Atrazine in Groundwater of Agricultural and Urban Areas in Serbia

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Abstract

Monitoring of pesticides in groundwater generally covers the area under intensive agricultural production, although the use of pesticides is not concentrated only on arable land. In urban areas pesticides are intensively used in communal hygiene (insecticides, rodenticides) and for complete of vegetation suppression, when herbicides are applied in very large quantities. Triazine based herbicide – atrazine, occupies a special place among pesticides that are present in water. This compound and its degradation products are very persistant and leaves residues in the environment.
This study was conducted in order to determine the presence of atrazine and its metabolites, deethylatrazine (DEA) and deisopropylatrazine (DIA) residues in groundwater in agricultural and urban regions on the entiry territory of the Republic of Serbia. The sampling was performed during 2008 on 327 localities. Groundwater samples of the first aquifer were taken from 249 wells surrounded by arable land and from 78 wells, distanced from agricultural area.
The extraction of atrazine and its metabolites from water was carried out with methanol using C-18 DSK 47mm (Supelco No.57171). Residue levels were analyzed by GC-NPD. Limit of quantification (LOQ) determined for this method was 0.01 μg L^{-1}.
Content of atrazine in groundwater samples taken from the localities under intensive agricultural production was 0.23 μg L^{-1}, DEA 0.20 μg L^{-1} and DIA 2.47 μg L^{-1}. In the groundwater samples from urban areas average values of atrazin was 0.10 μg L^{-1}, DEA 0.05 μg $L^{-1}$and DIA 1.78 μg L^{-1}. Presence of atrazine and its metabolites above 0.1 μg L^{-1}, in region under intensive agricultural productions and in city areas, is the consequence of intensive and long-term usage of atrazine based herbicides in the amounts up to 10 kg ha^{-1}. The results indicate that both agricultural and urban areas are probable source of pesticides in groundwater.

Keywords : *Atrazine; DEA; DIA; Groundwater; Monitoring*

Introduction

Monitoring of pesticides in soil and water covers mostly areas under intensive agricultural production, although the pesticides are not use only on arable land. According to recent researches, urban areas are very important source of groundwater contamination as well (1-3). Since 1990`s, when a large percentage of pesticide residues was detected in urban areas, this problem has gained in importance.

Atrazine and one of its metabolite, deethylatrazine, are the products most frequently detected in groundwater of urban areas and with the highest concentrations (4-7). Residue of atrazine are found in rivers, lakes, groundwaters, reservoirs and rainwater as a result of its extensive use in agriculture (8-11). Its persistence, mobility in certain soil types and not sufficient absorption of soil particles cause the contamination of surface and groundwater. The atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is a selective systemic herbicide from the triazine group (12), in use since 1952 (13). In the Republic of Serbia, it is applied to maize for weed control in the amount of 2-2.8kg ha^{-1} and as a total herbicide in the doses up to 20kg ha^{-1} (13). The intensive application of herbicides based on atrazine has brought about the accumulation of the residues of this herbicide and its degrading products, particularly deethylatrazine (DEA) (2-amino-4-chloro-6-isopropylamino-1,3,5-triazine) and deisopropylatrazine (DIA) (2-amino-4-chloro-6-ethylamino-1,3,5-triazine), in the environment in the past decades.

The European Union (COUNCIL DIRECTIVE 98/83/EC) specifies a limit of 0.1 μg L^{-1} for individual pesticides with a maximum pesticide total of 0.5 μg L^{-1} in water intended for human consumption (14).

The frequency with which it was detected at levels exceeding 0.1 μg L^{-1} in drinking water was one of the principal reasons for its ban in many EU countries (15). Consequently, the general population could be exposed to atrazine through ingestion of contaminated drinking water, as well as consumption of contaminated food or aerial drifts from spraying.

In the previous research in our country the pesticide residues were usually measured in surface water (16), while pesticide residues in groundwater were not systematically monitored up to the late '80s (17). Intensive study of this problem is being implemented since 2001 (18-20). After atrazine application has ended, the evolution of groundwater contamination must be monitored in order to characterize the response of natural systems, particularly the time it takes for concentrations to return to levels below the EU drinking-water threshold.

The aim of the article was monitoring the residues of atrazine and its metabolites, deethylatrazine (DEA) and deisopropylatrazine (DIA) in the groundwater of the Republic of Serbia in the areas under the intensive agricultural production, where the atrazine herbicides have been applied for many years.

Experimental

Study area and sampling
The monitoring programme was carried out on the whole teritory of the Republic of Serbia. The sampling was performed during spring 2008 in the localities where the herbicides based on atrazine were intensively applied for a number of years. In total there were 327 samples of groundwater (Fig. 1) – 249 samples from the localities under agricultural area and 78 from urban zone. Groundwater aquifer was collected from the initial welling up in the wells and pumps of the average depth of 12.95 m.

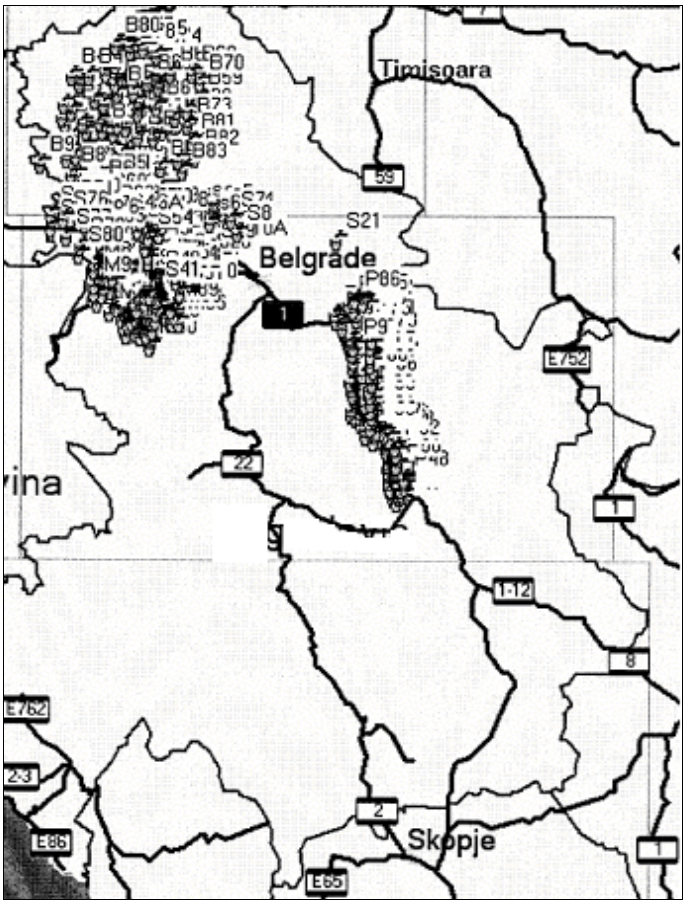

Figure 1. Geographical position of localities from which the water was sampled (MapSource)

Chemicals

In the analysis of the residues the analytical standards of atrazine (99.5 %), deethylatrazine (96.0 %) and deisopropylatrazine (99.0 %) produced by Dr.Ehrenstorfer GmbH (Augsburg, Germany) were used. The standard solution of atrazine, DEA and DIA (100 μg ml^{-1}) was prepared in the methanol (HPLC grade, JT Baker, Germany) whereas the working solutions (0.01 μg mL^{-1} – 1 μg mL^{-1}) were prepared by the appropriate dilution of the standard. All the solutions were protected from light and kept in a refrigerator until being used.

SP disc extraction

The extraction of atrazine and metabolites from water was carried out with ENVI-18 DSK (47mm) (Supelco No. 57171) (4,21). The disc was previously conditioned with methanol and deionized water (5 mL / 5 mL). Under vacuum (10 mL min^{-1}) 500 mL of the sampled water, to which methanol (2.5 mL) as polarity modificator was added, was filtered through the disc. After the disc was dried (30 min) the analytes were eluated with methanol in portions (2x3 mL) and evaporated to dryness. The extract was diluted in 1ml of methanol and analyzed on GC-NPD. Each sample was analyzed in three replications.
For the determination of the recovery deionized water with the addition of standard atrazine mixture, DEA and DIA in five concentrations (0.01 μg mL^{-1} – 1 μg mL^{-1}) was used. The analysis was done in three replications.

GC/NPD analysis

For the analysis of atrazine and its metabolite residues the gas chromatograph with the nitrogen-phosphorus detector (GC-NPD), (HP 5890, serie II with NP detector) were used. The separation was carried out on the capillary column HP Ultra 1 (Dimetil-polisiloksan 100 %), 30 m x 0.32 mm x 0.52 μm).

LOQ

Limit of quantification (LOQ is 10σ above the blank) were calculated using Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry (21).

Results and discussion

Residue levels of atrazine, DEA and DIA were analyzed by GC-NPD. Injected volume was 2 μL. Determination conditions presented in Table 1.

Table 1. Determination conditions of GC-NPD

Temperature programme	Temperature
Injector	250 °C
Detector	280 °C
Initial column temperature	150 °C u trajanju od 5 min
Heating rate of the column	30 °C min^{-1}
Final column temperature	250 °C u trajanju od 5 min

Average value of the recovery for atrazine was 91 %, DEA 87 % and DIA 73 %. Limit of quantification (LOQ) determined for this method was 0,01 μg L^{-1}. Typical chromatograms obtained for a mixed pesticide standard are shown in Fig. 2. The retention times obtained for the components of the mixture are listed in Table 2.

Table 2. Retention times of atrazine and its metabolites

Analyte	Retention times (min)
Atrazine	**20.700**
DEA	**19.142**
DIA	**18.974**

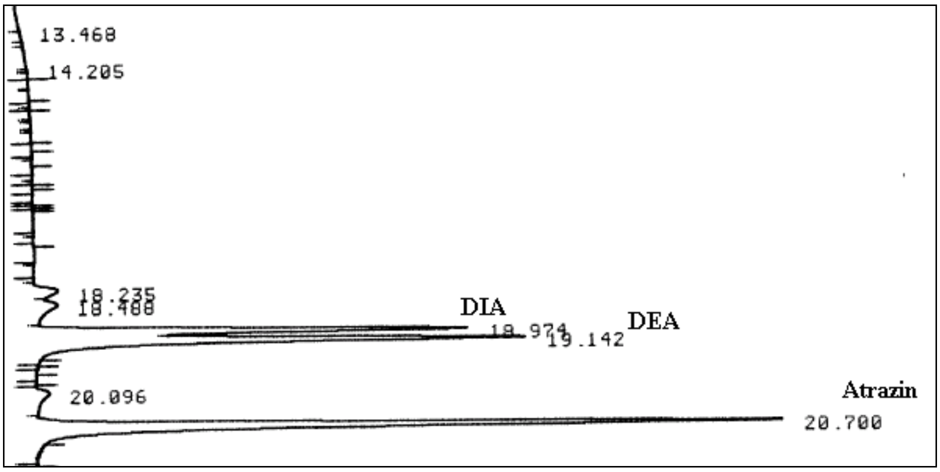

Figure 2. GC-NPD chromatogram of standard solution of atrazine, DEA and DIA

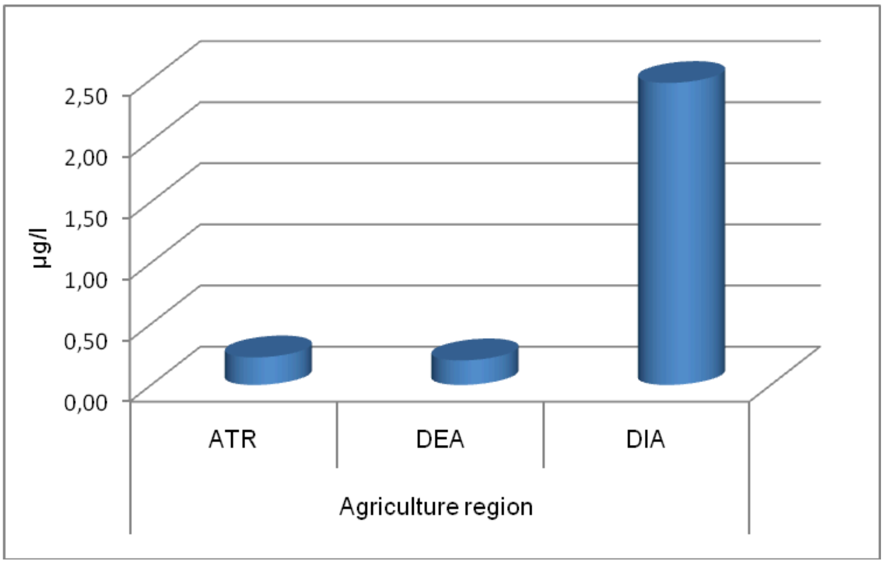

Figure 3. Average values of atrazine and its metabolites in agricultural areas of Serbia

Long-term and intensive use of atrazine-based herbicides in the Republic of Serbia has led to the accumulation of atrazine and its metabolites deetil and deizopropil-atrazine residues in groundwater. Given the importance of atrazine for weed control in raw crops, its occurrence in samples of groundwater from localities under agricultural production was expected. The analysis of atrazine, DEA and DIA from 249 samples of groundwater collected from agricultural regions showed that the average value of all tested analytes was above the EU MRL in water for human usage (0.1 µg L^{-1}) (14).

Average values of atrazine (0.23 µg L^{-1}) and DEA (0.20 µg L^{-1}) are a result of recent atrazine-based herbicides application. DIA was detected in the amount of 2.47 µg L^{-1} which indicates that atrazine was applied in large quantities in last few years. The application of the atrazine in the amounts of 4-6 kg ha^{-1} was common in weed control in orchards and vineyards. Having in mind that orchards and vineyards are mainly located on sandy soil, atrazine transport through deeper layers of soil to ground water is alleviated. As this soil type is characterized by low organic matter content, molecules of atrazine and its metabolites do not bind to humus intensively, thus reach the ground water with small losses. At this type of localities we took samples of groundwater with the highest content of atrazine (3.12 µg L^{-1}), DEA (1.09 µg L^{-1}) and DIA (13.29 µg L^{-1}). A high groundwater levels and precipitation shortly after the application create additional favorable conditions for atrazine and its metabolites occurrence in groundwater.

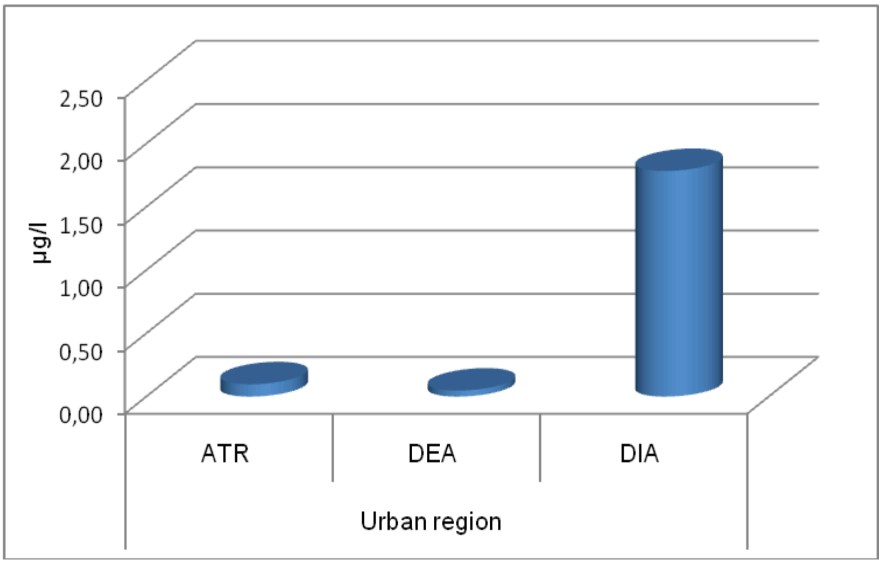

Figure 4. Average values of atrazine and its metabolites in urban areas of Serbia

Along with previous research, the presence of atrazine and its metabolites, DEA and DIA was assessed in groundwater from urban areas of Serbia. The groundwater aquifer was sampled from 78 sites in urban areas, distended from arable land.

The analysis determined that the average values of atrazine were 0.10 µg L^{-1}, DEA 0.05 µg L^{-1} and DIA 1.78 µg L^{-1}. The detected levels of atrazine and its metabolite DEA were equal or slightly lower than the limit (0.1 µg L^{-1}), while the level of DIA was significantly above the MRL.

The occurrence of herbicides in the environment of urban areas derives from their application during roads, railways and urban greenery maintenance. For this purpose, total herbicides are usually used and in large quantities. A high level of DIA found in groundwater samples is the result of intensive atrazine use in large amounts in previous years, while now its use in communal hygiene is reduced or completely suspended. As a total herbicide atrazine was applied in quantities up to 10 kg ha^{-1}. This has led to the accumulation of this compound and its metabolites in the environment, which particularly endangers groundwater.
Besides atrazine and its metabolites, some other pesticides, such as alachlor, metolachlor, and chlorpyrifos, which are used in crop protection from weeds and pests, were also detected in wastewater from urban areas, distended from arable land (22).
The fact that groundwater courses are connected can also explain the presence of herbicides used primarily in crop protection, in groundwater from urban areas.

Conclusion

The results indicate that both agricultural and urban areas are probable source of pesticides in groundwater. Presence of atrazine and its metabolites above 0.1 µg L^{-1}, in region under intensive agricultural productions and in city areas, is the consequence of intensive and long-term usage of atrazine based herbicides in the amounts 2-6 kg ha^{-1} and up to 10 kg ha^{-1}. Considering the fact that the atrazine based herbicides have been excluded from use in R. Serbia since 2008, we can expect a gradual reduction of its residues in this region.

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References

(1) B.W. Bruce and P.B. McMachon, Journ. Hidrol., 186, 129-151 (1996)

(2) T.D. Bucheli, S.R. Muller, A. Boegelin and R.P. Schwarzenbach, Environ. Sci. Technol., 22, 3465-3471 (1998)

(3) P.D. Capel, A.H. Spexet and S.J., Larson, Environ. Sci. Technol., 33, 5, (1999)

(4) G.M. Clark, D.A. Goolsby and W.A. Battaglin, Environmental Science and Technology, 33, 7, 981–986 (1999).

(5) J.E. Barbash, G.P. Thelin, D.W. Kolpin, R.J. Gilliom, Journal of Environmental Quality, 30, 831–845 (2001).

(6) W. Tappe, J. Groeneweg, B. Jantsch, Biodegradation, 13, 3–10 (2002).

(7) IFEN, 2004. Pesticides in Water. Sixth Annual Report, 2002 Data, Etudes et Travaux n°42.

(8) International Agency for Research on Cancer (IARC). Some chemicals that cause tumors of the kidney or urinary bladder in rodents and some other substances, IARC monographs on the evaluation of carcinogenic risks to humans. Lyon: IARC Scientific Publications, 73, (1999).

(9) D. Quaghebeur, B.D. Smet, E.D. Wulf, Journal of Environmental Monittoring, 6 (1) 82-90 (2004)

(10) Z. Kuang, L.L. Mcconnell, A. Torrents, Jounral of Environmental Quality, 32 (16) 11-22 (2003)

(11) T.R. Steinheimer, K.D. Scoggin, Journal of Environmental Monittoring, 3 (1) 26–32 (2001)

(12) C. Tomlin: The Pesticide Manual (14th ed). British Crop Protection Council, Farnham, 2006.

(13) V. JANJIĆ (Ed.): Triazinski herbicidi. Beograd, Srbija, 1996.

(14) THE COUNCIL OF THE EUROPEAN UNION, Council Directive (80/778/EEC) on the Quality of Water Intended for Human Consumption, of 15 July 1980.

(15) C.M. Villanueva, G. Durand, M-B. Coutte´, C. Chevrier, S. Cordier, Occup. Environ. Med., 62, 400–405 (2005)

(16) R. Šovljanski, S. Lazić, Contemporary Agriculture, 39, 5, 39-44 (1991)

(17) M. Mojašević, A. Bata, Pesticidi, 10, 197-212 (1995)

(18) M. Pucarevic, R. Sovljanski, S. Lazic, N. Marjanovic, Water Research, 36, 5120-5126 (2002)

(19) D. Šunjka, S. Lazić, M. Pucarević, V. Bursić, S. Vuković, The 16th International Symposium on analytical and environmental problems, Szeged, Hungary, September, 235-238 (2009)

(20) S. Lazić, D. Šunjka, M. Pucarević, V. Bursić, S. Vuković, VI Congress of Plant Protection with Symposium about biologicalcontrol of invasive species, Zlatibor, Serbia, November, 154-155 (2009)

(21) ACS Committee on Environmental Improvment and Subcommittee on Environmental Analytical Chemistry. Guidelines for data acquisition and data quality evaluation in environmental chemistry. Anal. Chem., 52, 2242– 2249 (1980)

(22) Wotzka, P., J. Lee, P. Capel and M. Lin. 1994. "Pesticide Concentrations and Fluxes in an Urban Watershed." *Proceedings AWRA National Symposium on Water Quality*. pp. 135-145