Effects of water matrix and ozonation on natural organic matter fractionation and corresponding disinfection by-products formation

ABSTRACT
In this study the influence of water matrix and oxidation treatment by ozone on natural organic matter (NOM) fractionation and corresponding disinfection by-products formation was investigated. Three water types were selected, based on their different NOM contents (5.16–9.85 mg/L dissolved organic carbon (DOC)) and structures (42–79% proportion of hydrophobic NOM fraction). It was determined that increasing the ozone dose (0.2–0.8 mg O3/mg DOC) generally led to reductions in DOC (2–26%) and trihalomethane formation potential values (4–58%). Results of NOM fractionation showed that the reactivity of all the individual NOM fractions towards trihalomethane formation decreased after ozone oxidation (0.8 mg O3/mg DOC) by 47–69%, relative to the raw waters.

Key words | aldehydes, groundwater, natural organic matter, ozonation, trihalomethanes

ACRONYMS
Natural organic matter (NOM); dissolved organic carbon (DOC); disinfection by-products (DBPs); trihalomethanes (THMs); trihalomethane formation potential (THMFP); chloroform formation potential (CFFP); bromodichloromethane formation potential (BDCMFP); dibromochloromethane formation potential (DBCMFP); bromoform formation potential (BFFP); specific trihalomethane formation potential (STHMFP); haloacetic acids (HAA); humic acid fraction (HAF); fulvic acid fraction (FAF); hydrophilic acid fraction (HPIA); nonacidic hydrophilic fraction (HPI-NA).

INTRODUCTION
The presence of natural organic matter (NOM) is very common in groundwaters which are used as water sources in the Banat Region (Republic of Serbia). The influence of NOM on drinking water quality is significant and its presence is undesirable for a variety of reasons: NOM influences the organoleptic quality of water, and can influence the regrowth of microorganisms in the distribution system, creating biologically unstable water, depending on the biodegradable NOM fraction present (Charnock & Kjønno 2000). Furthermore, if present in water resources, NOM can have a negative influence through the increase of coagulant and disinfectant demand in drinking water treatment (Bekbolet et al. 2008).

Due to their complicated origin-dependent composition, different NOM fractions (hydrophobic or hydrophilic) may have different reactivities to various treatment processes and have different potentials to form disinfection by-products (DBPs) (Matilainen et al. 2011; Lin & Wang 2011). More than 600 different compounds have already been identified in drinking water as a consequence of disinfection of water containing NOM (Krasner et al. 2006). The diversity of molecules that constitute NOM make any general conclusions about their structure and influence on water treatment very hard to draw. Generally, hydrophobic and high molecular weight NOM fractions are considered the main NOM fractions which react with chlorine and give the most DBPs (Liang & Singer 2003; Hua & Reckhow 2006).
aldehydes as by-products of the reaction between ozone and NOM compounds, short-chained carboxylic acids, keto-acids and other oxidation mechanisms and DBPs speciation.

Different NOM characteristics to better understand NOM precursors properties (Molnar et al. 2013). Thus, in order to comply with increasingly strict regulations for drinking water quality, good knowledge of the NOM present in source water and its influence on the structure of DBP precursors structure during various drinking water treatments is essential.

In drinking water treatment ozonation has been applied for more than 100 years. Ozone is used in drinking water treatment for multiple purposes: primary disinfection, taste and odour control (Rodríguez et al. 2008; Seo et al. 2010; Yuan et al. 2013), improving coagulation/flocculation and oxidation of emerging contaminants (Matilainen et al. 2010; Papageorgiou et al. 2014). Ozone can oxidize THM or HAA precursors (Li et al. 2008; Rodríguez et al. 2012), but ozone transformation products can also have a higher affinity to generate DBPs than the starting material (Hua & Reckhow 2013; Bond et al. 2014; Liu et al. 2014). The effects of ozone oxidation on DBPs formation depend on the water quality and NOM characteristics, especially precursors properties (Molnar et al. 2013; Hua & Reckhow 2013). It is therefore necessary to investigate waters with different NOM characteristics to better understand NOM oxidation mechanisms and DBPs speciation.

Using ozonation can cause the formation of carbonyl compounds, short-chained carboxylic acids, keto-acids and aldehydes as by-products of the reaction between ozone and NOM (Can & Gurol 2003; Dąbrowska et al. 2005; Jurado-Sánchez et al. 2014). Such polar compounds may represent about 30% of ozonation by-products (Richardson 2003), and are very significant due to their toxicity. Thus, formaldehyde is classified as carcinogenic to humans and acetaldehyde as possibly carcinogenic to humans (I.A.R.C. 2012), and acetaldehyde, formaldehyde, glyoxal and methyl glyoxal in water have been recognized as possible mutagenic compounds (Richardson et al. 2007).

In a recent study by Papageorgiou et al. (2014) it has been reported that the exact mechanism of aldehydes formation is not clearly established, but it has been established that ozone cleaves larger organic molecules into smaller ones, and reacts with unsaturated aliphatic chain compounds or aromatic groups of NOM to produce carbonyl compounds such as aldehydes (Weinberg 1999). The ozonation conditions generally employed in drinking water treatment are rarely sufficient to form high concentrations of toxic aldehydes (WHO 2011), but they are high enough to make NOM more biodegradable, which is one of the key factors influencing the efficiency of subsequent water treatment as well as the microbiological quality of the water.

The aim of this paper was to investigate the influence of different water matrices and ozone doses on NOM fractionation and corresponding DBPs formation. Particular emphasis is placed on the formation of aldehydes during ozonation due to their toxicity, as well as the impact of oxidation treatment on different NOM fractions towards THM formation.

**EXPERIMENTAL AND METHODS**

**Samples and reagents**

Groundwater from the Banat Region which is used as raw water source for three municipalities (Kikinda – A, Zrenjanin – B and Senta – C) was investigated. Standards for THMs (chloroform, CF; bromodichloromethane, BDCM; dibromochloromethane, DBCM and bromoform, BF) analysis and internal standard fluorobenzene were purchased from Supelco in concentrations of 2,000 μg/mL. Standards for aldehydes analysis (formaldehyde, acetaldehyde, glyoxal, methylglyoxal solutions) and O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride for aldehydes derivatization were purchased from Fluka. All solvents were obtained from J.T. Baker for Organic Residue Analysis. Resins for NOM fractionation (Supelite™ DAX-8 and Amberlite® XAD4) were purchased from Supelco. All other chemicals were analytical grade and were used without further purification.

**Ozonation**

The raw water was treated with ozone in a 2 L glass column using an Argentox ozone generator (1 g/h capacity). Ozone was introduced to the water via a diffuser at the bottom of the column at a flow rate of 8 L/h. At the end of ozonation, excess ozone was removed by nitrogen flow. The applied ozone doses were in the range of 0.2–0.8 mg O3/mg DOC,
and were calculated in relation to the initial concentrations of DOC in the water. After treatment, water samples were analyzed for DOC content, UV\textsubscript{254} absorbance, aldehydes content and THM formation potential (THMFP), while specific UV absorbance (SUVA) values were calculated: SUVA = UV\textsubscript{254} × 100/DOC.

**NOM fractionation**

NOM fractionation of the raw and ozone treated water was carried out using XAD resins according to the procedure given in Goslan et al. (2002). Using this method, the hydrophobic (humic acid fraction – HAF and fulvic acid fraction – FAF) and hydrophilic (hydrophilic acid fraction – HPIA and nonacidic hydrophilic fraction – HPI-NA) NOM fractions were isolated.

**Analytical methods**

Water samples were analysed for DOC content by Elementar LiquiTOCII, with oxidation by platinum catalysed combustion at 850°C. UV\textsubscript{254} absorbance measurements were performed in accordance with Standard Methods (APHA 2012) on a UV-1800 Shimadzu spectrophotometer at a wavelength of 254 nm, with a 1 cm quartz cell, and the specific UV absorbance (SUVA, L mg\textsuperscript{-1} m\textsuperscript{-1}/C\textsuperscript{0} 1 m\textsuperscript{-1}/C\textsuperscript{0} 1) was calculated.

The ozone content in the inlet and outlet gases was determined by iodometric procedure (APHA 2012), and the transferred ozone dose calculated from the difference. THMFP was determined according to Standard Methods (APHA 2012). At the end of the 7 day reaction period, the samples were dechlorinated, and THMs were analysed. THMs in the water samples were directly analysed with a purge and trap system (Tekmar 3100) coupled to a gas chromatograph equipped with mass selective detector (Agilent Technologies 7890A/5975C), after derivatization with O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (Glaze et al. 1989; Agbaba et al. 2004). MDLs for formaldehyde, acetaldehyde, glyoxal and methylglyoxal were 0.40, 0.16, 0.40 and 0.34 μg/L, respectively.

pH was measured by portable instrument (WTW InoLab pH). Water alkalinity (p- and m-alkalinity) was measured by Standard Methods (APHA 2012).

**RESULTS AND DISCUSSION**

**Characteristics of the raw groundwaters**

The investigated groundwaters contain high amounts of NOM (Type A – 5.16 mg/L DOC; Type B – 9.85 mg/L DOC and Type C – 7.46 mg/L DOC). The UV absorbance at 254 nm and SUVA values indicate the mainly hydrophobic character of NOM in water types A and B (4.31–4.53 L mg\textsuperscript{-1} m\textsuperscript{-1}/C\textsuperscript{0} 1 m\textsuperscript{-1}/C\textsuperscript{0} 1 SUVA) while water C contains a higher share of hydrophilic NOM (3.86 L mg\textsuperscript{-1} m\textsuperscript{-1}/C\textsuperscript{0} 1 m\textsuperscript{-1}/C\textsuperscript{0} 1 SUVA) (Table 1). Detailed characterisation of NOM using XAD resins also suggests that the main fraction of NOM in water type A and water type B is mostly of hydrophobic character (71–79%) (Figure 1). Groundwater type C has a greater amount of NOM with hydrophilic character (58%). Only water B contains the humic acid fraction (14%) in addition to the FAF. As a consequence of the high NOM content, a significant amount of THM precursors are present in the investigated waters (Type A – 270 μg/L; Type B – 373 μg/L and Type C – 263 μg/L THMFP). Aldehydes (2.4–50.2 μg/L) were also found in the waters investigated, with the highest amounts being detected in water C, in accordance with its hydrophilic character.

**Effects of water matrix and ozone doses on the NOM content and fractionation**

The results in Figure 2 show that DOC removal (Type A – 14–26%, Type B – 2–14% and Type C – 13–18%) depends upon the applied ozone dose, as well as the NOM content and fraction distribution. It is known that the stability of ozone in water and the efficacy of the ozonation process largely depend not only on the applied ozone dose and
the content and characteristics of NOM, but also on pH and water alkalinity, which have an influence on the decomposition of ozone into OH radicals (von Gunten 2003). The investigated waters are slightly basic and have high alkalinitites (Table 1), so it may be supposed that these conditions favour selected oxidation by ozone. Accordingly, in the water with the lowest alkalinity and DOC content and the highest pH (water A), the greatest degree of DOC removal was observed, suggesting that in this case reactions with other radical species in addition to ozone may be involved, improving NOM oxidation.

As expected, ozonation also led to THMFP reduction (4–58%). However, different trends in changes in THMFP were observed depending on the ozone dose and NOM fraction distribution. Thus, in waters A and C, THMFP decreased with increasing ozone dose. The greatest

Table 1 | Characteristics of the investigated water matrices (waters A–C)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit of measurement</th>
<th>Water A</th>
<th>Water B</th>
<th>Water C</th>
<th>No. of measurements (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>8.19 ± 0.16</td>
<td>7.48 ± 0.10</td>
<td>7.84 ± 0.11</td>
<td>7</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg CaCO₃/L</td>
<td>475 ± 10</td>
<td>745 ± 12</td>
<td>631 ± 11</td>
<td>5</td>
</tr>
<tr>
<td>DOC</td>
<td>mg C/L</td>
<td>5.16 ± 0.80</td>
<td>9.85 ± 0.99</td>
<td>7.46 ± 1.18</td>
<td>7</td>
</tr>
<tr>
<td>UV₂₅₄</td>
<td>cm⁻¹</td>
<td>0.211 ± 0.007</td>
<td>0.446 ± 0.080</td>
<td>0.288 ± 0.010</td>
<td>7</td>
</tr>
<tr>
<td>SUVA</td>
<td>L/mg-m</td>
<td>4.31 ± 0.50</td>
<td>4.53 ± 0.33</td>
<td>3.86 ± 0.60</td>
<td>7</td>
</tr>
<tr>
<td>THMFP</td>
<td>μg/L</td>
<td>270 ± 73</td>
<td>373 ± 70</td>
<td>263 ± 48</td>
<td>5</td>
</tr>
<tr>
<td>CFFP</td>
<td>μg/L</td>
<td>257 ± 37</td>
<td>344 ± 39</td>
<td>219 ± 39</td>
<td>5</td>
</tr>
<tr>
<td>BDCMFP</td>
<td>12.2 ± 5.3</td>
<td>27.5 ± 9.6</td>
<td>40.7 ± 7.2</td>
<td>5</td>
<td></td>
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<tr>
<td>DBCMFP</td>
<td>0.81 ± 0.40</td>
<td>1.44 ± 0.61</td>
<td>2.82 ± 1.3</td>
<td>5</td>
<td></td>
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<tr>
<td>Bromoform formation potential</td>
<td>&lt;MDL</td>
<td>&lt;MDL</td>
<td>&lt;MDL</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Total aldehydes</td>
<td>μg/L</td>
<td>2.4 ± 1.8</td>
<td>10.1 ± 4.4</td>
<td>50.2 ± 6.1</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 1 | Distribution of DOC in the NOM fractions (humic acid fraction – HAF; fulvic acid fraction – FAF; hydrophilic acid fraction – HPIA; nonacidic hydrophilic fraction – HPI-NA) of the raw waters: (a) water A, (b) water B, (c) water C.

Figure 2 | The effect of O₃ dose on changes in DOC and THM precursors contents for waters with different NOM structure.
degree of THMFP reduction by ozonation was achieved in water A, as was the case for DOC removal. In water type B, ozonation at doses less than 0.4 mg O$_3$/mg DOC led to a decrease in THMFP, and with further increases in ozone dose, the THMFP increased. It can be assumed that these changes are a consequence of the unique presence of HAF in water type B, which are oxidized when higher ozone doses are applied, producing new THM precursor material. For a detailed examination of the changes in the structure and reactivity of NOM, fractionation of NOM was carried out after ozonation with 0.8 mg O$_3$/mg DOC, the dose which generally achieved optimal DOC and THMFP reductions for all investigated waters.

The distributions of DOC in the raw waters and in the waters treated by ozone (0.8 mg O$_3$/mg DOC) are shown in Figure 3. These results indicate that the proportion of DOC in all the NOM fractions of ozone treated water was very similar for all waters. The hydrophobic fraction of NOM (HAF and FAF) from waters A and B was dominantly oxidized by ozone, resulting in an increase of the hydrophilic NOM content to 62 and 67% of the total DOC, respectively, which is significantly higher than the share of the hydrophilic fraction in the raw water (29 and 35%, Figure 1). Moreover, the share of hydrophilic NOM in water C was not significantly changed after oxidation relative to the raw water, remaining at 60%. It has been proved that ozonation causes significant fragmentation of high-molecular weight NOM components for each individual NOM fraction, and alters the molecular distribution towards smaller molecules (Zhang et al. 2008). In addition, Hammes et al. (2007) indicate that ozonation increases the concentration of oxygen-containing low molecular weight compounds by oxidative breakdown of complex NOM structure. The lower degree of NOM oxidation for water C could be explained by its NOM characteristics, which are mainly hydrophilic in character compared with the NOM from water A and B, which have easily oxidized fulvic and humic acid fractions (Hua & Reckhow 2015).

The increase in the hydrophilicity of the residual NOM content in ozone treated waters (waters A and B) is followed by increasing total aldehydes content (from 11.4 to 38.4 μg/L in water type A and from 14.9 to 50.7 μg/L in water type B, Figure 4). In contrast, there were no significant changes in the NOM structure in the ozone treated water for water C, where a slight decrease in the total aldehydes content
(about 20%) was observed, compared with the raw water. A more detailed analysis of the aldehydes measurements (Figure 4) also confirms the general similarity in the NOM structure originating from waters A and B, as a similar trend in changing aldehyde contents with increasing ozone dose was observed. However, some differences were also found, with the ozone treated water A predominantly forming formaldehyde and glyoxal (especially at doses above 0.4 mg O₃/mg DOC), whereas water B contained similar amounts of formaldehyde, acetaldehyde and glyoxal after ozonation (except at a dose of 0.6 mg O₃/mg DOC, when formaldehyde dominated). Unlike waters A and B, the NOM in water C more readily gave acetaldehyde (26.4–88.2 μg/L), and then methylglyoxal (7.99–19.1 μg/L). Maximum aldehydes production was observed at different ozone doses for all water types (0.8, 0.6 and 0.2 mg O₃/mg DOC for waters A, B and C, respectively). Papageorgiou et al. (2014) also indicate that during ozone treatment aldehydes content could increase relative to the raw water. The results given indicate that ozone treatment requires oxidation process optimization according to the NOM content as well as the specific oxidation by-products content. The results also indicate that significant changes in the character of NOM, particularly increasing its hydrophilicity, can increase the contents of polar oxidation by-products such as aldehydes. Note that during water treatment, ozonation is often followed by other processes (coagulation, sorption, etc.). In this case, biological filtration could be used to prevent undesirable aldehydes and other biodegradable compounds from passing into the water supply. Such residual NOM removal would also be important to decrease NOM reactivity during chlorination (Matilainen et al. 2010).

The share of THM precursors in all NOM fractions of the ozone treated waters is given in Figure 5. Like the DOC distribution results (Figure 3), they are very similar for all water types. Generally, the reactivity of all the individual NOM fractions towards THM formation, according to the STHMFP, decreased after ozone oxidation by 47–69%. Even though applying 0.8 mg O₃/mg DOC resulted in a total THM reduction only for waters A and C and not for B, the STHMFP of the individual NOM fractions indicates that the reactivity of all NOM fractions with chlorine decreases after ozone treatment.
The STHMFP, presented as the sum of all individual NOM fractions, has the highest value for the water with the highest NOM content (196 μg/mg DOC for water B in contrast to 130 and 166 μg/mg DOC for waters A and C). After treatment with ozone, the STHMFP were very similar (58.4–68.8 μg/mg DOC), pointing to selective ozone attack. When it comes to the individual THMs, chloroform was the most abundant species in ozone treated water, as well as in the raw water, with a slightly higher contribution in the hydrophobic fraction and HPI-A than in the HPI-NA. However, HPI-NA was the most reactive fraction towards brominated THM formation, such as BDCM and DBCM.

**CONCLUSION**

The influence of different water matrices and ozone doses on NOM fractionation and THMs and aldehydes formation was investigated. Application of ozone reduced DOC and THMFP values, with removal efficacy depending on the applied ozone dose and NOM character. In the water with the lowest alkalinity and DOC content and the highest pH, the highest degree of DOC and THMFP reduction was observed, suggesting that in this case reactions with other radical species in addition to ozone may be involved, improving the oxidation of NOM. It was shown that ozone preferentially oxidizes the hydrophobic NOM fraction, leading to an increase in residual hydrophilic content, which is more reactive to THM formation compared with the hydrophobic fraction. Significant changes in the NOM characteristics during ozonation, such as increasing the hydrophilicity of the residual NOM, causes an increase in polar oxidation by-products such as aldehydes, some of which have mutagenic activity. In raw waters with high hydrophobic NOM contents and after their ozone treatment, formaldehyde was dominantly formed, whereas in
the water of a more hydrophilic nature, acetaldehyde was the most abundant, in the raw and ozone treated waters. Regardless of the raw water quality, the distribution of DOC and THM precursors in all NOM fractions of the ozone treated water was nearly the same for all water types, with the highest contribution of brominated THMs coming from the hydrophilic non-acidic fraction.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. III43005), and the Provincial Secretariat for Science and Technological Development of Vojvodina (for the project No. APV114-451-1985 and their support No. 114-451-3718/2011-01 to IPA project HUSRB/1002/121/075).

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First received 16 May 2014; accepted in revised form 11 August 2014. Available online 23 August 2014.