

Effect of photochemical advanced oxidation processes on the formation potential of emerging disinfection by-products in groundwater from part of the Pannonian Basin

Jelena Molnar Jazić, Jasmina Agbaba, Aleksandra Tubić, Malcolm Watson, Tajana Đurkić, Dejan Krčmar and Božo Dalmacija

ABSTRACT

This study evaluates the effect of photochemical advanced oxidation processes (AOPs) (O_3/UV , H_2O_2/UV and $O_3/H_2O_2/UV$) on the formation potential (FP) of emerging disinfection by-products including nitrogenous by-products (N-DBPs) and halo ketones (HKs) in groundwater from part of the Pannonian Basin (AP Vojvodina, Republic of Serbia). Among the N-DBPs, the haloacetonitrile (HAN) precursor contents were $9.83 \pm 0.59 \mu\text{g/L}$ while precursors of halonitromethanes, particularly trichloronitromethane (TCNM) were not detected. Similarly, precursors of HKs as carbonaceous DBPs were also not detected in raw water. Ozonation alone and the H_2O_2/UV process with a lower UV dose maximally decomposed HAN precursors (about 70%) while during O_3 -based AOPs, HANFP varied significantly. Application of UV photolysis and H_2O_2/UV processes with increasing UV dose doubled the HANFP. Ozone alone, O_3/UV and H_2O_2/UV slightly increased HK formation potential, particularly 1,1-dichloro-2-propanone FP (0.93 ± 0.21 to $2.01 \pm 0.37 \mu\text{g/L}$). None of the investigated treatments influenced the formation of TCNM precursors. The effect of the applied treatments on bromide incorporation was most evident for HANs.

Key words | bromide incorporation, emerging disinfection by-products, ozone, photochemical advanced oxidation processes

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ABBREVIATIONS

| | | | |
|--------|---------------------------------------|--------|--------------------------------------|
| AOPs | advanced oxidation processes | HANs | haloacetonitriles |
| BCAN | bromochloroacetonitrile | HKs | halo ketones |
| C-DBPs | carbonaceous disinfection by-products | HNMs | halonitromethanes |
| DBAN | dibromoacetonitrile | N-DBPs | nitrogenous disinfection by-products |
| DBPs | disinfection by-products | NOM | natural organic matter |
| DCAN | dichloroacetonitrile | RW | raw water |
| DCP | 1,1-dichloro-2-propanone | TCAN | trichloroacetonitrile |
| DOC | dissolved organic carbon | TCP | 1,1,1-trichloropropanone |
| DON | dissolved organic nitrogen | THMs | trihalomethanes |
| FP | formation potential | TOC | total organic carbon |
| HAAs | haloacetic acids | | |

INTRODUCTION

Natural organic matter (NOM) is ubiquitously present in all water types including drinking water sources and has been recognized as containing the main precursors of disinfection by-products (DBPs) such as trihalomethanes (THMs) since the mid-1970s (Agbaba *et al.* 2012). It is important to note that among them, unregulated DBPs are considered as emerging DBPs (Yang & Zhang 2016). Therefore, more recently increasing attention has been paid to the nitrogenous (N)-DBPs detected in drinking water or chlorinated natural waters simulated in laboratory conditions, including haloacetonitriles (HANs), halonitromethanes (HNMs) and nitrosamines (Bond *et al.* 2011). Although the emerging N-DBPs have been detected at significantly lower concentrations compared with the carbonaceous (C)-DBPs such as THMs and haloacetic acids (HAAs), they are of emerging importance due to their cytotoxicity or genotoxicity, which is orders of magnitude higher than the regulated THMs and HAAs (Chiang *et al.* 2010; Zeng *et al.* 2016). The nitrogen involved in N-DBP formation can derive either from organic precursors such as dissolved organic nitrogen (DON), which reacts with the disinfectant (e.g. chlorine, chloramines) or from the disinfectant itself such as in the case of chloramination (which is of high importance for *N*-nitrosodimethylamine formation). Free amino acids are amongst the DON components considered as significant precursors to N-DBPs (WHO 2011; Chu *et al.* 2016). Bond *et al.* (2011) in their review paper indicate that among the three major groups of N-DBPs, haloacetonitriles were detected at the highest concentrations, in the range of 1–36 µg/L. Measured concentrations are related to the water characteristics, bromine content, influence of wastewater, etc. In drinking water, the concentration of *N*-nitrosodimethylamine is typically observed in the low ng/L range while concentrations of chloropicrin (trichloronitromethane, TCNM) in drinking water are usually less than 5 µg/L (WHO 2011).

From the group of halogenated acetonitriles, guideline values for drinking water are set only for dibromoacetonitrile (DBAN) and dichloroacetonitrile (DCAN) (70 and 20 µg/L, respectively). Guideline values for bromochloroacetonitrile (BCAN), trichloroacetonitrile (TCAN) and TCNM have not been established due to the fact that available data are still inadequate to permit derivation of

health-based guideline values (WHO 2011). Maximum permissible concentrations for haloacetonitriles are set for DBAN, DCAN and TCAN (100 µg/L, 90 µg/L and 1 µg/L) by Serbian national regulation (Official Gazette SRJ 42/98 and 44/99). Haloacetones (HKs), which belong to the important unregulated volatile fraction, can be formed in ozone and chlorine treated water, including chloramines and chlorine dioxide treatment, or in water treated by combination of ozone and chlorine agents (Serrano *et al.* 2014).

The best way to control DBP formation is effective control and removal of their precursors before disinfection. It has been found that N-DBP precursors are hard to remove by conventional coagulation/sedimentation and filtration processes due to the poor removal of low molecular weight DON (Chu *et al.* 2016; Yimeng *et al.* 2017). Recently, a large number of drinking water treatment studies have investigated the use of advanced oxidation processes (AOPs) in order to control NOM content and minimize DBP formation. Recent studies have demonstrated that ozone pre-oxidation can decrease HAN formation, but can also increase HNM formation. Additionally, in the presence of hydroxyl radicals, formed during AOPs, greater formation of all DBP groups has been observed (De Vera *et al.* 2015). Molnar *et al.* (2012) showed that the application of ozonation and catalytic ozonation at pH 6 resulted in an increase in HAN formation potential compared with raw water. Chiang *et al.* (2010) indicated that application of ozonation prior to chlorination can cause a negative effect on TCNM and HK reduction. Chu *et al.* (2016) reported that UV did not have significant influence on HAN formation during subsequent chlorination, while UV/H₂O₂ AOPs could alter DBP formation. Srithep & Phattarapattamawong (2017) suggested that among the photo-based AOPs, UV/H₂O₂/O₃ was the most effective process for removing HAN precursors, followed by UV/H₂O₂ and UV/O₃.

Due to the different treatment conditions and variety in raw water characteristics, data about emerging DBPs, their associated health side-effects, formation and behaviour during different treatment stages is still relatively limited. Therefore, the aim of this study was to investigate the impact of photochemical AOPs using ozone, UV light and hydrogen peroxide (O₃/UV, H₂O₂/UV and O₃/H₂O₂/UV) on the formation potential (FP) of N-DBPs and HKs in water rich in NOM. Bromide incorporation into DBPs was also considered.

EXPERIMENT AND METHODS

Groundwater samples

The investigated groundwater originated from Maglić (Autonomous Province (AP) of Vojvodina, Republic of Serbia) and was sampled from a 110-m-deep well. AP Vojvodina is a northern region of the Republic of Serbia, geographically belonging to the southern part of the Pannonian Basin, together with Hungary, Romania, Slovakia and Slavonia in Croatia. In this area the quality of groundwater is highly affected by the presence of NOM and varies from aquifer to aquifer and also depends on the location. The investigated groundwater characteristics were as follows: pH 8.01 ± 0.10 ; total alkalinity 753 ± 24 mg CaCO_3/L ; turbidity 1.82 ± 0.09 NTU; electrical conductivity $1,407 \pm 103$ $\mu\text{S}/\text{cm}$; TOC 5.82 ± 0.39 mg C/L ; total iron 0.24 ± 0.04 mg/L, manganese 0.074 ± 0.005 mg/L; bromide 623 ± 21 $\mu\text{g}/\text{L}$; chloride 19.2 ± 5.1 mg/L; nitrate <0.005 mg/L as N; nitrite <0.002 mg/L as N.

Chemicals

The analytical standard mix contained HANs (BCAN, DBAN, DCAN, TCAN), TCNM and HKs (1,1-dichloro-2-propanone – DCP and 1,1,1-trichloropropanone – TCP) in acetone in concentrations of 2,000 $\mu\text{g}/\text{mL}$ were purchased from Supelco. The internal standard used was 4-bromofluorobenzene (2,000 $\mu\text{g}/\text{mL}$ in methanol, Supelco). All solvents (J. T. Baker) were for organic residue analysis. Hydrogen peroxide (30% w/w, reagent grade) was purchased from POCH S.A.

Water treatment

UV photolysis and UV AOPs were performed in a stainless steel photochemical reactor with a quartz reaction vessel at the reactor centre equipped with a low pressure mercury lamp (Philips TUV 16 W) (more details are given in Molnar *et al.* 2015). The raw water (RW) was ozonated in a 2 L glass column (85 mm diameter) and ozone was generated electrochemically by an Argentox ozone generator. For the O_3/UV treatment, ozonated water was immediately subject to the

UV treatment in the photochemical reactor. For the $\text{H}_2\text{O}_2/\text{UV}$ treatment, hydrogen peroxide solution was added to the water prior to UV irradiation. For the $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ treatment, hydrogen peroxide solution was added to ozonated water which was then subject to UV light. A more detailed procedure for the applied treatments is given in Agbaba *et al.* (2016). All experiments were carried out in duplicate and the results reported as average values with standard deviation. Treatment lines were as follows: O_3 – ozonation (0.5 mg O_3/mg dissolved organic carbon (DOC)); UV_1 – photolysis (600 mJ/cm^2); UV_2 – photolysis (3,000 mJ/cm^2); O_3/UV_1 (0.5 mg O_3/mg DOC; 600 mJ/cm^2); O_3/UV_2 (0.5 mg O_3/mg DOC; 3,000 mJ/cm^2); $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}_1$ (0.5 mg O_3/mg DOC; 10 mg $\text{H}_2\text{O}_2/\text{L}$; 600 mJ/cm^2); $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}_2$ (0.5 mg O_3/mg DOC; 10 mg $\text{H}_2\text{O}_2/\text{L}$; 3,000 mJ/cm^2); $\text{H}_2\text{O}_2/\text{UV}_1$ (10 mg $\text{H}_2\text{O}_2/\text{L}$; 600 mJ/cm^2); $\text{H}_2\text{O}_2/\text{UV}_2$ (10 mg $\text{H}_2\text{O}_2/\text{L}$; 3,000 mJ/cm^2).

Analytical methods

HANFP, TCNMFP and HKFP were determined according to the standard method for measurement of THMFP (APHA 2012). Emerging DBPs were determined by liquid-liquid extraction using methyl tert-butyl ether followed by analysis by GC/ μECD (Agilent 6890N), according to USEPA method 551.1. The specific emerging DBP FPs were calculated as the ratios between the DBP FPs and the total organic carbon (TOC) content presented in our previous study (Agbaba *et al.* 2016).

Bromide and chloride anion content was determined using a Dionex ICS-3000 Ion Chromatography System according to DIONEX Application Note 154. The pH and turbidity measurements were carried out using the InoLab pH/ION 735 and Hanna HI 93703 portable instruments. Electrical conductivity of water was measured with the aid of a Hanna model HI 933000 field conductometer. Water alkalinity was measured according to the standard methods (APHA 2012). Iron and manganese concentrations were determined by graphite furnace atomic absorption spectroscopy (Perkin Elmer AAnalyst 700) according to USEPA Method 7010. Inorganic nitrogen substances (nitrite and nitrate) were analysed according to the SRPS ISO 7890-3:1994 and SRPS EN 26777:2009 methods.

RESULTS AND DISCUSSION

Effects of photochemical AOPs on the emerging DBP formation potential

Our previous work has shown that the investigated groundwater is rich in mostly hydrophobic natural organic matter which is characterized by a high content of fulvic acids (75%) relative to the 25% hydrophilic acid and non-acidic structures. Total NOM content according to the TOC value and UV absorbance at 254 nm was 5.82 ± 0.39 mg C/L and 0.231 ± 0.05 cm⁻¹, respectively. The NOM present is highly reactive towards forming C-DBPs such as THMs and HAAs (305 ± 44 µg/L THMFP and 348 ± 53 µg/L HAAFP) (Agbaba *et al.* 2016). This paper presents a continuation of research in which the impact of photochemical AOPs on the emerging DBP formation is addressed. Control experiments using ozone and photolysis alone were also conducted. When it comes to the N-DBPs, HAN precursor contents (9.83 ± 0.59 µg/L HANFP) were significantly lower than the C-DBPs. The dominant HAN compound formed during chlorination of raw water is DCAN (6.76 ± 0.35 µg/L DCANFP), followed by DBAN (3.07 ± 0.24 µg/L DBANFP), while precursors of TCAN and BCAN were not detected. TCNM precursors, as representative of HNMs, were also not detected (<0.400 µg/L). It can be supposed that amino acids, the main constituents of DON in drinking water sources, are responsible for the formation of HANs. Other authors have reported similar contents of HAN precursors in chlorinated water samples (Krasner *et al.* 2006; Zeng *et al.* 2016). Precursors of HKs, particularly TCP and DCP were also not detected in raw water samples (<0.300 µg/L).

The influence of UV photolysis, ozone oxidation and AOPs involving O₃, UV and H₂O₂ (O₃/UV, H₂O₂/UV and O₃/H₂O₂/UV) on the HAN precursor content is presented in Table 1. Treatment by ozone alone decreased HANFP by 71% whereby the precursors of DCAN were dominantly reduced. During O₃-based AOPs (O₃/UV and O₃/H₂O₂/UV) HANFP varied significantly (3.49 ± 0.14 – 10.1 ± 0.82 µg/L). Among the ozone-based AOPs, only the O₃/UV process (at the lower UV dose) was able to oxidize HAN precursors, reducing the HANFP by 64% compared with the raw water. However, it is obvious that the addition of H₂O₂ and UV

light did not have a further positive influence on decreasing HANFP compared with the ozone oxidation alone. The H₂O₂/UV process with a lower UV dose decomposed HAN precursors by 65% similar to ozone alone. During the UV photolysis and UV/H₂O₂ processes, increasing the UV dose doubled the HANFP. In all the treatments, of the haloacetoneitriles, only DCAN and DBAN precursors were detected in water. None of the investigated treatments, UV photolysis, ozone oxidation or AOPs, had any effect on the formation of TCNM precursors (<0.400 µg/L). Additionally, it is worth noting that the HANFP levels determined, which were used to assess the level of HANs in a worst-case scenario, were below Serbian national regulation and WHO guideline values.

De Vera *et al.* (2015) also demonstrated that application of ozone with a similar dose (0.75 mg/mg TOC) can decrease total HAN formation in water with high TOC content. Mitch *et al.* (2009) demonstrated that ozone can have extreme effects on HNM formation when followed by chlorination, reporting an increase in median chloropicrin occurrence of 226%, which was not observed in our study. According to Chu *et al.* (2016), UV photolysis alone at a dose up to 585 mJ/cm² followed by chlorination for selected amino acids did not significantly alter HAN formation, while UV/H₂O₂ may alter DBP formation. Srithep & Phattarapattamawong (2017) showed that in water with lower DOC content than in our study, UV/H₂O₂/O₃ was the most effective process for removing HAN precursors, followed by UV/H₂O₂ and UV/O₃. The better control of HAN precursors in our study could be attributed to the different characteristics of the NOM and DON, which are specific for every water body.

Concerning HKFP, application of the ozone and O₃/UV processes led to the generation of DCP precursors (0.600 µg/L). HKs can be formed from NOM structure, as a consequence of ozone oxidation, which may explain the obtained results. The DCP formed could be further oxidized to TCP, which was not observed in our study. Additionally, no relationship between UV dose and H₂O₂ addition in ozone-based AOPs was observed. Enhanced formation of HK precursors was observed as a consequence of UV/H₂O₂ process application (0.93 ± 0.21 to 2.01 ± 0.37 µg/L DCPFP) indicating that NOM oxidation favoured by free radicals can also promote HK formation. UV photolysis alone has no influence on the formation of HK precursors.

Table 1 | Emerging DBP FPs (actual and normalized to the measured TOC) in raw and treated water samples

| Water treatment | DCANFP | DBANFP | HANFP ^a | TCNMFP | HKFP ^b |
|--|------------------|------------------|--------------------|--------|-------------------|
| $\mu\text{g/L}$ | | | | | |
| RW | 6.76 ± 0.35 | 3.07 ± 0.24 | 9.83 ± 0.59 | <0.400 | <0.300 |
| O ₃ | 0.670 ± 0.20 | 2.18 ± 0.51 | 2.85 ± 0.56 | <0.400 | 0.600 ± 0.15 |
| UV ₁ | 6.76 ± 1.78 | 1.46 ± 0.47 | 8.22 ± 1.05 | <0.400 | <0.300 |
| UV ₂ | 12.1 ± 1.63 | 5.06 ± 1.34 | 17.2 ± 0.28 | <0.400 | <0.300 |
| O ₃ /UV ₁ | 0.940 ± 0.18 | 2.55 ± 0.33 | 3.49 ± 0.14 | <0.400 | 0.600 ± 0.12 |
| O ₃ /UV ₂ | 6.90 ± 1.07 | 1.58 ± 0.27 | 8.48 ± 0.81 | <0.400 | <0.300 |
| O ₃ /H ₂ O ₂ /UV ₁ | 8.21 ± 0.37 | 1.85 ± 0.25 | 10.1 ± 0.82 | <0.400 | <0.300 |
| O ₃ /H ₂ O ₂ /UV ₂ | 4.65 ± 0.64 | 2.44 ± 0.81 | 7.09 ± 1.10 | <0.400 | <0.300 |
| H ₂ O ₂ /UV ₁ | 1.08 ± 0.27 | 2.39 ± 0.54 | 3.47 ± 0.66 | <0.400 | 2.01 ± 0.37 |
| H ₂ O ₂ /UV ₂ | 13.6 ± 2.08 | 8.61 ± 1.94 | 22.2 ± 0.14 | <0.400 | 0.93 ± 0.21 |
| $\mu\text{g/mg TOC}$ | | | | | |
| RW | 1.16 ± 0.10 | 0.528 ± 0.06 | 1.69 ± 0.15 | nc | nc |
| O ₃ | 0.124 ± 0.04 | 0.403 ± 0.11 | 0.527 ± 0.12 | nc | 0.110 ± 0.02 |
| UV ₁ | 1.27 ± 0.37 | 0.272 ± 0.08 | 1.54 ± 0.24 | nc | nc |
| UV ₂ | 2.18 ± 0.34 | 0.903 ± 0.22 | 3.08 ± 0.11 | nc | nc |
| O ₃ /UV ₁ | 0.185 ± 0.03 | 0.506 ± 0.09 | 0.691 ± 0.06 | nc | 0.118 ± 0.02 |
| O ₃ /UV ₂ | 1.36 ± 0.16 | 0.312 ± 0.06 | 1.67 ± 0.10 | nc | nc |
| O ₃ /H ₂ O ₂ /UV ₁ | 1.55 ± 0.02 | 0.350 ± 0.06 | 1.90 ± 0.10 | nc | nc |
| O ₃ /H ₂ O ₂ /UV ₂ | 0.891 ± 0.10 | 0.471 ± 0.17 | 1.36 ± 0.25 | nc | nc |
| H ₂ O ₂ /UV ₁ | 0.206 ± 0.05 | 0.455 ± 0.09 | 0.661 ± 0.11 | nc | 0.381 ± 0.06 |
| H ₂ O ₂ /UV ₂ | 2.76 ± 0.52 | 1.74 ± 0.33 | 4.50 ± 0.18 | nc | 0.188 ± 0.04 |

^aTCANFP < 0.700 $\mu\text{g/L}$; BCANFP < 0.300 $\mu\text{g/L}$; ^bTCPPFP < 0.300 $\mu\text{g/L}$; nc – not calculated (corresponding DBP FPs were below the method detection limit).

None of the investigated treatments had any influence on TCP formation (Table 1). Generally low values for HKFP are somewhat expected because haloketones are important intermediate DBPs which are rapidly formed as soon as the water is chlorinated and may be finally converted to THMs or HAAs via hydrolysis or reactions with residual chlorine (Fu et al. 2017). The highest formation of HKs was observed in UV/H₂O₂-treated water with higher UV dose, where in our previous study the highest THMFPP was also observed (Agbaba et al. 2016).

DBP FPs normalized to the measured TOC can provide a better insight into the variations in the reactivity of organic matter towards DBP formation than actual FPs (Table 1). HANFPs, when normalized by TOC content (presented in our previous study by Agbaba et al. 2016) follow the same trend. The ozone and H₂O₂/UV process with a lower UV dose maximally reduced the reactivity of HAN precursors up

to 70%, while the highest reactivity toward HAN formation was observed in water treated by the H₂O₂/UV process with a high UV dose. HKFP normalized to the TOC was even lower than HANFP (0.110 ± 0.02 – 0.381 ± 0.06 $\mu\text{g/mg TOC}$) indicating lower reactivity of residual NOM after oxidation treatments toward HK formation relative to HAN formation.

Insight into distribution of DBPs and bromide incorporation

The distributions of individual DBP groups formed during chlorination (THMFPP, HAAFP, HANFP, THNMFP and HKFP) in the raw water and after the investigated treatments are presented in Figure 1. The bromide incorporations for these groups are presented in Figure 2. In both Figures 1 and 2, previously published data (Agbaba et al. 2016) relating to THMFPP and HAAFP was used for the calculations. Emerging

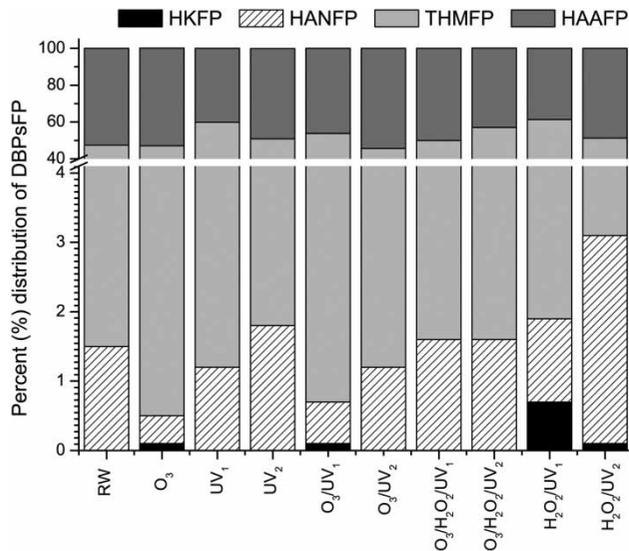


Figure 1 | Percent distribution of investigated DBP FPs in raw and treated water samples.

DBP precursors were only 1.5% of the total sum of DBPs formed in DBP FPs tests in the raw water samples, increasing slightly during $\text{H}_2\text{O}_2/\text{UV}$ treatment and reaching a maximum of 3.1% after the $\text{H}_2\text{O}_2/\text{UV}$ process with higher UV dose. The lowest share of emerging DBPs (only 0.4%) was observed after chlorination of ozonated water. In all water samples THM and HAA were dominantly formed during subsequent chlorination (over 97% of the DBPs investigated).

Taking into account the high bromide ion content ($623 \pm 21 \mu\text{g/L}$) of the investigated groundwater, there is an increased risk of brominated DBP formation through Br

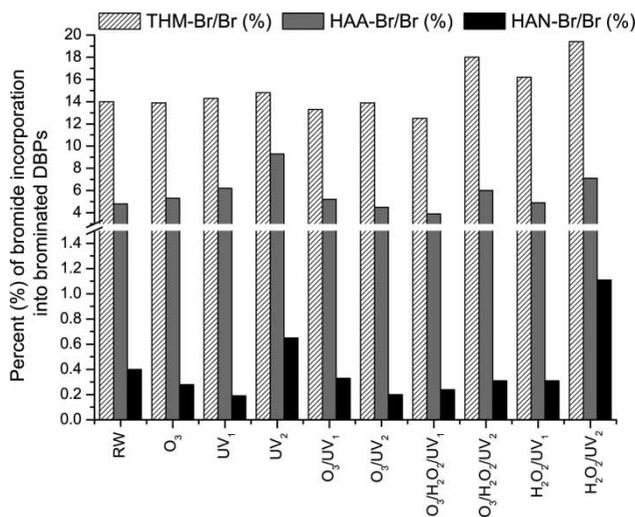


Figure 2 | Percentage of bromide incorporation for THMs, HAAs and HANs in raw and treated water samples.

oxidation to bromine and further reaction with organic precursors in water. The percentage of bromide ion incorporation into brominated DBPs was calculated according to the equations given by Sohn *et al.* (2006). It was found that the applied treatments have no significant influence on the changes in percentage of bromide incorporation into DBPs compared with the raw water (Figure 2). The influence of the applied treatments on bromide incorporation was most evident for emerging DBPs, particularly HANs, where bromide incorporation increases up to three times after $\text{H}_2\text{O}_2/\text{UV}$ treatment but only with the higher UV dose. Similar results were obtained for THMs and HAAs, which led to a 1.5-times increase in bromine incorporation. It may be supposed that in the $\text{H}_2\text{O}_2/\text{UV}$ system with a high UV dose and in the absence of ozone, highly reactive and unselective hydroxyl radicals are the main oxidation species. Through the contribution of photolysis and hydroxyl radical attack, NOM oxidation occurs, forming new, more hydrophilic species which are prone to further bromide incorporation. Additionally, UV photolysis using the higher UV dose of $3,000 \text{ mJ/cm}^2$ almost doubled bromine incorporation, while other treatments generally have no further influence on changing bromine incorporation compared with the raw water.

Results were also correlated between N-DBP FPs and: (a) total organic matter according to the TOC, UV_{254} and SUVA and (b) specific DBP precursors: THMFP, HAAFP and the total aldehydes and carboxylic acids (Agbaba *et al.* 2016). There was no correlation between HANFP and the total organic matter parameters. Additionally, the absence of a correlation between N-DBPs and the C-DBPs and oxygen containing DBPs indicates the completely different nature of their precursors. The formation of HAN before and after the treatments could be mostly attributed to the transformation of DON containing combined amino acids such as oligopeptides and proteins as the main precursors of nitrogenous DBPs. N-DBP formation was significantly lower than that of C-DBPs, which was expected as DON contents are usually lower than dissolved organic carbon contents (Chu *et al.* 2016). The influence of wastewater effluents on the DON content and subsequent N-DBP formation may be excluded in the case of this type of water. TCNM precursors were not detected after any of the oxidation treatments, indicating a different formation mechanism for halonitromethane and haloacetonitrile in water.

For evaluation of the optimal treatment conditions for the investigated groundwater, it is necessary to consider bromate formation, which is classified by IARC in group 2B as possibly carcinogenic to humans. Previous study has shown that bromate formation in concentrations above guideline values (10 µg/L) is significant in ozone-based advanced oxidation processes. Thus, despite the fact that maximal reduction of THMFP and HAAFP was achieved by the O₃/H₂O₂/UV process, in ozone-based processes there is an increased risk of bromate occurrence. Thus, the H₂O₂/UV process after optimizing treatment conditions (primarily UV dose) could be a possible choice to treat such challenging groundwater and to avoid bromate formation. Application of the H₂O₂/UV process would also reduce the cost of ozone generation. In the Strategy of water supply and water protection in AP Vojvodina (Official Gazette APV No. 1/2010) it is indicated that this type of water is the most difficult for processing to meet relevant norms for drinking water (Official Gazette SRJ 42/98 and 44/99). The quality of raw water requires, apart from the degasification/aeration and oxidation treatment used in the first stage of treatment, additional application of coagulation/flocculation and filtration (sand filtration and/or granulated activated carbon filtration) followed by membrane separation for the final phase of treatment and disinfection. Water supply strategy also emphasizes that for such complex technology of preparation it is necessary to carry out investigations using a pilot plant in order to optimize processes which would enable savings in the investment and exploitation costs of the plant. Thus, results of the conducted investigations are valuable for further treatment line investigations. Additionally, based on the available data in the Republic of Serbia there is generally a lack of data regarding the emerging DBP formation in drinking water. Besides that, apart from ozonation, UV-based advanced oxidation processes are still not applied in large water plants in the Republic of Serbia and so the conducted investigation contributes to understanding the possibility of using these processes with their benefits and disadvantages for treatment of water with similar characteristics.

CONCLUSION

The influence of photochemical advanced oxidation processes (O₃/UV, H₂O₂/UV and O₃/H₂O₂/UV) on the formation

potential of emerging disinfection by-products in NOM rich water was investigated. The content of HAN precursors in the raw water was significantly lower compared with the C-DBPs, representing just 1.5% compared with the total DBPs formed, while TCNM and HK precursors were not detected. Treatments with ozone and H₂O₂/UV with lower UV dose were shown to be the most effective in reducing HANFP with no significant influence on the changes in percentage of bromide incorporation into DBPs compared with the raw water. None of the oxidation treatments led to TCNM formation, indicating a different formation mechanism for halonitromethane and haloacetonitrile in water. In general, the absence of a correlation between the emerging DBPs with C-DBPs and the oxygen containing DBPs (previously investigated) demonstrates how the behaviour of different NOM functional groups strongly depends on the oxidation process applied, resulting in widely different reactivity towards chlorine and promoting the formation of different groups of DBPs. Considering all investigated oxidation/disinfection by-product formation and available guideline values, H₂O₂/UV could be a possible choice to treat such challenging groundwater and avoid bromate formation. Further pilot-scale investigations are needed to define the combination of optimal processes and their conditions.

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