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FATE OF ATRAZINE AND SIMAZINE RESIDUES IN POLLUTED GROUNDWATERS: RESULTS OF MONITORING INVESTIGATION OF POZNAŃ VOIVODESHIP WELLS IN 1993-1998

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Abstract. In the period of 1993-1998 six wells known as being contaminated were monitored 3-6 times per year (a total of 143 samples) for the presence of atrazine, simazine and respective chloro-dealkyl metabolites. Samples were prepared for analysis by solid phase extraction (SPE) and determination was by HPLC/UV or GC/NPD techniques, GC/MSD and HPLC/DAD were employed as secondary (confirmatory) techniques. Residues of analysed compounds were present in more than 90% of samples with exception for DeDiA that was found in 81.6% of samples. The highest concentrations of atrazine, simazine, DeA, DiA, and DeDiA were 16.80; 18.60; 7.49; 2.98 and 3.43 µg/l respectively. New inputs of atrazine and simazine were observed in ground water of three wells occasionally, probably resulting from fresh herbicide treatments. In the other wells contamination was rather stagnant at lower levels (0.X mg/l).

Key words: atrazine, simazine, residues, ground water, monitoring

I. INTRODUCTION

Use of pesticides, especially if it takes place against the rules of good agricultural practice, pose a potential risk for groundwaters, which was confirmed in studies conducted in the USA (e.g. Cohen et al. 1986), and Western Europe (e.g. Leistra and Boesten 1989). The pilot survey in 1989 also revealed contamination of some Polish groundwaters mainly by triazine herbicides and their metabolites (Dąbrowski et al. 1992). There was then an urgent need to initiate a more extensive investigation of this subject in Poland. Therefore, during the years 1993-1994 fourty wells in rural areas of 3 voivodeships were sampled nine times for a survey on pesticides in groundwater (Dąbrowski 1995).

All sampling points were drilled wells located in highly productive agricultural areas (ca. 50% close to orchards) on soils of good and medium permeability. Samples were subjected to analysis by GC/NPD, ECD and HPLC/UV. In case of positive findings GC/MSD was used as a confirmatory technique for all compounds amenable to gas chromatography and HPLC/DAD for those amenable only to liquid chromatography. From among 50 of monitored compounds, comprising 40 pesticides and 10 related substances, 27 were determined in analysed samples. Most frequently and at relatively high concentrations deisopropyl atrazine (DiA), simazine, atrazine, deethyl atrazine (DeA) and deethyl-deisopropyl atrazine (DeDiA) were detected in 22, 21, 19, 17 and 8% of samples respectively. Apart from them prometryn, lenacil, pirymicarb, napropamide, fenarimol, triadimefon, dichlofluanid and triadimenol were found but the frequency of these findings was much lower and did not exceed 4.7% of analysed samples.

Most frequently pesticide residues occured in the most vulnerable groundwaters of the Poznań voivodeship, where the depth of the wells mostly did not exceed 8 meters and the triazine herbicide residues were confirmed in 13-35% of analysed samples. Six most polluted wells were selected for further long term observations, and the results comprising the years 1993-1998 are reported in this paper.

II. MATERIAL AND METHODS

In the reported period of time 6 wells were sampled 22-26 times (3-6 times per year), thus 143 samples of groundwater were analysed on total. Pesticides and related compounds were isolated by solid phase extraction (SPE) technique using charcoal ENVI-Carb microcolumns based on the procedure of Di Corcia et al. (1991). The determinations were done by our own method using gas chromatography with nitrogen phosphorous detection (GC/NPD) and high performance liquid chromatography with ultra violet detection (HPLC/UV). Positive findings were confirmed by GC/MS and HPLC/DAD techniques. Performance of the method was evaluated by recovery studies and the rates ranged from 80% to 110% with coefficients of variation less than 10%. Limits of determination were set at 0.05 μg/l.

III. RESULTS

In the period 1993-1998 143 groundwater samples were taken from six wells, known as being contaminated, for triazine herbicide residues monitoring purposes. A total of 638 positive results, confirmed by GC/MS and HPLC/DAD techniques were obtained. In the groundwater samples residues of all five monitored compounds were found: most frequently – atrazine, DeA and simazine, and somewhat rarely – DiA and DeDiA. Detailed occurence frequencies are shown in Fig. 1. The statistical characteristics of atrazine and simazine residues detected in this survey are shown in Table .

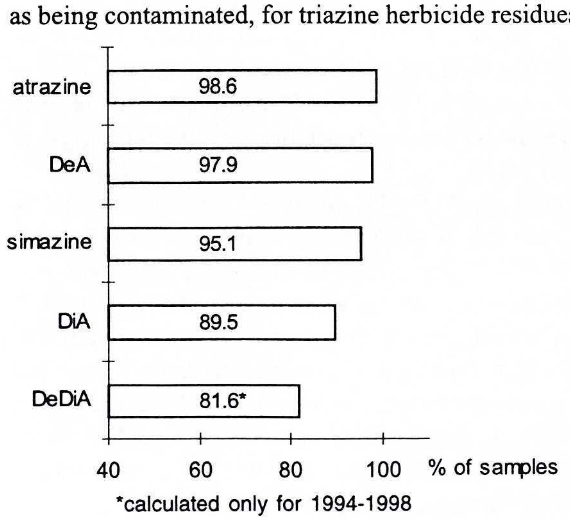

Fig. 1. Occurrence frequency of atrazine, simazine and their chlorodealkyl – metabolites in contaminated groundwaters of Poznań voivodship (1993-1998)

In the period of 1993-1998 the highest concentrations of atrazine, DeA and DiA (16.80; 7.49; and 2.98 μg/l respectively) were measured in well No. 23, and of simazine and

Table

Statistical characteristics of atrazine and simazine residues (µg/l) in contaminated groundwaters of Poznań voivodeship wells

	year	N	DeDiA				DiA				DeA				atrazine				simazine			
			min	max	aver.	Me	min	max	aver.	Me	min	max	aver.	Me	min	max	aver.	Me	min	max	aver.	Me
well 8	1993	5					0.85	2.19	1.54	1.54	1.11	3.89	2.15	1.88	0.44	0.62	0.54	0.56	0.14	0.37	0.28	0.28
	1994	3	2.22	3.41	1.88	2.22	1.03	1.86	1.35	1.16	1.71	2.83	2.39	2.62	0.27	0.44	0.34	0.30	0.12	0.26	0.18	0.17
	1995	3	1.87	2.32	1.40	1.87	0.72	1.08	0.84	0.73	1.41	2.34	1.85	1.79	0.13	0.64	0.45	0.59	0.30	0.32	0.21	0.30
	1996	6	1.20	2.19	1.81	1.83	0.41	1.33	0.84	0.72	0.14	0.99	0.41	0.33	0.88	2.03	1.47	1.48	0.19	0.25	0.22	0.22
	1997	3	1.54	2.40	2.09	2.33	1.17	1.45	1.31	1.30	1.90	2.66	2.28	2.29	0.36	1.34	0.74	0.53	0.26	0.37	0.31	0.29
	1998	5	1.22	1.50	1.37	1.41	0.83	1.26	1.04	1.03	1.56	2.25	1.80	1.75	0.23	0.40	0.31	0.30	0.14	0.22	0.18	0.18
well 13	1993	5					0.07	0.50	0.16	0.09	0.68	6.10	2.35	1.46	0.14	1.01	0.43	0.44	0.15	0.22	0.17	0.17
	1994	4	0.05	1.77	0.55	0.22	0.07	0.76	0.38	0.34	0.54	0.80	0.64	0.62	0.06	0.27	0.14	0.11	0.10	1.73	0.52	0.17
	1995	2	0.95	0.95	0.48	0.48	0.20	0.28	0.24	0.24	0.73	0.80	0.77	0.77	0.22	0.66	0.44	0.44	0.19	0.19	0.10	0.10
	1996	6	0.49	1.78	1.21	1.38	0.25	0.73	0.45	0.45	0.06	0.29	0.17	0.20	0.14	0.91	0.62	0.68	0.06	0.16	0.12	0.12
	1997	3	1.95	2.68	2.37	2.48	0.56	1.02	0.74	0.74	0.27	1.36	0.86	0.95	0.21	2.75	1.07	0.24	0.15	0.20	0.18	0.19
	1998	3	0.82	1.37	0.73	0.82	0.17	0.83	0.41	0.51	0.64	1.27	0.97	1.01	0.16	0.30	0.23	0.24	0.10	0.72	0.31	0.12
well 15	1993	5					0.04	1.17	0.29	0.04	0.16	0.47	0.25	0.16	0.04	0.88	0.32	0.09	0.12	0.36	0.20	0.25
	1994	4	0.10	0.28	0.10	0.05	0.04	0.13	0.06	0.05	0.13	0.44	0.25	0.21	0.03	0.34	0.14	0.09	0.09	1.64	0.52	0.17
	1995	3	0.17	0.17	0.06	0.00	0.15	0.15	0.05	0.00	0.27	0.40	0.22	0.27	0.05	0.15	0.11	0.13	0.19	0.55	0.35	0.30
	1996	6	0.14	0.14	0.02	0.00	0.08	0.21	0.07	0.04	0.16	0.48	0.35	0.40	0.09	0.22	0.16	0.17	0.10	0.18	0.15	0.15
	1997	2	0.30	0.59	0.45	0.45	0.23	0.28	0.26	0.26	0.58	0.80	0.69	0.69	0.04	0.46	0.41	0.41	0.18	0.18	0.18	0.18
	1998	2	0.09	0.17	0.13	0.13	0.37	0.60	0.49	0.49	0.42	0.64	0.53	0.53	0.03	0.79	0.55	0.56	0.18	0.22	0.70	0.70
well 4	1993	5					0.20	0.46	0.21	0.20	0.17	0.76	0.49	0.51	0.30	1.30	0.62	0.41	0.11	11.40	2.51	0.15
	1994	4	0.10	0.51	0.25	0.24	0.21	0.31	0.19	0.23	0.46	0.92	0.61	0.53	0.03	0.19	0.11	0.11	0.26	18.26	5.12	0.98
	1995	3	0.03	0.72	0.35	0.34	0.21	0.24	0.23	0.23	0.39	0.95	0.58	0.40	0.58	0.97	0.79	0.82	0.31	0.83	0.50	0.36
	1996	6	0.46	0.73	0.55	0.51	0.10	0.28	0.47	0.38	0.20	1.50	0.62	0.54	0.38	0.59	0.48	0.48	0.09	0.80	0.32	0.21
	1997	3	0.51	0.86	0.65	0.58	0.33	0.58	0.45	0.45	0.54	0.81	0.71	0.77	0.20	15.14	5.20	0.27	0.14	3.76	1.35	0.16
	1998	4	0.43	0.58	0.49	0.48	0.38	0.70	0.50	0.45	0.44	0.56	0.50	0.50	0.22	2.26	0.83	0.42	0.22	4.82	1.50	0.48
well 7	1993	4					0.83	1.10	0.99	1.01	1.35	6.50	4.78	5.64	3.90	6.31	5.43	5.76	0.27	0.77	0.54	0.57
	1994	3	0.13	1.67	0.60	0.13	0.06	0.82	0.36	0.21	0.42	2.67	1.83	2.40	0.10	0.43	0.31	0.40	0.37	18.60	6.32	0.37
	1995	3	0.67	0.98	0.55	0.67	0.46	0.75	0.57	0.51	1.10	2.38	1.62	1.38	0.26	1.15	0.78	0.93	0.24	0.74	0.49	0.48
	1996	6	0.61	3.43	0.94	0.62	0.29	1.67	0.43	0.30	0.28	1.63	0.80	0.80	0.52	2.38	1.34	1.37	0.56	1.04	0.80	0.78
	1997	2	1.23	1.28	1.26	1.26	0.41	0.63	0.52	0.52	1.79	1.99	1.89	1.89	0.66	0.81	0.74	0.74	0.16	0.21	0.19	0.19
	1998	4	0.66	1.73	1.01	0.82	0.47	0.68	0.55	0.54	1.05	1.60	1.25	1.17	0.38	0.60	0.46	0.43	0.13	0.27	0.18	0.17
well 23	1993	5					0.92	2.04	1.47	1.52	3.42	7.49	5.16	4.81	6.86	11.20	9.12	8.68	0.26	0.55	0.43	0.50
	1994	4	0.16	1.64	0.57	0.25	0.56	0.77	0.73	0.73	2.12	7.46	4.46	4.13	2.14	16.80	6.75	4.02	0.12	0.54	0.28	0.23
	1995	3	0.50	0.50	0.17	0.00	0.28	0.48	0.25	0.28	1.75	2.58	2.15	2.15	1.07	1.94	1.00	1.07	0.16	0.16	0.05	0.00
	1996	6	0.53	1.06	0.72	0.68	0.29	1.58	0.64	0.33	0.17	3.04	1.49	1.33	1.13	2.36	1.60	1.48	0.74	1.60	1.11	1.03
	1997	3	0.67	2.48	1.56	1.52	0.44	1.28	0.91	1.02	0.27	4.59	2.33	2.14	0.91	2.75	1.86	1.93	0.15	0.37	0.25	0.22
	1998	5	0.96	1.15	1.04	1.04	0.64	2.98	1.39	0.87	2.76	4.53	3.42	2.90	0.75	14.34	6.36	1.91	0.15	1.27	0.62	0.50

N – number of analysed samples; min – minimum concentration; max maximum concentration; aver. – average concentration; Me – median concentration

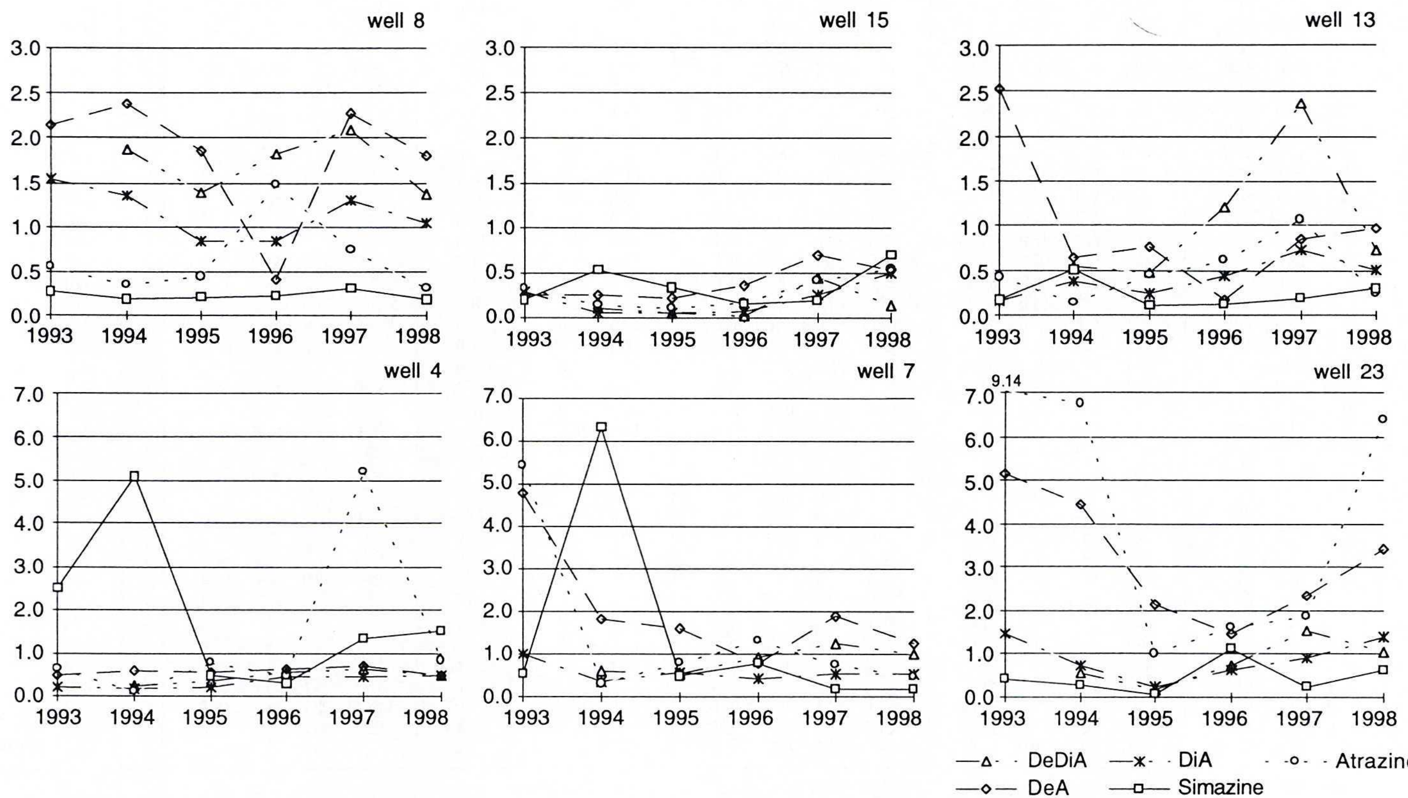

Fig. 2. Annual avarge concentrations of atrazine and simazine residues in contaminated wells of Pozı

DeDiA (18.60 and 3.43 μg/l respectively) - in well No. 7. Also average and median concentrations of atrazine and DeA (ranging from 2.04 to 3.20 μg/l were the highest in well No. 23 wheras those of DiA and DeDiA (ranging from 1.08 to 1.88 μg/l were the highest in well No. 8. Relatively high fluctuation of concentrations for all analysed compounds was observed all over the investigation period except for well No. 15 where for all determined compounds the highest concentration did not exceed 1.64 μg/l and the average and median values where not higher then 0.37 and 0.40 μg/l respectively.

In some wells even peak concentrations appeared primarily of atrazine and simazine most probably caused by fresh herbicide treatment of the neighbouring orchards. In the most polluted well No. 23 in the period from May 1993 till October 1994 the atrazine concentrations in groundwater, during seven sampling terms, ranged from 6.86 to 5.57 μg/l with a maximum of 16.80 μg/l in April 1994. This atrazine disappearance curve was accompanied by a similar disappearance pattern of its main metabolite DeA, which reached its highest concentrations between October 1993 and June 1994 (5.25-7.49 μg/l). In September and October 1998 two new peaks of atrazine concentrations were observed (14.34 and 12.95 μg/l) in well No. 23.

Disappearance curves of atrazine and DeA were observed also in well No. 7. In the period from May till October 93 disappearance curves of atrazine and DeA ranged from 6.31 to 3.90 μg/l and from 1.10 to 0.99 μg/l respectively. In June 1994 a single peak concentration of simazine (16.6 μg/l) appeared. In other sampling terms (a total of 22 in 1993-1998) the simazine concentration did not exceed the level of 0.X μg/l.

Also in well No. 4 single concentration peaks appeared: in April 1994 – 18.26 μg/l of simazine and in December 1997 – 15.14 μg/l of atrazine but in both cases no disappearance pattern was observed. Noteworthy is that concentrations of atrazine and simazine metabolites in this well only in two samples out of 25 slightly exceeded the level of 0.X μg/l.

A compact survey of the pollution of six selected Poznań voivodeship wells by atrazine and simazine residues is given in Fig. 2. Diagrams presented in this figure are to a quite good degree coincident with the permeability of the soils surrounding individual wells. Taking into account this permeability the contamination vulnerability of individual wells can be put in the following rising order: low permeability – well No. 15, low/medium permeability – well No. 8 and 7, medium permeability – well No. 13, medium/good permeability – well No. 4, good permeability – well No. 23.

All of the wells are shallow, their depth range from 3.30 to 10.1 m and the water table from 1.7 m to 5.3 m.

IV. DISCUSSION

First of all it should be emphasised that the presented results in no case should be considered as representative for groundwaters of the whole Poznań voivodeship because for examination six most vulnerable wells were selected. These results rather may be useful for estimation of pesticide residue levels, which could be expected in groundwaters under adverse conditions.

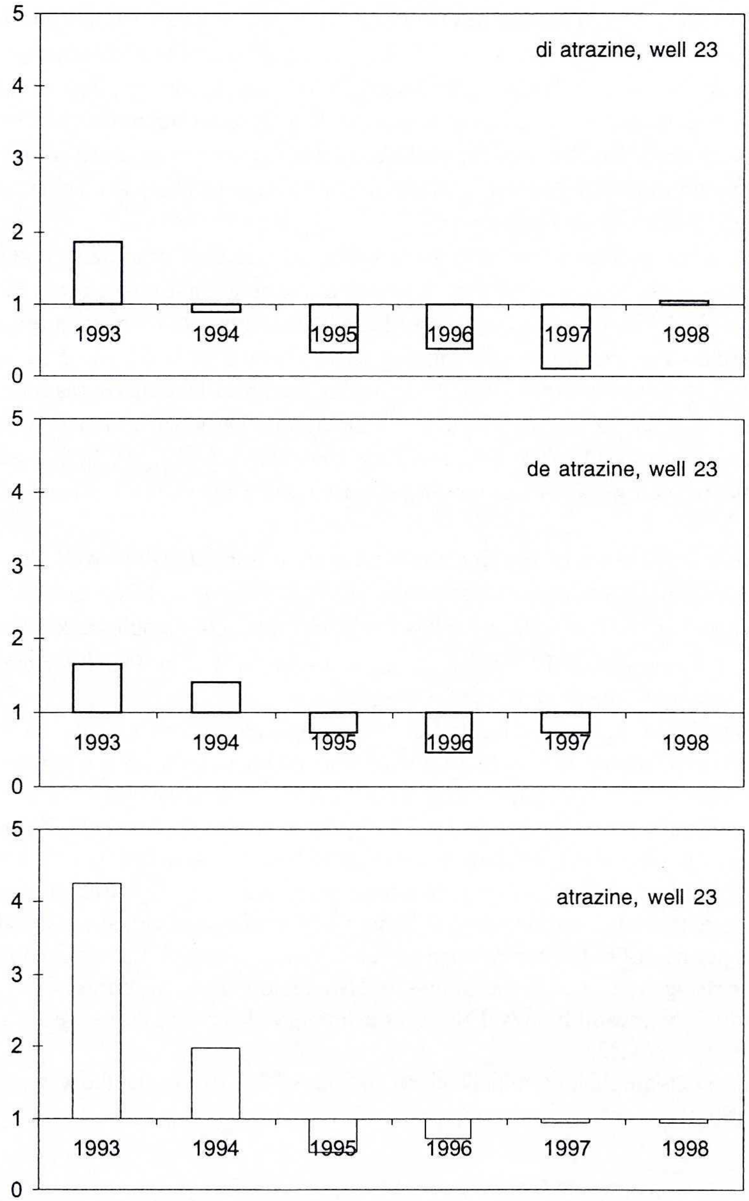

Fig. 3. Ratios of annual median values of atrazine residue concentrations in groundwater to the common median concentrations calculated for well No. 23 in the whole period 1993-1998

Until 1994 atrazine and simazine application for grass weed control in orchards of up to 3 kg a.i./ha and in older orchards even up to 6 kg a.i./ha were allowed. Since 1995 the dose is officialy reduced to 1.5 kg a.i./ha. Generally, our investigation reflect this situation quite good. Namely in wells, in which during 1993-1998 fresh herbicide inputs were observed (wells

No. 4, 7, 23) most of their peak concentrations appeared in the groundwaters before 1995 but afterwards there is still a remarkable residues fluctuation and it needs some more time to get a precise picture of the tendency in triazine herbicide residues fate in the environment. Nevertheless in Fig. 3 for the most vulnerable and polluted well No. 23 ratios of annual median values of atrazine residue concentrations to the median value common for the whole period 1993-1998 are shown. On the diagrames one can clearly see a decrease of atrazine, DeA and DiA after 1994.

V. LITERATURE

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LOS POZOSTAŁOŚCI ATRAZYNY I SYMAZYNY W SKAŻONYCH WODACH PODZIEMNYCH: WYNIKI BADAŃ MONITORINGOWYCH STUDNI WOJEWÓDZTWA POZNAŃSKIEGO W LATACH 1993-1998

STRESZCZENIE

W okresie 1993-1998 monitorowano sześć skażonych studni 3-6 razy w roku (suma próbek 143) na obecność atrazyny i symazyny oraz ich chlorodealkilo-metabolitów. Próbki wody przygotowano do analiz stosując technikę adsorbcji/ekstrakcji na mikrokolumienkach (SPE). Końcowe oznaczenia wykonano metodami HPLC/UV lub GC/NPD do potwierdzania wyników stosując techniki (GC/MSD i HPLC/DAD).

Pozostałości analizowanych związków występowały w ponad 90% próbek z wyjątkiem DeDiA znalezionym w 81,6% próbek. Najwyższe oznaczone stężenia atrazyny, symazyny, DeA, DiA, DeDiA wynosiły odpowiednio 16,80; 18,60; 7,49; 2,98 i 3,43 µg/l. W trzech studniach parokrotnie stwierdzono wzrost stężeń atrazyny i symazyny prawdopodobnie będący rezultatem aktualnych zastosowań herbicydów w praktyce rolniczej. W pozostałych studniach skażenia pozostałościami herbicydów raczej zmieniały się nieznacznie w zakresie niskich stężeń (0,X µg/l).