Formation of Genotoxic Compounds by MP UV treatment of Pre-treated Surface Water and Groundwater

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Introduction

To cost effectively inactivate Cryptosporidium and Giardia as well as to avoid disinfection by-product (DBP) formation by chlorination and ozonation, the application of UV technology has increased significantly. Many papers describe the primary benefits of UV technology: disinfection and organic contaminant control. For MP UV technology, formation of the inorganic reaction product nitrite in nitrate rich waters has been widely reported (Mack and Bolton, 1999). However, formation of harmful organic reaction products has not been well documented. Initially in preliminary research efforts, no positive Ames test response was found after UV treatment of IJssel Lake water, pre-treated by coagulation, sedimentation and rapid sand filtration. However, in research using MP UV with synthetic quartz sleeves that did not cut-off UV light at wavelengths below 240 nm, a significant response in the Ames test was found (Martijn and Kruithof, 2012). This paper explores the formation of genotoxic compounds by MP UV treatment of several water types, and examines the relation between Ames II test results and water constituents. To assess the possible health impact of the Ames test results of the UV/H_2O_2 treated water, the Ames test response was compared with the response of a well-known genotoxic compound 4-nitro quinoline oxide (4-NQO). This shows that a health impact cannot be excluded.

Materials and Methods

Water Samples

To study the impact of MP-UV photolysis and MP UV-AOP on formation of genotoxic compounds, water samples from a surface water source and groundwater source after different pre-treatment methods were used. The origin and pre-treatment method of the studied water samples give a representation of different natural organic matter content and initial nitrate contents.

Surface Water

Surface water samples originating from the IJssel Lake were taken after conventional pre-treatment by coagulation sedimentation and filtration (CSF), and advanced pre-treatment by ion exchange microfiltration (IX-MF). IXMF pre-treatment has greater inorganic and organic constituent removals compared to CSF. Nitrate concentrations in the CSF pre-treated sample were 12 mg NO_3/L and 2 mg NO_3/L in the IXMF pre-treated sample.

Groundwater

Groundwater samples with pre-treatment by aeration were taken from two sampling points. One of the samples had a low nitrate content (2.2 mg NO_3/L), while the other had a high nitrate content (22.8 mg NO_3/L).

Reconstituted Water

In addition to these actual water matrices, reconstituted water with natural organic matter (International Humic Substances Society - Pony Lake NOM) with and without nitrate addition has been studied. This sample was used to provide a better understanding of the reaction mechanisms, as the NOM constituents are well characterized and the nitrate addition was controlled. The reconstituted water with NOM and nitrate contained 12 mg NO_3/L.

MP UV Process Conditions

The water samples were irradiated by a 3kW MP UV lamp in a collimated beam apparatus. The UV dose was calculated according to the method proposed by Bolton (Bolton and Linden, 2003). The treatment scenarios included disinfection conditions with a UV dose of 40 mJ/cm^2, photolysis conditions with a UV dose of 600 mJ/cm^2, and advanced oxidation conditions (AOP) with a UV dose of 600 mJ/cm^2 and 6 mg/L H_2O_2.

Analysis and Testing

The formation of genotoxic compounds were characterized by Ames testing (Flückiger et al., 2004). Water samples before and after UV treatment were concentrated by solid phase extraction (SPE) by a concentration factor of 20,000. In addition, experiments with a known genotoxic compound 4-nitro quinoline oxide (4-NQO) were performed. This compound was used to establish a dose effect curve, allowing conversion of the Ames test

response in the water samples to a 4-NQO equivalent dose in an effort to relate the Ames test response to potential impacts to human health.

To further increase our understanding of the formation mechanisms of the genotoxic compounds, the inorganic and organic water matrix fractions were assessed. Determination of the inorganic compounds nitrate, nitrite and total inorganic nitrogen content were measured using the Hach Lange spectrophotometric cuvette test. Organic parameters were analysed by liquid chromatography and organic carbon detection (LC-OCD) analysis to assess impacts to total organic carbon, dissolved organic nitrogen and aromaticity.

Results

Ames II Test Response

Pre-treated Surface Water

MP UV collimated beam experiments to CSF pre-treated IJssel Lake water with a UV Photolysis dose (600 mJ/cm^2) and UV AOP (600 mJ/cm^2 with 6 mg/L H_2O_2) confirmed the prior full scale findings- in nitrate rich water a significant response in the Ames test is found as shown in Figure 1. Significant effects were found after UV Photolysis and UV AOP treatments. However, a significant effect was also found for the much lower UV disinfection dose (40 mJ/cm^2) which had not been widely reported before this work.

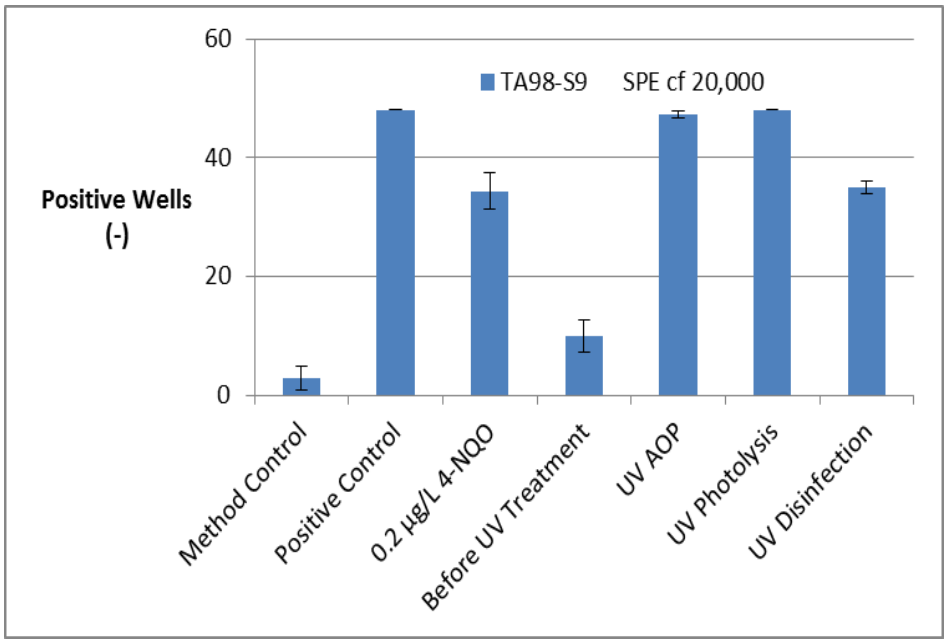

Figure 1- Ames II Test Response after UV AOP (600 mJ/cm^2 + 6 mg/L H_2O_2), UV Photolysis (600 mJ/cm^2), and UV Disinfection (40 mJ/cm^2) in CSF pre-treated surface water.

Application of IX-MF pre-treatment of IJssel Lake water reduced the nitrate content to about 2 mg NO_3/L. The pre-treatment processes had a significant effect on the Ames test response (Figure 2).

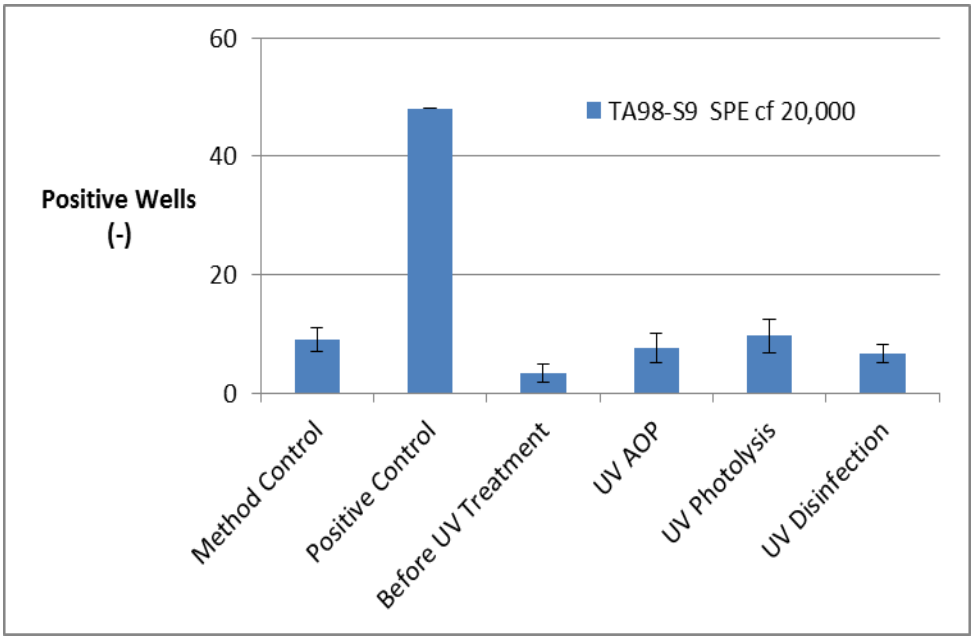

Figure 2- Ames II Test Response after UV AOP (600 mJ/cm2 + 6 mg/L H2O2), UV Photolysis (600 mJ/cm2), and UV Disinfection (40 mJ/cm2) in IXMF pre-treated surface water.

All three types of UV treatment on IX-MF pre-treated IJssel Lake water caused a lower Ames test response relative to the responses in CSF pre-treated water.

Reconstituted Water

MP UV treatment of reconstituted water containing IHSS Pony Lake NOM as an organic water matrix showed a significant response in the Ames test only when inorganic nitrogen in the form of nitrate was added (Figure 3).

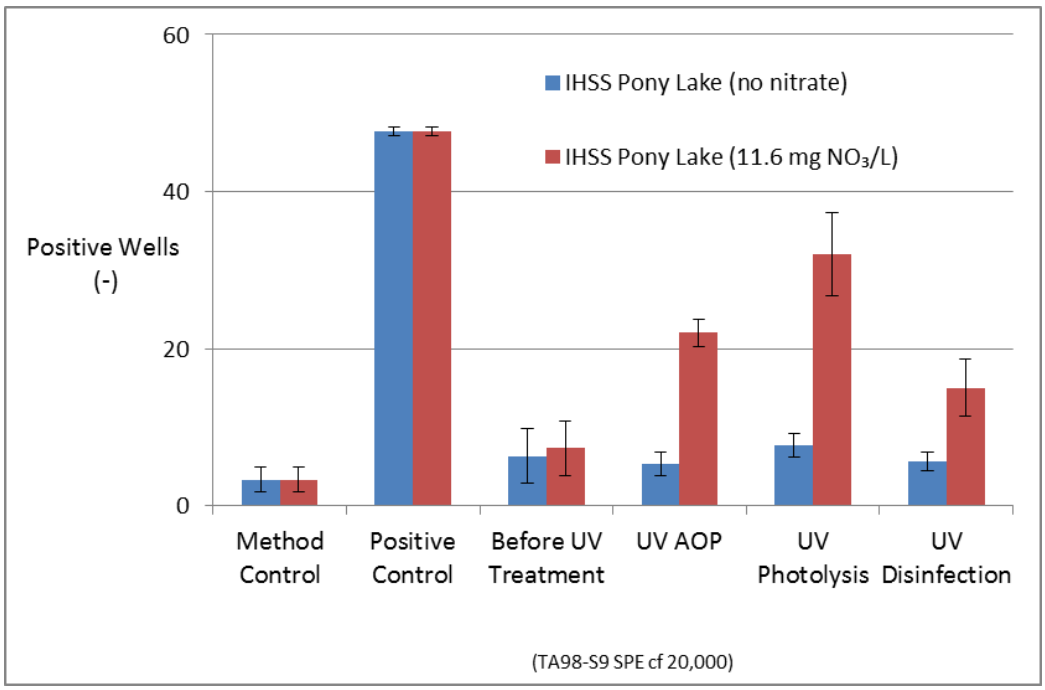

Figure 3 – Ames II Test Response after UV AOP (600 mJ/cm^2 + 6 mg/L H_2O_2), UV Photolysis (600 mJ/cm^2), and UV Disinfection (40 mJ/cm^2) in IHSS Pony Lake synthetic NOM samples with and without nitrate addition.

No significant response in the Ames test was observed in the sample without nitrate added. This once more shows the important role nitrate photolysis is playing in the extent of the Ames test response. It is hypothesized that, besides nitrite formation, intermediates produced by UV photolysis of nitrate caused the formation of genotoxic compounds giving the Ames test response. This may be nitrated and nitrosated aromatic compounds originating from the organic water matrix.

Aerated Groundwater with high and low nitrate content

In addition to two pre-treated surface water and reconstituted water with surface water constituents two pre-treated groundwaters were investigated. One groundwater had a low nitrate content (2.2 mg NO_3/L) and the other had a high nitrate content (22.8 mg NO_3/L). MP UV treatment of the two selected groundwater samples also showed a significant increase in Ames test response. The highest response was found for UV treatment of the aerobic groundwater containing low nitrate (Figure 4).

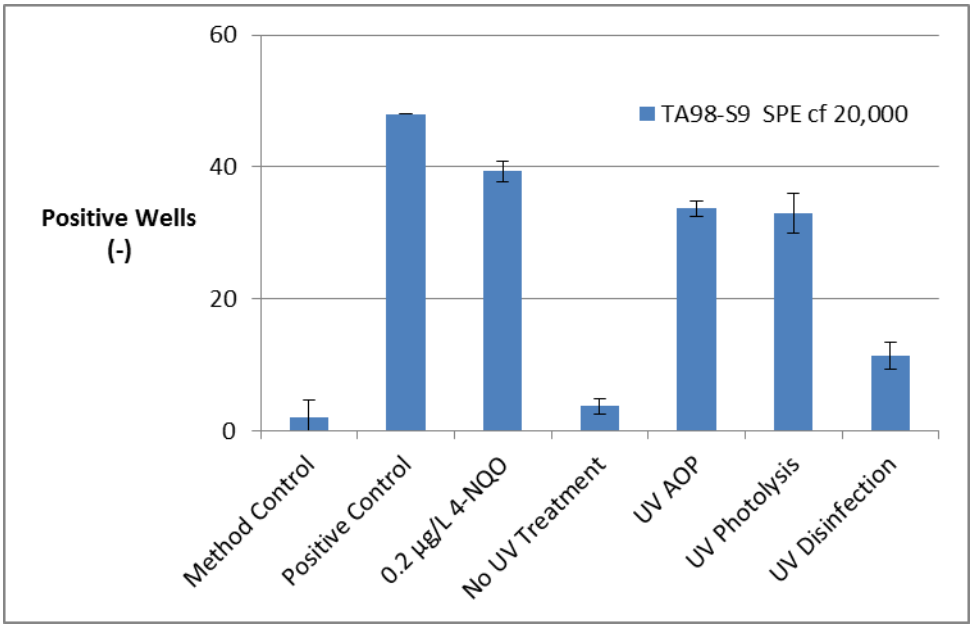

Figure 4 - Ames II Test Response after UV AOP (600 mJ/cm^2 + 6 mg/L H_2O_2), UV Photolysis (600 mJ/cm^2), and UV Disinfection (40 mJ/cm^2) aerobic groundwater pretreated by aeration with low nitrate.

Contrary to the experiments with surface water, the highest Ames test response was found for the lowest nitrate concentration. This suggests that the composition of the organic water matrix plays an important role as well. The reactivity of the organic water matrix towards UV photolysis intermediates of nitrate seems to be affected by the soil passage. Further research is needed to support this hypothesis.

Inorganic Parameters

A significant response in the Ames test was observed only when nitrate was present in the solution, containing organic matter as well. Therefore the fate of inorganic nitrogen was studied in further detail. In all water types where nitrate was present a significant nitrite formation was observed after MP UV irradiation. Figure 5 shows the nitrate-nitrite content after MP UV treatment for CSF pre-treated IJssel Lake water.

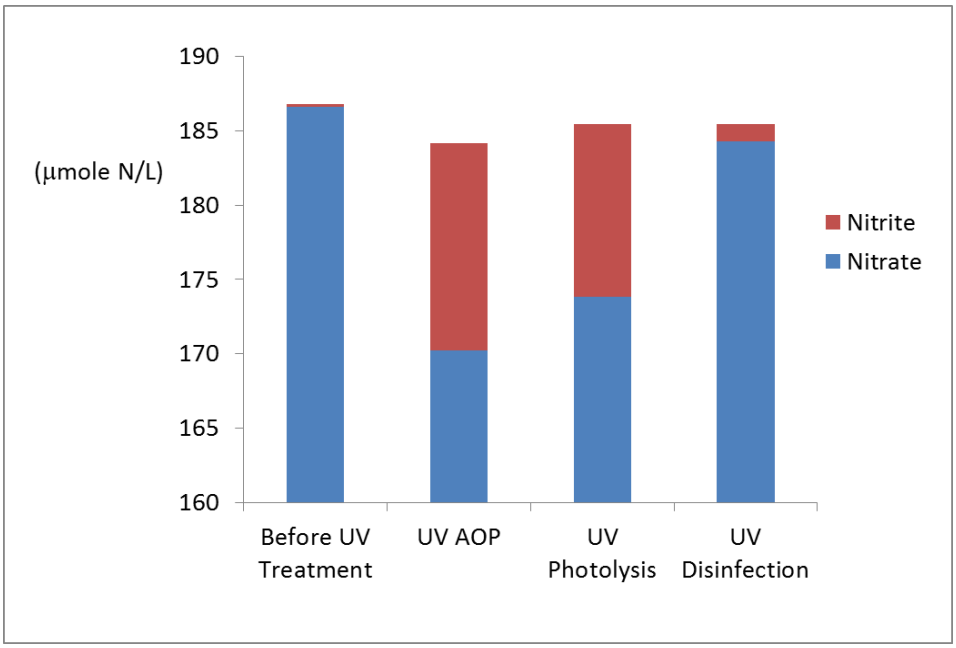

Figure 5 – Inorganic nitrogen balance for CSF pretreated IJssel Lake water after UV AOP (600 mJ/cm^2 + 6 mg/L H_2O_2), UV Photolysis (600 mJ/cm^2), and UV Disinfection (40 mJ/cm^2).

Significant nitrite formation was observed even at the low UV dose of 40 mJ/cm^2 used for disinfection applications. The highest nitrite formation was found for a UV dose of 600 mJ/cm^2 both in the presence and absence of hydrogen peroxide. The inorganic nitrogen balance showed only small insignificant changes in the total amount of inorganic nitrogen measured which was well within the limits of the accuracy of test methods used.

Organic Parameters

All water types contained dissolved organic nitrogen, where the highest content was in CSF pre-treated IJssel Lake water and IHSS Pony Lake NOM reconstituted water, and the lowest for IX-MF pre-treated IJssel Lake water and in both groundwater types. No substantial effect of MP UV treatment on the dissolved organic nitrogen was found (Figure 6).

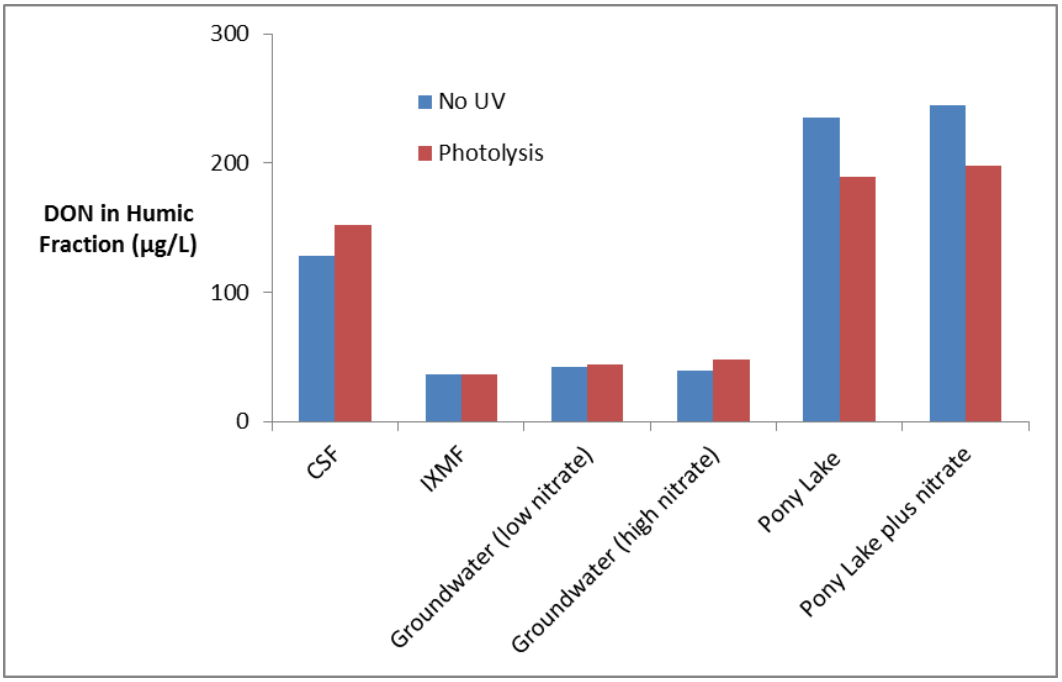

Figure 6 - Dissolved organic nitrogen in the humic fraction after no UV treatment and UV Photolysis (600 mJ/cm^2) for CSF pretreated IJssel lake water, IXMF pretreated IJssel lake water, groundwater with low nitrate, groundwater with high nitrate, IHSS Pony Lake NOM without nitrate, and IHSS Pony Lake NOM with nitrate.

Discussion

Ames Test Results and Chemical Analyses

As already mentioned it is hypothesized that intermediates produced by UV photolysis of nitrate play an important part. These intermediates are amongst others nitro- and nitroso radicals (Goldstein and Rabani, 2007). On one hand they cause nitrite formation, and on the other hand they react with the organic water matric potentially producing nitro- and nitroso aromatic compounds (Mack and Bolton, 1999), which are expected to cause the increase in the Ames test response.

The data presented in this paper suggests a relation between the formation of genotoxic compounds and nitrate photolysis by MP UV treatment of water containing organic matter. Figure 7 presents a direct correlation between nitrite formation and increased Ames response in IHSS Pony Lake NOM sample with nitrate addition after the three MP UV treatments.

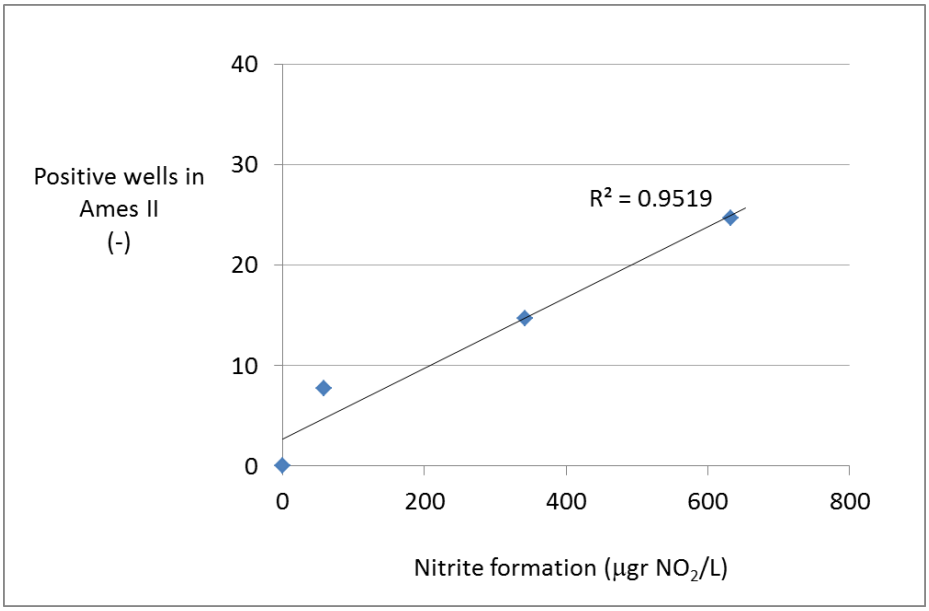

Figure 7 – Correlation for nitrite formation and positive Ames test wells in IHSS Pony Lake NOM with nitrate after UV AOP (600 mJ/cm^2 + 6 mg/L H_2O_2), UV Photolysis (600 mJ/cm^2), and UV Disinfection (40 mJ/cm^2).

A correlation between increased nitrite formation and increased Ames test response was found for each water type studied, although the relationship between the nitrite formation value and the number of positive Ames wells was not the same for all the water types.

Besides the formation of nitrate photolysis intermediates, the reactivity of the organic matrix towards these intermediates plays an important part. This suggests that the character of the organic fraction plays a role. The dissolved organic nitrogen (DON) and aromaticity were determined to investigate this aspect, though the results were not specific enough to clarify this relationship.

Possible health impact

After MP UV treatment a significant response in the Ames test was observed, indicating the presence of genotoxic compounds. However it was not clear if and how this response represented a human health impact. In an attempt to interpret the Ames test response in the concentrated water samples, an equivalent dose of a compound that is similar to the class of compounds that was expected to be formed by nitrate photolysis in the presence of organic matter, was proposed.

4-NQO is a carcinogenic and genotoxic compound, commonly used as positive control in the Ames test and a nitro aromatic compound was selected as equivalent. Figure 8 presents the dose effect relationship to correlate an Ames test response to a 4-NQO equivalent dose.

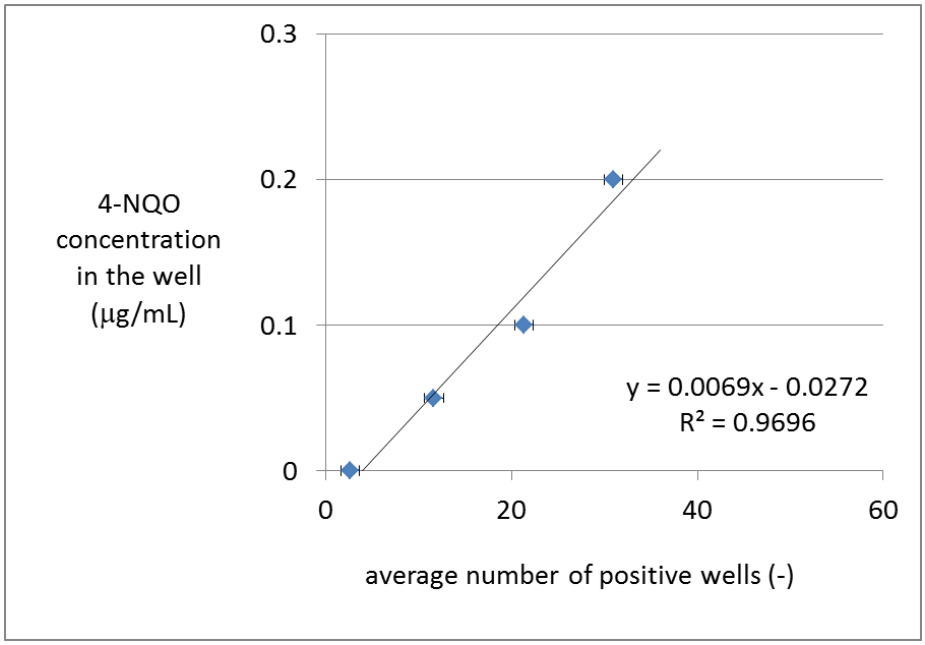

Figure 8 – Calibration curve with 4-NQO concentration in the well and Ames II test response (TA98-S9) for the water samples from IHSS Pony Lake NOM plus nitrate water samples

The 4-NQO dose effect equation in Figure 8 was applied to the Ames test results (mean positive wells) after MP UV treatments on the IHSS Pony Lake NOM plus nitrate sample. This conversion gives results in terms of 4-NQO equivalents after MP UV treatment and is shown in Figure 9.

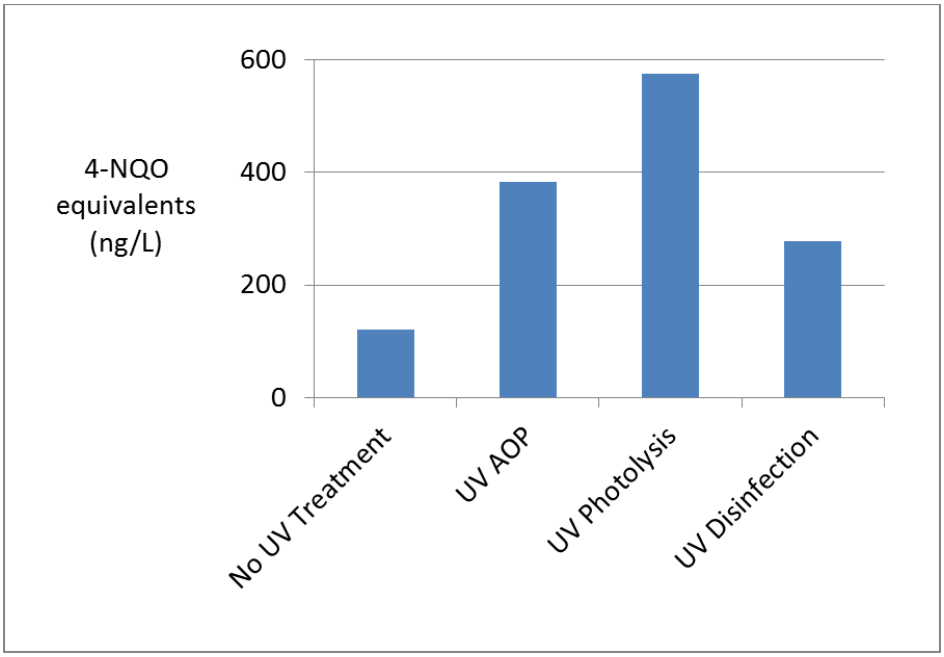

Figure 9 - 4-NQO equivalent concentration for IHSS Pony Lake NOM plus nitrate after UV AOP (600 mJ/cm^2 + 6 mg/L H_2O_2), UV Photolysis (600 mJ/cm^2), and UV Disinfection (40 mJ/cm^2).

For the MP UV Disinfection dose (40 mJ/cm^2), 280 ng 4-NQO equivalents per litre was found in IHSS Pony Lake NOM with nitrate, increasing up to almost 600 ng 4-NQO equivalents per litre for MP UV Photolysis (600 mJ/cm^2). A potential health impact of this range of 4-NQO equivalents per litre cannot be ignored. Therefore post treatment should be applied to reduce this effect. Currently, PWN applies biologically active GAC filters following UV/H_2O_2 treatment to lower the both the Ames test response and nitrite concentration. Further research is needed to quantify this effect.

Conclusions

The results from this paper give rise to the following conclusions:

- MP UV treatment increases the Ames toxicity response in nitrate rich water in the presence of organic matter;
- A relationship was found between the Ames test response and the nitrite formation, indicating that nitrate photolysis plays an important part;
- No relationship was found between the Ames test response and the measured group organic parameters (TOC, DON, Aromaticity) typically used in the drinking water field which can only detect milligram per liter changes in organics;
- A health evaluation based on the determination of 4-NQO equivalents per litre shows that a health impact of MP UV treatment cannot be excluded. Therefore post treatment may be needed to further protect human health;
- Further research is needed to more clearly understand the nitrite and organic matter interactions at the micro or nanogram per liter levels that cause increased Ames toxicity and relate these mechanisms to potential public health impacts.

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