

# UV AND UV/H<sub>2</sub>O<sub>2</sub> TREATMENT: THE SILVER BULLET FOR BYPRODUCT AND GENOTOXICITY FORMATION IN WATER PRODUCTION

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## Abstract

Since Rook showed the production of trihalomethanes by drinking water chlorination, reaction product formation by chemical disinfection/oxidation has been thoroughly investigated. Originally the focus was on the formation of individual organic products. After chlorination trihalomethanes (THMs), haloacetic acids (HAAs) and many other halogenated compounds were found. After ozonation, ultraviolet (UV) disinfection and advanced oxidation, biodegradable organic byproducts such as carboxylic acids were identified. All reaction products were formed by reaction with the organic water matrix (natural organic matter).

Formation of reaction products from the inorganic water matrix proved to be an important issue as well. By ozonation and ozone based advanced oxidation processes bromate was formed in bromide rich water. By UV and UV/H<sub>2</sub>O<sub>2</sub> treatment, nitrite was formed in nitrate rich water, especially when medium pressure UV lamps were applied.

In addition to chemical characterization of individual reaction products the side effects of disinfection/oxidation were investigated by genotoxicity testing. After chlorination a high response was found in the classic Ames test. After ozone and ozone based advanced oxidation a decrease of the response in the classic Ames test was observed, while after UV disinfection and UV based advanced oxidation no significant effect was found.

Modified genotoxicity testing such as in vitro Ames-II has been developed and applied on UV/H<sub>2</sub>O<sub>2</sub> treated water. Once again no or just a small significant genotoxic response was observed after MP UV/H<sub>2</sub>O<sub>2</sub> treatment in a system equipped with natural quartz sleeves. However a substantially higher response was found after MP UV/H<sub>2</sub>O<sub>2</sub> treatment in a system equipped with synthetic sleeves with a higher transmittance at lower wavelengths. The genotoxic response and the nitrite formation increased in the same order of magnitude, suggesting a relationship with the UV photolysis of nitrate. This was confirmed by UV photolysis of natural organic matter (NOM) and nitrate containing reconstituted water. The genotoxic effect was removed completely by post treatment with granular activated carbon (GAC) filtration and/or dune infiltration.

## Introduction

Since the beginning of the last century, chlorine has been used for drinking water disinfection. Originally, the use of chlorine, “a poisonous chemical”, was accepted with great reluctance, but soon drinking water chlorination was generally applied without any concern about harmful aspects (McGuire, 2008).

In 1974 this situation changed completely when Rook (1974), followed by Bellar et al (1974) showed the production of trihalomethanes (THMs) suspect human carcinogens by drinking water chlorination. Since Rook's discovery formation of disinfection byproducts (DBPs) and their potential threat for public health have been a major concern.

After Rook showed THM formation by chlorination, numerous halogenated DBPs have been found such as haloacetic acids (HAAs), haloacetonitriles (HANs), etc. (Cooney, 2008).

To characterize the health risks genotoxicity testing (i.e., by classic Ames testing) has been carried out. Standards have been set for THMs (worldwide) and HAAs (North America).

To restrict chlorination byproduct formation, measures have been taken. In The Netherlands, originally maintenance of chlorination was pursued, restricting the DBP formation by optimizing the chlorine dose and by removing the produced DBPs by granular activated carbon (GAC) filtration. Also, much attention has been paid to the removal of DBP precursors by (enhanced) coagulation and GAC filtration. In The Netherlands gradually the use of chlorine for both primary and post disinfection has come to a complete stop.

For primary disinfection a shift from chlorine to ozone (O<sub>3</sub>) use took place. For ozonation, formation of numerous organic reaction products such as aldehydes and carboxylic acids was established. These organic reaction products were biodegradable rather than harmful for public health. For many years ozone was accepted as the best available alternative for chlorine as the primary disinfectant. This situation changed after Kurakawa et al (1990) showed that the inorganic DBP bromate, formed by ozonation of bromide containing water, was a suspect human carcinogen. Much research has been carried out to control bromate formation. A significant reduction could be achieved, but bromate formation could not be avoided completely (Kruithof and Kamp, 1997).

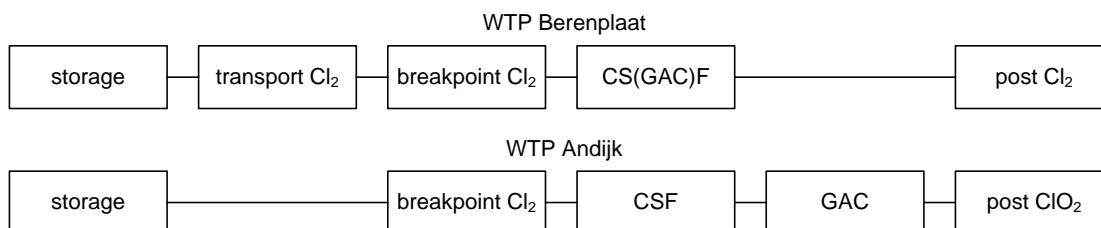
The detection of *Cryptosporidium* oöcysts in drinking water sources had a strong impact on drinking water disinfection. Under practical conditions chlorine was unable to inactivate *Cryptosporidium*. Ozone was able to inactivate *Cryptosporidium* but in many cases bromate formation was prohibitive. It was shown that UV disinfection inactivated *Cryptosporidium* already at a very low UV dose (Bolton et al, 1998). Until now, no individual harmful organic DBPs have been found. A point of attention is the formation of nitrite in nitrate rich water, especially when medium pressure UV lamps are used.

Besides disinfection, organic contaminant control has gained a lot of interest caused by the increasing presence of pesticides, endocrine disruptors, pharmaceuticals, algae toxins, solvents, etc. in drinking water sources (Kruithof et al, 2007). Much attention has been paid to the application of ozone, either in combination with GAC filtration ( $O_3$ -GAC) or with  $H_2O_2$  and GAC ( $O_3/H_2O_2$ -GAC). No harmful organic DBPs have been established until now, but once again bromate formation caused a switch from ozone to UV based processes (UV-GAC, UV/ $H_2O_2$ -GAC) (Kruithof, 2005). Much research has been carried out into the field of bromate, nitrite and genotoxicity. Bromate is not produced by UV based processes. Nitrite formation may be a concern in nitrate rich water, especially for medium pressure (MP) UV lamps.

This paper describes research carried out in The Netherlands. The results of two Dutch drinking water supply companies, EVIDES and PWN Water Supply Company North Holland are presented focussing on the formation of individual organic and inorganic DBPs and especially the formation of genotoxicity.

## Plant Information

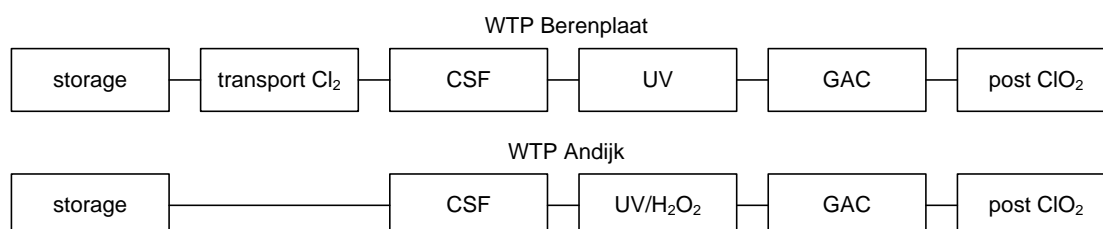
The treatment schemes of the Berenplaat (EVIDES) and the Andijk (PWN) water treatment plants (WTPs) before implementation of UV respectively UV/ $H_2O_2$  are presented in Figure 1.



**Figure 1: Process schemes at WTP Berenplaat and WTP Andijk before retrofit**

At WTP Berenplaat river Meuse water after storage in the Biesbosch reservoirs was treated by breakpoint chlorination, coagulation, sedimentation and filtration (CSF) and post chlorination. For organic contaminant control the media in the rapid filtration step were replaced by GAC. At WTP Andijk IJssel Lake (river Rhine) water was treated after storage on site by breakpoint chlorination, CSF, GAC filtration and  $ClO_2$  dosage.

Both water supply companies decided to upgrade primary disinfection and organic contaminant control (Kamp et al, 1997). EVIDES investigated replacement of breakpoint chlorination by ozonation and installation of GAC filtration with a longer empty bed contact time (EBCT). PWN focused on the implementation of  $O_3/H_2O_2$  treatment. Both processes were not implemented because of bromate formation. Subsequently EVIDES pursued the application of UV disinfection once again followed by GAC filtration with a longer EBCT. PWN focused the research on the feasibility of  $UV/H_2O_2$  treatment. Both treatment options have been installed in 2006 (Berenplaat) and 2004 (Andijk) respectively (see Figure 2).



**Figure 2: Process schemes at WTP Berenplaat and WTP Andijk after retrofit**

DBP formation by reaction of both the organic and inorganic water matrix and genotoxicity testing are presented for the original plants, the research phase and the retrofit plants. Some water matrix parameters relevant for the DBP formation in both pre-treated Biesboschwater (WTP Berenplaat) and IJssel Lake water (WTP Andijk) are presented in table 1.

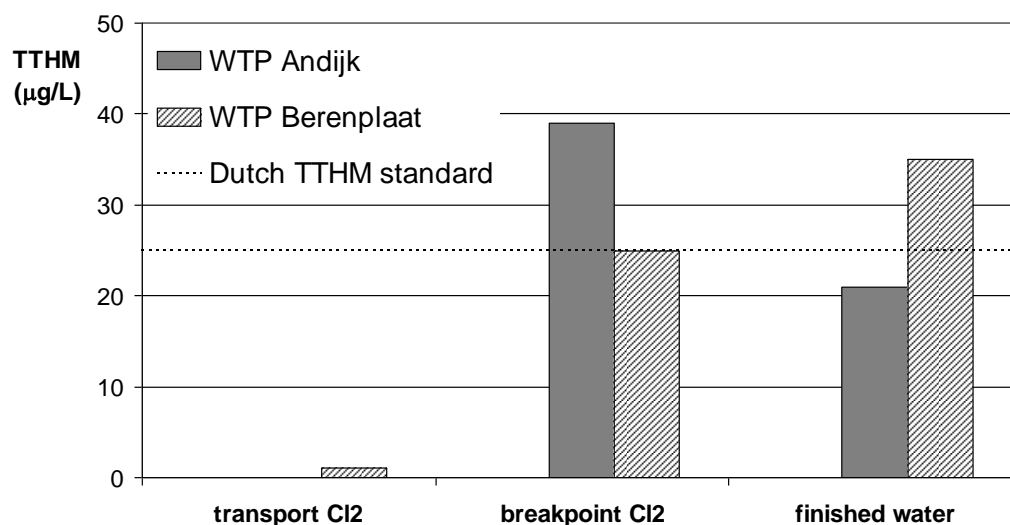
**Table 1: UV-influent water quality parameters for WTP Berenplaat and WTP Andijk**

parameter	WTP Berenplaat	WTP Andijk
DOC (mg/L)	3.2	3.0
Nitrate (mg $NO_3/L$ )	3.0	2-13
Bromide ( $\mu g/L$ )	150	300-500
$UVT_{254}$ ( $cm^{-1}$ )	88%	85%

## Disinfection Byproducts

### Formation of Reaction Products from the Organic Matrix

Major chlorination reaction products THMs and other halogenated compounds are produced by reaction of chlorine with the organic water matrix (natural organic matter). Since 2006 the Dutch standard for individual THMs in drinking water is 10  $\mu g/L$  while the total THMs (TTHMs) standard is 25  $\mu g/L$ . Profiles for the average TTHM content at both WTP Berenplaat (EVIDES) and WTP Andijk (PWN) during the application of breakpoint chlorination are presented in Figure 3.



**Figure 3: Average TTHM content before and after breakpoint chlorination and in the finished water (data WTPs Berenplaat and Andijk)**

Figure 3 shows that at both plants the standard for the TTHM content in the finished water may be exceeded. Lowering this TTHM content was one of the objectives of both water supply companies.

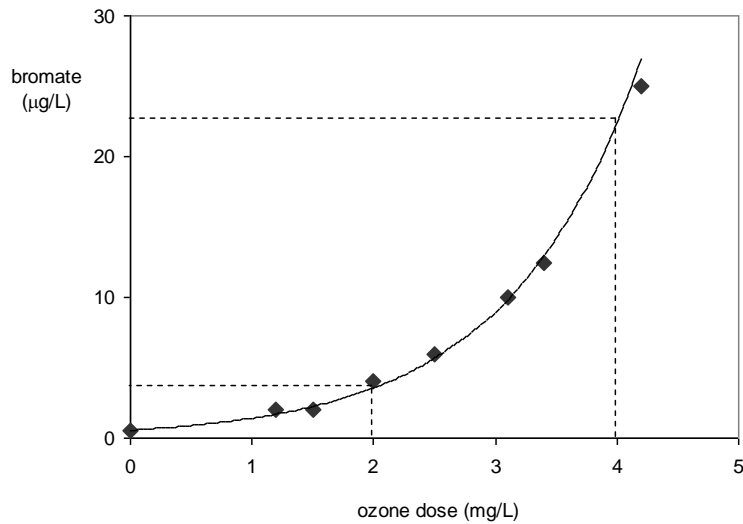
By both  $O_3$  and  $O_3/H_2O_2$  numerous aldehydes, aldehydic acids and carboxylic acids were formed by degradation of the organic water matrix. These compounds are biodegradable rather than harmful for public health as can be seen by the strong increase of assimilable organic carbon (AOC) content. The same types of compounds were produced by  $UV/H_2O_2$  treatment in concentrations of the same order of magnitude. By UV radiation only, the formation of these types of compounds was much less although still significant. No individual genotoxic compounds were detected.

Summarizing, it can be said that organic reaction product formation was based on reaction of the disinfectants / oxidants with the organic matrix (natural organic matter). Chlorination caused the formation of halogenated compounds such as THMs. All other processes,  $O_3$ ,  $O_3/H_2O_2$ , UV and  $UV/H_2O_2$ , reacted with the organic matrix under formation of biodegradable rather than harmful compounds.

### **Formation Reaction Products from the Inorganic Matrix**

Formation of inorganic compounds by chlorination was insignificant. However the bromide content of the water played an important part in the composition of the organic DBPs. In bromide rich water more brominated THMs were formed. The amount of more brominated species increased as a function of the Br-/DOC ratio (Kruithof, 1986).

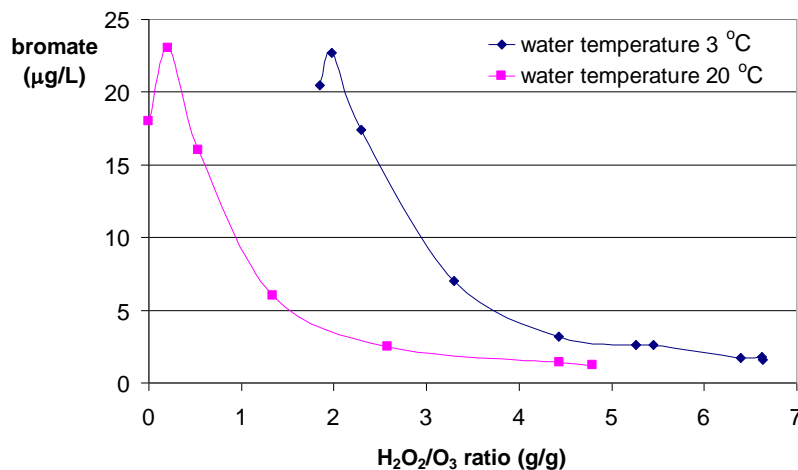
The bromide content also played an important part for ozone based processes. Ozonation of bromide rich water caused the formation of bromate. EVIDES studied the application of ozone for the primary disinfection of pretreated Biesbosch water. The bromate formation as a function of the ozone dose is presented in Figure 4.



**Figure 4: Bromate formation as a function of the ozone dose (pilot experiments EVIDES WTP Berenplaat, bromide content 150 µg/L)**

For a 2 log *Giardia* inactivation an ozone dose of about 2 mg/L was required causing a bromate formation of 3 µg/L lower than the Dutch standard of 5 µg/L. However for a 2 log *Cryptosporidium* inactivation an ozone dose of 4 mg/L was required causing a bromate content of about 25 µg/L; much higher than the bromate standard.

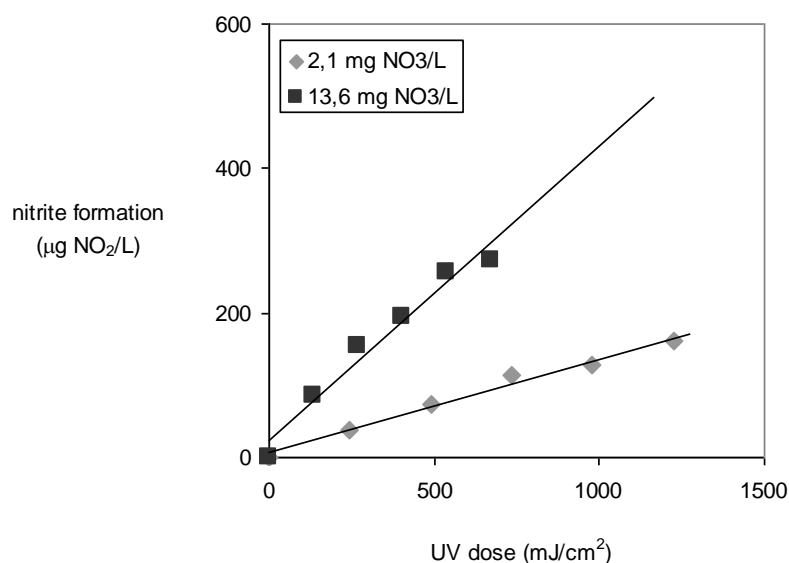
PWN investigated the feasibility of  $O_3/H_2O_2$  treatment for pretreated IJssel Lake water. The required pesticide degradation of 80% could be achieved by ozone/peroxide treatment at economically feasible  $O_3/DOC$  and  $H_2O_2/O_3$  ratios. In view of the high bromide concentration of the water (300-500µg/L), bromate formation was studied extensively. Figure 5 shows the dominant role of the water temperature on the bromate formation. At low  $H_2O_2/O_3$  ratio the synergistic effect of ozone and hydrogen peroxide on the bromate formation, as previously shown by Von Gunten et al (1994), could be confirmed (see Figure 5).



**Figure 5: Bromate formation by  $O_3/H_2O_2$  treatment of pretreated IJssel Lake water (pilot plant research PWN).**

PWN's bromate guideline value of 0.5  $\mu\text{g/L}$  was exceeded for all  $\text{H}_2\text{O}_2/\text{O}_3$  ratios at both water temperatures, while a pH increase did not lower the bromate formation significantly (Martijn et al 2006). Therefore PWN did not pursue the application of  $\text{O}_3/\text{H}_2\text{O}_2$  treatment. Because of potential bromate problems no full scale drinking water ozone projects were realized in The Netherlands the last 15 years.

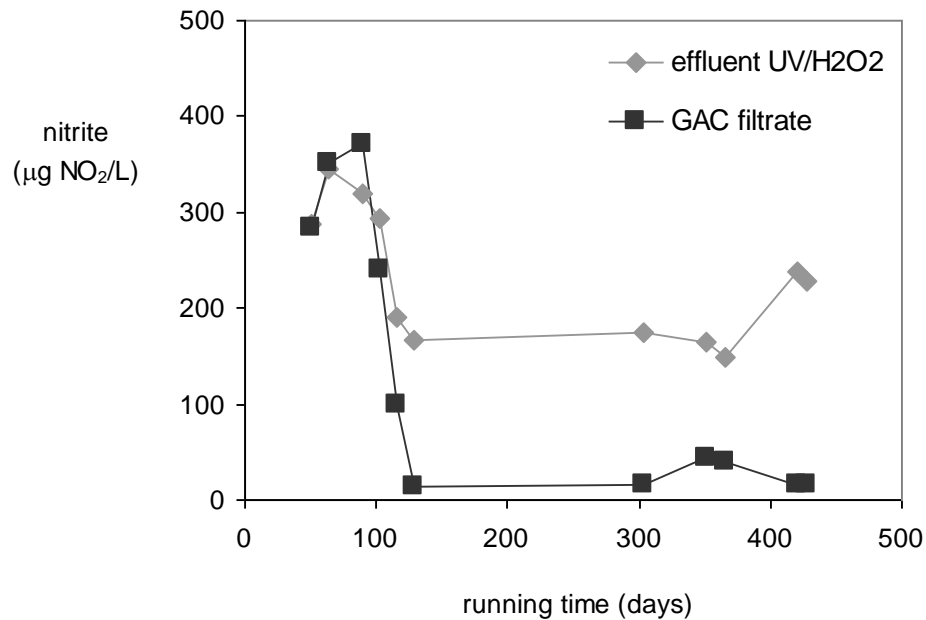
Subsequently EVIDES and PWN investigated the feasibility of UV disinfection and  $\text{UV}/\text{H}_2\text{O}_2$  treatment respectively. Nitrite formation may be an important issue for UV treatment of nitrate rich water. Nitrite formation was very restricted when LPUV lamps were used but was very significant when MPUV lamps in combination with natural quartz GE214 were used (see Figure 6).



**Figure 6: Nitrite formation by MPUV lamps in pretreated Biesbosch water for two nitrate concentrations (pilot plant research EVIDES)**

Figure 6 presents the nitrite formation in pretreated Biesbosch water with nitrate concentrations of 2.1 and 13.6 mg/L. For UV disinfection with a dose of 90 mJ/cm<sup>2</sup> the nitrite concentration did not exceed the E.C. standard of 0.1 mg/L. For advanced oxidation by  $\text{UV}/\text{H}_2\text{O}_2$  (UV dose 600 mJ/cm<sup>2</sup>,  $\text{H}_2\text{O}_2$  dose 6 mg/L) the nitrite standard was exceeded significantly, so post treatment was necessary to lower the nitrite concentration. An option to achieve this goal was chemical oxidation (i.e. by chlorine). PWN selected biological activated carbon filtration (BACF) to reoxidize nitrite to nitrate.

For virgin carbon nitrite oxidation proved to be problematic at low water temperature. By BACF in a biologically active mode with an empty bed contact time of 30 minutes nitrite was converted to concentrations below the EC standard of 0.1 mg/L, even at low water temperatures (see Figure 7).



**Figure 7: Nitrite formation by UV/H<sub>2</sub>O<sub>2</sub> (MPUV lamps) and reoxidation by BACF in pretreated IJssel Lake water (pilot plant research PWN)**

In summary, besides the organic matrix the inorganic water matrix played an important part in reaction product formation as well. This concerned especially the bromide and nitrate content. High bromide levels caused the formation of more brominated DBPs by chlorination. No inorganic DBPs were produced by chlorination. In some cases bromate was found in the finished water caused by impurity of the used sodiumhypochlorite (Hutchison, 1993).

When applying ozone and UV-based disinfection/oxidation a number of individual inorganic DBPs deserved special attention: bromate and nitrite. A major concern in view of the suspect carcinogenic properties of bromate was the formation of bromate by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. No bromate was produced by UV disinfection and UV/H<sub>2</sub>O<sub>2</sub> treatment. For these processes nitrite formation was a relevant issue for nitrate rich water, especially when MPUV lamps were applied.

## Genotoxicity

### Classic Ames Testing

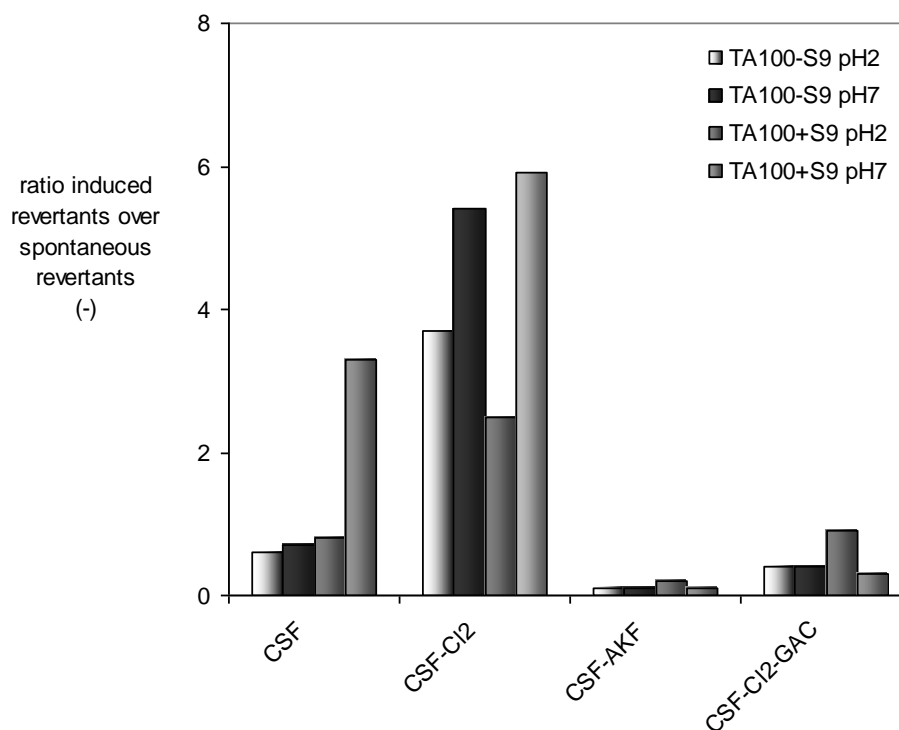
Worldwide genotoxicity research is carried out to characterize raw water quality and effects of treatment, specifically oxidative treatment and disinfection. The most commonly applied method for genotoxicity testing is the classic Ames test (Ames et al, 1972).

The classic Ames test is an in vitro test, using bacteria to detect DNA damage (point mutation). The test is performed with and without metabolic activation to mimic the effect of the liver, detecting both direct genotoxic compounds and compounds that become genotoxic after passing the liver. Results from the Ames test cannot be translated directly into human health risk. Chemical identification of the (group of) formed compounds is necessary for that.



KWR Water Cycle Research Institute developed a methodology for classic Ames testing of concentrated water samples, based on isolation onto XAD resins at two pH values. In the isolates, classic Ames testing was applied with two bacterial strains, TA98 and TA100 with and without metabolic activation by adding S9 mix (Noordsij et al, 1999). The TA98 strain detects frame shift mutations, the TA100 strain base pair substitution.

Applying the classic Ames test with strain TA100 on chlorinated, CSF pretreated river Rhine water showed an increase of the genotoxic effect. The strongest genotoxic effect was observed in the neutral pH isolate for strain TA100 with metabolic activation (Kruithof, 1986; see Figure 8). The observed genotoxicity was much higher than the genotoxic response caused by the present THMs. By GAC filtration all genotoxic response was removed.



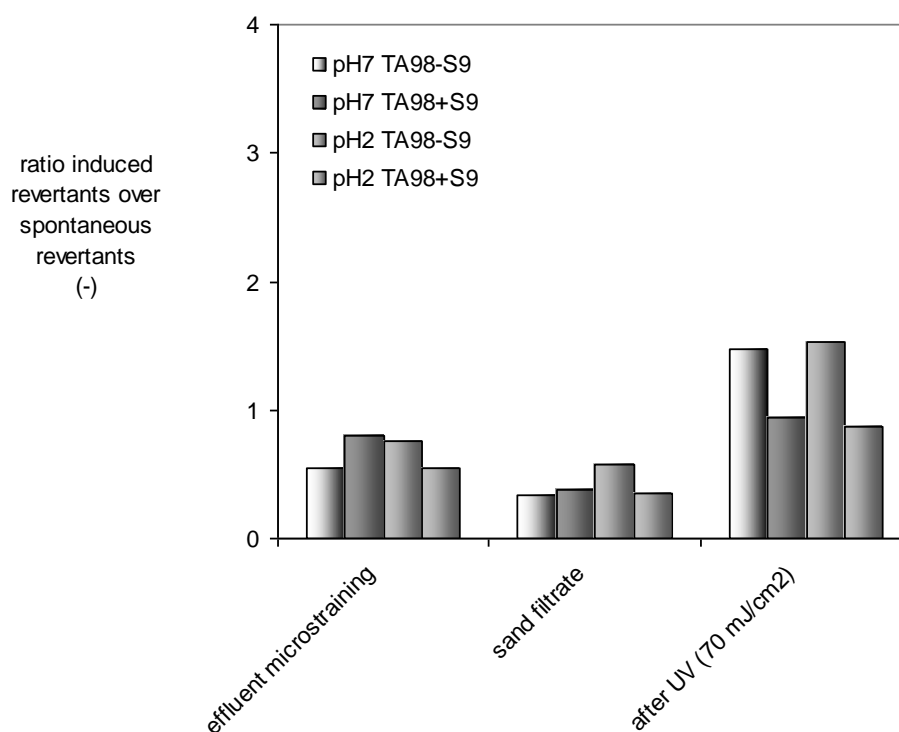
**Figure 8: Genotoxic response in the classic Ames test for strain TA100 caused by chlorination of pretreated river Rhine water (pilot plant research KWR)**

Classic Ames tests have also been carried out in  $O_3$  and  $O_3/H_2O_2$  treated water. In view of the applied isolation method the effect of bromate is not detected. The found genotoxic effect is caused by the isolated organic fraction. For standard process conditions a significant decrease in genotoxic response for strain TA98 was observed (Zoeteman et al, 1982).

By ozonation organic compounds are degraded into more polar, lower molecular weight compounds. For example aromatic compounds are degraded into aldehydes, carboxylic acids etc. These compounds are biodegradable rather than genotoxic.

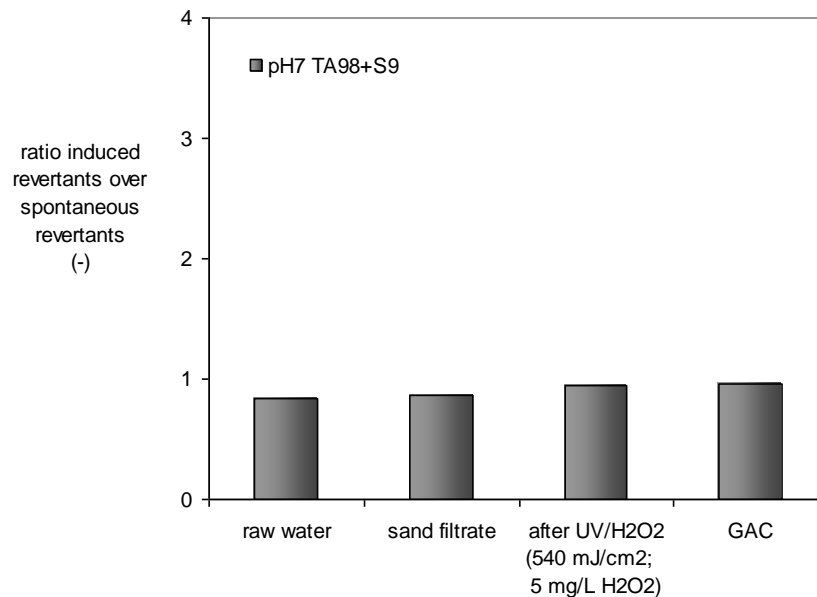
Classic Ames tests have also been carried out to determine the effect of UV-disinfection. In concentrates of water samples from the Biesbosch reservoir after CSF and GAC treatment for both LP and MP UV radiation (UV-dose 32 mJ/cm<sup>2</sup>) the genotoxic activity was insignificant (Kruithof et al, 1992).

More recently, in concentrates of CSF pretreated Biesbosch water after UV disinfection using MP UV lamps and natural quartz GE214 sleeves (UV-dose 70 mJ/cm<sup>2</sup>) the response in the classic Ames test was determined. In all samples, the response for strain TA100 was insignificant, while for strain TA98 the response was very low. The strongest response was observed in strain TA98 without metabolic activation (see Figure 9). However the response was not regarded as a genotoxic effect since the ratio of induced over spontaneous revertants was <2.



**Figure 9: Genotoxic response in the classic Ames test for strain TA98 caused by UV disinfection (70 mJ/cm<sup>2</sup>) of CSF pretreated Biesbosch water (pilot plant research EVIDES)**

A restricted number of classic Ames tests with strain TA98 has been carried out on concentrates of CSF pretreated IJssel Lake water after UV/H<sub>2</sub>O<sub>2</sub> treatment with MP UV lamps and natural quartz GE214 sleeves (UV dose 540 mJ/cm<sup>2</sup>, H<sub>2</sub>O<sub>2</sub> dose 5.0 mg/L). Once again no significant increase was observed (see Figure 10).



**Figure 10: Genotoxic response in the classic Ames test for strain TA98 caused by UV/H<sub>2</sub>O<sub>2</sub> treatment of pretreated IJssel Lake water (pilot plant research PWN)**

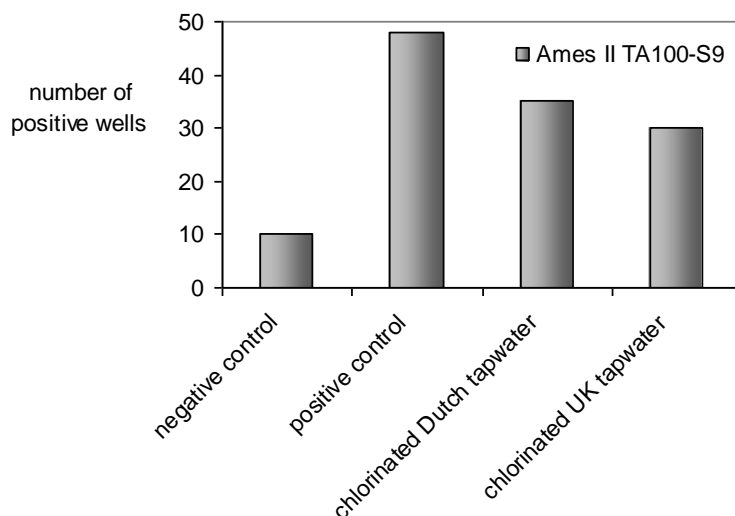
The genotoxic response in strain TA98 for a MP UV dose of 540 mJ/cm<sup>2</sup> combined with a H<sub>2</sub>O<sub>2</sub> dose of 5.0 mg/L was either lower or in the same order of magnitude as the response caused by a MP UV dose of 70 mJ/cm<sup>2</sup> only.

Summarizing, it can be said that chlorination caused a strong genotoxic effect in the classic Ames test, especially for strain TA100 with metabolic activation. Ozone caused a significant decrease of the response in the classic Ames test. The response observed for UV based processes was either not or hardly significant. For medium pressure UV lamps and natural quartz GE214 sleeves a slightly stronger response was observed than for low pressure UV. There was no significant difference between disinfection conditions (70 mJ/cm<sup>2</sup>) and advanced oxidation conditions (540 mJ/cm<sup>2</sup> and 5.0 mg/L H<sub>2</sub>O<sub>2</sub>).

### Advanced Genotoxicity Testing

To characterize the potential harmful side effects of UV treatment and UV based AOP treatment, similar to the efforts regarding harmful side effects of chlorination, the classic Ames test was applied (Figure 9 and Figure 10). No or a hardly significant response was observed. The applied methodology, based on the plate incorporation method in combination with XAD sample concentration (10,000-40,000 times), may not be sensitive enough to detect UV and UV/H<sub>2</sub>O<sub>2</sub> induced genotoxicity.

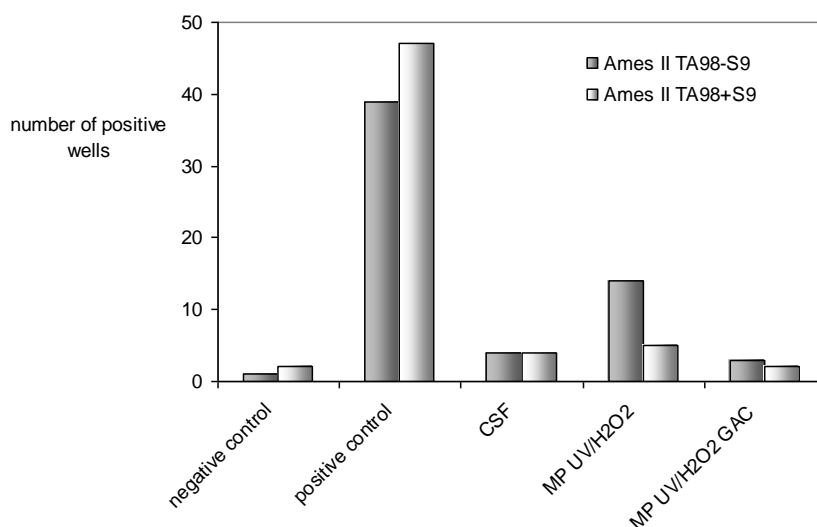
One of the reasons may be the inadequate adsorption by the applied XAD isolation of (hydrophilic) reaction products formed by UV and / or UV/H<sub>2</sub>O<sub>2</sub> treatment. This was modified by applying solid phase extraction with standard cartridges from OASIS (Heringa et al, 2009). In addition, a modified Ames test, Ames II, was applied, a micro array technique based on colour change of the micro wells where the classic Ames test is based on plate counting (Fluckinger et al, 2003). The induced genotoxic response in the Ames II test was determined in chlorinated Dutch and UK tap water (see Figure 11).



**Figure 11: Response in Ames II TA100-S9 for chlorinated Dutch and UK tap water (bench scale experiments)**

In agreement with the classic Ames test results a significant response was observed for strain TA100 in both Dutch and UK chlorinated water samples.

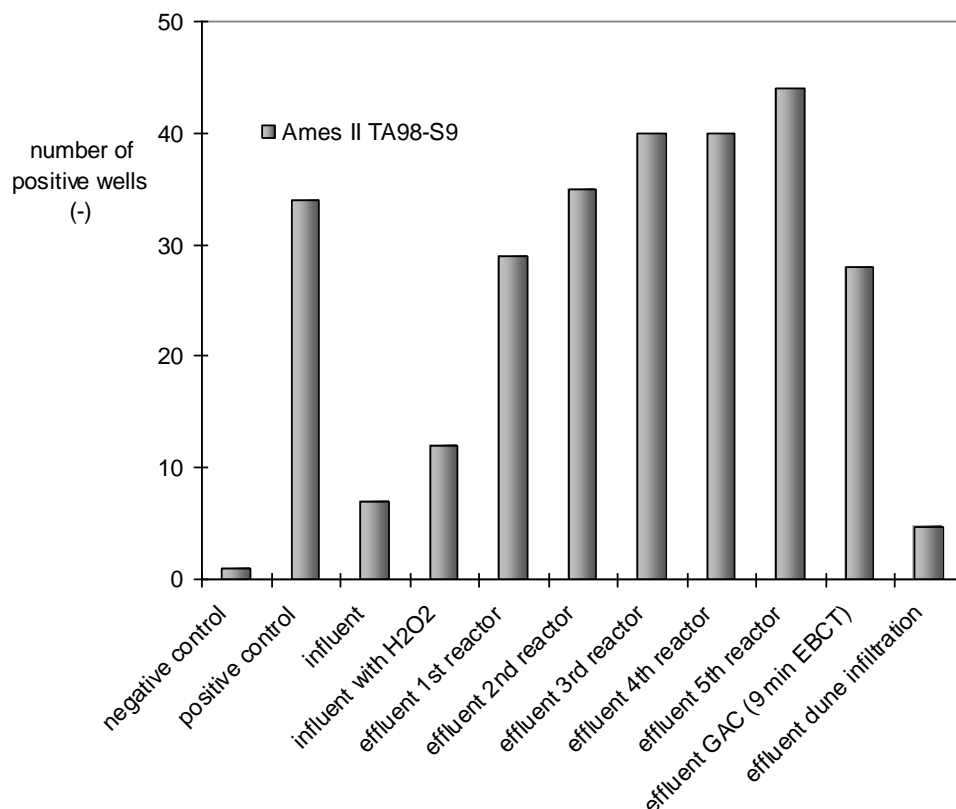
For IJssel Lake water after CSF treatment, after UV/H<sub>2</sub>O<sub>2</sub> treatment (MP UV lamps and natural quartz GE214 sleeves) and after GAC filtration, Ames II testing with TA98 with and without metabolic activation was performed on concentrated water samples (see Figure 12).



**Figure 12: Response in the Ames II test for strain TA98 in CSF pretreated IJssel Lake water after MP UV/H<sub>2</sub>O<sub>2</sub> treatment (UV-dose 540 mJ/cm<sup>2</sup>) and after GAC filtration (data WTP Andijk)**

Relative to the negative control a small but significant genotoxic response was observed after MP UV/H<sub>2</sub>O<sub>2</sub> treatment (natural quartz sleeves) in the TA98 strain without metabolic activation, For the Ames II strain TA98 with metabolic activation, no significant increase was observed. The genotoxic response was removed by biologically active GAC filtration (EBCT 30 minutes).

Additional Ames II experiments have been performed with strain TA98 without metabolic activation (-S9). The response in Ames II TA98-S9 was determined after each UV reactor of the full scale Heemskerk plant using MP UV lamps and synthetic quartz sleeves with a cut-off at a lower wave length than natural quartz GE214 sleeves (see Figure 13).

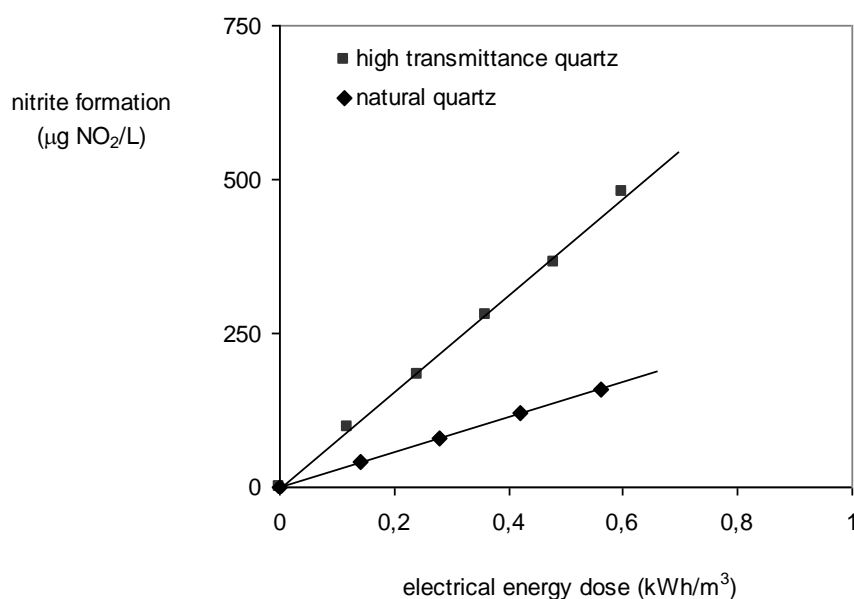


**Figure 13: Response in Ames II TA98 without metabolic activation in concentrated water samples after MP UV/H<sub>2</sub>O<sub>2</sub> treatment for several EEDs, GAC filtration and dune infiltration (WTP Heemskerk)**

Although the UV/H<sub>2</sub>O<sub>2</sub> treatment process conditions were the same as for the experiments presented in Figure 12, Figure 13 shows a substantial higher response in the Ames II TA98. The only difference between these experiments was the application of natural quartz GE214 sleeves at the Andijk plant (Figure 13) opposed to synthetic sleeves at the Heemskerk plant (figure 13).

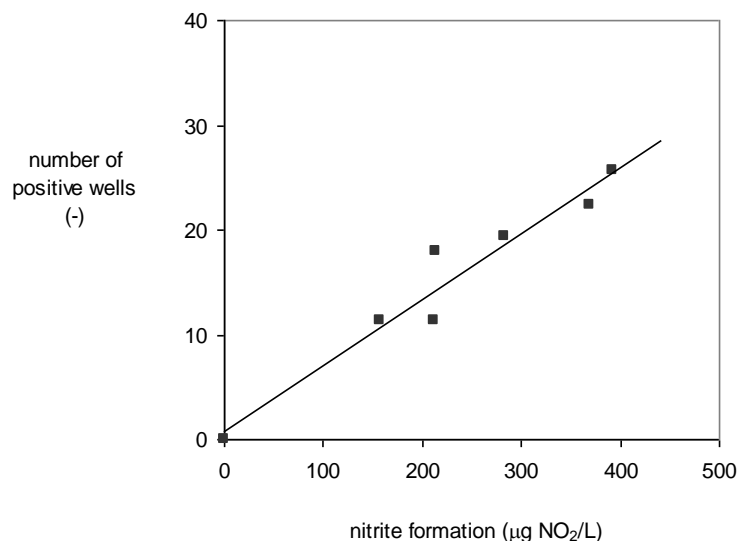
Post treatment at the Heemskerk plant (Figure 13) is catalytic quenching of the surplus  $\text{H}_2\text{O}_2$  by high surface load (50 m/h) GAC contacting (EBCT 9 min) and dune infiltration to obtain biological stability. This post treatment removed the generated response in the Ames II test completely (Figure 13).

The standard electrical energy dose (EED) for the UV/ $\text{H}_2\text{O}_2$  process at PWN is  $0.56 \text{ kWh/m}^3$ . At this EED the nitrite formation in the MP UV/ $\text{H}_2\text{O}_2$  system with synthetic quartz sleeves was substantially higher than the nitrite formation when natural quartz GE214 sleeves was applied (Figure 14). With the application of natural quartz GE 214 sleeves,  $160 \mu\text{g NO}_2/\text{L}$  was formed, while application of synthetic quartz sleeves resulted in the formation of  $480 \mu\text{g NO}_2/\text{L}$ .



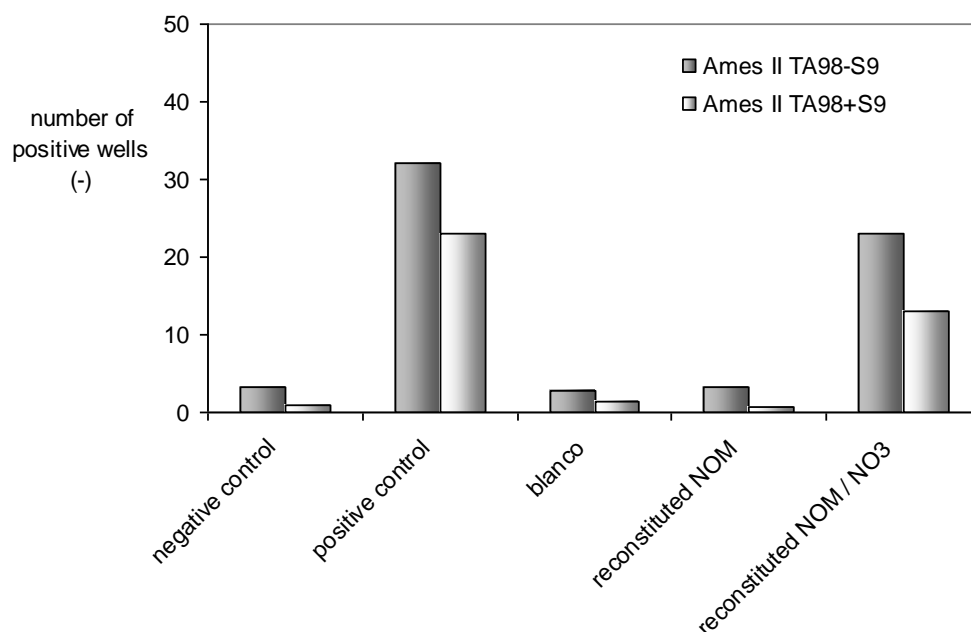
**Figure 14: Nitrite formation by MP UV as a function of the electrical energy dose in full scale UV equipment for natural and synthetic quartz at  $9 \text{ mg NO}_3/\text{L}$  (WTP Heemskerk)**

The response in the Ames II test increased in the same order of magnitude as the nitrite formation (Figure 15). The data was derived from UV equipment with both natural quartz GE214 sleeves and synthetic quartz sleeves. The same trend in the nitrite formation and the Ames II test response suggests that the increase in the Ames II results is somehow related to the nitrate degradation by MP UV photolysis causing the formation of genotoxic organic compounds in addition to the formation of nitrite.



**Figure 15: Response in the Ames II test on concentrated water samples of UV/H<sub>2</sub>O<sub>2</sub> treated pretreated IJssel Lake water as a function of the nitrite formation for both natural GE214 and synthetic quartz sleeves (WTP Heemskerk)**

Collimated beam experiments on reconstituted water were performed. NOM (Nordic NOM, IHSS, 3 mg C/L) was dissolved in demineralized water with NO<sub>3</sub> (11 mg/L) and without NO<sub>3</sub>. Standard PWN UV/H<sub>2</sub>O<sub>2</sub> process conditions were applied (500 mJ/cm<sup>2</sup>; 6.5 mg/L H<sub>2</sub>O<sub>2</sub>). The Ames II test with and without metabolic activation was applied on concentrated water samples (Figure 16).



**Figure 16: Response in the Ames II strain TA98 with and without metabolic activation on concentrated water samples after UV photolysis of reconstituted water (bench scale experiments)**

MP UV/H<sub>2</sub>O<sub>2</sub> treatment of NOM containing water in the absence of nitrate showed no elevated response in the Ames II test, relative to the blank and the negative control. In the presence of nitrate, a significant increase in response in the Ames II test was observed after MP UV/H<sub>2</sub>O<sub>2</sub> treatment (Figure 16). This indicates that nitrate photolysis in the presence of NOM generates a response in the Ames II strain 98 in concentrated water samples. This suggests the formation of N-DBPs by the reaction of the organic matrix and nitrogen containing intermediates formed by the photolysis of nitrate. The formation of individual N-DBPs has not been identified yet, but will be pursued in follow up studies.

In summary no genotoxicity in the classic Ames test was detected after MP UV and MP UV/H<sub>2</sub>O<sub>2</sub> treatment. Introduction of the Ames II test in combination with a modified concentration method showed a genotoxic response in strain TA100 after chlorination in the same order of magnitude as earlier found in the classic Ames test. Contrary to the results from the classic Ames test, Ames II strain TA98 without metabolic activation showed a significant response after MP UV/H<sub>2</sub>O<sub>2</sub> treatment when synthetic quartz sleeves were used. The genotoxic response increased as a function of the MP UV dose in the same order of magnitude as the nitrite content. This suggests that the genotoxic response is related to the UV photolysis of nitrate. This was confirmed in collimated beam experiments with NOM and nitrate containing reconstituted water. All responses were removed after biological GAC filtration and/or dune infiltration.

### **Perspective Chemical Disinfection / Oxidation**

In the last 40 years extensive research into the application of chemical disinfection and oxidation to restrict/avoid DBP formation has been carried out. Originally for both primary and post disinfection chlorine was used. Formation of THMs, other organohalogenes and a genotoxic response in the classic Ames test stopped the absolute confidence in chlorine. Drinking water standards have been set for DBPs especially THMs and HAAs. In The Netherlands use of chlorine has been stopped completely. In Dutch surface water treatment for post disinfection a low ClO<sub>2</sub> dose is applied. Also worldwide the chlorine use is restricted i.e. by replacing post chlorination by chloramination.

After chlorination, THMs and HAAs represent the two major classes of DBPs. The use of alternative disinfectants such as chloramines and ozone minimized the formation of regulated THMs and HAAs but several other priority DBPs are formed such as iodinated THMs, nitromethanes, acetamides and brominated furanones (Krasner et al, 2006). Therefore the formation of DBPs by chlorine and alternative disinfectants is a continuously growing concern.

In many cases for primary disinfection chlorine has been replaced by ozone. Ozonation and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment are also interesting options for organic contaminant control. Application of ozone and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was hampered by the formation of bromate. Concerns about the lowering of the bromate standard prevented realization of full scale drinking water ozone projects in The Netherlands in the last 15 years. Worldwide, lowering the bromate standard from 10 to 5 µg/L may cause problems as well. Recently relevant issues have been presented to reconsider the bromate standard.



Important aspects are reduction of bromate in the stomach (low pH), in the liver and in blood (reduction by  $\text{H}_2\text{S}$ , thiols, etc.). Only a very restricted part of all consumed bromate reaches the kidneys, where tumour formation may occur. In addition, there are indications that the human body itself already produces low concentrations of bromate in the same order of magnitude as the intake by the consumption of ozonated drinking water (Cotruvo et al, 2008). The results of this research effort and the subsequent strategy of USEPA and WHO will be crucial for future applications of ozone. Stabilizing or relaxing the bromate standard may have a very positive impact on future ozone projects both for primary disinfection and organic contaminant control by  $\text{O}_3/\text{H}_2\text{O}_2$ .

Recently UV based technologies were introduced for the inactivation of *Cryptosporidium* (UV) and control of organic micropollutants (UV/ $\text{H}_2\text{O}_2$ ). No harmful individual organic DBPs have been detected yet. Application of MP UV caused nitrite formation in nitrate containing water. Especially for MP UV/ $\text{H}_2\text{O}_2$  nitrite formation may exceed the drinking water standard. Produced nitrite can be removed by chemical oxidation and by biological post treatment (BACF). After UV and UV/ $\text{H}_2\text{O}_2$  no significant response in the classic Ames test was found. However recent results from Ames II tests in combination with an optimized isolation method indicated formation of genotoxic compounds after MP UV treatment utilizing synthetic quartz sleeves with a cut off at lower wave lengths than the natural quartz GE214 sleeves. The more open synthetic quartz sleeves enable a stronger nitrate photolysis for the same UV dose. This effect may be even stronger using supracil sleeves with an even lower cut off wave lengths. These sleeves are not used in this research effort.

The same trend of the nitrite formation and the Ames II test response suggests that the increase in the Ames II results is somehow related to the nitrate degradation by MP UV photolysis causing the formation of genotoxic organic compounds by reaction of UV photolysis intermediates with the organic water matrix in addition to the formation of nitrite. All responses in both the classic Ames test and the Ames II test were removed by GAC filtration and/or dune infiltration.

The byproduct formation will be further decreased by an improved pretreatment, removing both NOM and nitrate. PWN will implement pretreatment by ion exchange and ceramic microfiltration in 2013 improving both the economics and the DBP formation of the UV/ $\text{H}_2\text{O}_2$  treatment (Martijn et al, 2010). Therefore in an integrated treatment approach both LP and MP UV and UV/ $\text{H}_2\text{O}_2$  are reliable barriers for primary disinfection and organic contaminant without a prohibitive reaction product formation.

Keywords: ozone, chlorination, ozonation, advanced oxidation, UV disinfection, UV/ $\text{H}_2\text{O}_2$  treatment, reaction product formation, genotoxicity testing

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