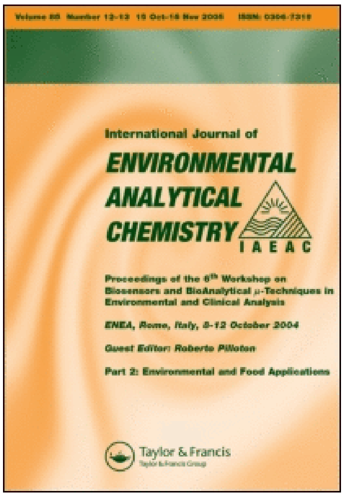

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Levels of atrazine and simazine in waters in the rural and urban areas of North-West Croatia

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To cite this Article Drevenkar, Vlasta , Fingler, Sanja , Mendaš, Gordana , Stipičević, Sanja and Vasilić, Zcaron elimira(2004) 'Levels of atrazine and simazine in waters in the rural and urban areas of North-West Croatia', International Journal of Environmental Analytical Chemistry, 84: 1, 207 — 216

To link to this Article: DOI: 10.1080/03067310310001149679

URL: http://dx.doi.org/10.1080/03067310310001149679

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 1–3, pp. 207–216, January–March 2004

LEVELS OF ATRAZINE AND SIMAZINE IN WATERS IN THE RURAL AND URBAN AREAS OF NORTH-WEST CROATIA

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(Received 29 September 2002; In final form 10 April 2003)

The triazine herbicides atrazine and simazine were measured in samples of surface, ground, drinking and rain/snow waters collected in the 1992–2001 period in rural areas north-west of Zagreb city and in the city area. Atrazine was detected in 367 and simazine in 40 out of the 477 water samples analysed. The highest atrazine concentrations (up to $8.28\,\mu g\,L^{-1}$) were measured in surface waters from the rural area in the 1992–1995 period. In the later sampling period (2001) a decreasing trend in atrazine concentrations was observed in surface and ground waters collected from privately owned wells. However, there were no great variations in levels of atrazine in drinking waters in either the rural or the urban area. The atrazine concentration exceeded $0.1\,\mu g\,L^{-1}$ in 29% of drinking water samples, reflecting the contamination of ground waters serving as drinking water supplies. The sorption intensity of atrazine and simazine was tested in soil and aquifer sediments collected close to the wells used for the public water supply systems. The values of Freundlich K_f sorption coefficients indicated more efficient retention of compounds in the surface soil and in the aquitard layer than within the three aquifer porous ground water layers of more or less balanced gravel, sand, and silt content and with 0.99–1.5% of organic matter. The incidence and concentrations (<0.01–$0.18\,\mu g\,L^{-1}$) in rain/snow samples collected in the Zagreb city and at a rural site about 20 km north-west of the city centre indicated that atmospheric transport was also involved in atrazine environmental distribution.

Keywords: Atrazine; Simazine; Surface, ground and drinking water; Rain/snow

INTRODUCTION

Because of their relatively high water solubility symmetric triazine herbicides are agrochemical agents with a potentially high risk of leaching into the surface and ground waters [1,2]. Widespread contamination of aquatic environment with atrazine, one of the most heavily used herbicides from this class, and its N-dealkylated and hydroxylated degradation products, has been established world-wide [3–15].

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000149679

To reduce the levels in different environmental compartments the use of atrazine was forbidden in several European countries over the last decade. In Croatia the use of atrazine for weed control along roads and railroads is not permitted but it is selectively used in croplands, especially in areas of intensive corn production. As a result, altrazine occurs not only in surface and ground waters but also in drinking water in both rural and urban areas [16,17].

In Croatia the monitoring of atrazine and other triazine pollutants in different waters has not been performed on a regular basis. Therefore knowledge of water contamination by these pollutants is limited. This article presents the results of atrazine and simazine determination in surface, ground and drinking waters collected in a rural and an urban (the city of Zagreb) area in north-west Croatia in the 1992–2001 period. The same compounds were analysed also in wet deposition samples (rain and snow) collected in Zagreb city and at a rural site lying about 20 km north-west of the Zagreb city centre. In addition the sorption intensity of atrazine and simazine was tested in soil and typical aquifer sediments collected close to the wells used for the public water supply systems.

EXPERIMENTAL

Chemicals

Atrazine (6-chloro-*N*-ethyl-*N*′-isopropyl-[1,3,5]triazine-2,4-diamine) 99.0%, and simazine (6-chloro-*N*,*N*′-diethyl-[1,3,5]triazine-2,4-diamine) 99.2%, were purchased as standards of Pestanal® quality from Riedel de Haën, Seelze, Germany.

n-Hexane for organic trace analysis, Suprasolv® was the product of E. Merck, Darmstadt, Germany. Sep-Pak C_{18} silica cartridges were purchased from Waters Associates, Milford, USA. Whatman GF/A glass microfibre filters were purchased from Whatman International, England. All other chemicals were products of p.a. purity obtained from Kemika, Zagreb, Croatia. Acetone was redistilled before use.

Chromatographic Equipment

Triazine compounds were analysed on a Varian 3400 Cx gas chromatograph (Varian, Walnut Creek, CA, USA) with a septum-equipped programmable injector (SPI) and a thermionic sensitive detection (TSD) system. The analytical fused-silica capillary columns (film thickness 0.25 μm) were a 30 m × 0.25 mm i.d. Supelcowax 10, a 30 m × 0.32 mm i.d. SPB-50, and a 60 m × 0.25 mm i.d. SPB-5 (Supelco, Bellefonte, PA, USA). The operating conditions of GC analyses were: Supelcowax 10 column temperature programmed from 70°C (with 1 min hold) up to 230°C at 50°C min^{-1} with a final hold of 30 min; SPB-50 column temperature programmed from 70°C (with 1 min hold) up to 200°C at 15°C min^{-1} with a final hold of 30 min; SPB-5 column temperature programmed from 60°C (with 1 min hold) up to 160°C at 40°C min^{-1} with a hold of 1 min, then from 160°C to 240°C at 2°C min^{-1}. SPI and TSD temperatures were 260 and 300°C, respectively. The carrier gas was hydrogen produced with an HG 200 hydrogen generator (Claind, Lenno, Italy). Column head pressure was 48 kPa for 30 m long columns and 165 kPa for 60 m long column. The injection volume was 2 μL.

The confirmation of compound identities was accomplished by gas chromatographic-mass spectrometric analysis using the 30 m × 0.25 mm i.d. SPB-5 column coupled to the ion trap detector in a Varian Saturn II GC/MS system. The SPI temperature was programmed from 50°C (with 0.1 min hold) to 300°C at 200°C min^{-1} with a final hold of 3 min. The carrier gas was helium and the column head pressure 103 kPa. The injected sample volume was 1 μL. The GC/MS transfer line and manifold temperatures were 260 and 170°C, respectively. The instrument was operating in the electron impact ionisation mode at an electron energy of 70 eV. Spectra of triazines were recorded in the full scan acquisition mode with mass range scanned from 45 to 500 m/z and a scan rate of 1 scan s^{-1}.

Water Sampling

Samples of surface, ground and drinking water were collected from June 1992 to October 1995 and from April to December 2001 in the Zagreb city area and in the rural area located north-west of Zagreb city between the Sava river and its tributaries the Sutla and Krapina rivers. Drinking water in the area of Zagreb was also sampled in June 1998. The water sampling locations were the same in all sampling periods.

The Sava river rises in Slovenia and before entering the Zagreb area it flows through rural and urban regions for a distance of about 200 km. The Sutla (total length 92.4 km, in Croatia 89 km) and Krapina (length 75 km) rivers flow into the Sava river 14 and 25 km, respectively, upstream of the Zagreb city central area. The Sutla and Krapina river water samples were collected at three locations along each river. The Sava river water was collected at two locations about 15 and 20 km upstream of Zagreb city. During the sampling periods one to four samples were taken every year at each river water sampling location.

Ground waters in the Zagreb city area are partly recharged through Sava river water. The ground water samples were collected at both rural and urban sites from approximately 10 m deep privately owned wells, and drinking water samples were tap water from the municipal water supplies.

All samples of surface, ground and drinking waters were collected in one-litre dark glass bottles and stored at 4°C before analysis.

Rain/snow waters were sampled from April to November 1996 at two locations: at an urban site in the northern part of Zagreb city and a rural site lying about 20 km north-west of Zagreb city centre. Rain water was collected on single occasions and during longer periods by using precleaned 2.5-L amber-coloured glass bottles and 0.29- and 0.18-m^2 stainless-steel funnels. The collectors were only open during the rainfall. Surface snow samples were collected from a known area with a glass plate and were melted in a glass beaker at room temperature. The samples were stored at 4°C before analysis.

Soil/Sediment Sampling

To test the sorption intensity of atrazine and simazine in soil and typical aquifer sediments in the investigated area, one surface soil at a depth of 0.05–0.20 m (A1) and four sediment samples at depths of 3.9–11.9 m (A2–A4 and B) were collected at two locations (A and B) close to the wells used for the public water supply systems. Three sediment samples were collected within the porous ground water layer (A2, A3

TABLE I Characteristics of the soil and sediment samples collected at locations A and B close to the wells used for public water supply systems near the Zagreb city area

Characteristic	*Soil A1*	*Sediment A2*	*Sediment A3*	*Sediment A4*	*Sediment B*
Depth (m)	0.05–0.20	3.9–4.2	10.2–10.4	11.7–11.9	6.8–7.0
SOM[a] (%)	7.71	1.50	0.99	5.75	1.02
SSA[b] ($m^2 g^{-1}$)	2.63	1.88	2.22	23.50	2.85
pH (in water)	7.7	8.2	8.3	8.0	7.9
Mean particle size[c] (μm)	493	31	96	3	297
Clay (%)	8	39	25	67	6
Silt (%)	19	22	19	31	24
Sand, (%)	29	20	31	2	36
Gravel (%)	44	19	25	1	35
Soil/sediment type	Sandy gravel	Gravelly sandy silty clay	Gravelly sandy silty clay	Silty clay	Sand–silt–gravel
Mineral composition[d]	Q, D, C, F, Ch	C, Q, D, F	C, D, Q, Mi, F	Q, D, Mi, Ch	C, D, Q, F

[a]Sorbent organic matter content; [b]Specific surface area; [c]Before grinding of original samples; [d]Dominant mineral species presented in decreasing order: Q, quartz; C, calcite; D, dolomite, F, feldspars; Ch, chlorite; Mi, micas.

and B) and one from the aquitard beneath the aquifer (A4). Characteristics of the soil and sediment samples are shown in Table I.

Accumulation of Triazines from Water

Surface and ground water samples were filtered through a sintered-glass filter of porosity 4 and rain/snow water samples through a Whatman GF/A glass microfibre filter. Triazine herbicides were accumulated from 500-mL water samples by C_{18} solid-phase extraction on a Sep-Pak C_{18} cartridge. The sample was forced through the cartridge using a positive air pressure and the retained compounds were eluted in the opposite direction with 2 mL of acetone. The eluate was evaporated under a stream of nitrogen and the residual water (0.2–0.3 L) was extracted with 2 mL of *n*-hexane by vortexing the sample for 1 min. For gas chromatographic analysis the extract was evaporated under a stream of nitrogen to 1.0 mL.

The C_{18} solid-phase extraction procedure enabled almost quantitative recoveries of atrazine and simazine from water. At concentrations ranging from 0.2 to 2.0 $\mu g\,L^{-1}$ the recoveries were (% ± *S.D.*) 83 ± 15 for atrazine and 83 ± 13 for simazine. Detection limit was 5–10 $ng\,L^{-1}$ for both herbicides depending on the gas chromatographic column used. Analytical quality control was performed by participation in a national interlaboratory comparison as well as in the proficiency testing exercises organised by the Institute for Agrobiotechnology, Tulln, Austria.

Accumulation of Triazines from Particles Isolated from Rain/Snow

Whole volumes of rain (0.5–5.56 L) and snow (1.0 L) waters were filtered through a weighed Whatman GF/A glass microfibre filter which collected particles with a diameter larger than 1.6 μm. After filtration, the filter was dried in air and weighed again to determine the mass of retained particles. To extract triazine herbicides from the retained particulate matter the glass fibre paper was extracted with two portions (20 and 10 mL) of acetone : *n*-hexane 2 : 1 mixture in an ultrasonic bath for 5 min.

The extracts were combined, centrifuged and the separated supernatant was evaporated under a stream of nitrogen to 1.0 mL for gas chromatographic analysis.

Sorption Experiments

The sorption intensities of atrazine and simazine in soil and sediment samples were determined as described elsewhere [18]. Briefly, sorption experiments were carried out by overnight equilibration of compounds in suspension of soil/sediment and 0.01 mol L^{-1} $CaCl_2$ (solid to liquid ratio 1:20). Initial concentrations of sorbates in the aqueous phase ranged from 0.17 to 3.98 nmol mL^{-1}. The equilibrium concentrations of triazines in the aqueous phase were determined by C_{18} solid-phase extraction and GC analysis. The sorption results were evaluated in terms of the Freundlich isotherm,

$$x/m = K_f C_e^{1/n}, \tag{1}$$

where x/m is the mass of compound sorbed per unit of sorbent, C_e is the equilibrium concentration in water, K_f is the sorption coefficient and $1/n$ is constant for a given compound and sorbent.

RESULTS AND DISCUSSION

Out of the total 107 surface, 111 ground and 212 drinking water samples collected in rural and urban areas in the 1992–2001 period, 103, 82 and 164, respectively, contained traces of atrazine (Tables II and III). In surface waters the maximum atrazine concentrations and the highest median values, exceeding 0.1 μg L^{-1}, were measured in river and stream waters collected in the rural area in the 1992–1995 period (Table II). Maximum atrazine concentrations, ranging from 3.02 to 8.28 μg L^{-1}, were comparable to those reported for surface waters in other European countries, e.g. in Belgium, France, Italy, The Netherlands and the United Kingdom in the 1989–1991 period [10]. The results obtained in 2001 indicated a decreasing trend in atrazine concentrations not only in river water but also in ground waters collected from private wells in the area between the Sutla and Krapina rivers (Table II). The same applies for the ground waters collected in the Zagreb city area in 1994 and 2001 (Table III). However, no great variations between samples were observed in atrazine levels in drinking waters in either the rural or the urban area. In the 1992–1995 period, atrazine was detected in 66% and in 2001 in 53% of drinking water samples collected in villages between the Krapina and Sutla rivers (Table II). The atrazine median concentration exceeded 0.1 μg L^{-1} in both sampling periods. Moreover, in 78% of positive samples atrazine concentrations were above this level. No seasonal variations were observed. The levels found were comparable with atrazine concentrations determined in drinking water collected in 1993 in a pig-breeding farm located in the same area [17]. In the Zagreb city area atrazine was identified in 86–100% of drinking water samples collected in 1995, 1998 and in spring 2001 (Table III). A lower incidence of atrazine (53%) was noticed only in drinking water samples collected in winter 2001 (Table III). The atrazine

TABLE II Atrazine mass concentrations in waters collected in the agricultural area between the Sutla and Krapina rivers north-west of Zagreb city

	N	*n*	*Mass concentration* (μg L^{-1})	
			Range[a]	*Median*
Surface water				
June 1992–October 1995				
Krapina river	28	28	0.02–4.35	0.10
Sutla river	30	28	0.04–3.02	0.23
Streams between the Sutla and Krapina rivers	16	16	0.05–8.28	0.25
April–October 2001				
Sutla and Krapina rivers	13	13	0.02–0.11	0.06
Ground water (private wells)				
June 1992–October 1995	37	23	0.01–0.37	0.02
May–October 2001	17	8	0.02–0.09	< 0.01
Drinking water				
June 1993–October 1995	50	33	0.01–0.34	0.11
April–October 2001	15	8	0.12–0.31	0.12
Rain/Snow water				
April–July 1996	10	8	0.03–0.18	0.05
August–November 1996	10	1	0.01	< 0.01

N = number of samples; *n* = number of positive samples; [a]Ranges apply to positive samples.

TABLE III Atrazine mass concentrations in waters collected in or near the Zagreb city area

	N	*n*	*Mass concentration* (μg L^{-1})	
			Range[a]	*Median*
Sava river up to 20 km upstream of Zagreb city				
March 1993–October 1995	17	16	0.02–0.73	0.04
April–October 2001	3	2	0.04–0.06	0.04
Ground water (private wells)				
June 1994	40	37	0.03–0.69	0.11
May–November 2001	17	14	0.01–0.61	0.06
Drinking water				
February–May 1995	46	46	0.01–0.18	0.09
June 1998	28	24	0.03–0.16	0.07
May 2001	37	34	0.01–0.14	0.06
November–December 2001	36	19	0.01–0.22	0.05
Rain/snow water				
April–July 1996	18	7	0.03–0.11	< 0.01
August-November 1996	9	2	0.01	< 0.01

N = number of samples; *n* = number of positive samples; [a]Ranges apply to positive samples.

concentration ranges determined in four sampling periods were comparable but the median concentrations, which were always below 0.1 μg L^{-1}, were slightly decreasing.

Compared to atrazine the incidence of less intensively used simazine was significantly lower in all investigated surface, ground and drinking waters. In the 1992–1995 period simazine was detected occasionally only in samples collected in the rural area including

TABLE IV Simazine mass concentration ranges in waters collected n the 1992–1995 period

	N	*n*	*Mass concentration*[a] ($\mu g\,L^{-1}$)
Surface water			
Krapina river	28	8	0.06–0.83
Sutla river	30	4	0.08–0.58
Streams between the Sutla and Krapina rivers	16	2	0.10–0.28
Sava river up to 20 km upstream of Zagreb	17	4	0.05–0.65
Ground water			
Private wells in the rural Area	37	11	0.05–0.68
Drinking water			
Municipal water supplies in the rural area	50	5	0.10–0.78

N = number of samples; n = number of positive samples; [a]Ranges apply to positive samples.

TABLE V Sorption of atrazine and simazine in soil A1 and sediments A2–A4 and B: Freundlich isotherm coefficients and log K_{om}

Soil/Sediment	*Atrazine*			*Simazine*		
	K_f	$1/n$	log K_{om}[a]	K_f	$1/n$	log K_{om}[a]
A 1	9.08	1.06	2.07	7.32	0.56	1.97
A 2	5.49	0.96	2.56	6.00	0.82	2.60
A 3	1.51	1.24	2.18	2.47	0.69	2.39
A 4	12.50	0.91	2.33	7.77	0.23	2.13
B	1.90	0.56	2.27	2.48	0.51	2.38

[a]Organic matter sorption coefficient calculated by normalization of K_f values for the sorbent organic matter content.

the samples of Sava river water upstream of Zagreb city (Table IV). In 2001 simazine was not detected in any water sample.

The appearance of atrazine in drinking water reflects the contamination of ground waters serving in the rural and urban areas as drinking water supplies. The levels of atrazine in ground waters collected from the private wells were in the range of those reported from other European countries and the United States [6]. The purity of ground waters in or near Zagreb city is likely to be affected by agricultural activities in surrounding areas and by infiltration of Sava river water, in which atrazine was regularly detected (Table III). To evaluate the potential of atrazine and simazine to leach through the soil and aquifer sediment layers and to contaminate the ground waters in the semi-rural area north-west of Zagreb city, the intensity of their sorption was tested in surface soil and sediment samples collected close to the wells used for public water supply systems (Table I). The results of sorption experiments are summarized in Table V. Atrazine and simazine sorption intensities varied at different horizons, according to considerable variations in sorbent properties. As was expected, the values of Freundlich K_f sorption coefficients indicated more efficient retention of compounds in surface soil A1 and aquitard layer A4 than within the three aquifer porous ground water layers of more or less balanced gravel, sand and silt content and with 0.99–1.50% of organic matter. The surface soil sorbent contained the highest (7.71%) and the aquitard sorbent the second highest (5.75%) amount of organic matter. The aquitard sorbent was characterized also by the highest specific surface area (23.50 $m^2 g^{-1}$) and the highest clay content of all sorbents, two properties which could also favour sorption intensity. The transport of pesticides, including triazine herbicides, in coarse-grained aquifers characterised by low organic carbon content was shown to be mainly influenced by convection and dispersion whereas pesticide adsorption and degradation were low [19]. Significantly higher persistence of atrazine and simazine in aquifer environments, compared to their behaviour in soils [20], could also contribute to the contamination of ground water.

Triazine herbicides enter the atmosphere by direct volatilization during and after their application or via wind erosion of soil particles with adsorbed herbicide from treated areas. Their removal from the atmosphere through wet deposition is also a possible source of pollution of terrestrial and aquatic ecosystem even in areas which are at considerable distances from the pollution sources [7–10]. We therefore compared the occurrence of triazine herbicides in rain/snow water samples collected at a rural site 20 km north-west of Zagreb city centre (Table II) and at an urban site in the northern residential part of Zagreb city (Table III). In total, 47 snow/rain water samples were analysed; 18 samples contained measurable concentrations of atrazine and 6 of simazine. Atrazine concentrations indicated a clear seasonal trend at both locations (Fig. 1(a) and (b)) showing that atmospheric transport was involved in its

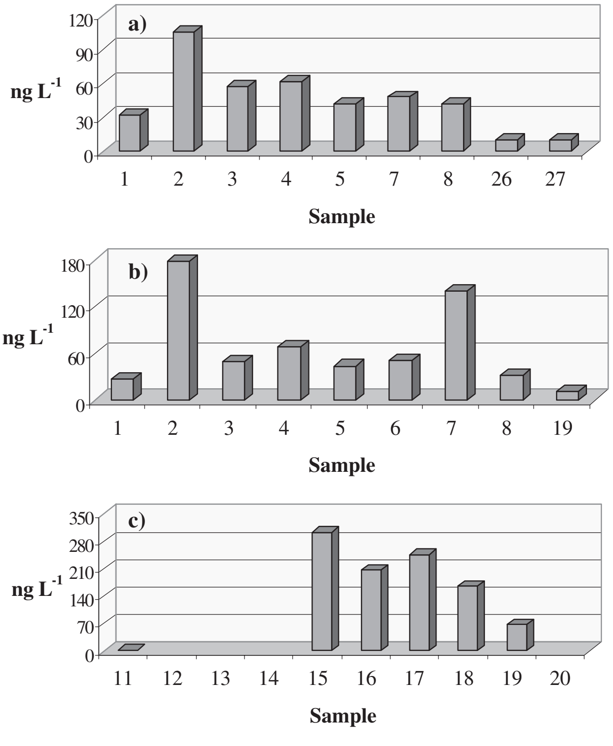

FIGURE 1 Concentration of atrazine and simazine in rain/snow water samples collected in 1996: (a) atrazine in rain/snow water samples collected at the urban location; (b) atrazine in rain/snow water samples collected at the rural location; (c) simazine in rain water samples collected at the rural location. Sampling dates: (a) **1**, 3 Apr; **2**, 20–30 Apr; **3**, 30 Apr–3 May; **4**, 3–13 May; **5**, 13–14 May; **7**, 22–29 May; **8**, 13 Jun; **26**, 14 Oct–11 Nov; **27**, 11–20 Nov. (b) **1**, 3 Apr; **2**, 30 Apr–6 May; **3**, 9 May; **4**, 10–14 May; **5**, 14–21 May; **6**, 22–29 May; **7**, 13 Jun; **8**, 14 Jun–10 Jul; **19**, 25 Oct–11 Nov; (c) **11**, 1–10 Aug; **12**, 12–16 Aug; **13**, 16 Aug–2 Sep; **14**, 2–15 Sep; **15**, 15–23 Sep; **16**, 24–29 Sep; **17**, 1–14 Oct; **18**, 14–25 Oct; **19**, 25 Oct–11 Nov; **20**, 11–20 Nov.

environmental distribution. All but three positive samples, including the snow samples at both locations, were collected in the April–June period. Concentrations higher than $0.1\,\mu g\,L^{-1}$ were determined in two samples collected in April and June at the rural location (Table II) and in one sample collected in April at the urban location (Table III). The analysis of rain samples in July, August and September failed to show detectable atrazine quantities. However, one sample from the rural location (Table II) and two from the urban location (Table III) collected in October and November still contained atrazine traces. The amounts of atrazine washed out from the atmosphere to the earth's surface by rain were $95–518\,ng\,m^{-2}$ at the Zagreb city location and $187–1221\,ng\,m^{-2}$ at the rural location.

Simazine occurred in only six rain samples collected at the rural location from August to November 1996 as the consequence of a local application (Fig. 1(c)). Its concentrations ranged from 0.02 to $0.30\,\mu g\,L^{-1}$ with a median value of $0.03\,\mu g\,L^{-1}$. The highest simazine concentration was measured in a rain sample collected in mid-September. Later in September and during October and November the simazine concentration in rain gradually decreased. Simazine amounts deposited on the earth's surface by rain at that location ranged from 62 to $4695\,ng\,m^{-2}$.

Out of the 47 particle samples isolated from snow and rain water only the sample with the extremely high mass of particles ($37.9\,mg\,L^{-1}$) isolated from the rain water, contained atrazine ($1.21\,ng\,mg^{-1}$). This sample was collected in June at the rural location during a short rain event after a two-week dry period, and atrazine was applied on a field near the sampling site immediately before sampling. The mass of atrazine (46 ng) on particles isolated from 1 L of rain water was one order of magnitude lower than that measured in the same volume of aqueous phase (140 ng). The absence of triazine herbicides on particulate matter in wet deposition samples suggested direct volatilisation from treated areas as the dominant source of atrazine and simazine in snow/rain samples.

CONCLUSIONS

Atrazine and simazine were analysed in a total of 477 water samples of different types collected in north-west Croatia in the 1992–2001 period. As a consequence of agricultural input, atrazine was detected in 349 (81%) and simazine in 34 (8%) of the 430 surface, ground and drinking water samples. In 29% of drinking water samples atrazine concentration exceeded $0.1\,\mu g\,L^{-1}$, the maximum allowable concentration for a single pesticide in drinking water in Croatia. Aquifer sediments in the investigated area are typically gravelly sandy silty clay and sand–silt–gravel in texture, and contain up to 1.5% organic matter providing moderate binding capacity for triazine herbicides. Wells used for the public water supply systems have a high potential for contamination through subsurface movement of these compounds. The use of herbicides on intensively cultivated agricultural land in this area should be rationalised in order to protect surface and ground waters supplying the public water distribution systems.

Direct volatilisation from treated areas seemed to be the dominant source of atrazine and simazine in snow/rain samples. Atrazine levels in samples collected at urban site, confirmed the atmospheric input as an important contamination source of the area with no direct atrazine application.

Acknowledgements

This work was supported by the Ministry of Science and Technology of the Republic of Croatia through the Project 00220203 and by the United States Department of Agriculture through funds made available to the U.S.-Croatian Joint Board on Scientific and Technological Co-operation (Grant no. JF 113). We thank Dr. Mladen Juračić from the Department of Geology, Faculty of Science, University of Zagreb, for providing the data on soil/sediments characteristics.

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