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# Treatability of chloro-s-triazines by conventional drinking water treatment technologies

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### Abbreviation:

ATZ: atrazine

DDA: didealkylatrazine

DEA: deethylatrazine

DI: distilled

DIA: deisopropylatrazine

EPA: US Environmental Protection Agency

GAC: granular activated carbon

GC-MS: gas chromatography-mass spectrometry

MCL: maximum contaminant level

MR: Missouri River

PAC: powdered activated carbon

PROP: propazine

SIM: simazine

SPE: solid-phase extraction

TCT: total chloro-s-triazine

## ABSTRACT

Recent research shows that herbicide atrazine (ATZ), simazine (SIM), and propazine (PROP), as well as their three chlorinated degradates—desethylatrazine (DEA), deisopropylatrazine (DIA), and didealkylatrazine (DDA)—may cause a common toxic effect in terms of endocrine disruption. The US Environmental Protection Agency (EPA) is currently considering a regulatory trigger based on the sum of these concentrations of these six chloro-s-triazines. While limited removal data exists for the parent compounds, little information is available for the degradates formed biologically and/or chemically in the environment and in the treatment plants. It is therefore critical to assess the removal efficiency in a typical water plant of the parent herbicides, as well as the daughter products. In this work, conventional drinking water treatment technologies were evaluated under typical water treatment plant conditions to determine their effectiveness in removing six chloro-s-triazines: ATZ, SIM, PROP, DEA, DIA, and DDA. Experiments were conducted using synthetic solutions prepared by spiking both distilled water and Missouri River water with the study compounds. Two powder activated carbons (PAC)—Calgon WPH and Norit HDB—were shown to be partially effective in removing the studied chloro-s-triazines. Ozonation efficiency varied, depending on different water sources, with respect to the removal of atrazine and didealkylatrazine. Coagulation/flocculation/sedimentation with alum and iron salts, excess lime/soda ash softening, and disinfection by free chlorine were all ineffective methods for removing chloro-s-triazines. It appears that chloro-s-triazine compounds are not readily removed by most conventional drinking water treatment processes, with the exception of use of activated carbon.

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## 1. Introduction

Atrazine (ATZ) is one of the most widely used herbicides worldwide. In the US alone, ATZ use is approximately 75 million pounds annually (US Environmental Protection Agency (USEPA), 1994). Due to its frequent use, ATZ and its metabolites are commonly found in groundwater and surface waters of the Midwestern, Southern and Eastern United States (Adams et al., 1990; Jiang et al., 2005; Thurman et al., 1991, 1992; Schottler et al., 1994; Barbash et al., 1999; Nelson et al., 2001). ATZ was categorized as a “possible human carcinogen” in the 1980s. As a result, the US Environmental Protection Agency (USEPA) promulgated a 3 µg/L maximum contaminant level (MCL) for ATZ (and 4 µg/L for simazine (SIM)) for drinking water (USEPA, 2003). In April of 2002, USEPA announced its preliminary determination that three triazine pesticides—ATZ, SIM, and propazine (PROP), and three metabolites—didealkylatrazine (DDA), deethylatrazine (DEA) and deisopropylatrazine (DIA)—share a common mechanism of toxicity with respect to endocrine disruption (USEPA, 2000). Because these compounds may act in the same manner to affect reproductive functions and development, regulations based on total chloro-s-triazines (TCT) are currently being considered by the USEPA (USEPA, 2000).

Conventional water treatment processes that are not effective for removing ATZ include chlorination, aeration, filtration, and coagulation (Lykins et al., 1986; Miltner et al., 1989). Technologies that are at least partially effective for ATZ in controlling chloro-s-triazine include powdered activated carbon (PAC) (Njam et al., 1991; Adams and Watson, 1996), granular activated carbon (GAC) (Hulsey et al., 1993; Pryor et al., 1999), ozonation (Adams and Randtke, 1992; Acero et al., 2000, Verstraeten et al., 2002), membranes (Devitt et al., 1998; Seacord et al., 1999), and biofiltration (Zhang et al., 1991; Galluzzo et al., 1999). These may be used individually as well as in integrated systems. For example, a study of GAC by Hulsey et al. (1993) showed that GAC can be effective in removing ATZ as well as DEA and DIA. Studies of the effectiveness of membranes show that their effectiveness varies significantly, although smaller membrane sizes (e.g.,

reverse osmosis and nanofiltration) are generally effective for controlling triazines (e.g., Devitt et al., 1998; Seacord et al., 1999). Adams (2003) presented a detailed literature review on control of TCT in conventional drinking water treatment plants.

Due to the likelihood that water utilities, in the future, may be required to remove both parent chloro-s-triazines as well as metabolites from drinking water, there is a need to assess the effectiveness of conventional treatment technologies for their removal. There is little information available about treatment of these chloro-s-triazine metabolites, especially DDA, for which only a few analytical methods exist. To address this need, bench-scale screening tests were performed in this work to evaluate the efficiency of removal of three parent herbicides—ATZ, SIM, PROP—and three major chlorinated metabolites—DIA, DEA and DDA—under typical drinking water treatment conditions.

## 2. Materials and methods

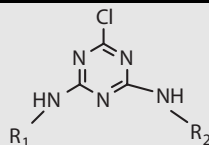
All water treatment chemicals were at least reagent grade and were obtained from Fisher Scientific (Fair Lawn, New Jersey, USA). Properties and structures of the six triazines investigated in this work—ATZ, SIM, PROP, DEA, DIA, and DDA—are presented in Table 1. Study compounds were obtained from Supelco (Bellefonte, PA, USA). Deuterated triazine standards were obtained from EQ Lab (Atlanta, Georgia, USA). Individual stock solutions of 500 mg/L ATR, PROP, DEA, and DIA were prepared by dissolving 15.0 mg of each respective triazine in 30.0 mL of methanol. Individual stock solutions of 100 mg/L SIM and DDA were prepared by dissolving 10.0 mg of each compound into 100.0 mL of methanol. The PACs used in this work, Calgon WPH Pulv and Norit HDB, were obtained directly from Calgon Carbon Corp. (Pittsburgh, PA, USA) and Norit American Inc. (Marshall, TX, USA), respectively. The BET surface areas are 1027 and 546 m<sup>2</sup>/g for the WPH and HDB, respectively (Jain et al., 2005). The total pore volume (< 400 Å) are 0.55 and 0.48 m<sup>3</sup>/g, respectively (Jain et al., 2005).

Table 1 – Selected properties and chemical structures of study compounds

Compound	CODE	CAS #	Formula	R <sub>1</sub>	R <sub>2</sub>	M.Wt. (Daltons)	pKa <sup>a</sup>	Aq. sol <sup>b</sup> (mg/L)
Atrazine	ATZ	1912-24-9	C <sub>8</sub> H <sub>18</sub> ClN <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub> -	(CH <sub>3</sub> ) <sub>2</sub> CH-	215.7	2.35 ± 0.50	33
Simazine	SIM	122-34-9	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub> -	CH <sub>3</sub> CH <sub>2</sub> -	201.7	3.10 ± 0.50	5
Propazine	PROP	139-40-2	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH-	(CH <sub>3</sub> ) <sub>2</sub> CH-	229.7	2.40 ± 0.50	3.8–8.6
Deethylatrazine	DEA	6190-65-4	C <sub>6</sub> H <sub>10</sub> ClN <sub>5</sub>	H-	(CH <sub>3</sub> ) <sub>2</sub> CH-	187.6	2.44 ± 0.40	3200
Deisopropylatrazine	DIA	1007-28-9	C <sub>5</sub> H <sub>8</sub> ClN <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub> -	H-	173.6	2.55 ± 0.50	670
Didealkylatrazine	DDA	3397-62-4	C <sub>3</sub> H <sub>7</sub> ClN <sub>5</sub>	H-	H-	147.5	2.61 ± 0.50	NA

<sup>a</sup> Scifinder Scholar 2004.

<sup>b</sup> <http://chemfinder.cambridgesoft.com/>



**Table 2 – Characteristics and background concentration of chloro-s-triazines of ground water and filtered Missouri River water used in this study**

Item	Missouri river water			Groundwater
	Oct. 2003	Feb. 2004	May 2005	
Temperature (°C)	22	10	21	19
pH	8	8	10	7
Alkalinity (mg/L as CaCO <sub>3</sub> )	155	203	210	225
Total hardness (mg/L as CaCO <sub>3</sub> )	223	258	264	310
Calcium hardness ((mg/L as CaCO <sub>3</sub> )	165	215	195	154
Turbidity (NTU)	51	23	126	0
DOC (0.45- $\mu$ m Nylon filter)	5	7	7	NA
TDS (mg/L)	370	362	273	277
DDA ( $\mu$ g/L)	0	0.04	0	0
DIA ( $\mu$ g/L)	0	0	0	0
ATZ ( $\mu$ g/L)	0.1	0.23	0.39	0
PROP ( $\mu$ g/L)	0	0	0	0
SIM ( $\mu$ g/L)	0	0.05	0	0
DEA ( $\mu$ g/L)	0.07	0.04	0	0

NA—not available.

### 3. Sample preparation

Two aqueous stock mix solutions containing 25 mg/L of four (i.e., ATZ, DEA, DIA and DDA) or six compounds (i.e., ATZ, SIM, PROP, DEA, DIA and DDA) were prepared from each individual methanol-based stock solution. Samples were taken from the standard mix or individual stock solutions (as appropriate) and prepared for various treatments by spiking either distilled (DI) water, groundwater, or Missouri River (MR) water. The MR water was collected from the MR near Jefferson City, MO, USA at three different times during the period of the experiment (October 2003, February 2004 and May 2005). Unfiltered MR water was used for coagulation experiments, while groundwater from local wells in Rolla, MO was used in softening experiments. The MR water was filtered through a 0.45- $\mu$ m filter for prior to the chlorination, PAC adsorption, and ozonation experiments. The characteristics of the waters and the background triazine concentration of MR water are provided in Table 2.

### 4. Analytical methods

After processing via a specific treatment method, samples were concentrated using solid-phase extraction (SPE) and analyzed using gas chromatography-mass spectrometry (GC-MS). In the SPE procedure, 125 mL of a sample was filtered and then passed through preconditioned Waters MCX (Milford, MA, USA) and Supelco Envi-Carb (Bellefonte, PA, USA) cartridges in a series under slight vacuum. The cartridges were eluted with methanol and methylene chloride and then evaporated to dryness under a nitrogen stream. The concentrated samples were then dissolved in acetone and quantitatively analyzed by GC-MS in selected ion monitoring (SIM) mode. Deuterated triazine standards were used as the internal quantitation standards. The GC-MS system was

equipped with an Agilent 6893 GC with a HP-5MS capillary column and an Agilent 5973 Mass Selective Detector (MSD). The limit of detection was 0.02  $\mu$ g/L for ATZ and PROP, and 0.01  $\mu$ g/L for SIM, DEA, DIA, and DDA (Jiang and Adams, 2005). The detailed SPE/GC-MS development and procedure validation is presented elsewhere (Jiang and Adams, 2005).

### 5. Experiment design

In these experiments, five common water treatment processes were examined for efficiency in removing chloro-s-triazines. Each of processes is described below.

#### 5.1. Metal salt coagulation

Aluminum sulfate [ $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ] and ferric sulfate [ $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ ] were studied as coagulants. Coagulation experiments were conducted in a six-gang stirrer (Phipps & Bird PB700) at a pH of 6.8. Coagulant dosages were 0, 20, 40, 64 and 107 mg/L of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  or 0, 25, 42, 85, 127, and 169 mg/L of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ .

ATZ, DDA, and a stock-mix standard solution was diluted into 1 L of MR water to create a solution with a concentration of 3  $\mu$ g/L of each compound. After addition of chemical, the samples were mixed at 100 rpm for 1 min ( $G = 100 \text{ s}^{-1}$ ), flocculated at 30 rpm for 20 min ( $G = 24 \text{ s}^{-1}$ ), and then allowed to settle for 3 h. Samples were then filtered through a 0.45- $\mu$ m Nylon filter prior to SPE and GC-MS analysis.

#### 5.2. Lime softening

In the lime softening experiments, the total, calcium and magnesium hardness of the tap water used was determined to be 310, 154, and 156 mg/L as CaCO<sub>3</sub>, respectively. The alkalinity of the groundwater was 225 mg/L as CaCO<sub>3</sub>. Excess lime/soda ash softening was used to remove both calcium

and magnesium hardness as  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . Required lime and soda ash dosages were determined to be 539 and 90 mg/L as  $\text{CaCO}_3$ , respectively.

The softening experiments were conducted as follows. DDA, ATZ or the stock-mix standard solution were diluted in 1 L of water to create a solution with a concentration of  $3\ \mu\text{g/L}$  of each compound. Next, the lime and soda ash solution were added and the pH was immediately adjusted to  $11.3 (\pm 0.25)$ , using a 20% sodium hydroxide solution. Next, the solutions were mixed/flocculated/settled in the manner described for coagulation above. Samples were filtered, concentrated and analyzed, as also described above.

### 5.3. Powered activated carbon adsorption

PAC adsorption experiments were conducted in a six-gang stirrer with both MR and DI water on  $3\ \mu\text{g/L}$  of DDA, ATZ, or the standard-mix solution. After placing the appropriate solution into five separate beakers, PAC was added at dosages of 0, 5, 10, 20, and 50 mg/L. The solutions were mixed for 4 h prior to sampling to simulate the retention time in an actual treatment plant. Additional experiments were conducted with  $3\ \mu\text{g/L}$  of the mix solution in both water matrixes using PAC dosages of 5 and 20 mg/L, at 24 h contact time. The samples were taken at 0.5, 4, and 24 h, respectively to test the effect of contact time on the removal of chloro-s-triazines. Samples were filtered, concentrated, and analyzed in the manner described for coagulation. Realizing that the common PAC dosage in a drinking water plant is on the order of 1–2 mg/L for odor and taste control, a set of additional experiments was conducted later in a 1, 2, 5, 10, and 30 mg/L dosage in MR and DI water with a 4-h contact time for both WPH and HDB carbon. The spiked compounds were either  $5\ \mu\text{g/L}$  of ATZ or  $5\ \mu\text{g/L}$  of a mix of ATZ, DEA, DIA, and DDA.

Sorption isotherm experiments were also conducted as follows. Stock solutions were diluted to 500 mL in glass bottles to create a concentration of  $15\ \mu\text{g/L}$  of DDA, ATZ, or the triazine mix in DI water (buffered with 10 mM of  $\text{K}_2\text{PO}_4$ ) or MR water. The pH of these solutions was adjusted to pH 7 by 2% of sodium hydroxide or 2% of sulfuric acid. The sample bottles were then placed in a tumbler and mixed continuously for 1 week to maintain sufficient sorption to PAC particles and to allow a condition of equilibrium to be achieved. The contact time selected was based on kinetic study (data not shown). Samples were filtered, concentrated, and analyzed in the manner described earlier for coagulation samples.

### 5.4. Chlorination

The chlorination experiments were conducted by placing 1 L of filtered MR or DI water (buffered with 20 mM phosphate) at a pH of 6.1 into beakers on a six-gang stirrer. After spiking with an appropriate standard triazine stock solution, chlorine was added in the form of hypochlorite ( $\text{OCl}^-$ ) ion. Oxidation of the study compounds by free chlorine was conducted at a chlorine concentration of 2.0 mg/L as  $\text{Cl}_2$ . Aliquots were collected for 30 min at 5-min intervals and immediately quenched using a 20% excess of sodium sulfite. SPE and GC-MS analysis was conducted on unfiltered samples.

### 5.5. Ozonation

The ozonation experiments were conducted in 500 mL amber glass bottles with no headspace using both DI (buffered with 10 mM  $\text{K}_2\text{PO}_4$ ) and MR water at pH 6 ( $\pm 0.25$ ) and 9 ( $\pm 0.25$ ). The aqueous phase ozone stock solution was produced using a PCI-WEDECO GLS-1 ozone generator (WEDECO Ozone Technologies, Inc. Charlotte, NC, USA). The ozone concentration was determined using a spectrophotometer at 254 nm based on an extinction coefficient of  $3000\ \text{M}^{-1}\text{cm}^{-1}$  (Liu et al., 2001). After spiking DDA and ATZ into reactors, an appropriate amount of ozone stock solution was then introduced to obtain ozone concentrations of 0, 1, 3, and 5 mg/L for DDA and 0, 0.2, 0.5, 0.7, 1, 3, and 5 mg/L for ATZ. The reaction bottles were then immediately capped, shaken for 1 min, and allowed to react for 30 min at room temperature before analysis.

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## 6. Results and discussion

### 6.1. Metal salt coagulation

Coagulation is the process by which chemicals are added to water to destabilize colloidal particles, allowing aggregation through flocculation, and followed by sedimentation. Concurrent removal of soluble species can occur through co-precipitation such as adsorption on the destabilized colloidal material, followed by concomitant removal of the colloids and the adsorbed species. At higher coagulant doses, precipitation of the coagulant metals as hydroxide was achieved, providing an opportunity for the triazines to co-precipitate on the hydroxide precipitate as well. The coagulation experiments were conducted in MR water to provide an opportunity for the co-precipitation of triazines to coagulated solids.

In this work, however, no significant removal ( $\alpha = 0.05$ ) of any of the triazines considered (including DDA) was achieved with alum or ferric salt coagulation (data not shown). This work suggests that the studied triazines (including DDA) are not likely to be effectively removed via a coagulation process alum or iron salts.

### 6.2. Excess lime/soda ash softening

The excess lime softening experiments were conducted on groundwater from Rolla, MO. During the precipitation processes, large specific surface areas are generated in solution due to the (initially) exceedingly small diameters of precipitate particles, thereby providing the opportunity for co-precipitation processes to occur (Letterman, 1999). Because this study employed excess lime softening, in which both  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  flocs were formed, the triazine compounds were presented with the opportunity to co-precipitate with at least two different types of solid.

In this work, however, no significant removal ( $\alpha = 0.05$ ) of any of the triazines was achieved during the softening process (data not shown). Thus, excess lime softening does not appear to be a significant means for use in removing the studied compounds in drinking water treatment plants.

6.3. Powered activated carbon adsorption

6.3.1. Plant simulation

Calgon WPH and Norit HDB PACs are commonly used in drinking water treatment plants for the removal of a wide range of synthetic organic chemicals, taste and odor compounds, and NOM. In these experiments, a 4-h contact time was employed with these two PACs to simulate typical processing conditions in water treatment plants. Additional samples were also taken at 0.5-, 4-, and 24-h contact times for a separate set of kinetic experiments.

In these experiments, the percent removal of DDA in DI water for WPH PAC dosages of 5 and 20 mg/L were 87% and 100%, respectively (Fig. 1, top). In MR water, significantly lower removal percentages were observed, specifically 69% and 100%, respectively, most likely due to competition with natural organic materials (NOM) in the water (Fig. 1, top). For Norit HDB, slightly lower DDA removals were observed than for Calgon WPH for both DI and MR waters, and lower capacities were again observed for NOM versus the DI waters (Fig. 1, bottom).

For ATZ, much higher removals were observed with both WPH and HDB than for DDA (Fig. 2). As with DDA, reduced capacity was observed in MR versus DI waters, presumably due to competition with NOM in the surface water.

Comparative and competitive sorption of the chloro-s-triazines were studied in a mixture in both DI and MR water with both PACs for a typical contact time of 4 h. At higher PAC dosages of 20–50 mg/L, removal of more than 90% of all triazines were observed for both PACs and in both DI and MR

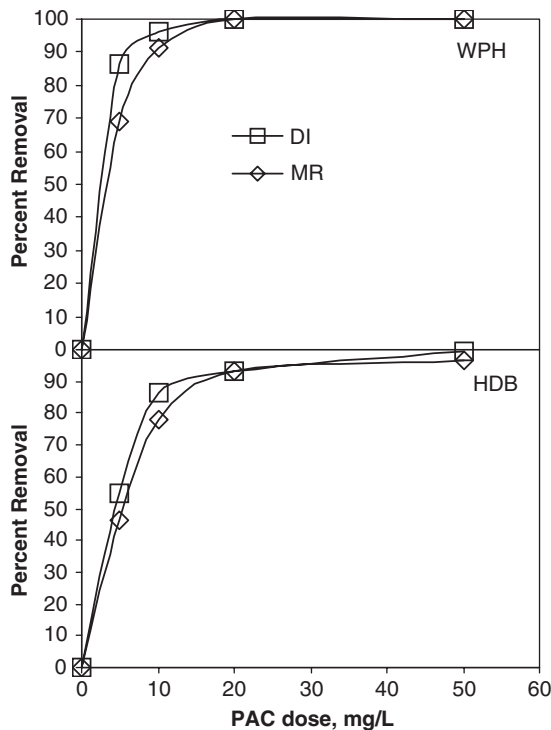


Fig. 1 – Removal of 3 µg/L of DDA by Calgon WPH and Norit HDB powder activated carbon with dosage of 0, 5, 10, 20 and 50 mg/L (at pH 7.5 and 4 h contact time) in DI and MR water.

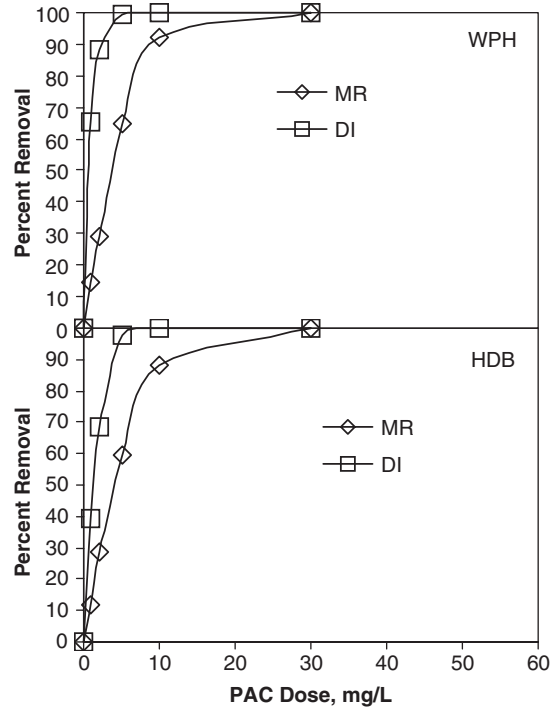


Fig. 2 – Removal of 5 µg/L of ATZ by Calgon WPH and Norit HDB powder activated carbon with dosage of 0, 1, 2, 5, 10 and 30 mg/L (at pH 7.5 and 4 h contact time) in DI and MR water.

waters, except for DDA and DEA in MR water by HDB (Fig. 3). At a PAC dosage of 5 mg/L, however, more than 80% and 35% removal rates were achieved for WPH and HDB, respectively (Fig. 3). At the low PAC dosages of just 1 or 2 mg/L that are commonly used in drinking water treatment plants for taste-and-odor control, very limited triazine removals were achieved (i.e., less than 40% in MR water and less than 60% in DI water) (Fig. 3).

The effect of contact time on triazine removal (from the mixture of triazines), with a PAC dosage of 5 mg/L, was studied for both PACs in DI and MR waters. Except for DDA, the adsorption of each triazine was more rapid in DI water than in MR water (Fig. 4). In some cases, the sorption at 1 or 24 h was significantly smaller or larger than at 4 h, respectively. In other cases, these differences were small. Because contact times are limited by the residence times of the water treatment plants (on the order of 4 h), these data suggest that water treatment operations should utilize as much contact time as is available to maximize efficiency of carbon utilization. Shorter contact times (e.g., 1 h) may result in significantly higher carbon utilization rates and, hence, increase costs and sludge production.

We can conclude from the above results that PAC can partially remove triazine compounds (parent compounds and their metabolites) from water. On the other hand, GAC used in a filter cap or post-filter contactor will typically come to equilibrium with the high influent concentration, rather than the lower effluent (treated water) concentration for a contaminant. Thus, the capacity of a GAC is greater than for an equivalent PAC which will generally be in equilibrium with the lower effluent (treated water) concentration. We can,

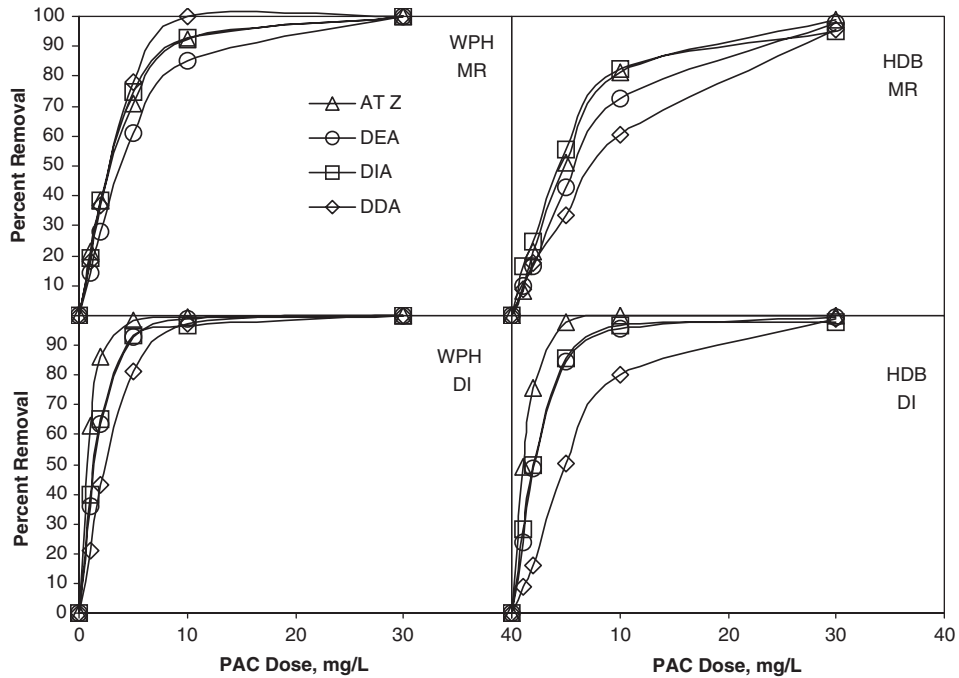


Fig. 3 – Removal of 5 µg/L of mix of ATZ, DEA, DIA and DDA by Calgon WPH and Norit HDB powder activated carbon with dosage of 0, 1, 2, 5, 10 and 30 mg/L (at pH 7.5 and 4 h contact time) in DI and MR water.

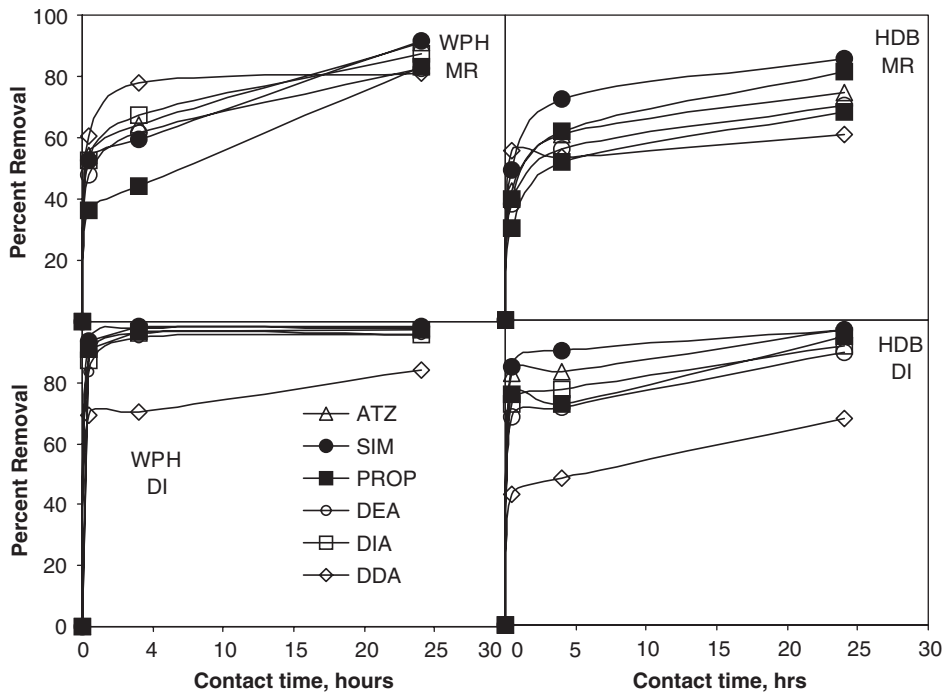


Fig. 4 – Removal of 3 µg/L of mix of six chloro-s-triazines by Calgon WPH and Norit HDB powder activated carbon in 0, 0.5, 4 and 24 h contact time (at pH 7.5 and 5 mg/L dose of carbon) in DI and MR water.

therefore, expect that GAC will have a greater removal potential for those compounds.

6.3.2. Isotherms

To better understand the sorption of the triazines on both WPH and HDB PACs in both waters, equilibrium isotherms were developed as described above. Adsorption data was fit to

the Freundlich isotherm model. Parameters were estimated using linear regression via the method of least squares, with units of µg/L for concentration and mg adsorbate per g adsorbent (mg/g) for capacity. The Freundlich isotherm is an empirical correlation of the form:  $q_e = k \times C_e^{1/n}$  where  $q_e$  is adsorption capacity (mg/g),  $C_e$  is equilibrium liquid phase concentration (µg/L); and  $K$  and  $1/n$  are Freundlich constants.

The parameter,  $K$ , is primarily related to the capacity of the adsorbent, with greater  $K$  corresponding to greater capacity. The Freundlich  $1/n$  is related to the strength of adsorption, where the smaller the value of  $1/n$  is, the stronger the adsorption bond is (Snoeyink and Summers, 1999).

The Freundlich isotherm model was fit to data (Figs. 5–8). The estimated model coefficients for WPH and HDB were calculated and are presented in Tables 3 and 4, respectively. Isotherms were conducted in a single solute phase (for DDA and ATZ) and for the triazine mixture (containing all six study compounds). In general, strong regressions were achieved for the isotherms (Tables 3 and 4).

The isotherm results for the ATZ only experiments show that ATZ in DI water WPH had a much higher adsorption capacity than HDB (Fig. 5). This is consistent with the BET surface area being approximately twice as great for WPH as HDB (Jain et al., 2005). In MR water, however, the observed capacities were very similar for the two carbons but were significantly lower than their capacities in DI water presumably due to competition by NOM. This would suggest that the pore fouling by the NOM prevented much of the additional surface area of the WPH from being utilized. Much lower Freundlich  $K$  values for WPH and HDB are seen in Tables 3 and 4, respectively, for MR versus DI waters.

Isotherm results for DDA only experiments showed that equilibrium capacities of DDA were much lower than those of ATZ in both DI and MR waters (Fig. 6). This fact would be consistent with the much greater solubility of DDA than for

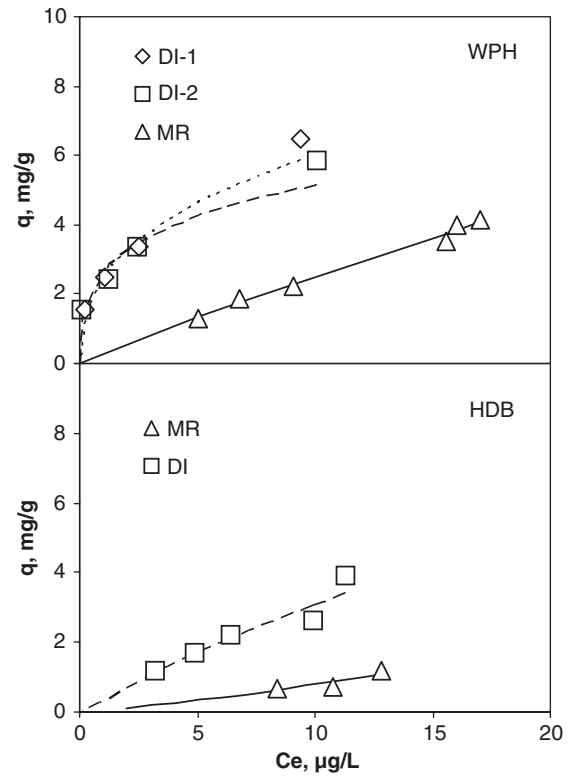


Fig. 6 – Adsorption isotherm of DDA on Calgon WPH and Norit HDB in DI and MR water (data fitted by Freundlich adsorption isotherm).

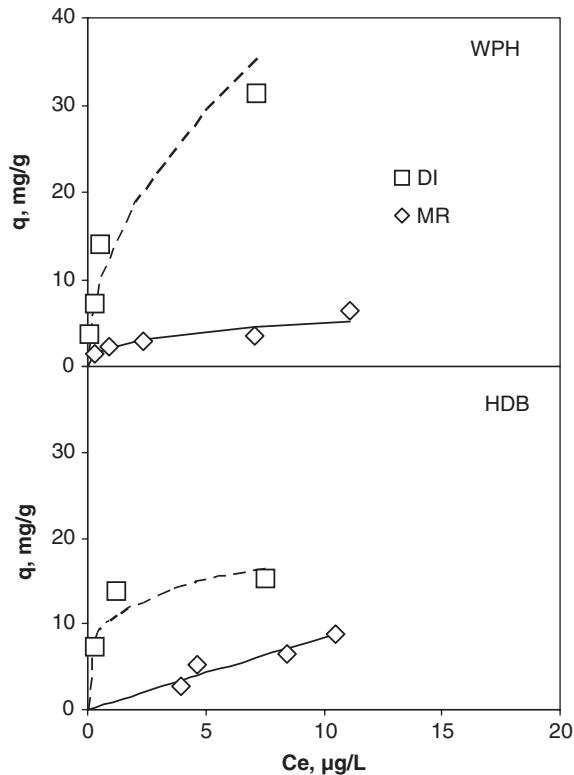


Fig. 5 – Adsorption isotherm of ATZ on Calgon WPH and Norit HDB in DI and MR water at pH 7 (data fitted by Freundlich adsorption isotherm).

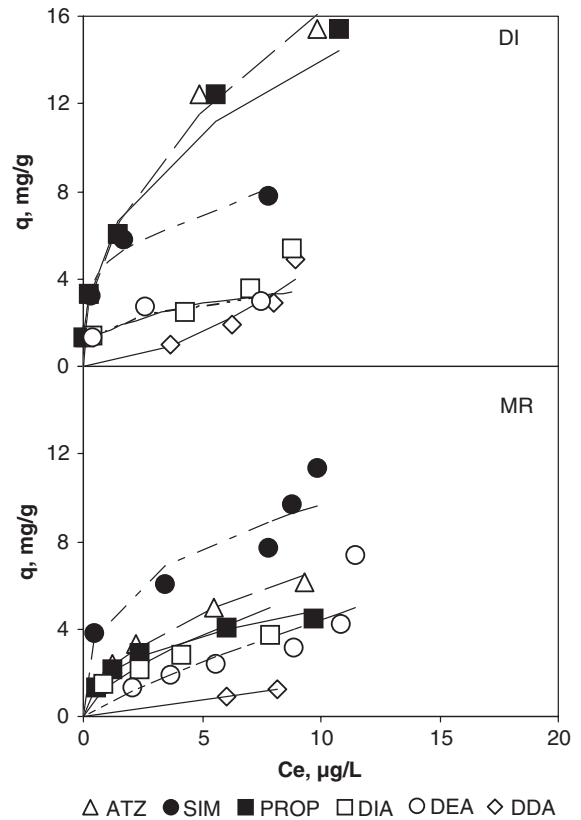
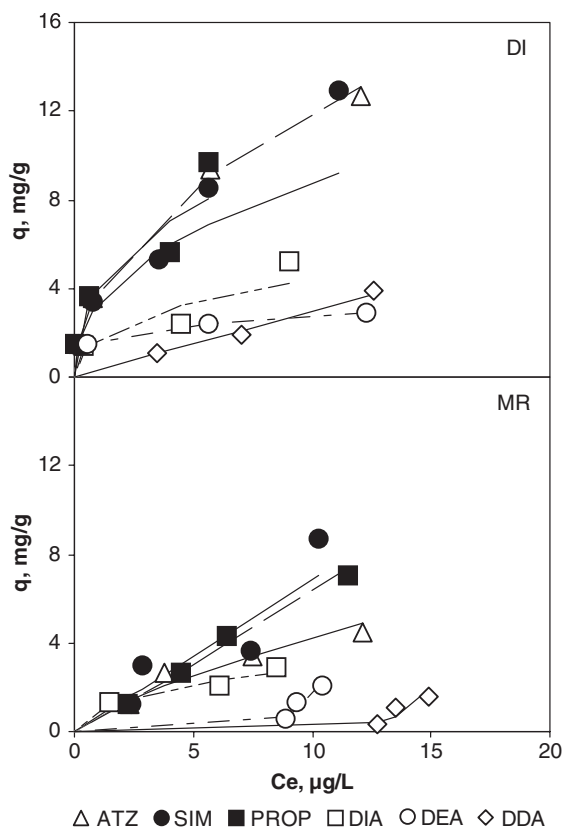


Fig. 7 – Adsorption isotherm of mix of six chloro-s-triazines on Calgon WPH in DI and MR water at pH 7 (data fitted by Freundlich adsorption isotherm).



**Fig. 8 – Adsorption isotherm of mix of six chloro-s-triazines on Norit HDB in DI and MR water at pH 7 (data fitted by Freundlich adsorption isotherm).**

**Table 3 – Experimental Freundlich isotherm coefficients for Calgon WPH PAC adsorption (based on minimum sum-of-squares for nonlinear regressed isotherm Units:  $C$ — $\mu\text{g/L}$ ;  $q$ — $\text{mg/g}$ )**

Compound	Calgon WPH					
	DI			MR		
	K	1/n	R <sup>2</sup>	K	1/n	R <sup>2</sup>
<i>Individual</i>						
ATZ	13.518	0.491	0.941	2.211	0.358	0.839
DDA	2.674	0.321	0.960	0.308	0.910	0.760
<i>Mix</i>						
ATZ	5.494	0.470	0.988	2.060	0.513	0.990
SIM	4.663	0.271	0.974	4.624	0.319	0.909
PROP	5.765	0.387	0.992	1.878	0.413	0.977
DIA	1.829	0.308	0.930	1.385	0.621	0.843
DEA	1.793	0.294	0.933	0.651	0.832	0.862
DDA	0.113	1.628	0.933	0.213	0.826	1.000

ATZ, due to the loss of two alkyl groups (ethyl and isopropyl) imparting greater hydrophobicity (lipophilicity) for ATZ, as compared with DDA. The results also showed that competition effects associated with MR water versus DI water significantly decreased the observed capacities of both carbons (Fig. 6). The calculated Freundlich K values for DDA

**Table 4 – Experimental Freundlich isotherm coefficients for Norit HDB PAC adsorption (based on minimum sum-of-squares for nonlinear regressed isotherm. Units:  $C$ — $\mu\text{g/L}$ ;  $q$ — $\text{mg/g}$ )**

Compound	Norit HDB					
	DI			MR		
	K	1/n	R <sup>2</sup>	K	1/n	R <sup>2</sup>
<i>Individual</i>						
ATZ	10.654	0.221	0.769	0.885	0.973	0.839
DDA	0.451	0.839	0.950	0.043	1.269	0.760
<i>Mix</i>						
ATZ	3.873	0.490	0.999	0.783	0.732	0.896
SIM	3.333	0.422	0.972	0.681	1.002	0.787
PROP	4.168	0.381	0.818	0.551	1.062	0.994
DIA	1.837	0.377	0.850	1.076	0.420	0.933
DEA	1.659	0.219	0.999	0.000	7.516	0.889
DDA	0.306	0.984	0.981	0.000	10.075	0.800

were just 14–20% of those that ATZ showed for the Calgon WPH (Table 3). On Norit HDB, the calculated Freundlich K values for DDA were only 4–5% of those for ATZ (Table 4). Overall, these data suggest that treatment efficiency of DDA may be significantly less than that of ATZ when using PAC.

Comparative sorption of the six study triazines in a mixture of WPH with both DI and MR waters showed that the metabolites—DEA, DIA, and DDA—had lower capacities in general than the parent compounds—ATZ, SIM and PROP (Fig. 7). This is expected due to the lesser hydrophobicity of the degradates than that of the parents due to the loss of the hydrophobic alkyl moieties. Similar results (i.e., lower capacities of degradates than those of the parents) was also observed for HDB (Fig. 8).

These results provide data that would support a hypothesis that TCT overall may be more difficult to remove via carbon adsorption than the parents alone if TCT is comprised of a significant fraction of these degradates. Thus, while there has been considerable treatment experience using PAC for the treatment of the parent chloro-s-triazine herbicides, this technology may be much less efficient in treating their degradates.

#### 6.4. Chlorination

Because free chlorine ( $\text{HOCl}/\text{OCl}^-$ ) is the most common chemical disinfectant used in drinking water plants, chlorination experiments were conducted using DI water and MR water. Typical CT (concentration  $\times$  time,  $\text{mgmin/L}$ ) values for free chlorination to achieve a 99.9% reduction in *Giardia lamblia* ranges from 56  $\text{mgmin/L}$  at 20°C (pH 7) to 312  $\text{mgmin/L}$  at 5°C (pH 9) (Letterman, 1999).

In this work, a free chlorine dosage of 2  $\text{mg/L}$  with a 30 min contact time (i.e.,  $\text{CT} = 60 \text{ mgmin/L}$  at pH 6.1) provided no significant removal ( $\alpha = 0.05$ ) of any of the study triazines (data not shown). The results suggest that DDA and the other studied triazine compounds are not likely to be degraded by free chlorine in drinking water treatment plants.



6.5. Ozonation

Ozonation results for DDA alone showed that DDA is recalcitrant to ozone in both DI and MR water at a dosage of up to 5 mg/L (Fig. 9) at pH values of 6 and 9. At pH 6, direct

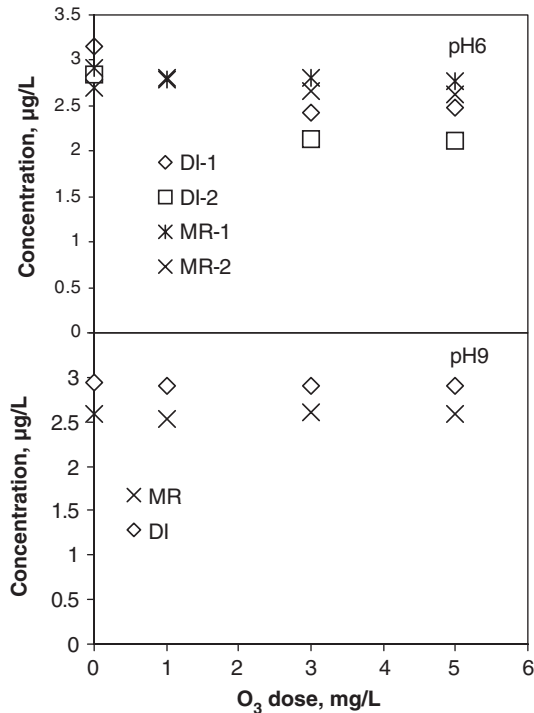


Fig. 9 – Removal of 3 µg/L of DDA by O<sub>3</sub> at 0, 0.2, 0.5, 0.7, 1, 3, 5 mg/L dosage in DI and MR water at pH 6 and pH 9.

ozonation reactions (with molecular ozone as the primary oxidant) predominated (Gottschalk et al., 2000). The observed lack of oxidation at pH 6 were consistent with extremely low second-order rate constants for DDA with a molecular ozone of  $<0.1 \text{ M}^{-1}/\text{s}$  (Acero et al., 2000). At pH 9, on the other hand, indirect ozonation reactions (with hydroxyl radical as the primary electrophile) predominated (Gottschalk et al., 2000). The observed slow oxidation at pH 9 was consistent with the relatively low second-order rate constants for DDA with a hydroxyl radical of  $<10^8 \text{ M}^{-1}/\text{s}$  (Acero et al., 2000).

Ozonation results for ATZ alone in DI and MR water showed that ATZ can be readily oxidized at a pH 6 by molecular ozone at dosages of 3–5 mg/L. The results at pH 6 showed that DEA is the primary degradate formed with little or no DIA or DDA formed in either DI or MR water (Fig. 10). The possibility that DDA is formed but rapidly degraded by molecular ozone is noted to be improbable due to the lack of DDA removal in the ozonation experiments using DDA-only. While ATZ was degraded by more than 90% with 5 mg/L ozone, the TCT only decreased by 70% and 32% in DI and MR water, respectively, due to the formation of degradates that were more recalcitrant and/or required larger ozone dosages to degrade than ATZ (Fig. 10). The recalcitrance of DEA and DIA were due to very low ozonation rate constants of 0.18 and  $3.1 \text{ M}^{-1}/\text{s}$ , respectively, at 20 °C, and 0.16 and  $0.2 \text{ M}^{-1}/\text{s}$ , respectively, at 11 °C (Acero et al., 2000).

Ozonation results for ATZ alone at pH 9 showed that ATZ was less efficiently removed at this higher pH, than it was at the low pH of 6 (Fig. 10). Specifically, an ozone dose of 5 mg/L achieved only 73% and 61% removal of ATZ in DI and MR water, respectively. As with the pH 6 results, DEA was the primary degradate with lesser amounts of DIA formation (Fig. 10). No DDA formation was observed; further, it is

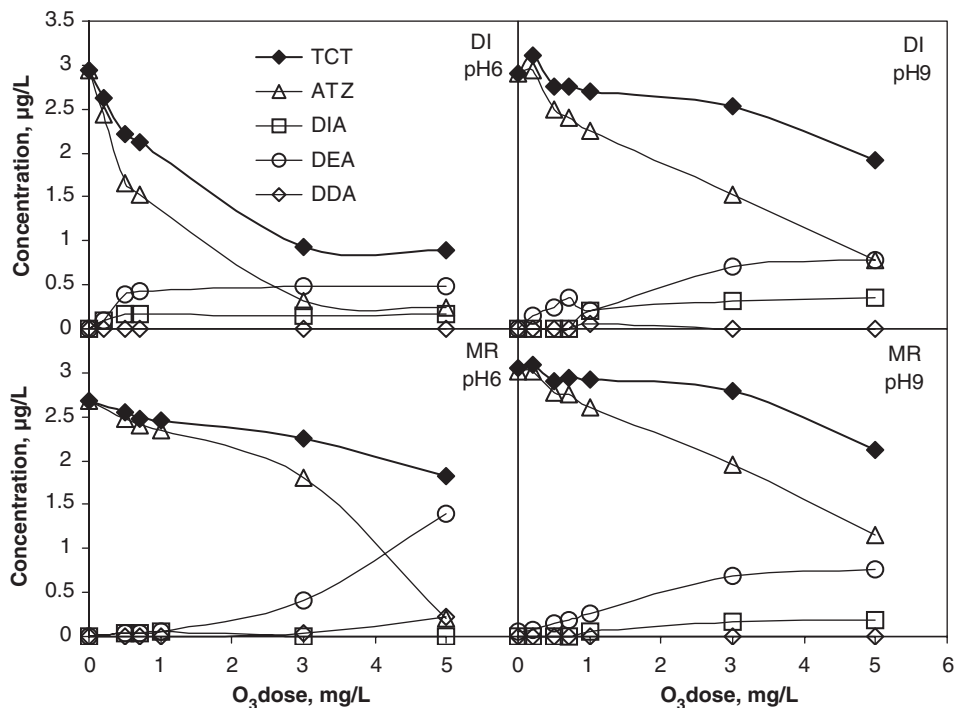


Fig. 10 – Removal of 3 µg/L of ATZ by O<sub>3</sub> at 0, 0.2, 0.5, 0.7, 1, 3, 5 mg/L dosage in DI and MR water at pH 6 and 9.

unlikely that any had formed and been removed (Fig. 10). Larger ozone dosages than those used in these experiments, or larger than those commonly used in water treatment plants, would probably have resulted in formation of more of the DDA. When the ozone dosage exceeded the range examined, the TCT was observed to be much more slowly removed than the ATZ due to the buildup of degradates that contributed to the TCT (Fig. 10).

Overall, these results showed that ozonation in water treatment plants is somewhat inefficient at removing ATZ (relatively high ozone dosages of 5 mg/L are required for removal). Furthermore, the results also showed that ozone is even less efficient at removing TCT due to DEA formation (and, to a lesser degree, DIA). A further issue with ozone for control of organic chemicals is the possibility for formation of ozonation byproducts such as bromate in high bromide waters.

## 7. Conclusions

With increased concern regarding a potential endocrine disruption effect, the removal from drinking water treatment plants of the chloro-s-triazine degradates—DEA, DIA, and DDA—as well as their parents, is increasingly important. The results of this study show that the parent and its metabolite chloro-s-triazines are only marginally removed in the conventional treatment processes examined in this work. Specifically, coagulation, softening and chlorine oxidation resulted in no significant amounts of any study compounds being removed. Relatively high dosages of ozone were found to be partially effective in removing ATZ, but conversion of ATZ to more recalcitrant metabolites (i.e., DEA, DIA and DDA) significantly limited the removal of the total chloro-s-triazine. DEA, followed by DIA, were major ozonation metabolites with very limited DDA formation being observed.

Adsorption of the parent and degradate chloro-s-triazines was relatively rapid on PAC, though relatively high PAC dosages of 5 mg/L (based on taste-and-odor control applications) were only partially effective in their removal. Higher PAC dosages (e.g.  $\geq 10$  mg/L) were highly effective in removing of all of the parents and metabolites. In these studies, no consistent and significant differences between the removal of parents and metabolites by PAC were apparent.

In drinking water plants where removal of chloro-s-triazines is needed, effective treatment approaches may include higher dosages of PAC, use of GAC-capped filters or GAC-post-filtration contactors, or membrane operations. Due to the costs associated with these options, watershed protection and proper controls of triazine herbicide application rates and methods may continue to play an important role in the effective control of total chloro-s-triazine concentrations in drinking water.

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