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PESTICIDE CONTENT IN DRINKING WATER SAMPLES COLLECTED FROM ORCHARD AREAS IN CENTRAL POLAND

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Abstract: Samples of drinking water collected in Warka-Grójec region of central Poland were tested for the presence of pesticides. Data obtained from analysis of water samples will be used for future epidemiological and environmental studies in the region. Samples were collected during spring and autumn of 2002-2003 from dug wells, deep wells and water mains in 81 randomly-selected rural households scattered throughout this region of extensive agriculture. The concentration of pesticides from four main chemical groups was determined by gas chromatography: organochlorines (lindane, DDT, methoxychlor), triazines (atrazine, simazine), organophosphates (acephate, diazinon, fenitrothion) and pyrethroids (alpha-cypermethrin, deltamethrin). Two-year monitoring of drinking water samples indicated the presence of DDT and methoxychlor contamination. Pyrethroids were generally not detected, with the exception of alpha-cypermethrin found in only a few samples. Triazines were also found in water samples collected in the course of the study with higher incidence during spring period. Organophosphates were by far the most common contaminants of drinking water in this region. Almost all samples were contaminated by significant amounts of fenitrothion. The present study reveals an urgent need for systematic monitoring of drinking water quality in regions of intensive agriculture, since they are highly vulnerable to pesticide contamination. Consumption of pesticide-contaminated water may have a negative impact on the population living in this area, which also requires scientific assessment.

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INTRODUCTION

Herbicides and pesticides are used for crop protection from weeds and insects. Chemical plant protection should be performed with specific agents applied at specific concentrations according to agrotechnical needs. Misuse of pesticides can lead to excessive contamination of the environment, i.e. soil, water or air. Accumulation of pesticides in the environment results in high levels of these dangerous chemicals in crops and animal feed, which ultimately leads to human exposure.

Potential toxicity of pesticides is the main hazard associated with their agricultural use. Human population can be exposed to these toxic chemicals via the gastrointestinal tract, respiratory system, as well as through the skin. Occupation or accidental exposure to high doses of pesticides can result in life-threatening poisoning. However, long-term environmental exposure also has a negative impact on health. This is particularly important when human populations are exposed to pesticides by drinking contaminated water [9].

There are several sources of drinking water contamination by pesticides. The main source is pesticide leaching to ground water following application on agricultural fields. Another important factor is inappropriate pesticide handling, storage and disposal [7]. Particularly dangerous could be improper equipment cleaning practices, storage and disposal of expired pesticides in unsealed pits.

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Clearly, rural populations sustain much higher exposures to pesticides, particularly due to consumption of contaminated water, than urban populations which are exposed mainly by consumption of food containing pesticide residues. Prolonged exposure to pesticides through consumption of contaminated water has been linked with increased risk of certain types of cancer [6]. Thus, contamination of drinking water by pesticides may have a damaging impact on public health and needs to be continuously monitored.

The aim of this study was to survey an area of intensive agriculture for the presence of pesticides in drinking water. Data obtained from analysis of water samples collected in this region may be very useful for future epidemiological and environmental studies.

MATERIALS AND METHODS

Sample collection. Samples of drinking water were collected in the Warka and Grojec region, located in central Poland. The area is characterized by extensive agriculture with total arable land of 117,000 ha, including 40,000 ha of orchards. Pesticide use in this region is one of the highest in the country. Approximately 16-20 kg/ha of various pesticides are being applied, whereas in the rest of country only 0.5-1 kg/ha is used [1, 11].

The households are loosely scattered throughout the study area in the immediate vicinity of large orchards. As such, pesticide residues can leak directly into the water intake that is usually located within the household. Moreover, dilution of pesticide concentrates and cleaning of the spaying equipment often takes place near the water intake, which creates a danger of direct contamination.

Single samples of drinking water were collected from 81 water intakes in the spring and autumn of 2002 and 2003. Specifically, samples were taken from water mains (20%), dug (40%) and deep wells (40%) located in the following settlements: Laski, Kazimierków, Wichradz, Opozdzew, Grzegorzewice, Nowa Wieś, Czachów, Pobierowice and Kępina.

The samples were analyzed in duplicate for the presence of organochlorines (lindane, DDT, methoxychlor), organophosphates (acephate, diazinon, fenitrothion), triazines (atrazine, simazine) and pyrethroids (alpha-cypermethrin, deltamethrin).

Analytical procedures. All analytical procedures were performed according to previously published methods [2, 8, 10]. Briefly, the extraction and concentration of water samples was performed by SPE (Solid Phase Extraction) method with Octadecyl C18 columns (BAKERBOND spe™; J. T. Baker, The Netherlands) [5]. The eluates were analyzed with a Hewlett-Packard 5890 Series II (Hewlett-Packard, Germany) gas chromatograph equipped with an electron capture detector and capillary RTX column [2]. The mean recovery was 92% for organochlorine compounds, 91% for organophosphates, 96% for triazines and 89% for pyrethroids. The detection limits for individual compounds were: lindane 0.01 µg/l; DDT 0.01 µg/l; methoxychlor 0.01 µg/l; acephate 0.50 µg/l; diazinon 0.10 µg/l; fenitrothion 0.01 ug/l; simazine 2.00 µg/l; atrazine 1.00 µg/l; alpha-cypermethrin 0.05 µg/l and deltamethrin 0.10 µg/l. Internal system of qulity control has been used throughout in the study. The control mixture of pesticide standards was run every 2 determined samples. All procedures and operations used complied with the principles of Good Laboratory Practice.

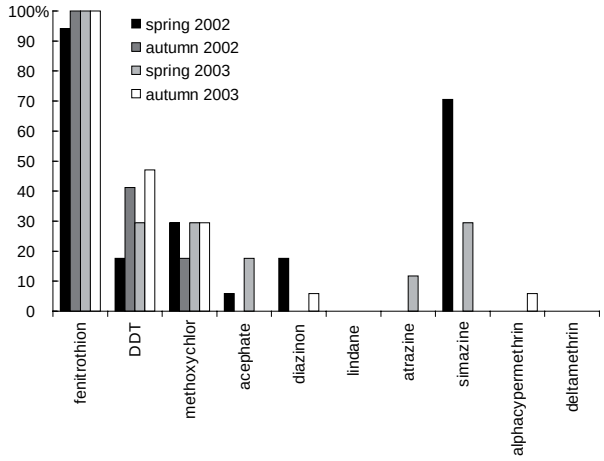

Figure 1. Prevalence of pesticide-contaminated samples collected from water mains in the Warka-Grójec region during spring and autumn of 2002/2003.

Statistics. Pesticide concentration in samples obtained during spring and fall of each year (2002 and 2003) was compared with Mann-Whitney non-parametric t-test.

RESULTS

Samples collected in 2002. During the spring of 2002, contamination of water samples with the following pesticides was observed: lindane, DDT, methoxychlor, acephate, diazinon, fenitrothion, atrazine and simazine. Alpha-cypermethrin and deltamethrin were not detected during this sampling period (Fig. 1, 2 and 3).

Water samples collected from water mains, dug and deep wells were most often contaminated with fenitrothion (nearly 100% samples), which has been commonly used for the past 30 years as insecticide in the orchard industry. Contamination with other organophosphates, such as diazinon, was less frequent: up to 25% of samples from deep wells and 12.5% samples from dug wells. Atrazine, however, was found only in about 3% of samples. Another most commonly detected pesticide was simazine. It was present in 70.6% samples collected from water mains, in 65.5% deep wells samples and in 56.6% dug well samples. DDT was found in samples from dug wells, deep wells and water mains: 28.1%, 18.8% and 17.7%, respectively. Another organochlorine compound, methoxychlor, was present in 21.9% samples from dug wells, in 29.4% samples from water mains and in 12.5% samples from deep wells.

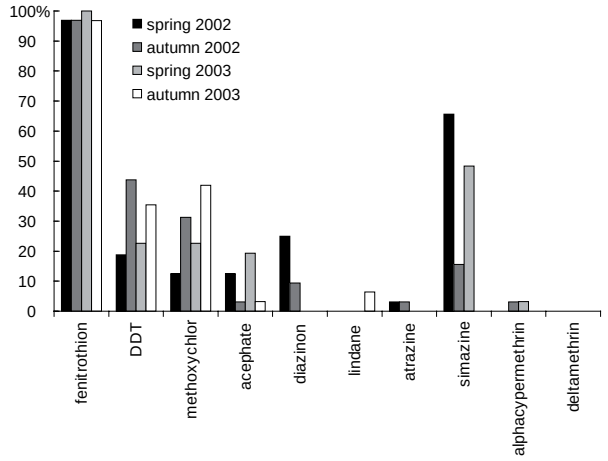

Figure 2. Prevalence of pesticide-contaminated samples collected from deep wells in the Warka-Grójec region during spring and autumn of 2002/2003.

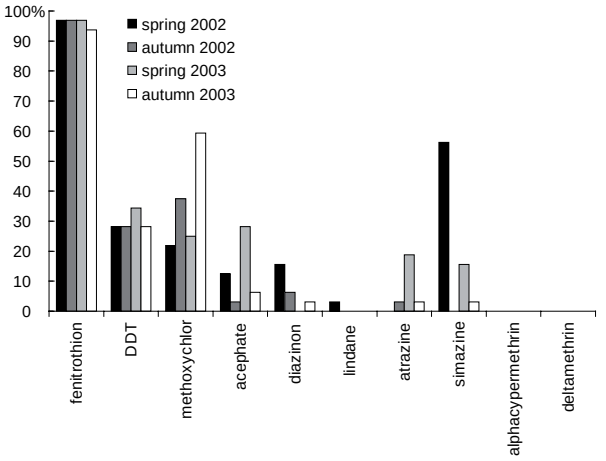

Figure 3. Prevalence of pesticide-contaminated samples collected from dug wells in the Warka-Grójec region during spring and autumn of 2002/2003.

The levels of pesticides in several water samples exceeded maximum admissible concentrations (MAC). MACs for simazine, fenitrothion and diazinon were exceeded in 51, 49 and 16 samples, respectively. MACs for other pesticides, i.e. DDT, methoxychlor, acephate and atrazine, were less frequently exceeded. It should be noted, however, that the MACs for different pesticides were exceed by several-fold to 140-fold in the case of simazine (Tab. 1, 2 and 3).

During the autumn of 2002, a profile of contamination different from that during the spring was observed. The

Table 1. Concentration and prevalence of pesticide-contaminated samples collected from water mains in the Warka-Grójec region during spring and autumn of 2002/2003.

Compounds	Total number of samples	Number of contaminated samples				Range of concentrations		Number of samples with exceeded MAC	
		spring		autumn		spring	autumn	spring	autumn
	N	n.	%	n.	%	µg/l	µg/l	n	n
2002									
lindane	17	0	0.0	0	0.0	not detected	not detected	0	0
DDT	17	3	17.7	7	41.2	0.0267-0.0402	0.0113-0.0184	0	0
metoxychlor	17	5	29.4	3	17.7	0.0423-0.9660	0.0675-0.2581	4	2
acephate	17	1	5.9	0	0.0	1.0699	not detected	1	0
diazinon	17	3	17.7	0	0.0	0.1357-0.2282	not detected	3	0
fenitrothion	17	16	94.1	17	100.0	0.0267-0.4234	0.0308-0.2608	8	5
atrazine	17	0	0.0	0	0.0	not detected	not detected	0	0
simazine	17	12	70.6	0	0.0	2.3510-7.0439	not detected	12	0
alphacypermethrin	17	0	0.0	0	0.0	not detected	not detected	0	0
deltamethrin	17	0	0.0	0	0.0	not detected	not detected	0	0
2003									
lindane	17	0	0.0	0	0.0	not detected	not detected	0	0
DDT	17	5	29.4	8	47.1	0.0106-0.0291	0.0372-0.1669	0	1
metoxychlor	17	5	29.4	5	29.4	0.0177-0.3950	0.0735-0.8053	1	2
acephate	17	3	17.7	0	0.0	0.8812-1.5303	not detected	3	0
diazinon	17	0	0.0	1	5.9	not detected	0.2145	0	1
fenitrothion	17	17	100.0	17	100.0	0.0777-0.2810	0.0306-0.7372	15	15
atrazine	17	2	11.8	0	0.0	3.3163-5.0837	not detected	2	0
simazine	17	5	29.4	0	0.0	2.1672-4.7296	not detected	5	0
alphacypermethrin	17	0	0.0	1	5.9	not detected	0.3013	0	1
deltamethrin	17	0	0.0	0	0.0	not detected	not detected	0	0

MAC (Maximal Admissible Concentration, currently 0.1 µg/l)

Table 2. Concentration and prevalence of pesticide-contaminated samples collected from deep wells in the Warka-Grójec region during spring and autumn of 2002/2003.

Compounds	Total number of samples	Number of contaminated samples				Range of concentrations		Number of samples with exceeded MAC	
		spring		autumn		spring	autumn	spring	autumn
	N	n.	%	n.	%	µg/l	µg/l	n	n
2002									
lindane	32	0	0.0	0	0.0	not detected	not detected	0	0
DDT	32	6	18.8	14	43.8	0.0150-0.1239	0.0142-0.0536	1	0
metoxychlor	32	4	12.5	10	31.3	0.0927-0.4043	0.0479-1.1507	3	4
acephate	32	4	12.5	1	3.1	0.7088-1.0168	2.6335	4	1
diazinon	32	8	25.0	3	9.4	0.1225-0.6321	0.1418-1.5079	8	3
fenitrothion	32	31	96.9	31	96.9	0.0108-0.4691	0.0386-0.3279	18	12
atrazine	32	1	3.1	1	3.1	3.5533	1.1597	1	1
simazine	32	21	65.6	5	15.6	2.7275-14.1381	2.0189-3.8238	21	5
alphacypermethrin	32	0	0.0	1	3.1	not detected	0.2070	0	1
deltamethrin	32	0	0.0	0	0.0	not detected	not detected	0	0
2003									
lindane	31	0	0.0	2	6.5	not detected	0.0130-0.0190	0	0
DDT	31	7	22.6	11	35.5	0.0133-0.0370	0.0164-0.1263	0	1
metoxychlor	31	7	22.6	13	41.9	0.0165-0.4030	0.0571-0.2434	3	6
acephate	31	6	19.4	1	3.2	0.7289-1.4736	1.2571	6	1
diazinon	31	0	0.0	0	0.0	not detected	not detected	0	0
fenitrothion	31	31	100.0	30	96.8	0.0135-0.3719	0.1159-1.8708	25	30
atrazine	31	0	0.0	0	0.0	not detected	not detected	0	0
simazine	31	15	48.4	0	0.0	1.8942-6.2723	not detected	15	0
alphacypermethrin	31	1	3.2	0	0.0	0.1213	not detected	1	0
deltamethrin	31	0	0.0	0	0.0	not detected	not detected	0	0

MAC (Maximal Admissible Concentration, currently 0.1 µg/l)

following pesticides were found in water samples: DDT, methoxychlor, acephate, diazinon, fenitrothion, atrazine, simazine and alpha-cypermethrin. Lindane and deltamethrin were not detected (Fig. 1, 2 and 3).

Again, nearly 100% of water samples, regardless of the source, were contaminated with fenitrothion. DDT has been also detected in 43.8% of water samples collected from deep wells, 41.2% water mains and 28.1% dug wells. Others, organochlorine, methoxychlor, were present in 37.5% samples from dug wells, 31.3% deep wells and 17.7% water mains. However, water samples collected from water mains were free from thiazines (atrazine, simazine) and pyrethroids (alpha-cypermethrin, deltamethrin). Among pyrethroids, however, only alpha-cypermethrin was detected in 3.1% of studied dug wells. This contrasted with more frequent contamination of dug wells with thiazines, i.e. simazine (15.6%) (Fig. 1, 2 and 3). Concentration of all pesticides, except DDT, exceeded MAC values up to 80 times.

Samples collected in 2003. During spring of 2003, the following pesticides were found in water samples: DDT, methoxychlor, acephate, fenitrothion, atrazine, simazine and alpha-cypermethrin. Lindane, diazinon and deltamethrin were not detected during this sampling period (Fig. 1, 2 and 3).

All samples collected from water mains and deep wells were contaminated with fenitrothion and this pesticide was also found in 96.9% of samples from dug wells. Approximately 20% samples from water mains and deep wells were polluted with acephate, while this pesticide was found in 28.1% samples of dug wells. All three types of water sources were also contaminated with DDT – most often in dug wells (34.4%). Water mains were frequently contaminated with methoxychlor (29.4%), while it was rarely found in samples from dug and deep wells. Simazine was detected in all types of water samples contaminating nearly 50% of deep wells. Several percent of samples from water mains and dug wells were contaminated with atrazine, but it was not found in deep wells (Fig. 1, 2 and 3).

MAC values were most often exceeded for fenitrothion, acephate and simazine; in some cases up to 230 times (Tab. 1, 2 and 3).

During the autumn of 2003, the following pesticides were found in water samples: lindane, DDT, methoxychlor, acephate, diazinon, fenitrothion, atrazine, simazine and alpha-cypermethrin. Deltamethrin was not detected (Fig. 1, 2 and 3).

Table 3. Concentration and prevalence of pesticide-contaminated samples collected from dug wells in the Warka-Grójec region during spring and autumn of 2002/2003.

Compounds	Total number of samples	Number of contaminated samples				Range of concentrations		Number of samples with exceeded MAC	
		spring		autumn		spring	autumn	spring	autumn
	N	n.	%	n.	%	µg/l	µg/l	n	n
2002									
lindane	32	1	3.1	0	0.0	0.0215	not detected	0	0
DDT	32	9	28.1	9	28.1	0.0106-0.0378	0.0146-0.0323	0	0
metoxychlor	32	7	21.9	12	37.5	0.0338-0.1911	0.0618-0.9672	2	7
acephate	32	4	12.5	1	3.1	0.5654-1.8486	2.4519	4	1
diazinon	32	5	15.6	2	6.3	0.2377-2.2493	0.6526-2.6229	5	2
fenitrothion	32	31	96.9	31	96.9	0.0214-0.4844	0.0279-0.3033	23	20
atrazine	32	0	0.0	1	3.1	not detected	8.0898	0	1
simazine	32	18	56.3	0	0.0	2.4786-10.8209	not detected	18	0
alphacypermethrin	32	0	0.0	0	0.0	not detected	not detected	0	0
deltamethrin	32	0	0.0	0	0.0	not detected	not detected	0	0
2003									
lindane	32	0	0.0	0	0.0	not detected	not detected	0	0
DDT	32	11	34.4	9	28.1	0.0102-0.0543	0.0237-0.1723	0	2
metoxychlor	32	8	25.0	19	59.4	0.0236-0.3042	0.0351-0.5290	4	15
acephate	32	9	28.1	2	6.3	0.7526-1.9131	1.2990-10.6112	9	2
diazinon	32	0	0.0	1	3.1	not detected	0.1955	0	1
fenitrothion	32	31	96.9	30	93.8	0.0232-0.4150	0.1525-1.5929	28	30
atrazine	32	6	18.8	1	3.1	2.4770-4.3997	4.3646	6	1
simazine	32	5	15.6	1	3.1	2.4491-22.7861	1.9642	5	1
alphacypermethrin	32	0	0.0	0	0.0	not detected	not detected	0	0
deltamethrin	32	0	0.0	0	0.0	not detected	not detected	0	0

MAC (Maximal Admissible Concentration, currently 0.1 µg/l)

Again, fenitrothion was by far the most frequently detected pesticide, contaminating 100% water main samples and up to 95% of samples collected from dug and deep wells. A high percentage of samples was also polluted with DDT and methoxychlor. For example, DDT was found in 47% and 35.5% samples obtained from water mains and deep wells, respectively. Dug wells were slightly less frequently contaminated with DDT (28.1%). Methoxychlor was found in 59.4%, 41.9% and 29.4% of dug wells, deep wells and water mains, respectively. The remaining pesticides, i.e. lindane, DDT, acephate, diazinon, atrazine, simazine and alpha-cypermethrin were detected in less than a few percent of water samples (Fig. 1, 2 and 3).

MAC values were most often exceeded for fenitrothion (75 samples) and methoxychlor (23 samples). MAC for acephate was exceeded by 106 times, while those values for other pesticides were exceeded several times (Tab. 1, 2 and 3).

DISCUSSION

The high incidence of organophosphates, pyrethroids and triazines in water samples clearly indicates that these pesticides are commonly used in the orchard industry and contaminate drinking water in the studied region. Organochlorines, which were banned in the 1970s, are still found in drinking water samples confirming that they are very persistent in the environment.

Among organochlorines, lindane was found in a small number of samples, mainly during spring (first year of the study) and autumn (second year of the study). Nevertheless, concentrations of lindane did not exceed MAC values. A much higher incidence of contamination was observed in the case of DDT, particularly during the autumn. Interestingly, methoxychlor was also more frequently found in samples collected during the autumn (both years of the study). It is not clear why these pesticides display such fluctuation during the year, but similar pattern was previously shown in this region several years ago [2, 4].

Contamination of water samples by organophosphates was the most prevalent among other pesticides analyzed in the present study. By far the most common pesticide was fenitrothion, present in nearly 100% of collected samples. The contamination with this pesticide was detected throughout the length of the study in all types of water sources. Evidently, such a high degree of contamination

with fenitrothion results from its common use in the orchard industry. Another organophosphate, acephate, was also found in samples collected during spring and summer throughout the study. In contrast, diazinon also belonging the organophosphate group, was only detected during the first year of the study, while during the second year it was infrequently found during the autumn. Earlier studies carried out in this area during the 1990s showed that fenitrothion was present in 90% of samples, and acephate in 50% of samples [4]. MAC values for these pesticides were exceeded several times in some water samples [4]. Studies performed in other regions also indicated the highest degree of contamination with fenitrothion and acephate in comparison to other pesticides [3].

Contamination of water samples with pyrethroids was very rare. Only alpha-cypermethrin was detected in a few samples, while deltamethrin was not detected at all. These results correspond well with data that have been obtained over last 10 years in this area [3, 4].

Triazines, simazine and atrazine showed a different pattern of contamination of water samples. Simazine was found throughout the entire study period with significantly higher prevalence in the spring. Atrazine, however, was found only in a very few samples. As in the case of organophosphates, the results concerning triazines were in line with previously collected data in this region [3, 4].

The present study, together with our previous reports [1-4], clearly indicates that drinking water in the regions of intensive agriculture is highly vulnerable to contamination by currently used pesticides, i.e. organophosphates. Seasonal fluctuations in the level of contamination may be a reflection of pesticides usage in a given period.

Surprisingly, we have not observed significant differences in the level of contamination of samples collected from various sources, i.e. dug and deep wells or water mains. Indeed, concentrations of pesticides were similar in samples collected either from wells or water mains. This fact suggests that water treatment practices may be insufficient. Thus, pesticides that leached to ground waters are not efficiently removed and distributed by existing water delivery system to households in the region.

MAC values recommended by European Union Directive (80/778/EEC) are much more stringent than those previously implemented by the Polish government. Consequently, current MAC values were exceeded in the great majority of water samples collected in the course of the present study.

CONCLUSIONS

1. The 2-year study carried out in the Warka-Grójec region in the years of 2002-2003 revealed a high degree of contamination of drinking water by several pesticides from various chemical groups.

2. The most common pesticides found in water samples were fenitrothion, DDT, methoxychlor and simazine. Concentration of these compounds significantly exceeded current MAC values recommended by European Union. Lindane and alpha-cypermethrin were only found in a few samples.

3. Water samples collected from different sources, i.e. dug and deep wells or water mains were almost equally contaminated by the same pesticides.

4. The present study reveals an urgent need for the systematic monitoring of drinking water quality in regions of intensive agriculture, since they are highly vulnerable to pesticide contamination.

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REFERNCES

1. Badach H, Majczakowa W: Skażenie środowiska (powietrze i powierzchnia gleby) po opryskaniu sadu wybranymi związkami fosforoorganicznymi. *Med Ogólna* 1995, **30**, 51-58.

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

3. Badach H, Nazimek T: Skażenie pestycydami wód pitnych w gospodarstwach zlokalizowanych na terenach sadowniczych. *Post Ochr Roślin* 2002, **42**, 758-760.

4. Badach H: Zanieczyszczenie wód pitnych środkami ochrony roślin w gospodarstwach rolnych na terenie o dużym zagęszczeniu plantacji chmielu i sadów. *Med Ogólna* 2004, **39**, 240-253.

5. Baker JT: *Bakerbonds spe. Application notes*. J.T. Baker Inc., USA 1998.

6. Cantor KP: Drinking water and cancer. *Cancer Causes Control* 1997, **8**, 292-308.

7. Dąbrowski J, Spieszalski W, Walorczyk S, Drożdżyński D: Zanieczyszczenie wód podziemnych pestycydami w województwie poznańskim na podstawie badań przeprowadzonych w latach 1993-1994. *Post Ochr Roślin* 1996, **1**, 160-166.

8. Juhler RK: Optimized method for the determination of organophosphorus pesticides in meat and fatty matrices. *J Chromatogr A* 1997, **786**, 145-153.

9. Kamińska IA, Oldak A, Turski WA: Geographical Information System (GIS) as a tool for monitoring and analysing pesticide pollution and its impact on public health. *Ann Agric Environ Med* 2004, **11**, 181-184.

10. LeBel GL, Williams DT, Griffith G, Benoit FM: Isolation and concentration of organophosphorus pesticides from drinking water at the ng/L level, using macroreticular resin. *J Assoc Off Anal Chem* 1979, **62**, 241-249.

11. Pomorska K, Badach H, Nazimek T: Skażenie pestycydami wybranych elementów środowiska w regionie sadowniczym. *Med Ogólna* 1997, **32**, 177-183.