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Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A Predictive Tool for Drinking Water Treatment

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The present study investigates the degradation of atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-*s*-triazine) by ozone and OH radicals during ozonation and advanced oxidation processes, with the identification of the main degradation products. Besides the dealkylated and amide degradation products (6-amino-2-chloro-4-isopropylamino-*s*-triazine, 6-amino-2-chloro-4-(ethylamino)-*s*-triazine, 4-acetamido-2-chloro-6-isopropylamino-*s*-triazine, 4-acetamido-6-amino-2-chloro-*s*-triazine, and chlorodiamino-*s*-triazine), two new degradation products with an imine group were identified (2-chloro-4-ethylimino-6-isopropylamino-*s*-triazine and 6-amino-2-chloro-4-ethylimino-*s*-triazine). The contribution of the different pathways (direct ozone and OH radical reaction) to the overall degradation process has been quantified, and the rate constants of the reactions of atrazine and its main degradation products with both oxidants have been measured. The ethyl group is more reactive than the isopropyl group (i.e. 19 times during ozonation and four times during OH radical attack). The ethyl group reacts in higher proportion through oxidation to acetamide or imine derivates than to dealkylation. In contrast, the isopropyl group reacts mainly through dealkylation to the free amino group. Acetamido and imino groups are found to be resistant to chemical oxidation. These reactivities were corroborated by the measured values of the rate constants with both oxidants. A combination of product distribution and the kinetic parameters together with ozone and OH radical concentrations allowed us to calculate the evolution of the concentration of the degradation products for a given ozonation process.

Introduction

The European Union has set pesticide standards for drinking waters, at a maximum permissible concentration for a particular pesticide at 0.1 ppb and the sum of all pesticides at 0.5 ppb (*1*). The new regulation establishes not only a maximum concentration of pesticides in drinking water but also includes their degradation products after drinking water treatment (*2*). There are no global maximum concentration levels (MCLs) for pesticides in the U.S.A. The regulation is based on toxicological evidence of single compounds. For atrazine the MCL in the U.S.A. is 3 μg/L (*3*). Due to their potential toxicity, the application of pesticides has been restricted in Switzerland over the last 10 years (*4*). There is a change in mentality of the convenience of agricultural control versus pollution of water resources with pesticides. Therefore, the development of ecological farming in Switzerland is encouraged.

If source control does not lead to satisfactory pesticides levels, water treatment has to be applied to comply with the drinking water standards. There are several processes which are currently used: activated carbon filtration, ozonation, microbial action, hydrolysis, photodecomposition, and advanced oxidation processes (AOPs) (*5*−*11*). In the present study we will focus on ozone-based oxidation processes for atrazine degradation. Atrazine is one of the most widely used agricultural herbicides (*12*) (i.e. about 36 000 metric t/year are applied only in the U.S.A. (*13*)). Because of its persistence and the large use, traces of triazine herbicides have been found in many ground and surface waters. Very often a 1:1 mixture of atrazine and deethylatrazine is found (*14, 15*). Due to the low reactivity of atrazine with molecular ozone (*16*), AOPs have a higher potential for the elimination of not only atrazine but also its first degradation byproducts. Ozone-based AOPs involve the generation of radical intermediates, in particular the hydroxyl radicals (•OH), which are highly reactive with most organic compounds including atrazine (*17*). The combination O_3/H_2O_2 is the most widely applied AOP in drinking water treatment, because of the simple adaptation of conventional ozonation processes to this AOP by addition of hydrogen peroxide in the ozonation reactor (*18*).

Attempts to identify and quantify the formation of degradation products during this AOP have been made (*6*−*8*). The most abundant degradation products found during degradation of atrazine with O_3 and •OH are listed in Table 1. In general, dealkylation and alkyl chain oxidation to acetamide are the predominant pathways when ozone, AOPs, photolytic degradation, and Fenton's reagent are applied (*6*−*11*). The formation of these degradation products can be explained by attacks of the side chains with ozone (*19*) and/or •OH (*20*). An attack of ozone to the N or the α-C atom leads to the formation of N-dealkyl and acetamide derivates (*19, 21*) over an unknown reaction pathway. OH radicals attack the α-C through hydrogen abstraction, forming a carbon centered radical. This radical, after addition of oxygen forming the peroxyl radical, decomposes through bimolecular reactions to N-dealkyl and acetamide derivates (*20, 21*). In contrast, when photodecomposition is utilized, hydroxy triazines are the predominant subproducts (*10*). Even though there is quite a lot of qualitative information about possible reaction pathways, there is still lack of information about the quantitative contribution of the different transformation pathways when ozone and •OH are present as oxidants. The knowledge of the quantitative evolution of degradation products during ozonation or an AOP will allow assessing the treatment with respect to drinking water regulations.

To define and calibrate an ozonation process with respect to its oxidation capacity, it is necessary to estimate the oxidant concentrations. Whereas ozone can be readily measured, there are no fast and easy methods to determine the •OH concentration during ozonation processes. An experimental approach has been developed in order to determine the

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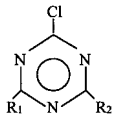
TABLE 1. Chemical Structure of Atrazine and Its Degradation Products



	R_1	R_2
atrazine (ATRA)	$NHCH_2CH_3$	$NHCH(CH_3)_2$
4-acetamido-2-chloro-6-isopropylamino-*s*-triazine (CDIT)	$NHCOCH_3$	$NHCH(CH_3)_2$
4-acetamido-2-chloro-6-ethylamino-*s*-triazine (CDET)	$NHCOCH_3$	$NHCH_2CH_3$
deethylatrazine (DEA)	NH_2	$NHCH(CH_3)_2$
deisopropylatrazine (DIA)	$NHCH_2CH_3$	NH_2
4-acetamido-6-amino-2-chloro-*s*-triazine (CDAT)	$NHCOCH_3$	NH_2
deethyldeisopropylatrazine (DEDIA)	NH_2	NH_2
2-chloro-4-ethylimino-6-isopropylamino-*s*-triazine (ATRA-imine)[a]	$N{=}CHCH_3$	$NHCH(CH_3)_2$
6-amino-2-chloro-4-ethylimino-*s*-triazine (DIA-imine)[a]	$N{=}CHCH_3$	NH_2

[a] First identified in the present investigation.

concentrations of both ozone and •OH during ozonation or AOPs (*22, 23*). This method is based on the measurement of the decrease of a probe compound which reacts fast with •OH and does not react with O_3. The selected probe compound was *p*-chlorobenzoic acid (pCBA), which reacts with •OH with a second-order rate constant $k = 5.2 \times 10^9\ M^{-1}\ s^{-1}$ (*24*). To assess the importance of ozone and •OH reactions a new parameter, the R_{ct}-value, has been defined as the ratio of the exposures of •OH and O_3 (i.e. concentration of oxidant integrated over the reaction time) and can be calculated from the decrease of pCBA:

$$\ln\left(\frac{[\mathrm{pCBA}]_t}{[\mathrm{pCBA}]_0}\right) = -k_{\bullet\mathrm{OH+pCBA}}\int_0^t [\bullet\mathrm{OH}]\mathrm{d}t = -k_{\bullet\mathrm{OH+pCBA}}R_{ct}\int_0^t [\mathrm{O_3}]\mathrm{d}t \quad (1)$$

The ozonation of several surface waters and groundwaters from different locations in Europe has been investigated, and the R_{ct}-value has been calculated. It has been observed that the R_{ct}-value was constant over a wide range of an ozonation process (*22, 23*). Therefore, it represents directly the ratio of the concentrations of •OH and O_3. Hence, the concentration of •OH during an ozonation experiment can be easily calculated from the measured ozone concentration.

The elimination of a degradation product (M), which reacts with both O_3 and •OH, can then be calculated by second-order kinetics and expressed as a function of R_{ct}, k_{O3}, $k_{\bullet OH}$, and the ozone exposure $\int[O_3]dt$:

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -\left(\int [\mathrm{O_3}]\mathrm{d}t\right)(k_{\bullet\mathrm{OH}}R_{ct} + k_{\mathrm{O_3}}) \quad (2)$$

$k_{\bullet OH}$ and k_{O3} are the second-order rate constants for the reactions of a degradation product M with •OH and O_3, respectively.

To predict the evolution of degradation products during an ozonation process by kinetic modeling the following steps are required: (1) identification of the primary byproducts of atrazine and its degradation products from degradation with ozone and •OH, (2) quantification of the contribution of each pathway for the reaction of both oxidants with atrazine and its degradation products, (3) determination of the rate constants for the reaction of each degradation product with ozone and •OH, (4) and application of the R_{ct}-value together with the above kinetic parameters.

Materials and Methods

Standards and Reagents. All chemicals used for solutions (buffer, eluent, etc.) were reagent grade and were used as received. Stock solutions were prepared in bidistilled water. Table 1 lists the structures and common names of atrazine and its degradation products. ATRA, DEA, DIA, DEDIA, were obtained from Novartis Crop Protection AG (Basel, Switzerland) with a purity higher than 98%. CDIT, CDET, and CDAT were synthesized according to procedures published previously (*6*). The purity was higher than 97% determined by GC-MS and LC-MS. ATRA-imine was synthesized as follows: 200 mg of DEA was added to 5 mL of acetaldehyde in the presence of 2 g of molecular sieve (4 Å). After 24 h, the solution was concentrated in a vacuum to near dryness, giving more than 90% yield of transformation from DEA to ATRA-imine. Because the exact concentration of the imine standards was not known, nominal concentrations of ATRA-imine and DIA-imine were estimated using the response factors of adjacent *s*-triazine compounds in the HPLC chromatogram. This approximation is based on the fact that the UV absorbance may be attributed to the resonance structure of the ring, which is basically identical (*7*). The calculated concentrations give us an estimation of the upper limit of the concentrations of these components.

Analytical Methods. Atrazine and *s*-triazine degradation products were measured by HPLC (Hewlett-Packard, 1050 series) equipped with a variable wavelength detector using a method adapted from ref *25*. Absorbance was measured at 220 nm. Separation was performed using gradient elution at a flow of 1 mL/min (column Hypersil ODS, 5 μm Florio). Initial conditions were 2% acetonitrile and 98% aqueous buffer (sodium acetate 1 mM, pH 6) with a linear gradient to 28% of acetonitrile within 40 min. After that, the initial conditions were reached within 2 min, and the system was equilibrated for 8 min. The sample volume injected varied from 25 to 250 μL depending on the *s*-triazine concentration, and the detection limit was 0.025 μM for atrazine and the degradation products (5 μg/L for atrazine). Acetophenone was analyzed with this method. pCBA was determined by HPLC (column: Merck Lichrospher 100, RP18−5 μm) with an eluent containing 45% 10 mM H_3PO_4 (pH = 2) and 55% methanol at 1 mL/min and detected at 234 nm.

The identification of atrazine and its degradation products DEDIA, CDAT, ODIT (4-acetamido-2-hydroxy-4-isopropylamino-*s*-triazine), DIA, DEA, and CDIT was performed by LC-MS. The mass spectra were in agreement with those obtained from the pure compounds and the mass fragmentation of atrazine degradation given by Arnold et al. (*26*). The method above-described was used for the separation of the degradation products by LC (Hewlett-Packard, 1100 series). The spectra were obtained on a Platform LC single quadrupole mass spectrometer equipped with an electrospray interface (ESI) from Micromass UK Ltd. (Manchester, UK). The spectra were acquired in the positive scan mode, over the m/z range 40−500 at 1 scan/s. The ESI interface temperature was set to 150 °C and the nitrogen gas flow to 500 L/h. The cone voltage was 15 V.

There were two unidentified compounds corresponding to the peaks at 9 and 26 min (ATRA-imine and DIA-imine, see below Figure 1). Their identification was not possible by LC-MS, probably because they were labile compounds and therefore destroyed in the source. The retention time did not coincide to any degradation product proposed in the literature (*6*−*11*). The identification of these degradation products was performed by GC-MS. Positive electron impact (EI+) mass spectra were obtained with a Fisons MD800 quadrupole mass spectrometer interfaced to a Fisons GC8000

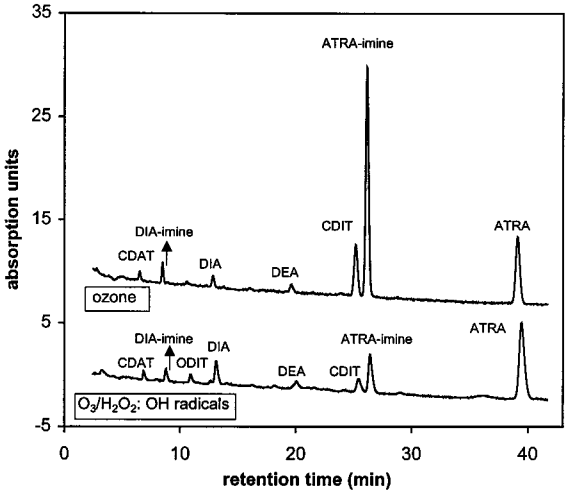


FIGURE 1. HPLC−UV chromatograms of atrazine solution treated with ozone and •OH (O_3/H_2O_2). Atrazine was degraded to around 70% of the original concentration. Experimental conditions in oxidation with ozone: pH = 7, T = 20 °C, $[O_3]_0$ = 10 mg/L, [*t*-BuOH] = 2 mM, $[ATRA]_0$ = 4.55 μM. Experimental conditions in oxidation with OH radicals: pH = 7, T = 20 °C, $[O_3]_0$ = 1 mg/L, $[H_2O_2]_0$ = 0.1 mM, [*t*-BuOH] = 25 μM, $[ATRA]_0$ = 4.1 μM.

gas chromatograph. Spectra were recorded at an electron energy of 70 eV. The source temperature was set at 200 °C. The mass spectra were scanned from 20 to 250 u at 0.4 scan/s. Samples (2 μL) were injected splitless onto a OV-240-OH column (phase: 33% cyanopropylphenyl and 67% dimethylpolysiloxane). The oven temperature started at 100 °C during 1 min and was increased to 180 °C at 20 °C/min. After 20 min at 180 °C the temperature was increased to 260 °C at 20 °C/min. The enrichment and extraction of the samples into an organic phase was achieved by solid-phase extraction (*25*). ATRA-imine has a parent ion at m/z 213 with the corresponding ^{37}Cl at m/z 215 and an abundant ion at m/z 212 (214) corresponding to the cleavage of the H in the α-C. Loss of methyl group yields the ions at m/z 198 (200). Cleavage of the isopropyl group gives DIA-imine, m/z 171 (173). Additional masses were found in good agreement with fragment of the mass spectra of atrazine (*27*) less 2 units of m/z. In addition, ATRA-imine was synthesized as described above, and its mass spectra was identical with that of the degradation product found in the reaction sample, corroborating its identification. DIA-imine was tentatively identified with a parent ion at m/z 171, with the corresponding ^{37}Cl at m/z 173, and an abundant ion at m/z 170 (172) corresponding to the cleavage of the H in the α-C.

Dissolved ozone was analyzed by the Indigo method (*28*). Hydrogen peroxide was determined by the peroxidase-DPD method (*29*).

Product Formation during Ozonation and the AOP O_3/H_2O_2. Conventional ozonation and AOP O_3/H_2O_2 experiments were performed with each degradation product in bidistilled water at 20 °C in order to establish the degradation pathway with ozone and with •OH, respectively. The initial concentration of the *s*-triazine was 4−5 μM in these experiments (by adding a certain volume of an aqueous stock solution).

Oxidation by Ozone. To study molecular ozone reactions, the pH was kept constant at 7 to mimic drinking water conditions (with 50 mM phosphate buffer). A high concentration of *tert*-butyl alcohol (*t*-BuOH, 2 mM) was added in order to suppress the reaction between •OH (formed from ozone decomposition) and *s*-triazines. Under these conditions approximately 99% of the •OH are scavenged by *t*-BuOH, which can be calculated by competition kinetics. The evolution of atrazine and its degradation products was measured after initiating the reaction by addition of a certain volume of a concentrated O_3 stock solution (1 mM) to the reactor. Samples were withdrawn with a dispenser system, and the reaction was stopped by purging the residual ozone with N_2 during 5 min. The initial O_3 concentration was varied from 5 to 10 mg/L in order to achieve a complete degradation of atrazine and the various degradation products under consideration.

Oxidation by OH Radicals. AOP O_3/H_2O_2 experiments were carried out by adding H_2O_2 (0.1 mM) to the *s*-triazine-containing solutions followed by addition of O_3. Under these conditions, •OH was the predominant oxidant. The pH was varied from 6 to 9 (with 50 mM phosphate buffer), and *t*-BuOH was added at a small concentration (2.5×10^{-5} M) to define the lifetime of •OH in the reaction medium. Even small concentrations of organic compounds could otherwise alter the experimental system significantly. *s*-Triazines were analyzed after total O_3 consumption in experiments with varying O_3 dosages (0.25−10 mg/L).

Experiments in Natural Waters. Some experiments were carried out with water form River Seine, France (DOC 2.5 mg/L, alkalinity 3.9 mM). The waters were filtered (0.45 μM cellulose acetate, Sartorius), and the pH was adjusted to 7 by addition of HCl. To increase the buffer capacity of the waters, 10 mM borate was added. To mimic real treatment conditions these experiments were performed at 11 °C. Atrazine was added in low concentration (0.5 μM) to avoid interference with respect to O_3 and •OH reactions with the natural water matrix. To calibrate the system with respect to •OH reactions, pCBA was added as a probe compound (0.5 μM). After addition of ozone (2 mg/L), samples were withdrawn after certain time intervals with a dispenser and quenched with indigo for residual ozone measurements (*30*). For *s*-triazines and pCBA analysis, residual ozone was quenched by nitrite.

Determination of Rate Constants for the Reactions of *s*-Triazines with Ozone and •OH. The rate constants of the reaction of ozone with atrazine and its degradation products have been determined by measuring the ozone decrease in excess of the compound (>10-fold) according to a procedure described previously (*16*, *31*). The temperature was varied from 5 to 20 °C, and the pH was kept constant at 2. In addition to *s*-triazine ($(1-2) \times 10^{-4}$ M) and ozone (1×10^{-5} M), *t*-BuOH (10 mM) was added to scavenge •OH. Ozone concentrations were monitored by the Indigo method (*28*) as a function of reaction time under pseudo-first-order conditions (*31*).

Rate constants of *s*-triazines with •OH were determined by competition kinetics (*17*). •OH radicals were generated by a combination of O_3 and H_2O_2 at pH 9 to keep the concentration of O_3 as low as possible. Acetophenone was chosen as a reference compound. The rate constant with •OH is 6×10^9 M^{-1} s^{-1} (*24*), which was checked by relative measurements with pCBA as reference compound. The rate constant of the direct ozone reaction of acetophenone is 3.5 M^{-1} s^{-1}. Under our experimental conditions the direct ozone reaction with acetophenone can be neglected because the half-life of ozone is very small (1 s). Therefore, reactions with •OH by far predominate the oxidation kinetics. The extend of the oxidation reaction was varied by changing the ozone dose. The relative decrease of atrazine and acetophenone was measured by HPLC after complete depletion of ozone.

Results and Discussion

Identification of Atrazine Degradation Products. To determine the degradation pathway of atrazine with both ozone and •OH, experiments were carried out at pH 7 in absence and in the presence of H_2O_2 (0.1 mM). The decrease of atrazine and formation of its degradation products was followed by HPLC analysis as described above. Figure 1 shows chromatograms of atrazine, which was degraded by ozone and

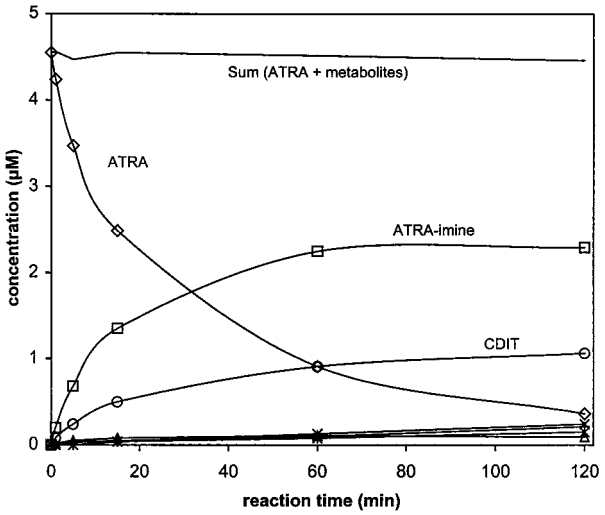


FIGURE 2. Evolution of the concentration of atrazine and its degradation products during ozonation. Lower curves stand for DEA, DIA-imine, CDAT, and DIA (from the lowest to the highest curve). Experimental conditions: pH = 7, T = 20 °C, $[O_3]_0$ = 10 mg/L, [t-BuOH] = 2 mM, $[ATRA]_0$ = 4.55 μM.

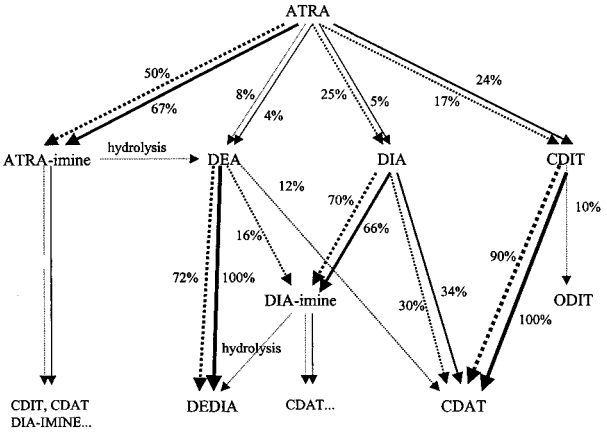


FIGURE 3. Atrazine degradation and formation of degradation products by ozone and OH radicals. Percentages given for the relative importance of a pathway. Solid lines: molecular ozone reactions; dashed lines: OH radical reactions.

by •OH. The degradation products formed in the reaction of ATRA with both oxidants are similar. However, molecular ozone attack leads to larger amounts of ATRA-imine and CDIT, and the mass balance (sum of atrazine and degradation product concentration) was very close to 100% even after total ATRA degradation. When compared to the oxidation by molecular ozone, during •OH degradation much less first generation degradation product formation is observed. In addition, some nonidentified degradation products appeared during •OH attack, and the mass balance was lower than that obtained with ozone. This is a result of the lower selectivity of •OH relative to O_3.

In the present study we identified two degradation products (ATRA-imine and DIA-imine) which were not found previously (*6*−*11*). Besides the dealkylation and alkyl oxidation with formation of acetamide, the formation of imine has been proposed when O_3 and •OH attack substituted amines (*19, 20*). In similar studies with amino acids, the formation of an imine group has been proposed after •OH attack (*32, 33*). During the degradation of ATRA with •OH, the peroxyl radical may decompose by monomolecular reaction to the formation of the imine group (*20*). Therefore, the formation of imine degradation products can occur by the attack of O_3 and •OH to substituted amino groups. These imine groups are expected to hydrolyze easily through dealkylation. The hydrolysis of the imines will be discussed below.

Molecular Ozone Reaction of Atrazine and Its Degradation Products. Figure 2 depicts the degradation of ATRA and the evolution of its degradation products during an ozonation experiment (ozone as only oxidant). ATRA-imine and CDIT were the predominant degradation products (see also Figure 1, where the chromatogram of the ozonated sample corresponds to a reaction time of 60 min). It can be assumed that during the first few minutes of the reaction, ozone attacks mainly ATRA, and the reaction with the degradation products only occurs when ATRA is partially degraded. Therefore, the percentage of each degradation product formed from ATRA degradation can be calculated during this initial phase (15 min). These investigations lead to the reaction scheme which is shown in Figure 3 (solid lines). The percentages stand for the fraction of ATRA oxidized to a particular product. For example the attack of ozone on the ethyl group was 19 times as likely to occur as attack on the isopropyl as determined from the ratio ([ATRA-imine] + [CDIT] + [DEA])/[DIA].

Similar experiments were performed with most of the identified degradation products (ATRA-imine, CDIT, DEA, DIA, DEDIA, and CDAT). Also for these compounds the partial contribution of the different oxidation pathways during the initial phase of the reactions is shown in Figure 3. Degradation of ATRA-imine by ozone was slow, and besides CDIT, DIA-imine, and CDAT, some unidentified byproducts were formed. The reaction of molecular ozone with CDIT lead to the formation of CDAT. This shows that the acetamide group is refractory to ozone attack. The ozonation of DEA lead to the formation of DEDIA, thus the dealkylation is the result of ozone attack to the isopropyl group. During direct ozonation of DIA, where the degradation pathway of the reactive ethyl group can be observed, the oxidation of the ethyl group to the formation of DIA-imine and acetamide were the predominant reactions, 66 and 34%, respectively. Dealkylation occurred after a certain extension of the degradation process, and DIA-imine was hardly degraded. DIA-imine was not synthesized, and, therefore, the ozone degradation could not be studied. CDAT and DEDIA were resistant to ozone attack, and, therefore, both were identified as final products. No hydroxy derivates were found in agreement with published studies of atrazine ozonation (*6, 7*).

Reaction of •OH with Atrazine and Its Degradation Products. The degradation of ATRA by •OH is shown in Figure 4A,B as a function of the ozone dosage. For •OH oxidation similar degradation products as for ozonation were found, and only small variations in the degradation product distribution were observed when the pH was modified. Figure 4A includes the decrease of the concentration of ATRA and the four primary degradation products as well as the mass balance. The concentrations of the second-generation degradation products are represented in Figure 4B. The reaction scheme of ATRA with •OH is shown in Figure 3 (dashed lines). •OH attack on the ethyl group was four times as likely to occur compared to the isopropyl. This has to be put into relation to 19 times for the molecular ozone reactions. The mass balance during •OH oxidation decreased to 90% of initial ATRA concentration after 50% degradation of ATRA and to 66% after 90% degradation. This loss in the mass balance is due to the formation of nonidentified degradation products (Figure 1, sample corresponds to 1 mg/L of O_3 in Figure 4) and products which may not be detected by our method.

The degradation pathway of the reaction of the main degradation products with •OH and its relative importance for product formation was also studied and is shown in Figure 3 as well. The degradation of ATRA-imine by •OH leads to the formation of CDIT, CDAT, and DIA-imine, together with a

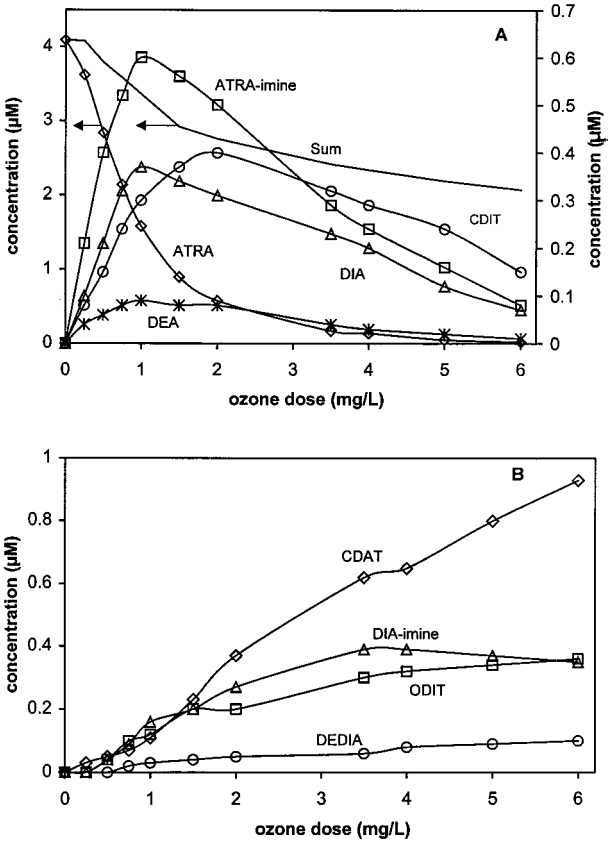


FIGURE 4. Evolution of the concentration of atrazine and its degradation products during the AOP O_3/H_2O_2 (•OH degradation). (A) ATRA, ATRA-imine, CDIT, DIA, and DEA. (B) CDAT, DIA-imine, ODIT, and DEDIA. Experimental conditions: pH = 7, T = 20 °C, $[H_2O_2]_0$ = 0.1 mM, [*t*-BuOH] = 25 μM, $[ATRA]_0$ = 4.1 μM.

minor fraction of unidentified products. During the oxidation of CDIT, the hydroxy-derivate ODIT was identified which accounts to 10% of the total process. This degradation product has been identified previously during degradation of ATRA by Fenton's reagent (*11*). CDAT and DIA-imine were the dominant degradation products during the reaction of DIA with •OH. In addition, CDAT was produced during DIA-imine degradation. DEDIA and CDAT were identified as the final degradation products.

In most previous studies, where the degradation product distribution has been studied, DEA has been identified as the degradation product with the highest concentration during the treatment of ATRA with ozone and •OH (*6*−*11*). The present study seems to be in disagreement with these previous investigations. However, the hydrolysis of the imine and acetamide groups may be an important process leading to the generally observed products (usually measurements are performed only after more than a few hours up to days). The hydrolysis of these compounds would also explain their absence in treated drinking waters and in natural water samples (*15*, *25*, *34*).

Hydrolysis of Acetamide and Imine Groups. The hydrolysis of the acetamide group leads to the formation of the dealkylated degradation product and acetic acid (*35*). This hydrolysis has been studied for CDIT and CDAT at different pHs, resulting in stable compounds in the pH range 6−8 (half-life of several days). CDIT hydrolyzes to DEDIA at pH 2 with a rate constant of 0.041 h^{-1} and a half-life of 17 h (data not shown).

The hydrolysis of the imine group leads to the dealkylated degradation product and acetaldehyde (*35*). To study the hydrolysis of ATRA-imine, this compound was formed

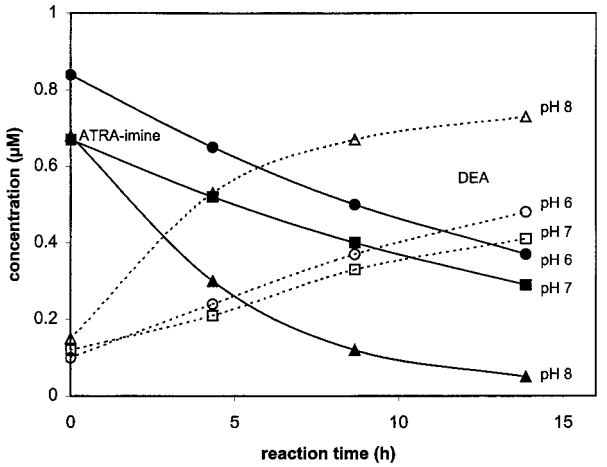


FIGURE 5. Hydrolysis of ATRA-imine (solid lines) and formation of DEA (dashed lines) in the pH range 6−8. Experimental conditions: T = 20 °C, $[O_3]_0$ = 1 mg/L, $[H_2O_2]_0$ = 0.1 mM, [*t*-BuOH] = 25 μM, $[ATRA]_0$ = 4.1 μM.

TABLE 2. Hydrolysis of ATRA-Imine[a]

pH	k_h (h^{-1})	$t_{1/2}$ (h)	pH	k_h (h^{-1})	$t_{1/2}$ (h)
5	0.078	9.0	8	0.19	3.6
6	0.060	11.6	9	1.20	0.6
7	0.060	11.6			

[a] Influence of pH on rate constants and half-life.

through partial degradation of ATRA by •OH. When the maximum concentration of ATRA-imine was reached, the decrease of ATRA-imine was measured together with the increase of DEA over 2 days until total disappearance (Figure 5). Such experiments were performed at pH 6, 7, and 8. The sum of the concentration of ATRA-imine and DEA remained constant over the entire reaction which is the result of a stoichiometric transformation. The rate constant for hydrolysis (k_h) and the half-life ($t_{1/2}$) of ATRA-imine at various pH values are given in Table 2. It can be observed that ATRA-imine has its highest stability in the pH range 6−7, decreasing both at lower and higher pH through acid and base catalysis. Our data suggests that during drinking water ozonation at near neutral pH and a residence time lower than an hour, the contribution of the hydrolysis is negligible compared the oxidation process itself. However, a half-life of 11 h is short enough to lead to a complete hydrolysis of this degradation product in drinking waters, since the residence times of waters from treatment to consumer are usually in the order of days. Therefore, to find this degradation product, samples would have to be analyzed immediately after withdrawing them from the reactor. The hydrolysis of DIA-imine has also been studied at pH 7. A k_h of 0.062 h^{-1} and a $t_{1/2}$ of 11.2 h have been obtained.

Rate Constants of ATRA and Its Degradation Products with Ozone and •OH. To perform a complete kinetic study of atrazine degradation by ozone and •OH not only the degradation products have to be known but also the rate constants of the reactions of atrazine and each degradation product with both oxidants have to be determined. The rate constants determined in the present study are shown in Table 3. When compared to values given in the literature (*36*, *37*), the main disagreement is the rate constant of the reaction of molecular ozone with DIA. According to our understanding this value should be lower than that of the reaction of ozone with ATRA. The higher rate constant of DIA compared to DEA with both oxidants shows the higher reactivity of the ethyl group. These results also show the high selectivity of

TABLE 3. Rate Constants for Reaction of Atrazine and Its Main Degradation Products with Ozone and •OH at 20 °C

compd	k_{O3} (M^{-1} s^{-1})[a]	k_{O3} (M^{-1} s^{-1})[b]	k_{OH} (M^{-1} s^{-1})[a]	k_{OH} (M^{-1} s^{-1})[c]
ATRA	6.0	6.3	3×10^9	2.4×10^9
ATRA-imine	<1		1.7×10^9	
CDIT	0.14		1.2×10^9	
DEA	0.18	0.19	1.2×10^9	1.2×10^9
DIA	3.1	7.51	1.9×10^9	1.9×10^9
CDAT	<0.1		$<1 \times 10^8$	
DEDIA	<0.1		$<1 \times 10^8$	$<5 \times 10^7$

[a] Determined in this work. [b] Reference *36*. [c] Reference *37*.

ozone versus a •OH (i.e. the ratio between rate constants of DIA and DEA with ozone is 17 and only 1.6 for •OH).

Similar rate constants of CDIT and DEA with O_3 shows the low reactivity of the acetamide group. The rate constant of ozone with ATRA-imine could not be measured because of the hydrolysis of this degradation product at low pH. However, due to the low reactivity shown in the experiments of atrazine ozonation (Figure 2), this rate constant may be similar to DEA. The rate constants of ozone with CDAT and DEDIA were lower than 0.1 M^{-1} s^{-1}, thus the contribution of these reactions to the overall process is negligible. These products can be considered as the final degradation products even for extensive ozonation.

The activation energy, E_{act}, of the reaction between ozone and atrazine has been calculated from an Arrhenius plot, varying the temperature from 5 to 20 °C. The resulting E_{act} of 36.5 kJ/mol lies in the range of 35−50 kJ/mol typically observed for molecular ozone reactions (*31*).

Concerning reactivities with •OH, similar rate constants were obtained for the main degradation products, which shows the low selectivity of •OH. The imine group is not very reactive with •OH, since the rate constant of the reaction of ATRA-imine with •OH is only slightly higher than that of DEA. The rate constants of •OH with CDAT and DEDIA could not be measured because of the very small rate constants ($<1 \times 10^8$ M^{-1} s^{-1}).

Prediction of Atrazine Degradation Product Formation during Drinking Water Ozonation. Once the pathways of degradation product formation for the reaction of atrazine with ozone and •OH has been established and the necessary rate constants have been measured, these results can be applied to drinking water ozonation to predict the evolution of atrazine and its degradation products. However, this is only possible if the O_3 and •OH concentrations are known. For that, experiments have been carried out with water from River Seine at 11 °C, applying both conventional ozonation and the AOP O_3/H_2O_2. Once the natural water was calibrated in terms of ozone decomposition and formation of •OH, the evolution of degradation products was determined by kinetic modeling according to the degradation processes established in the present study and compared to experiments.

To contemplate the contribution of the several degradation pathways and estimate the formation of degradation products, the global rate constants of each degradation product have been split up according to the partial contribution of each pathway. Table 4 shows the fractional rate constants of atrazine with O_3 and •OH. It should be noted that the rate constant of the reaction of ATRA with ozone at 11 °C is 4.0 M^{-1} s^{-1} (mass balance 100%). In the presence of H_2O_2 (•OH degradation) 90% of atrazine degradation leads to the mentioned degradation products formation (mass balance 90%, being the 10% unidentified degradation products), and, therefore, a value of 2.7×10^9 M^{-1} s^{-1} instead of 3×10^9 M^{-1} s^{-1} has been assumed for the rate constant of its reaction with •OH.

TABLE 4. Rate Constants for Reaction of Atrazine with Ozone and •OH Forming Primary Generation Degradation Products at 11 °C

degradation product	k_{O3} (M^{-1} s^{-1})	k_{OH} (M^{-1} s^{-1})
ATRA-imine	2.68	1.35×10^9
CDIT	0.96	0.46×10^9
DEA	0.16	0.22×10^9
DIA	0.2	0.67×10^9
ATRA	4.0	2.7×10^9

TABLE 5. Ozone Decomposition Kinetics and R_{ct}-Values for Treatment of River Seine Water with Ozone and O_3/H_2O_2.

$[O_3]$ (mg/L)	$[H_2O_2]$ (mg/L)	k (s^{-1})	R_{ct}
2	0	2.2×10^{-3}	1.5×10^{-8}
2	0.8	3.8×10^{-2}	2.8×10^{-7}

The characterization of the River Seine water with respect to ozone stability and •OH oxidation is shown in Table 5. The experimental values for the first-order rate constants for ozone decomposition (k) and the R_{ct}-value calculated by applying eq 1 define the system completely with respect to O_3 and •OH concentrations. The O_3 concentration was calculated applying first-order kinetics with the experimental value of k. The •OH concentration was derived from the calculated O_3 concentration and the experimental R_{ct}-value (i.e. $[•OH]/[O_3]$). With these determined oxidant concentrations, the concentration of atrazine and its degradation products have been determined by applying eq 2 using the computer program ACUCHEM (*38*).

Figure 6A,B shows the experimental results (symbols) and model calculations (lines) for atrazine removal and degradation products formation in water from River Seine during conventional ozonation and the AOP O_3/H_2O_2, respectively. The dashed line stands for the total mass balance (i.e. sum of the concentration of ATRA and all the identified degradation products). The total mass balance was above 90% of the initial ATRA concentration in all samples. The atrazine degradation was around 60%, similar to values observed during full-scale ozonation (*39*). It should be noted that the same degradation in both processes is reached after different reaction times. Whereas in the conventional ozonation process (Figure 6A) 30 min are required, it takes only 2 min in the AOP (Figure 6B). With this low degradation level, only the formation of the first generation of degradation products is relevant, which account for 75% of the degraded ATRA. The good agreement between model calculations and experimental results supports this kinetic formulation to predict not only micropollutant degradation but also the formation of degradation products.

Therefore, for a given micropollutant, the evolution of the concentration of its degradation products can be predicted by a combination of kinetic parameters (reactivity toward ozone and •OH and the degradation pathway with both oxidants) and the decomposition of ozone into •OH in this particular system (k and R_{ct}). The application of the present method is important for drinking water treatment, since e.g. EU regulations include, besides the original pesticides, the degradation products formed during drinking water treatment (*2*). From our results it gets evident that the new EU regulation for atrazine cannot be met by the oxidation processes under consideration here (both conventional ozonation and the AOP O_3/H_2O_2) if the level of the raw water is above 0.1 μg/L. However, our method allows for predicting the product distribution for ozonation processes (AOPs) that are applied for different purposes (disinfection, taste and odor removal, etc.).

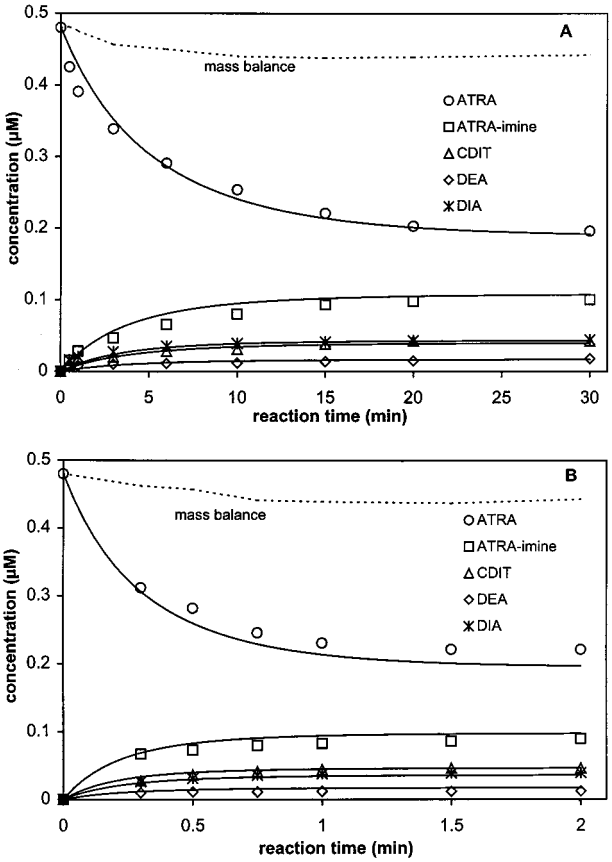


FIGURE 6. Evolution of atrazine and degradation products during (A) conventional ozonation and (B) AOP (O_3/H_2O_2) of River Seine water. Symbols stand for experimental results and lines for model calculations (note different time scales). The dashed lines represent the total mass balance. DOC = 2.5 mg/L, alkalinity = 3.9 mM, T = 11 °C, pH = 7, $[O_3]_0$ = 2 mg/L, $[H_2O_2]_0$ = 0.8 mg/L (only (B)).

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