

ORGANOCHLORINE PESTICIDES CONCENTRATION IN THE DRINKING WATER FROM REGIONS OF EXTENSIVE AGRICULTURE IN POLAND

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Badach H, Nazimek T, Kamiński R, Turski WA: Organochlorine pesticides concentration in the drinking water from regions of extensive agriculture in Poland. *Ann Agric Environ Med* 2000, 7, 25–28.

Abstract: Considerable amounts of organochlorine pesticides (DDT, lindane, heptachlor and methoxychlor) were detected in drinking water samples during a two-year study in Warka-Grójec rural region of Poland. The average incidence of drinking water sources with detectable levels of pesticides ranged from 20 to 30%. According to Polish regulations concerning water quality, individual concentrations did not reach the maximum admissible level. However, the levels of pesticides in most cases exceeded the maximum admissible concentrations recommended by the European Union.

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Key words: pesticides, water pollution, water quality.

INTRODUCTION

Water, an essential for life on earth, is one of our most precious natural resources. With the growth of our civilisation, the demand for water has increased dramatically and its uses have become much more extensive. Large volumes of water are used in industry, agriculture and for personal consumption. Each of these uses requires a different level of quality and drinking water should possess the highest purity except for some very specific industrial uses. The most common and harmful impurities include bacteria, viruses and different chemical substances including pesticides.

Nowadays, the contamination of water by pesticides is a very important ecological problem, especially in regions with intensive agriculture where leaking of these highly toxic substances into the water supplies may cause strong effects on human and animal health.

Organochlorine compounds are chlorinated hydrocarbons that had been used in agriculture as insecticides. These substances vary in structure and among them are hexachlorocyclohexanes - lindane (γ -hexachlorocyclohexane),

chlorinated ethane derivatives - DDT (dichlorodiphenyl-trichloroethane) or methoxychlor and cyclodienes - heptachlor [15].

Organochlorines possess a cumulative capacity, slow degradation rate, and their residues are present in the soil environment even several years after application [11]. Moreover, these insecticides express strong neurotoxic effects and potential to induce developmental disabilities [5, 16]. The evidence on the relation between pesticide contamination of drinking water and cancer was also postulated [3]. Due to the above-mentioned properties the use of organochlorines has sharply decreased but they are still the active ingredients of some pest control products [10].

Many countries of Central and Eastern Europe have water quality problems, especially in rural areas where the water networks are small and consumers depend mainly on private wells. Water quality standards are difficult to achieve because the treatment of drinking water in these regions is not sufficient. Consequently, drinking water may accumulate high levels of toxic substances including pesticides [9].

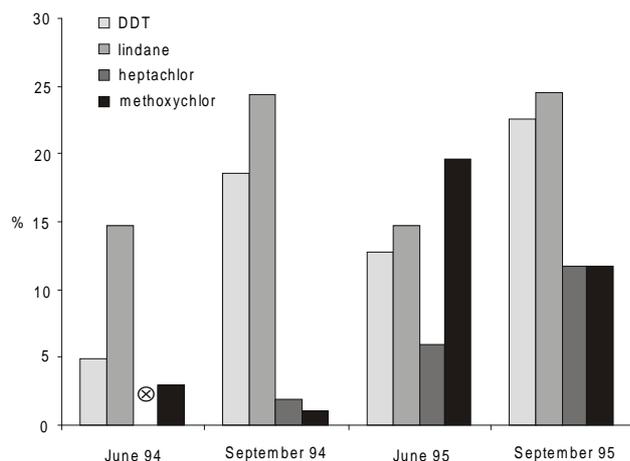


Figure 1. Percentage of samples with detectable levels of pesticides obtained from household water intakes of Warka-Grójec rural region. Samples were collected from the same water intakes during a two-year period, 1994–1995, in June and September each year. ⊗ - concentration of heptachlor in all studied samples was below the detection limit for this compound (see Materials and Methods).

The Warka and Grójec region, where the observations were carried out, is located in the central part of Poland in the vicinity of Warsaw. It is characterised by extensive agriculture with the total arable land of 117,000 ha, whereas the area of orchards is estimated at 40,000 ha. The households are scattered in the area of large orchards, which are adjacent to each other. Main water intakes in this region are either dug or deep wells, which are situated near households. Pesticide usage in this region is very high and reaches 12.9 kg/ha whereas the average usage of pest control products in Poland is 0.5 kg/ha [1]. Therefore, we decided to examine the organochlorine pesticides concentrations in the drinking water of this region.

MATERIALS AND METHODS

Sample collection. Samples of water were collected from water intakes located within fruit growing farms during a two-year period, 1994–1995, in June and September each year. The examined water supplies were deep wells whose depth ranged from 30–58 m and dug wells which ranged from 4–28 m. About 70% of wells were situated in yards near houses, whereas the remainder were a considerable distance from houses. The samples were obtained from the same 102 water intakes each year. The following organochlorine pesticides were selected for analytical determinations: lindane, DDT, heptachlor and methoxychlor. Water samples of 1 l were taken from the tap located at home, usually in the kitchen, or directly from a well. Samples were collected according to the rules described in Circular 703 of University of Florida [8]. Water samples kept in glass bottles were stored in a cold, dark room for no longer than 2 weeks until pesticide determination.

Analytical procedure. The extraction and concentration of water samples were performed by SPE method (Solid Phase Extraction) with C₁₈ (Backerbond spe-1000 columns). All organic solvents (Merck, Germany) and water (J.T. Baker, The Netherlands) used during the extraction and elution procedures were HPLC grade. Pesticide standards were obtained from Promochem, Poland. The column was conditioned by the gradual passing of 6 ml of hexane. It was then desiccated under vacuum (25 mm Hg) for 2 min. Once the column was dry, 12 ml of methanol was aspirated throughout, followed by 6 ml water passage. Water samples were poured into the pre-treated column at a flow rate not greater than 5 ml/min. Subsequently, the column was washed with 1 ml HPLC grade water. The column was dried again under vacuum for 10 min. When the vacuum was turned off 2.5 ml hexane was added. The solvent was allowed to percolate into the column for 1 min. Finally, aspiration of 2.5 ml hexane through the column was performed three times. The eluate was evaporated to dryness in a vacuum vortex evaporator (type 350 P Unipan, Poland) at 30°C. The residue was dissolved in 1 ml hexane and 1 µl of this solution was subjected to gas chromatography analysis.

Gas chromatography. Analysis was carried out with a Hewlett-Packard Series II (Hewlett-Packard, Germany) gas chromatograph equipped with an electron capture detector (ECD-Ni⁶³). A fused-silica capillary column HP-5 (5% PhMe Silicone; 10 m × 0.53 mm internal diameter, 2.65 µm film thickness) was used. The oven temperature program for optimal component resolution was as follows: initial temperature 185°C for 4 min then 230°C for 4.5 min and 270°C for 3 min. Temperature programmed ramp rate was set at 70°C/min. The injector port and detector temperatures were set at 270°C and 300°C, respectively. Purified nitrogen was used as the carrier gas with the flow-rate being 63 ml/min. The retention times for examined substances were: 2.5 min - lindane, 3.7 min heptachlor, 7.1 min DDT and 9.8 min - methoxychlor. The mean recovery of the organochlorine compounds was 91–93%. The detection limits for individual compounds were: lindane 0.001 µg/l; DDT 0.01 µg/l, heptachlor and methoxychlor 0.02 µg/l. The control mixture of pesticide standards was run every 5 determined samples. All procedures and operations used complied with the principles of Good Laboratory Practice.

RESULTS

Figure 1 shows the percentage of contaminated water intakes during the entire sampling period. The highest incidence of contamination can be seen in the case of lindane. Percentage of water intakes polluted by lindane ranged from 15 to 30%. Moreover, a large number of water samples contaminated with DDT was observed during the study. The percentage of heptachlor or methoxychlor pollution in 1994 was lower. However, in 1995 the incidence of contaminated water intakes was

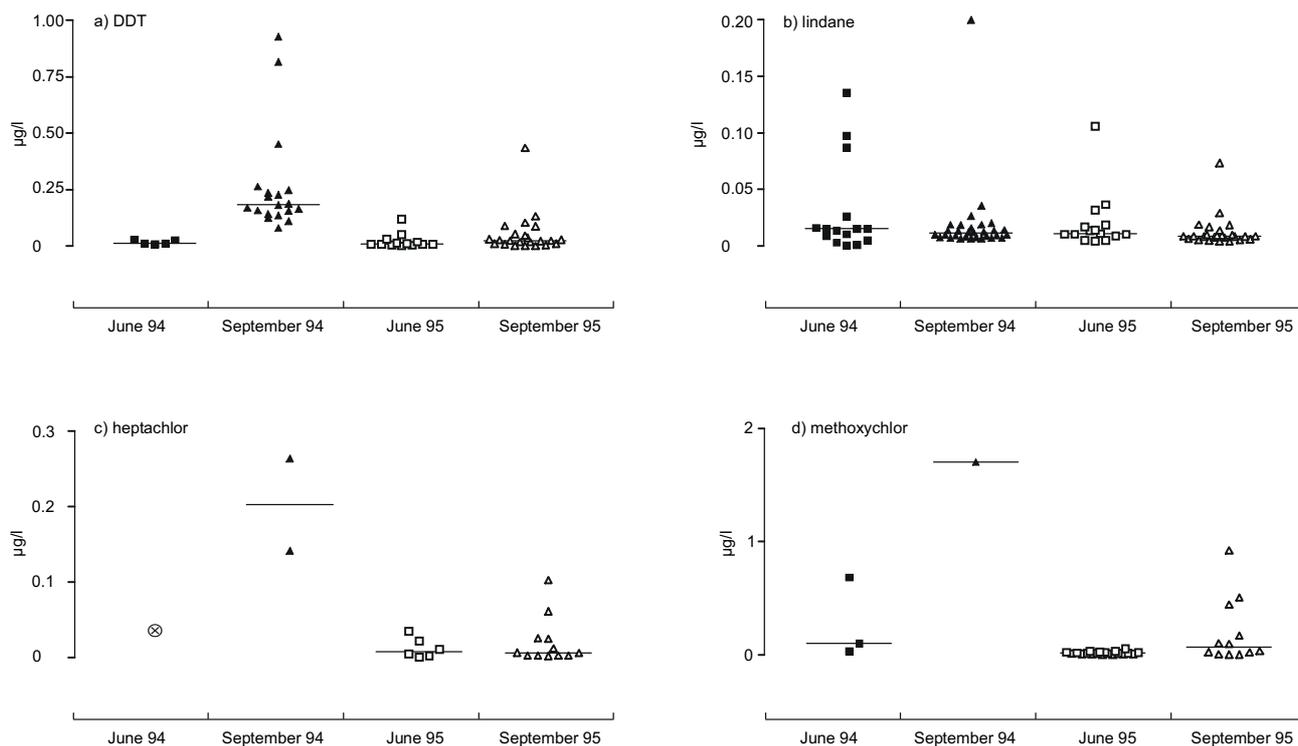


Figure 2. Concentrations of organochlorine pesticides in samples with detectable levels of pesticides obtained from household water intakes of Warka-Grójec rural region. Graphic symbols represent concentrations of individual pesticide after single measurement, while solid line describe the median value. Samples were collected from the same water intakes during a two-year period, 1994–1995, in June and September each year. ⊗ - concentration of heptachlor in all studied samples was below the detection limit for this compound (see Materials and Methods).

high and these pesticides were found in approximately 10–20% samples.

Concentrations of pesticides and their median values in contaminated water intakes, given by sampling period, are shown in Figure 2. As can be seen (Fig. 2a) concentration of DDT reached the highest level in September 1994 with median value of 0.18 $\mu\text{g/l}$. In remaining sampling periods median levels of DDT ranged from 0.01–0.02 $\mu\text{g/l}$ (Fig. 2a). During the two-year study, concentrations of lindane in every sampling time were comparable with medians close to 0.01 $\mu\text{g/l}$ (Fig. 2b). In June 1994, concentrations of heptachlor in all examined samples were below the detection limit. Only two water intakes were found to be contaminated with heptachlor in September 1994. In 1995, the median levels of heptachlor did not exceed 0.01 $\mu\text{g/l}$ (Fig. 2c). The content of methoxychlor in water samples was relatively low (Fig. 2d). However, in September 1994, one of the studied water intakes was polluted by this pesticide with concentration as high as 1.7 $\mu\text{g/l}$ (Fig. 2d).

DISCUSSION

Ground water is the principle source of fresh water for both rural and industrial regions. In Warka and Grójec rural region the sources of drinking water are wells located mainly within the household area. Considerable

amounts of organochlorine pesticides were detected in this area. Moreover, a high incidence of pollution of water intakes by these pesticides (particularly DDT and lindane) was observed.

General drinking water quality standards are recommended by World Health Organisation - WHO [6, 7]. Regulations of European Union countries concerning the maximum admissible concentration of water impurities are derived from the Council Directive [4]. Polish regulations are given in the dispositions of Ministry of Health and Welfare [13, 14].

The European Union Council Directive [4] and Polish dispositions of Ministry of Health and Welfare [13, 14] are generally in agreement and the highest admissible concentrations of individual contaminants of drinking water are similar [17]. However, significant differences exist in the case of pesticides. According to Polish regulations [13, 14] the maximum admissible concentrations of DDT, lindane and methoxychlor are 1.0, 5.0 and 30.0 $\mu\text{g/l}$, respectively, while in European Union countries the level of individual pesticide in drinking water should not exceed 0.1 $\mu\text{g/l}$, and the total amount of pesticides should be lower than 0.5 $\mu\text{g/l}$. The maximum admissible concentration of heptachlor in drinking water is 0.1 $\mu\text{g/l}$, both in Poland and the European Union. Determined levels of pesticides in most cases exceeded the maximum admissible concentration recommended by the European

Union Directive [4]. However, Polish regulations concerning water quality were fulfilled [13, 14] and the concentrations of pesticides did not reach the highest admissible level.

The median level of pesticides did not change considerably during the two-year observation period. Nevertheless, in several cases high levels of these compounds were detected. This, apparently, could be associated with improper dilution or disposal of pesticide concentrates. Moreover, washing spraying equipment near water intakes was a common practice in this area. Finally, the leakage of waste pesticides stored in tomb-like containers can not be excluded.

The high percentage of contaminated samples observed in this study may be related to extensive application of organochlorines in Warka-Grójec region. Environmental and agricultural use of organochlorines in Poland has been banned by the Ministry of Agriculture [12]. High occurrence of DDT and lindane in water samples reaching 20-30% confirms that these two pesticides are still persistent in the environment although their distribution and usage was prohibited in Poland in 1975 and 1990, respectively.

It is clear that agricultural activity can lead to contamination of ground water found in spaces between soil particles and rocks. There are several factors that determine pesticide movement to ground water. These include properties of the pesticide, properties of the soil, rainfall and depth to ground water, method and rate of application of pesticide [2]. Organochlorine pesticides examined in this study persist for many years in soil and are refractory to degradation by microorganisms, chemical reactions and sunlight [11]. The health effects of occupational and general population exposures to organochlorine compounds include neurologic deficits, cancer - especially non-Hodgkin's lymphoma and leukaemia, developmental and reproductive impairment [10].

CONCLUSIONS

It may be concluded that the presence of organochlorine pesticides in high concentrations may cause important sanitary and ecological problems in Warka-Grójec area. Moreover, since these toxic substances strongly influence human health and are persistent in the environment, improved educational and control activity is needed in this region.

Acknowledgements

The authors thank to Mr Jan Prach and Mr Kazimierz Pieczykolan for their helpful assistance in samples collection, extraction and analysis. We are grateful to the Institute of Agriculture Medicine for financial support (grant 2.24).

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