

Seasonal exposures to triazine and other pesticides in surface waters in the western Highveld corn-production region in South Africa

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Concentrations of atrazine in an agricultural region vary greatly and are influenced by rainfall amounts.

Abstract

The objective of this study was to characterize concentrations of atrazine, terbuthylazine, and other pesticides in amphibian habitats in surface waters of a corn-production area of the western Highveld region (North-West Province) of South Africa. The study was conducted from November 2001 to June 2002, coinciding with the corn-production season. Pesticide residues were measured at regular intervals in surface water from eight ponds, three in a non-corn-growing area (NCGA) and five within the corn-growing area (CGA). Measured atrazine concentrations differed significantly among sites and between samples. In the five CGA sites, the maximum atrazine concentrations measured during the study ranged from 1.2 to 9.3 µg/L. Although no atrazine was recorded as being applied in the catchment of the three NCGA sites, maximum concentrations from 0.39 to 0.84 µg/L were measured during the study, possibly as a result of atmospheric transport. Maximum measured concentrations of terbuthylazine ranged from 1.22 to 2.1 µg/L in the NCGA sites and from 1.04 to 4.1 µg/L in the CGA sites. The source of terbuthylazine in the NCGA sites may have been in use other than in corn. The triazine degradation products, deisopropylatrazine (DIA) and deethylatrazine (DEA) and diaminochlorotriazine (DACT) were also found in water from both the CGA and NCGA sites. Concentrations of DIA were ≥ 1 µg/L throughout the season, while DEA concentrations were mostly < 0.5 µg/L before planting but increased after planting and application of herbicides to concentrations > 2 µg/L in some locations. Concentrations of DACT were highly variable (LOD to 8 µg/L) both before and after planting and application, suggesting that they resulted from historical use of triazines in the area. Other herbicides such as simazine and acetochlor were only detected infrequently and pesticides such as S-metolachlor, cypermethrin, monocrotophos, and terbuphos, known to be used in the CGA, were not detected in any of the samples. Because of dilution by higher than normal rainfall in the study period, these concentrations may not be predictive of those in years of normal rainfall.

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1. Introduction

Atrazine (Fig. 1) is used for the control of broadleaf and grass weeds in corn and other crops and is used as a pre- and/or post-emergence herbicide. Herbicidal S-triazazines such as atrazine have been on the market for more than 47 years; simazine (Fig. 1) was introduced in 1956 and atrazine in 1957 (Kneusli, 1970). Since that time, they have become widely used in agriculture and forestry (Graymore et al., 2001). In 1995, $149\text{--}160 \times 10^6$ kg of atrazine was applied worldwide (Short and Colborn, 1999). Atrazine is sold as the active ingredient in a number of wettable, flowable powder, and water-dispersible granular formulations under a variety of trade names as a broadleaf herbicide (Meister, 1994). Today, the most cost-effective and preferred herbicides used for corn production in South Africa are atrazine and herbicide formulations containing atrazine as an active ingredient (Hassett et al., 1987). In South Africa, atrazine is used in combination with various other herbicides including terbuthylazine, S-metolachlor, and simazine (Fig. 1).

The study area is located in the western Highveld which covers large parts of the Free State and North-West Provinces and is recognized as one of two major corn-production areas in South Africa. Agricultural activities dominate land-use in this area, and specifically the production of corn (maize), the predominant crop. However, in the study area, atrazine was the predominant active ingredient because of its effectiveness in the practice of mulch tillage (no-till). In addition to

atrazine and terbuthylazine, a number of insecticides and herbicides are used in the study area. The study area receives summer rainfall and corn is usually planted in late October–early November and triazine herbicides are applied during planting and again shortly thereafter. Corn is usually treated with atrazine and terbuthylazine in a 1:1 mixture with a total application equal to 1–1.5 times the recommended rate (Table 1).

Atrazine can reach surface water systems through various pathways such as surface run-off, seepage flow, artificial drain-flow, aerial drift during application, and re-deposition in waters upon volatilization and precipitation (Chung and Gu, 2003). Herbicides such as atrazine have been reported to be relative persistent in freshwater (Detenbeck et al., 1996; Solomon et al., 1996). Consequently, atrazine has been detected in surface water, ground water, and even rainfall, since its first use in 1959 (Richards et al., 1987; Hatfield et al., 1996). Due to the extensive use, persistence, water solubility and relatively weak adsorption to soil, atrazine is present in the aquatic environment via agricultural run-off, leaching and atmospheric input and is therefore regularly and most frequently detected in surface water (Gfrerer et al., 2002). The objective with this study was to determine concentrations of atrazine, terbuthylazine, their breakdown products, and other pesticides in surface waters in amphibian habitats in the study areas during the 2001–2002 field use season.

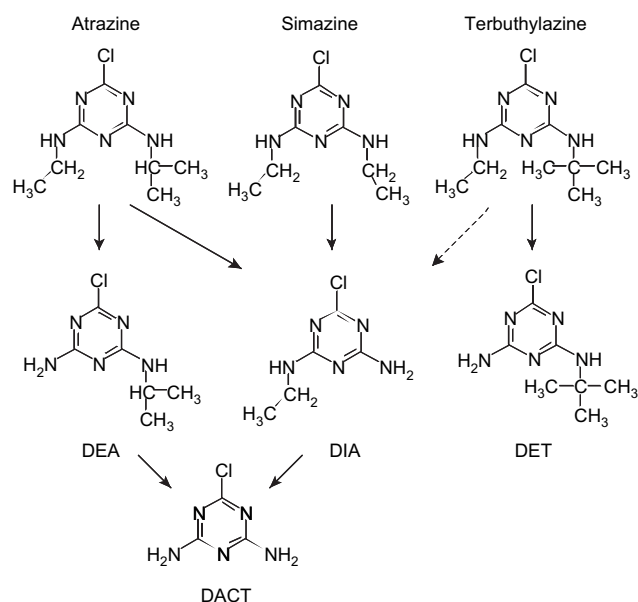


Fig. 1. Structure of atrazine, terbuthylazine, simazine, deisopropylatrazine (DIA), deethylatrazine (DEA), diaminochlorotriazine (DACT), and deethylterbuthylazine (DET) showing the pathways of formation of the degradation products.

Table 1
Herbicides used on corn in the study area (2001–2002)

Registered trade name	Active ingredient	Application rate
With planting		
Dual Gold	916 g/L S-metolachlor	0.25–0.45 L/ha at 33% of surface
Gardomil Gold	103 g/L S-metolachlor	2.2 L/ha at 33% of surface
Bullet	249 g/L Atrazine	2.75 L at 33% of surface
	249 g/L Terbuthylazine	
Guardian	250 g/L Acetochlor	0.75 L at 33% of surface
	125 g/L Atrazine	
	125 g/L Terbuthylazine	
3–6 weeks after planting		
Gardomil Gold	103 g/L S-metolachlor	2.2 L/ha
	249 g/L Atrazine	
	249 g/L Terbuthylazine	
Metagan Gold	916 g/L S-metolachlor	0.6 L/ha
A-mazing	250 g/L Acetochlor	3.0 L/ha
	125 g/L Atrazine	
	125 g/L Terbuthylazine	
Ipondess	900 g/L Acetochlor	0.6 L/ha
Gesaprim super	300 g/L Atrazine	2.0 L/ha
	300 g/L Terbuthylazine	
Atrazine	500 g/L Atrazine	2.5 L/ha

Study sites in the corn-growing area (CGA sites) are situated in the Viljoenskroon area while reference sites are located in a non-corn-growing area (NCGA sites), located 50 km to the North, in the Potchefstroom area. The surface area and watershed areas for sites are given in Table 2. Of the three NCGA ponds, R1 and R3 received water from intermittent springs whereas the only source of water for R6 was rainfall and surface runoff. Ponds R1 and R6 are large, earth-walled dams with muddy water. Vegetation in ponds R1 and R6 was limited to the periphery. Pond R3 was shallow and had dense stands of vegetation throughout the pond. Ponds R1 and R6 are semi-permanent ponds, while R3 dries up every two to three years. The surrounding vegetation for all three NCGA sites consisted of wooded, natural vegetation, with no field crops in the catchment. Both R1 and R3 were situated on cattle farms whereas R6 was located in a security buffer zone outside a munitions factory. Ponds in the CGA varied from small (sites E4 and E8), to medium (site E1), to large (sites E3 and E6). All sites were heavily vegetated around the periphery. All sites had clear water with light penetrating to the bottom in sites E1, E3, E4 and E8. The surrounding vegetation for all five CGA sites consisted of natural grassland for the first 10–100 m surrounding the ponds, but the remainder of the catchment area was dominated by cornfields (Fig. 2).

2. Materials and methods

2.1. Sampling and sample storage

At each site, four 1-L sub-samples of water, one from each quadrant of the water body, were collected. These were combined in a 5-L glass jar and, from this, two 1-L sub-samples were collected in labeled 1-L solvent-rinsed (acetone and hexane) glass bottles, pre-rinsed with surface water from the sampling site. Water samples were transported in cool-boxes and stored at 4 °C until analyzed. Water samples for pesticide analysis were taken every week from November 05, 2001 until February 18, 2002 and from then at approximately

2-week intervals until June 10, 2002. Sediment samples were also taken each month at each site and analyzed for pesticides. In addition, water and sediment samples were taken and analyzed for a number of elements and several major ions every month from November 2001 to March 2002, the major portion of the growing season. In May, water was only analyzed for nitrate and nitrite and in June for nitrate only.

During sampling of the water, the air temperature was measured in the shade at a height of 1 m using a digital thermometer. Water temperature (°C), conductivity (µS/cm), dissolved oxygen (mg/L) and pH-readings were recorded at a reference point using a YSI multi-parameter logger. Data were later uploaded to a personal computer for processing. All readings were also recorded on site on data sheets for quality control and assurance. The monitoring program described the seasonal variation in parameters from November 2001 to the middle of June 2002 including the ranges of concentrations of atrazine and other herbicides observed. This period of study included both the period prior to application of herbicides through the period of application and maximum rainfall into the dry season when rainfall had ceased and the corn was being harvested. Thus, the differences in concentrations of atrazine as well as changes in the seasonal and physico-chemical properties of the sites were investigated.

2.2. Analytical methods

Measurements of concentrations of the pesticides, their degradation products, elements, and major ions were conducted on water as well as sediment samples. Atrazine concentrations were measured by use of two types of extractions, a standardized C-18 SPE procedure as described by Eisenreich et al. (1994) and a liquid–liquid extraction (Yokley and Cheung, 2000). The values reported here for atrazine were determined by calculating the mean value for the two sets of data. All standards were of analytical grade and prepared by weighing 10.0 mg of analytical grade standard (corrected for percent purity) and dissolving in 100 mL of methanol. A 5.0 µg/mL mixed standard was prepared and serially diluted in acetone to produce calibration standards of 0.05, 0.10, 0.20, 0.50, 1.00, and 2.00 µg/mL. Injections of 1.00 µL of each standard produced a calibration range of 0.05–2.00 ng. All analyses were performed using an Agilent model 6890 series II-Plus gas chromatograph interfaced to a 5973 mass selective detector (GC/MSD operated in the selected ion monitoring (SIM) mode). The MSD transfer line was maintained at 280 °C and tuning was performed on a daily basis with PFTBA to ensure accurate mass calibration. The GC was

Table 2
Surface and watershed area of NCGA and CGA sites

Site	Surface area of pond (ha)	Watershed area (ha)
R1	2.05	244
R3	0.20	170
R6	1.49	480
E1	0.74	1990
E3	4.61	1046
E4	0.22	448
E6	6.87	515
E8	0.24	1100

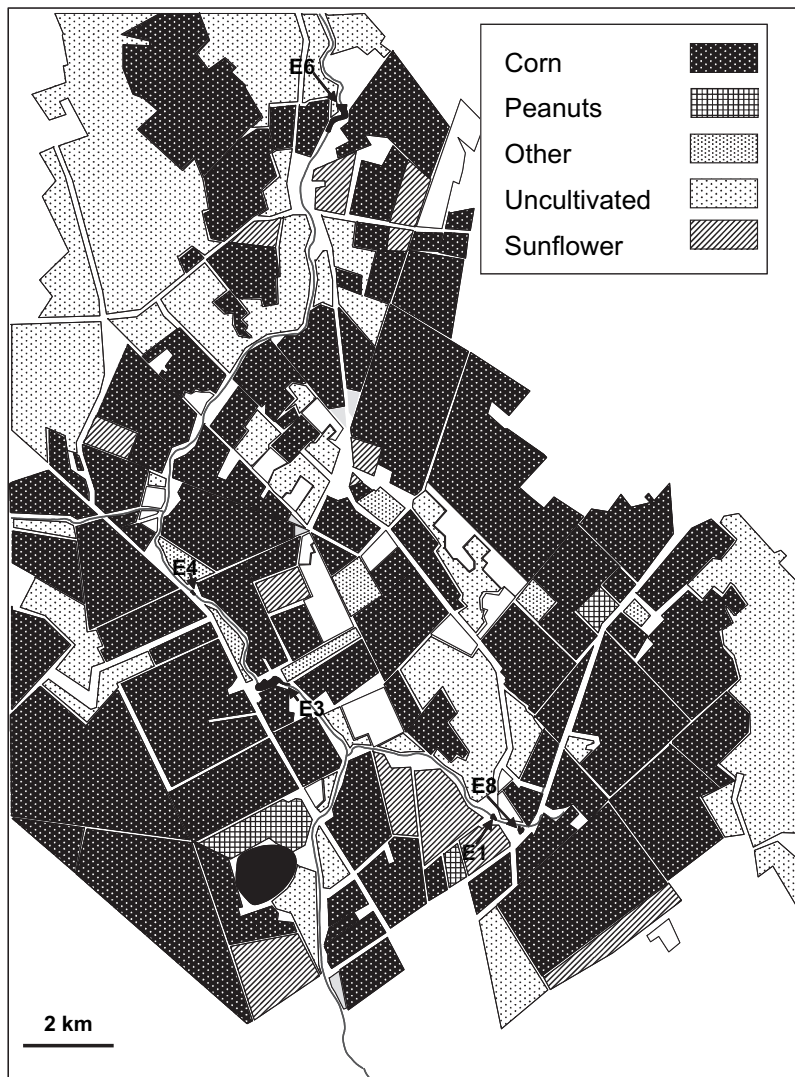


Fig. 2. Map of the CGA study area showing crops planted in the catchment area.

equipped for splitless injection and an Agilent HP-5 (0.25 mm i.d., 30 m, 0.25- μ m film thickness) was used for the separation. Electronic pressure programming was utilized in conjunction with a temperature program. The level of detection (LOD) for atrazine and terbuthylazine was 0.1 μ g/L. The LOD for the triazine degradation products (Fig. 1) deisopropylatrazine (DIA) and deethylatrazine (DEA) and diaminochlorotriazine (DACT) was 0.1 μ g/L. Standards were not available for deethylterbuthylazine (DET) and it could not be analyzed for, although it has been reported to be formed in soils (Navarro et al., 2003).

Analysis of elements in both water and sediment samples were conducted at SGS Laboratories (Midrand, South Africa). Other pesticides were analyzed for at the Council for Scientific and Industrial Research Laboratory (CSIR, Pretoria, South Africa). Both analytical laboratories are GLP accredited by the South African National Accreditation System (SANAS). The LODs

for simazine, acetochlor, S-metolachlor, cypermethrin, monocrotophos, and terbuphos were 0.5 μ g/L.

As is normal for field sampling, a proxy value of half the LOD was assigned to concentrations < LOD when plotting the data or calculating mean or time-weighted means.

2.3. Climatological data

Rainfall data were obtained from individual farmers in the study area. Additional data for rainfall, minimum and maximum temperatures, average wind speed, evaporation and hours of sunlight were obtained from the Agricultural Research Council of South Africa. For the CGA, these data were recorded at the Rietpan Weather Station (27°09' S, 26°54' E) and for the NCGA sites data were recorded at the Naschem Weather Station (26°33' S, 27°08' E).

2.4. Agricultural activities

A crop and pesticide use survey was conducted throughout the study area to characterize the types of crop planted in the catchment area of all the experimental and reference sites. Data on pesticide use were obtained from individual farmers and from representatives of agrochemical companies.

2.5. Quality assurance

The entire study was conducted according to good laboratory practice (GLP) and the raw data and electronic files were subjected to quality assurance verification by external quality assurance.

3. Results

3.1. Climatological and physical data

The seasonal pattern in water temperatures observed (Fig. 3) is typical of that of reservoirs. The highest temperature was observed in early December 2001 (30.0 °C), while the lowest temperature was observed on 10 June 2002 (9.3 °C). The pH increased during the sampling period (Fig. 3). The pH of the CGA ponds was, on average, slightly higher than that of the NCGA ponds. The conductivity (EC) of the NCGA ponds differed from those of the CGA ponds (Fig. 3). Throughout the season and study period, the EC for ponds R1, R3 and R6 was less than 100 $\mu\text{S}/\text{cm}$, despite the changes in water depth and flushing of the ponds caused by sporadic and heavy rainfall. The EC at site R6 increased with inflow of water early in the study and then declined to values similar to the other NCGA sites. For the CGA ponds, the initial EC ranged from 580 to 1413 $\mu\text{S}/\text{cm}$. At the time of the first rainfall in late November 2001, the EC for the CGA sites had decreased to between 400 and 800 $\mu\text{S}/\text{cm}$, while there was little change in the EC-values in the NCGA ponds during this period. The EC remained relatively stable throughout the season except for E4 where an increase to 1567 $\mu\text{S}/\text{cm}$ during mid-April 2002 was observed.

Concentrations of dissolved oxygen (DO) in all of the ponds were greatest during the first rainfalls of November 2001. DO concentrations decreased in all of the ponds during December and January, followed by an increase in DO concentrations between February and June 2002 (Fig. 4).

Due to the rainfall in November and December 2001, there was an overall increase in the depth of all the ponds (Fig. 3). From late-December through June 2002, the water depth in the ponds decreased. Some of the ponds overflowed during the rainy season; therefore, the depths observed during December 2001 and January

2002 were greater than the 100% capacity for most of the ponds. The overflowing of the CGA ponds, except pond E6, ceased in early January 2002. The only exception was NCGA pond R6, where an increase in depth was observed during February and March 2002. The rainfall observed in October, November, and December 2001 (Fig. 4) was more than double the long-term average. For the remainder of the study period, the rainfall was close to the long-term average.

3.2. Elements in water and sediment samples

A summary of results of the elemental analyses conducted on water samples are presented in Table 3

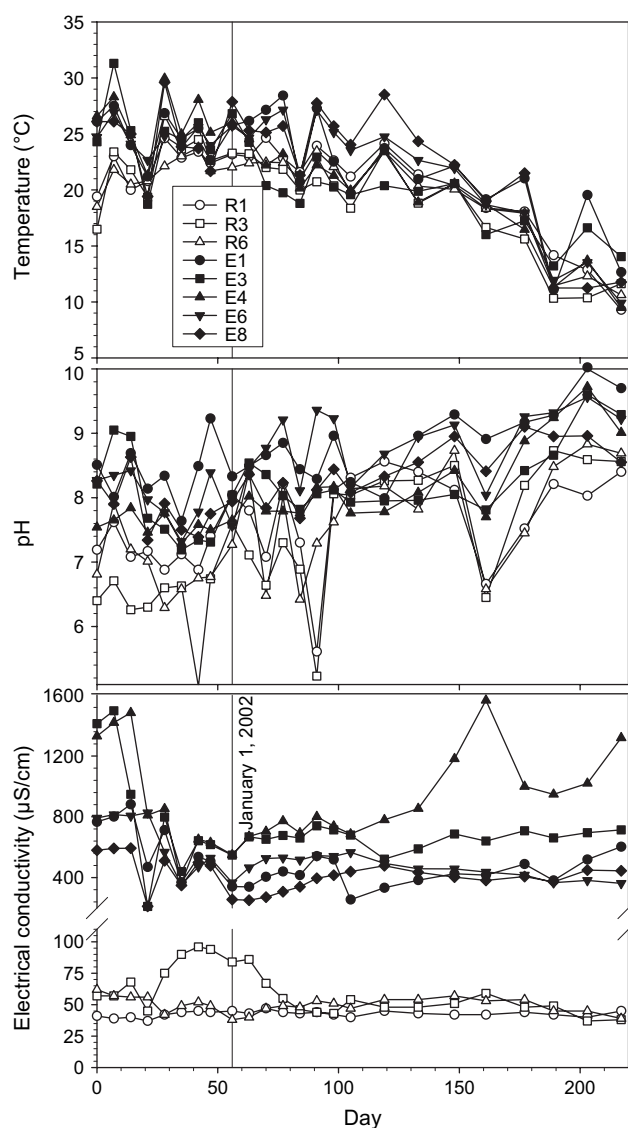


Fig. 3. Temperature, pH, and electrical conductivity for both the NCGA and CGA sites. The vertical line indicates January 01, 2002, the date around which planting of corn and application of herbicides took place. Each point represents a single analysis.

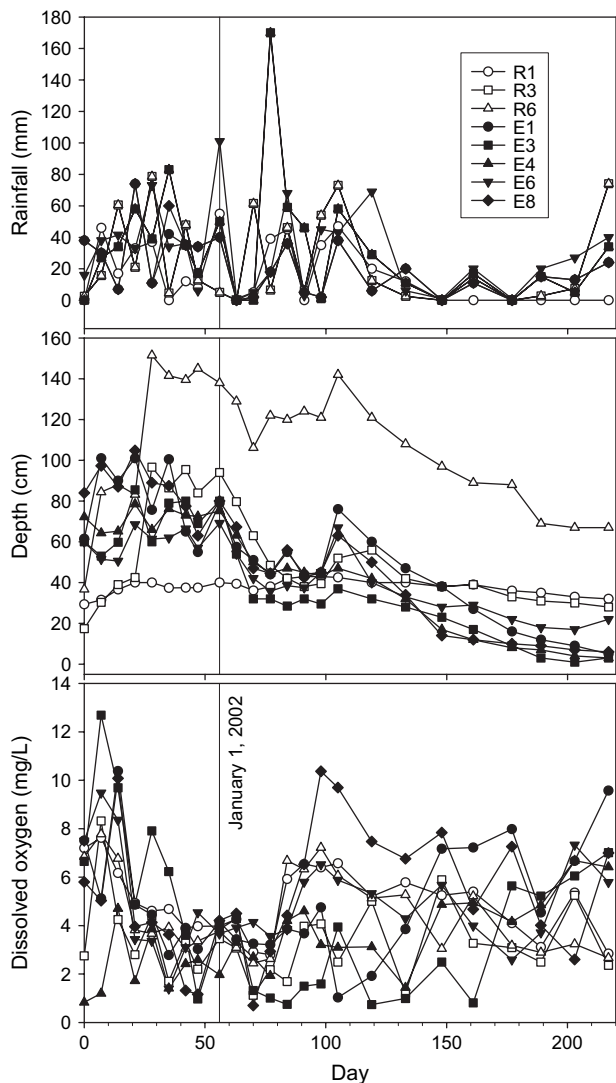


Fig. 4. Dissolved oxygen, depth at reference point and rainfall for both the NCGA and CGA sites. Each point represents a single analysis.

and those on sediment samples in Table 4. There were differences in concentrations of several elements between the CGA and the NCGA sites. These observations are consistent with differences in the EC (Fig. 3) and are probably related to differences in the geology of the sites. Some of the elements detected in the water analyses occurred in concentrations exceeding published water quality guidelines (CWQG, 1999 and the South African Water Quality Guidelines for Aquatic Ecosystems), however, this is likely because suspended minerals were included in the analyses of the water. Some elements, such as lead and chromium, were only detected sporadically during the study. Other elements, such as aluminum, iron, and silica, were present in relatively large concentrations in site R6 as compared to the other sites.

3.3. Applications of triazines and other pesticides

Due to higher than average rainfall during November and December 2001, farmers were not able to plant much sunflower, sorghum, wheat or peanuts in the catchment area of the CGA sites. As a result, the majority of the catchment area was planted with corn (Fig. 2). While the normal corn-planting season is from 1 November to 10 December 2001, the excessive rains delayed the planting and some farmers planted as late as the first week of January 2002. As a result, the application of herbicides was delayed. The herbicides applied during the study period as well as the amounts of atrazine applied in the CGA are summarized in Table 1 and Fig. 5.

3.4. Exposures to triazines and other pesticides

Although no herbicides were applied in the catchment of any of the NCGA ponds, only trace amounts of atrazine with an average concentration of $0.4 \mu\text{g/L}$ were detected during the study, except for the unexpected spike in R3 during May 2002 (Fig. 6). The finding of trace amounts of atrazine in NCGA ponds was surprising as these sites were shown to be free from atrazine residues in the previous year (Du Preez et al., submitted for publication). The lowest concentrations of atrazine in waters from locations in the CGA were observed from October through December. Atrazine concentrations increased after corn was planted and herbicides were applied (Fig. 6). During December and early January, concentrations of atrazine increased values ranging from 4 to $10 \mu\text{g/L}$. After the high water period in April, atrazine concentrations decreased. Terbutylazine was detected in the CGA sites at concentrations up to $4.1 \mu\text{g/L}$ and also in the NCGA sites, although at lower concentrations (Fig. 5). Simazine was occasionally detected in CGA sites E1 and E8 at maxima of 1 and $3.2 \mu\text{g/L}$, respectively.

The triazine degradation products, deisopropylatrazine (DIA) and deethylatrazine (DEA) were detected at all the sites at one or more times during the monitoring period (Fig. 7). Concentrations of DEA were generally $<0.5 \mu\text{g/L}$ prior to planting and application but increased later in the season, including values up to $2.2 \mu\text{g/L}$ observed in site R3. DIA concentrations ranged from the $<\text{LOD}$ to $\leq 1 \mu\text{g/L}$ throughout the monitoring period and did not increase after planting and application. Concentrations of the triazine degradate diamino-chlorotriazine (DACT) ranged from $<\text{LOD}$ to $\approx 8 \mu\text{g/L}$ high at both the CGA and NCGA sites and the highest concentrations were observed prior to planting and application of herbicides in 2001 (Fig. 7).

Acetochlor was detected only at CGA site E8 at a maximum concentration of $1 \mu\text{g/L}$. S-metolachlor, cypermethrin, monocrotophos, and terbuphos, known

Table 3
Mean concentrations of elements and ions (mg/L) in unfiltered water at reference and exposed sites

Elements and ions ^a	R1	R3	R6	E1	E3	E4	E6	E8	Guideline ^b
Aluminum as Al	6.0	2.0	33.8	1.3	0.2	0.1	0.02	0.03	0.1
Antimony as Sb	ND	ND	ND	ND	ND	ND	ND	ND	NA
Arsenic as As	ND	ND	ND	ND	ND	ND	ND	ND	0.005
Barium as Ba	0.01	0.1	0.2	0.1	0.02	0.1	0.1	0.1	NA
Beryllium as Be	ND	ND	ND	ND	ND	ND	ND	ND	NA
Bismuth as Bi	ND	ND	ND	ND	ND	ND	ND	ND	NA
Boron as B	ND	ND	ND	ND	ND	ND	ND	ND	NA
Cadmium as Cd	ND	ND	ND	ND	ND	ND	ND	ND	0.000017
Calcium as Ca	2.3	4.0	4.5	25.4	31.6	30.8	33.2	33.2	NAp
Chromium as Cr	0.012	0.010	0.016	0.028	0.014	0.014	0.004	0.004	0.001
Cobalt as Co	ND	ND	ND	ND	ND	ND	ND	ND	NA
Copper as Cu	ND	ND	ND	ND	ND	ND	ND	ND	0.002
Iron as Fe	4.5	2.1	21.3	0.8	0.2	0.7	ND	ND	0.3
Lead as Pb	0.018	0.016	0.034	ND	ND	ND	ND	ND	0.001
Lithium as Li	ND	ND	ND	ND	ND	ND	ND	ND	NA
Magnesium as Mg	3.1	3.8	3.2	28.6	27.4	27.0	28.4	28.4	NAp
Manganese as Mn	ND	ND	0.1	ND	ND	0.2	ND	ND	NA
Mercury as Hg	ND	ND	ND	ND	ND	ND	ND	ND	NA
Molybdenum as Mo	ND	ND	ND	ND	ND	ND	ND	ND	0.073
Nickel as Ni	ND	ND	ND	ND	ND	ND	ND	ND	0.025
Nitrate as NO ₃	0.4	0.4	0.6	0.6	0.7	0.7	0.3	0.4	NA
Nitrite as NO ₂	0.3	0.4	0.4	0.5	0.5	0.5	0.4	0.4	0.06
Phosphorus as P	0.01	0.1	0.1	0.1	0.7	0.9	0.4	0.3	NAp
Potassium as K	1.2	2.5	7.4	12.2	19.0	19.2	11.4	11.4	NAp
Selenium as Se	ND	ND	ND	ND	ND	ND	ND	ND	0.001
Silica as Si	8.7	4.7	49.2	5.5	5.8	4.8	4.3	4.3	NAp
Silver as Ag	ND	ND	ND	ND	ND	ND	ND	ND	0.0001
Sodium as Na	2.4	2.8	1.3	63.6	106.4	115.8	55.2	55.2	NAp
Strontium as Sr	ND	0.02	0.03	0.1	0.2	0.2	0.2	0.2	NA
Sulphate as SO ₄	3.0	3.2	6.2	23.6	29.5	25.7	26.7	26.7	NAp
Sulphur as S	1.6	2.0	2.1	9.1	10.7	10.4	9.6	9.6	NA
Thallium as Tl	ND	ND	ND	ND	ND	ND	ND	ND	0.0008
Tin as Sb	0.2	ND	0.2	ND	0.2	0.6	0.6	0.6	NA
Titanium as Ti	0.1	0.03	0.6	0.1	0.01	ND	ND	ND	NA
Vanadium as V	0.01	ND	0.01	ND	ND	0.002	ND	ND	NA
Zinc as Zn	ND	ND	ND	ND	ND	ND	ND	ND	0.03
Zirconium as Zr	ND	ND	ND	ND	ND	ND	ND	ND	NA
Total hardness as CaCO ₃	18.2	25.0	24.6	182.0	191.4	188.2	200.4	200.4	NAp

^a Mean of five monthly samples except for nitrate and nitrite which are based on seven samples.

^b From (CWQG, 1999). NA = not available. NAp = not applicable.

Table 4
Concentrations of elements in sediments at NCGA and CGA sites

Element ^a	Units	R1	R3	R6	E1	E3	E4	E6	E8
Arsenic as As	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND
Cadmium as Cd	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND
Chromium as Cr	mg/kg	7.01	ND	100.50	7.51	20.00	22.00	19.00	57.50
Copper as Cu	g/100 g	ND	0.01	0.01	0.06	0.01	0.17	0.03	0.02
Iron as Fe	g/100 g	2.89	3.16	1.05	7.06	5.06	2.61	5.05	9.38
Lead as Pb	mg/kg	0.31	0.18	ND	ND	0.02	ND	ND	0.10
Mercury as Hg	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND
Molybdenum as Mo	mg/kg	0.03	0.04	0.02	ND	ND	ND	0.01	0.01
Nickel as Ni	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND
Selenium as Se	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND
Silver as Ag	mg/kg	ND	ND	ND	ND	ND	ND	ND	ND
Thallium as Tl	mg/kg	ND	ND	ND	ND	ND	ND	0.01	ND
Zinc as Zn	g/100 g	ND	ND	ND	0.25	0.09	0.03	ND	ND

^a Based on the mean of five monthly samples.

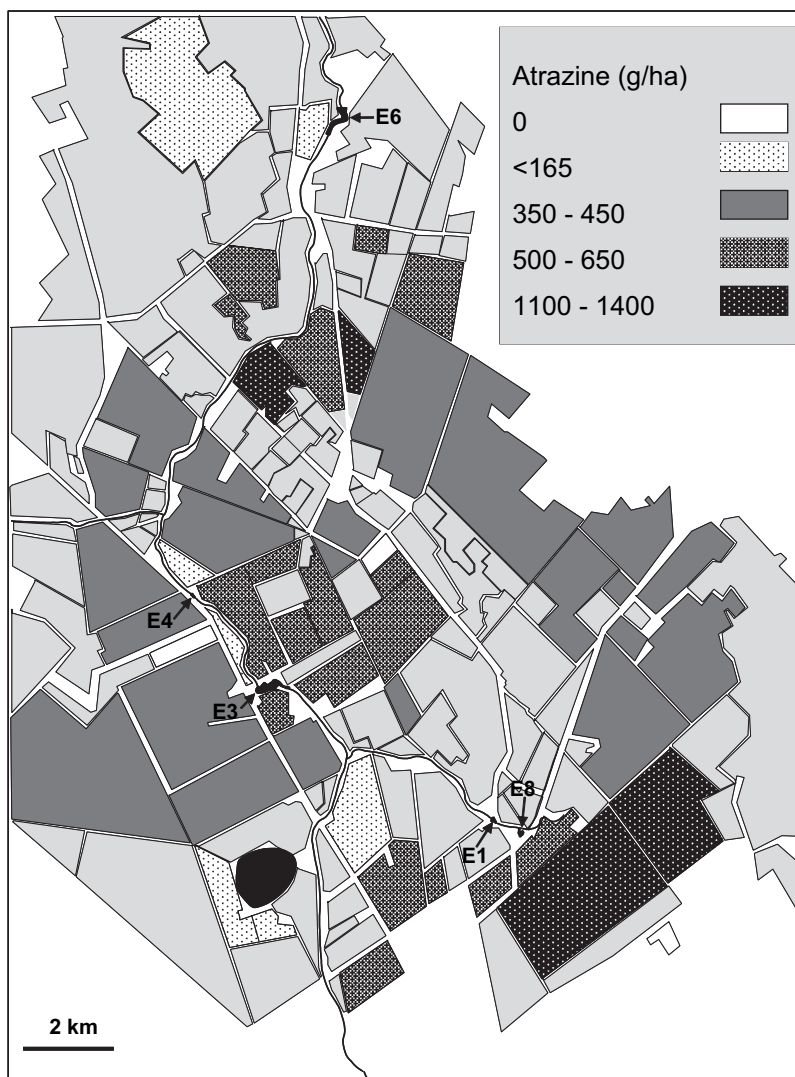


Fig. 5. Map of the CGA study area indicating the amount of atrazine applied during the 2001–2002 study period.

to be used in the general area, were not found in any of the samples at a detection limit of $> \text{LOD}$ ($0.5 \mu\text{g/L}$). None of the cattle located on the NCGA sites R1 and R3 received any growth promoters or hormones such as 17- α -trenbolone. At both sites, the herds consisted of one bull and a number of female animals. None of the ponds had inputs from urban sewage treatment or septic systems and exposure to hormones of anthropogenic origins would not be expected.

4. Discussion

Reinhart and Hugo (1997) conducted a study on soil types and, of the 23 soil samples taken throughout the corn-production area in South Africa, the Viljoenskroon area had the fourth highest percentage (81%) of sand. Due to the surface run-off and lateral movement, especially in sandy soils, water-bodies in corn-production

areas usually can be expected to contain residues of atrazine and other triazines. Atrazine has often been detected in flowing surface waters in agricultural areas of the USA between late spring and midsummer (Goolsby et al., 1997). However, only limited field studies (Tauler et al., 2000) have been conducted to understand the fate of atrazine in surface water because they are costly and technically difficult (Kolpin and Kalkhoff, 1993). A study conducted in South Africa in 1991 reported the presence of atrazine in groundwater and water-bodies ranging from small farm ponds to large reservoirs. Concentrations of atrazine as high as $14 \mu\text{g/L}$ were observed in groundwater of the corn-growing areas of South Africa (Jansen van Rensburg, unpublished data). In another study, conducted during 1992 in South Africa, atrazine was detected in concentrations ranging from 0.73 to $14.97 \mu\text{g/L}$ in surface water and 0.49 to $3.89 \mu\text{g/L}$ in groundwater (Pick et al., 1992). Current annual application rates of atrazine and other triazines are lower

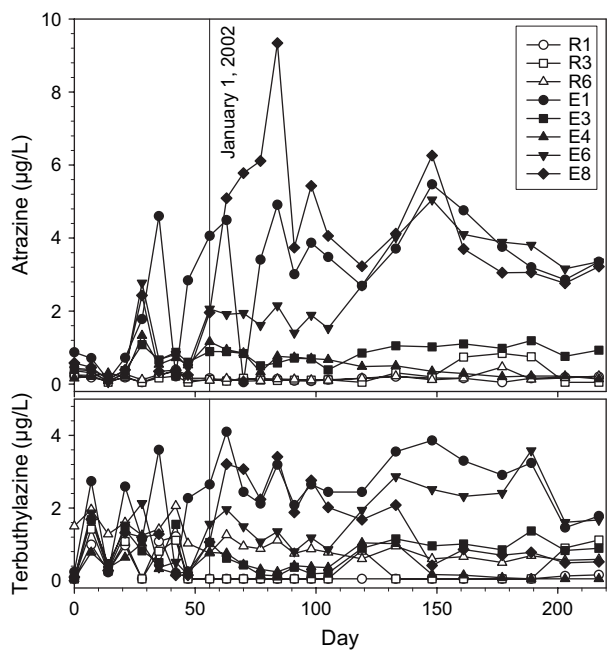


Fig. 6. Atrazine and terbutylazine concentrations measured at the NCGA and CGA sites. Each point represents a single analysis.

(≤ 1.5 kg/ha) compared to those used in the early 1980s (≤ 2.5 kg/ha). In our study, the higher than normal rainfall (twice the seasonal average) and prolonged overflowing of the ponds during the study season likely resulted in dilution of atrazine concentrations in comparison to what had previously been measured in years of normal rainfall.

Due to unusually large amounts of rainfall, the 2001–2002 planting season was delayed for approximately one month, with some farmers planting until mid January 2002. The delayed planting season resulted in greater planting of corn than was anticipated as the planting season for sunflower, peanuts and other crops was over by the time the farmers could get into the fields. As a result, more fields would have been treated with atrazine and terbutylazine than normal.

The higher concentrations of atrazine and other triazines in sites E1 and especially E8 (Fig 6) were expected as the farmer adjacent to site E8 applied greater rates of these herbicides (1.1–1.4 kg/ha). Sites E3 and E4 overflowed for a longer period and atrazine concentrations were ≤ 1.2 $\mu\text{g/L}$ after application (Fig 6). Site E6 was the largest site (6.87 ha) with post-application concentrations of atrazine ranging from 2 to 5 $\mu\text{g/L}$ (Fig. 6). The small atrazine concentrations measured in the NCGA sites are probably the result of wet or dry deposition from nearby areas of application. None of the CGA and NCGA sediment samples contained any atrazine or other triazines at concentrations above the LOD (0.5 $\mu\text{g/kg}$). Given the low soil binding ($K_d = 0.2$ for atrazine, Giddings et al., in press)

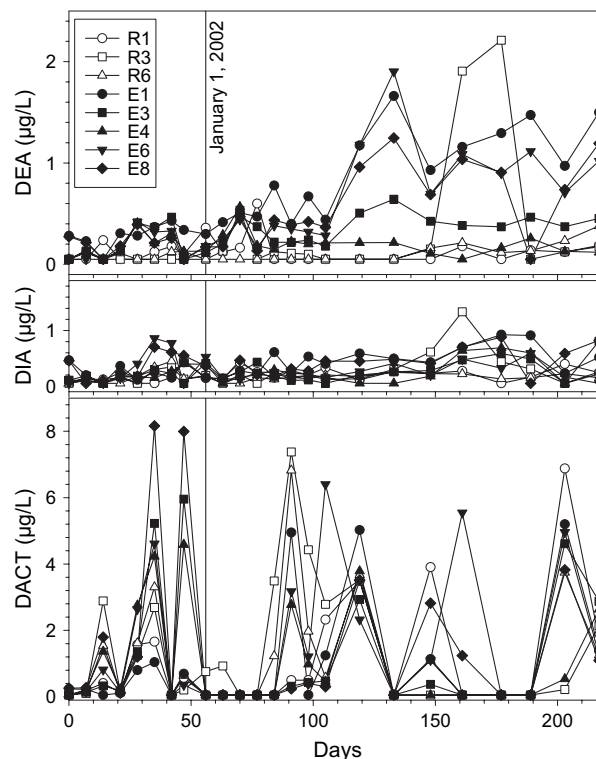


Fig. 7. Concentrations of the triazine degradation products, DEA, DIA, and DACT measured at the NCGA and CGA sites. Each point represents a single analysis.

this would be expected. At some sites, such as E1, E4, and E8, pulses of atrazine were observed in the water early in the season, prior to planting and application. These may have been due to mobilization of atrazine from previous applications by higher than normal rainfall early in the season. At the pHs measured in these ponds (Fig. 3), atrazine would be expected to have a half-life of >300 days (Giddings et al., in press), suggesting that the changes in concentration were the result of hydrological events rather than degradation. The persistence of atrazine has not been reported to be greatly affected by other parameters such as DO, temperatures in the ranges we measured, or the presence of other substances and elements observed in the ponds (Table 3).

The reason for the detection of terbutylazine at the NCGA sites is not clear. The ratios of the time-weighted mean concentrations of atrazine to terbutylazine in the NCGA and CGA sites were 0.28 and 1.33, respectively, suggesting that terbutylazine in the NCGA sites may have originated from non-corn uses such as vegetation control or from rainfall (Huskes and Levensen, 1997). The mobility of terbutylazine relative to that of atrazine in the study environments is not known, however, it has been reported to have a half-life >300 days in groundwater (Navarro et al., 2004) and to be mobile in sandy soils (Maloszewski et al., 2003).

The presence of relatively high concentrations of triazine degradation products (Fig. 7) in both the CGA and NCGA sites was unexpected, especially the values observed for DACT. The greatest concentrations of DIA and DEA observed in a data set of 6600 samples of surface waters in Ohio, USA were $\approx 11 \mu\text{g/L}$ and 99% were $< 5 \mu\text{g/L}$ (Giddings et al., in press). Maximum concentrations of DEA in other data sets (5100 samples) from surface waters in the USA were smaller $\leq 1.1 \mu\text{g/L}$ (Giddings et al., in press). Concentrations of DACT in surface waters have not been reported in the literature.

DEA could only be formed from atrazine since it retains the isopropyl group (Fig. 1). Concentrations of DEA increased after planting and herbicide application, which is consistent with formation from atrazine applied during the current season. DIA could be formed from atrazine, simazine, and, to a small extent, from terbuthylazine (Esser et al., 1975) since it retains the ethyl group (Fig. 1), however, concentrations were not high, were relatively constant, and did not increase markedly later in the season as might be expected from degradation of parent herbicides applied during the growing season. Concentrations of DACT were inconsistent over time and did not show clear temporal trends such as would be expected from application of triazines during the study season. DACT could be formed from atrazine, simazine, and terbuthylazine and is the “terminal” chlorinated degradation product for all three compounds (Fig. 1). The persistence of atrazine degradation products in soils from North America has been reported to be short ($t_{1/2}$ from 17 to 26 days) but persistence in water has not been measured (Giddings et al., in press). Persistence of DACT in water and soils of the CGA region is not known specifically, however, the concentrations we observed could be the result of build-up in soil and groundwater over several years with flushing out occurring as a result of the higher than average rainfall that occurred during the study season.

A range of concentrations of atrazine, terbuthylazine, and their degradation products were measured at the sites in the CGA and NCGA. Because of dilution by higher than normal rainfall in the study period, these concentrations are likely lower than those in previous years with more typical rainfall patterns. Because of extensive historical use of atrazine and other triazines in this area, these substances have probably been present for a number of years such that the current values include possible residue accumulations from past uses, when larger amounts were applied.

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