

Krzna River Basin Pollution by Chosen Chloroorganic Pesticides

Marcin Nowik^{1*}, Andrzej L. Dawidowicz²

¹County Sanitary and Epidemiological Station in Biała Podlaska,
Kopernika 7, 21-500 Biała Podlaska, Poland

²Faculty of Chemistry, Maria Curie Skłodowska University,
Marii Curie Skłodowskiej 3, 20-031 Lublin, Poland

Received: 15 November 2010

Accepted: 15 April 2011

Abstract

Chloroorganic pesticides belong to a group of compounds whose specific characteristics classify them as one of the most dangerous for the environment. Although the use of chloroorganic pesticides was banned in Poland and other countries many years ago, regular monitoring of these compounds in the natural environment is still required due to their exceptional toxicity and significant durability. Our paper presents and discusses the concentration levels of selected chloroorganic pesticides [p, p'-DDT and its metabolites (p, p'-DDE, p, p'-DDD), HCH isomers (α -HCH, γ -HCH), heptachlor, epoxide heptachlor, hexachlorobenzene (HCB), endrin, aldrin, and dieldrin] in soil, river sediment, and water samples taken from the Krzna River, the biggest left-hand tributary of the Bug River, and from its bank. The results indicate that the concentrations chloroorganic pesticides in the examined samples are generally low. Some increase of the accepted pesticide concentration level is observed in the vicinity of Rzeczycza village, which points to the necessity of continuous monitoring of this region.

Keywords: chloroorganic pesticides, Krzna River basin pollution

Introduction

The term *pesticides*, proposed by The Food and Agriculture Organization of the United Nations, is applied to a wide spectrum of natural and synthetic compounds used against the action and activity of organisms that are dangerous for human beings, man-made, and man-used products [1]. Among the large number of pesticides are insecticides named chloroorganic pesticides that deserve special attention. p, p'-DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane) and its metabolites (p, p'-DDE – 1,1-bis-(4-chlorophenyl)- 2,2-dichloroethene), p, p'-DDD – 1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl) ethyl]benzene), hexachlorocyclohexane (HCH) isomers (α -HCH, β -HCH, γ -HCH, δ -HCH), heptachlor, aldrin, and dieldrin are the most representative in this group. These chlorohydrocarbons are still used in some countries to destroy insects in fields, forests and buildings, as well as insect parasites of people and animals. They differ in respect to the structure and the chlorine level, which influences their different toxic and physico-chemical properties [2].

It should be stated that chloroorganic pesticides in Poland were replaced a long time ago by other groups of compounds of similar effectiveness, but that are much more easily degradable (e.g. phosphoroorganic insecticides). In spite of this fact, levels of chloroorganic pesticides are still continuously monitored throughout the country, due to the danger they pose.

A characteristic feature of chloroorganic pesticides is the long period of their degradation, both in the natural

*e-mail: onet_nowmar@poczta.onet.pl

environment and in living organisms. This results mainly from their resistance to enzymatic transformation. Chloroorganic pesticides are hardly metabolized and therefore are only slowly removed from the organism. They tend to store up in the cells of organisms on all the subsequent levels of the food chain [3]. Many of them exhibit carcinogenic, mutagenic, and teratogenic activity (i.e. they may be dangerous to embryos and fetuses). They can cause disorders of the nervous system, cancer, shortness of breath, and damage bone marrow [4-6]. Another characteristic of pesticides is their mobility in the environment, e.g. in a soil [7] or from soil to crops [8]. Pesticides penetrate the atmosphere relatively easily due to their high vapor pressure [9]. Pesticides applied in tropical climates are transported with the air into the cooler regions of the world [10, 11].

Before revealing negative activity of chloroorganic pesticides, their production was massive and they were widely applied in many countries. For example, ca. 75,000 tons of *p,p'*-DDT was produced by Polish factories in the period 1949-78 [12]. Despite the straightforward ban concerning the use and production of chloroorganic pesticides [13], they are still applied in many developing countries and their presence is found in foods of animal origin [14]. The extremely toxic properties of chloroorganic pesticides and their considerable durability make necessary regular monitoring of these compounds, even today [15].

The Research Area

Our paper presents and discusses the results of quantification analysis of typical chloroorganic pesticides such as *p,p'*-DDT and its metabolites (*p,p'*-DDE, *p,p'*-DDD), HCH isomers (α -HCH, γ -HCH), heptachlor, heptachlor epoxide, hexachlorobenzene (HCB), endrin, aldrin, and dieldrin in soil, sediment, and water sampled from the Krzna River and its banks.

Krzna, the largest left tributary of the Bug, flows through central-eastern Poland (Fig. 1). It is 125 kilometers long and has a mean discharge of 10.5 m³/s at its mouth [16]. The basin of the Krzna (about 3,300 km²) is a typical farming area with numerous small farms inhabited by a populace of ca. 340,000. The existence of farms in the area has a significant influence on the pesticide contamination level in the area, as most pesticides in the soil, sediment, and surface waters come from farming. The considerable fragmentation of the farm area limits the possibilities of thorough control of plant and animal protection agents applied in the area. The Krzna flows through several towns, including: Biała Podlaska, Łuków, and Międzyrzec Podlaski, where it is a source of drinking water. Some fragments of the river run have been included in natural reserve areas. It is worth noting additionally that in Kalińów and Adamki, villages located in the Krzna basin, are the waste repositories containing traces of chloroorganic pesticides. The last fact additionally support the necessity of the Krzna basin control with respect to the pesticide level, despite the fact that repositories were cleared in 2001. It is worth mentioning that the water in the Krzna is systematically monitored [17]; however, no detailed analysis for chloroorganic pesticides have yet been performed [18-20].

Experimental

Validation of Analytical Procedure Applied for the Estimation of Chloroorganic Pesticides in Soil, Sediment, and Water

The procedure combining SPE technique (employing octadecyl-modified silica bed) with further analysis of SPE extract by means of gas chromatography with ECD detection is one of the most popular methods applied for the analysis of chloroorganic pesticides [21-24]. This proce-

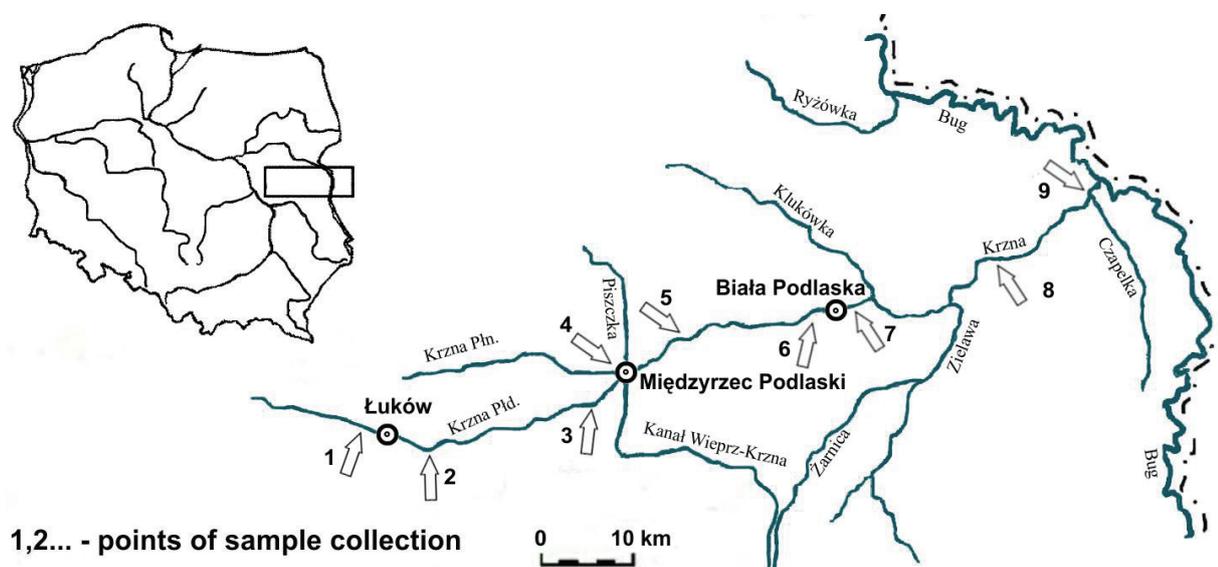


Fig. 1. Krzna River and points of sample collection.

cedure was applied for analysis of water, soil, and sediment samples from the Krzna basin. In order to estimate the reliability of results obtained in our laboratory, a validation of the procedure was performed [25, 26]. Such parameters as detection limit, the quantification limit, the range of method, method sensitivity, linearity, recovery, uncertainty, and precision in repetitive conditions were evaluated. All these elements were calculated separately for each pesticide and for each matrix (soil, water, sediment) following the same sample preparation procedure as that described below. Certified reference materials (CRM) were used, as well as reference materials prepared on the basis of pesticide matrices (RM) relevant to the analyzed samples. The parameters established in the process of validation are presented in Table 1.

The limit of detection (LOD) and the limit of quantification (LOQ) involved measurements of 10 independent samples, where the level of the analyzed compound was close to the expected limit of detection. The results thus acquired were subjected to the Q-Dixon Test for identification and rejection of outliers, and then standard deviation was calculated for them. The triple standard deviation and the six-times standard deviation were accepted for the limit of detection and for the limit of quantification, respectively.

The method range, its linearity, and the method sensitivity were established on the basis of the calibration curve and curve equation. Measurements of solution matrices on three levels of concentration were performed five times. The accuracy of the chosen range of measurement was verified by performing five measurements for the smallest and five for the largest concentrations. The obtained results served as a basis for calculations of standard deviations, which in turn were verified by means of the F-Snedecor Test. Linearity was established on the basis of the regression coefficient. Method sensitivity was established as the gradient of the calibration curve.

Precision in repetitive conditions was calculated from five measurements on three levels of concentration. The largest coefficient of variation calculated from the standard deviations on the given level of concentration was accepted as the method precision.

In order to establish recovery, an analysis of samples enriched with a given compound was performed on three concentration levels for a working method range and was repeated six times.

Method uncertainty was evaluated with regard to such elements as: preparation sample to analysis, sample weight uncertainty, calibration phase uncertainty, repeatability, and recovery uncertainty. The largest uncertainty among the ones calculated on three levels of concentration within the range of measurement was accepted as method uncertainty.

Sample Preparation Method

The examined samples of soil, sediment and water were collected in summer 2009 from 9 places positioned along the Krzna River sites (Fig. 1). The collected samples were subjected to the following sample preparation procedures:

Soil Samples

Soil samples were collected by hand using a metal spatula at a depth of 0-15 cm and 1 m from the shore. They were initially purified from larger contaminants (stones, plant parts) and transported to the laboratory in glass containers. Collected samples were dried at about 100°C to constant weight. The dried soil samples were crushed in a mortar and fractionated using sieves. A grain fraction less than 2 mm was used in the studies. The samples prepared in the above way were stored in glass containers at +4°C.

Sample preparation procedure was as follows: to 5 g of analyzed soil 50 µl solution of tetrachloro-m-xylene (LGC Standards) in acetone (J.T. Baker) was added as an internal standard (50 ng/ml). The sample was then shaken for 30 min with 10 ml of methanol (J.T. Baker). The resulting extract was filtered into a 50 ml volumetric flask using the 3 h filter (Filtrak). Residual sludge was poured again with a new portion of methanol, and extraction was repeated twice, each time pouring the extract into the flask so that each sample of the soil was extracted three times. The flask with the combined extracts was filled up to its volume with methanol. The resulting solution was subjected to SPE procedure using the SPE 12G chamber (J.T. Baker) and SPE column filled with 500 mg octadecyl-bonded silica gel (J.T. Baker) previously conditioned according to manufacturer's instructions. The SPE column was next dried for 30 min, sucking the air thru it. The elution of the sorbed pesticides was performed by washing the SPE column with 3 ml of hexane (J.T. Baker). The eluate was collected into a 5ml flask, dried with anhydrous sodium sulfate (Merck) and then concentrated to a volume of about 0.5 ml in a stream of inert gas (nitrogen) and transferred to 1 ml volumetric flask. The 1 ml flask was supplemented with hexane to its volume.

Sediment Samples

River sediment samples were collected 1 m from the shore using a metal bucket. The samples were initially purified from larger contaminants (larger stones and other plant parts) and transported to the laboratory in glass containers. Further handling of sediment samples was the same as in the case of the soil samples.

Water Samples

Water samples were collected from the river into glass containers. The samples were analyzed within 24 hours after collection. Before analysis the samples were stored at +4°C. In the case of water samples the following sample preparation procedure was employed. To water sample (1 L), 1 ml of methanol and 50 µl tetrachloro-m-xylene solution in acetone (50 ng/ml) were added. The obtained mixture was filtered through 3-h paper filter (Filtrak) and subjected to SPE procedure using the SPE 12G chamber and the extraction disks filled with octadecyl-bonded silica gel previously conditioned in accordance with the manufacturer's instructions. Further steps of the pesticide determination were the same as in the case of soil and river sediment samples.

Table 1. The validation results for pesticide analysis in soil sediment and water samples.

Pesticide	Matrix	Method range µg/kg or µg/l	Linearity	Calibration curve ng/ml	Method sensitivity	Limit of detection µg/kg or µg/l	Limit of quantification µg/kg or µg/l	Accuracy	Precision	Recovery	Uncertainty
α-HCH	Soil, sediment	1.50-40	0.9992	12-200	44.77	0.75	1.50	9.60%	21%	62%	35%
	Water	0.012-0.200				0.006	0.012	7.37%	17%	82%	32%
HCB	Soil, sediment	1.90-40	0.9991	10-200	42.05	0.95	1.90	9.11%	24%	65%	30%
	Water	0.010-0.200				0.005	0.010	6.92%	24%	85%	25%
γ-HCH	Soil, sediment	1.80-40	0.9995	12-200	38.30	0.90	1.80	11.31%	19%	75%	37%
	Water	0.012-0.200				0.006	0.012	8.53%	22%	85%	32%
Heptachlor	Soil, sediment	1.40-40	0.9995	8-200	34.83	0.70	1.40	8.31%	20%	81%	34%
	Water	0.008-0.200				0.004	0.008	6.39%	22%	95%	29%
Aldrin	Soil, sediment	1.50-40	0.9994	8-200	35.76	0.75	1.50	10.15%	20%	81%	33%
	Water	0.008-0.200				0.004	0.008	7.81%	20%	90%	26%
Heptachlor epoxide	Soil, sediment	1.80-40	0.9991	10-200	45.40	0.90	1.80	15.87%	22%	63%	38%
	Water	0.010-0.200				0.005	0.010	12.21%	16%	90%	25%
p,p'-DDE	Soil, sediment	1.60-40	0.9998	13-200	32.16	0.80	1.60	10.23%	18%	75%	38%
	Water	0.013-0.200				0.007	0.013	7.87%	15%	76%	26%
Dieldrin	Soil, sediment	1.90-40	0.9997	12-200	33.90	0.85	1.90	9.84%	17%	68%	36%
	Water	0.012-0.200				0.006	0.012	6.80%	18%	81%	26%
Endrin	Soil, sediment	1.40-40	0.9995	9-200	26.05	0.70	1.40	9.54%	24%	74%	33%
	Water	0.009-0.200				0.005	0.009	2.08%	16%	87%	31%
p,p'-DDD	Soil, sediment	1.30-40	0.9999	8-200	23.28	0.65	1.30	7.69%	23%	79%	37%
	Water	0.008-0.200				0.004	0.008	4.89%	16%	90%	31%
p,p'-DDT	Soil, sediment	2.00-40	0.9991	11-200	26.63	1.00	2.00	8.15%	21%	82%	30%
	Water	0.011-0.200				0.006	0.011	6.27%	19%	83%	26%

Table 2. Concentrations of examined chloroorganic pesticides in soil samples.

	Poważe	Strzyżew	Rzeczyca	Międzyrzec Podlaski	Puchacz	Porosiuki	Biała Podlaska	Małowa Góra	Neple
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	µg/kg								
α-HCH	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HCB	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
γ-HCH	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Heptachlor	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD
Aldrin	< LOD	< LOQ	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD
Heptachlor epoxide	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
p,p'-DDE	< LOD	< LOQ	75.59±29.05*	3.61±1.39*	< LOQ	< LOD	< LOQ	< LOQ	< LOD
Dieldrin	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Endrin	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD
p,p'-DDD	< LOD	< LOD	11.19±4.14*	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
p,p'-DDT	< LOD	< LOD	93.15±27.78*	3.40±1.01*	< LOQ	< LOD	< LOD	< LOD	< LOD

*uncertainty calculated for a coverage factor $k=2$, with a level of confidence of approximately 95%.

Chromatographic Measurements

The obtained samples were analyzed using a gas chromatograph Agilent 6890 N equipped with a μ -ECD detector and capillary column DB-5 from Agilent (30 m \times 0.25 mm i.d. with 0.25 mm film of stationary phase).

Helium (grade 5.0) was used as a carrier gas. 1 μ L of the sample was injected by Agilent 7683B Series Automatic Liquid Sampler. The injector's temperature was 250°C. The following temperature program was applied: 2 min at 80°C, 20°C/min to 180°C, and then a linear temperature increase up to 250°C at the rate 6°C/min and hold 10 min.

Results and Discussion

Concentrations of the examined chloroorganic pesticides in the soil samples (collected from the sites marked on the map in Fig. 1) are presented in Table 2. As results from the presented data, for most analyzed samples the concentration of pesticides is lower than their quantification limit. In many cases even the detection limit of examined pesticides is not reached, which is marked in individual table slots by the abbreviation (<LOD). Despite the generally low contamination level of soil with the analyzed pesticides in the Krzna basin, the DDT concentrations Rzeczyca and Międzyrzec Podlaski are significantly higher. Especially in the first mentioned place, Rzeczyca, the DDT concentration exceeds 37 times its accepted norm [27]. As stated in the Introduction, the use of p,p'-DDT in the European Union has been illegal since the 1970s. The high level of this pesticide in the soil samples collected in the above-mentioned regions shows that it is either the effect of the massive DDT

application in the period before the DDT ban, or it results from illegal use of agents containing p,p'-DDT in recent times. As is known from the available literature [28], p,p'-DDT contaminations are accompanied by p,p'-DDT degeneration products such as p,p'-DDD and p,p'-DDE. The proportion of these compounds in the environmental sample is often treated as an indicator allowing further investigation of how long the p,p'-DDT-containing agents were used in a given area. The period of p,p'-DDT half-degradation in the soil equals several years. The high level of p,p'-DDT concentration in relation to its metabolites in the soil samples from Rzeczyca suggests that agents containing this pesticide were in the area used recently. The concentration values of p,p'-DDT and p,p'-DDE in Międzyrzec Podlaski also suggest recent application of these insecticides; however, the concentrations of these compounds in the latter area are not as high as in Rzeczyca.

Sediment samples, in the context of pesticide concentration, are significantly different. Even though the concentrations of the studied pesticides in sediment are much lower than in the soil, in the case of three compounds – α -HCH, p,p'-DDE and endrin – their levels are much over the limit of quantification. It can be said that the concentrations, after considering the range of uncertainty, evaluated in the phase of method validation, do not exceed the acceptable levels. It is worth mentioning that the levels of p,p'-DDT and its metabolites in the sediment samples collected in Rzeczyca and Międzyrzec Podlaski are low, despite the high concentrations of these pesticides in the soil samples from these locations. It is likely that the process of washing out of DDT and its metabolites from the soil to the neighboring sediment was short. This additionally suggests that DDT was applied in these places recently.

Table 3. Concentrations of the examined chloroorganic pesticides in sediment samples.

	Poważe	Strzyżew	Rzeczyca	Międzyrzec Podlaski	Puchacze	Porosiuki	Biała Podlaska	Malowa Góra	Neple
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	µg/kg								
α-HCH	< LOD	< LOD	< LOD	2.58±0.91*	< LOD	< LOD	< LOD	< LOD	< LOD
HCB	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
γ-HCH	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Heptachlor	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Aldrin	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD
Heptachlor epoxide	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
p,p'-DDE	< LOD	< LOD	< LOD	3.18±1.22*	2.71±1.04*	< LOD	< LOD	< LOD	< LOQ
Dieldrin	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Endrin	< LOD	< LOD	< LOD	6.36±2.04*	2.44±0.78*	< LOD	< LOD	< LOD	< LOD
p,p'-DDD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
p,p'-DDT	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOD

*uncertainty calculated for a coverage factor $k=2$, with a level of confidence of approximately 95%.

Table 4. Concentrations of the examined chloroorganic pesticides in water samples.

	Poważe	Strzyżew	Rzeczyca	Międzyrzec Podlaski	Puchacze	Porosiuki	Biała Podlaska	Malowa Góra	Neple
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	µg/l								
α-HCH	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
HCB	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOQ	< LOD
γ-HCH	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Heptachlor	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ
Aldrin	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOD	0.010±0.004*	< LOD
Heptachlor epoxide	< LOD	< LOQ	< LOD	< LOD	< LOD	< LOQ	< LOQ	< LOD	< LOD
p,p'-DDE	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Dieldrin	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
Endrin	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
p,p'-DDD	< LOQ	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOD	< LOD
p,p'-DDT	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

*uncertainty calculated for a coverage factor $k = 2$, with a level of confidence of approximately 95%.

The data concerning the contamination of Krzna water with the discussed chloroorganic pesticides are presented in Table 4. According to these data only the samples collected in Malowa Góra contain 0.010 µg/L aldrin. The levels of other pesticides in all the analyzed water samples from Krzna are below the pesticide quantification level.

As is known from literature [28], the period of half-degradation of p,p'-DDT in water is significantly shorter (a few days) than in the soil and sediment. The absence of the pesticide and its metabolites in water with its simultaneously significant concentration level in the soil in the areas of Rzeczyca and Międzyrzec Podlaski suggests that the

p,p'-DDT-containing agents has been sporadically used regardless of the obligatory ban of their application.

The analysis of the results of chloroorganic pesticide levels in the Krzna samples makes it visible that, generally, the levels of contamination with these compounds are minimal. Only the area around Międzyrzec Podlaski should become the focus of attention, due to the high concentration of p,p'-DDT and its metabolites. The basin of Krzna in analysis for the presence of chloroorganic pesticides in Poland can be regarded as one of the least contaminated by these compounds [18, 29-31].

References

1. Food and Agriculture Organization of the United Nations, International Code of Conduct on the Distribution and Use of Pesticides, Rome **2002**.
2. BIZIUK M. Pesticides. Occurrences, determination and neutralizing, Scientific and Technical Publishing **2001** [In Polish].
3. RÓŻAŃSKI L. The transformations of pesticides in living organisms and the environment, Agricultural And Forestry State Publishing; **1992** [In Polish].
4. FISHBEIN L. Overview of potential mutagenic problems posed by some pesticides and their trace impurities, Environmental Health Perspectives **27**, 127, **1978**.
5. MCGLYNN K. Serum Concentrations of 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) and 1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) and Risk of Primary Liver Cancer, Journal Of The National Cancer Institute, **98**, 1005, **2006**.
6. NASTERLACK M. Pesticides and childhood cancer: An update, International Journal of Hygiene and Environmental Health **210**, 645, **2007**.
7. LOPEZ-BLANCO M. C., CANCHO-GRANDE B., SIMAL-GANDARA J., LOPEZ-PERIAGO E., ARIAS-ESTE VEZ M. Transport of commercial endosulfan through a column of aggregated vineyard soil by a water flux simulating field conditions, J. Agric. Food Chem. **53**, 6738, **2005**.
8. LOPEZ-PE REZ G. C., ARIAS-ESTE VEZ M., LOPEZ-PERIAGO E., SOTO-GONZALEZ B., CANCHO-GRANDE B., SIMAL-GANDARA J. Dynamics of pesticides in potato crops J. Agric. Food Chem., **54**, 1797, **2006**.
9. ARIAS-ESTEVEZ M., LOPEZ-PERIAGO E., MARTINEZ-CARBALLO E., SIMAL-GANDARA J., MEJUTO J.C., GARCIA-RIO L. The mobility and degradation of pesticides in soils and the pollution of groundwater resources, Agriculture, Ecosystems and Environment, **123**, 247, **2008**.
10. RAMAMOORTHY S., RAMAMOORTHY S. Chlorinated organic compounds in the Environment; Lewis Publishers **1997**.
11. JAWARD F., FARRAN N., HARNER T. Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe, Environ. Sci. Technol., **38**, (1), 34, **2004**.
12. KOŁSUT W. The report. The results of the inventory of production, import and export of POPs under the Stockholm Convention, Institute of Environmental Protection **2004** [In Polish].
13. CRAVEN A. Bound residues of organic compounds in the soil: the significance of pesticide persistence in soil and water: a European regulatory view, Environmental Pollution **108**, 15, **2008**.
14. RADZYMIŃSKA M., SMOCZYŃSKI S. S., KOPEĆ M. Persistent organochlorine pesticide, lead, cadmium, nitrate (v) and nitrate (iii) in polish milk and dairy products, Pol. J. Environ. Stud. **17**, (1), 95, **2008**.
15. GONZALEZ-LOPEZ N., RIAL-OTERO R., CANCHO-GRANDE B., SIMAL-GANDARA J., SOTO-GONZALEZ B. Occurrence of organochlorine pesticides in stream sediments from an industrial area, Arch. Environ. Contam. Toxicol. **48**, 296, **2005**.
16. <http://pl.wikipedia.org/wiki/Krzna>.
17. Environmental report of the Lublin voivodeship in 2007. Library of Environmental Monitoring Lublin **2008** [In Polish].
18. BOJAKOWSKA I., GLIWICZ T. Chlorinated pesticides and polychlorinated biphenyls in river sediments of Poland, Geological Review **53**, (8), 649, **2005** [In Polish].
19. WOLSKA L., NAMIESNIK J., MICHALSKA M., BARTOSZEWICZ M. Preliminary study on toxicity of aquatic ecosystems in Bug river basin, Pol. J. Environ. Stud. **17**, (5), 811, **2008**.
20. TUZIMSKI T. Determination of pesticides in water samples from the Wieprz-Krzna Canal in the Leczynsko-Wlodawskie Lake District of southeastern Poland by TLC-DAS and HPLC-DAD, Journal of AOAC International **91**, (5), 1203, **2008**.
21. MOTTALEB M. A., ABEDIN M.Z. Determination of chlorinated pesticides in soil by solid phase extraction-gas chromatography, Analytical Sciences, **15**, (3), 283, **1999**.
22. CONTE, MILANI, MORALI, ABBALLE, Comparison between accelerated solvent extraction and traditional extraction methods for the analysis of the herbicide diflufenican in soil, Journal of Chromatography A, **765**, (1), 121, **1997**.
23. SANGHI, KANNAMKUMARATH, Comparison of extraction methods by Soxhlet, sonicator, and microwave in the screening of pesticide residues from solid matrices, Journal Of Analytical Chemistry **59**, (11), 1032, **2004**.
24. Application Note J.T. Baker nr EN-026.
25. NAMEŚNIK J., KONIECZKA P. Evaluation and quality control of measurement results, Scientific and Technical Publishing **2007** [In Polish].
26. BULSKA E. Chemical metrology, Malamut Publishing **2008** [In Polish].
27. Regulation of the Minister of Environment of September 9, **2002** J. Law. No. 165, Item 1359 [In Polish].
28. U.S. Department Of Health And Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry "Toxicological profile for DDT, DDE, and DDD" **2002**.
29. FALANDYSZ J., STARNBERG B. Persistent organochlorine compounds in sludge and sediments from the Gdańsk Region, Baltic Sea, Pol. J. Environ. Stud. **13**, (2), 133, **2004**.
30. POLKOWSKA Ż., ZABIEGAŁA B., GÓRECKI T., NAMEŚNIK J. Contamination of runoff waters from roads with high traffic intensity in the urban region of Gdańsk, Poland, Pol. J. Environ. Stud. **14**, (6), 799, **2005**.
31. TOMZA-MARCINIAK A., WITCZAK A. Bioaccumulation of DDT and Its Metabolites in the Międzyodrze Ecosystem, Poland, Pol. J. Environ. Stud. **18**, (3), 467, **2009**.

