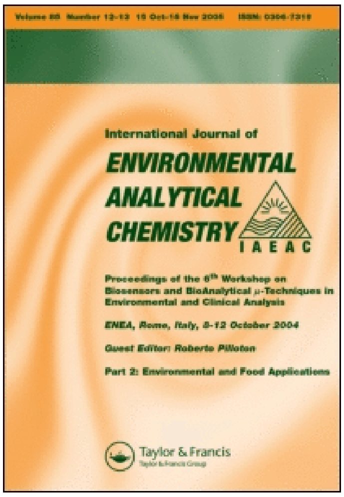

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ATRAZINE AND PARATHION-METHYL REMOVAL BY UV AND UV/O_3 IN DRINKING WATER TREATMENT

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The degradation of atrazine and parathion-methyl by UV-light in the presence of O_2(UV/O_2) and by a combination of UV-light and ozone in the presence of O_2(UV/O_2/O_3) was studied at a pilot plant for drinking water treatment. The photolysis rate of parathion-methyl increased with UV/O_2/O_3 compared to the treatment with UV/O_2 only, while the photodecomposition rate of atrazine was not enhanced by the UV/O_2/O_3 combination under the working conditions applied.

In field experiments with a large-scale plant the degradation of atrazine and desethylatrazine was studied at a drinking water supply. The applied ozone dose rates were smaller and the residence time of the liquid phase in the UV-reaction unit was shorter than in the pilot plant. The degradation rate of both atrazine and desethylatrazine increased with increasing ozone dose rates and increasing radiant power. At a continuous flow rate of 70 m^3/h of contaminated raw water atrazine could be degraded below the threshold limit for pesticides (0.1µg/L) at optimum operation conditions, whereas the resulting desethylatrazine concentration exceeded this limit. At a continuous flow rate of 30 m^3/h desethylatrazine could be degraded below the threshold limit, too.

KEY WORDS: Pesticide, degradation, atrazine, parathion-methyl, UV/O_3, advanced oxidation.

INTRODUCTION

In Germany about 30000 t of pesticides are annually used for agricultural purposes[1]. Thus, pesticide residues are present in soils, in surface and ground water[2,3,4]. The threshold limit for pesticide concentration in drinking water (0.1 µg/L for individual pesticides, given by the EC Drinking Water Directive) is exceeded in many cases. For usage as drinking water a pretreatment of the contaminated water sources is required, in order to reduce the concentrations of micro-pollutants[5].

In addition to conventional water treatment techniques (filtration, chlorination, ozonation, flocculation and adsorption on activated carbon)[6,7] great importance was directed to new water treatment techniques, especially applying "advanced oxidation processes"

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(AOP)[8,9,10]. Hydroxyl radicals, generated during the AOP, play a fundamental role in the destruction of pollutants present in water. For instance the combination of UV/O_3 was employed for the removal of TOC[11], trihalomethane precursors[12] and formulated pesticides[13], UV/H_2O_2 was used for degradation of atrazine[14,15,16] and other organochlorinated pesticides[17] in water. UV/TiO_2 was employed for the destruction of hydrocarbons[18], haloorganics[19], chloroaromatics[20] and triazines[21] and UV/TiO_2 plus oxidizing species (H_2O_2, $S_2O_8^{2-}$) for the decomposition of chloroaromatics and atrazine[22,23]. Additionally, the degradation efficiency of the systems H_2O_2/O_3, H_2O_2/UV and H_2O_2/Fe^{2+}[24], and of the systems O_3, O_3/H_2O_2 and O_3/TiO_2[25] were compared.

According to the results of Prados *et al.*[26] the UV/O_3 combination process proves to be efficient for the degradation of different pesticides. Hence we report data from two plants for water treatment with UV/O_3 for degradation experiments on pilot-plant-scale and on large-scale. A systematic investigation on the degradation effects of UV-light and UV/O_3 were carried out for the pesticides parathion-methyl and atrazine, employing the pilot plant. The degradation of atrazine and desethylatrazine was investigated under field conditions at a drinking water supply, applying a large-scale UV/O_3 plant under various operational conditions.

Chemical reactions involved in the UV/O_3 oxidation process

In order to produce OH-radicals, a combination of UV-light and ozone was applied to the water. Photolysis of aqueous ozone yields hydrogen peroxide directly (Eqn. 1), which is photo-decomposed into hydroxyl radicals (Eqn. 2)[27,28]. In neutral solution hydrogen peroxide (pK_a = 11.7) dissociates to HO_2^- (Eqn. 3), which may initiate further decomposition of residual ozone into hydroxyl radicals[29] (Eqns. 4 and 5).

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 \tag{1}$$

$$H_2O_2 + h\nu \rightarrow 2\cdot OH \tag{2}$$

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \tag{3}$$

$$HO_2^- + O_3 \rightarrow HO_2\cdot + O_3\cdot^- \tag{4}$$

$$O_3\cdot^- + H^+ \rightarrow \cdot OH + O_2 \tag{5}$$

In acidic media, chain reactions of ozone with hydrogen peroxide are inhibited. The UV-decomposition of aqueous ozone however yields almost stoichiometric amounts of hydrogen peroxide which accumulates in acidic solutions, because photodecomposition of H_2O_2 is about 100 times slower than photolysis of ozone at 254 nm due to the low extinction coefficient of H_2O_2 ($\varepsilon_{254} = 18.6$ L mol^{-1} cm^{-1}) compared to ozone ($\varepsilon_{254} = 2900$ L mol^{-1} cm^{-1}).

OH-radicals are non-selective oxidants, which react with most organic molecules close to diffusion-controlled rate constants ($k = 10^9$ L mol^{-1} s^{-1}; for a compilation see Buxton *et* *al.*[30]). The main mechanisms are hydrogen atom abstraction (Eqn. 6) and addition of OH-radical to unsaturated compounds or an aromatic nucleus (Eqn. 7). In the presence of dioxygen the organic radicals formed (Eqns. 6 and 7) are converted to their corresponding hydroperoxyl radicals (Eqn. 8) which undergo further decomposition to give products with C=O, HC=O and OH functions[31]. Repeated OH-attack on these products can gradually lead to the mineralization of the compound. Almost all solutes, present in the water, compete for the OH-radicals and withdraw thereby OH-radicals from reactions with the pesticide, to be degraded. Moreover reactions of excess ozone with OH-radicals have to be taken into consideration[32] (Eqns. 9 and 10). The formed HO_2-radical shows low reactivity towards typical pollutants.

$$RH + \cdot OH \rightarrow R\cdot + H_2O \tag{6}$$

$$RR'C = CR''R''' + \cdot OH \rightarrow RR'C(OH) - (\cdot C)R''R''' \tag{7}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{8}$$

$$O_3 + \cdot OH \rightleftarrows HO_4\cdot \tag{9}$$

$$HO_4\cdot \rightarrow HO_2\cdot + O_2 \tag{10}$$

Moreover the oxidative effect of OH-radicals is reduced by the presence of OH-radical scavengers in a water matrix. Bicarbonate and carbonate ions play a dominant role as OH-radical scavengers[33,34], because they can be present at concentrations of several millimoles per liter and react with high rate constants with OH-radicals ($k_{Bicarbonate} = 1.1 \times 10^7$ L mol^{-1} cm^{-1}; $k_{Carbonate} = 3.9 \times 10^8$ L mol^{-1} cm^{-1}) to give the carbonate radical anion $CO_3\cdot^-$ (Eqns. 11 and 12), which shows much lower reactivity compared to the OH-radical[35].

$$\cdot OH + HCO_3^- \rightarrow CO_3\cdot^- + H_2O \tag{11}$$

$$\cdot OH + CO_3^{2-} \rightarrow CO_3\cdot^- + OH^- \tag{12}$$

Guittonneau *et al.*[36] describe the rate, at which OH-radicals oxidize pesticide P in the presence of HCO_3^- and other OH-radical scavengers S_i (Eqn. 13),

$$-\frac{d[P]}{dt} = \frac{n(d[O_3])}{dt} \cdot \frac{k_p[P]}{k_p[P] + k_{HCO_3^-}[HCO_3^-] + \sum k_i[S_i]} \tag{13}$$

where $n(d[O_3]/dt)$ represents the rate of OH-radical production by photolytic decomposition of ozone and the second term represents the fraction of OH-radicals that oxidize the pesticide P besides HCO_3^- and other OH-radical scavengers. Eqn. 13 reveals that the degradation rate of the pesticide $d[P]/dt$ decreases with increasing concentrations of OH-radical scavengers (e.g. HCO_3^-, S_i) and increasing the reaction rate constants of these scavengers.

According to Peyton *et al.*[37] the influence of the UV/O_3 process on the rate of pesticide disappearance is given by Eqn. 14. The rate of pesticide degradation may be represented by a linear combination of terms from the contributing processes during application of UV/O_3: Photolysis, ozonation and photolytic oxidation,

$$- \frac{d\,[P]}{dt} = k_p\, I^a\, [P]^b + k_O\, [O_3]_l^c\, [P]^d + k_u\, I^e\, D^f\, [P]^g \tag{14}$$

where [P] is the pesticide concentration, I the flux of irradiation, $[O_3]_l$ the concentration of ozone in the liquid phase, D the dose rate of ozone, k the reaction rate constants for photolysis (k_p), ozonation (k_o) and photolytic oxidation (k_u), a-g represent the reaction orders.

In the photolysis term (first term of Eqn. 14) k_p includes the quantum yield of pesticide degradation. The ozonation term (second term of Eqn. 14) represents direct reaction of ozone with the pesticide in the liquid phase. The photolytic oxidation term (third term of Eqn. 14) represents both the generation of OH-radicals by photo-decomposition of aqueous ozone and the reaction of OH-radicals with pesticide molecules.

From Eqn. 14 the effect of I, $[O_3]_l$ and D on the degradation rate can be estimated qualitatively, even if the numerical values of the rate constants (k_p, k_o, k_u) and the reaction orders (a–g) are not known. Therefore a technical process for water purification should be adapted on the specific problem (e.g. pesticide, water matrix).

In order to estimate the effect of OH-radicals in the UV/O_3 process, we employed a pesticide which is scarcely degraded by UV-light only (parathion-methyl, 1), and another one which is degraded by UV-light to a much higher extent (atrazine, 4). Figure 1 shows the pesticides used for the degradation experiments and their oxidation products investigated in this study.

EXPERIMENTAL

Chemicals

Atrazine (98.4%), desethylatrazine (99%), desisopropylatrazine (98.5%) and desethyldesisopropylatrazine (96.9%) were purchased from Dr. Ehrenstorfer (Augsburg, FRG), parathion-methyl (99%), paraoxon-methyl (96%), parthion-ethyl (99%) from Riedel-de Haën (Seelze, FRG) and p-nitrophenol (98%) from Aldrich (Steinheim, FRG). $Na_2S_2O_3$ p.a. (Merck, Darmstadt, FRG), $TiOSO_4{\cdot}xH_2SO_4{\cdot}xH_2O$ (Aldrich, Steinheim, FRG), indigo-5,5′,7-trisulfonate tripotassium salt (Fluka, Buchs, CH), methanol, ethylacetate and acetone, all 'Distol' grade (Fisons from Müller, Fridolfing, FRG) were used as received.

Analysis

Samples were taken in glass bottles containing $Na_2S_2O_3$ with a final concentration of 1 g/L. $Na_2S_2O_3$ reduces immediately residual ozone and hydrogen peroxide. Extraction and pre-concentration of the samples were carried out by solid phase extraction with 2 g octadecyl

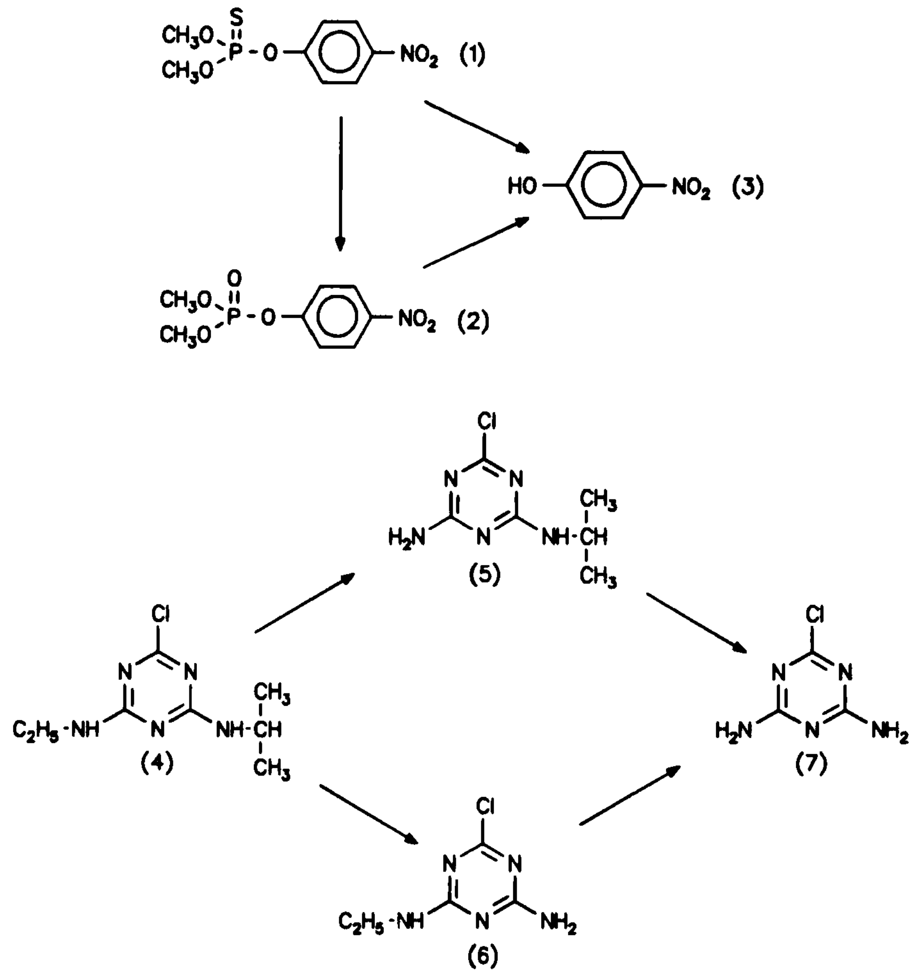

Figure 1 Pesticides used for degradation experiments and their oxidation products investigated in this study. - (1) parathion-methyl, (2) paraoxon-methyl, (3) p-nitrophenol, (4) atrazine, (5) desethylatrazine, (6) desisopropylatrazine, (7) desethyldesisopropylatrazine.

silica (C_{18}) 40 µm, 60 Å (Baker, Deventer) in glass cartridges, percolating 0.1 L up to 1 L sample at a flow rate of 4 mL/min. After drying by a stream of nitrogen the solid phase material was eluted with two 5 mL portions of acetone, then the organic solution was evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved either with 1 mL acetone containing methylatrazine (synthesis by Weller[38], C = 50 µg/L) as internal standard for the triazine determination, or with 200 µL ethylacetate containing parathion-ethyl (C = 1 mg/L) as internal standard for the determination of phosphorus pesticides. At 1 L sample volume the extraction recovery is 61 ± 3.5 % (n = 6) for atrazine, 68 ± 6.5 % (n = 6) for desethylatrazine and 30 ± 5 % (n = 6) for desisopropylatrazine. At 100 mL sample volume the extraction recovery is 105 ± 6 % (n = 6) for parathion-methyl, 109 ± 7 % (n = 6) for paraoxon-methyl and 100 ± 5 % (n = 6) for p-nitrophenol. The extraction recoveries were checked with spiked water samples.

Atrazine and its degradation products were analyzed by HRGC on a Hewlett Packard HP 5890 gas chromatograph with a thermionic detector (NPD) and a DB 5 column (J & W Scientific, 30 m × 0.32 mm, film thickness 0.25 µm). The injector temperature was set at 240°C, the detector temperature at 280°C, the oven temperature was programmed in three ramps (50 °C isothermal for 1 min, with 30°C/min to 160°C/min to 160°C, with 4°C/min to 200°C, with 30°C/min to 280 °C, 5 min isothermal) to obtain sufficient separation.

Parathion-methyl and its degradation products were analyzed by HRGC/MS on a Hewlett Packard HP 5890 series II gas chromatograph interfaced to a HP 5971 mass selective detector (MSD) and equipped with a Ultra-2 column (Hewlett Packard, 50 m × 0.2 mm, film thickness 0.33 µm). The sample was injected via temperature programmed vaporization (PTV, Gerstel, Mühlheim; program: 50 °C, isothermal for 3 s, with 12°C/s to 280 °C, isothermal for 300 s), oven temperature was programmed (90 °C, isothermal for 3 min, with 8 °C/min to 280 °C, isothermal for 5 min) and MS interface was set at 280 °C, resulting in a MS source temperature of 190 °C. Quantitative determinations were carried out in the SIM (selected ion monitoring) mode with electron impact ionization (EI) at 70 eV, recording the appropriate abundant ions (m/z 109 and 110 for all phosphorus containing compounds, m/z 139 for p-nitrophenol).

UV/VIS absorption measurements were carried out on a Zeiss PM 6 spectrophotometer. Ozone was determinated by the indigo method[39] and hydrogen peroxide after reaction with $TiOSO_4$[40].

UV/O_3 pilot plants

For UV/O_3 degradation experiments two plants from Wedeco Umwelttechnologie (Herford, FRG) were used: The pilot plant SWO 70/UV for experiments carried out at our institute and the plant LWO 1000 for experiments on large-scale at a drinking water supply.

The technological characteristics for both plants are presented in Table 1 and a schematic diagram of the pilot plant SWO 70/UV is shown in Figure 2. Both plants are equipped with medium pressure mercury vapor lamps, which provide almost equal UV-radiant power (in the UV-C region) per irradiated reactor volume. The emission spectrum ranges from 220 to 440 nm. The calculated mean hydraulic residence time in the UV-reaction unit is much shorter in the large-scale plant LWO 1000. In addition to that the maximum ozone dose rate applied to the total water flow (flow through the plant plus backflow) is smaller in the plant LWO 1000.

Mode of operation

Ozone is generated by dark discharge of dioxygen (O_3 generator in Figure 2) and an ozone/dioxygen mixture is introduced via an injector (it works like a water jet pump) by an

Table 1 Technological characteristics of the UV/O_3 plants.

Characteristic	*Pilot plant* *SWO 70/UV*	*Large-scale plant* *LWO 1000*
Mercury vapor lamp (Heraeus, Hanau), type	UVH 4122	UVH 10022
Electrical power (kW)*	4	10
Radiant power in the UV-C region (kW)*	0.4	1
Available radiant power/reactor volume (kW/L)	0.1	0.085
Light path length in the reactor (cm)	2	2
Hydraulic residence time in the UV-reactor (s)	5	1.8
Ozone dose rate applied to the water flow (g/m^3)	47	11
Continuous flow rate (m^3/h)	0–3	70
Back flow rate (m^3/h)	1.5	20
System pressure (bar)	5	5

*manufacturer data

excessive pressure of water (10 bar) into the backflow. The backflow is conducted through two vessels, for complete O_3 absorption and for blowing off the excessive pressure, respectively. At the inlet of the plant the raw water is mixed with the ozonized water from

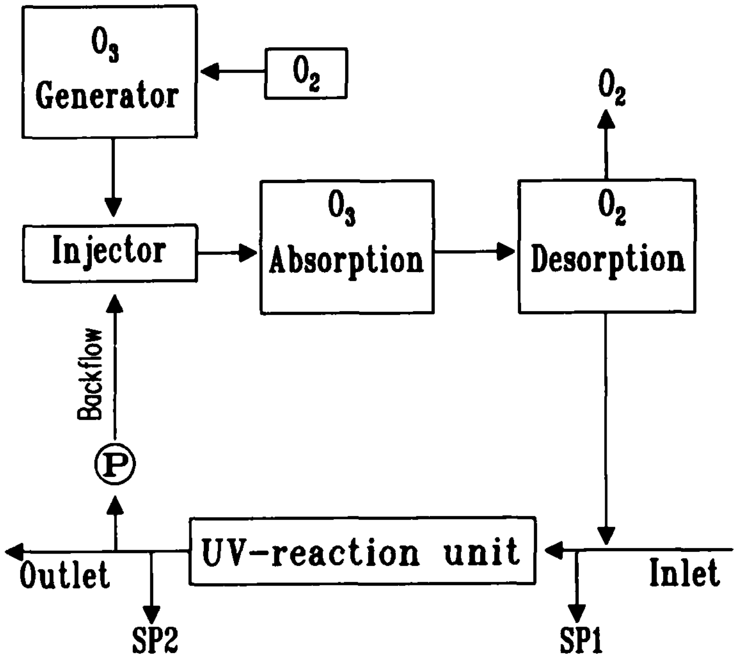

Figure 2 Schematic diagram of the UV/O_3 pilot plant. - P: circulation pump; SP: sampling port (1 before, 2 after the UV-reaction unit).

the backflow and reaches the UV-reaction unit. There the ozonated raw water flows round a tube lamp, which is fixed in axial position in the annular reactor. In the UV-reactor aqueous ozone is decomposed by UV-light to yield high-reactive OH-radicals. The sampling ports SP1 and SP2 (indicated in Figure 2) are placed directly at the UV-reaction unit. Sampling at this ports provide data describing the degradation effect after one passage through the UV-reaction unit.

RESULTS AND DISCUSSION

Degradation experiments with the UV/O_3 pilot plant SWO 70/UV

All experiments with the pilot plant SWO 70/UV were carried out under batch operation conditions (no influx and efflux; backflow was maintained at 1.5 m^3/h and is equal to the flow rate through the UV-reaction unit).

The pilot plant was fed with Munich tap water ($pH = 7.8$; $C(HCO_3^-) = 4$ mmol/L; $C(NO_3^-) = 0.065$ mmol/L; C(dissolved organic carbon) = 0.2 mg/L, calculated as carbon).

In order to describe the photodecomposition of ozone in the UV-reaction unit (the first reaction step of OH-radical generation), ozone concentration was measured at the sampling ports SP1 and SP2 (sampling ports indicated in Figure 2). The ozone dose rate applied to the backflow (theoretically expected concentration) was linearly correlated with the measured ozone concentration at SP1, with a slope of 0.44 (44% of the ozone injected was found as dissolved ozone at SP1). This result may be due to incomplete dissolution of ozone in the water, the autodecomposition of ozone at higher concentrations and the ozone destruction by surfaces and dissolved organic matter[41].

At different ozone dose rates the measured ozone concentration at SP2 was in all cases below 0.05 mg/L, when the applied UV-C radiant power was 80 W/L. This indicates that the aqueous ozone was completely decomposed by the UV-irradiation applied in the reaction unit.

The measured hydrogen peroxide concentration at SP2, generated by photodecomposition of aqueous ozone (Eqn. 1), correlates linearly with the ozone concentration at SP1 with a slope of 0.30 (30% of decomposed ozone were observed as H_2O_2). These data show that there is no complete reaction of HO_2^- with O_3 according to Eqn. 2 and OH-radical generation works with a loss of $\geq$ 40%.

UV and UV/O_3 degradation of parathion-methyl (1) and atrazine (4) - a comparison

The degradation efficiency of UV/O_2 and UV/O_2/O_3 in the pilot plant SWO 70/UV was evaluated for the pesticides parathion-methyl (1) and atrazine (4, see Figure 1). Pesticides were dissolved in methanol and subsequently transferred into an aqueous matrix. Homogenization of the solution was obtained by recirculation in the plant and provides pesticide concentrations of 10 µg/L (at a methanol/water ratio of 10^{-5}). No effect of the methanol on the degradation efficiency and the formation of by-products could be observed for both parathion-methyl (1) and atrazine (4) in blank experiments. Sampling was done at SP1 and SP2, directly at the UV-reaction unit, in order to describe the degradation after one UV-reactor passage. For 3 single experiments with the pilot plant we estimated a relative standard deviation of 8%. The resulting pesticide concentration C at SP2 was normalized to the concentration C_0 at SP1, describing the degradation rate by the ratio C/C_0.

After one UV-reactor passage (5 s hydraulic residence time) the reaction of ozone and of H_2O_2 alone with the pesticide was negligible and therefore we investigated only the effect of UV-light/dioxygen and $UV/O_2/O_3$ on the degradation efficiency. The effect of the UV-radiant power (at oxygen saturation without any ozone dosage) on the degradation rate is shown in Figure 3. Parathion-methyl (1) is scarcely degraded by UV-light only. At the maximum UV-radiant power (80 W/L) applied, the concentration ratio C/C_0 was still 0.92 for parathion-methyl (1). For atrazine (4) we determined an increasing degradation rate with increasing UV-radiant power. C/C_0 was 0.15 after a treatment with 80 W/L UV-radiant power (Figure 3). These data are due to the different quantum yields Φ for pesticide degradation. According to Nick *et al.* [42] the quantum yield for atrazine (4) was estimated to be $\Phi = 50$ mmol/Einstein (dye laser experiments at a wavelength of 260 nm [43]). Comparable data reports Zepp *et al.* [44] for degradation of parathion-methyl (1) in natural water under sunlight irradiation ($\Phi = 0.17$ mmol/Einstein). However, at a wavelength of 254 nm the extinction coefficient of atrazine ($\varepsilon = 3860$ L mol^{-1} cm^{-1}) and parathion-methyl ($\varepsilon = 5130$ L mol^{-1} cm^{-1}) in aqueous solution are of the same order of magnitude.

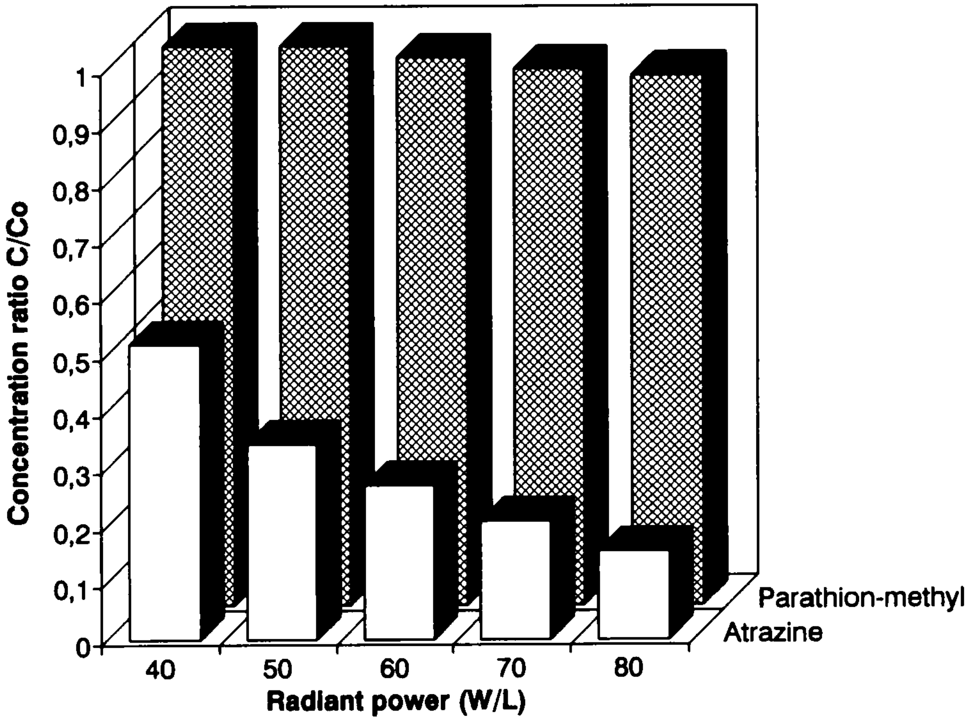

Figure 3 Effect of UV-radiant power on pesticide degradation by UV/O_2 in the pilot plant. - $C_0 = 10$ µg/L.

For an accurate calculation of the UV-degradation rate of a pesticide, the amount of light absorbed per unit time, at all wavelengths emitted by the UV-lamp, is necessary[45]. Since there were no data available of the photon fluxes at all wavelengths emitted by the employed lamp type, no calculation of photolysis rates have been carried out.

Further the effect of UV-light in combination with dioxygen and ozone ($UV/O_2/O_3$) on the degradation rate of atrazine (4) and parathion-methyl (1) was investigated. At the highest UV-radiant power (80 W/L) we applied increasing ozone dose rates and investigated the effect on the degradation rate. For parathion-methyl (1) an increasing degradation rate with increasing ozone dose rates was found (Figure 4). The concentration ratio C/C_0 was reduced from 0.93 to 0.47 by rising the ozone dose rate from 0 to 6 g/m^3 and to 0.23 applying an ozone dose rate of 32 g/m^3 (Figure 4).

The effect of ozone dose rate on the degradation efficiency of atrazine (4) was inversely related. The concentration ratio C/C_0 was affected scarcely by rising the ozone dose rate from 0 to 6 g/m^3 (Figure 4).

The different effect of ozone on the degradation rate of atrazine (4) and parathion-methyl (1) could be due to an inner filter effect of ozone. Hence ozone shows an high molar absorption coefficient ($\varepsilon = 2900\ L\ mol^{-1}\ cm^{-1}$ at $\lambda_{max} = 260$ nm). At an ozone concentration of 10 mg/L (0.21 mmol/L) 70% of the irradiation at 260 nm are absorbed by ozone at a path length of 2 cm. As a consequence there are two contrary effects on the degradation rate of pesticides at increasing ozone dose rates: Diminution of the UV-degradation by the inner

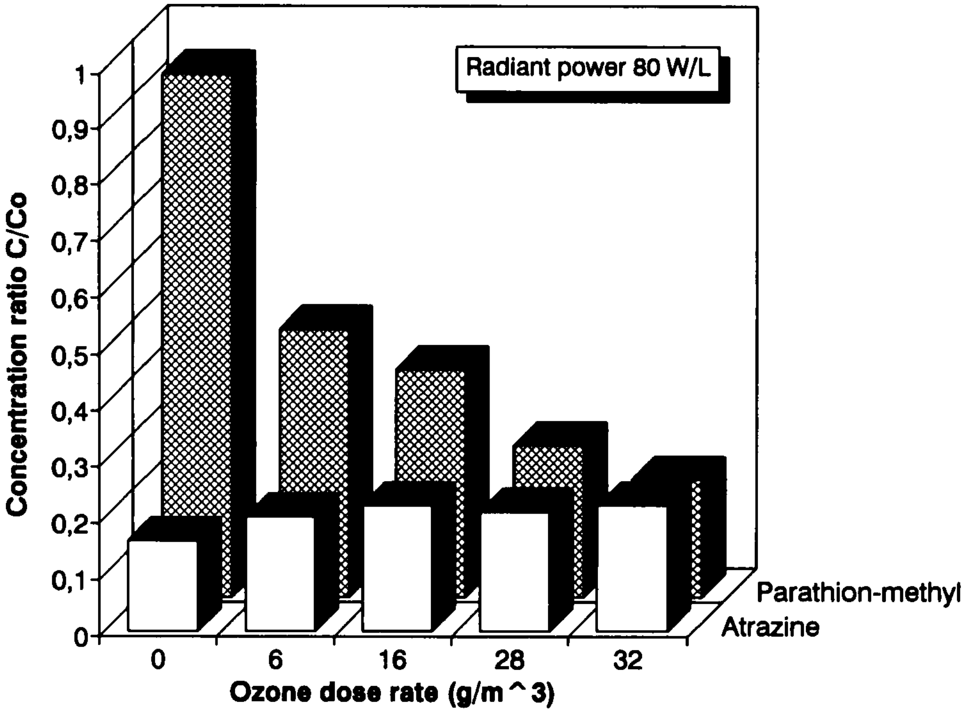

Figure 4 Effect of ozone dose rate on pesticide degradation by $UV/O_2/O_3$ in the pilot plant. - $C_0 = 10$ µg/L.

filter effect of ozone and increase of OH-radical production, followed by an increased OH-radical mediated degradation.

By-product formation

The effect of ozone dose rate on by-product formation in the pilot plant SWO 70/UV was investigated for parathion-methyl (1). In laboratory experiments p-nitrophenol (3) and paraoxon-methyl (2) were found as the major degradation products (see Figure 1). They were formed by photochemically induced solvolysis of the phenol ester bond and formal by oxidation of the P = S group, respectively. The by-product formation during the degradation of parathion-methyl (1) is shown in Figure 5. At an ozone dose rate of 32 g/m^3 we determined the lowest residual concentration of parathion-methyl (1) and not any by-product. Therefore we concluded that the generated by-products were further degraded at high rate constants.

Ozonation of aqueous atrazine (4) solutions (without any UV) yields desethylatrazine (5) as major product in amounts up to 30% of initial atrazine (4) concentration. However, the desalkylated atrazine derivatives (5, 6 and 7, see Figure 1) are not formed during the treatment with UV/O_2/O_3 in amounts greater than 2%. Hydroxy derivatives of atrazine (4), the major degradation products after UV-irradiation[42], were not investigated yet.

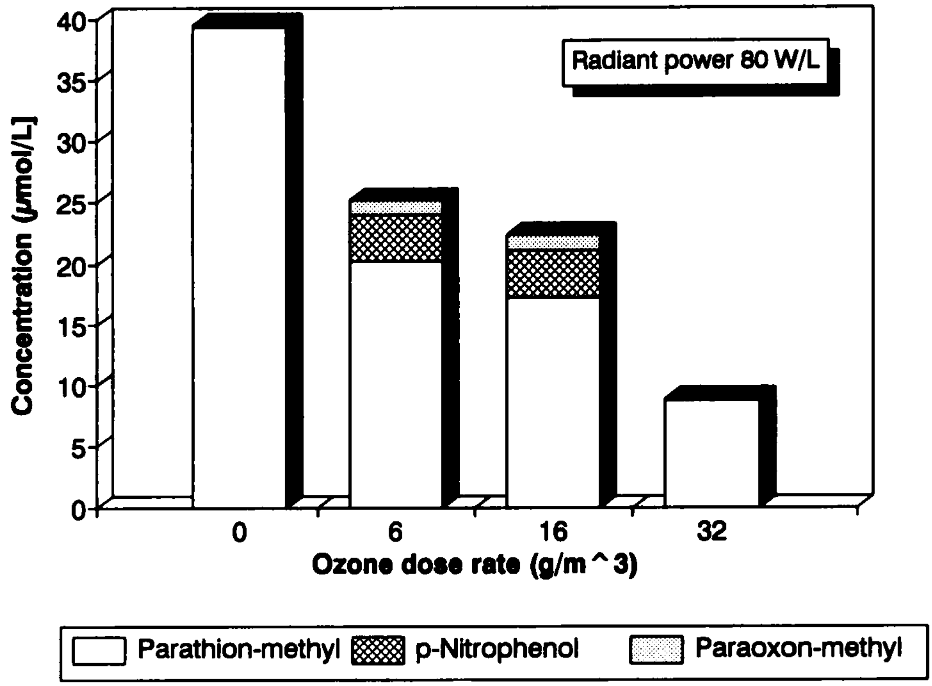

Figure 5 Effect of ozone dose rate on by-product formation during the degradation of parathion-methyl by UV/O_2/O_3 in the pilot plant. - C_0 = 10 mg/L.

However, the identified by-products do not provide any information about the OH-radical action during the UV/O_2/O_3 degradation. According to Eqns. 6, 7 and 8 the OH-radical attack, the formation of an organic radical R· and subsequently the formation of an hydroperoxyl radical RO_2· are only the first steps of by-product formation, which are followed by a diversity of decomposition pathways[31]. In this way the formation of p-nitrophenol and desalkylated atrazine can only be explained by the oxidation of a molecule moiety, which is subsequently split off.

Field experiments with the large-scale plant

Experiments with the large-scale plant LWO 1000 were performed under field conditions at a drinking water supply. The plant was fed with ground water (pH = 7.2; C(HCO_3^-) = 7.6 mmol/L; C(NO_3^-) = 0.8 mmol/L; C(dissolved organic carbon) = 0.6 mg/L, calculated as carbon), contaminated with atrazine (4) (C_0= 0.28 µg/L) and desethylatrazine (5) (C_0= 0.60 µg/L) at a continuous flow rate of 70 m^3/h. In order to describe the degradation rate of UV-light/dioxygen and the UV/O_2/O_3 combination, sampling was done at the inlet and the outlet of the plant. The estimated relative standard deviation for 6 samples was 4% for

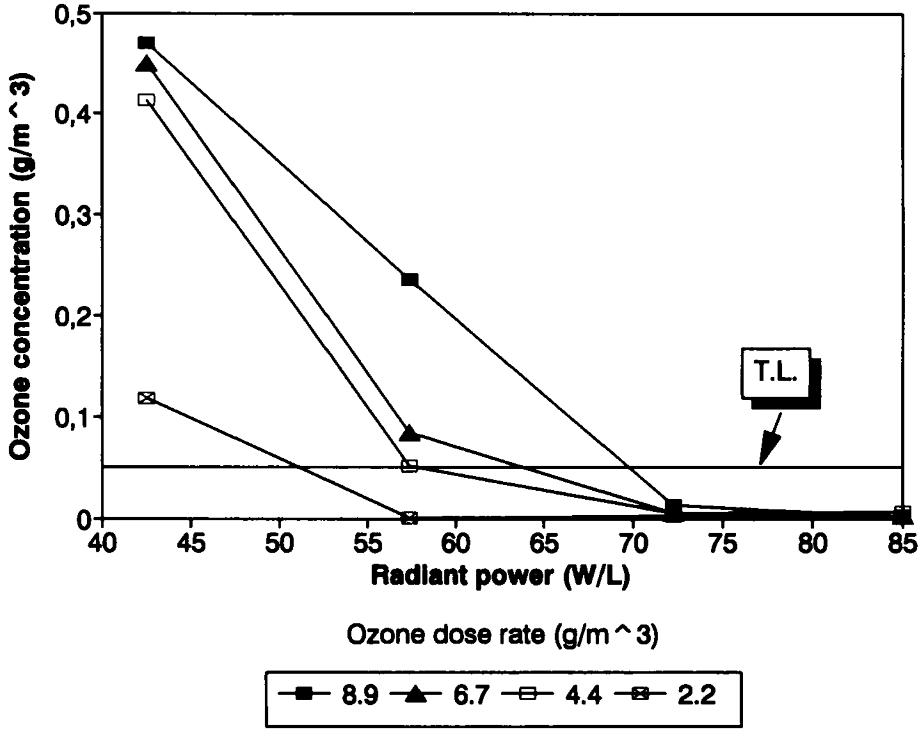

Figure 6 Ozone concentration at the outlet of the large-scale plant at variation of radiant power and ozone dose rates applied. - T. L.: Threshold limit for ozone in drinking water.

atrazine (4) and 7% for desethylatrazine (5). Again degradation was described by the concentration ratio C/C_0, with the concentration C at the outlet and C_0 at the inlet of the plant.

The threshold limit for ozone in drinking water is 0.05 mg/L. Hence the completeness of the ozone decomposition in the UV-reaction unit was investigated evaluating the ozone concentration at the outlet. The threshold limit for ozone at the outlet of the plant was reached only after application of a radiant power of 72.25 and 85 W/L for all ozone dose rates (Figure 6). In spite of this fact, experiments were done, applying all combinations of UV-radiant powers (42.5, 54.6, 72.25 and 85 W/L) and ozone dose rates (2.2, 4.4, 6.7 and 8.9 g/m^3).

The effect of ozone dose rate on atrazine (4) degradation rate is shown in Figure 7 applying different UV-radiant power. We could find a distinct drop of the concentration ratio (e.g. C/C_0 from 0.63 to 0.4, from 0.34 to 0.25) comparing the UV/O_2 degradation (0 g/m^3 ozone dose) with the UV/O_2/O_3 degradation at lowest ozone dose rate (2.2 g/m^3). At increasing ozone dose rates (2.2, 4.4, 6.7 g/m^3) we observed decreasing concentration ratios C/C_0 of atrazine (4), e.g. from 0.3 to 0.17 (at a radiant power of 54.6 W/L), from 0.25 to 0.12 (at a radiant power of 85 W/L). At low ozone dose rates the inner filter effect of ozone can be neglected. The degradation efficiency is improved by the elevated OH-radical generation from photolytic ozone decomposition. A further increase of the ozone dose rate

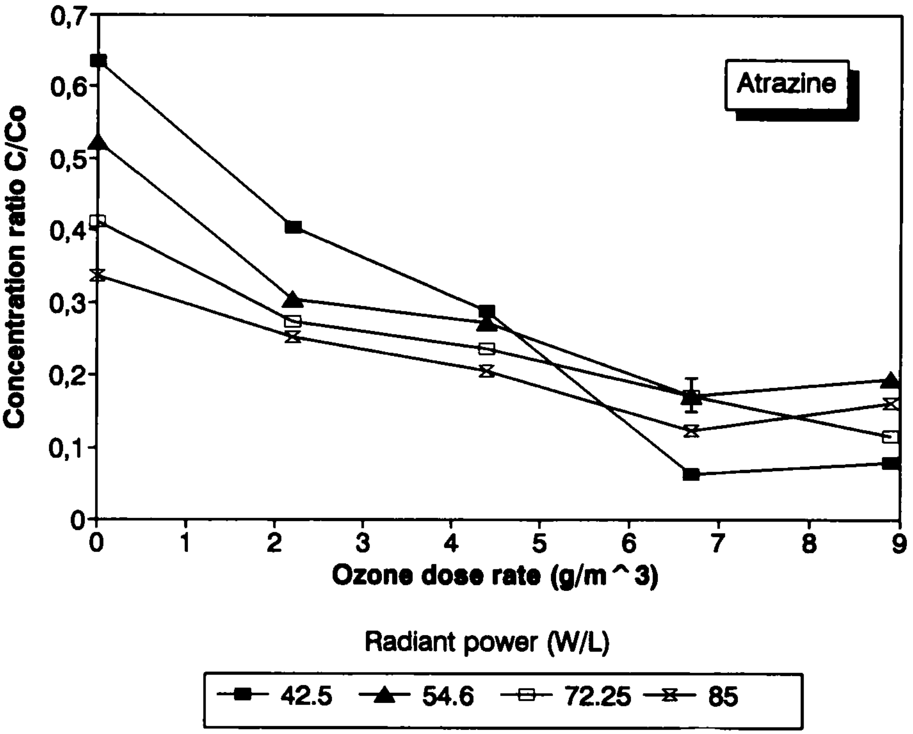

Figure 7 Effect of ozone dose rate on atrazine degradation at variation of radiant power applied in the large-scale plant. - Indicated is a typical error bar (3s, n = 6).

(8.9 g/m^3) did not result in a further decrease of the degradation rate, according to the results obtained for the degradation of atrazine (4) in the pilot plant.

Increasing radiant power resulted in a decreasing concentration ratio at low ozone dose rates at 2.2 and 4.4 g/m^3 (Figure 7). At higher ozone dose rates (6.7 and 8.9 g/m^3) this relation has not been observed. However one has to keep in mind, that at high ozone dose rates there is residual ozone in the water at the outlet (Figure 6). Residual ozone may react with HO_2^- (from residual H_2O_2) to yield OH-radicals (according to Eqns. 3–5). In this way residual atrazine (4) may react with ozone and OH-radicals after the UV-reaction unit on the way to the outlet and the sampling port of the plant. Therefore the measured atrazine (4) concentration was affected also by reactions after the UV-reaction unit. This might be an explanation for the unexpected low concentration ratios of 0.1 at 42.5 W/L radiant power (6.7 and 8.9 g/m^3 ozone dose rate) compared to 0.15 at 85 W/L (8.9 g/m^3).

For desethylatrazine (5) the dependence of the degradation rate on ozone dose rate and UV-radiant power is shown in Figure 8 and is similar to that of atrazine (4). However the lowest concentration ratios obtained for desethylatrazine (5) after $UV/O_2/O_3$ treatment were 0.25 (applying 8.9 g/m^3 ozone and 85 W/L radiant power) and 0.32 (applying 8.9 g/m^3 ozone and 54.6 W/L radiant power) and therefore higher than obtained for atrazine (4) degradation. The concentration ratio after UV/O_2 were also higher for desethylatrazine (5) (0.48 at 85 W/L) than for atrazine (4) (0.34 at 85 W/L).

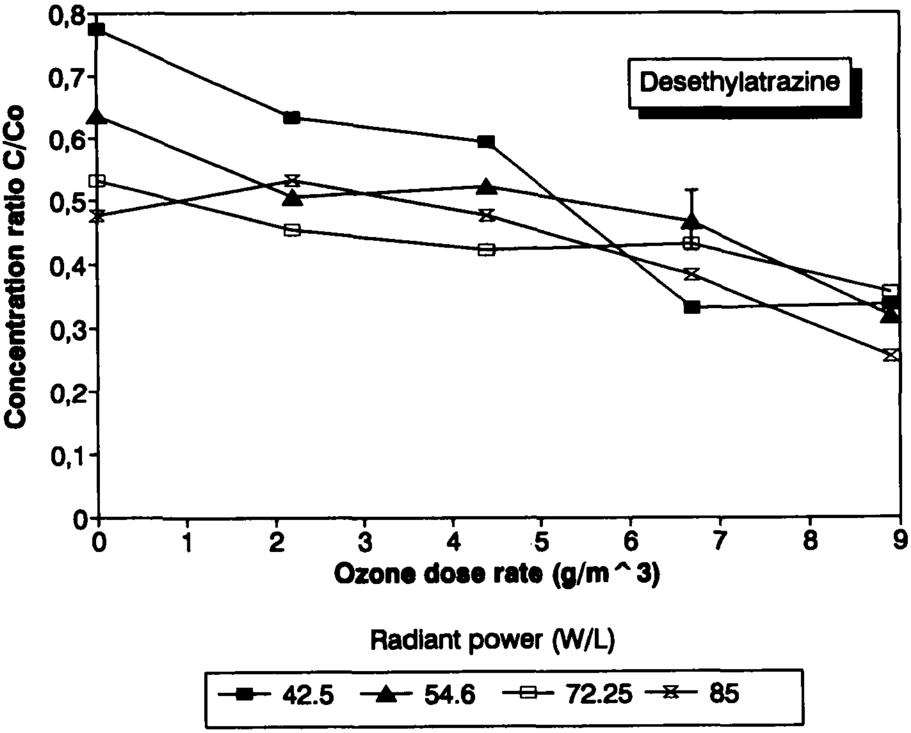

Figure 8 Effect of ozone dose rate on desethylatrazine degradation at variation of radiant power applied in the large-scale plant. - Indicated is a typical error bar (3s, n = 6).

Employing a radiant power of 85 W/L, the dosage of ozone first does not lead to a decrease of the concentration ratio, namely C/C_0 is 0.48 (UV-degradation at 0 g/m^3 ozone) and 0.53 (2.2 g/m^3 ozone). Nevertheless it has to be taken into consideration that desethylatrazine (5) is formed as a by-product of the degradation of atrazine (4) by ozone. For that reason the concentration of desethylatrazine (5) could be elevated by ozonation of atrazine (4) in the plant before the UV-reaction unit was reached. For that reason the concentration ratio of desethylatrazine (5) can be elevated by increasing the ozone dose rate (Figure 8).

The combination of low UV-radiant power (42.5 W/L) and high ozone dose rates (6.7 and 8.9 g/m^3) yielded unexpected low concentration ratios, 0.33 and 0.34, respectively (cf. atrazine (4) degradation applying these combination).

Was field application of drinking water treatment by UV/O$_3$ successful?

The concentration of atrazine (4) at the outlet of the plant fell below the threshold limit for pesticides applying the highest ozone dose rates 8.9 and 6.7 g/m^3 combined with radiant power of 42.5 up to 85 W/L (Figure 9). However, combinations of high ozone dose rates with high UV-radiant power are the only useful applications, on account of minimizing the residual ozone concentration in the outlet (see Figure 6).

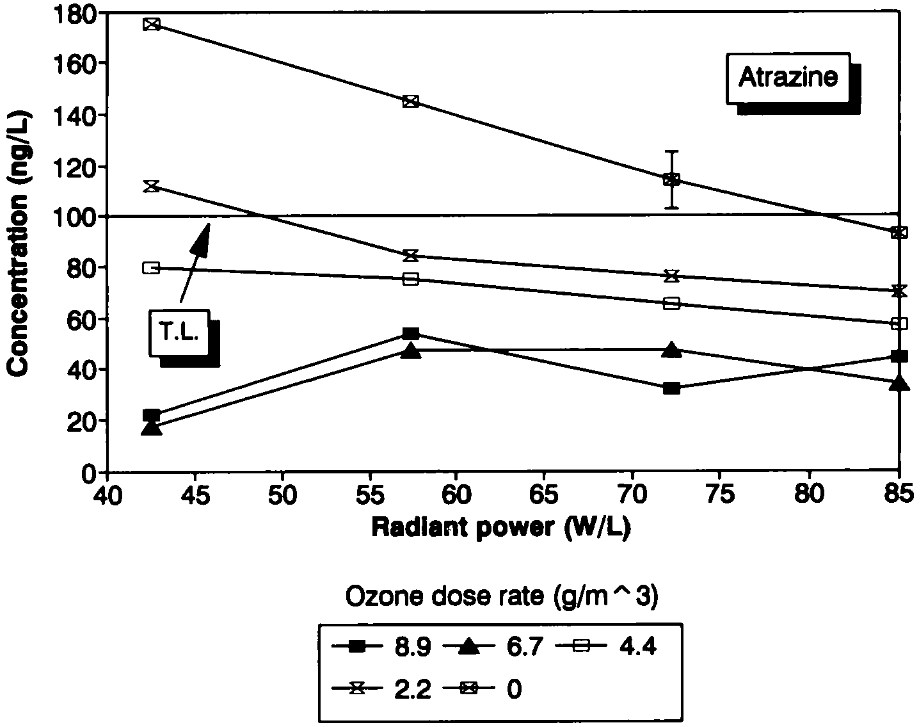

Figure 9 Effect of radiant power on atrazine concentration in the outlet of the large-scale plant at variation of ozone dose rates. - T. L.: Threshold limit for pesticides in drinking water. Indicated is a typical error bar (3s, n = 6).

For desethylatrazine (5) the threshold limit could not be reached at any combination of ozone dose rate and UV-radiant power (Figure 10). The lowest desethylatrazine (5) concentrations attained at an ozone dose rate of 8.9 g/m^3 were 200 ng/L (42.5 W/L radiant power) and 150 ng/L (85 W/L radiant power).

The degradation rate could be improved by decreased inflow and by this means increased hydraulic residence times in the UV-reaction unit and higher ozone dose rate. At a continuous flow rate of 30 m^3/h of the incoming ground water the desethylatrazine (5) concentration was decreased to 90 ng/L (atrazine concentration < 10 ng/L) at a radiant power of 85 W/L and an ozone dose rate of 16 g/m^3 (hydraulic residence time in the UV-reaction unit: 3.2 s).

CONCLUSION

In the pilot plant SWO 70/UV, parathion-methyl (1) was scarcely degraded by UV-light only ($C/C_0 = 0.92$), compared to atrazine (4) ($C/C_0 = 0.16$). For parathion-methyl (1) an increasing degradation rate at increasing ozone dose rates was found. The degradation rate

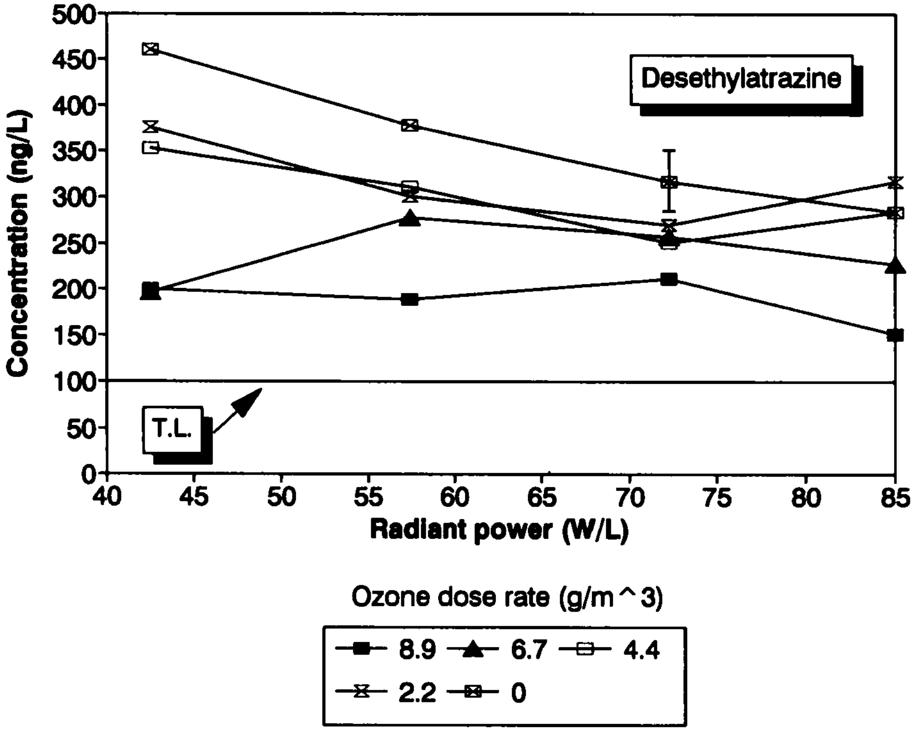

Figure 10 Effect of radiant power on desethylatrazine concentration in the outlet of the large-scale plant at variation of ozone dose rates. - T. L.: Threshold limit for pesticides in drinking water. Indicated is a typical error bar (3s, n = 6).

of atrazine (4) could not be improved by $UV/O_2/O_3$ in the pilot plant. An explanation of this effect might be the inner filter effect of ozone and as a consequence, diminution of the UV-degradation. This filter effect does not affect the degradation of parathion-methyl (1), because of the low quantum yield of the parathion-methyl (1).

In field experiments with the large-scale plant LWO 1000 atrazine (4) could be degraded below the threshold limit for pesticides in drinking water (0.1 µg/L), whereas the residual desethylatrazine (5) concentration exceeded this limit, at a continuous flow rate of 70 m^3/h. At a flow rate of 30 m^3/h the desethylatrazine (5) concentration could be decreased to 90 ng/L. Applying UV-light only, desethylatrazine (5) ($C/C_0 = 0.48$ at 85 W/L) is less degraded than atrazine (4) ($C/C_0 = 0.34$ at 85 W/L). The degradation efficiency of atrazine (4) and desethylatrazine (5) could be improved by applying the combination of UV-light, dioxygen and ozone ($UV/O_2/O_3$) compared to UV-light.

In a further study the nitrite formation during the $UV/O_2/O_3$ process (photolysis of nitrate) and the breakdown of the triazine ring during the $UV/O_2/O_3$ process will be studied.

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