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Formation of genotoxic compounds by medium pressure ultraviolet treatment of nitrate-rich water

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ABSTRACT

Genotoxic compounds were produced by full-scale medium pressure (MP) ultraviolet hydrogen peroxide (UV/H_2O_2) treatment of nitrate-rich pretreated surface water. It was hypothesized that this formation was caused by the reaction of nitrate photolysis intermediates with natural organic matter (NOM). An increase in the Ames test response was also found after MP UV photolysis of water containing Pony Lake NOM from the International Humic Substances Society (IHSS) and nitrate, while no increase in the Ames test response was found when nitrate was absent. The same trend in an Ames test response and nitrite formation was observed for both nitrate-rich pretreated surface water and reconstituted water containing NOM and nitrate. Therefore, the conversion of nitrate by MP UV photolysis was studied in several water types. In organic-free water, nitrate was completely converted into nitrite, while no inorganic nitrogen was lost. Also in nitrate-rich surface water, nitrite was found as the only inorganic reaction product, while a small decrease of the inorganic nitrogen content was observed. When NOM was replaced by phenol, MP UV photolysis caused a restricted nitrite formation only, together with a large loss of inorganic nitrogen. The formation of the nitrated phenol derivatives, 2- and 4-nitrophenol and 4-nitrocatechol, was observed with highest concentrations under practical UV conditions. It is hypothesized that the formation of nitrated aromatic compounds is the cause of the increased Ames test response by MP UV treatment.

Keywords: Ames test; UV; Nitrate photolysis; Genotoxicity; Nitration; Nitrosation

1. Introduction

Since Rook [1] showed the formation of trihalomethanes (THMs) by drinking water chlorination, reaction product formation by chemical disinfection/oxidation has been investigated thoroughly. THMs and many other reaction products were formed by the reaction of chlorine with the organic water matrix. Ozonation and ozone-based advanced oxidation caused the formation of biodegradable compounds such as carboxylic acids, once again by reaction with the organic water matrix. Besides, the inorganic water matrix played an important part. Kurokawa et al. [2] showed that bromate, formed by ozonation of bromate-rich water was a suspect human

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carcinogen. Also UV disinfection and UV-based advanced oxidation caused the formation of biodegradable compounds, while in nitrate-rich water, nitrite was formed, especially when medium pressure (MP) UV lamps were applied. In addition to chemical characterization, the side effects were determined by genotoxicity testing. After chlorination, a high response in the Ames test was observed, while after ozone and UV-based processes no significant effect was found [3,4]. For many years, no formation of genotoxic compounds was observed for UV-based processes. However, when natural quartz sleeves were replaced by synthetic quartz sleeves allowing passage of UV light with wavelengths <240 nm in MP UV treatment, a significant Ames test response was found in nitrate-rich water. It was hypothesized that the Ames test response was caused by the reaction of MP UV photolysis intermediates of nitrate with the organic water matrix [5]. In this paper, the research on the formation of genotoxic compounds by MP UV treatment is described in more detail. The role of the photolysis of nitrate on genotoxicity formation and the production of nitrated reaction products, which may be responsible for the genotoxic response, are described for practical and reconstituted matrices. To show the incorporation of inorganic nitrogen in the organic matrix, experiments were carried out with an organic model compound phenol.

2. Nitrate and nitrite photolysis by UV light in organic-free water

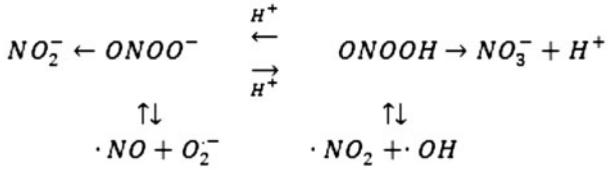
Nitrate has two absorption bands in the UV region, one in the near UV region from 260 to 350 nm with a maximum at 300 nm and a much more intensive band below 260 nm with a maximum at 200 nm [6]. Nitrite formation by the application of low pressure (LP) UV in water treatment is insignificant due to the low absorbance of nitrate at the major LP UV emission wavelength (254 nm). MP UV light with wavelengths between 200 and 300 nm causes a significant nitrate photolysis, resulting in a substantial nitrite formation. Especially the emitted UV light with wavelengths < 250 nm causes a strong nitrite formation [7]. Photolysis of nitrate takes place according to two pathways:

$$\mathrm{NO_3^-} \overset{hv}{\rightarrow} {}^{\bullet}\mathrm{NO_2^-} + \mathrm{O^{\bullet -}} \quad \Phi = 0.08$$

$$\mathrm{O^{\bullet -}} + \mathrm{H_2O} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{OH^-}$$

$$\mathrm{NO_3^-} \overset{hv}{\rightarrow} \mathrm{ONOO^-} \quad \Phi = 0.48$$

In view of the quantum yield $\Phi = 0.48$, the major intermediate reaction product of nitrate photolysis is peroxynitrite, giving the following consecutive reaction [8]:



$$\begin{tikzcd}
NO_2^- & ONOO^- \arrow[l] \arrow[r, shift left, "H^+"] \arrow[d, shift left] & ONOOH \arrow[l, shift left, "H^+"] \arrow[r] \arrow[d, shift left] & NO_3^- + H^+ \\
& \cdot NO + O_2^- \arrow[u, shift left] & \cdot NO_2 + \cdot OH \arrow[u, shift left] &
\end{tikzcd}$$

$${}^{\bullet}\mathrm{NO} + {}^{\bullet}\mathrm{NO_2} \rightarrow \mathrm{N_2O_3} + \mathrm{H_2O} \rightarrow 2\mathrm{NO_2^-} + 2\mathrm{H^+}$$

$${}^{\bullet}\mathrm{NO_2} + \mathrm{O_2^{\bullet -}} \rightarrow \mathrm{O_2NOO^-} \rightarrow \mathrm{NO_2^-} + \mathrm{O_2}$$

Disproportionation of peroxynitrite produces nitroso-, nitro- and hydroxyl radicals as intermediates. The stable inorganic end product of nitrate photolysis by MP UV light is nitrite.

Mack and Bolton [7] give a detailed description of the nitrite photolysis by UV. The major reactions are:

$$\mathrm{NO_2^-} + \mathrm{H_2O} \overset{hv}{\rightarrow} \mathrm{NO^{\bullet}} + \mathrm{OH^{\bullet}} + \mathrm{OH^-}$$

$$\mathrm{NO_2^-} + \mathrm{OH^{\bullet}} \rightarrow \mathrm{NO_2^{\bullet}} + \mathrm{OH^-}$$

$$2\mathrm{NO_2^{\bullet}} + \mathrm{H_2O} \rightarrow \mathrm{NO_2^-} + \mathrm{NO_3^-} + 2\mathrm{H^+}$$

So, UV photolysis of nitrite causes the formation of nitrate as a stable end product. The intermediate nitro- and nitroso radicals produced by both nitrate and nitrite photolysis may react with the organic water matrix as well to form nitrogenous organic reaction products.

3. Photolysis of nitrate and nitrite in the presence of natural organic matter

Many authors have described the impact of nitrate/nitrite photolysis in natural waters. The focus was on nitrate/nitrite photolysis as a potential source for hydroxyl radical formation rather than nitration or nitrosation reactions. Only Thorn et al. studied nitration and nitrosation reactions. Thorn and Mikita [9] showed nitrite fixation by humic substances, applying ^{15}N Nuclear Magnetic Resonance. Thorn and Cox [10] showed that nitrate and nitrite nitrogen were incorporated in aquatic natural organic matter (NOM) by irradiation of ^{15}N-labelled nitrate in aqueous solution.

Because hardly any nitrosation/nitration reactions of NOM are described in the literature, a review was carried out on the effect of nitrate/nitrite photolysis in the presence of low molecular organic compounds. The photolysis of nitrate and nitrite in the presence of low molecular weight organics was studied for a broad variety of compounds. In particular, the interaction with aromatics such as benzene, biphenyl, and phenol was studied [11–14]. Hydroxylation, nitration and nitrosation were observed when nitrate and/or nitrite were photolysed in the presence of these organic substances. For radiation with wavelengths <260 nm, hydroxylation and nitration were intensified. The mechanism of the reactions is not completely clear yet, although a radical pathway for both hydroxylation and nitration was hypothesized. A strong mutagenicity was attributed to some nitrated compounds [15].

4. Materials and methods

4.1. Full-scale experiments

The full-scale MP ultraviolet hydrogen peroxide (UV/H_2O_2) installation, located at PWN's water treatment plant (wtp) Andijk in The Netherlands, was consisting of three parallel UV process trains. In each UV train, four UV reactors were placed in series. Each UV reactor was equipped with 16 12 kW MP UV lamps. Immediately downstream of each UV reactor, a sample port was installed. The MP UV/H_2O_2 treatment had an electrical energy consumption of 0.54 kWh/m^3, corresponding with a UV dose of 560 mJ/cm^2, combined with 6 mg/L H_2O_2, to meet the treatment target of 80% atrazine degradation.

4.2. Collimated beam experiments

Irradiations were performed in a collimated beam (CB) apparatus equipped with a 3 kW medium pressure Hg lamp. The UV dose delivered to the solution was calculated using the UV dose calculation method developed by Bolton and Linden [16]. A sample volume of 55 mL was irradiated in a crystallizing dish. The irradiation path length was approx. 19.5 mm. For the Ames test, multiple samples were irradiated under identical conditions, utilizing an automated sample carousel, placed under the CB apparatus.

4.3. Ames testing

The Ames II™ Assay was used, based on the same principle as the standard Ames Assay [17]. The Ames II test with strain TA98 without metabolic activation (-S9) was conducted on concentrated water samples extracted through SPE according to the method described by Heringa et al. [18], yielding 20,000-fold concentrated extracts. Quality control of the Ames II test was ensured by the positive control (0.5 μg/mL 4-nitroquinoline N-oxide plus 2.0 μg/mL 2-nitrofluorene) and solvent dimethylsulfoxide (DMSO) control included in the assay. Mineral water was added as an additional procedure control including SPE. The positive control for the test strain TA98 in the absence of metabolic activation must be equal to, or larger than, 25 positive wells. The solvent control should result in 8 or less positive wells.

5. Results

5.1. Ames test response for pretreated surface water samples

The Ames II test was conducted on concentrated water samples, taken from a full-scale MP UV/H_2O_2 treatment train, utilizing synthetic quartz sleeves (Fig. 1). The influent of MP UV/H_2O_2 is the effluent from the conventional surface water pretreatment, including coagulation, sedimentation and filtration of surface water from the IJssel Lake.

After each UV reactor, the response in the Ames test increased. According to the general approach for genotoxicity in the Ames test, a sample is genotoxic when the response exceeds two times the procedure control. According to this approach, the response after UV reactor four was genotoxic. After MP UV/H_2O_2 treatment, the response in the Ames test was removed to the level of the procedure control by posttreatment with biologically activated carbon filtration.

A response in the Ames test was also found when nitrate was photolysed in the presence of International Humic Substances Society (IHSS) Nordic Lake NOM [5]. To confirm the role of nitrate, MP UV CB experiments in reconstituted water using 2.5 mg C/L IHSS Pony Lake NOM without nitrate and in the presence of 12 mg NO_3/L were conducted. Three UV treatment conditions were applied: MP UV disinfection with a

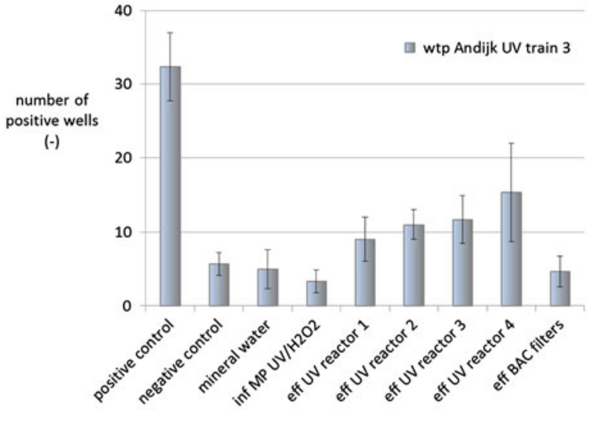


Fig. 1. Ames test response ($n = 3$) in strain TA98 (-S9) after consecutive UV reactors in a MP UV/H_2O_2 treatment train at wtp Andijk.

UV dose of 40 mJ/cm^2, MP UV photolysis with a UV dose of 600 mJ/cm^2 and MP UV/H_2O_2 treatment with a UV dose of 600 mJ/cm^2 in combination with 6 mg H_2O_2/L (Fig. 2).

In the presence of nitrate, it was observed that the number of positive wells increased with the UV dose. Already a UV dose of 40 mJ/cm^2, generally applied for disinfection, generated a significant Ames test response relative to the negative control. MP UV photolysis with 600 mJ/cm^2 caused the highest number of positive wells, while after MP UV/H_2O_2 treatment the number of positive wells was significantly lower than after MP UV photolysis only. In the absence of nitrate, no increase in the number of positive wells in the Ames test was observed, regardless of the MP UV treatment conditions, supporting the crucial role of nitrate photolysis in the generated response in the Ames test.

MP UV photolysis of nitrate resulted in nitrite formation. Both practical and CB measurements showed an increased nitrite formation with increasing MP UV dose. Fig. 3 shows the observed response in the Ames II test for both full-scale and CB data as a function of the formed nitrite by MP UV irradiation.

A clear relation was observed between the Ames II test response and the nitrite formation, supporting the impact of UV nitrate photolysis on both the nitrite formation and the Ames test response. Therefore, the UV photolysis of nitrate and nitrite was studied in both organic-free water and water containing a natural and a synthetic organic matrix.

5.2. Photolysis of nitrate and nitrite in organic-free water

Nitrate photolysis experiments in demineralized water were carried out to investigate the formation of stable reaction products and the possible loss of inorganic nitrogen from the system. Sample volumes of 55 mL containing 11 mg NO_3/L (180 μM) or 13.5 mg NO_2/L (290 μM) solutions in demineralized water were irradiated in a MP UV CB set-up. The irradiance at the centre of the beam was 1.93 mW/cm^2, and irradiation times were 30, 60, 180 and 420 min. An irradiation time of about 10 min represents practical MP UV doses applied for UV/H_2O_2 treatment. In Fig. 4(A), the results for nitrate photolysis and in Fig. 4(B) the results for nitrite photolysis, both in demineralized water, are shown.

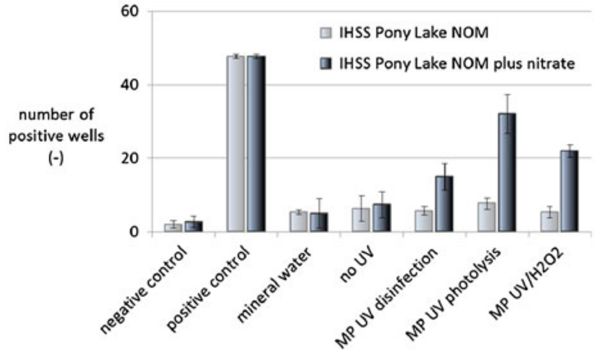


Fig. 2. Ames test response ($n = 3$) in strain TA98 (-S9) in MP UV CB experiments with reconstituted water IHSS Pony Lake NOM (2.5 mg C/L) without and with nitrate (12 mg NO_3/L).

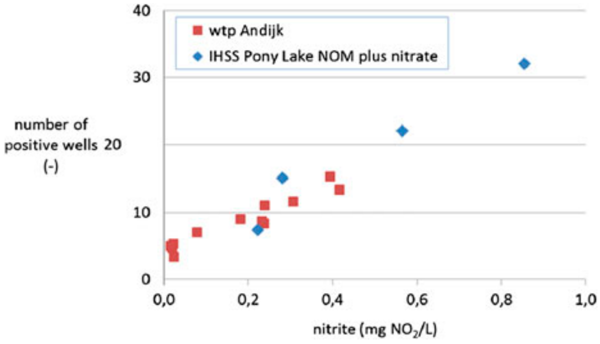


Fig. 3. Ames test response in water samples (20,000 cf) as a function of the nitrite formation by MP UV treatment wtp Andijk and in CB experiments with IHSS Pony Lake NOM.

During the UV regime used in practice, photolysis of nitrate caused a linear increase of the nitrite concentration as a function of the UV irradiation time (UV dose). At long UV irradiation times, nitrite formation from nitrate photolysis and nitrate formation from nitrite photolysis reached equilibrium (Fig. 4(A)). Photolysis of a nitrite solution initially caused a linear increase of the nitrate concentration as a function of the UV dose. At long UV irradiation times, the nitrite and nitrate concentration reached equilibrium (Fig. 4(B)). In both experiments, no nitrogen was lost from the system, confirming that the only two stable reaction products from nitrate and nitrite photolysis were nitrite and nitrate.

5.3. Inorganic nitrogen loss by photolysis of nitrate in the presence of an organic matrix

A gap in the inorganic nitrogen mass balance suggests the incorporation of inorganic nitrogen into the organic matrix. The effect of full-scale MP UV/H_2O_2 treatment on the total inorganic nitrogen content was investigated. The initial nitrate content (9.6 mg NO_3/L; 155 μM) represented a high but still representative concentration. Fig. 5 shows the concentration of nitrate and nitrite in the influent of the MP UV/H_2O_2 treatment and after each consecutive UV reactor in the process train. The sample times and locations were identical to the conditions presented in Fig. 1.

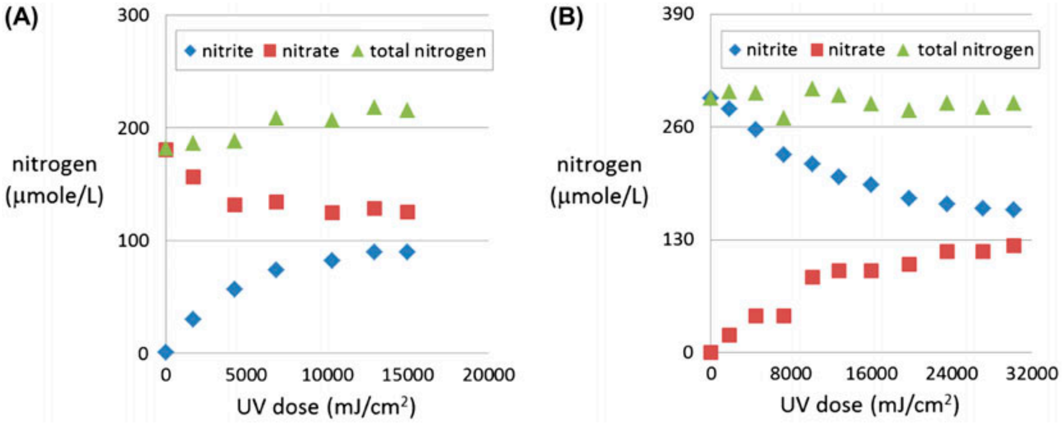


Fig. 4. CB experiments: (A) MP UV photolysis of a nitrate solution (11 mg NO_3/L; 180 µM); (B) MP UV photolysis of a nitrite solution (13.5 mg NO_2/L; 290 µM).

After each UV reactor, with increasing UV dose, the nitrite concentration increased. The total inorganic nitrogen content, combined nitrate and nitrite, showed a small, although not statistically significant, decrease of approximately 4 µM N (Fig. 5). This suggests the formation of nitrated compounds by the incorporation of inorganic nitrogen into NOM.

Liquid Chromatography-Organic Carbon Detection analysis suggested that some incorporation of inorganic nitrogen in the organic matrix took place (data not shown). However, characterization of individual reaction products was not achieved yet.

Therefore, MP UV CB experiments were performed with an aromatic model compound, phenol, to show the loss of inorganic nitrogen caused by nitration of the aromatic ring. Fig. 6 shows the nitrate and nitrite concentration as a function of MP UV irradiation times in CB experiments with phenol/nitrate solutions. The initial phenol concentration was 0.25 mM, the initial nitrate concentration 0.18 mM, the irradiance in the centre of the beam was 1.4 mW/cm^2. An irradiation time of about 10 min represented the process conditions commonly applied for MP UV/H_2O_2 treatment.

With increasing irradiation times, the total inorganic nitrogen concentration, represented by nitrate and nitrite, decreased strongly. This suggests incorporation of inorganic nitrogen into the phenol ring. Therefore, the formation of nitrated reaction products was pursued by Ultra Performance Liquid Chromatography.

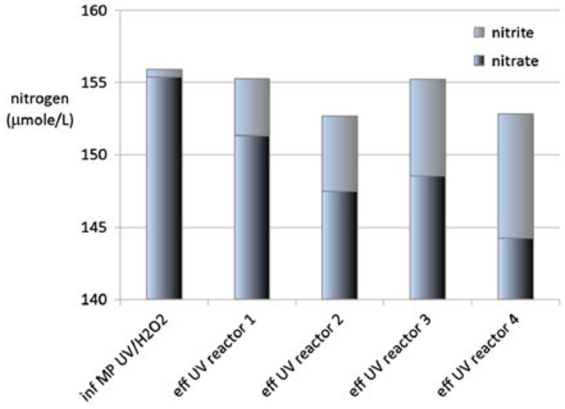


Fig. 5. Concentration of nitrate, nitrite and total inorganic nitrogen content after consecutive MP UV reactors at wtp Andijk.

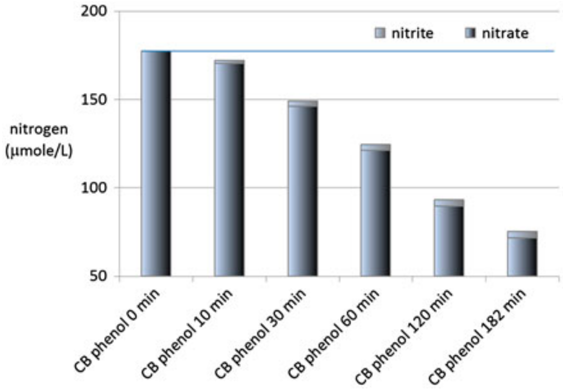


Fig. 6. Nitrate and nitrite concentration and total inorganic nitrogen content after MP UV CB experiments with phenol (0.25 mM) and nitrate (0.18 mM).

5.4. Nitrated reaction product formation by nitrate photolysis in the presence of phenol

The formation of nitrophenols was investigated for a solution with an initial phenol and nitrate concentration of 0.25 mM and of 0.18 mM, respectively, as a function of the MP UV irradiation time in CB experiments (Fig. 7).

With an MP UV irradiance of 1.4 mW/cm^2, the formation of nitro phenols was observed after short irradiation times. A UV dose applied for practical MP UV/H_2O_2 process conditions resulted in the strongest formation. Under these conditions 2.2 μM 2-nitrophenol, 2.1 μM 4-nitrophenol, and 2.4 μM 4-nitrocatechol were found next to 1.7 μM nitrite. Approximately 3%, respectively, 5% of the original reactants nitrate and phenol was converted into nitro aromatics.

6. Discussion

Until recently it was generally accepted that no formation of genotoxic compounds was caused by MP UV applications. Toxicity was observed by combination of UV radition and chlorine [19]. The focus of this paper is on the formation of genotoxic compounds by the application of MP UV only. An increase in the Ames test response, indicating the formation of genotoxic compounds was observed after full-scale MP UV/H_2O_2 treatment, utilizing synthetic quartz sleeves of nitrate-rich surface water. The Ames test response showed a relation between nitrite formation as shown before by Martijn and Kruithof [5].

CB experiments with reconstituted water containing NOM in the presence and absence of nitrate were conducted. MP UV irradiation of NOM did not show an increase in the Ames test response, while MP UV irradiated water samples with NOM in the presence of nitrate did show a response, already at a UV dose commonly applied for disinfection of 40 mJ/cm^2. With increasing UV dose, the Ames test response increased. MP UV irradiation of nitrate and NOM with a UV dose of 600 mJ/cm^2 in the presence of H_2O_2 caused a lower Ames test response than MP UV irradiation with the same UV dose without H_2O_2 dosage.

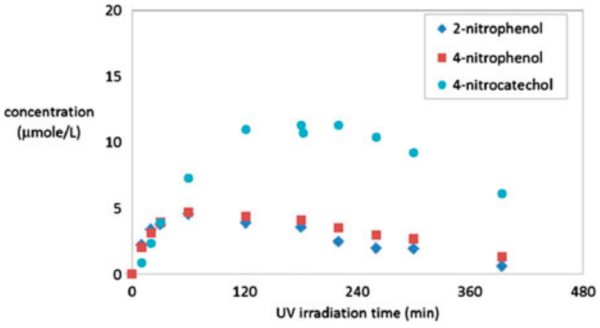


Fig. 7. Formation of nitro phenols in MP UV CB experiments with a phenol (0.25 mM)—nitrate (0.18 mM) solution in demineralized water.

The reaction mechanism of nitrate degradation by MP UV photolysis involves the formation of peroxynitrite as the major intermediate specie. Peroxynitrite decomposes into nitro- and nitroso radicals producing nitrate and nitrite as stable end products [7,8].

This research showed that in organic-free water, after MP UV irradiation, all inorganic nitrogen in the system was found back as nitrate and nitrite, so no inorganic nitrogen was lost from the system. Upon MP UV irradiation of a practical water matrix containing nitrate and NOM, a small but not significant decrease in inorganic nitrogen (nitrate plus nitrite content) was observed, due to the incorporation of inorganic nitrogen into the organic matter. By MP UV irradiation of phenol in nitrate-rich water, a strong decrease of the inorganic nitrogen content was achieved, indicating a significant incorporation of inorganic nitrogen into the organic matrix.

Thorn and Cox [10] showed incorporation of inorganic nitrogen in the organic water matrix, but were unable to identify any low-molecular nitrogen-containing organics. Parallel research efforts to identify low-molecular nitrogen-containing organic compounds after MP UV/H_2O_2 treatment of NOM-containing water have not been successful until now. Therefore, within the framework of this research effort the focus was on the formation of nitrated organics by MP UV/H_2O_2 treatment of an aromatic model compound, phenol, in nitrate-rich water.

Niessen et al. [13] and Machado and Boule [14] showed the formation of nitrated reaction products by UV photolysis of high phenol concentrations under extreme UV conditions. In this research effort, the focus was on process conditions more suitable for UV disinfection, UV photolysis and advanced oxidation. Under these conditions hydroxylation and nitration of phenol were confirmed. The strongest formation of hydroxylated and nitrated phenols was found at conditions similar to practical MP UV/H_2O_2 treatments.

Formation of nitrated aromatic compounds by MP UV photolysis is most probably the cause of the observed Ames test response, because nitro aromatics are well-known genotoxic compounds [19]. Wollin and Dieter [20] derived health based drinking water guideline values for a number of nitro aromatics. For these genotoxic substances, estimations of excess lifetime cancer risk were derived. For instance, for 2,6 dinitrotoluene, a toxicology-based drinking water guideline value of 50 ng/L (0.27 nM) was derived for an additional 5.86×10^{-6} cancer risk over a life-span of 70 years. After identification and quantification of formed nitrated organics from the organic water matrix by MP UV treatment under practical conditions, risk assessment for these compounds should be carried out to quantify the possible health impact.

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References

[1] J.J. Rook, Formation of haloforms during chlorination of natural water, Water Treat. Exam. 23 (1974) 234–245.
[2] Y. Kurokawa, A. Maekawa, M. Takahashi, Y. Hayashi, Toxicity and carcinogenicity of potassium bromate—a new renal carcinogen, Environ. Health Perspect. 87 (1990) 307–335.
[3] J.C. Kruithof, Chlorination by Products: Production and Control, AWWARF Report Denver, 1986, pp. 137–141.
[4] J.C. Kruithof, E.J. Oderwald-Muller, R.T. Meijers, Control strategies for the restriction of bromate formation, in: Proceedings of the 12th World Congress of the International Ozone Association, 1992, pp. 209–233.
[5] A.J. Martijn, J.C. Kruithof, UV and UV/H_2O_2 treatment: The silver bullet for by product and genotoxicity formation in water production, Ozone: Sci. Eng. 34 (2012) 92–99.
[6] K.S. Krishnan, A.C. Guha, The absorption spectra of nitrates and nitrites in relation to their photodissociation, Proc. Indian Acad. Sci. -Sect. A 1(4) (1934) 242–249.
[7] J. Mack, J.R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: A review, J. Photochem. Photobiol. A: Chem. 128 (1999) 1–13.
[8] S. Goldstein, J. Rabani, Mechanism of nitrite formation by nitrate photolysis in aqueous solutions: The role of peroxynitrite, nitrogendioxide and hydroxyl radical, J. Am. Chem. Soc. 129 (2007) 10597–10601.
[9] K.A. Thorn, M.A. Mikita, Nitrite fixation by humic substances, Soil Sci. Soc. Am. J. 64 (2000) 568–582.
[10] K.A. Thorn, L.G. Cox, Ultraviolet irradiation effects incorporation of nitrate and nitrite nitrogen into aquatic natural organic matter, J. Environ. Qual. 41 (2012) 865–881.
[11] D. Vione, V. Maurino, C. Minero, M. Lucchiari, E. Pelizzetti, Nitration and hydroxylation of benzene in the presence of nitrite/nitrous acid in aqueous solution, Chemosphere 56 (2004) 1049–1059.
[12] J. Suzuki, T. Sato, A. Ito, S. Suzuki, Photochemical reaction of biphenyl in water containing nitrite or nitrate ion, Chemosphere 16 (1987) 1289–1300.
[13] R. Niessen, D. Lenoir, P. Boule, Phototransformation of phenol induced by excitation of nitrate ions, Chemosphere 17 (1988) 1977–1984.
[14] F. Machado, P. Boule, Photonitration and photonitrosation of phenolic derivatives induced in aqueous solution by excitation of nitrite and nitrate ions, J. Photochem. Photobiol. A: Chem. 86 (1995) 73–80.
[15] J. Suzuki, H. Okazaki, T. Sato, S. Suzuki, Formation of mutagens by photochemical reaction of biphenyl in nitrate aqueous solution, Chemosphere 11 (1982) 437–444.
[16] J. Bolton, K. Linden, Standardization of methods for fluence (UV Dose) determination in bench-scale UV experiments, J. Environ. Eng. 129(3) (2003) 209–215.
[17] S. Flückiger-Isler, M. Baumeister, K. Braun, V. Gervais, N. Hasler-Nguyen, R. Reimann, J. Van Gompel, H.G. Wunderlich, G. Engelhardt, Assessment of the performance of the Ames II assay: A collaborative study with 19 coded compounds, Mutat. Res. 558(1–2) (2004) 181–197.
[18] M.B. Heringa, D.J.H. Harmsen, E.F. Beerendonk, A.A. Reus, C.A.M. Krul, D.H. Metz, G.F. Ypelaar, Formation and removal of genotoxic activity during UV/H_2O_2-GAC treatment of drinking water, Water Res. 45 (2011) 366–374.
[19] H.S. Rosenkranz, R. Mermelstein, The genotoxicity, metabolism and carcinogenicity of nitrated polycyclic aromatic hydrocarbons, J. Env. Sci. Health C3 (1985) 221–272.
[20] K.-M. Wollin, H.H. Dieter, Toxicological guidelines for monocyclic nitro-, amino- and aminonitroaromatics, nitramines, and nitrate esters in drinking water, Arch. Environ. Contam. Toxicol. 49 (2005) 18–26.