

# Controlling the formation of halogenated byproducts in the chlorination of source waters by oxidative pre-treatment with the Fe(II)/Fe(III)-S(IV)-air system

Alexandra Truzzi<sup>a,b</sup>, Boglárka Kovács<sup>c</sup>, Ildikó Bodnár<sup>a</sup>, István Fábián<sup>d,e,\*</sup>

<sup>a</sup> Department of Environmental Engineering, University of Debrecen, Óttemető u. 2–4., Debrecen H-4028, Hungary

<sup>b</sup> Doctoral School of Chemistry, University of Debrecen, Egyetem tér 1., Debrecen H-4032, Hungary

<sup>c</sup> Debrecen Waterworks Ltd., Benczúr Gyula u. 7., Debrecen H-4032, Hungary

<sup>d</sup> Department of Inorganic and Analytical Chemistry, University of Debrecen, Egyetem tér 1., Debrecen H-4032, Hungary

<sup>e</sup> ELKH-DE Mechanisms of Complex Homogeneous and Heterogeneous Chemical Reactions Research Group, University of Debrecen, Egyetem tér 1, 4032 Debrecen, Hungary

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## ABSTRACT

Breakpoint chlorination is a generally accepted method for removing ammonium ion from source waters in drinking water treatment technologies. This process is often accompanied by the formation of halogenated organic byproducts. The presence of these compounds in potable water is of primary concern. In this paper, we demonstrate that the concentration of the precursors of the halogenated species can sufficiently be decreased by oxidizing the organic pollutants with the Fe(II)/Fe(III) – S(IV) – air system. Pre-oxidative treatment of the source waters results in a substantial reduction of chemical oxygen demand, while the ammonium ion concentration remains unaffected. The breakpoint chlorination produces substantially less trihalomethanes (THMs) and adsorbable halogenated organic compounds (AOXs) in oxidatively pre-treated source waters than in raw waters. These results offer a possibility to improve drinking water treatment technologies for better controlling the formation of antagonistic byproducts. It is demonstrated that reaching the regulated concentration levels of THMs is feasible with this method even in source waters containing organic pollutants at relatively high concentration levels. The main advantage of the procedure is that the reagents used for the oxidative pre-treatment are converted into non-toxic products (Fe(III) and  $\text{SO}_4^{2-}$ ) by the end of the process.

## 1. Introduction

Disinfection is an essential part of drinking water treatment technologies for reducing the risk of water-borne infectious diseases (Cabral, 2010; Mazhar et al., 2020). The use of chlorine to disinfect water is one of the great health successes of the 20th century (Mazhar et al., 2020). Furthermore, chlorine is used in many parts of the water supply system for different purposes. The main objective of the breakpoint chlorination is the removal of ammonia by converting it to  $\text{N}_2$  (Pressley et al., 2002). This technological step can be introduced at the beginning, at an intermediate location, at the end of the water treatment system or by using a combination of these locations depending on the water quality and needs. During breakpoint chlorination, chlorine gas or sodium hypochlorite ( $\text{NaOCl}$ ) is added to the raw water (Halling-Sorensen and Jorgensen, 1993). Apart from the removal of ammonia, parallel oxidation

and chlorination reactions also occur with inorganic and organic components. Notably, low valence metal ions, such as  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  are oxidized. Typically, the chlorine demand of these side reactions is negligible compared to the amount consumed by ammonia. Another use of chlorine is the post or transport chlorination of the finished water. It aims to prevent the increase of the pressure loss caused by organisms that proliferate in the transmission line (e.g., excessive proliferation of biofilm, migratory mussels, mosses) and to keep the drinking water safe (Byun et al., 2021). A common feature of these chlorination operations is that sequential processes take place depending on the precursors, chlorine dose, the presence of chlorine-requiring substances, and the contact time (Driss and Bouhelassa, 2013).

Contaminants of source water used for drinking water supply can be suspended ( $> 1 \mu\text{m}$ ) and colloidal ( $0.001\text{--}1 \mu\text{m}$ ) solids as well as dissolved materials. Various inorganic, organic compounds,

\* Corresponding author at: Department of Inorganic and Analytical Chemistry, University of Debrecen, Egyetem tér 1., Debrecen H-4032, Hungary.  
E-mail address: [ifabian@science.unideb.hu](mailto:ifabian@science.unideb.hu) (I. Fábián).

microorganisms (viruses, bacteria, fungi), as well as algae can be present in the source water in different forms (Bai et al., 2019; Latchmore et al., 2020; Lipczynska-Kochany, 2018). The main organic matter constituents of the pollutants are humic substances, which are the products of chemical and biological processes in soil, natural waters, bottom sediments, and persist for centuries or longer (Cabral, 2010). Humic substances are low to medium molecular weight anionic polyelectrolytes featuring aromatic and aliphatic moieties. They can be classified into the groups of more soluble fulvic acids and less soluble humic acids (Lipczynska-Kochany, 2018; Matilainen and Sillanpaa, 2010; Mokhtar Kamal et al., 2019). The yellow or brown colors of raw water with a high content of organic matter are caused mainly by humic substances. The great many functionalities of these compounds give rise to various oxidation reactions during the chlorination processes (Lipczynska-Kochany, 2018; Rahman et al., 2010). It is important to note that humic substances are the dominant precursors of saturated and unsaturated chlorinated aliphatic acids as compared to compounds of aromatic origin (Kali et al., 2021).

The main concern regarding breakpoint chlorination is the formation of antagonistic disinfection byproducts (DBPs) from various substances in water (Wistrom et al., 1996). These DBPs include volatile compounds, mostly trihalomethanes (THMs), and a few hundred nonvolatile compounds, mainly formed from fulvic acids (Gilca et al., 2020; Mazhar et al., 2020; Srivastav et al., 2020; Stefán et al., 2019). The molecular structures of the latter compounds are still unknown, but it was confirmed that many DBPs are mutagenic and carcinogenic (Kimura and Ortega-Hernandez, 2019; Tak and Vellanki, 2018). The concentration of THMs varies significantly in the treated water depending on the quality of the source water. The formation of adsorbable halogenated organic compounds (AOXs) is also closely monitored in water treatment technologies. The concentration of AOXs is a non-specific parameter that corresponds to a family of organic compounds (Xie et al., 2020). These species are also toxic, but their concentration can be reduced by filtration with activated carbon (Çapar and Yetiş, 2002; Erdem et al., 2020). Nevertheless, their formation should be avoided or at least minimized to keep the operational cost of potable water production low. The concentrations of THMs and AOXs are important quality indicators of the finished water, and they need to be reduced below the permitted level in accordance with public health requirements (Childress et al., 1999; Mohd Zainudin et al., 2018; Mokhtar Kamal et al., 2019).

It is a plausible strategy that the precursors of the halogenated DBPs are removed from the source water prior to the breakpoint chlorination (Yang et al., 2005). However, considering their diverse properties, it is not a trivial task (Childress et al., 1999; Zhu et al., 2019). There are several indicator parameters for the organic pollutants such as the total organic carbon (TOC), chemical oxygen demand (COD), UV absorbance etc. (Charrois and Hrukey, 2007; Driss and Bouhelassa, 2013; Karthik et al., 2020; Lu et al., 1993). Several methods based on chemical or biological technologies are available to reduce the precursors of THMs and AOXs. Some of them are as follows: adsorption, coagulation/flocculation (McKie et al., 2015; Mohd Zainudin et al., 2018; Shi et al., 2007; Wang et al., 2013; Zhao et al., 2013), nanofiltration (Lin et al., 2006, 2007; Sutherland et al., 2015), advanced oxidation processes (AOPs) utilizing  $O_3$ , UV,  $H_2O_2$ /UV,  $H_2O_2$ / $O_3$  and UV/ $O_3$  (Deeudomwongsa et al., 2017; Matilainen and Sillanpaa, 2010; Rahman et al., 2010), oxidation by Fe(VI) (Liu et al., 2020; Rouge et al., 2020) etc. Many of these technologies suffer from high operational cost (Matilainen and Sillanpaa, 2010).

Recently, we have reported a novel method for reducing the concentration of organic matter in source waters extracted from deep wells (Truzzi et al., 2022). The procedure is based on the iron(II/III) catalyzed auto-oxidation of the sulfite ion. This reaction yields highly reactive radicals which act as strong oxidizing agents and react with the contaminants. COD is practically the measure of oxidizable organic pollutants in source water. We have thoroughly studied the removal efficiency of COD (CODR%) upon adding S(IV) and Fe(II)/Fe(III) to the

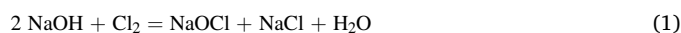
source water while replenishing  $O_2$  by purging it with air. The optimum conditions for COD removal were established by using the response surface methodology (RSM). We have confirmed that typically well over 80% of the initial organic matter content of the source water samples could be removed with this method. Now we present results on how the oxidative pre-treatment of the source waters, i.e., the removal of a great part of COD affects the formation of THMs and AOXs in subsequent breakpoint chlorination. For comparison, control experiments with untreated source waters were also performed.

## 2. Materials and methods

### 2.1. Materials

All chemicals –  $Na_2SO_3$  (Sigma-Aldrich),  $Fe_2(SO_4)_3$  (VWR Chemicals),  $FeSO_4$  (Reanal),  $KMnO_4$  (P.P.H. Polskie Odczynniki Chem.),  $Na_2(COO)_2$  (Reanal), sodium salicylate ( $C_7H_5NaO_3$ , VWR Chemicals), sodium citrate ( $Na_3C_6H_5O_7$ , VWR Chemicals), sodium pentacyanonitrosylferrate(III) dihydrate ( $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ , VWR Chemicals) and sodium dichloroisocyanurate ( $C_3Cl_2N_3NaO_3$ , VWR Chemicals) – were of analytical grade and used without further purification. For the gas chromatographic experiments, THMs standard solution containing TCM, BDCM, CDBM, and TBM (2000  $\mu g/mL$  each in methanol) was obtained from Restek. The standard was stored at  $-18^\circ C$  and diluted as required with ultra-pure methanol (Merck). Synthetic air (21%  $O_2$ , 78%  $N_2$ , and 1% other) was purchased from Linde. Reagent solutions were prepared with ultrapure water (18.2  $M\Omega\ cm$ ) obtained from a Synergy® UV Water Purification System (Millipore).

For the breakpoint chlorination experiments, alkaline sodium hypochlorite solution was prepared by introducing chlorine gas into NaOH solution (Eq. (1)).



The concentrations of hypochlorite ion and excess NaOH were determined as described earlier (Szabó et al., 2015).

### 2.2. Water samples

Source waters were obtained from deep-drilled wells from the following locations: Apátfalva, Földeák, Királyhegyes, Kismarja, Makó, Nagyer, Pocsaj (Hungary). These water samples were processed as received, their composition and pH were not altered before the experiments. The main part of this study was made with the water from Királyhegyes (EOV: 770635.8 m, EOVx: 104066.9 m) which is characterized by relatively high COD (7.02 mg/L). Once the general features of the applied methods were established the overall applicability of the results was tested with the samples obtained from other locations. The characteristic parameters of these waters are shown in Table 1. The oxidative pre-treatment of the source waters, as well as the breakpoint chlorination experiments, were made at ambient temperature,  $\sim 25^\circ C$ .

### 2.3. Analytical methods

All analytical measurements in this study were carried out at least in triplicates. In some cases, additional parallel experiments were also made. The error of the experimental results was always well within the expected reproducibility of a given method as indicated by the standard deviation of the reported data.

The COD of the samples was obtained by the standard  $KMnO_4$  method with  $\pm 2.5\%$  standard error (Geerdink et al., 2017). The concentration of ammonium ion was determined with  $\pm 3.0\%$  error in accordance with the ISO 7150-1:1984 standard (Standardization, 1984). Essentially this method is based on the modified Berthelot reaction using salicylate and dichloroisocyanurate (Krom, 1980). The water sample is mixed with a reagent solution containing sodium

**Table 1**

Some of the characteristic parameters of the source waters used in this study.

Location	COD (mg/L)	pH	NH <sub>4</sub> <sup>+</sup> (mg/L)	Fe (μg/L)	Mn (μg/L)	As (μg/L)	CH <sub>4</sub> (L/m <sup>3</sup> )	T (°C)
Apátfalva	5.21	8.0	1.39	75.8	16.1	3.09	4.46	22.1
Földeák	2.70	8.0	1.58	151.1	22.6	21.9	2.47	31.1
Királyhegyes	7.02	8.2	1.11	97.5	22.1	7.70	7.16	18.5
Kismarja	6.52	7.9	0.71	138.0	78.0	< 0.5	–	13.8
Makó	2.30	7.8	1.56	129.1	37.8	34.8	3.45	26.3
Nagyér	3.20	8.0	0.20	774.0	161.0	25.1	1.70	14.8
Pocsaj	6.80	8.0	1.31	98.0	29.0	< 0.5	–	25.1

salicylate, sodium citrate, sodium pentacyanonitrosylferrate(III), and sodium dichloroisocyanurate. Under alkaline conditions, a dye forms from these reagents with the involvement of ammonia within 60 min. The solution turns in blue and the absorbance at 655 nm is proportional to the concentration of ammonium ion. For these measurements, an HP 8453 diode array UV/VIS spectrophotometer was used.

After the breakpoint chlorination, samples were collected and quenched i) in 40 mL screw-capped glass vials containing 5 mg of sodium thiosulfate pentahydrate (0.0125% w/v) for the determination of THMs and ii) in 250 mL screw-capped bottles containing 2.5 mL of sodium-sulfite solution for the determination of AOXs. These samples were stored in a refrigerator at 4 °C until THM and AOX analysis.

The concentrations THMs were measured in accordance with the ISO 10301:1997 standard (Standardization, 1997) by using a Thermo TRACE GC Ultra analyzer equipped with an electron capture detector (ECD) and capillary columns RTX-624 30 m × 0.32 mm × 1.8 μm (Restek) or ZB-SemiVolatiles 30 m × 0.25 mm × 0.25 μm (Zebron, Phenomenex). Helium was used as carrier gas with a flow rate of 1.0 mL min<sup>-1</sup> and nitrogen was used as makeup gas with a flow rate of 30 mL min<sup>-1</sup>. The oven was held at 40 °C for 6 min, then it was ramped first at 6 °C min<sup>-1</sup> to 82 °C, and next at 10 °C min<sup>-1</sup> to the final temperature of 100 °C at where it was held for 5 min. The injector and detector temperature was 140 °C (Maia et al., 2014). The standard error of these measurements was ±8.0%.

AOXs were measured using the microcoulometric titration method (ISO 9562:2004) (Standardization, 2004) with an ECS 1200 AOX, EOX, POX analyzer (Thermo Fisher Scientific). In brief, first 100 mL of water sample was measured into a 250 mL Erlenmeyer flask. Then 5 mL NaNO<sub>3</sub>-HNO<sub>3</sub> solution and 50 mg activated carbon (Thermo Trace Elemental) were added. The flask was shaken at 120 min<sup>-1</sup> for 1 h, and then the mixture was filtered through a quartz frit (Thermo Scientific). Inorganic halides were removed by washing the retained activated carbon with 25 mL of 20-times diluted NaNO<sub>3</sub>-HNO<sub>3</sub> solution. The quartz frits were transferred to the AOX analyzer. After incineration, the concentrations of AOXs were obtained from the amount of halogenide ions (predominantly chloride ion) formed (Xie et al., 2018). The standard error of these measurements was ±5.0%.

**Table 2**

The COD of raw (RSW) and oxidatively pre-treated (OSW) source waters, COD removal efficiency, and the concentration of ammonium ion prior to and after the oxidative treatment.

Location	COD <sub>RSW</sub> (mg/L)	COD <sub>OSW</sub> (mg/L)	CODR% (%)	c (NH <sub>4</sub> <sup>+</sup> ) <sub>RSW</sub> (mg/L)	c (NH <sub>4</sub> <sup>+</sup> ) <sub>OSW</sub> (mg/L)
Apátfalva	5.21 ± 0.02	0.60 ± 0.02	88.5	1.39 ± 0.01	1.38 ± 0.01
Földeák	2.70 ± 0.01	0.39 ± 0.01	85.6	1.58 ± 0.01	1.60 ± 0.01
Királyhegyes	7.02 ± 0.01	0.89 ± 0.01	87.5	1.11 ± 0.01	1.11 ± 0.01
Kismarja	6.52 ± 0.02	1.19 ± 0.01	81.7	0.71 ± 0.02	0.72 ± 0.02
Makó	2.30 ± 0.01	0.34 ± 0.01	85.4	1.56 ± 0.01	1.55 ± 0.01
Nagyér	3.20 ± 0.01	0.39 ± 0.01	87.8	0.20 ± 0.02	0.21 ± 0.02
Pocsaj	6.80 ± 0.01	1.29 ± 0.02	81.0	1.31 ± 0.01	1.24 ± 0.01

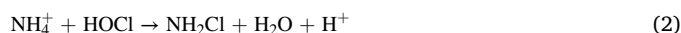
### 3. Results and discussion

#### 3.1. The removal of COD

Two sets of experiments were carried out with each source water. In one set, the COD of the sample was reduced by oxidative pre-treatment with the Fe(II)/Fe(III) – S(IV) – air system using the optimum conditions established earlier: c<sub>Fe</sub> = 1.7 mM, Fe(II)% = 20%, c<sub>S(IV)</sub> = 0.9 mM t<sub>air</sub> = 42 min, v<sub>air</sub> = 200 mL min<sup>-1</sup> (Truzzi et al., 2022). Briefly, the reagents were added to a 250 mL aliquot of the treated water, which was continuously purged with air. In the end, the precipitate was filtered off and COD was determined. The general concept of this method is provided in the [Supplementary Material](#). As expected, substantial COD removal was achieved under such conditions. The results also confirm that the oxidative pre-treatment does not affect the concentration of ammonium ion (Table 2). Thus, as expected, ammonium ion is not generated in the oxidative process; not removed from the reaction mixtures by purging with air; and not reacting with the oxidizing system.

#### 3.2. Breakpoint chlorination

During breakpoint chlorination, the ammonium ion is converted to NCl<sub>3</sub> in a stepwise process (Eqs. (2)–(4)) (White, 1992).



Trichloramine decomposes in a subsequent, relatively slow reaction step (Eq. (5)).



In this process, the use of appropriate amount of chlorine is imperative. In the case of under-dosing, chloramines remain in the finished water that could be the source of odor issues. On the other hand, the use of excess chlorine enhances the possibility of the formation of antagonistic chlorinated products. Thus, in accordance with Eqs. (2)–(4), the ideal mass ratio of HOCl to NH<sub>4</sub><sup>+</sup> is 8.7 : 1 which is generally maintained in water treatment technologies when the concentration of other

oxidizable components, most notably  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , is negligible. It follows that, the applicable hypochlorite concentration predominantly depends on the ammonium concentration of the treated water. In this paper, the 100% sodium hypochlorite dose corresponds to the 8.7 : 1 HOCl to  $\text{NH}_4^+$  mass ratio.

The time profiles of the breakpoint chlorination of the raw source water (RSW) and the oxidatively pre-treated source water (OSW) were obtained by adding sodium hypochlorite solution to 20 mL water and analyzing the reaction mixture for  $\text{NH}_4^+$  at different reaction times. The corresponding time profiles indicate that the reaction with OSW is somewhat slower (Fig. 1). A detailed quantitative explanation of this observation would require the identification, characterization, and the analysis of the kinetic role of each component of the contaminants before and after the pre-oxidative treatment. Considering the large number and diversity of these components, this is clearly not feasible. In general, the composition of the source waters is significantly altered by reducing COD e.g., potential catalyst of chlorination is removed, the ionic strength is altered etc. All of these changes may affect the actual course of breakpoint chlorination. While the specific reasons for the difference in the time profiles could not be identified, the results in these and other experiments confirmed that the process completes in 90 min and this contact time was used for breakpoint chlorination in all cases.

The breakpoint chlorination efficiently removes ammonium ion from the treated water, and significant differences were not found between RSW and OSW in this respect. For example, in the case of the source water from Királyhegyes, the ammonium ion concentration drops from 1.11 mg/L to 0.05 and 0.02 mg/L in the non-treated and the pre-oxidized samples, respectively. The same kind of results were found in the case of other source waters. Because alkaline NaOCl solution was used, the pH increased by about 0.2 unit during the breakpoint chlorination, which is negligible as far as the quality of the treated water is concerned.

### 3.3. The formation of halogenated DBPs

In general, breakpoint chlorination is associated with chlorination side reactions. This leads to the formation of various chlorinated organic species. The specific reaction sequences leading to these DBPs are difficult to identify. The precursors of AOXs and THMs are present at considerably lower concentration levels than ammonium ion. Still, these compounds are formed in measurable amounts. This implies that the reactions of the precursors efficiently compete with the reaction of ammonium ion and other inorganic constituents with hypochlorite. The corresponding reaction rates are dependent on the concentrations of the

precursors as well as the oxidant. The required amount of hypochlorite for breakpoint chlorination is determined by the concentration of ammonium ion and varies accordingly. Consequently, the rate of the chlorination reactions of organic substrates may differ even if they are present at the same concentration level but the concentrations of ammonium ion differ. Thus, a strict correlation cannot be expected between COD and the formation of chlorinated DBPs. Nevertheless, it is reasonable to state that the higher concentration of organic contaminants leads to the formation of THMs and AOXs at higher concentration levels (Fig. 2).

As demonstrated in Fig. 3a and b, the removal of organic contaminants from the source waters by oxidative pre-treatment with the Fe(II)/Fe(III) – S(IV) – air system has a profound effect on the formation of halogenated DBPs. After the treatment, 60–85% less AOX and 40–85% less THM formed during breakpoint chlorination (Table S2). A multi-dimensional regression analysis was performed to explore how COD and the HOCl dosage affects the formation of chlorinated DBPs by using ANOVA. It was assumed that the concentrations of the DBPs are linearly dependent on both COD and the concentration of HOCl added. The model predicts that the concentrations of the AOXs and THMs increase rather erratically as a function of COD and no obvious trend emerges as a function of HOCl dosage. According to the calculations, the 95% confidence intervals of the predicted parameters are unrealistically broad, and a strict correlation between CODR% and the decline in the concentrations of AOXs and THMs was not found. This finding is corroborated by the plots of the corresponding predicted vs. experimental concentrations of DBPs (Fig. S1 a-d).

These results are not quite unexpected by considering that the source waters were obtained from wells at different locations. Thus, the composition of the contaminants, i.e., the concentrations of the precursors of AOXs and THMs may differ significantly. This is clearly manifested in the lack of clear-cut correlation between COD and the concentrations of THMs and AOXs. The data also reveals that the pre-oxidative treatment significantly reduces the amount of oxidizable organic components (over 80%), but it is less effective in the removal of the precursors of the chlorinated DBPs. In other words, the drop in the concentrations of AOXs and THMs is always smaller than the change of COD.

As shown in Fig. 4a and b, there is a reasonable linear correlation between the concentrations of AOXs and THMs in the raw and the pre-oxidized source waters. This is a strong indication that the redox properties of the precursors of both types of DBPs are similar and their concentrations are equally affected by the pre-oxidative treatment.

In a recent study, the effects of pre-oxidative treatment of water by using  $\text{ClO}_2$ , Fe(VI),  $\text{O}_3$  and  $\text{MnO}_4^-$  on the formation on halogenated DBPs

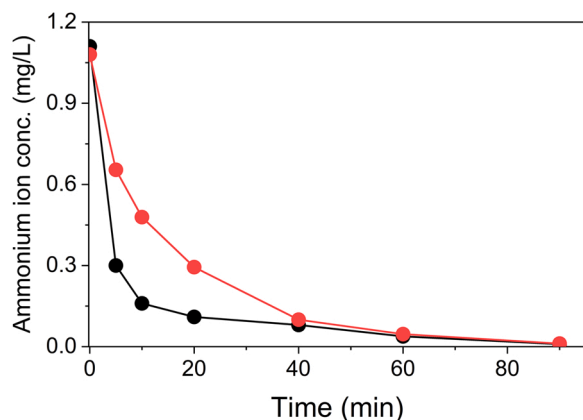


Fig. 1. Sodium hypochlorite was used in 100% dose which corresponds to the 8.7 : 1 HOCl to  $\text{NH}_4^+$  mass ratio. (a) The time dependence of breakpoint chlorination of the raw source water (RSW, black) and the oxidatively pre-treated source water (OSW, red). (b) Source water is from Királyhegyes containing 1.11 mg/L  $\text{NH}_4^+$ .

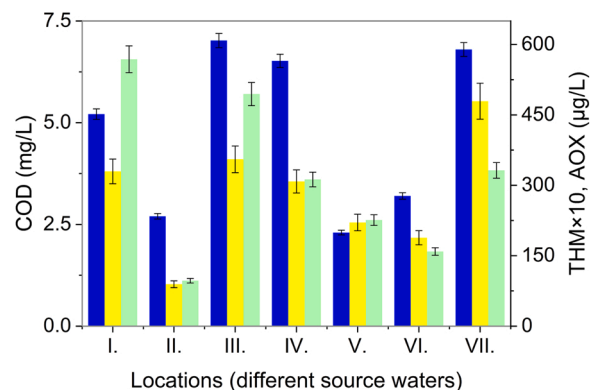
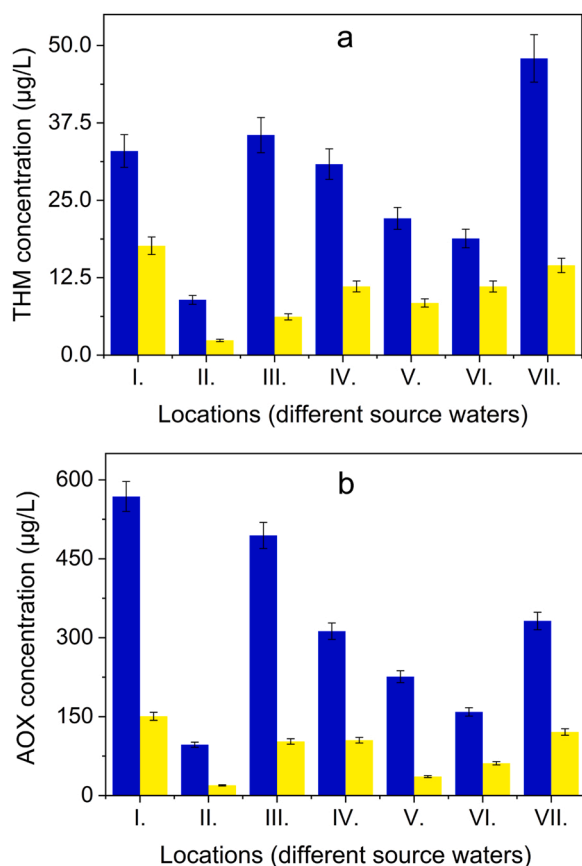


Fig. 2. The COD (blue) of different source waters and the concentration of THMs (yellow) and AOXs (green) generated during breakpoint chlorination. Locations: I: Apátfalva, II: Földeák, III: Királyhegyes, IV: Kismarja, V: Makó, VI: Nagyér and VII: Pocsaj. Sodium hypochlorite was used in 100% dose which corresponds to the 8.7 : 1 HOCl to  $\text{NH}_4^+$  mass ratio.

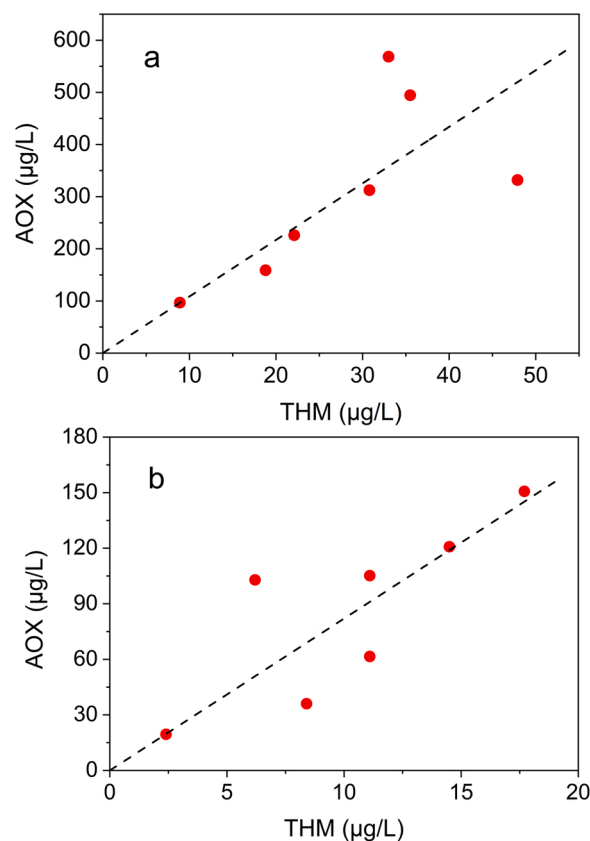




**Fig. 3.** The comparison of the formation of THMs (a) and AOXs (b) in raw (RSW, blue) and oxidatively pre-treated (OSW, yellow) source waters after breakpoint chlorination. Locations: I: Apátfalva, II: Földeák, III: Királyhegyes, IV: Kismarja, V: Makó, VI: Nagyér and VII: Pocsaj. Sodium hypochlorite was used in 100% dose which corresponds to the 8.7 : 1 HOCl to  $\text{NH}_4^+$  mass ratio.

were studied in detail (Rouge et al., 2020). Because of the differences in the experimental approaches, the results from that and our studies are difficult to compare directly. However, it is reasonable to conclude that the system used here decreases the formation of AOXs as or even more efficiently than the other oxidants in real source waters. In contrast, while the formation of THMs increased after pre-oxidation with all the strong oxidants mentioned, a substantial decrease was found in THMs by using the Fe(II)/Fe(III) – S(IV) – air system in this study. This difference is related to the differences of the redox chemistry of these systems. Apparently, the degradation of the organic contaminants leads to the generation of the precursors of the halogenated DBPs with the strong oxidants. A further benefit offered by the Fe(II)/Fe(III) – S(IV) – air system is the use of relatively inexpensive and easily applicable reactants. In comparison, the preparation and stabilization of a reagent ferrate solution is not a trivial task, and in situ generation of chlorine dioxide or ozone also present significant challenges. Under certain conditions the oxidation by permanganate is not efficient enough. The products formed from the reagents in the case of the Fe(II)/Fe(III) – S(IV) – air system (sulfate ion and Fe(III)) are considered to be non-toxic which is also a significant advantage. In accordance with these arguments, now we present a versatile new pre-oxidative method for drinking water treatment.

The acceptable concentration level of volatile halogenated hydrocarbons and THMs is regulated between 10 and 100 µg/L in European countries and the USA (Joint Research Centre, 1997). As shown in Table S2, satisfying the strictest limits is not feasible when the raw source water is chlorinated. Pre-oxidative treatment of the source waters with the Fe(II)/Fe(III) – S(IV) – air system makes possible to keep the



**Fig. 4.** The correlation between the concentrations of AOXs and THMs in the raw (a) and the pre-oxidized (b) source waters.

concentrations of the halogenated DBPs at the regulated or lower concentration levels.

#### 4. Conclusions

In this study, the concentration of oxidizable organic contaminants was significantly reduced with the Fe(II)/Fe(III) – S(IV) – air system in source waters. The results confirm that due to the oxidative pre-treatment halogenated DBPs (AOXs and THMs) form at considerably lower concentration levels during breakpoint chlorination. These results may serve as a basis for modifying drinking water treatment technologies for better controlling the formation of antagonistic halogenated DBPs. Reaching the regulated concentration levels of THMs is also feasible with this method. The main advantage of the procedure is that the reagents used for the oxidative pre-treatment are converted into non-toxic products (Fe(III) and  $\text{SO}_4^{2-}$ ) by the end of the process.

The obvious benefit of introducing the pre-oxidative process into water treatment technologies is the production of higher quality potable water. (Rouge et al., 2020) However, increased costs associated with this extra step raises valid concerns. In this respect, it is important to note that relatively inexpensive chemicals are used in the case of the Fe(II)/Fe(III) – S(IV) – air system. The products of the reactions may also enhance the coagulation of suspended materials, thus, reducing the required amounts of coagulants. More importantly, considerably less antagonistic products are formed during breakpoint chlorination in the oxidatively pre-treated water. Consequently, the savings in the cost of their removal from the treated water may substantially overcompensate the expenses of the oxidative pre-treatment. As an example, the reduced level of AOXs requires less frequent regeneration of activated carbon in the technology. An exact assessment of the financial balance would require detailed tests in a water treatment plant under optimized conditions.

## CRediT authorship contribution statement

**Alexandra Truzzi:** Investigation, Methodology, Data curation, Writing – original draft. **Boglárka Kovács:** Investigation, Methodology, Validation. **Ildikó Bodnár:** Resources, Supervision, Writing – original draft. **István Fábrián:** Conceptualization, Funding acquisition, Resources, Supervision, Writing – original draft.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2022.114036](https://doi.org/10.1016/j.ecoenv.2022.114036).

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