

**BY-PRODUCT FORMATION DURING UV DISINFECTION OF A
PRE-TREATED SURFACE WATER**

**Dr. G.F. IJpelaar¹, Ir. B. van der Veer²,
Dr. G.J. Medema¹, Dr. J.C. Kruithof³**

**¹ Kiwa N.V. Water Research,
P.O. Box 1072, 3430 BB Nieuwegein, the Netherlands**

**² N.V. Water Supply Company Europoort
P.O. Box 59999, 3008 RA Rotterdam, the Netherlands**

**³ N.V. PWN Water Supply Company North Holland
P.O. Box 2113, 1990 AC Velserbroek, the Netherlands**

ABSTRACT

A low-pressure (LP-UV) and medium-pressure UV lamp (MP-UV) were compared on the formation of nitrite, AOC and mutagenicity using pre-treated surface water in a bench-scale UV unit. The results have been compared with the by-product formation in a MP-UV pilot installation at WTP Berenplaat of Water Supply Company Europoort. It was found that although significant nitrite formation occurred in the MP-UV bench-scale experiments, it remained below the standard (0.1 mg/L NO₂⁻) in the pilot plant. LP-UV gave no or very low amounts of nitrite. The AOC and mutagenicity increase with LP-UV was negligible. However, the AOC content and mutagenicity after MP-UV irradiation in the bench-scale unit was significant. AOC formation also occurred in the pilot installation.

The mutagenicity was elevated but not significant. Distribution of biologically stable water is realized by reducing the AOC concentration using GAC filtration after UV disinfection.

KEYWORDS

AOC, biosimetry, by-products, LP-UV, MP-UV, mutagenicity, nitrite, UV.

INTRODUCTION

Since the early eighties of the last century, water utilities in the Netherlands are using ultraviolet radiation primarily for groundwater disinfection (*E. coli*, *Aeromonas*) and for reduction of heterotrophic plate counts (HPC) in riverbank filtrate after GAC filtration. UV fluences between 200 and 400 J/m² were applied. Examples are the locations of De Landeus (*E. coli*) and Hardinxveld (HPC). For post disinfection of surface water at location Zevenbergen Water Supply Company North-West-Brabant (nowadays Brabant Water) built a demonstration UV plant for the reduction of HPC counts up to 5000/ml (22 °C) in GAC filtrate. UV was studied on full scale as an alternative for post chlorination to avoid side effects like mutagenicity and the formation of significant amounts of adsorbable organohalogenes (AOX). At UV fluences above 100 J/m² a 3.5-log reduction was achieved, while a complete elimination was measured at UV fluences of 160 – 230 J/m². At this fluence level, by-products measured as AOC and mutagenicity (Ames) were insignificant (1).

Since the early nineties several studies have been started on the applicability of direct photolysis and UV-driven oxidation of dissolved micropollutants (2 – 5). During application of these processes (MP-UV, 7500 – 15000 J/m², up to 25 g/m³ H₂O₂) for the degradation of recalcitrant compounds like pesticides and solvents (i.e. 1,4-dioxane), AOC formation occurs up to concentrations of 100 µg AcC eq/L or higher (4). Although these UV-doses are much higher than those currently applied for disinfection purposes, it suggests that by-product formation may occur to a certain extent during UV disinfection at fluences >400 J/m².

Until a few years ago, UV disinfection was not considered applicable for primary disinfection of surface water because of the extremely high doses needed to inactivate protozoan oocysts.

Campbell and co-workers reported that UV fluences of 87480 J/m² were needed to realize >2 log inactivation of *Cryptosporidium parvum* oocysts (6). However, the discovery in 1998 that *Cryptosporidium parvum* oocysts are readily inactivated by medium-pressure UV irradiation has rendered UV as a primary disinfection barrier, since these oocysts are highly resistant to conventional disinfectants (7).

Recently, Water Supply Company Europoort studied the applicability of UV for primary disinfection of surface water for WTP Berenplaat. It was found that an UV fluence of 1200 J/m² was needed to achieve a 1.5-log inactivation of sulfite-reducing clostridia spores (SSRC).

This paper focuses on the side effects of UV disinfection of pre-treated water using both low (LP-UV) and medium-pressure UV (MP-UV) lamps for fluences up to 900 J/m². The formation of biodegradable organic carbon, measured as assimilable organic

carbon (AOC), formation of nitrite by reduction of nitrate as well as the effect of UV radiation on mutagenicity are presented.

MATERIALS AND METHODS

Experiments on by-product formation using low (LP-UV) and medium-pressure (MP-UV) UV lamps were performed with a bench-scale UV unit. This unit was equipped with one UV lamp surrounded by 3 small quartz cells which could be used in series. The water depth is very low (~ 2 – 3 centimeter) causing the water to pass the lamp at very short distances. The UV lamps used were a LP-UV (B160VIK from Berson, 130 W output) and a MP-UV (B2020 from Berson, output 2 kW, F200 quartz tubes). The pilot UV installation (180 m³/h) was equipped with 4 MP-UV, which were identical to the MP-UV as applied in the bench-scale unit. Figure 1 shows the emission spectra of the UV lamps used in this research.

Biesbosch water, after storage pre-treated by microstraining, coagulation (Fe(III)) and floc blanket clarifying in the full-scale WTP Berenplaat was applied for this study. During all experiments the UV transmission (254 nm, 1 cm path length) of the pre-treated water was 90%.

Biodosimetry tests were performed using *Bacillus subtilis* spores (ATCC 6633) calibrated by the University of Vienna. The spores were either dosed to a large volume of water (bench-scale unit) or injected to the water flow (pilot installation). The concentration of the spores was measured in the non-irradiated and in the UV-irradiated water. For the AOC analyses strains of P17 and Nox were applied, using the standardized method as described by Van der

Kooij (8). Nitrate was analyzed with ion chromatography and nitrite was measured spectrophotometrically. Mutagenicity was measured with the Ames test (*Salmonella typhimurium* strain TA98, with and without in vitro microsomal activation (S9 mix) and extracted at pH2 and pH7).

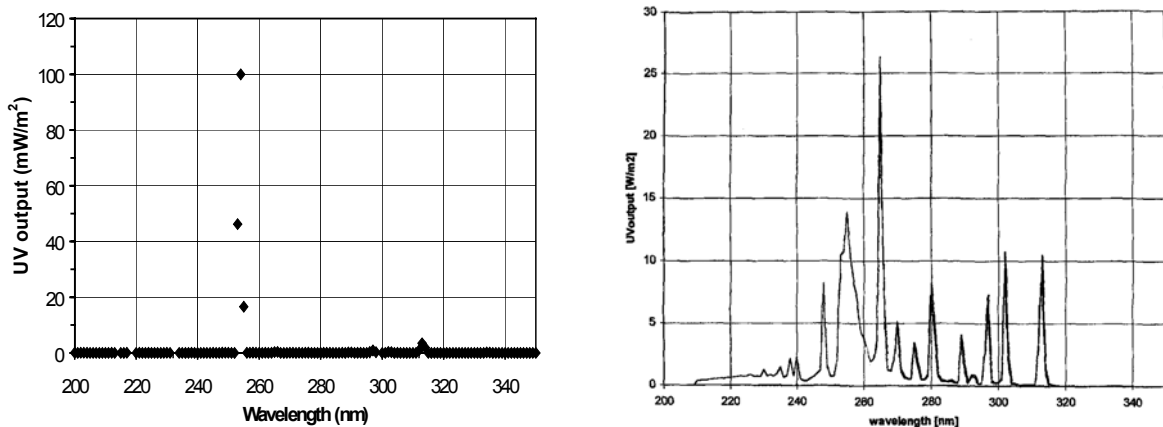


Figure 1: Emission spectra of the LP-UV (left) and MP-UV (right) lamps.

RESULTS OF MEASUREMENTS

BIODOSIMETRY

The delivered UV fluences in both the bench-scale UV unit and the pilot installation were measured by means of biodosimetry with *Bacillus subtilis* spores as described in the previous section. Table 1 shows the corresponding Reduction Equivalent Fluences (REF)

using the low-pressure (LP-UV) and medium-pressure UV lamps (MP-UV).

Table 1: REF by biosimetry with *Bacillus subtilis* spores in the bench-scale UV unit.

Type of UV lamp	Log inactivation <i>Bac. subtilis</i> spores	REF (J/m ²)
LP-UV	2.52	470
	4.56	760
	5.56	910
MP-UV	1.18	270
	4.35	730
	5.55	910

BY-PRODUCT FORMATION

Nitrite

The formation of nitrite was measured with both the low and the medium-pressure UV lamp under disinfection conditions with REF's between 200 and 900 J/m² (see figure 2 and table 2). Figure 3 shows the concentrations of nitrite in the water after UV treatment in the pilot installation.

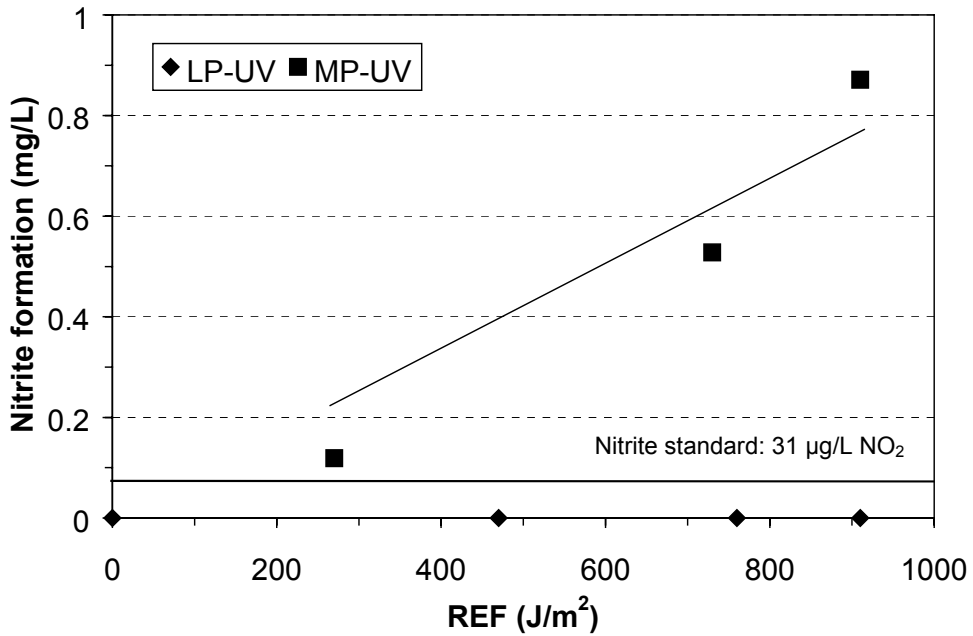


Figure 2: Nitrite concentrations in UV irradiated pre-treated surface water measured in the bench-scale UV unit.

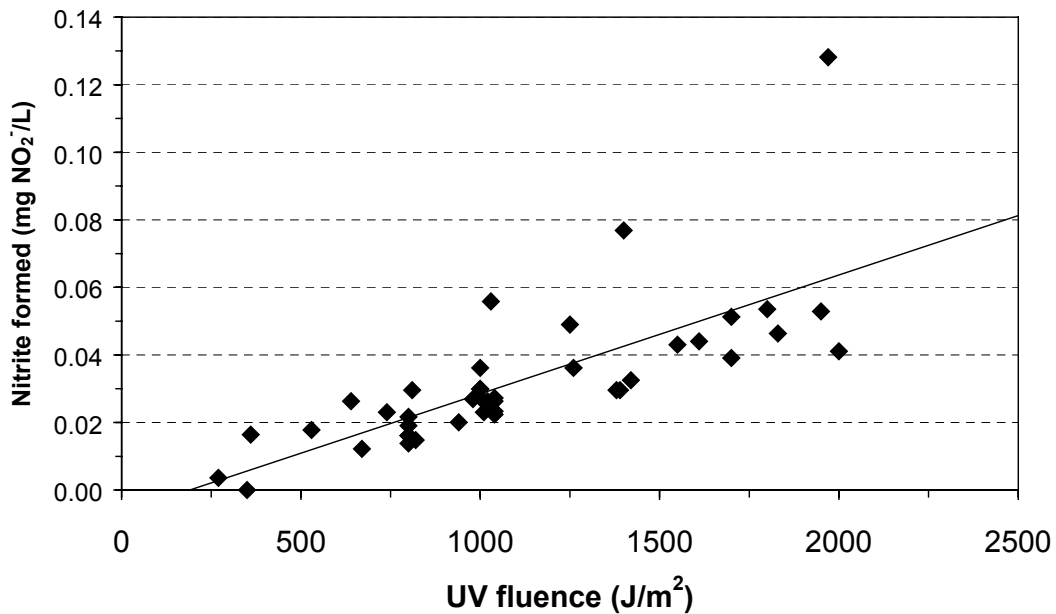


Figure 3: Nitrite concentrations in UV irradiated pre-treated surface water measured in the MP-UV pilot installation. [NO₃] = 13 – 15 mg/L.

Table 2: Nitrite and AOC formation in the bench-scale unit and in the pilot installation.

UV fluence (J/m ²)	Nitrite formation (µg/L)		AOC formation (µg AcC eq/L)	
	Bench-scale unit	Pilot unit	Bench-scale unit	Pilot unit
Low-pressure UV lamp				
470	< 31	-	3.6	-
760	< 31	-	4.0	-
910	< 31	-	4.7	-
Medium-pressure UV lamp				
270	119	3.6	8.7	-
600	-	~ 23	-	10 – 18
730	528	~ 23	11	-
910	871	~ 20	18	-

Assimilable Organic Carbon (AOC)

Organic matter as present in any kind of natural water absorbs UV radiation mainly at wavelengths below 250 nm (see figure 4). This might result in degradation of natural organic matter causing the formation of low-molecular or assimilable organics, in particular on application of MP-UV. It is well known that the formation of such organics may cause regrowth in the distribution network (9). Figure 5 presents the AOC formation in the MP-UV pilot installation whereas figure 6 shows the AOC concentrations versus the REF in the bench-scale unit.

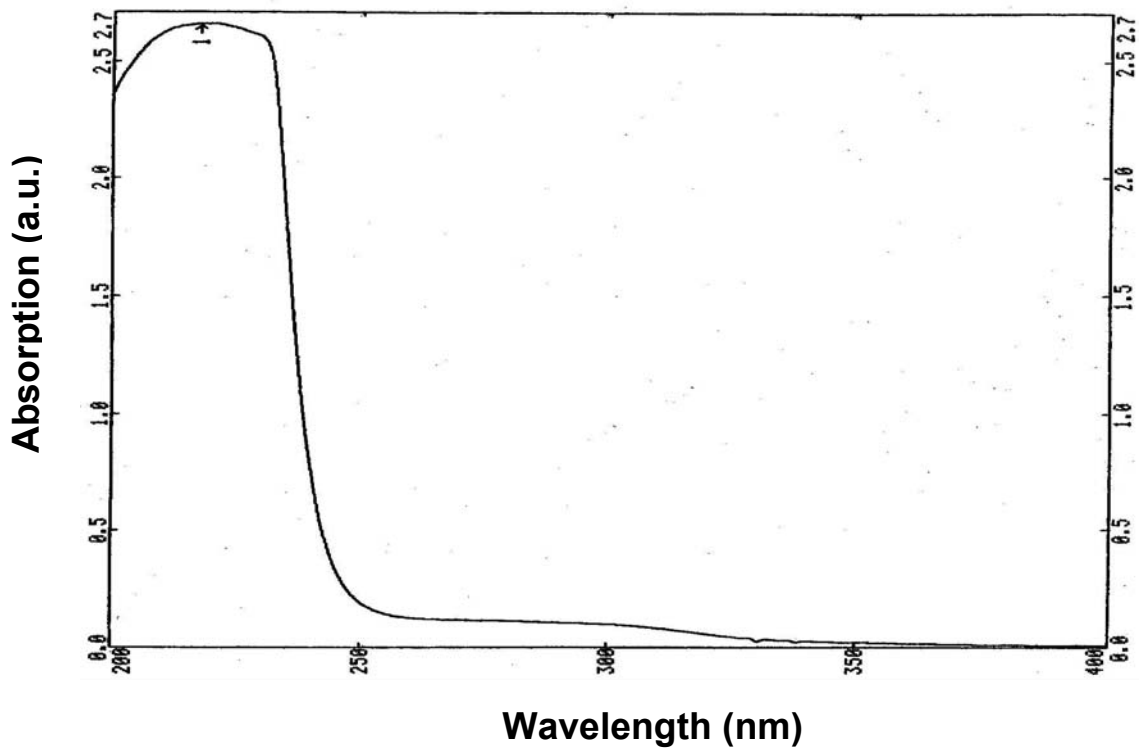


Figure 4: UV scan of a typical natural water.

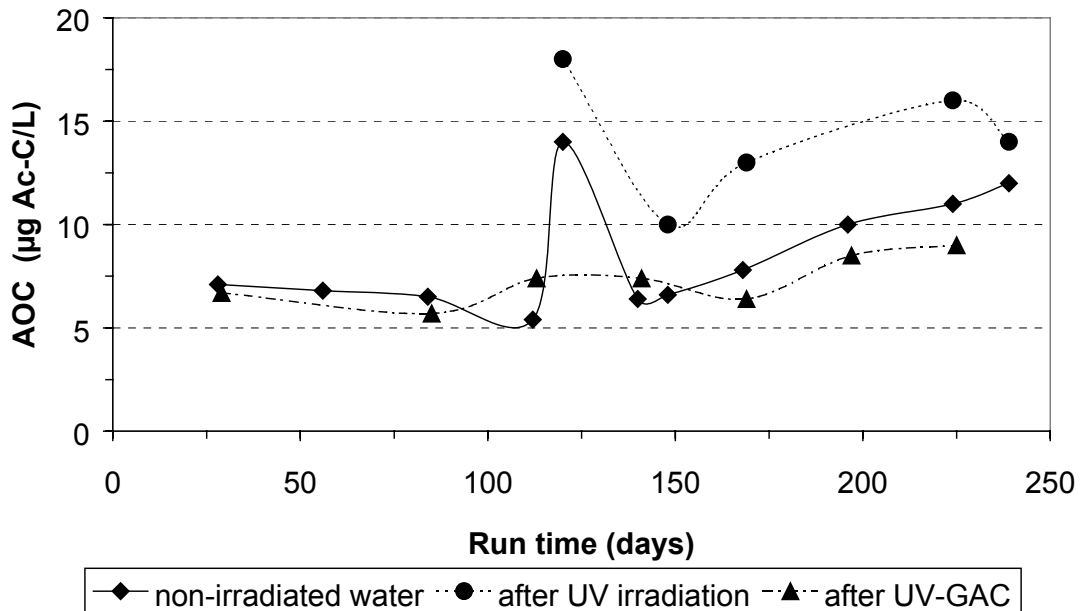


Figure 5: Amount of AOC in the untreated and UV treated water in the UV pilot installation at a REF of 600 J/m².

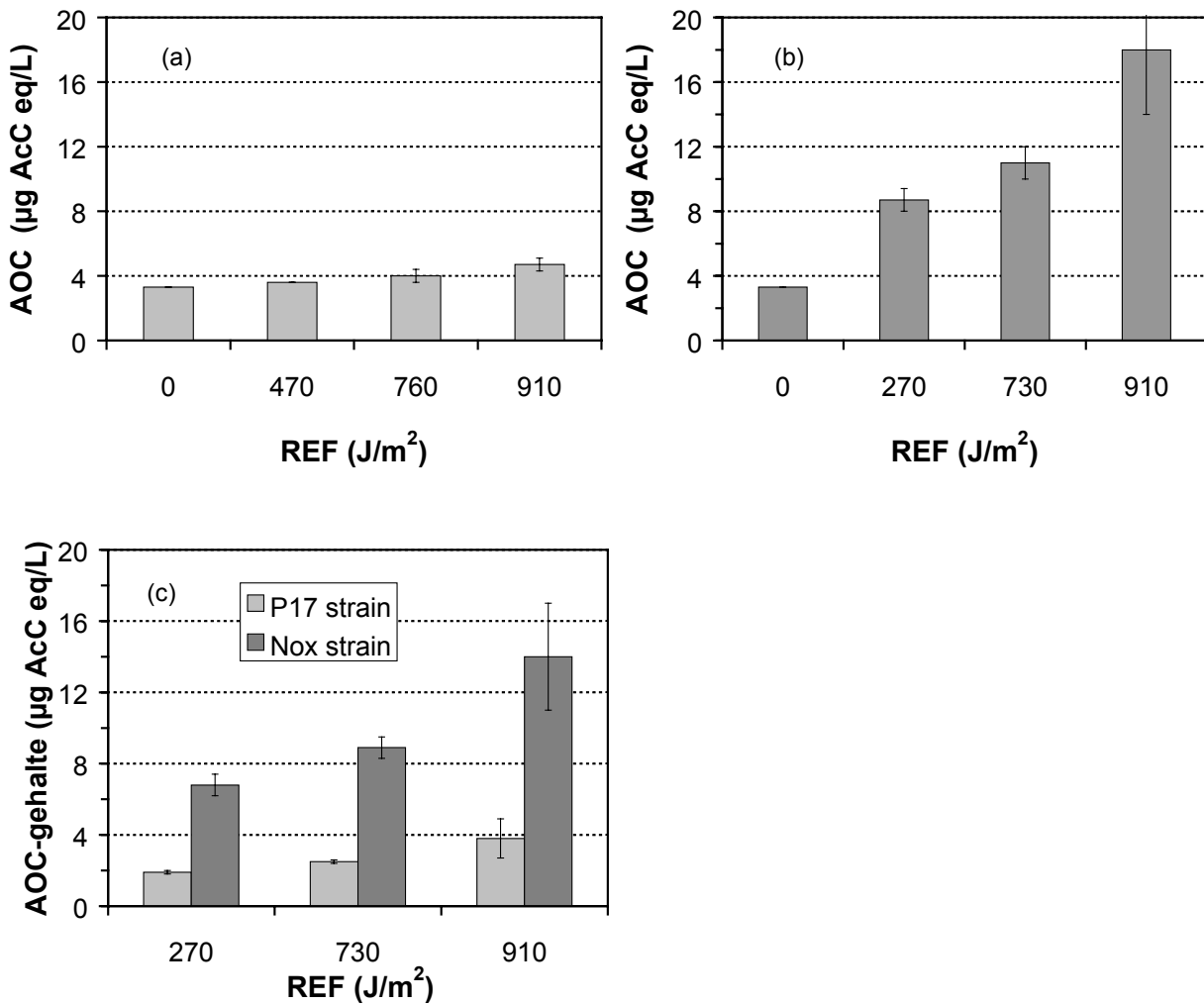


Figure 6: Amount of AOC in the raw (0 J/m²) and irradiated water (a) LP-UV, (b) MP-UV, and (c) MP-UV discriminating between the P17 and Nox strain. Markers in the bars indicate the analysis error.

Mutagenicity

The number of spontaneous revertants and induced revertants after UV irradiation are presented in table 3.

Table 3: Number of revertants in pre-treated water before and after UV irradiation at pH 7 based on the TA98 strain without S9.

Type of UV lamp	REF (J/m ²)	Mutagenicity (revertants/L)	
		Bench-scale unit	Pilot plant
LP-UV	470	17	-
	910	20	-
MP-UV	270	109	-
	600	-	42
	910	142	-
-	-	17 (spontaneous revertants)	30

DISCUSSION

NITRITE FORMATION

Research performed by Von Sonntag and co-workers (10) showed that UV radiation at wavelengths <240 nm enables the cleavage of a nitrogen – oxygen bond in a nitrate molecule resulting in the formation of nitrite. Also DOC and dissolved inorganic carbon like CO₂ seem to have significant effects on the nitrite level in the UV-irradiated water during photolysis of nitrate-containing water (11). From this it is expected that nitrite formation will occur during UV irradiation of nitrate in waters using non-filtered MP-UV

(200 – 320 nm). No or very low levels of nitrite will be formed by LP-UV.

The results of the measurements with the bench-scale UV unit show significant amounts of nitrite after irradiation with MP-UV using UV fluences up to 910 J/m². However, the nitrite concentrations found in the water after UV irradiation at 600 J/m² in the MP-UV pilot installation are considerably lower, 0.03 mg NO₂⁻/L (pilot) versus 0.53 mg/L NO₂⁻ in the bench-scale unit (730 J/m²), respectively. The standard for nitrite in drinking water in the Netherlands is 0.1 mg NO₂⁻/L. Based on this study, it can be concluded from these results that nitrite formation can be controlled under practical conditions.

In contrast to the fluence in the bench-scale unit and the pilot installation (730 vs. 600 J/m²), the nitrite formation in the bench-scale unit is more than 20 times higher than in the pilot unit (see table 2). Considering this might be due to the difference in set-up of both UV-units, the effect of the absorption of nitrate between 200 – ~250 nm on the average irradiance through the water was modeled (12). Using an arbitrary lamp flux, absorption coefficients of natural water, a nitrate factor (instead of the germicidal factor) and a divergence factor, it was found that the average irradiance in the bench-scale unit was only a factor of about 2 higher than in the pilot unit. Since this does not account for the large difference in nitrite formation as described above, an explanation for this discrepancy has not been found.

AOC FORMATION

As predicted AOC formation may occur during UV irradiation of pre-treated water. The majority of AOC formed originates from dissolved organic carbon (DOC) which absorbs UV radiation predominantly between 200 and 250 nm (see figure 4). Using the LP-UV (bench-scale unit) at REF's of 760 and 910 J/m² AOC increases of 0.7 and 1.4 were measured, respectively. Based on the analytical error of both values, e.g. 0.4 µg AcC eq/L, these values cannot be fully distinguished. Therefore, it can be concluded that using LP-UV systems AOC formation is limited. The AOC concentration increased to about 18 µg AcC eq/L in the bench-scale UV unit using MP-UV at 910 J/m². On application of MP-UV in the pilot installation an AOC concentration of 10 – 18 µg AcC eq/L (influent AOC concentration 5 – 15 µg/L) was measured at a REF of 600 J/m². This suggests that the AOC formation in the pilot system is less prominent than in the bench-scale system as has been observed for nitrite formation. Moreover, after GAC filtration, the concentration of 15 – 20 µg AcC eq/L was reduced to <10 µg AcC eq/L (see figure 5). From the AOC analyses it was found that especially the Nox strain contributes to the AOC concentrations found in the treated water. It is well known that the Nox strain grows pre-dominantly by consumption of carboxylic acids (13), suggesting that these compounds are produced by UV irradiation of this type of water. If UV-GAC treated water has a biofilm formation potential, additional precautionary actions (measures) may be necessary. On the other hand, the formation of AOC out of DOC may be limited by using quartz tubes with coatings filtering out wavelengths lower than 240 or 250 nm.

MUTAGENICITY

The number of induced revertants as measured with the MP-UV in the bench-scale UV unit and in the pilot installation were 142 (versus 17 spontaneous revertants) and 42 (versus 30 spontaneous revertants) respectively. This indicates that the results obtained concerning mutagenicity are comparable to the results with nitrite and AOC formation in the bench-scale installation: no or negligible increase with LP-UV but significant increases with MP-UV. The number of revertants was increased in the MP-UV pilot installation but this was not significant. It may be concluded that, although limited, mutagenicity may occur using MP-UV systems. As concluded earlier with the formation of AOC, application of GAC filtration and coated quartz tubes with a cut-off at 240 nm may prevent the occurrence of mutagenicity in such systems. No increase in mutagenicity was found using low-pressure UV lamps (14).

As is for nitrite and AOC formation, the cause of the significant difference in mutagenicity of the UV-irradiated water in the bench-scale unit compared to the pilot installation is unclear.

CONCLUSIONS

During UV disinfection of pre-treated natural waters by-product formation may occur. This research focussed on the formation of nitrite, assimilable organic carbon (AOC) and mutagenicity using a low-pressure (LP-UV) and a medium-pressure UV lamp (MP-UV) in a bench-scale UV unit. The results have been compared with the

results of a pilot UV installation equipped with the same medium-pressure UV lamps as the one used in the bench-scale UV unit.

On application of the LP-UV (bench-scale unit), AOC and nitrite formation and mutagenicity was insignificant. However, with the MP-UV bench-scale set-up AOC and nitrite formation as well as mutagenicity appeared to be significant. Concerning these by-products, the formation level in the MP-UV pilot installation was either insignificant (nitrite, mutagenicity) or controllable based on an additional post GAC treatment (AOC).

LITERATURE

1. KRUIHOF, J.C., LEER, R.Chr. VAN DER, HIJNEN, W.A.M., 'Practical experiences with UV disinfection in the Netherlands', J Water SRT – Aqua, Vol. 41, nr. 2, pp. 88 – 94, 1992
2. HESSLER, D.P., GORENFLO, V., FRIMMEL, F.H., 'Degradation of Aqueous Atrazine and Metazachlor Solutions by UV and UV/H₂O₂ - Influence of pH and Herbicide Concentration', Acta Hydrochim. Hydrobiol., vol. 21, no. 4, 1993, pp. 209 – 214
3. BOURGINE, F.P., CHAPMAN, J.I., 'Pesticide Reduction in Drinking Water by UV Photolysis', IOA Regional Conference on Ozone, Ultraviolet Light, Advanced Oxidation Processes in Water Treatment, Amsterdam 1996.
4. KRUIHOF, J.C., KAMP, P.C., 'UV/H₂O₂: The Ultimate Solution for Pesticide Control', Annual AWWA Conference, Denver USA, 2000
5. IJPELAAR, G.F., KRUIHOF, J.C., 'Advanced Oxidation Processes for the Degradation of Pesticides in Ground Water

and Surface Water', Proceedings World Water Conference IOA, London UK 2001.

6. Campbell, A.T., Robertson, L.J., Snowball, M.R., Smith, H.V., 'Inactivation of Oocysts of *Cryptosporidium Parvum* by Ultraviolet Irradiation', *Wat. Res.*, vol. 29, no. 11, 1995, pp. 2583 – 2586.
7. KORICH, D.G., MEAD, J.R., MADORE, M.S., SINCLAIR, N.A., STERLING, C.R., 'Effects of Ozone, Chlorine Dioxide, Chlorine, and Monochloramine on *Cryptosporidium parvum* Oocyst Viability', *Appl Env. Microbiol.*, May 1990, pp. 1423 – 1428.
8. KOOIJ, D. VAN DER, 'Assimilable Organic Carbon as an Indicator of Bacterial Regrowth', *Journal AWWA*, February 1992, pp. 57 – 65.
9. KOOIJ, D. VAN DER, HIJNEN, W.A.M., KRUIHOF, J.C., 'The Effects Of Ozonation, Biological Filtration And Distribution On The Concentration Of Easily Assimilable Organic Carbon (AOC) In Drinking Water', *Ozone Sci & Eng.*, Vol. 11, 1989, pp. 297 – 311.
10. SONNTAG, C. VON, SCHUCHMANN, H-P., 'UV disinfection of drinking water and by-product formation – some basic considerations', *J. Water SRT – Aqua*, vol. 41, nr.2, 1992, pp. 67–74.
11. SHARPLESS, C.M., Linden, K.G., 'UV Photolysis of Nitrate: Effects of Natural Organic Matter and Dissolved Inorganic Carbon and Implications for UV Water Disinfection', *Env. Sci. Technol.*, vol. 35, pp. 2949 – 2955, 2001.
12. BOLTON, J.R., UVCalc, Version 2, www.boltonuv.com, February 2002.

13. KOOIJ, D. VAN DER, HIJNEN, W.A.M., 'Substrate Utilization of an Oxalate-Cosuming Spirillum Species in Relation to Its Growth in Ozonated Water', Appl. Environ. Microbiol. Vol. 47, 1984, pp. 551-559.
14. HAIDER, T., SOMMER, R., KNASMULLER, S., ECKL, P., PRIBIL, W., CABAJ, A., KUNDI, M., 'Application of a test combination of three different bioassays for the investigation of genotoxic effects induced by UV-irradiation in water', Proceedings of the 'Intern. Conf. on UV Technologies', Washington DC, USA, 14–16 june 2001.