

RESEARCH ARTICLE

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# Ionizing radiation induced degradation of diuron in dilute aqueous solution

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## Abstract

**Background:** Cutting edge technologies based on Advanced Oxidation Processes (AOP) are under development for the elimination of highly persistent organic molecules (like pesticides) from water matrices. Among them, ionizing radiation treatment represents a promising technology that requires no additives and can be easily adapted to an industrial scale. In these processes several reactive species are produced, mainly powerful oxidizing radicals inducing the degradation. This paper investigates the reactions taking place in dilute aqueous solutions of a hazardous pollutant (diuron) during irradiation.

**Results:** Irradiation of aqueous diuron solutions resulted in effective degradation of the solute mainly due to the reactions of hydroxyl radicals formed in water radiolysis. Hydroxyl radical reacts with diuron with a second order rate constant of  $(5.8 \pm 0.3) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . The main reaction is addition to the ring forming hydroxycyclohexadienyl radical. 30 – 50% of hydroxyl radical reactions induce dechlorination. Reactions with the methyl groups or with the  $\alpha$ -amino group have low contribution to the transformation. The presence of dissolved oxygen enhances the rate of degradation; one hydroxyl radical on average induces five-electron oxidations. The high oxidation rate is attributed to the reaction of some of the primarily formed organic radicals with dissolved  $\text{O}_2$  and the subsequent reactions of the peroxy radicals.

**Conclusion:** The presence of dissolved oxygen is highly important to achieve efficient ionizing radiation induced degradation of diuron in dilute aqueous solution.

**Keywords:** Diuron, Hydroxyl radical, Degradation, Advanced oxidation processes, Irradiation technology

## Background

Diuron, a phenylurea herbicide, has been used worldwide in agriculture to control broadleaf and grassy weeds in cereals and other crops for more than 50 years. Diuron is highly persistent in the aquatic environment due to its photochemical stability. As a consequence, it has been detected in wastewater effluents and in surface waters at low concentrations up to the  $\mu\text{g dm}^{-3}$  level. As a potentially carcinogenic substance, its occurrence in such reservoirs poses serious threat to human health and it is also toxic to microorganisms. The European Water Framework Directive classifies diuron as one of the priority substances, being a hazardous pollutant [1].

Diuron is also included in the drinking water contaminant candidate list of the U.S. Environmental Protection Agency [2], to enforce further research and data collection.

Advanced Oxidation Processes (AOP) are suggested for the elimination of persistent organic compounds from water matrices. The radical induced degradation of diuron has been investigated formerly using several AOP [3-7]. In these experiments, with the exception of direct photodegradation, hydroxyl radical was the main oxidizing agent. Mazellier and Sulzberger [8] observed only one product in heterogenous photo-Fenton system (3-(3,4-dichlorophenyl)-1-formyl-1-methylurea), indicating  $\cdot\text{OH}$  attack on the methyl group. In other experiments using ozonation or photocatalytic oxidation, the  $\cdot\text{OH}$  attack took place on the aromatic ring leading to hydroxylated or dechlorinated products.

The ionizing radiation treatment is one of the AOP. In establishing reaction mechanisms radiation chemistry

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provides the advantage of investigating the radical intermediates by electron pulse radiolysis (their yields can be easily calculated) and additionally achieving the final products by utilizing  $^{60}\text{Co}$   $\gamma$ -irradiation. Radiation technology can be applied on an industrial scale [9]. The aim of the present study is to investigate both the intermediates and the final products of diuron degradation induced by water radiolysis techniques. In order to promote the practical application we also determined sum parameters important in wastewater analysis: chemical oxygen demand (COD), total organic carbon (TOC) and total nitrogen content (TN). To the best of our knowledge, there is only one publication reporting the radiation induced degradation of diuron [10]. In a previous paper we have already reported on the degradation of fenuron [11].

## Materials and methods

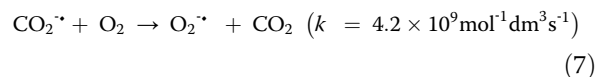
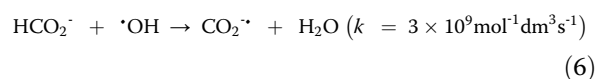
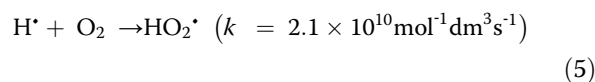
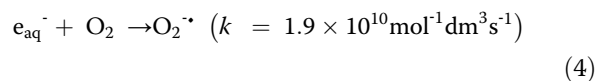
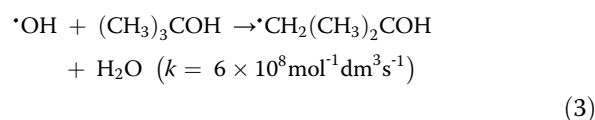
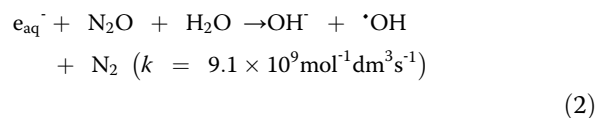
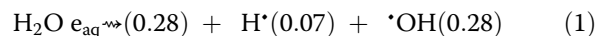
### Chemicals and equipment

Diuron and other chemicals were purchased from Spectrum-3D or Carlo Erba and used without further purification. HPLC grade eluents for liquid chromatographic analysis were obtained from Fischer Chemicals. All solutions were prepared at their natural pH. The absorption spectra of the irradiated samples were recorded on a JASCO 550 UV-Vis spectrophotometer in a 1 cm cell. Appropriate dilutions were applied in order to stay within the linear range of the Lambert-Beer relation. An Agilent Technologies 6410 Triple Quad HPLC-MS/MS system was used for final product identification. Liquid chromatographic separations were carried out on a Phenomenex Kinetex Phenyl-Hexyl column (100 mm  $\times$  2.1 mm  $\times$  2.6  $\mu\text{m}$ ) using isocratic elution mode at a flow rate of 0.25  $\text{cm}^3 \text{min}^{-1}$ . The mobile phase composed of 45% methanol and 55% water. The concentration of adsorbable organic halides (AOX) and free chloride ions were monitored by AOX equipment and perfectION<sup>TM</sup> Combination Chloride Electrode, respectively. COD measurements were performed with a Behrotest TRS 200 COD system. TOC and TN were measured using Shimadzu TOC-VCSN equipment.

### Pulse radiolysis and steady-state gamma irradiation

Pulse radiolysis was performed using 800 ns pulses of a linear accelerator, and an optical detection system with a cell having 1 cm light path length [12]. Pulse dosimetry was carried out in air-saturated,  $1 \times 10^{-2} \text{ mol dm}^{-3}$  KSCN solutions by monitoring the absorbance of  $(\text{SCN})_2^{\cdot-}$  at  $\lambda_{\text{max}}$  480 nm. The absorbed doses per pulse were 20 Gy. A  $^{60}\text{Co}$  gamma facility with 1.8 PBq activity was used for steady-state gamma irradiation. The dose rate was measured to be  $\sim 10 \text{ kGy h}^{-1}$  using ethanol-monochlorobenzene (ECB) dosimetry.

In the radiolysis of water, hydrated electron ( $e_{\text{aq}}^-$ ), hydrogen atom ( $\text{H}^\cdot$ ) and hydroxyl radical ( $^\cdot\text{OH}$ ) form as reactive intermediates as shown in Eq. (1) [13,14].



In Eq. (1) the numbers in parentheses are the radiation chemical yields ( $G$ -values) in  $\mu\text{mol J}^{-1}$ . Standard radiation chemical techniques were applied in the experiments in order to observe the individual reactions of the intermediates. The  $^\cdot\text{OH}$  reactions were followed in  $\text{N}_2\text{O}$ -saturated solutions to convert  $e_{\text{aq}}^-$  to  $^\cdot\text{OH}$  in Reaction (2). Reactions between  $e_{\text{aq}}^-$  and diuron were investigated in  $\text{N}_2$ -saturated solutions containing 5 vol. % *tert*-butanol to convert  $^\cdot\text{OH}$  to the less reactive  $^\cdot\text{CH}_2(\text{CH}_3)_2\text{COH}$  in Reaction (3). When the solution was purged with  $\text{N}_2$  in the absence of *tert*-butanol, all the three primary species reacted with diuron. In the presence of dissolved  $\text{O}_2$  (air or  $\text{O}_2$  saturated solutions),  $e_{\text{aq}}^-$  and  $\text{H}^\cdot$  are converted to superoxide radical anion/perhydroxyl radical pair in Reactions ((4) and (5)). Hence, in these solutions  $^\cdot\text{OH}$  as well as the  $\text{O}_2^{\cdot-}/\text{HO}_2^\cdot$  pair induce the transformations ( $\text{p}K_{\text{a}} (\text{O}_2^{\cdot-}/\text{HO}_2^\cdot) = 4.8$ ). Experiments were also made in  $\text{O}_2$  saturated solutions containing Na formate ( $0.05 \text{ mol dm}^{-3}$ ). In such solutions (in addition to  $e_{\text{aq}}^-$  and  $\text{H}^\cdot$ )  $^\cdot\text{OH}$  is transformed to  $\text{O}_2^{\cdot-}/\text{HO}_2^\cdot$  in Reactions (6) and (7).

In most of the experiments  $\sim 1 \times 10^{-4} \text{ mol dm}^{-3}$  diuron solutions were investigated, they were saturated with appropriate gases ( $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$  or air) before irradiation.

## Results

### Pulse radiolysis

In the transient absorption spectra taken on samples investigating the  $\cdot\text{OH}$  reaction ( $\text{N}_2\text{O}$  saturated), three absorption bands were observed: two shorter wavelength bands peaking at  $\sim 330$  nm and  $\sim 360$  nm and a longer wavelength band with maximum around 460 nm (Figure 1). The build-up of these three bands was similar. In separate experiments we added  $\text{K}_3\text{Fe}(\text{CN})_6$  to the solution with equal concentration as diuron. In these solutions the  $\sim 360$  nm band had smaller intensity and it decayed quickly. The decay of the  $\sim 460$  nm band took place on the ms time scale.

In general,  $\cdot\text{OH}$  is a highly reactive electrophilic radical, in its reaction with diuron, however, direct oxidation (electron transfer) hardly occurs [5]: the basic reactions are addition to the ring and H-abstraction from one of the  $\text{CH}_3$  groups or from the N-H group. The absorption band at  $\sim 360$  nm is typical for the hydroxycyclohexadienyl radicals: e.g. for the chloroanilines the maxima of the bands are around 360 nm [15]. For fenuron the maximum is at 350 nm [11]. Therefore, we assign the  $\sim 360$  nm band to hydroxycyclohexadienyl radical isomers. Ring-hydroxylated products identified by HPLC-MS/MS technique provide further confirmation. In addition, this identification is in agreement with the fast decrease of this absorption band in the presence of  $\text{K}_3\text{Fe}(\text{CN})_6$ . This additive is known to oxidize cyclohexadienyl type radicals to phenols in fast reactions.

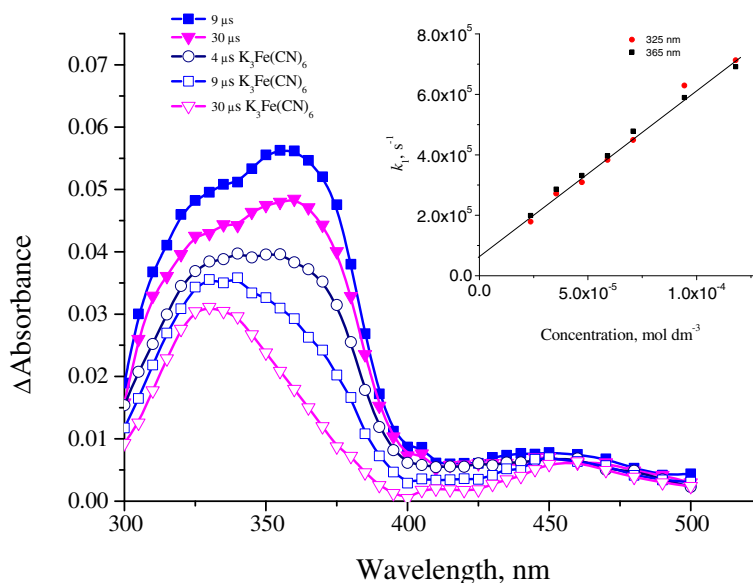
The longer wavelength band at  $\lambda_{\text{max}} \sim 460$  nm (and partly the band at 330 nm) may belong to (oxygen

centred) phenoxyl radicals or to (nitrogen centred) aminyl radical. As it will be discussed later, phenoxyl radical may form after release of HCl from the  $\cdot\text{OH}$  adducts. In the case of hydroxyanilines the  $\lambda_{\text{max}}$  of phenoxyl radicals are around 440 nm [15]. Aminyl radical can form in H-abstraction from N-H group. These radicals are observed in the reaction of  $\text{SO}_4^{\cdot-}$  with phenylureas and also in photoionization experiments. In the case of diuron  $\lambda_{\text{max}} \approx 450$  nm and  $\epsilon_{\text{max}} \approx 2000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  are suggested [3]. Based on the absorption spectra we cannot make a clear assignment for the longer wavelength band. Based on end product experiments (phenol formation) this absorbance can be attributed to phenoxyl radical. Considering the band intensity we can also safely say that H-abstraction from N-H is less important than the other reactions of  $\cdot\text{OH}$ .

The radical that forms in H-abstraction from a  $\text{CH}_3$  group is expected to exhibit UV absorbance below 300 nm. However, under our circumstances it is invisible since below 300 nm the absorbance of diuron disturbs observing the transient absorbance.

The rate constant of the diuron +  $\cdot\text{OH}$  reaction was determined by varying the diuron concentration and measuring the build-up of radical absorbance. The slope of the pseudo-first-order rate constant *versus* diuron concentration plot suggests a second order rate constant of  $(5.8 \pm 0.3) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (Figure 1, Inset). This value is in agreement with the rate constants published previously: their average is calculated to be  $6.0 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  [16].

In pulse radiolysis experiments with  $\text{N}_2$ -saturated solution containing *tert*-butanol ( $e_{\text{aq}}^-$  reaction) low transient



**Figure 1** Transient absorption spectra in  $\text{N}_2\text{O}$  saturated,  $1 \times 10^{-4} \text{ mol dm}^{-3}$  diuron solutions. Closed symbols in the absence, open symbols in the presence of  $1 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{K}_3\text{Fe}(\text{CN})_6$ , dose/pulse 20 Gy. Inset: concentration dependence of pseudo-first-order rate constant of absorbance build-up at 325 and 365 nm.

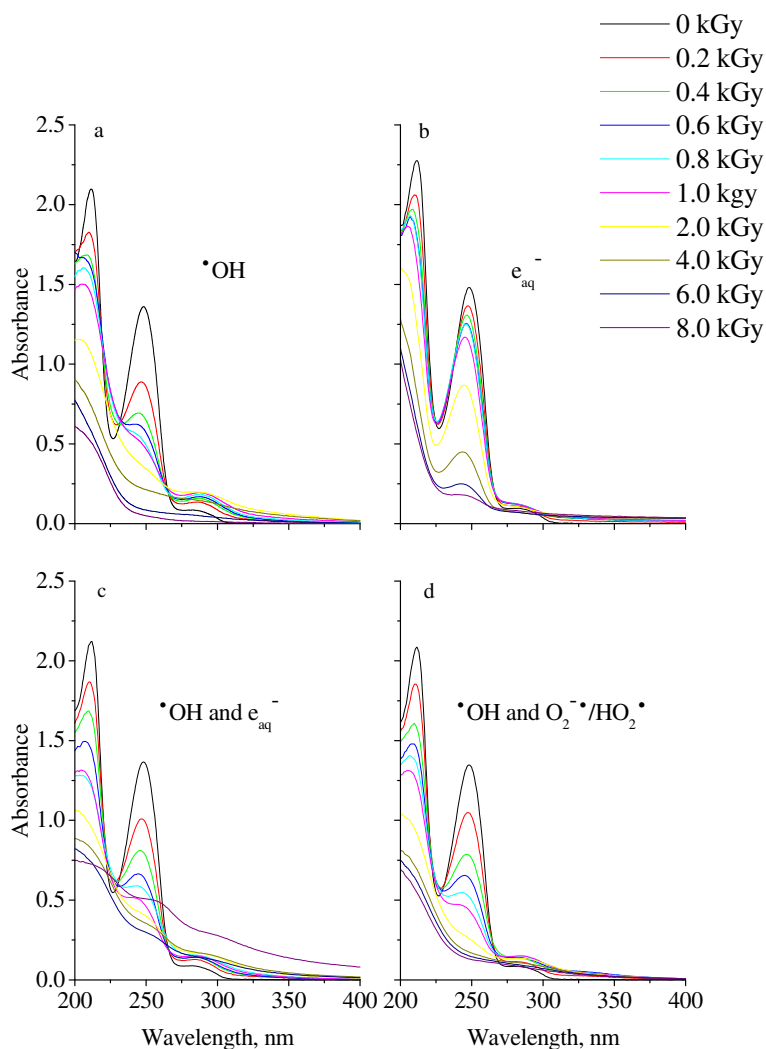
absorbance was obtained in the 300 – 400 nm range (not shown) with maximum at  $\sim 350$  nm. Based on the hydrated electron absorbance decay at 600 nm, we calculated a rate constant of  $1.0 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for the  $e_{\text{aq}}^- + \text{diuron}$  reaction. Canle Lopez et al. [3] measured  $(9.4 \pm 0.6) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  previously.

### Steady-state gamma radiolysis

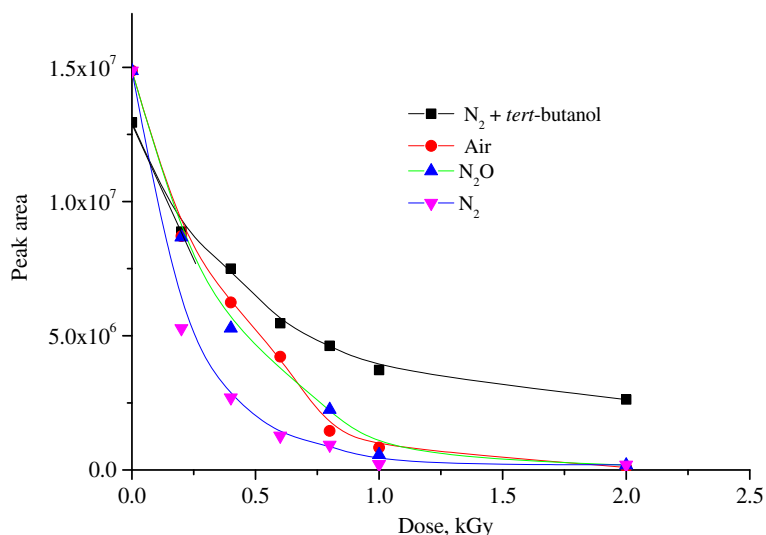
The degradation of diuron in gamma radiolysis was followed by UV-Vis spectroscopy and by COD, TOC and TN measurements. Product analysis was also performed using HPLC-MS/MS technique. The band between 230 and 270 nm in the UV spectrum is assigned to the characteristic  $\pi \rightarrow \pi^*$  transition of the aromatic ring,  $\lambda_{\text{max}}$  is at 248 nm with  $\epsilon_{\text{max}}$  of  $17000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ . The absorbance decreased faster when  $\cdot\text{OH}$  was the reacting species (Figure 2a) than in  $e_{\text{aq}}^-$  reaction (Figure 2b).

Moreover, in  $\cdot\text{OH}$  reaction at  $\sim 300$  nm increase in absorbance was observed, this build-up was absent in  $e_{\text{aq}}^-$  reaction. In both  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$  reactions the absorption band slightly shifted to shorter wavelength. This shift may reflect dehalogenation.  $\lambda_{\text{max}}$  for the monohalogenated monuron and the non-halogenated fenuron are at 245 and 238 nm ( $\epsilon_{\text{max}}$  15377 and  $13104 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , respectively).

As the integrated chromatographic peak areas (diode array detection) show in Figure 3, at a dose of 1 kGy the majority of diuron degraded in  $\text{N}_2\text{O}$  ( $\cdot\text{OH}$ ),  $\text{N}_2$  ( $\cdot\text{OH} + e_{\text{aq}}^-$ ) and air saturated ( $\cdot\text{OH} + \text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ ) solutions, only a few percent of the intact molecules remained. In  $\text{N}_2$  saturated *tert*-butanol containing solutions ( $e_{\text{aq}}^-$ ), however, the degradation was much slower; the initial yield was  $\sim 0.15 \mu\text{mol J}^{-1}$ . In air and  $\text{N}_2\text{O}$  saturated solutions the values were estimated to be  $\sim 0.2 \mu\text{mol J}^{-1}$  and  $\sim 0.3 \mu\text{mol J}^{-1}$ , respectively.



**Figure 2** Absorption spectra of  $1.6 \times 10^{-4} \text{ mol dm}^{-3}$  diuron solution. Irradiation with 0–8 kGy doses, the spectra were obtained in  $\cdot\text{OH}$  (a),  $e_{\text{aq}}^-$  (b),  $\cdot\text{OH} + e_{\text{aq}}^-$  (c) and in  $\cdot\text{OH} + \text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$  (d) reactions.

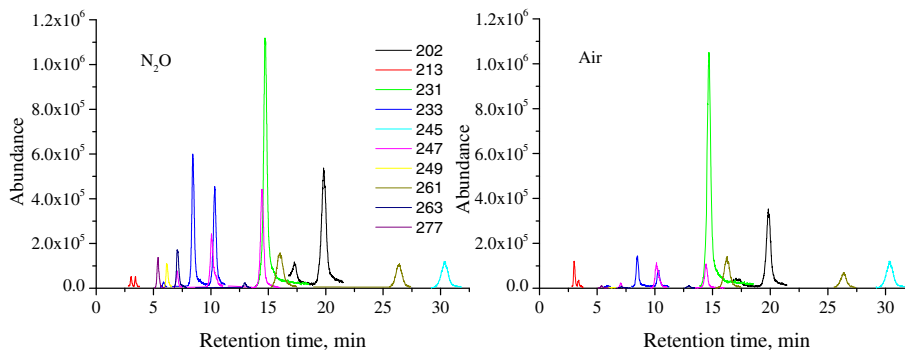


**Figure 3** Integrated diuron peaks obtained after HPLC-MS/MS analysis (optical detection).  $1 \times 10^{-4}$  mol dm $^{-3}$  solution was irradiated under different conditions indicated in the Figure.

#### Identification of by-products by HPLC-MS/MS

A large number of products were observed on the chromatograms, their composition changed gradually as a function of dose. The distribution was different in air- and N<sub>2</sub>O saturated solutions (Figure 4). At 0.5 kGy dose in both solutions about 50-70% of the starting molecules transformed to products: 14 different compounds were separated. The large variation is partly due to the possible presence of isomers and also to the thermal instability and decomposition of some of the products. Diuron eluted at 14.34 min and in negative ionization mode had a parent ion with m/z 231. Two compounds with m/z 247 eluted earlier than diuron at 6.89 and 14.13 min, respectively. We identified these molecules as ring hydroxylated derivatives of diuron. The ion at m/z 247 had an intensive fragment with m/z 202. This m/z 202 ion appeared also for the ring hydroxylated products with modified -N(CH<sub>3</sub>)<sub>2</sub> unit: with one CH<sub>3</sub> group missing (parent ion at m/z 233, 8.37 and 10.12 min),

and hydroxylated molecules with one CH<sub>3</sub> oxidized to -CHO (m/z 261, 16.31 and 25.89 min). In the case of two products at 16.93 and 19.50 min no ion with higher m/z than 202 appeared, indicating a complete ionic degradation of the parent ion in the mass spectrometer. In the case of molecules with one Cl only (parent ion m/z 213, 2.19 and 2.32 min), m/z 202 was not present and another fragment at m/z 168 indicated a chlorine loss (m/z 202-Cl). In the case of ring dihydroxylated molecule (parent ion at m/z 263, 7.01 min) the MS/MS spectra revealed a fragment at m/z 218 (m/z 202 + OH), which contains one more hydroxyl group compared to m/z 202. The product with parent ion m/z 249 at 6.08 min was identified as ring dihydroxylated molecule with one methyl group missing, while the one with m/z 277 at 5.31 min as ring dihydroxylated molecule with one methyl group oxidized to -CHO. Fragments with m/z 202, m/z 218 (m/z 202 + OH) and m/z 168 (m/z 202-Cl) are characteristic for ring hydroxylated



**Figure 4** Chromatogram of  $1 \times 10^{-4}$  mol dm $^{-3}$  diuron solutions. Irradiation with 0.5 kGy dose in N<sub>2</sub>O or air atmosphere. The peak of each selected ion is depicted with different colour and its m/z value is indicated.

molecules. They form isocyanate ion in the collision chamber, e.g. in the case of diuron:  ${}^-\text{O}(\text{Cl}_2)\text{C}_6\text{H}_2\text{NHCON}(\text{CH}_3)_2 \rightarrow {}^-\text{O}(\text{Cl}_2)\text{C}_6\text{H}_2\text{N}=\text{C}=\text{O} + \text{HN}(\text{CH}_3)_2$ . Similar reaction (isocyanate ion formation) has also been observed in the thermal degradation of diuron [6] and during the mass spectrometric analysis of irradiated fenuron samples [11].

In the case of the molecule with elution time 29.64 min at  $m/z$  245, the aromatic ring remained intact and one of the methyl groups was oxidized to -CHO.

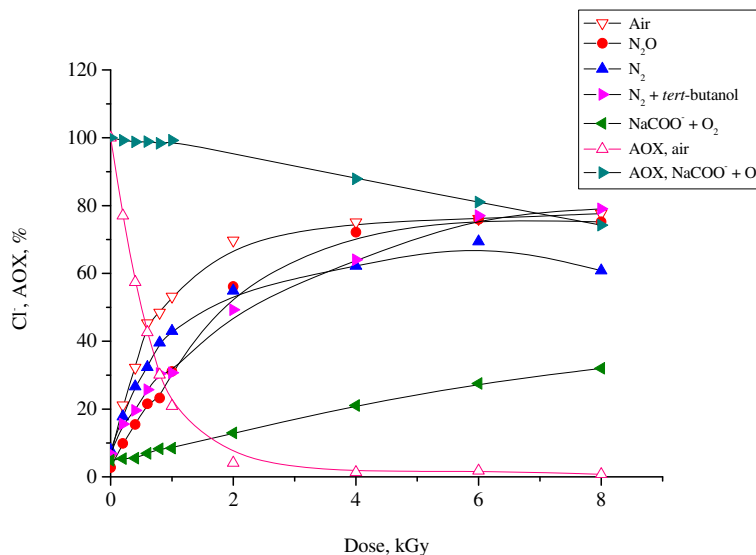
The products reveal that  $\cdot\text{OH}$  attack takes place both on the ring and also on the methyl groups attached to the terminal N atom. Most of these products were observed also in previous studies where hydroxyl radicals were the initiating reactants [4,7,10]. According to Tahmassebi et al. [4] "The disubstitution of the phenyl ring by chlorine atoms reduces its susceptibility towards any electrophilic and/or radical attack which in counterpart makes the attack on the urea N-terminus group more competitive." However, our results clearly show the predominance of ring hydroxylation reactions for diuron similarly to the reactions with fenuron [11].

Figure 4 suggests that the rate of hydroxylated product formation is higher in  $\text{N}_2\text{O}$ -saturated solution than under aerated condition. This difference may be due to the higher yield of hydroxyl radicals in the former solution than in the latter ( $0.56$  and  $0.28 \mu\text{mol J}^{-1}$ ) and also to the reaction of the dissolved  $\text{O}_2$  with the organic radicals in aerated solution, opening up by that new reaction pathways at the expense of hydroxylated product formation (see later). Most of the products had maximum concentrations between  $0.3$  and  $0.7$  kGy dose. At  $1$  kGy dose strong decrease in product concentrations was observed.

### Chloride release and AOX

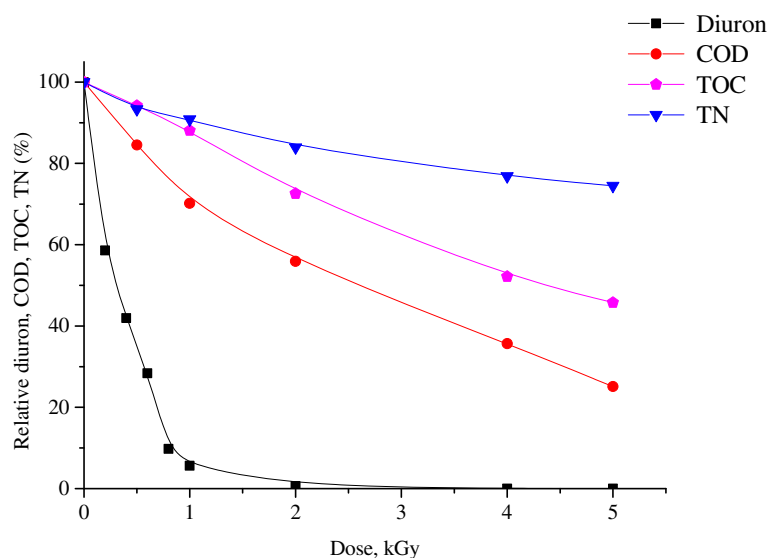
Chloride release is an important indicator for the degradation of chlorinated molecules. It facilitates the understanding of the attack of reactive radicals on special sites of the molecule studied. Chloride release was observed under all conditions investigated (Figure 5), in the reactions of  $\cdot\text{OH}$ ,  $e_{\text{aq}}^-$ ,  $\cdot\text{OH} + e_{\text{aq}}^-$ , and  $\cdot\text{OH} + \text{O}_2^-/\text{HO}_2$ . The percentages in the figure are calculated by taking into account both of the chlorine atoms in diuron. The initial (low-dose) yields for air saturated ( $\cdot\text{OH} + \text{O}_2^-/\text{HO}_2$ ),  $\text{N}_2$  saturated ( $e_{\text{aq}}^- + \cdot\text{OH}$ ),  $\text{N}_2$  saturated containing *tert*-butanol ( $e_{\text{aq}}^-$ ) and  $\text{N}_2\text{O}$  saturated ( $\cdot\text{OH}$ ) solutions are  $\sim 0.15$ ,  $\sim 0.1$ ,  $\sim 0.08$  and  $\sim 0.07 \mu\text{mol J}^{-1}$ . In  $\text{O}_2$ -free solutions about 15–30% of  $\cdot\text{OH}$  attack on diuron yields chloride ion, while this value is about 60% in solutions containing dissolved  $\text{O}_2$ . The efficiency of  $\text{Cl}^-$  release for  $e_{\text{aq}}^-$  reaction is about 25%.

We investigated the question whether the  $\text{O}_2^-/\text{HO}_2$  pair directly induces chloride release. In order to examine the possibility of  $\text{O}_2^-/\text{HO}_2$  reaction with diuron, measurements were conducted in  $\text{O}_2$  saturated Na formate containing solutions. In such solutions all the three reactive intermediates of water radiolysis transform to the  $\text{O}_2^-/\text{HO}_2$  pair in Reactions (4)–(7). In solutions with Na formate the absorbance slightly decreased with increasing absorbed dose and the maximum slightly shifted to shorter wavelengths (not shown). However, the effect was small and was observable only at higher doses. As Figure 5 shows in Na formate solutions both the yield of chloride release and decrease of AOX were small at low doses.



**Figure 5** Chloride release ( $\text{Cl}^-$ ) and the adsorbable organic chloride (AOX). Chloride release was measured in different solutions (indicated in the Figure) AOX was measured in air and  $\text{O}_2$  saturated (Na-formate added) solution (diuron  $1.1 \times 10^{-4} \text{ mol dm}^{-3}$ ).





**Figure 6** TOC, COD and TN results and removal of diuron. All of the experiments were carried out in  $1.2 \times 10^{-4}$  mol  $\text{dm}^{-3}$  diuron solutions before irradiation and after irradiating with various doses.

### Removal of COD, TOC and TN

By measuring the changes of COD and TOC after irradiation, we monitored the rates of oxidation and mineralization. The TN measurements show whether the N content remains in the solution after degradation, or it leaves the solution in the form of  $\text{N}_2$ . These measurements were conducted on samples saturated with air. COD and TOC decreased steadily with the absorbed dose (Figure 6), the decrease in COD was higher than in TOC. Partly oxidized molecules need less  $\text{O}_2$  for complete mineralization than the intact ones; however, their organic carbon content is similar to those of the starting molecules. For instance, in air saturated solutions at 1 kGy dose the decrease of COD and TOC was 30% and 7%, respectively. At this dose, about 95% of diuron was depleted. This result is similar to the one obtained by Zhang et al. [10] using  $7.9 \times 10^{-5}$  mol  $\text{dm}^{-3}$  diuron concentration; they found practically 100% removal of the starting molecules and 34 % TOC removal. TN decreased only slightly during the treatment showing that nitrogen mainly remained in the liquid phase.

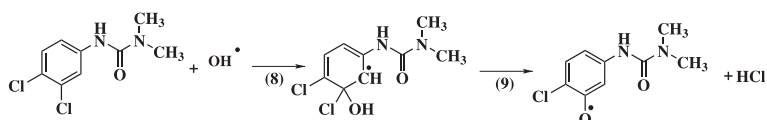
The initial slope of the COD-dose plot is c.a.  $11 \text{ mg dm}^{-3} \text{ kGy}^{-1}$ , so at 1 kGy dose  $\sim 3.4 \times 10^{-4}$  mol  $\text{dm}^{-3}$   $\text{O}_2$  was built in the products. At this dose  $2.8 \times 10^{-4}$  mol

$\text{dm}^{-3}$   $\cdot\text{OH}$  was introduced into the solution, the  $\text{O}_2$  molecules built-in/ $\cdot\text{OH}$  introduced into the solution molar ratio is c.a. 1.2. When an  $\text{O}_2$  is incorporated in a product four-electron oxidation occurs. Therefore  $\cdot\text{OH}$ , the one-electron oxidant, induces more than four-electron oxidations.

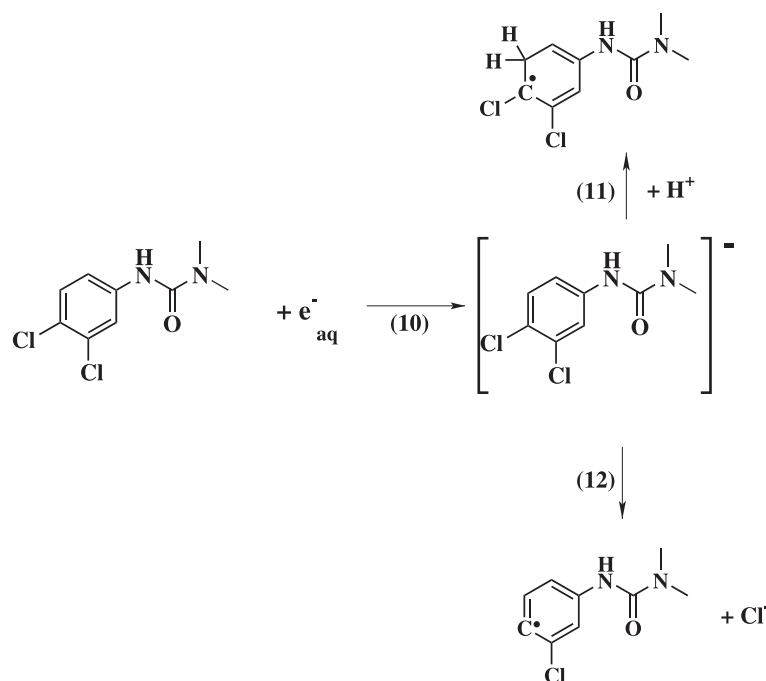
### Discussion

Using the UV spectroscopic and LC-MS/MS results, the yields of diuron degradation are calculated to be in the  $0.15 - 0.3 \mu\text{mol J}^{-1}$  range. The  $G$ -values of chloride release are between  $0.07 - 0.15 \mu\text{mol J}^{-1}$  (two Cl-atom elimination). Based on the COD values measured in air saturated solution the  $\text{O}_2/\cdot\text{OH}$  ratio is c.a. 1.2. The value is much higher than the ratio established for fenuron,  $\sim 0.7$  [11] and it is also higher than found for the majority of molecules studied so far in our laboratory ( $0.25 - 1.0$  [17-19]). The high ratio in the present study indicates effective diuron degradation in air saturated solution.

$\cdot\text{OH}$  is expected to add to any of the carbon atoms of the aromatic ring. The addition at a carbon atom bearing the chlorine atom (8), may be followed by HCl elimination (9) as it was shown e.g. for diclofenac [20,21]. Canle Lopez et al. [5] suggest such chlorine release in



**Scheme 1**  $\cdot\text{OH}$  attack to diuron at the *meta*-position.



**Scheme 2** Reactions of  $e_{aq}^-$  with diuron.

photocatalytic oxidation of diuron, too.  $\cdot OH$  attack at the *meta*-position is shown in Scheme 1.

This reaction ultimately gives rise to phenoxyl type radical formation, the absorption bands in the transient spectrum at  $\sim 330$  nm and at  $\sim 460$  nm are probably due to this transient intermediate (Figure 1). The dechlorination yields in both  $N_2O$  bubbled and air saturated solutions are smaller than the  $\cdot OH$  yields. Only a small fraction of  $\cdot OH$  reaction leads to dechlorination. Based on the higher dechlorination yield in aerated solution compared to  $N_2O$ -saturated solution, one may think that the  $O_2^{\cdot -}/HO_2^{\cdot}$  pair also induces dechlorination.  $O_2^{\cdot -}$  is a reductive radical with standard one-electron reduction potential of  $-0.33$  V (vs. NHE) [22], while the standard one-electron reduction potential of diuron is calculated to be  $1.72$  V [23]. The dechlorination of chloroanilines in microbial experiments is demonstrated in several papers [24]: in the case of dichloroanilines first the *para*- and then the *meta*-chlorines are involved in the process. In our experiments carried out in the presence of Na formate, when  $O_2^{\cdot -}$  is the main reactive species, just a small dechlorination was found. Because of the low yield one may also think that the dechlorination is due to some side reaction in these solutions, e.g. small fraction of  $\cdot OH$  or  $e_{aq}^-$  is not scavenged by  $HCO_2^-$  or  $O_2$ , respectively, and reacts with diuron inducing dechlorination. In the photocatalytic experiments of Canle Lopez et al. [5] a competition was found between the reactions of  $e^-$ , transferred to the conduction band, with  $O_2$  and with diuron. Based on our

experiments we may say that dissolved  $O_2$  in the solution promotes the  $Cl^-$  elimination from the adduct. Low reactivity of the  $O_2^{\cdot -}/HO_2^{\cdot}$  pair with aromatic molecules was also reported in other works [18,25].

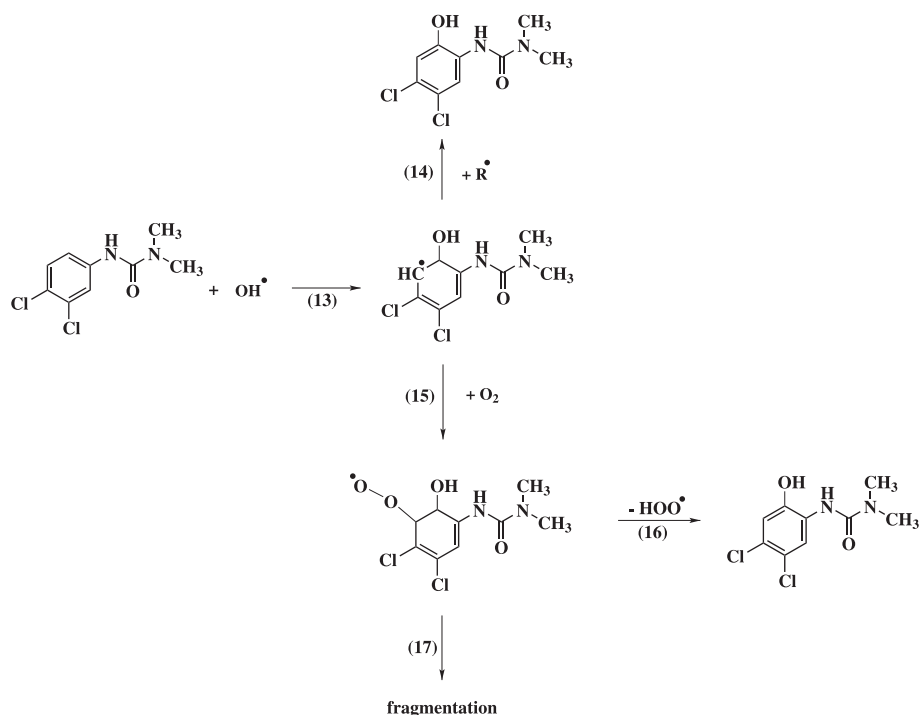
The rate coefficient of hydrated electron reaction with diuron is one order of magnitude higher than with fenuron due to the enhanced electron-withdrawing effect of the two Cl atoms attached to the aromatic ring. The electron is accommodated on the ring and the adduct undergoes reversible protonation with  $pK_a$  of  $4.30 \pm 0.04$  [3]. The results in Figure 3 show that about 25% of the  $e_{aq}^-$  reactions induce chloride release. The mechanism suggested for chloride release is shown in Scheme 2, Reaction (12).

The phenyl radicals formed in (12) may be stabilized in bimolecular radical-radical or radical-molecule reactions. The expected products are molecules with one chlorine atom on the ring in *para*- (monuron) or in *meta*-position. These products were observed in our LC-MS/MS investigations, however, with quite low yields.

In the present work and also in most of other AOP experiments, where  $\cdot OH$  played important role in the degradation [3-7], phenol type molecules were observed as important intermediate products. These phenols may form through the identified transient intermediates, hydroxycyclohexadienyl radicals shown in Scheme 3, Reaction (13).

In the absence of dissolved  $O_2$  the hydroxycyclohexadienyl radicals decay in bimolecular reaction with other





**Scheme 3** Reactions of  $\cdot\text{OH}$  with diuron in the presence and in the absence of  $\text{O}_2$ .

radicals ( $\text{R}^\cdot$ ) present: the reaction may yield phenol type molecules (Scheme 3, Reaction (14)). In the presence of dissolved  $\text{O}_2$  the transient radicals can transform to peroxy radicals (Reaction (15)). The peroxy radicals formed from hydroxycyclohexadienyl radicals may either eliminate  $\text{HO}_2^\cdot$  forming phenol compounds (Reaction (16)) or may undergo stepwise oxidation to open-chain carboxylic acids. These reaction pathways are well known for different aromatics [26,27]. The high degradation rate in air saturated solutions, as compared to reactions under other conditions, can be attributed to the involvement of oxygen in the process.

Products that reflect  $\cdot\text{OH}$  reaction with a methyl group were also observed in the presence of dissolved  $\text{O}_2$ . However, based on the abundances it seems that  $\cdot\text{OH}$  predominantly reacts with the aromatic ring and not with the methyl groups.

## Conclusions

During irradiation of dilute diuron solutions effective degradation was observed, which was higher under oxidative than reductive conditions. Under oxidative circumstances the intermediate products observed were similar to those found in other Advanced Oxidation Processes: hydroxylation in the ring, hydroxylation coupled to chlorine release and products reflecting reactions on one of the methyl groups. The presence of dissolved oxygen enhanced the rate of degradation. As

the COD values show, the one-electron-oxidant  $\cdot\text{OH}$  on average induces five-electron oxidations. The high oxidation rate is attributed to the reactions of the primarily formed radicals with dissolved  $\text{O}_2$  and the subsequent reactions of the peroxy radical.

## Competing interest

The authors declare that they have no competing interest.

## Authors' contributions

K.K. carried out the pulse radiolysis, the AOX, COD, TOC, and TN measurements and evaluated the results. S.H. took the UV-Vis spectra, participated in the pulse radiolysis experiments and drafted part of the manuscript. V.M. participated in the pulse radiolysis experiments. T.C. carried out the HPLC-MS/MS measurements and evaluated the results of this measurement. E.T. and L.W. participated in evaluation of the results and prepared the final draft of the manuscript. All authors read and approved the final manuscript.

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