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Journal of Hydrology 266 (2002) 190–208

Journal of Hydrology

www.elsevier.com/locate/jhydrol

Changes in concentrations of triazine and acetamide herbicides by bank filtration, ozonation, and chlorination in a public water supply

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Received 1 April 2001; revised 10 August 2001; accepted 4 January 2002

Abstract

The changes in triazine and acetamide concentrations in water during natural and artificial treatment by bank filtration, ozonation, filtration, and chlorination were measured at the well field and drinking water treatment plant of Lincoln, Nebraska, USA. The city's groundwater supply is affected by induced infiltration and transport of triazines and acetamide herbicides from the Platte River in late spring and early summer. The objective of the study was to evaluate the effect of infiltration and treatment on the presence of triazines and acetamides in drinking water. Samples of river water, well water, and public supply water at various stages of water treatment were collected from 1997–1999 during spring-runoff when the presence of herbicides in the Platte River is largest. In 1999, parent compounds were reduced by 76% of the concentration present in river water (33% by bank filtration, 41% by ozonation, and 1.5% by chlorination). Metabolites of herbicides for which analytical techniques existed were reduced by 21% (plus 26% by bank filtration, minus 23% by ozonation, and minus 24% by chlorination). However, increases in concentrations of specific metabolite compounds were identified after bank filtration and ozonation. After bank filtration, increases in cyanazine amide, cyanazine acid, and deethylcyanazine acid were identified. After ozonation, concentrations of deisopropylatrazine, deethylatrazine, didealkylatrazine, atrazine amide-I, hydroxydeethylatrazine, hydroxydeisopopylatrazine, deethylcyanazine acid, and deethylcyanazine increased. Concentrations of cyanazine acid and ethanesulfonic and oxanilic acids of acetamides decreased during ozonation. Our findings suggest that bank filtration and ozonation of water in part can shift the assessment of risk to human health associated with the consumption of the water from the parent compounds to their degradation products. Published by Elsevier Science B.V.

Keywords: Triazines; Acetamides; Metabolites; Bank filtration; Ozonation; Public water supply; Water treatment

1. Introduction

Filtration and disinfection are very important steps in the treatment of drinking water. River-bank filtration, herein referred to as bank filtration, and ozonation have been documented as having positive effects on drinking water (Katz, 1980; Kühn, 1999). In the United States, increased exploitation of water from alluvial aquifers along river banks is expected,

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0022-1694/02/$ - see front matter Published by Elsevier Science B.V.
PII: S0022-1694(02)00163-4

given the rise in demand for drinking water (Solley et al., 1998), the ease of withdrawal of water from alluvial aquifers, and the positive effects of bank filtration on the quality of surface water. However, concerns about the effectiveness of river-bank filtration as pretreatment for drinking water have increased partly because of recent developments in the construction of large capacity collector wells near the banks of large rivers and increased understanding of the transport and fate of contaminants in hydrologic systems, and their resulting effects on human health.

Field studies of herbicide degradation products have identified not only the presence of DEA, DIA, and HA (Table 1), but also that the dealkylated hydroxymetabolites HDEA, HDIA, and DDA can be present in soils (Baluch et al., 1993; Panchin et al., 2000) and water (Lerch et al., 1998; Scribner et al., 2000; Thurman et al., 1991; Thurman et al., 1992; Thurman et al., 1996). Metabolites of herbicides could be more important contaminants in the environment than the parent compounds (Anderson, 1990; Baluch et al., 1993; Scribner et al., 2000). They tend to be more water soluble than the parent compounds, and tend to leach more rapidly (Scribner et al., 2000). Atrazine metabolites accounted for nearly 60% of the load of herbicides in northern Missouri streams, and sulfonic and oxanilic metabolites of ALA, ACET, and METO were present in 75% of all the samples and had a larger summed concentration than their parent compound (Lerch et al., 1998; Kalkhoff et al., 1998). The presence of metabolites in pore water and groundwater has serious implications for surface water and groundwater monitoring because the effect of herbicide application and its influence on the environment tends to be underestimated when samples are analyzed for the parent compounds only (Panchin et al., 2000; Lerch et al., 1998).

Treatment of drinking water with chlorine is being replaced with ozone and chlorine dioxide treatment, two strong oxidizing agents, because of the adoption of federal regulations governing the exposure of humans to chlorine and its by-products in drinking water (Katz, 1980). Ozonation studies have focused on organic carbon loss or disappearance of parent compounds (Neukrug et al., 1983) and, in some cases, have focused on identification of by-products under aqueous ozonation conditions. Ozone reacts with a wide variety of organic materials, oxidizing the parent compounds to form a range of metabolites without much ring cleavage or dechlorination (Acero et al., 2000; Hapeman-Somich, 1991, 1992; Hapeman, 1994).

Triazine and acetamide herbicides in the Platte River in Nebraska, USA, are transported from the river into the City of Lincoln public water supply (Verstraeten et al., 1999a). The City of Lincoln well field consists of 38 active production wells. Two wells are horizontal collector wells each with a capacity of about 25 m^3d^{-1}, on an island in the Platte River, and 36 wells are vertical wells each with a capacity of as much as 1 m^3d^{-1}, on the west bank of the Platte River (Fig. 1). The production wells are completed in alluvial sand, gravel, silt and clay with a saturated thickness of about 27 m underlain by shale. The horizontal wells consist of a caisson with an outside diameter of 4.9 m that is attached to seven laterals with well screens having diameters of 30 cm and total lengths of up to 430 m set at depths of about 25 m. The distance of underground passage between river-bank and the collector well is about 25 m with a mean residence time estimated at about 6 days. Bank-filtered water is transported in about 20– 60 min from the collector wells to the treatment plant (site 2 and 3 to site 4).

The treatment plant of interest (East Treatment Plant) has a capacity of 190 m^3d^{-1}. The plant receives groundwater from the horizontal and vertical wells, with a river-infiltration component in the collector wells at times in excess of 90% (Steele and Verstraeten, 1999). Treatment of water in the treatment plant consists of ozonation, filtration, chlorination, fluoridation, ammoniation, and residence in the reservoir (Fig. 2). For the ozonation process, air is prepared in three high-volume low-pressure air compressors capable of producing 10 SCMM (standard cubic meters per minute) with a typical air pressure less than 138 kPa. The typical ozone dosage is about 1.5 mg l^{-1}, dependent upon demand by organic and inorganic compounds. The typical residence time in the ozonation basin is 20 min, but can vary from 12 to 32 min. After ozonation, polymer is added and the water flows through dual-media filters consisting of a 0.5 m anthracite cap and 0.56 m of sand and gravel. Then the water flows to a clear well where 2.2 mg l^{-1} chlorine gas is added. Fluoride (0.6 mg l^{-1}) is added after the clear well is passed.

Table 1
Chemical name, abbreviation, and IUPAC name of selected herbicides and metabolites

Chemical name	Abbreviation	IUPAC name	Analytical method	Reporting limit ($\mu g\ l^{-1}$)
Atrazine	ATR	2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine	GC/MS	0.05
Atrazine amide I	ATRM-I	4-acetamido-2-chloro-6-ethylamino-*s*-triazine	GC/MS	0.05
Atrazine amide II	ATRM-II	4-acetamido-2-chloro-6-isopropylamino-*s*-triazine	–	–
Deethylatrazine	DEA	6-amino-2-chloro-4-(isopropylamino)-*s*-triazine	GC/MS	0.05
Deisopropylatrazine	DIA	6-amino-2-chloro-4-(ethylamino)-*s*-triazine	GC/MS	0.05
Intermediate product	–	2-chloro-4,6-diacetamido-*s*-triazine	–	–
Atrazine amide III	ATRM-III	4-acetamido-6-amino-2-chloro-*s*-triazine	–	–
Didealkylatrazine	DDA	2-chloro-4,6-diamino-*s*-triazine	LC/MS	0.10
Atrazine imine	ATR-imine	2-chloro-4-ethylimino-6-isopropylamino-*s*-triazine	–	–
Deisopropyl imine	DIA-imine	6-amino-2-chloro-4-ethylimino-*s*-triazine	–	–
Hydroxyatrazine	HA	2-hydroxy-4-ethylamino-6-isopropylamino-*s*-triazine	LC/MS	0.20
Hydroxydeethylatrazine	HDEA	2-hydroxy-4-amino-6-isopropylamino-*s*-triazine	LC/MS	0.20
Hydroxydeisopropylatrazine	HDIA	2-hydroxy-4-ethylamino-6-amino-*s*-triazine	LC/MS	0.20
Ammeline	–	2-hydroxy-4,6-diamino-*s*-triazine	–	–
Ammelide	–	Aminodihydroxy-*s*-triazine	–	–
Cyanuric acid	–	Trihydroxy-*s*-triazine	–	–
Cyanazine	CYA	2-((4-chloro-6-(ethyl-amino)-1 triazine-2-yl)-amino)-2-methylpropionitrile	GC/MS	0.01
Deethylcyanazine	DEC	2-((4-amino-6-chloro-1 triazine-2-yl)-amino)-2-methylpropionitrile	GC/MS	0.01
Cyanazine amide	CAM	2-chloro-(1-carbamyl-1-methyl-ethylamino)-6-ethylamino-*s*-triazine(LC/MS in 1999)	GC/MS	0.05
Deethylcyanazine amide	DCAM	2-chloro-(1-carbamyl-1-methyl-ethylamino)-6-amino-*s*-triazine	GC/MS	0.01
Cyanazine acid	CAC	2-chloro-(1-carboxylic-1-methyl-ethylamino)-6-ethylamino-*s*-triazine	GC/MS	0.01
Deethylcyanazine acid	DCAC	2-chloro-(1-carboxylic-1-methyl-ethylamino)-6-amino-*s*-triazine	GC/MS	0.01
Propazine	PROP	2-chloro-4,6-bis(isopropylamino)-*s*-triazine	GC/MS	0.05
Simazine	SIM	2-chloro-4,6-bis(ethylamino)-*s*-triazine	GC/MS	0.05
Alachlor	ALA	2-chloro-2′-6′-diethyl-*N*-(methoxymethyl)-acetanilide	GC/MS	0.05
Alachlor ethanesulfonic acid	ALA ESA	2-((2,6-diethylphenyl) (methoxymethyl)amino)-2-oxoethanesulfonic acid	HPLC/DAD	0.02
Alachlor oxanilic acid	ALA OXA	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid	HPLC/DAD	0.02
Acetochlor	ACET	2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6methyl-phenyl)acetamide	GC/MS	0.05
Acetochlor ethanesulfonic acid	ACET ESA	2-[2-ethyl-6-methylphenyl)(ethoxymethyl)-amino]-2-oxoethanesulfonic acid	HPLC/DAD	0.02
Acetochlor oxanilic acid	ACET OXA	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)-amino]-2-oxoacetic acid	HPLC/DAD	0.02
Metolachlor	METO	2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide	GC/MS	0.05
Metolachlor ethanesulfonic acid	METO ESA	2-[(2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid	HPLC/DAD	0.02
Metolachlor oxanilic acid	METO OXA	2-[(2-ethyl-6-methylphenyl) (2-methoxy-1-methylethyl)amino]-2-oxoacetic acid	HPLC/DAD	0.02
Dimethenamid	–	(2-chloro-*N*-(2,-dimethyl-3-thienyl)-*N*-(2-methoxy-1-methylethyl)acetamide	GC/MS	0.05
Flufenacet	–	*N*-(-fluorophenyl)-*N*-(1-methylethyl)-2-((5-(trifluoromethyl)-1,3,4-thiadiozol-2-yl)oxy)-acetamide	GC/MS	0.05

IUPAC, International Union of Pure and Applied Chemistry; GC, gas chromatography; MS, mass spectrometry; –, no abbreviation or analytical method; LC, liquid chromatography; HPLC, high performance liquid chromatography; DAD, diode array detection.

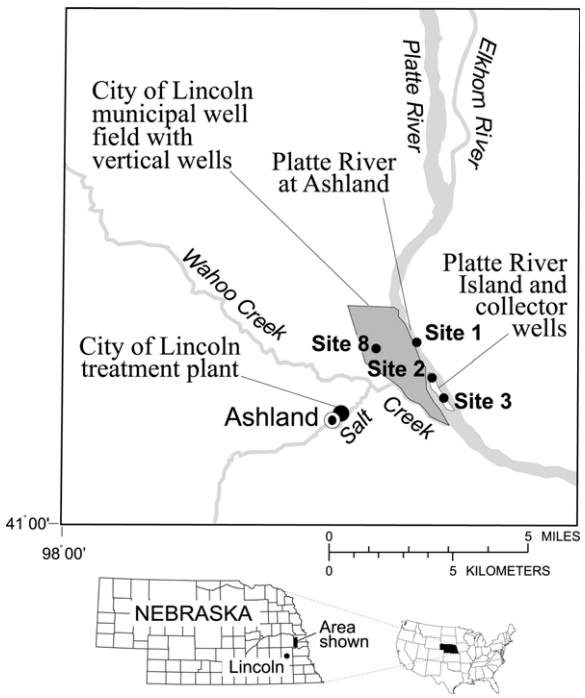


Fig. 1. Location of well field, selected well sites, and municipal treatment plant.

Anhydrous ammonia (0.38 mg l^{-1}) is added where water flows into a reservoir, which discharges into the distribution system. Then the treated water is piped through approximately 40 km of steel and concrete distribution system pipes to the City of Lincoln.

To evaluate the degradation of selected triazine and acetamide herbicides during bank filtration, ozonation, and chlorination, a study was conducted by the US Geological Survey (USGS) in cooperation with the City of Lincoln from 1997–2000. This paper describes the effect of bank filtration, ozonation, and, to a lesser extent, chlorination on the presence of the aforementioned herbicides in the drinking water of the City of Lincoln, with special emphasis on the interpretation of those data collected during a worst-case scenario in 1999.

2. Methods

This study was performed during spring-runoff, typically occurring from April–June, when concentrations of herbicides in the river significantly affect the quality of surface water, groundwater, and drinking water. The horizontal collector wells each were pumped at about 50 $m^3 d^{-1}$. During the 1999

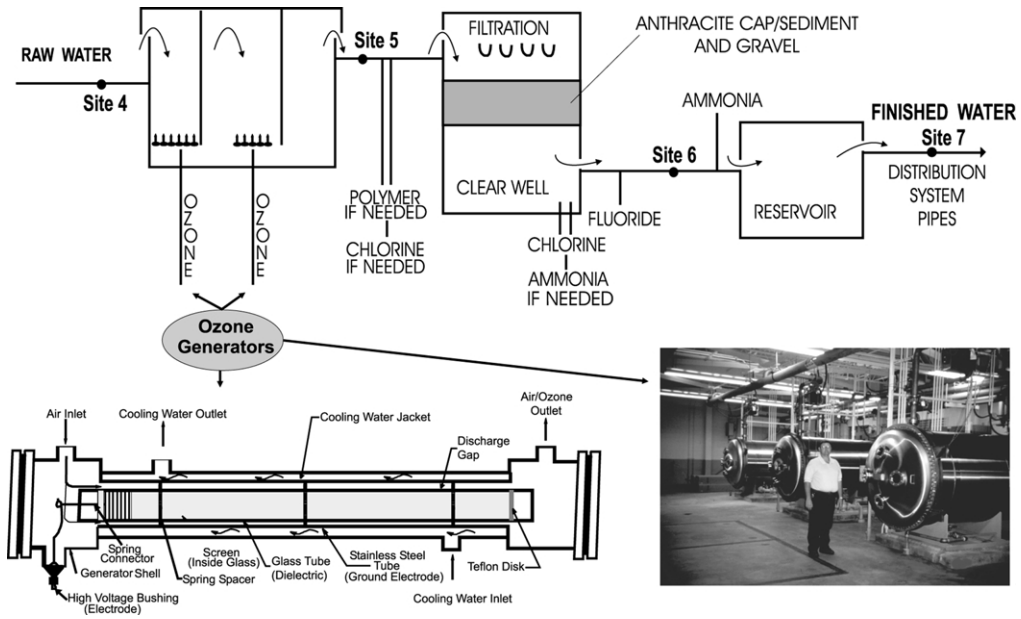


Fig. 2. Flow diagram of the East Treatment Plant, ozone generators, and sampling sites.

tests, the effect of bank filtration was decreased to ensure that researchers could assess the effect of ozonation and chlorination on concentrations of herbicides in the treatment plant by encouraging less attenuation during the bank-filtration process. During these tests, only laterals that extend under the river were used, thereby encouraging the presence of infiltrated surface water in the collector wells (about 100%). The shortest possible subsurface travel distances (25 m) and times (6 days or less) were used, thereby discouraging the formation of metabolites through chemical and biological degradation. In general, the pH of the river varies from 7.5 to more than 8.0 and the temperature of the river varies largely during the year. Water in the river generally is well oxygenated, whereas water from the collector wells generally has low dissolved oxygen (less than 1 mg l^{-1}) resulting in part in anaerobic conditions in the subsurface.

2.1. Sample-collection procedures

Equal-width integrated samples (Wells et al., 1990) were collected from the Platte River (site 1), and representative samples were collected from the collector wells (sites 2 and 3) (bank-filtered water), prior to treatment (site 4), after ozonation (site 5), after chlorination and minor filtration (site 6), and after ammoniation and short residence time (minor filtration) in the reservoir (site 7) (Figs. 1 and 2). The same aliquot of water was sampled at all the sampling sites to the best extent possible dependent upon the flow rate of wells and the treatment system. Travel time from the Platte River to the collector wells during all sampling times was estimated to be about 6 days (Verstraeten et al., 1999a). For example, on June 9, 1999, starting at 12:30 in the afternoon samples were collected from: sites 2 and 3, 6 days after collecting samples from the river; site 4, 2 h after collector wells, site 5, 37 min. after site 4; site 6, 11 min. after site 5; and site 7, 31 min. after site 6. Samples were collected during one spring-runoff event in June 1997 and two spring-runoff events in June 1998 and June 1999 (the samples from the event with the largest herbicide concentrations were quantified). The collector wells were pumped starting 1 day after the onset of the runoff event at a combined pumping rate of about 98.4 m^3d^{-1}. In 1997 and 1998, the water from the collector wells generally was mixed with approximately 50% groundwater from vertical wells on the west bank of the Platte River and a sample was collected from a vertical well (site 8) representing the water-quality of groundwater. In addition, field measurements, including pH, temperature, specific conductance, and dissolved oxygen, were collected at all sites (Table 2). Quality assurance-quality control consisted of the collection of a duplicate sample and an equipment blank during the 1998 sampling at site 4 (before ozonation). In 1999, a duplicate sample was collected at site 5 (after ozonation). Results from the equipment blanks indicated no contamination above reporting levels. Duplicate sample analyses showed very small variations in concentrations.

In 1999, the normal plant procedures were modified for the study to ensure that large concentrations of herbicides went through the treatment plant to increase the confidence in our findings. The four most northern laterals from site 2 and the four most eastern laterals from site 3 were used. In addition, on June 9, 1999, the conditions of the plant were altered such that the incoming bank-filtered water in the plant consisted of 100% collector well water in approximately equal amounts from the two collector wells. The ozone residence time during the test was 32 min. After these conditions were in place for about 2 h, samples were collected from the plant. At least 2 l of sample water was collected in a 1-gallon glass container and was filtered onsite using a baked-glass fiber filter into four 125 ml brown baked-glass bottles. Samples were sent overnight on ice to the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas, and were extracted within 7 working days.

2.2. Analytical procedures

Samples from the river collected during the events were analyzed for ATR, the most commonly detected compound in largest concentration in the municipal water shortly after spring-runoff events (Verstraeten et al., 1999a), using an immunoassay technique (Aga et al., 1994). Subsequent quantitative analyses were done on the samples associated with the event showing the largest concentration of ATR in water from the Platte River. Samples were analyzed for ATR, DEA, DIA, ATRM-I, CYA, CAM, PROP, SIM,

Table 2
Concentrations of triazine herbicides and metabolites, June 1997–1999

Analyte	Year	R (site 1)	W1 (site 2)	W2 (site 3)	U (site 4)	O (site 5)	CF (site 6)	T (site 7)	GW (site 8)
pH (pH units)	1999	8.2	6.7	6.9	7.4	7.0	7.1	7.2	–
Water temperature (°C)	1999	17.7	18.0	15.5	20.0	17.2	17.8	17.0	–
Specific conductance ($\mu S\ cm^{-1}$ at 25 °C)	1999	398	502	521	556	536	563	560	–
Dissolved oxygen ($mg\ l^{-1}$)	1999	9.75	0.05	0.31	0.42	0.62	0.80	0.85	–
Atrazine (ATR)	1997	9.64	1.50	1.50	0.77	0.50	0.50	0.50	0.11
	1998	7.80	4.79	3.82	2.27	0.57	1.35	0.78	<0.05
	1999	12.50	9.39	10.70	11.60	4.40	3.50	4.10	–
Deethylatrazine (DEA)	1997	0.46	0.14	0.12	0.08	0.16	0.17	0.18	<0.05
	1998	0.74	0.52	0.41	0.22	0.42	0.60	0.49	<0.05
	1999	0.85	0.86	0.86	0.85	1.60	1.41	1.55	–
Deisopropylatrazine (DIA)	1997	0.23	0.07	<0.05	<0.05	0.09	0.07	0.09	<0.05
	1998	0.45	0.31	0.24	0.11	0.23	0.31	0.28	<0.05
	1999[a]	0.48	0.37	0.42	0.41	0.69	0.61	0.64	–
Atrazine amide I (ATRM-I)	1999[a]	<0.20	<0.20	<0.20	<0.20	0.50	0.31	0.41	–
Hydroxyatrazine (HA)	1997	0.97	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	1998	1.16	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	1999[a]	0.61	0.18	0.38	0.21	0.09	0.12	–	–
	1999[b]	0.61	0.73	0.73	–	0.10	0.08	0.09	–
Hydroxydeethylatrazine (HDEA)	1999[a]	0.20	0.15	0.25	0.13	0.25	0.29	–	–
	1999[b]	0.20	0.22	0.93	–	0.19	0.18	0.17	–
Hydroxydeisopropylatrazine (HDIA)	1999[a]	0.12	0.14	0.12	0.11	0.20	0.11	–	–
	1999[b]	0.12	0.10	0.41	–	0.05	0.08	0.10	–
Didealkylatrazine (DDA)	1999[a]	0.26	0.19	0.25	0.21	0.65	0.29	–	–
	1999[b]	0.26	0.22	0.12	0.10	0.25	0.19	0.17	–
Cyanazine (CYA)	1997	3.49	0.35	0.33	0.16	0.19	0.18	0.19	0.09
	1998	1.35	0.92	0.96	0.58	0.34	0.25	0.24	<0.01
	1999[a]	1.36	1.03	1.23	1.15	0.52	0.39	0.50	–
Deethylcyanazine (DEC)	1999[a]	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	0.04	–
Cyanazine amide (CAM)	1997	0.43	0.22	0.41	0.19	0.12	0.12	0.14	<0.05
	1998	0.40	1.87	1.95	1.32	0.81	0.34	0.25	<0.05
	1999[a]	0.15	0.76	0.63	0.50	0.36	0.22	0.38	–
Deethylcyanazine amide (DCAM)	1999[a]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	–
Cyanazine acid (CAC)	1999[a]	0.13	0.30	0.26	0.27	0.15	0.15	0.14	–
Deethylcyanazine acid (DCAC)	1999[a]	<0.01	0.34	0.46	0.27	0.34	0.19	0.38	–
Propazine (PROP)	1999[a]	0.12	0.14	0.12	0.11	0.05	~0.04	0.05	–
Simazine (SIM)	1999[a]	0.05	~0.04	~0.03	~0.03	~0.015	~0.01	~0.02	–
Deethyl-to-atrazine ratio (DAR), dimensionless	1997	0.05	0.09	0.08	0.10	0.32	0.34	0.36	–
	1998	0.09	0.11	0.11	0.10	0.74	0.44	0.63	–
	1999[a]	0.07	0.09	0.08	0.07	0.36	0.40	0.38	–

R: Platte River; W1, northern collector well; W2, southern collector well; U, bank-filtered water; O, post-ozonation; CF, post-chlorination and filtration; T, treated water; GW, groundwater; <, less than; –, no data; ~, about; concentrations in $\mu g\ l^{-1}$.

[a] 100% water from vertical wells collected in 1999.

[b] About 50% water from collector wells mixed with 50% water from vertical wells collected in 1999.

ACET, ALA, and METO in accordance with Thurman et al. (1990) and Meyer et al. (1993); ACET ESA, ACET OXA, ALA ESA, ALA OXA, HA, METO ESA, and METO OXA in accordance with Ferrer et al. (1997), Kolpin et al. (1998) and Hostetler and Thurman (1999); CYA, DEC, CAM, DCAM, CAC, and DCAC in accordance with Thurman et al. (1990) and Meyer et al. (1993); HA, HDEA, and HDIA in accordance with Lerch et al. (1998); and dimethenamid and flufenacet in accordance with Kish

et al. (2000). Analyses of in-laboratory replicates also were completed regularly.

A new analytical method was developed for extraction of DDA. Samples consisted of 240 ml of water spiked with 200 μl of 1.23 mg l^{-1} D_5-atrazine as a surrogate. The pH was adjusted to approximately 1.6 with 1.0 ml concentrated HCl. Controls were spiked with an appropriate volume of 1.0 mg l^{-1} DDA in methanol (MeOH). A 150 mg, 6 cc mixed-mode cation exchange (MCX) cartridge (OASIS, Waters, Milford, MA) was used for the solid phase extraction. The cartridges were preconditioned with 3 ml MeOH, 3 ml 1.0 N HCl, and 3 ml distilled water. The samples then were loaded onto the cartridges at approximately 10 ml min^{-1}. After the samples were loaded, the cartridges were washed with 2 ml of 0.1 N HCl to lock the DDA to the cartridge, then washed with 3 ml 25/75 H_2O/MeOH to wash off humic materials. The samples then were eluted with 3 ml of 5% NH_4OH in MeOH, and 100 μl of 1.23 mg l^{-1} simatone were added as an internal standard. This solution was reduced under N_2 to a final volume of 50 μl before adding 75 μl of 0.5% acetic acid in water.

Analyses of DDA were completed with LC/MS. A C18, 150 mm × 2.0 mm, 5 μm particle size, 100 Å pore size analytical column was used to separate the analytes. Mobile phase A consisted of 0.5% acetic acid in 50/50 MeOH/HCN, and phase B consisted of 0.5% CH_3COOH in water. At a flow of 0.40 ml min^{-1}, a gradient was used whereby mobile phase B was held at 80% for the first 5 min, then decreased to 50% for 15 min, then to 0% for 20 min. A 6-min reequilibration time elapsed between runs. The absorbance of light at 254 nm was detected using a diode array detector. The 1100 MSD (mass selective detector) series B was operated in APCI (atmospheric pressure chemical ionization) positive under selected ionization mode. Nitrogen was used as the drying gas with a flow of 10-ml min^{-1} at 40 °C. The nebulizing pressure was set at 300 psig. The capillary voltage was set at 4000 eV and the fragmentor was set at 70 eV. Increasing the fragmentor did not result in increased fragment ions greater than *m/z* 100, but did result in a decrease in signal. The ions 146 and 148 were monitored for DDA; the ions 216, 218, 174, 176, 146, and 148 were monitored for the parent atrazine; the ions 221 and 223 for D_5-atrazine; and the ion 198 was monitored for simatone. A blank and a minimum of three controls were run with each sample set. Calculations were based on the DDA-to-simatone ratio.

3. Results and discussion

Herbicides and metabolites were affected differently by bank filtration and chemical treatment depending upon the herbicide and the treatment process (Tables 2 and 3). Total herbicide concentration—in this case, parent and metabolite compounds of triazines and acetamides for which analytical methods exist—was lowered by 65% during the treatment processes from a concentration of 29.35 μg l^{-1} in the river to a concentration of 10.15 μg l^{-1} in treated water in 1999 (Table 4). In 1999, concentrations of total herbicides (parent compounds and metabolites) decreased by 22% during bank filtration, another 38% (48% of herbicides present in bank-filtered water) during ozonation, and another 5% (14% of herbicides present in ozonated water) during chlorination, filtration, and residence in reservoir prior to distribution. Ammoniation and addition of fluoride did not affect the presence of herbicides in the water during treatment. Chlorination had some effect on the presence of parent compounds and metabolites.

In 1999, in post-ozonated water, concentrations of parent compounds of triazines and acetamides had decreased by 76% (about 33% during bank filtration, 41% (62% of parent compounds in bank-filtered water) during ozonation, and 1.5% (5% of concentrations in ozonated water) during chlorination and minor filtration. Overall, the data indicate that metabolites, for which analytical procedures exist, were both destroyed and created during the treatment processes (plus 26% during bank filtration, minus 23% during ozonation, and minus another 24% during chlorination and minor filtration) resulting in an overall decrease of 21% in quantified metabolite concentrations.

In general, relative amounts of parent compounds decreased while relative amounts of metabolites increased during the treatment processes. Parent compounds composing 81% (23.80 μg l^{-1}) of the sum of all compounds (29.35 μg l^{-1}) analyzed for in

Table 3
Concentrations of acetamide herbicides, 1997–1999

Analyte	Year	R (site 1)	W1 (site 2)	W2 (site 3)	U (site 4)	O (site 5)	CF (site 6)	T (site 7)	GW (site 8)
Alachlor (ALA)	1997	0.60	0.20	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	1998	0.38	0.09	0.08	<0.05	<0.05	<0.05	<0.05	<0.05
	1999	0.99	–	0.24	0.19	0.08	0.06	0.07	–
Alachlor ethanesulfonic acid (ALA ESA)	1997	0.29	0.25	0.24	0.23	<0.20	<0.20	<0.20	0.25
	1998	0.35	0.34	0.32	0.29	<0.20	<0.20	<0.20	0.24
	1999	0.26	–	0.27	0.31	<0.20	<0.20	<0.20	–
Alachlor oxanilic acid (ALA OXA)	1997	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	1998	0.26	0.26	0.21	<0.20	<0.20	<0.20	<0.20	<0.20
	1999	0.28	–	0.39	1.17	<0.20	<0.20	<0.20	–
Acetochlor (ACET)	1997	4.35	0.20	0.19	0.08	<0.05	<0.05	<0.05	0.20
	1998	1.46	0.37	0.35	0.22	0.07	0.06	<0.05	<0.05
	1999	3.7	–	1.04	0.70	0.31	0.24	0.28	–
Acetochlor ethanesulfonic acid (ACET ESA)	1997	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	1998	0.46	0.38	0.25	0.25	0.25	0.44	<0.20	<0.20
	1999	0.49	–	0.51	0.55	0.25	0.21	0.22	–
Acetochlor oxanilic acid (ACET OXA)	1997	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	1998	0.60	0.49	0.43	0.25	<0.20	<0.20	<0.20	<0.20
	1999	1.04	–	1.31	1.17	0.41	0.40	0.39	–
Metolachlor (METO)	1997	4.72	0.69	0.69	0.30	0.13	0.12	0.12	<0.05
	1998	3.60	1.80	1.55	1.04	0.30	0.29	0.15	<0.05
	1999	4.33	–	2.08	1.62	0.64	0.48	0.56	–
Metolachlor ethanesulfonic acid (METO ESA)	1997	0.62	<0.20	0.51	<0.20	<0.20	<0.20	<0.20	<0.20
	1998	0.55	0.44	0.39	0.37	<0.20	<0.20	<0.20	<0.20
	1999	0.29	–	0.43	0.47	<0.20	<0.20	<0.20	–
Metolachlor oxanilic acid (METO OXA)	1997	0.37	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	1998	0.45	0.27	0.24	0.23	<0.20	<0.20	<0.20	<0.20
	1999	0.38	–	0.42	0.40	0.20	0.21	0.21	–
Dimethenamid	1999	0.56	0.43	0.51	0.36	<0.05	<0.05	0.16	–
Flufenacet	1999	0.19	0.07	0.08	0.07	0.05	<0.05	0.05	–

R: Platte River; W1, northern collector wells; W2, southern collector well; U, bank-filtered water; O, post-ozonation; CF, post-chlorination and filtration; T, treated water; GW, groundwater; –, no data; <, less than; concentrations in $\mu g\,l^{-1}$.

surface water decreased to 57% (5.79 $\mu g\,l^{-1}$) of the sum of all compounds (10.15 $\mu g\,l^{-1}$) analyzed for in treated drinking water (Table 4). Conversely, metabolites composing 19% (5.55 $\mu g\,l^{-1}$) of the sum of compounds (29.35 $\mu g\,l^{-1}$) analyzed for in surface water increased to 43% (4.36 $\mu g\,l^{-1}$) of the sum of all compounds (10.15 $\mu g\,l^{-1}$) analyzed for in treated drinking water. These findings confirmed data collected in 1997 and 1998.

However, these data, when discussed as the sum of parent compounds and metabolites, may mislead the water resource manager and consumer. Discussion of concentrations by class of compounds and, more specifically, by analyte, including all potential metabolites, provides better understanding of whether parent compounds and metabolites truly are created or destroyed during treatment. Some metabolites decreased during ozonation, others increased. However, uncertainties in mass-balance calculations arise from a lack of analytical procedures for a large number of metabolites (or disinfection by-products) created through natural or anthropogenic physical, chemical, or biological treatment processes. Toxicological data for all herbicide compounds, including known and unknown metabolites, also are lacking. The discussion regarding the effect of chemical and physical treatment of the herbicides in the plant therefore focuses on the data collected in 1999, because changes in concentrations are the

Table 4
Summary of concentrations herbicides and metabolites and ratio of herbicide concentration of sampling site to river site, 1999

Analytes	R (site 1)	W1 (site 2)	W2 (site 3)	U (site 4)	O (site 5)	CF (site 6)	T (site 7)
Parent triazines	14.03	10.60	12.08	12.89	4.99	3.94	4.67
Triazine metabolites	2.81	3.29	3.63	2.96	4.86	3.70	3.54
All triazines	16.84	13.89	15.71	15.85	9.85	7.64	8.21
Parent acetamides	9.77	–	3.95	2.94	1.08	0.78	1.12
Metabolites of acetamides	2.74	–	3.33	4.07	0.86	0.82	0.82
Acetamides	12.51	–	7.28	7.01	1.94	1.60	1.94
All parent compounds	23.80	–	16.03	15.83	6.07	4.72	5.79
All metabolites	5.55	–	6.96	7.02	5.73	4.52	4.36
All herbicides (parent compounds and metabolites)	29.35	–	22.29	22.86	11.79	9.24	10.15
Ratio of all parent compounds at sampling site to river site (%)	100	–	67	67	26	20	24
Ratio of all metabolites at sampling site to river site (%)	100	–	125	126	103	81	79
Ratio of all herbicide concentrations (parent compounds and metabolites) at sampling site to river site (%)	100	–	78	78	40	31	35

R: Platte River; W1, northern collector wells; W2, southern collector well; U, bank-filtered water; O, post-ozonation; CF, post-chlorination and filtration; T, treated water; –, no data; concentrations in $\mu g\ l^{-1}$ unless otherwise indicated.

most obvious—largest concentrations present in bank-filtered water and largest differences in values between treatment steps.

3.1. Triazines

Concentrations of ATR decreased 14% from the ATR concentration observed in the Platte River during bank filtration in 1999, when nearly undiluted river water was present in the water collected from the collector wells (Table 2). Concentration of ATR decreased 84% from the ATR concentration observed in the Platte River during bank filtration in 1997, when the collector wells pumped a mixture of river and groundwater. These data illustrate how well construction (distance of laterals from the river) and well management (pumping rates and selection of laterals) can alleviate the effects of contaminants present in a river (Verstraeten et al., 1999a).

In water from the river and the collector wells, DEA, DIA, HA, HDEA, HDIA, and DDA (metabolites of ATR), and CAM and CAC (metabolites of CYA) were detected. Concentrations of parent compounds, especially ATR, decreased through bank filtration. In 1998, concentrations of parent compounds decreased by 51% for ATR and 29% for CYA. Because a larger component of river water was pumped in 1999 than in 1998, attenuation of ATR through bank filtration decreased from 51% in 1998 to 14% in 1999. Similarly, attenuation of CYA decreased from 29% in 1998 to 10% in 1999.

DEA and DIA were attenuated by about 45% during bank filtration in 1998 and less than 15% in 1999. Concentrations of the other triazine metabolites generally remained less affected and concentrations of the acids generally remained unchanged. In 1998, increases in CAM, CAC, DCAC of up to 488% were documented. Overall, larger percentages of metabolites of CYA than of ATR were created during bank filtration. The DAR, the deethylatrazine-to-atrazine ratio (Table 2), of water from the river and collector well sites were very similar and remained below 0.20, indicating relatively low degradation rates of ATR to DEA in agricultural soils and during bank filtration. The DAR generally is about 0.10 in soil water soon after application (Scribner et al., 2000).

During ozonation, concentrations of ATR decreased by about 62% in 1999 (Fig. 3). This

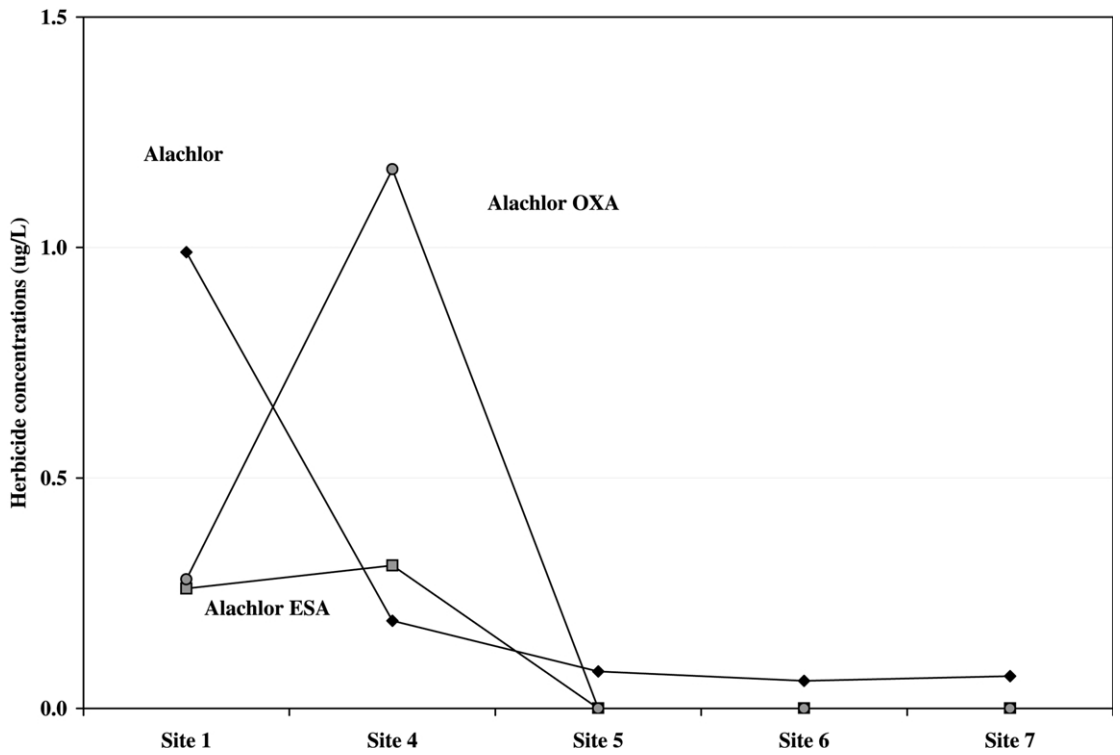
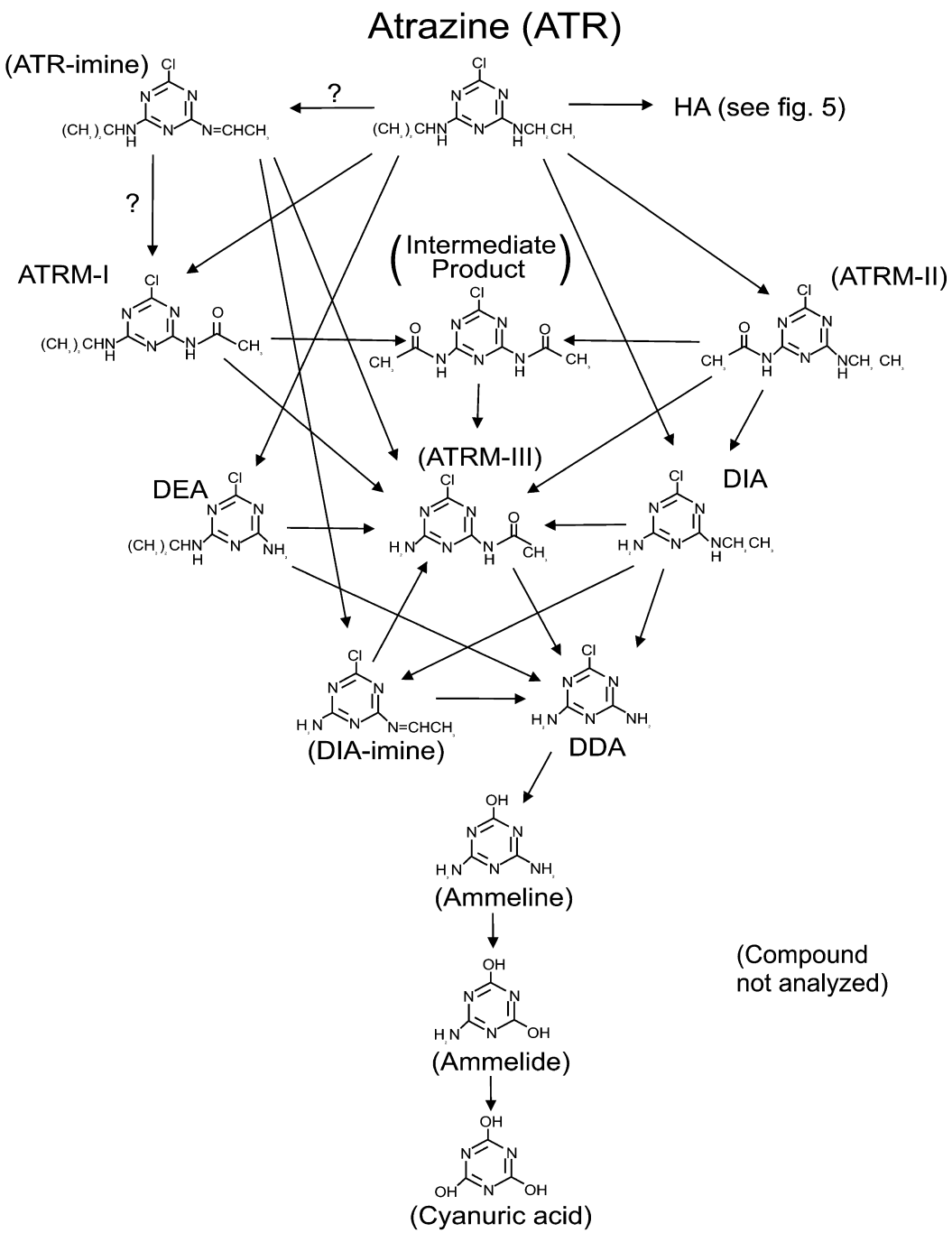


Fig. 3. Concentrations of atrazine, total organic carbon, and atrazine metabolites through the drinking water treatment process, 1999.

decrease depends on the ozone demand of the water, which, in turn, is affected by other water-quality factors (Verstraeten et al., 1999b). Comparison of total organic carbon (TOC) concentrations to triazine concentrations indicates that organic components present in river water may be reduced by bank filtration but generally are more stable in solution than the triazines. In 1999, TOC varied from 11.0 mg C l^{-1} in the Platte River (site 1), to 8.3 and 8.8 mg C l^{-1} in the collector wells (sites 2 and 3, respectively), 8.3 mg C l^{-1} in bank-filtered water (site 4), 7.3 mg C l^{-1} after ozonation (site 5), and 7.4 mg C l^{-1} in finished water (site 7). These data also indicate that a substantial amount of ozone may have been consumed by the overall organic components present in the bank-filtered water (Fig. 3) which agrees with findings of Hapeman et al. (1998) and Ma and Graham (1999).

Degradation of ATR proceeds during oxidation by dealkylation, deamination, and dehalogenation and tends to shift towards the more polar compounds as the pH increases (Kearney et al., 1988). Four primary and three secondary products of ATR are created through ozonation by removal or oxidation of the alkyl groups (Fig. 4). Hapeman-Somich (1991, 1992) and Hapeman (1994) in laboratory studies concluded that: (1) the alkyl chains of *s*-triazines and acetamides were oxidized or removed; (2) in some cases the aromatic ring was oxidized and cleaved without dechlorination; (3) amino alkylgroups were the first site of attack and are removed or converted to the acetamide; and (4) the ozonation rate of *N*-ethyl was five times faster than the ozonation rate of *N*-isopropyl. Recently, in a laboratory study, Acero et al. (2000) identified two additional by-products with an imine group. These researchers also suggested that the *N*-ethyl group seems to be more reactive than the *N*-isopropyl group and, while the ethyl group mainly reacts to acetamide or imine derivatives, the isopropyl group reacts mainly through dealkylation of the free amino group and that acetamides tended to be refractory to ozone attack (Acero et al., 2000).

In our study, the oxidation of atrazine and its by-products occurred through the oxidation of the



Modified from Hapeman-Somich, *et. al.* (1992) and Acero *et. al.* (2000)

Fig. 4. Ozone degradation pathway of atrazine (compounds in parentheses not analyzed).

N-acetyl groups, and, to a lesser extent, the *N*-isopropyl groups of ATR, DIA, and DEA. In 1999, DEA concentrations increased from 0.85 to 1.60 $\mu g\,l^{-1}$ (188%), DIA concentrations increased from 0.41 to 0.69 $\mu g\,l^{-1}$ (168%), and DDA concentrations increased from 0.21 to 0.65 $\mu g\,l^{-1}$ (309%) through ozonation. Consequently, the DAR was modified from a value of about 0.07 in bank-filtered water to 0.36, a value not commonly found in surface water and generally larger than those of groundwater (Table 2). Therefore, the value of the DAR not only is an indicator of nonpoint-source pollution, but also can be used to indicate degradation of herbicides during water treatment. Analyses of ATRM-I confirm the presence of this product only after ozonation (Table 2; Fig. 3), at concentrations of about 0.50 $\mu g\,l^{-1}$. Samples were not analyzed for the other two amides (ATRM-II and ATRM-III) or either of the imines (ATR–imine and DEA–imine) (Fig. 4).

The average difference in the combined amount of ATR and its analyzed metabolites plus propazine and simazine before (13.67 $\mu g\,l^{-1}$) and after (8.36 $\mu g\,l^{-1}$) ozonation is 5.31 $\mu g\,l^{-1}$ in samples collected in 1999, suggesting that 39% of the original amount of ATR and its metabolites are in the form of ATRM-II, DDA, ATRM-III, ATRM-I, and other unidentified compounds or that ring cleavage could have occurred. Through ozonation, the following products increased by: 8% DEA, 5% ATRM-I (0.50 $\mu g\,l^{-1}$), 3% DIA (0.27 $\mu g\,l^{-1}$), and 5% DDA (0.44 $\mu g\,l^{-1}$). In these calculations, the degradation of CYA to DIA and further degradation to other metabolites were not identified. Most of the metabolites that were not quantified in this study are hypothesized to be in the ****form of the imines and amides, especially the ATR–imine. ATR–imine probably is present in about the same concentrations ($\sim$4.00 $\mu g\,l^{-1}$ or $\sim$43% of the ATR, PROP, plus SIM metabolites) as ATR, consistent with the findings of Acero et al. (2000). Assuming our hypothesis is correct, one could infer that dechlorination of the parent compound is not significant. The order of importance of the metabolites of ATR, excluding HA, that were identified during this study is DEA > DDA and ATRM-I > DIA.

The strongest difference between the results of this study and Hapeman's study (Hapeman et al., 1995) is the formation of less DEA. In our study, the ozonation rates of *N*-ethyl group were about two times faster than *N*-isopropyl group, instead of five times faster as suggested by Hapeman and others (1995), in part because of dissimilar kinetic conditions between field and laboratory environments. Imines have been shown to be important, but short-lived, by-products of ATR through ozonation (Acero et al., 2000). These researchers suggested that at an ozone dosage of 2 $mg\,l^{-1}$, the main metabolites of ATR would be ATR–imine (67%) > ATRM-II (24%) $\gg$ DIA (5%) > DEA (4%) $\gg$ ATRM-III > DIA–imine > DDA.

Degradation of parent products strongly depends on pH (Acero et al., 2000). However, differences in pH probably do not affect the relative amounts of metabolites that are formed, notably when the parent compound is exposed to ozone for less than 1 h. In general, Acero et al. (2000) concluded that the higher the pH, the more DEA, instead of DIA, would be formed; in other words, degradation through the *N*-isopropyl group is more important than degradation through *N*-acetyl group. Formation of DIA and DEA also increased with reaction time. In our study, the pH of the surface water was greater than 8.5 and more DEA than DIA was formed, confirming their findings (Acero et al., 2000). Kearney et al. (1988) reported that at a pH of above 8.0 there was a major shift toward the more oxidized products and an acceleration of the oxidation process. The differing results of our study with those of other studies might be related to differences in a field study versus a study conducted within a laboratory environment and the presence of differing concentrations of TOC.

It is possible that a similar degradation process occurs for HA (Fig. 5), because dealkylated by-products were generated through ozonation. HDEA concentrations increased about twofold (192%) from 0.13 to 0.25 $\mu g\,l^{-1}$, and HDIA concentrations increased slightly less than twofold (182%) from 0.11 to 0.20 $\mu g\,l^{-1}$, respectively (Table 2). Here again, ozonation through the oxidation of the *N*-acetyl groups and the *N*-isopropyl groups occurred. In this case, the groups appeared to have had similar reaction times. The hypothesis is that similar amounts of ammeline and DDA are created through ozonation. However, no data exist to confirm this hypothesis.

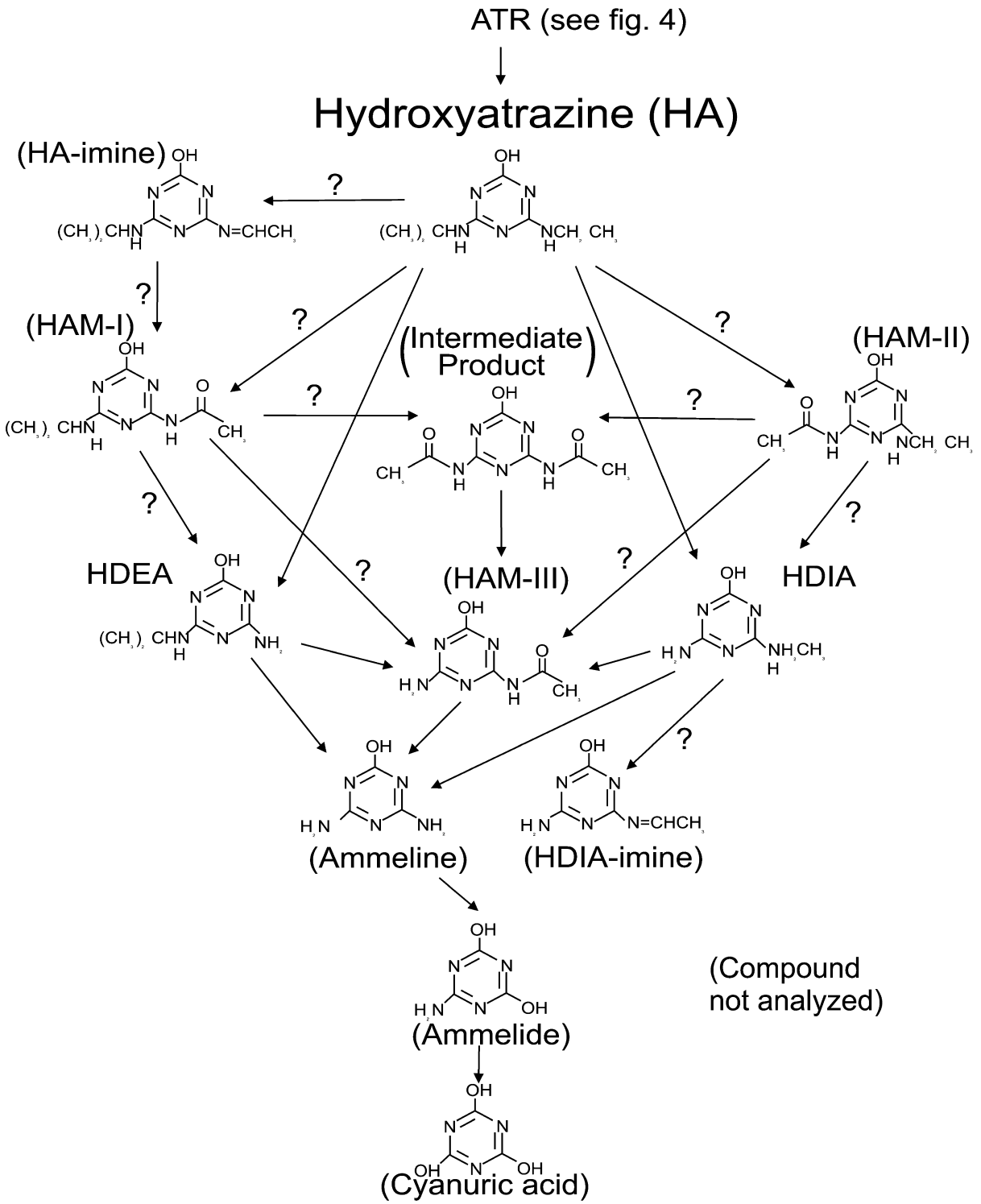


Fig. 5. Proposed ozone degradation pathway of hydroxyatrazine.

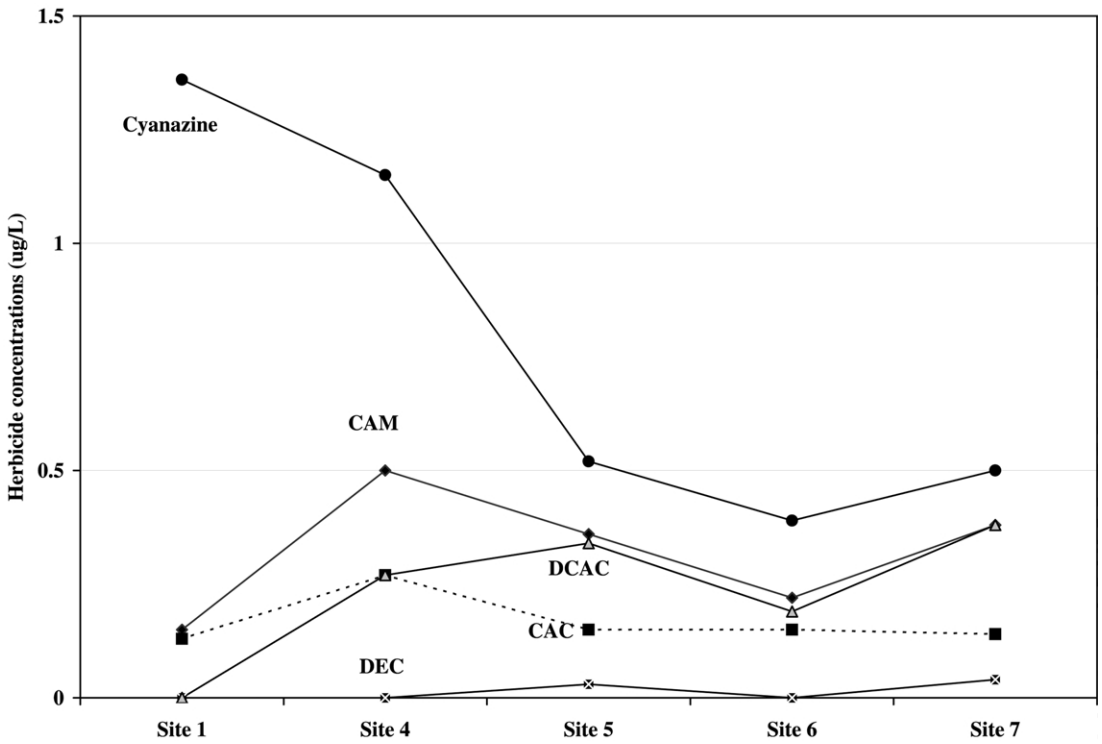


Fig. 6. Concentrations of cyanazine and cyanazine metabolites through drinking water treatment, 1999.

It is also possible that CYA underwent a similar degradation process as ATR through ozonation (Figs. 6 and 7). The data illustrate that while CYA concentrations decreased through ozonation, very small amounts of DEC ($<0.01-0.03\ \mu g\ l^{-1}$; unknown %) and DCAC (from 0.23 to $0.34\ \mu g\ l^{-1}$; 130%) increased, and CAC ($0.27-0.15\ \mu g\ l^{-1}$; 56%) concentrations decreased. Because DIA is a known metabolite of CYA, CYA probably also contributed to the generation of DIA and DDA, as did ATR.

3.2. Acetamides

During bank filtration, concentrations of parent acetamides decreased. In 1998, concentrations of parent acetamides decreased by 60% (76% ALA, 72% ACET, 52% METO, 9% dimethenamid and 58% flufenacet) from site 1 to site 4 (Table 3) more than parent triazine compounds (14%). The decreases in these parent compounds were similar in 1999. Increases in concentrations of the ESA and OXA (degradation products) of ALA (4 and 39%), ACET (4 and 26%), and METO (48 and 11%) (Table 3) ranging from 104 to 148% were observed in 1999. These changes in concentrations were smaller, or decreases were noted, during the 1998 sampling event. The 1999 data suggest that the parent acetamides generally are less stable or tend to be more adsorbed to sediments than the triazines—60% versus 24% removal—and, therefore, tend to be more attenuated during bank filtration. Thus, acetamides (half-life of 15–30 days) not only are less stable than triazines (half-life of 30–60 days) in a soil environment, but also when exposed to ozone.

During ozonation, the acetamides—ALA, ACET, METO, dimethenamid, and flufenacet—generally decreased about 63% in 1999 (Fig. 8; Tables 3 and 4), similar to the triazines. The metabolites created during the ozonation process were not quantified because of a lack of analytical methods, but substituted anilines probably are formed. ESA and OXA metabolites generally decreased in concentration by 79% in 1999. Ozonation of acetamide compounds typically does not involve dehalogenation, but does create

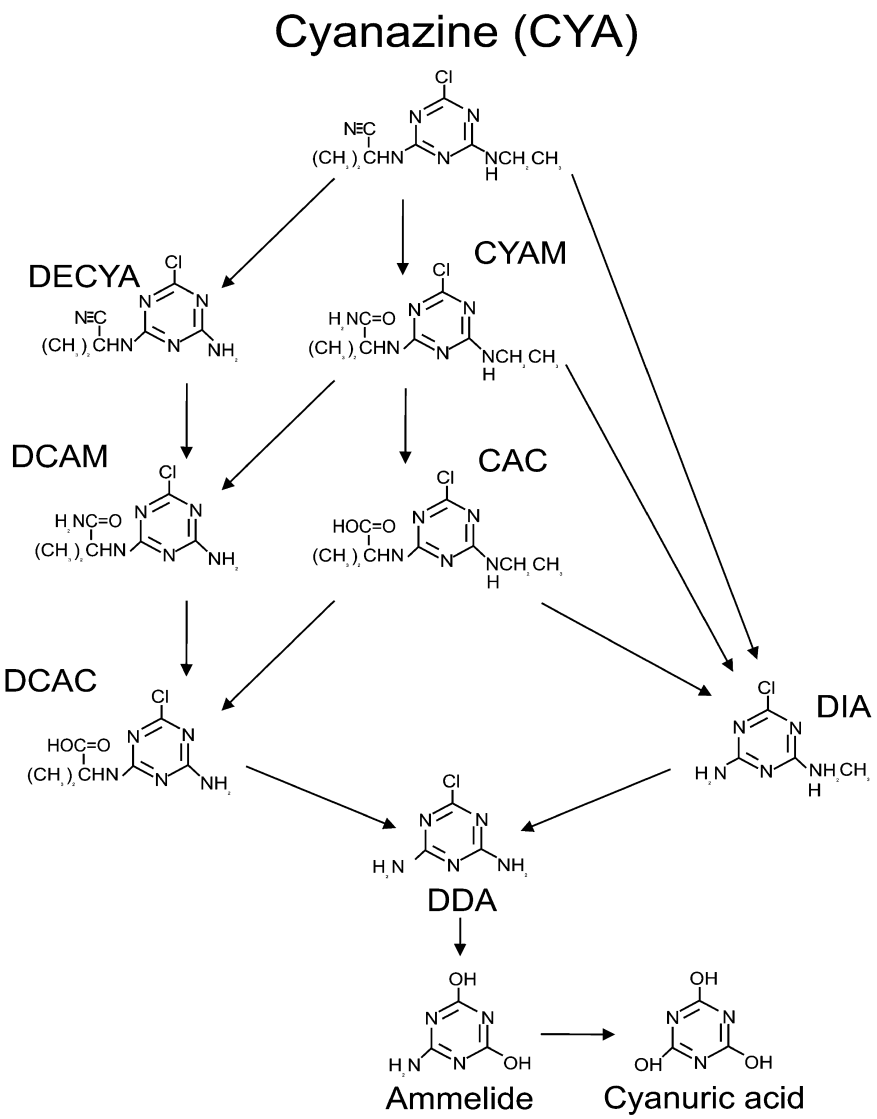


Fig. 7. Proposed ozone degradation pathway of cyanazine.

alcohols, carbonyls, and carboxylic acids by cleaving of double bonds, opening of aromatic rings, and removal or oxidation of alkyl groups (Hapeman-Somich, 1991). Hapeman-Somich (1991) suggested that: (1) the primary product of ALA from ozonation in water was a compound with one of the ethyl chain converted to an acetyl group; (2) METO underwent oxidation at the ethyl-side chain; and (3) the methoxy carbon and the carbon is attached to the methoxy group. More investigation and methods development is needed to further identify and quantify the metabolites of acetamides created during bank filtration, ozonation, and chlorination.

Implications for drinking water regulations in the United States. Analyzing for parent compounds alone precludes a full understanding of the transport and fate of herbicides and their impact on the ecosystem and human health. Although significant amounts of parent compounds probably can be removed by bank filtration and ozonation, the toxicity of the remaining

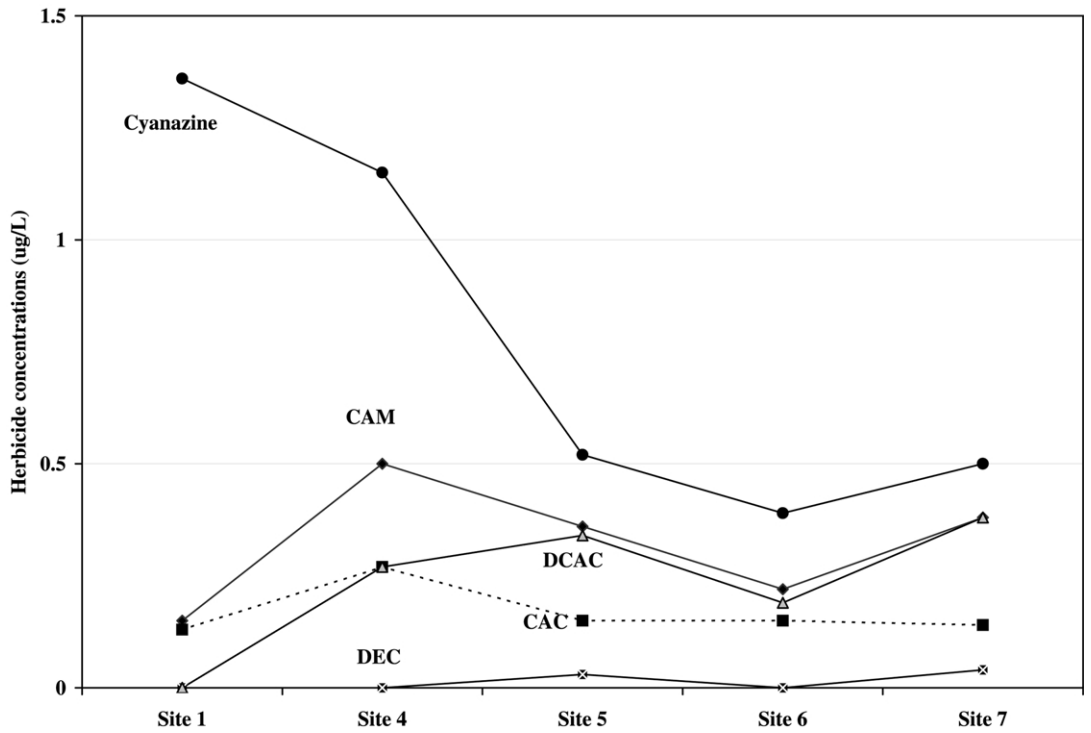


Fig. 8. Concentration of alachlor and their metabolites through drinking water treatment, 1999.

compounds is of concern as long as no ring cleavage occurs. It is important for municipalities actively using or intending to use bank filtration or ozonation as part of their drinking water treatment processes to understand: (1) to what extent the herbicides degrade during drinking water treatment, (2) which by-products are created during drinking water treatment, (3) to what extent these by-products are simultaneously created and destroyed, and (4) the toxicological implications of the treatment procedures (Hapeman-Somich, 1992).

In some cases, pesticide metabolites may be several times more toxic than the original compound (US Environmental Protection Agency Science Advisory Panel, Federal Insecticide, Fungicide, and Rodenticide Act, written communication, 2000). Metabolites of herbicides could be phytotoxic and toxic to animals (Behki and Khan, 1986; Day, 1991; Kaufman and Kearney, 1970; Stratton, 1984). A study by Papilloud et al. (1996) suggested that DIA and DEA are less toxic than their parent compound. ESA metabolites might be less toxic than their parent compounds (Dapson, 1992), but the toxicity of acetanilide metabolites, which are dehalogenated compounds, generally remains unknown because these by-products have been identified and documented only recently (Kalkhoff et al., 1998).

Differences in pH, temperature, turbidity, and dissolved organic materials in water make predictions of removal or attenuation of any herbicide and its metabolites during bank filtration very difficult. Moreover, varying conditions in a treatment plant such as chemical and physical treatment procedures, flow rate, filter rate, and chemical dose also affect the presence of herbicides in the drinking water. Currently, the best-known methods for treatment of pesticides, including herbicides, are (1) high pH in combination with oxidation processes—UV/H_2O_2, O_3/H_2O_2, or Fenton's reagent (ferrous salts/H_2O_2, a hydroxyl radical generating system) reactions, or (2) the use of granular (GAC) or powder (PAC) activated carbon (Hapeman-Somich, 1992; Lambert et al., 1996; Orlandini et al., 1996).

Other means of destroying triazines and acetamides

exist. Hapeman-Somich (1991) suggested that complete mineralization of herbicides could be obtained by ozonation in concert with microbial degradation processes with specific organisms rather than indigenous soil microbes. Another way to improve the drinking water-quality is to alleviate the problem at the source through coordinated efforts between state and local governments and agricultural producers.

In the United States, the pesticide regulations have been set for a few parent compounds but not metabolites. The US Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for ATR is 3.00 $\mu g\,l^{-1}$ and for ALA is 2.00 $\mu g\,l^{-1}$. Additional herbicides and metabolites on the Contaminant Candidate List of USEPA include metolachlor, acetochlor, alachlor ESA, and metabolites of ATR (Thomas Speth, US Environmental Protection Agency, written communication, 2000). An MCL for total triazine of 20 $\mu g\,l^{-1}$ is currently under discussion in the United States because the health risk associated with the consumption of metabolites of pesticides may be similar to those of the parent pesticides. In Europe, the pesticide standards for drinking water have been set at $<0.10\ \mu g\,l^{-1}$ for concentrations of individual parent and metabolites after drinking water treatment, e.g. atrazine and metabolites, and $<0.50\ \mu g\,l^{-1}$ for the sum of all pesticides and metabolites present in drinking water.

In summary, large concentrations of parent compounds, such as triazines and acetamides, decreased during bank filtration and ozonation, probably with minor dechlorination. Metabolites, either existing prior to treatment or created during ozonation, decreased or increased during drinking water treatment. Our findings suggest that ozonation of water containing herbicides in a public water supply potentially shifts the assessment of the risk of human consumption of the parent compound to its degradation products and identifies the need for additional analytical methods development, evaluation of the presence of metabolites in drinking water, and determination of the toxicological character of the most common metabolites in drinking water. Nevertheless, when concentrations of herbicides are of concern, treatment processes, such as use of higher doses of ozonation, additional means of oxidation (chlorination) in combination with granular or powdered activated carbon, or microbial degradation, could be used. Furthermore, improving management practices at the source when feasible and thereby reducing herbicide concentrations in streams ultimately would alleviate the risk to human health associated with their consumption in drinking water.

Acknowledgments

We thank the City of Lincoln for their support of this study. We also thank Betty Scribner and Lisa Zimmerman of the US Geological Survey for ensuring the integrity of the data and Drs David Eckhardt and Michael Meyer of the US Geological Survey for their review of this document.

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