

RESIDUES AND TRANSFER OF TRIAZINE HERBICIDES IN GROUND WATERS OF INTENSIVELY EXPLOITED ARABLE LAND IN WIELKOPOLSKA PROVINCE OF POLAND

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Abstract: Analyses of the ground waters in respect of presence of residues of plant protection products, i.e. active substances as well as environmental metabolites thereof are performed in the Institute of Plant Protection since the end of 80ties of the past Century. Based on the results obtained in 1993–1994 for 40 wells located in administrative territories of former Poznań, Toruń and Bydgoszcz voivodeships, in the vicinity of intensive agricultural production areas (orchards, farms), wells where significant amounts of residues of triazines group and dealkylated metabolites thereof had been found previously were qualified to further studies. There were 6 wells in which triazine residues were determined most often. Additionally, based on hydrogeological maps, directions of underflows in the areas of well's locations were determined as well. The aim of the above was to find the additional places for sampling waters distant from pollution sources and estimation of the level of residues of target compounds depending on distance from the basic wells.

Seven triazine compounds including basic active substances (atrazine, simazine) and their metabolites [desethyl atrazine, desisopropyl atrazine, desethyldeisopropyl atrazine, hydroxyatrazine and hydroxysimazine] were selected for the presented studies. Residues were analyzed using methodologies designed in the Institute, i.e. solid-phase extraction (SPE) followed by determination by chromatographic techniques HPLC-PDA, GC-NPD and GC-MS. Generally, during 11 years of investigations (1993–2003) samplings were performed 52 times and 323 samples of groundwater including that from additional wells were analyzed. Most often residues of atrazine and deethylatrazine in wells located in environs of Poznań were detected.

Key words: residues, plant protection products, herbicides, sampling, SPE, HPLC, GC

INTRODUCTION

Since 1945 when one of the first herbicides, 2,4-D was applied, a great progress in agriculture especially in highly developed countries was observed. Thousands of

chemicals were tested in respect of their herbicide activity and several hundred being more or less effective were introduced to the common use. Unfortunately, along with increase of usage of chemical fertilizers and plant protection products (PPP), residues unknown before chemicals, menace of the natural environment including surface and ground waters as well as soil appeared.

Important questions from an ecological viewpoint are in what extend PPP might be hazardous for ground waters, what transformations could occur during their passage through the soil profile, and what is an ability of residues of active substance and products of its degradation under field conditions to migration with underflows and/or which products of its metabolism would be a final one at aqueous conditions. Residues of active substances as showing a high resistance in the environment, easily bind to the components of the soil sorption complex and being of a high solubility in water are most interesting for researchers of groundwater pollutants. Above criteria have been met by herbicides of the triazine group, especially the most important ones like as atrazine and simazine. Moreover, the following arguments promoted the selection of the above substances:

- both herbicides are produced by domestic manufacturers therefore, they belongs to most inexpensive ones so, they are most common active substances used as components of herbicide preparations;
- compounds described are easily transformed in the environment and their metabolites have similar toxicity to the substrates;
- studied active substances are listed as the compounds that should be withdrawn from the common use for crop protection (Directive 2000/60/EC 2000);
- selected herbicides, their metabolites and decay thereof can be observed in the natural conditions therefore, use of any special, artificial experimental field is not necessary.

Harmfulness of triazine herbicides residues to humans and other living organisms is known a long time. Atrazine as well as simazine and products of their transformations in the natural environment are considered as potential carcinogens (Tchounwou 2000; Oh 2003).

MATERIALS AND METHODS

Method for sampling well's water was designed using directions given by Dąbrowski (1995a, b) and Siepak (1997).

1. Method for sampling well's water

One-liter probe bottles were carefully washed with detergent containing water, then rinsed with water, treated with chromic acid cleaning mix, rinsed with distilled water several times, dried and finally stoppered with polypropylene stoppers to prevent an accidental contamination. Each drawn four-liter sample was poured into the bottles. In the case of wells equipped with hydrophore or lifting pump *ca.* 5l of water were drain off followed by rinsing the bottles with 3 one-liter portions of water before sampling. If the well was equipped with bucket hanging on the rope, the first portion of water was used for rinsing the bucket and then bottles were rinsed (three times, *ca.* 1l portions) followed by sampling.

2. Handling the collected samples
Samples that obtained (paragraph 1) were marked immediately after drawing and bottles stoppered. The samples were stored at 2–4°C before use. According to the recommendations of US EPA (United States Environmental Protection Agency) and UK SCA (United Kingdom Standing Committee of Analysis) extraction of the collected triazine samples was performed within 7 days from sampling. When chromatography process could not be done immediately after extraction, samples were only extracted to the solid phase and SPE columns refrigerated at –20°C. As per literature data, triazine xenobiotics adsorbed at the columns packed with an active charcoal could be stored even one year without losses of triazines (Sabik 2000).
3. Extraction of triazine compounds from water
Developed analytical methodology based mainly on publications of Di Corcia (1991; 1992) and concerned an application 1.5l water of an active charcoal as a packing for SPE cartridges. Investigated substances were eluted from SPE cartridges with methanol/dichloromethane mixture (v/v 2:8). To optimize extraction conditions and recovery for spiked samples of hydroxyatrazine and hydroxysimazine during extraction, studies of Berg et al. (1995) and personal information from other researchers (Denmark, Germany) were applied. Modifications of Di Corcia methodology allowed for designing the routine method for analysis of triazines and products of their degradation (dealkylated and hydroxylated ones) and method validation data were described in the author's Ph. D. thesis (Drożdżyński 2004).
4. Determination of triazine residues
Residues of selected triazine herbicides as well as products of their transformations in the environment were determined using gas chromatography with nitrogen-phosphorus detection (GC-NPD) and high performance liquid chromatography with photodiode array detection (HPLC-PDA). Use of two independent chromatography methods avoided mistakes in interpretation of the results. Moreover, gas chromatography-mass spectroscopy method (GC-MS) was used to confirm results for samples where very high quantities of triazine residues and/or their metabolites were detected. An application of the above methods complementary allowed for obtaining most objective image of groundwater pollution in Poznań environs from 1993 to 2003.

RESULTS AND DISCUSSION

In the period between 1993 and 2003 (11 years) 3–7 samplings of water from selected wells of Wielkopolska Province were performed yearly. The samplings were done usually from April to November with the exception of few years when samples were drawn to the middle of December. Until 1998, 143 samples were drawn during 26 samplings. 1998 was the last year when samplings were made for all six initially selected wells. Unfortunately, due to lack of an access to one of them, in 1999 samples from only five wells were taken and additional places located in the closest neighborhood of the selected ones were looked for samplings to determine dependence of concentration of triazine herbicides on distance from the source of pollution. In 2000, based on hydrogeological maps of resorts Stęszew and Pamiątkowo located near the places where the highest amounts of triazines had been found before, and

co-operation with hydrogeologists additional wells along the directions of underflows were found. Examination of these wells was made at the same time as in case of the basic ones. From 1999 to 2003, in 26 terms decimal, 150 samples were drawn from underflows. Moreover, in 1994 fifteen wells located from 200 to 1000m from all triazine-polluted wells were examined and 15 additional samples drawn between December 5 and 19. On July 24 and September 5, 2003 fourteen samples were drawn from the wells of Stęszew and Pamiątkowo neighborhood. During 11 years of our studies, samplings were done in 52 regular and 3 additional terms and generally 323 samples of groundwater were drawn.

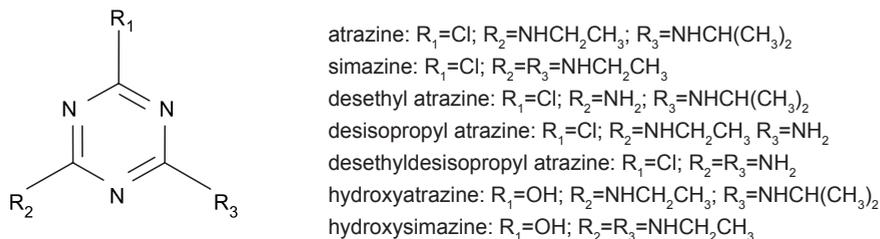


Fig. 1. Structures of triazine compounds investigated in wells of Wielkopolska

Seven triazine compounds (Fig. 1) including two herbicides, atrazine and simazine, three dealkylated metabolites thereof, i.e. desethyl atrazine (DEA), desisopropyl atrazine (DIA) and desethyl desisopropyl atrazine (DACT) as well as two their hydroxyl products of transformation in the environment named hydroxyatrazine and hydroxysimazine were selected. Residues of atrazine and DEA were detected most often. Both of them were determined in 91% of analyzed samples. Residues of simazine was found in 85.4%, DIA in 82.7% while DACT was detected in 76.2% of examined underground water samples. The highest determined residue values for particular triazine xenobiotics were as followed: atrazine, 16.87 $\mu\text{g/l}$ (April 1994); simazine, 11.40 $\mu\text{g/l}$ (May 1993); DEA, 7.49 $\mu\text{g/l}$ (May 1993); DIA, 4.05 $\mu\text{g/l}$ (September 1998); DACT, 3.45 $\mu\text{g/l}$ (April 1996); hydroxyatrazine, 0.68 $\mu\text{g/l}$ (May 1998); hydroxysimazine, 0.34 $\mu\text{g/l}$ (May 1998). As we can observe all high values were noticed until 1998 when maximum permissible dose of triazine herbicides for phytosanitary treatment was limited from 5.0 to 1.5 kg/ha. Directive 98/83/EC (1998) has defined permissible concentration of residues of pesticides (Maximum Residue Level, MRL) in water intended for human consumption as 0.1 $\mu\text{g/l}$ for single compound and 0.5 $\mu\text{g/l}$ in case of sum of residues in the examined water sample. Both atrazine and simazine determined in well samples significantly exceeded MRLs established by European Union in many cases. It is worthy of note that all norms, maximum permissible value for water concern exclusively an active substances of the herbicides i.e. atrazine and simazine but not products of their transformation in the environment. Metabolites thereof despite frequent significantly higher level in groundwater are not a subject for any limitation by any code. As comparing above monitoring data with those obtained in other countries there are noticeable similarities in both quantities and proportions of determined residues of triazines for well samples analyzed in

Portugal (Cerejeira 2003), Greece (Papastergiou 2001) or United States (Smith 1999). Figure 2 presents detection frequency of the selected active substances of triazine group and their metabolites occurring in wells of Wielkopolska Province.

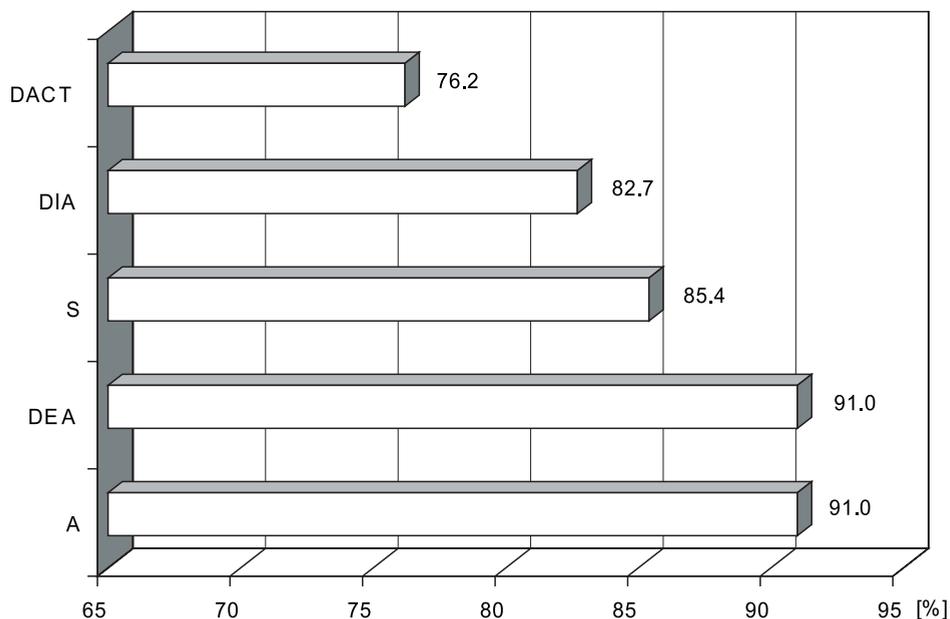


Fig. 2. Occurrence of residues of the selected triazines in Wielkopolska wells Abbreviations: A – atrazine; S – simazine; DEA – desethyl atrazine; DIA – desisopropyl atrazine; DACT – desethylde-sisopropyl atrazine

Hydroxy derivatives were determined sporadically. In the period 1998–2003 only 12 samples of water were polluted with the residues of hydroxyatrazine while hydroxysimazine traces were confirmed in two cases. Taking into consideration an ability of these products to adsorption to the soil particles of surface layer of the soil profile, we can suppose that their presence in monitored wells was due to rinsing out triazine residues of preparations from the topsoil layer after application. This supposition based on observation that most of well casings reached only the level of ground therefore, wells could be supplied with surface waters from the neighboring fields during intensive precipitations. Also interviews given by fruit-farmers, owners of the wells, confirmed the possibility of direct transfer of rainwater bearing soil particles to the wells.

Generally, eleven years of studies on triazine residues in wells of the environs of Poznań can be divided into two periods: 1993–1998 and 1999–2003. The first one was characterized by significant amounts of detected residues of herbicides, both in respect of concentration levels and frequency of determination of selected residues (Dąbrowski 2000). After 1998 considerable decrease of the pollution level with residues of triazine xenobiotics in examined wells was noticed. In 2000–2003 studied herbicides were detected at lower and lower amounts therefore we can anticipate that in few years they would disappear completely in ground waters of Wielkopolska Province. However, first of all, the reserves of residues of triazines in non-extractable form

but liberated by soil microorganisms should soon run out. Now, concentrations of detected herbicide residues practically meet limitations concerning MRLs in water.

As analyzing pollution of selected wells with residues of triazines, frequency and concentration of DEA attract the attention. This dealkyl metabolite should appear in lower concentrations than DIA or DACT as far as it was the product of atrazine degradation only while other abovementioned compounds derived from simazine as well. Nevertheless, due to the mobility of DEA in the soil, the metabolite easily passes through the soil profile to the groundwater. Above is in agreement with observation of other researchers (Kolpin et al. 1997) who also noticed a higher level of this derivative in groundwaters in 106 wells in the State of Iowa, USA compared to others.

There are difficulties in the drawing an exact diagram of amount of herbicides in dependence on precipitations based on comparison of detected triazine residues and rainfalls. The most abundant falls in Wielkopolska Province were observed in 1997 and 1998. They were the years when mainly products of triazine xenobiotic degradation in significant amounts were found however not as high as before. In December 1997 in one well sudden increase of atrazine residue level was noticed as an effect of the herbicide application after termination of production cycle in the orchards. Very likely, sampling was performed soon after the late-fall treatment during which fruit-farmer could liquidate surplus of triazine preparations knowing restrictions for doses of atrazine and simazine planned for 1998. Data concerning the precipitations were taken from weather station of Poznań International Airport at Ławica located near area of investigation.

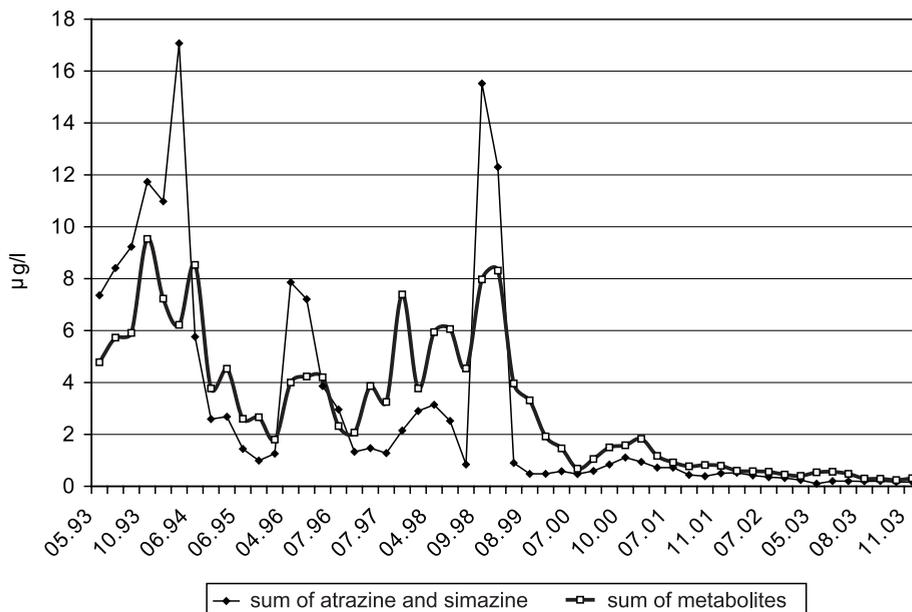


Fig. 3. Comparison of the proportions between residues of basic pesticides and their metabolites (sum of atrazine and simazine vs. sum of the 5 metabolites) for Stęszew environ

Taking into account proportions between residues of studied herbicides and products of their transformations, significant changes in amount of detected compounds can be noticed. As during the first before mentioned period (1993–1999) residues of basic active substances of triazine preparations i.e. atrazine and simazine were predominant, starting from 1996 tendency to higher contribution of dealkylated metabolites in total pool of detected residues of triazines was observed. Figure 3 displays a comparison of proportion of residues of the basic pesticides with products of their transformations (the sum of residues of atrazine and simazine vs. sum of metabolites) for wells located at Stęszew environs.

Amongst analyzed triazines in additional wells, residues of degradation of atrazine and simazine were mainly detected, especially DIA. Interestingly, this metabolite, common for atrazine and simazine, was quite often detected at places located a bit farther from basic wells and less frequently and at lower concentrations in wells examined in the beginning of the investigation. Above can be connected with a high mobility of this compound in groundwater. Hydroxyatrazine as well as hydroxysimazine were not found in any additional sample that was in agreement with information concerning easiness of these compounds to be adsorbed to the topsoil particles. Residues of basic compounds were found sporadically probably due to distance from the source of contamination to additional wells. Figure 4 shows a comparison of atrazine, simazine, DEA, and DIA residues amounts in one of basic wells and additional one located 200 m farther in 2000–2003.

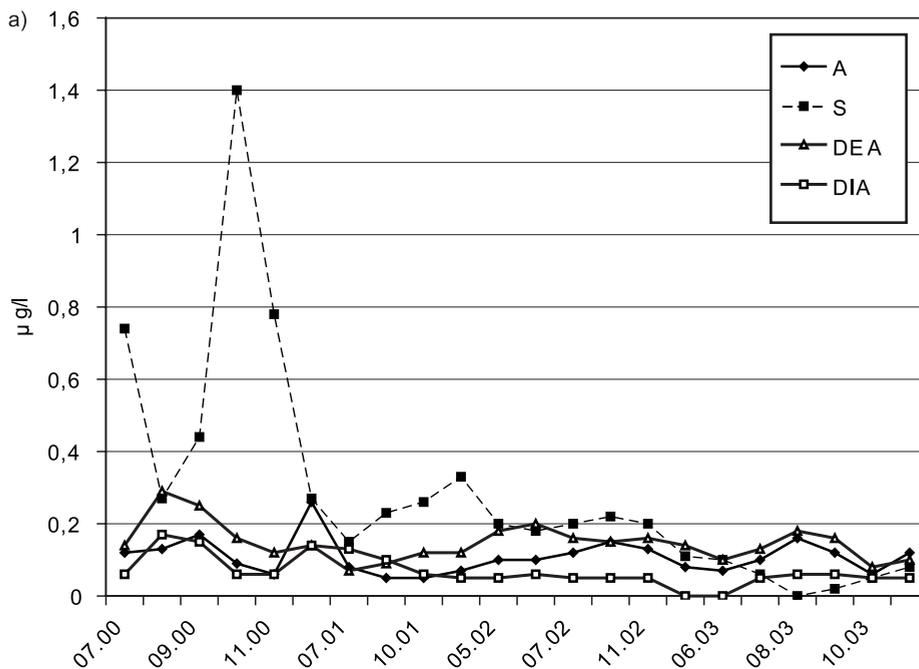


Fig. 4. Comparison of residues of atrazine, simazine, DEA and DIA in the basic well (a) and additional one (b) located 200 m farther (2000–2003). For abbreviations see caption to the Figure 2

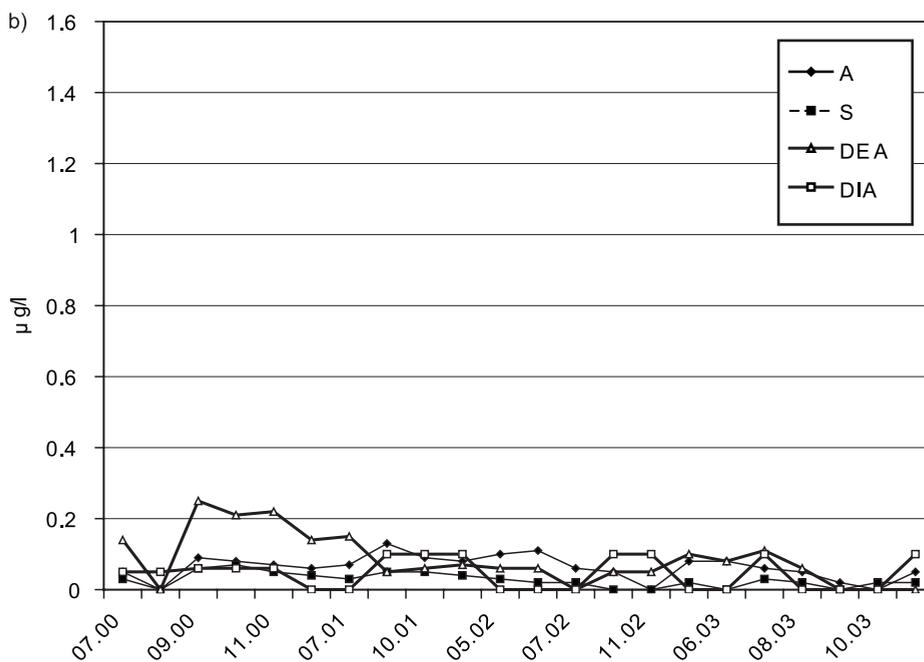


Fig. 4. Comparison of residues of atrazine, simazine, DEA and DIA in the basic well (a) and additional one (b) located 200 m farther (2000–2003). For abbreviations see caption to the Figure 2

CONCLUSIONS

In course of 11 years of monitoring wells of Poznań environs, most often residues of atrazine and DEA were detected. As many as 91% of 323 samples were contaminated with these compounds. It can be concluded that triazine herbicides were most popular PPP in Wielkopolska Province. If we make such assumption that only some part of applied active substances reached groundwaters, while most of them was bound to the soil components forming non-extractable complexes, we can expect that residues of triazines, mainly products of herbicide degradation can last in Wielkopolska wells for a long time.

Hydroxy derivative residues were detected in Wielkopolska wells sporadically. Only 12 samples of well water drawn in 1998–2003 were contaminated with hydroxyatrazine residues while hydroxysimazine residues was hardly found in two cases. Literature data support evidences that residues of triazine metabolites are the main products in surface layer of soil and easily adsorbed in biologically active soil layer (Moreau 1997; Lerch 1999). Most likely, an appearance of the residues was not a result of vertical transfer through the soil profile but was caused by surface water run-off in the consequence of intensive rainfalls. Moreover, all above samples were drawn from wells that were not sufficiently protected against support with surface water after rainfalls or storms.

After 1998 significant decrease of determined amounts of residues of triazine herbicides was observed due to reduction of maximum permissible dose for application

of atrazine and simazine from 5.0 to 1.5 kg/ha that year. It evidenced that farmers operating in Wielkopolska region followed recommendations of plant protection inspectorates and significantly limited or abandoned application of triazine herbicides in agricultural practice, which evidently changed the proportion between residues of herbicides and their metabolites.

Noticeable change of proportion of detected triazine compounds residues in selected wells causes that more and more frequently products of atrazine and simazine have been detected instead of the original substances themselves. Probably presently detected residues of triazines are a result of rinsing off the metabolites of herbicides produced by soil microorganisms and stored in sorption soil complex. Products of triazine transformations are less phytotoxic and their occurrence in waters is rather more profitable for agricultural environment than the presence of original herbicides. However, there is still problem of an influence of the residues of triazine herbicides and their metabolites on humans and animals. The metabolites can be potentially hazardous for consumer's health but there are not any regulation(s) concerning their MRLs, etc. in potable water that is, in my opinion, a gross negligence and deep ignorance of the legislature.

Just a little distance between basic wells located in the areas of intensive agricultural production and additional ones placed in closest neighborhood results in lower concentrations of residues of triazine herbicides and metabolites in water. This is a quite strong evidence for easiness with which herbicides of this group can be bound to the soil components. Therefore, a higher triazine residues hazard could be expected in case of surface waters because in this kind of water resources of active substances of this PPP group would transfer better.

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POLISH SUMMARY

POZOSTAŁOŚCI ORAZ PRZEMIESZCZANIE SIĘ HERBICYDÓW TRIAZYNOWYCH W WODACH PODZIEMNYCH INTENSYWNIE UŻYTKOWANYCH ROLNICZO OBSZARÓW WOJEWÓDZTWA POZNAŃSKIEGO

Badania wód podziemnych na obecność pozostałości środków ochrony roślin są prowadzone w Instytucie Ochrony Roślin od końca lat osiemdziesiątych ubiegłego stulecia. W oparciu o wyniki uzyskane w latach 1993–1994 dla 40 studni zlokalizowanych na terenach ówczesnych województw poznańskiego, toruńskiego i bydgoskiego, położonych w pobliżu miejsc intensywnej produkcji rolniczej (sady, gospodarstwa rolne), wytypowano do dalszych badań te, w których wcześniej stwierdzono obecność znacznych ilości pozostałości herbicydów z grupy triazyn oraz ich dealkilowych metabolitów. Ostatecznie do dalszych prac wybrano sześć studni w których najczęściej oznaczano triazyny. Jednocześnie na podstawie map hydrogeologicznych wyznaczone zostały kierunki spływu wód podziemnych na terenach na których zlokalizowane były studnie. Miało to na celu znalezienie dodatkowych miejsc poboru próbek wód, położonych na kierunku spływu wód podziemnych, oddalonych od źródła zanieczyszczeń i co za tym idzie możliwość oszacowania poziomu pozostałości poszukiwanych związków w zależności od odległości od studni podstawowych.

Siedem związków triazynowych w tym dwa związki podstawowe (atrazyna i symazyna) oraz pięć produktów przemian (deetyloatrazyna, deisopropyloatrazyna, deetylodeisopropyloatrazyna, hydroksyatrazyna i hydroksysymazyna) zostało wybranych do badań. Pozostałości herbicydów triazynowych były oznaczane z wykorzystaniem metodyki analitycznej opracowanej w Instytucie. Podstawą metody było wyekstrahowanie poszukiwanych związków przy pomocy ekstrakcji do fazy stałej (SPE), a następnie oznaczenie z użyciem technik chromatograficznych: wysokosprawnej chromatografii cieczowej z detektorem wielodiodowym (HPLC-PDA), chromatografii gazowej z detektorem azotowo-fosforowym (GC-NPD) oraz chromatografii gazowej z detektorem mas (GC-MS).

W trakcie jedenastu lat badań (1993–2003) pobrano łącznie 323 próbki wody (ze studni podstawowych i dodatkowych) w 52 terminach. Najczęściej w próbkach wód ze studni z okolic Poznania znajdowano pozostałości atrazyny oraz jej dealkilowego metabolitu deetyloatrazyny.

