convention are pesticides. All nine pesticides are banned in Poland. The Stockholm convention was signed in May 2001. It has to be ratified by at least 50 countries so that it would be introduced. Poland was one of the signing countries. In mid-seventies Poland, almost 500,000 tons of DDT were used. The accumulation of organochlorine compounds (OCs) in environment and foods [11] is still a matter of major concern although the use of most OCs has been banned or restricted in most of the countries due to possible adverse effects that those residues may have after a lengthy exposure at low doses.

To the best of our knowledge, samples in the latest study on organochlorine pesticides pollution in the soil in Kazakhstan area were collected before 2002 and the pollution status had not been monitored and evaluated for many years, it is necessary to conduct a new and comprehensive survey. Currently in Kazakhstan there is no official control of pesticide residues in agricultural crops. However, some studies have been carried out to check the contamination status of organochlorinated pesticides (OCPs) in agricultural soils and cereals, vegetables and fruit in Poland.

Since OCPs have been used in agriculture in Poland and Kazakhstan over a long period of time, an attempt to compare the occurrence of organochlorine pesticide in both countries seems quite interesting. The objectives of this study were to investigate and compare the concentrations of OCPs in agricultural soils and selected crops.

2. Materials and methods

Laboratory analysis was conducted by the Laboratory of Pesticide Residues, Plant Protection Institute–National Research Institute in Bialystok, Poland using accredited methods. Sampling sites are illustrated in Fig. 1. Soil samples (0–10 cm soil layer, 1 kg each) were collected in 2012–2014 with a stainless-steel scoop and stored in PE bags from the north-eastern part of Poland (89 samples), and Almaty region of Kazakhstan (32 samples). Each sample was mixed of six sub samples. All soil samples were placed in dark and transported to the laboratory. Soil samples were air dried, thoroughly mixed, sieved through a 100-mesh. Polish vegetables (beans—52 samples, lupine—1, carrots—148, parsley—78, celery—34, and cucumber—76), fruits (black currant 235 samples) and grain (wheat 146 samples, barley—57 and rye—21) (1 kg each samples) were obtained under the official control of residues of plant PPP conducted in 2008–2013 by the Ministry of Agriculture and Rural Development, implemented in cooperation with regional inspectorates of Plant Protection and Seed. These samples were collected by the inspectors according to a predetermined schedule for a given year. Kazakh vegetables (1 kg each sample) were collected from local supermarkets and open markets during 2011–2013 from Almaty region (cucumber—21 samples, tomatoes—23, and sunflower—2). Samples of grain (wheat—49 samples), were taken from some areas of Kazakhstan, Almaty. All samples were appropriately prepared and stored at −18°C then analyzed and sent to the Polish laboratory.

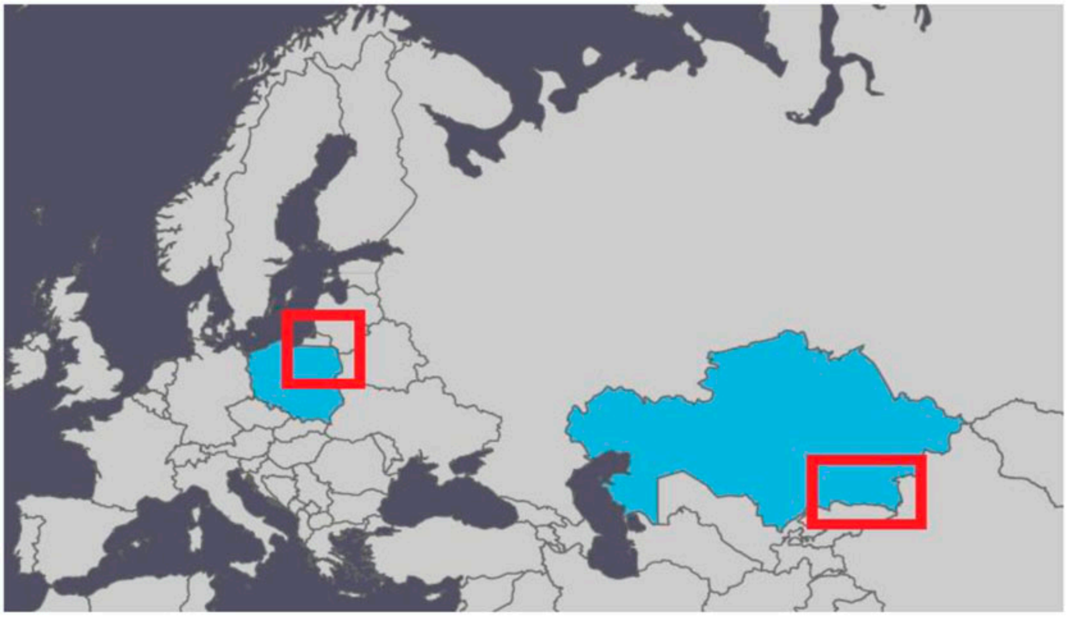

Fig. 1. Sampling sites (http://commons.wikimedia.org/wiki/File:Europe_map_kazakhstan.png).

2.1. Pesticide standards

The standard solution of OCPs including HCH-alpha, HCH-beta, HCH-gamma, HCH-delta, DDD-p,p´, DDE-p,p´, DDT-p,p´, DDT-o,p´, DDD-o,p´, DDE-o,p´, methoxychlor, heptachlor, heptachlor epoxide, endosulfan-alpha, endosulfan-beta, endosulfan-sulfate, aldrin, hexachlorobenzene (HCB), cis-chlordane, trans-chlordane, dieldrin and endrine was purchased from the Dr Ehrenstorfer Laboratory (Germany). Standard stock solutions of various concentrations were prepared in acetone and stored at 4℃ (purity > 95%). The working standards were prepared by dilution with *n*-hexane/acetone (9:1, v/v) mixture (concentration range 0.001–2.5 mg/kg).

2.2. Sample preparation procedure

2.2.1. Soil sample preparation procedure

Two grams of the soil sample was put in a mortar with 4 g of Florisil. This was manually blended using a pestle to produce a homogeneous mixture which was packed into a glass macro column (300 × 12 mm I.D.) with anhydrous sodium sulphate (5.0 g) and silica gel (2.5 g). The adsorbed analytes were eluted using 15 mL hexane/acetone (8:2, v/v) and 15 mL of hexane/acetone/diethyl ether (1:2:2, v/v/v) and collected [12]. The extract was dried by evaporation at a temperature of about 40℃, and dried residue was dissolved in the 2 mL of hexane/acetone (9:1, v/v) and then transferred to 2 mL vials for further GC analysis.

2.2.2. Fruit/vegetables sample preparation procedure

A representative portion of the sample was chopped up and blended. Two grams of a homogenized sample vegetables/fruit was put in a mortar with 4 g of solid support (Florisil). This was manually blended using a pestle to produce a homogeneous mixture which was packed into a glass macro column (300 × 12 mm I.D.) with anhydrous sodium sulphate (2.0 g) and silica gel (4.0 g). The adsorbed analytes were eluted using 15 mL hexane/acetone (8:2, v/v) and 15 mL of acetone/diethyl ether (2:8, v/v). The extract was dried by evaporation at a temperature of about 40℃, and dried residue was dissolved in the 2 mL of hexane/acetone (9:1, v/v) and then transferred to 2 mL vials for further GC analysis.

2.2.3. Grain sample preparation

A representative portion of grain was blended. Two grams of the grain sample was put in a mortar with 4 g of Florisil. This was manually blended using a pestle to produce a homogeneous mixture which was packed into a glass macro column (300 × 12 mm I.D.) with anhydrous sodium sulphate (2.5 g) and silica gel (2.5 g). An additional layer of anhydrous sodium sulphate (2.0 g) was put on the bottom of a column. The adsorbed analytes were eluted using 25 mL of an acetone/methanol mixture (9:1, v/v). The extract was evaporated at a temperature of about 40℃ and then diluted in 2 mL of hexane/acetone (9:1, v/v). 1.7 mL of extract was placed in an SPE C-18 column, which had been rinsed twice with 5 mL acetonitrile earlier, however, it should not dry. Analytes were eluted with 15 mL acetonitrile. The extract was collected in a round-bottomed flask. The extract was dried by evaporation at a temperature of about 40℃, and dried residue was dissolved in the 2 mL of hexane/acetone (9:1, v/v) and then transferred to 2 mL vials for further GC analysis [13].

2.3. GC–EC conditions (two a fused silica capillary columns)

Quantitative estimation of OCPs pesticide residues in all extracts was done by an Agilent 7890 gas chromatograph (Santa Clara, CA, USA) equipped with a Model HP 7683 automatic split-splitless injector, a ^{63}Ni micro-electron capture detector (μEC). Data acquisition and processing were performed with Chemstation (Hewlett-Packard, version A.10.2) software. The DB-35, a midpolarity fused silica column (35%-phenyl)-methylpolysiloxane) with low bleed (30 m × 0.32 mm I.D. × 0.5 μm film thickness), supplied by Agilent (Little Falls, DE, USA), was employed. High purity helium was used as a carrier gas at a constant flow of 1.9 mL/min and nitrogen as a make-up gas (57 mL/min), hydrogen 3.0 mL/min and air 60 mL/min. Details of gas chromatography operating parameters were as follows: the injector and detector temperature was 300℃, oven program: the initial temperature being 120℃ increased to 190℃ at 13℃/min, then to 240℃ at 8℃/min and finally to 295℃ at 168℃/min and it was maintained at that level for 20 min. Two microliters of each sample was injected at 210℃ in a splitless mode (purge off time 2 min). The total time of analysis: 35 min and equilibration time 2 min. Individual OCPs were identified by comparing the retention time between samples and the standard solution. Quantification was performed by comparing the height of peaks obtained in samples with those found in matrix-matched calibration standards for the mixture (±0.005 min for positive match). In the case of positive peaks of pesticides detected above LODs, the results were confirmed by the analysis on a different polarity column. A fused silica capillary column, HP-5, with 5% phenyl methyl siloxane as the nonpolar stationary phase (30 m × 0.32 mm I.D. × 0.25 μm film thickness) was found to be ideal for a conformational analysis under the following conditions: high purity helium was used as a carrier gas at a constant flow of 3.0 mL/min and nitrogen as a make-up gas (57 mL/min), hydrogen 3.0 mL/min and air 60 mL/min. The oven temperature program was as follows: the injector and detector temperatures were 210 and 300℃, respectively, the oven—the initial temperature: 120℃ increased to 190℃ at 16℃/min, then to 230℃ at 8℃/min and finally to 285℃ at 18℃/min and maintained for 10 min.

2.4. Quality assurance (QA) and quality control (QC)

The correlation coefficients (*r*) of calibration curves of OCPs were all higher than 0.995. The limits of detection were detected with a signal-to-noise (S/N) of three, ranging from 0.001 to 0.214 mg/kg. Method blanks were run using the same solvents as for real samples. No contaminants of organochlorine pesticides were found in the method blanks. The procedure was checked for recovery efficiencies by spiking the concentrations of OCPs standards in a matrix blank. The method blank and spiked blank were used to check for the interference and cross contamination. GC analysis was repeated twice for each replicate sample. The spiked recoveries of OCPs ranged from 87.10 to 100.64% and the relative standard deviation (RSD) was less than 14%. These parameters confirmed the practicability of the analytical protocol in the determination of OCPs in the soil/vegetables/fruit/bees/meat.

The laboratory of pesticide residues in Bialystok regularly participates (2–4 times per year) in proficiency tests. This is an important way of meeting the requirements of ISO/IEC 17025 in the area of quality assurance of laboratory results. It is also mandated by PCA (Polish accreditation bodies) that laboratories participate in proficiency testing programs for all types of analyses undertaken in the laboratory provided that suitable programs exist.

3. Results and discussion

This study involved examination of 937 fruit, vegetables and soil samples from the north-eastern part of Poland and 159 vegetables and soil samples from the south-eastern Kazakhstan (Fig. 1). Additionally, we included in this study 28 Polish samples of bees and 18 Kazakhs samples of beef meat have been prepared according to the methodology described earlier [14]. The chloro-organic insecticides: HCH (alfa and beta), DDT and metabolites, endosulfan and metabolites, aldrine, dieldrin and dicofol were detected in soil, vegetables, fruit, bees and meet samples. The occurrence and concentration of pesticides are presented in Tables 1 (soils samples) and 2 (fruit, vegetables, grain, bees and meat).

The total concentrations of tested organochlorine pesticides in Polish samples ranged between 0.001and1.19 mg/kg, and in Kazakh 0.001–0.62 mg/kg. Tables 1 and 2 showed that DDE-p,p´, DDD-p,p´, DDT-o,p´, DDT-p,p´, HCH (alfa and gamma), dicofol, aldrin and endosulfan were detected most frequently in Kazakh samples and DDE-p,p´, DDD-p,p´, DDT-o,p ´, DDT-p,p´, HCH (alfa and gamma), dieldrin and endosulfan in Polish samples.

Most of the analyzed samples were contaminated by DDT. DDT is an organochlorine insecticide with a broad spectrum of activity which is used to control agricultural crops, insects in forest, household pests and to control insect-transmitted diseases. Due to its effectiveness, long residual persistence, low acute toxicity and low cost, the application of DDT was once very popular. Commercial or technical DDT usually contain DDT-p,p´ as the main component (65–80%), together with smaller amounts: -DDT-o,p´ (15–21%), p, p´-dichlorodiphenyldichloroethane (DDD-p,p´) (up to 4%) and the contaminant, 1-(p-chlorophenyl)-2,2,2-trichloroethanol (up to 1.5%).

Average total concentrations of DDT in Polish and Kazakh soil samples were 0.104 and 0.097 mg/kg appropriately. Compared with other countries, it was higher than those in agricultural soil in Argentina (0.026 mg/kg) [15], Brazil (0.005 mg/kg) [16], China (0.014 mg/kg) [17], US (0.009 mg/kg) [18], Pakistan (0.039 mg/kg) [19] and Germany (0.023 mg/kg) [20], but lower than those in agricultural soil of Romania (0.226 mg/kg) [21] and India (0.939 mg/kg) [22]. In comparison with China, the mean value of ΣDDTs (0.104 mg/kg and 0.097 mg/kg) in this study was higher than those in agricultural soils in China such as Pear River Delta region (0.0376 mg/kg) [23], Taihu Lake region (0.050 mg/kg) [24], Beijing (0.032 mg/kg) [25].

DDTs and HCHs were still the predominant pesticides in soil. DDT-p,p´ degrades to -DDE-p,p´ in aerobic environment and to DDD-p,p´ in anaerobic environment. Surface soil samples in aerobic environment were collected in this study and this might elucidate the highest detection frequency of DDE-p,p´ (Fig. 2). The ratio of DDT-p,p´/(DDE-p,p´ + DDD-p,p´) can be used to indicate whether DDT -p,p´ in soils is

Table 1
The occurrence and concentration of pesticides in soils samples

Poland (89)					Kazakhstan (32)				
No. of sample	Pesticide	Concentration (mg/kg)	F1	F2	No. of sample	Pesticide	Concentration (mg/kg)	F1	F2
1	DDT-p,p´	0.03			1	DDT-p,p´	0.043		
	DDT-o,p´	0.004				DDT-o,p´	0.006		
	DDD-p,p´	0.008				DDD-p,p´	0.017		
	DDE-p,p´	0.009				DDE-p,p´	0.054		
	DDT-sum	0.051	1.76	0.13		DDT-sum	0.12	0.61	0.14
2	DDT-p,p´	0.036			2	DDT-p,p´	0.06		
	DDT-o,p´	0.004				DDT-o,p´	0.03		
	DDD-p,p´	0.008				DDD-p,p´	0.03		
	DDE-p,p´	0.021				DDE-p,p´	0.12		
	DDT-sum	0.069	1.24	0.11		DDT-sum	0.24	0.40	0.50
3	DDT-p,p´	0.084			3	DDT-p,p´	0.02		
	DDT-o,p´	0.019				DDT-o,p´	0.005		
	DDD-p,p´	0.006				DDD-p,p´	0.009		
	DDE-p,p´	0.043				DDE-p,p´	0.03		
	DDT-sum	0.152	1.71	0.23		DDT-sum	0.064	0.51	0.25
4	DDT-p,p´	0.254			4	DDT-p,p´	0.011		
	DDT-o,p´	0.043				DDT-o,p´	0.004		
	DDD-p,p´	0.107				DDD-p,p´	0.008		
	DDE-p,p´	0.006				DDE-p,p´	0.026		
	DDT-sum	0.41	2.25	0.17		DDT-sum	0.049	0.32	0.36
5	DDT-p,p´	0.018			5	DDT-p,p´	0.009		
	DDT-o,p´	0.004				DDT-o,p´	0.004		
	DDD-p,p´	0.003				DDD-p,p´	0.005		
	DDE-p,p´	0.003				DDE-p,p´	0.012		
	DDT-sum	0.028	3.00	0.22		DDT-sum	0.03	0.53	0.44
6	DDT-p,p´	0.112			6	DDT-p,p´	0.121		
	DDT-o,p´	0.019				DDT-o,p´	0.057		
	DDD-p,p´	0.009				DDD-p,p´	0.043		
	DDE-p,p´	0.004				DDE-p,p´	0.321		
	DDT-sum	0.144	8.62	0.17		DDT-sum	0.542	0.33	0.47
7	DDT-p,p´	0.028			7	DDT-p,p´	0.008		
	DDT-o,p´	0.007				DDT-o,p´	0.003		
	DDD-p,p´	0.004				DDD-p,p´	0.003		
	DDE-p,p´	0.003				DDE-p,p´	0.018		
	DDT-sum	0.042	4.00	0.25		DDT-sum	0.032	0.38	0.38
8	DDT-p,p´	0.365			8	DDT-p,p´	0.021		
	DDT-o,p´	0.068				DDT-o,p´	0.004		
	DDD-p,p´	0.026				DDD-p,p´	0.007		
	DDE-p,p´	0.006				DDE-p,p´	0.085		
	DDT-sum	0.465	11.41	0.19		DDT-sum	0.117	0.23	0.19
9	DDT-p,p´	0.195			9	DDT-p,p´	0.006		
	DDT-o,p´	0.031				DDE-p,p´	0.008		
	DDD-p,p´	0.017				DDT-sum	0.014	0.75	
	DDE-p,p´	0.004			10	DDT-p,p´	0.004		
	DDT-sum	0.247	9.29	0.16		DDE-p,p´	0.008		
10	DDT-p,p´	0.118				DDT-sum	0.012	0.50	
	DDT-o,p´	0.047			11	DDT-p,p´	0.006		
	DDD-p,p´	0.033				DDE-p,p´	0.011		
	DDE-p,p´	0.214				DDT-sum	0.017	0.55	
	DDT-sum	0.412	0.48	0.40	12	DDE-p,p´	0.015		

(*Continued*)

Table 1 (*Continued*)

Poland (89)					Kazakhstan (32)				
No. of sample	Pesticide	Concentration (mg/kg)	F1	F2	No. of sample	Pesticide	Concentration (mg/kg)	F1	F2
11	DDE-p,p´	0.005			13	DDT-p,p´	0.007		
	DDT-p,p´	0.006			14	HCH-alfa	0.006		
	DDT-sum	0.011	1.20		15	HCH-gamma	0.007		
12	DDE-p,p´	0.004							
	DDT-p,p´	0.006							
	DDT-sum	0.01	1.50						
13	DDE-p,p´	0.007							
	DDT-p,p´	0.009							
	DDT-sum	0.016	1.29						
14	DDE-p,p´	0.015							
	DDT-p,p´	0.01							
	DDT-sum	0.025	0.67						
15	DDD-p,p´	0.005							
16	DDT-p,p´	0.01							
17	HCH-gamma (lindan)	0.004							
18	HCH-gamma (lindan)	0.006							

F1 = DDT-pp´/DDE-pp´ + DDD-pp´.

F2 = DDT-op´/DDT-pp´.

"aged (degraded)" or "new (input recently)" [26]. A ratio less than 1 indicates historical DDT or no input in the environment while a value much greater than 1 indicates fresh application [27]. In this study, the ratios of DDT-p,p´/(DDE-p,p´ + DDD-p,p´) varied from 0.23 to 11.41 (Table 1). Some differences were observed in DDT-p,p´/(DDE-p,p´ + DDD-p,p´) in the soil from both countries. This value was higher for Polish samples and ranged between 0.48 and 11.41 than Kazakh ones ranged between 0.23 and 0.75.

The ratio of DDT-o,p´/DDT-p,p´ was applied to distinguish whether DDT contamination was caused by the usage of technical DDT or dicofol. Generally, DDT-o,p´/DDT-p,p´ ranges from 0.2 to 0.3 in technical DDT and from 1.3 to 9.3 or higher in dicofol [28]. In this study, the minimum ratio of DDT-o,p´/DDT-p,p´ was similar in Kazakh and Polish samples 0.14 and 0.11, and the ratios of DDT-o,p´/DDT-p,p´ ranged from 0.11 to 0.50 (Table 1). It was higher than 0.3 for eight of the Kazakh samples indicating that the recent application of DDT has been mainly introduced by dicofol and in the case of Polish samples it indicated that the recent application of DDT has been mainly introduced by the use of technical DDT. Organochlorine pesticides do not readily degrade in the environment and are lipophilic with a tendency to bioaccumulate. Therefore, they can be found in plants, fatty foods including the cow milk and meat. The presence of fats and oils promotes absorption and enhances the toxicity of organochlorine pesticides subsequently [29]. DDT is not genotoxic [30] and experimental studies suggested that DDE-p,p´ is anti-androgenic and that DDT-o,p´ is estrogenic.

Lindane is a persistent organic pollutant: it is relatively long-lived in the environment, it is transported to long distances by natural processes such as global distillation, and it can bioaccumulate in food chains. Thus, the determination of levels in tissues can reflect the magnitude of local environment pollution [31]. In our research, Kazakh samples (18) of beef meat contained HCH-gamma in the concentration 0.005–0.009 mg/kg. HCH-gamma (lindane) has been used to treat food crops and forestry products as powders for seed treatment, a soil treatment, and to treat livestock and pets. Alfa and gamma isomers of HCH in Kazakh samples: soil, wheat and sunflower and in Polish samples: soil, beans, celery and one sample of lupine were detected in the highest concentration 1.19 mg/kg. The World Health Organization classifies lindane as "Moderately Hazardous" and its international trade is restricted and regulated under the Rotterdam Convention on Prior Informed Consent. In 2009, the production and agricultural use of lindane was banned under the Stockholm Convention on POPs.

Table 2
The occurrence and concentration of pesticides samples in samples of fruits, vegetables, grain, bees, and meat

Kazakhstan				Poland			
Commodity (number of samples)	No. of sample	Pesticide	Concentration (mg/kg)	Commodity (number of samples)	No. of sample	Pesticide	Concentration (mg/kg)
Wheat (49)	1	DDT-p,p´	0.05	Wheat (146)	1	DDT-p,p´	0.008
		DDT-o,p´	0.03			DDT-o,p´	0.007
		DDE-o,p´	0.09			DDD-p,p´	0.01
		DDT-sum	0.17			DDE-p,p´	0.004
	2	DDT-p,p´	0.06			DDT-sum	0.029
		DDT-o,p´	0.04		2	DDT-p,p´	0.012
		DDE-o,p´	0.1			DDT-o,p´	0.008
		DDT-sum	0.2			DDE-p,p´	0.005
	3	DDT-p,p´	0.13			DDT-sum	0.025
		DDT-o,p´	0.06	Barley (57)	1	DDT-p,p´	0.007
		DDE-o,p´	0.15	Rye (21)	1	DDT-p,p´	0.003
		DDT-sum	0.34			DDT-o,p´	0.004
	4	HCH-gamma	0.12			DDT-sum	0.007
	5	Aldrin (I)	0.08	Beans (52)	1	HCH-alpha	0.164
Sunflower (2)	1	HCH-alpha	0.005			HCH-gamma	0.520
Cucumber (21)	1	Endosulfan-alpha	0.004		2	HCH-alpha	0.041
		Endosulfan-beta	0.001			HCH-gamma	0.569
		Endosulfan-sulfate	0.003		3	HCH-gamma	0.622
		Endosulfan-sum	0.008		4	HCH-gamma	0.404
	2	Endosulfan-alpha	0.04	Lupine (1)	1	DDD-p,p´	0.09
		Endosulfan-beta	0.02			HCH-gamma	1.19
		Endosulfan-sulfate	0.02	Carrots (148)	1	Dieldrin	0.12
		Endosulfan-sum	0.08		2	DDE-p,p´	0.005
Tomato (23)	1	Endosulfan-alpha	0.03	Parsley (78)	1	DDT-p,p´	0.01
		Endosulfan-beta	0.02		2	DDT-o,p´	0.006
		Endosulfan-sulfate	0.01	Celery (34)	1	HCH-gamma	0.01
		Endosulfan-sum	0.06	Cucumber (76)	1	Endosulfan-alpha	0.004
	2	Endosulfan-alpha	0.03			Endosulfan-beta	0.002
		Endosulfan-beta	0.02			Endosulfan-sulfate	0.003
		Endosulfan-sulfate	0.01			Endosulfan-sum	0.009
		Endosulfan-sum	0.06	Blackcurrant (235)	1	Endosulfan-alpha	0.08
	3	Endosulfan-alpha	0.04			Endosulfan-beta	0.04
		Endosulfan-beta	0.03			Endosulfan-sulfate	0.05
		Endosulfan-sulfate	0.01			Endosulfan-sum	0.17
		Endosulfan-sum	0.08		2	Endosulfan-alpha	0.006
	4	Endosulfan-alpha	0.12			Endosulfan-beta	0.004
		Endosulfan-beta	0.62			Endosulfan-sulfate	0.004
		Endosulfan-sulfate	0.06			Endosulfan-sum	0.014
		Endosulfan-sum	0.80	Bee (28)	1	DDT-p,p´	0.08
	5	Endosulfan-alpha	0.04			DDT-o,p´	0.03
		Endosulfan-beta	0.02			DDE-p,p´	0.09
		Endosulfan-sulfate	0.01			DDT-sum	0.2
		Endosulfan-sum	0.07			HCH-gamma	0.01
	6	Endosulfan-alpha	0.1			Cypermethrin	5.91
		Endosulfan-beta	0.1		2	DDT-p,p´	0.09
		Endosulfan-sulfate	0.08			DDT-o,p´	0.05
		Endosulfan-sum	0.28			DDE-p,p´	0.1

(*Continued*)

Table 2 (*Continued*)

Kazakhstan				Poland			
Commodity (number of samples)	No. of sample	Pesticide	Concentration (mg/kg)	Commodity (number of samples)	No. of sample	Pesticide	Concentration (mg/kg)
	7	Endosulfan-alpha	0.09			DDT-sum	0.24
		Endosulfan-beta	0.04			Cypermethrin	3.51
		Endosulfan-sulfate	0.02				
		Endosulfan-sum	0.15				
	8	Dicofol	0.08				
	9	Dicofol	0.06				
Meal (18)	1	HCH-gamma	0.009				
	2	HCH-gamma	0.005				

Distribution of organochlorine pesticides has been reported by authors in different types of samples [32–34].

In our study, 28 samples of bees poisoning were examined. For example, we found organochlorine pesticides (one sample: HCH-gamma, DDE-p,p´; DDT-o,p´; DDT-p,p´; sum DDT 0.2; second sample: DDE-p,p´; DDT-o,p´; DDT-p,p´; sum DDT 0.24) along with the pesticides responsible for beehive extinctions, such as cypermethrin 5.91 and 3.51 mg/kg, in body of bees. This fact proves that DDT and lindane are still present in the environment, and that bees are a perfect bioindicator of environmental pollution. Honey bees are good biological indicators because they indicate the chemical impairment of the environment they live in through two signals: the high mortality (in the case of pesticides) and the residues present in their bodies or in beehive products (in the case of pesticides and other contaminants like heavy metals and radionuclides) [35] that may be detected by suitable laboratory analyses [14].

The background contamination of grains with residues of DDT and HCH has been observed in 4 samples (among 224 samples) collected from Poland, and 4 samples (among 49) from Kazakhstan. The mean levels of DDT residues were 0.03; 0.025; 0.007 mg/kg in Polish and 0.17; 0.20; 0.34 mg/kg in Kazakh samples of wheat, barley and rye grains, while the corresponding levels of HCH was 0.12 mg/kg in one Kazakh sample. This contamination has been ascribed to the ubiquitousness of these insecticides in the environment rather than to their deliberate usage.

Another technical grade insecticide, dicofol was proved to contain DDT-p,p´ and DDE-p,p´ as contaminants. Dicofol is an acaricide used to control many species of phytophagous mite especially red spider mite, on a range of food and ornamental crops and it is still produced and used in China [36]. Exposure to dicofol causes some adverse health effects including poisoning and the US EPA classified dicofol as a possible human carcinogen. Dicofol was detected in two Kazakh samples of tomatoes in the range of concentration: 0.06–0.08 mg/kg.

The results showed that endosulfan was present in three polish plants samples: cucumbers (1) and black currant (2). The concentrations were as follows: alpha isomers: 0.004–0.08 mg/kg, endosulfan-beta 0.002–0.04 mg/kg and sulfate 0.003–0.05 mg/kg. The average concentration was 0.064 mg/kg for all isomers, and the highest concentration for individual samples of tomatoes was 0.17 mg/kg.

In Kazakh samples, endosulfan was present in nine vegetables samples: tomatoes (7) and cucumbers (2). The concentrations were as follows: alpha isomers: 0.004–0.12 mg/kg, beta endosulfan 0.001–0.62 mg/kg and sulfate 0.001–0.08 mg/kg. The average concentration was 0.176 mg/kg for all isomers, and the highest concentration for individual samples of tomatoes was 0.8 mg/kg.

The commercial technical endosulfan consists of 70% endosulfan-alpha and 30% endosulfan-beta, which have similar insecticidal properties but different physicochemical properties [37]. Endosulfan has become a highly controversial agrichemical due to its acute toxicity, potential for bioaccumulation, and being an endocrine disruptor. Because of its threats to human health and the environment, a global ban on the manufacture and use of endosulfan was negotiated under the Stockholm Convention in April 2011. It is still used extensively in India, China [38], and in a few other countries (USA, Florida). Endosulfan is a broad-spectrum nonsystemic insecticide and acaricide with contact and stomach action. It is used to control sucking, chewing and boring insects on a wide variety of vegetables, fruits, grains, cotton, and tea, as well as ornamental shrubs, vines and trees. Endosulfan is

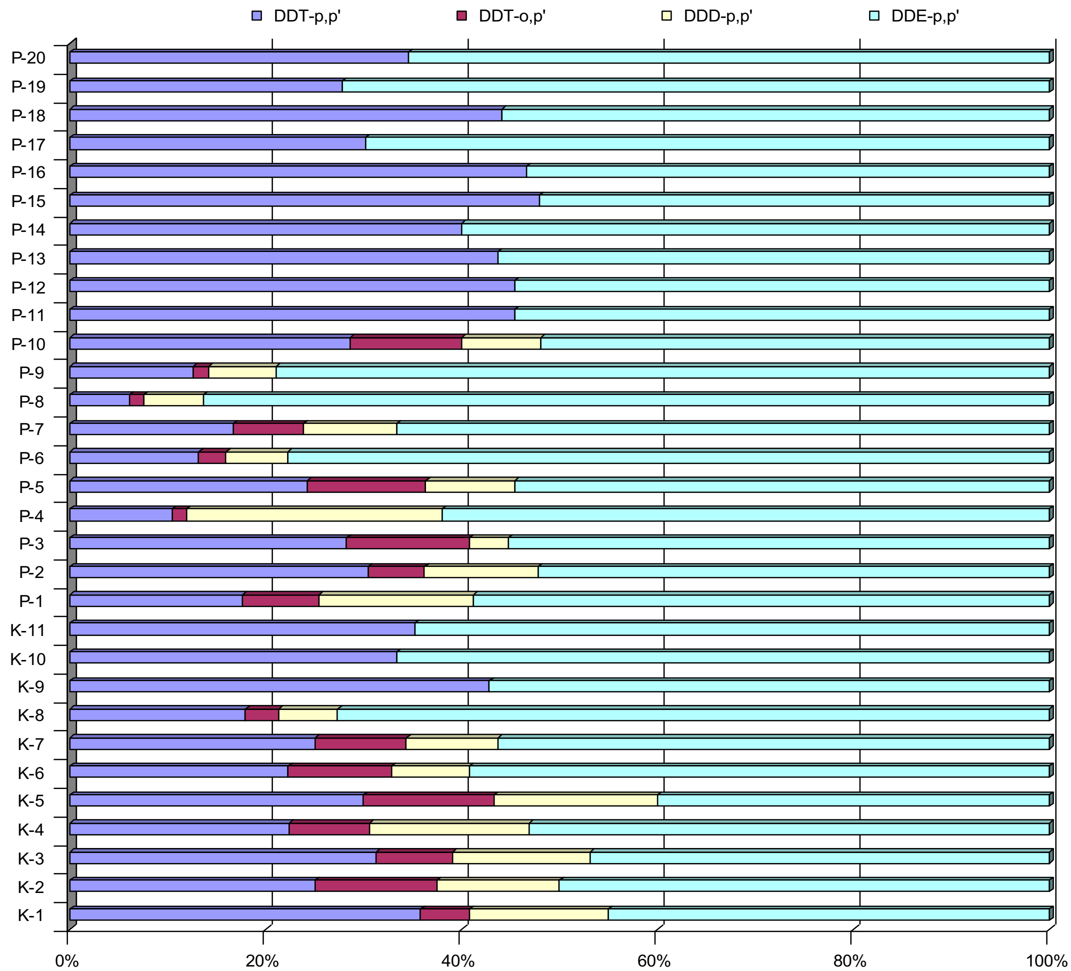

Fig. 2. Percentage composition of DDT metabolites in soils samples.

extremely toxic to fish and aquatic invertebrate and it has been implicated increasingly in mammalian gonadal toxicity [39], genotoxicity, and neuro toxicity [40] and moderately persistent in the soil environment [41]. The two isomers have different degradation times in soil, for the alpha isomer is 35 d, and is 150 d for the beta-isomer. While the usage of endosulfan in agriculture was banned in Kazakhstan in 1983. Nothing is known about its illegal use.

Aldrin was determined in one sample of Kazakhs wheat in the concentration of 0.08 mg/kg. Aldrin was developed as a pesticide to control soil insects. Its use is now banned in the European Union, but it is still used in some developing countries. Although aldrin is banned in the EU, it still may be released to the environment from products or materials which have been treated with it elsewhere. In those countries where it is still used as a pesticide, it directly contaminates the soil. At an international level, aldrin is the subject of two proposed UN treaties. It is banned under the UNECE POPs protocol and proposed for elimination under the UNEP POPs Convention [42]. Dieldrin was detected only in one Polish sample of carrots in the concentration of 0.12 mg/kg.

4. Conclusion

DDT levels found in the soil from the north-eastern Poland and the south-eastern Kazakhstan were generally low in comparison to values regarding the agricultural soil around the world. Despite the fact that organochlorine has been restricted worldwide and for long periods of time in many countries, it continues to be a ubiquitous contaminant whose environmental concentrations are reported not to have declined in some areas. Overall, this study has contributed to update the current knowledge about the occurrence and the impact of organochlorine on two agricultural areas, Poland and especially in Kazakhstan. Given that the main route of human exposure to organochlorine is via dietary intake, monitoring of organochlorine in soil and especially in those used for human food crops should be regarded still today as a necessary precaution. Routine monitoring of these pollutants in foods is required for the prevention, control and reduction of pollution as well as for legal decisions to minimize potential health hazards.

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