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Bromate formation potential during ozonation of wastewater treatment plant effluents

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ABSTRACT

Ozonation is an established advanced treatment process to transform organic micropollutants present in wastewater treatment plant effluents. In the presence of bromide, ozone treatment can cause formation of the oxidation byproduct bromate. Due to its potential carcinogenicity, its concentration in drinking water is regulated and limited to 10 μg/L in the European Union. Understanding relevant influences on bromate formation and potential control options is crucial to ensuring surface water quality and safe drinking water in case of semi-closed water cycles. This study investigates the bromate formation potential for four wastewater treatment plant effluents of the largest German city Berlin. Laboratory-scale ozonation experiments were conducted with varying ozone doses and bromide concentrations to determine bromate formation for different conditions that might occur during real operation. The results show native bromide concentrations of 0.14 to 0.32 mg/L and bromate concentrations of 0.3 to 1.3 μg/L for ozone consumptions around 0.7 mg/mg O_3/DOC at pH values between 7 and 8. This corresponds to bromate yields of 0.2 to 0.6% (mg/mg bromate/bromide). Splitting the ozone dose into multiple smaller doses proved to be an efficient bromate control option for high specific ozone consumptions, with up to 48% less bromate formation. The results underline that the bromate formation potential in Berlin wastewater treatment plants does not limit ozonation as advanced wastewater treatment, since bromate concentrations of all plants were significantly below the drinking water limit of 10 μg/L for specific ozone consumptions around 0.7 mg/mg O_3/DOC, even at artificially elevated bromide concentrations.

1. Introduction

Organic micropollutants (OMPs) such as pharmaceuticals, industrial chemicals, or pesticides are insufficiently removed by conventional wastewater treatment [1]. Thus, municipal wastewater treatment plants are major point sources of OMPs that affect the receiving surface waters and subsequent compartments of the water cycle [2,3]. Ozonation is an established advanced wastewater treatment process that reduces OMPs and partially transforms them into more biodegradable compounds [4,5]. The reduction of UV absorbance at 254 nm (ΔUVA_{254}) has been shown to be a suitable surrogate parameter for the removal of OMPs [6–8]. Aromatic moieties, often present in OMPs, and humic substances absorb light at the wavelength of 254 nm. The same moieties are attacked by the reaction of ozone, resulting in a decrease of both the UVA_{254} and the concentration of OMPs [3,8,9]. Information about aromaticity can be obtained from the ratio of UVA_{254} and DOC, which is called specific UV absorbance at 254 nm (SUVA) [10].

During ozonation, not only the targeted OMPs, but also other organic and inorganic compounds react with the highly reactive oxidant ozone. This can lead to the formation of undesired oxidation byproducts such as bromate (BrO_3^-). Bromate is formed during ozonation when bromide (Br^-) is present [11]. Residual waste incineration and subsequent wet scrubbers represent one of the main bromide sources in urban wastewater [12]. Other common bromide sources are chemical industries, landfills, and coal-fired power plants [12,13]. Therefore, the level of bromide concentrations strongly depends on the catchment area of a wastewater treatment plant (WWTP).

Bromate is classified as potentially carcinogenic and poses a risk for humans and animals [14]. Hence, a drinking water limit of 10 μg/L in the European Union (EU) and a recommended threshold of 50 μg/L in surface waters to protect aquatic environments were adjusted [15,16]. A much stricter surface water quality standard for bromate of 1 μg/L as

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annual average is in place in the Netherlands [17]. Therefore, it is important to understand its formation and to keep bromate formation low.

Bromate is formed by the oxidation of a bromide ion during water treatment with ozone. There are different bromate formation pathways, either directly with ozone, or indirectly with secondary oxidants such as hydroxyl (OH) radicals [11,18]. The direct reaction with ozone represents the main formation pathway [18,19]. The first step is usually the oxidation of the bromide ion to hypobromite and hypobromous acid that are in a pH dependent equilibrium. Due to higher reactivity, hypobromite reacts faster with ozone [11]. By further oxidation, hypobromite is oxidized to bromite and finally to bromate [11,18,19]. To assess bromate formation in the water, bromate yields are commonly used, which describe the ratio of the formed bromate concentration to the initial bromide concentration [20]. These yields can be expressed on either mass or molar basis; both are widely applied in wastewater treatment studies.

Bromate reduction measures and control options can be of substantial interest in wastewater treatment. The first option is to control the main drivers of bromate formation: bromide concentration and ozone dose. Moreover, the pH determines the equilibrium between hypobromite and hypobromous acid. One bromate formation reduction measure is pH decrease, slowing down bromate formation due to a shift to hypobromous acid [11,19]. Another reduction measure encompasses the addition of ammonia which inhibits bromate formation due to the fast reaction of ammonia with hypobromous acid to monobromamine [21]. Subsequent reaction with ozone causes an oxidation back to bromide and nitrate [18,21]. Another option to reduce bromate formation is the addition of hydrogen peroxide, which belongs to advanced oxidation processes (AOPs). Addition of hydrogen peroxide leads to a shorter lifetime of ozone due to the fast transformation of ozone to OH radicals. In addition, it reacts with the bromide intermediate hypobromous acid back to bromide, minimizing bromate formation [18,19,22]. Cheng et al. [23] demonstrated that in waters with low DOC concentrations, less bromate is formed with multiple lower ozone doses compared to one single dose. In practice, mostly the splitting of the ozone dose, as well as attempts to control bromide concentrations, are applied to mitigate bromate formation. All other measures have drawbacks, such as relatively high costs or chemical demands [19].

If bromate is formed in wastewater treatment processes, it only degrades under anoxic conditions [18]. Since oxygen concentrations are typically very high after ozonation (mostly above 20 mg/L), common biological post-treatment steps following ozonation, such as sand filtration, are not able to remove bromate [24–26].

This study investigates the bromate formation potential of four WWTPs in Berlin with a focus on ozonation experiments with varying bromide concentrations and ozone doses. Multi-stage dosing is examined as a bromate reduction measure. UVA_{254} reduction is used as a surrogate parameter for the efficiency of ozonation or OMP removal, respectively. Additional parameters such as pH and organic carbon composition are investigated to find potential correlations to bromate formation. Moreover, the analytical methods ion chromatography with conductivity detection and liquid chromatography-tandem mass spectrometry are assessed for bromate quantification in wastewater applications.

2. Material and methods

2.1. WWTP effluents

All investigated WWTPs follow a conventional treatment train, consisting of mechanical pretreatment, sand trap, primary sedimentation, activated sludge process including nitrogen and phosphorus removal, and secondary sedimentation. Standard quality parameters such as chemical oxygen demand (COD), dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP), total suspended solids (TSS), and pH of the effluents for 24-h composite samples are presented in Table 1.

Data from regular effluent monitoring was used to analyze bromide concentrations in the effluents of the four WWTPs within the period 2019–2024. Moreover, potential temporal trends (yearly, monthly, weekly, daily) were investigated. For most WWTPs, measurements originated from 24-h composite samples, while for WWTP C, only 2-h composite samples were available.

2.2. Laboratory-scale ozonation experiments

For the ozonation experiments, 80 L effluent grab samples were taken at each WWTP, brought to the laboratory and ozonated within the subsequent day. The samples of WWTP D were stored below 8 °C and ozonated within two days.

Bromide concentrations were adjusted by spiking respective volumes of a bromide stock solution (1000 mg/L in pure water) to obtain 0.3 mg/L, 0.6 mg/L, and 1.0 mg/L besides the native concentrations. For native bromide concentration equal to or higher than 0.3 mg/L, only three different concentrations (i.e., native, 0.6 mg/L, and 1.0 mg/L) were tested.

The ozonation experiments were conducted with a laboratory-scale ozonation plant (Fig. 1). The ozonation plant consists of a 4 L glass reactor, electric stirrer, diffusor, water trap to dehumidify the airflow before detection, ozone generator (Modular 8 HC from Wedeco GmbH), and residual ozone destructor. Measurement devices (ozone analyzer BMT 964 from BMT Messtechnik) measure the ozone concentration in the in- and outflow constantly which enables an automatic calculation of the ozone consumption by a mass balance.

The reactor was filled with 4 L of the unfiltered water sample and closed. The ozone inflow concentration ($C_{O3,\ in}$) in the ozone generator was adjusted to around 10 mg/L and the gas flow was set to 1 L/min. The ozone generator stopped automatically when the target dosage was reached, and ozone was stripped with the oxygen flow. Samples were taken after the ozone concentration in the off-gas reached 0.0 mg/L.

For each bromide concentration, three experiments with varying ozone doses were conducted. Specific ozone consumptions (CN) were adjusted to target values of 0.3, 0.7, and 1.0 mg/mg O_3/DOC, which present common ozone consumptions in water treatment and OMP removal [27]. Additional experiments were conducted for 1.0 mg/L bromide with three individual ozone doses to achieve specific consumptions of 0.33 mg/mg O_3/DOC each.

The ozone dose (D), required to reach a target specific ozone consumption (CN_{target}), was calculated based on ozone-consuming water quality parameters, the measured DOC and nitrite concentrations (c_{DOC} and $c_{NO2\text{-}N}$), according to Eq. (1). Nitrite reacts quickly with ozone and therefore leads to additional ozone consumption, which was considered by the value 3.43 mg/mg O_3/NO_2-N [25]. Since the ozone consumption is lower than the ozone dose due to ozone losses with the off-gas, the formula was adjusted by a factor (f) of 1.3 to 1.5, depending on experience. Higher factors were used for higher target ozone consumptions, the exact factors can be found in Table S1 in the supporting information.

$$D = \left(CN_{target} * c_{DOC} + 3.43 * c_{NO2-N}\right) * f \tag{1}$$

2.3. Analytical methods

All samples were filtered by vacuum filtration with cellulose nitrate filters with 0.45 μm pore size (Sartorius Stedim Biotech GmbH, Germany) and stored in glass bottles at temperatures below 8 °C until analyses.

Bromide, nitrite, and DOC were measured before the ozonation experiments to calculate the respective ozone doses. Bromide and nitrite were measured by ion chromatography (IC) for anions and conductivity detection [28]. The DOC was also measured based on the respective standard [29]. With the ozone consumption obtained from the

Table 1

Standard quality parameters for each WWTP effluent (2023) with standard deviations and number of measurements indicated in brackets.

Parameter	WWTP A	WWTP B	WWTP C	WWTP D
COD [mg/L]	40.4 ± 4.2 (178)	36.0 ± 5.3 (116)	32.5 ± 4.6 (181)	37.2 ± 5.4 (175)
DOC [mg/L]	13.4 ± 2.4 (24)	11.9 ± 2.0 (31)	11.2 ± 2.5 (46)	13.2 ± 3.2 (38)
TN [mg/L]	11.7 ± 1.9 (62)	10.9 ± 2.1 (91)	10.6 ± 1.8 (48)	11.4 ± 3.3 (46)
TP [mg/L]	0.3 ± 0.1 (63)	0.4 ± 0.2 (116)	0.4 ± 0.1 (24)	0.6 ± 0.1 (46)
TSS [mg/L]	4.2 ± 1.9 (178)	7.2 ± 8.9 (117)	3.8 ± 1.5 (48)	4.5 ± 1.4 (46)
pH [−]	7.8 ± 0.2 (12)	8.1 ± 0.2 (16)	7.6 ± 0.2 (12)	7.9 ± 0.2 (12)

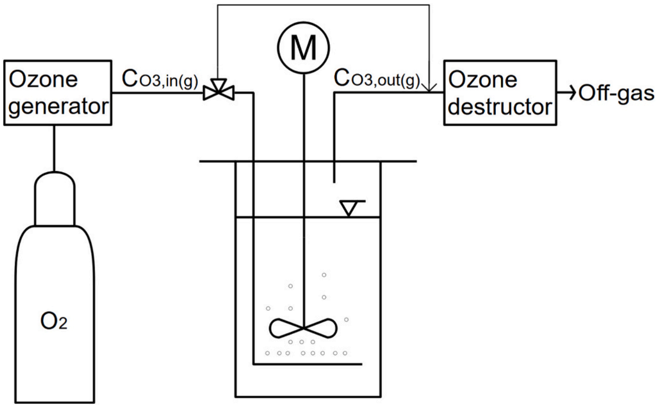

Fig. 1. Ozonation plant with a simplified gas flow.

ozonation experiments, and the measured oxidation of nitrite, the corrected DOC specific ozone consumption (CN_{DOC}) could be examined according to Eq. (2). For all nitrite concentrations below the limit of detection (LOD) of 0.05 mg/L, complete consumption (0 mg/L) was assumed.

$$CN_{DOC} = CN - 3.43^{*}\left(\frac{c_{NO2-N,in} - c_{NO2-N,out}}{c_{DOC}}\right) \tag{2}$$

The pH was measured for all samples after filtration by electrochemical measurement using a pH meter at ambient temperature.

Organic carbon was characterized by LC-OCD (liquid chromatography-organic carbon detection), a size-exclusion chromatography with continuous carbon analyses.

UVA_{254} was measured for all water samples by the UV/VIS spectrophotometers Perkin-Elmer Lambda 2 and Nanocolor UV/VIS II from Macherey-Nagel.

Bromate concentrations were determined for the ozonated samples, as well as the native samples (not treated with ozone) in order to preclude contamination. Since ion chromatography with conductivity detection (IC-CD) is a common measurement method for assessing bromate in drinking water [30,31], this method was examined for the application in wastewater. Measurement and detection were performed by 930 Compact IC Flex from Metrohm with the separation columns Metrosep A Supp 7–250/4.0 and Metrosep A Supp 16 Guard/4.0. According to Metrohm, the columns should provide a limit of quantification (LOQ) of 1 μg/L of bromate if chloride can be separated sufficiently [32]. Additional measurements by IC-CD were conducted (by an external laboratory) with pretreatment by silver cartridges in order to precipitate chloride and avoid a potential overlapping of the bromate peak [31]. Diluted samples (1:2 with ultrapure water) were measured as well to decrease potential influences of high chloride concentrations. Additionally, the peak recognition was decreased to be able to quantify lower concentrations. Due to inconclusive results from IC-CD measurements and potential problems with the wastewater matrix, an alternative measurement method was necessary.

Additional measurements were conducted with liquid chromatography-tandem mass spectrometry (LC-MS/MS) using a Thermo Scientific mass spectrometer with a limit of quantification of 0.2 μg/L. An internal bromate standard (100 μg/L with ^{18}O, Cambridge Isotope Laboratories) was added to all samples. The reversed phase column Phenomenex Synergi 4u MAX-RP 80 A was used in combination with ultrapure water with 0.1% formic acid and varying amounts of methanol as mobile phases.

For bromate concentrations below LOD, it was assumed that no bromate was formed (measured with LC-MS/MS). Since targeted specific consumptions were not achieved, bromate formations were interpolated for comparison.

3. Results and discussion

3.1. Bromide concentrations in WWTP effluents

Box-plots of the bromide concentrations from 2019 to 2024 presented in Fig. 2 exhibit median bromide concentrations between 0.1 and 0.2 mg/L for WWTPs B to D. WWTP A had significantly higher bromide concentrations, mostly exceeding 0.3 mg/L. All WWTPs showed strong variations of bromide concentrations with maximum values of almost 1 mg/L. The measured bromide concentrations are in a reasonable range for a large city as Berlin, since bromide concentrations up to 0.1 mg/L can be explained by background concentrations, whereas higher concentrations can be related to anthropogenic sources [12]. Bromide effluent concentrations in the range of 0.1 to 0.4 mg/L can be related to small and medium bromide sources in the catchment area, such as industries using bromide-containing biocides. Typical big bromide sources that may explain elevated bromide effluent concentrations are residual waste incineration, coal-fired power plants in the catchment area, or internal sludge incineration [12,13]. Internal investigations indicate that some airlines use bromide-containing disinfectants for airplane toilets, which are discharged into the sewer system leading to WWTP A. Moreover, brominated flame retardants are commonly used in airplanes

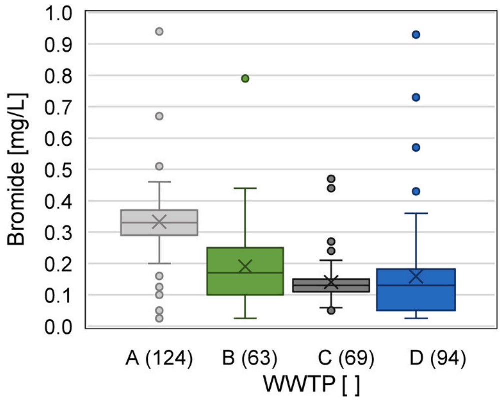

Fig. 2. Distribution of bromide concentrations 2019–2024 for the four WWTPs A, B, C, D with number of measurements indicated in brackets.

[33]. Through cleaning procedures at the airport, these bromide-containing compounds could be released into the sewage system.

Long-term, seasonal, weekly, and daily bromide concentrations showed no clear variation pattern (Fig. S1 and S2, in the supporting information). Slightly higher bromide concentrations in colder months can be related to varying weather conditions and the potential use of bromide-containing road salt, even though common de-icing agents are sodium chloride and calcium chloride [34,35]. Industrial production processes can explain marginally higher bromide concentrations during working days. Daily bromide concentrations were stable but increased steeply on Thursday night for WWTP D (Fig. S2). A potential reason could be a bromide containing discharge in one industrial batch. This measurement underlines the large variety of bromide concentration depicted in the box-plots (Fig. 2).

3.2. *Ozonation experiments*

The pH measurement results showed constant pH values of all WWTP effluents, independent of the ozone consumption (Fig. S3). Multi-stage dosing of ozone seemed to increase the pH slightly, which might be caused by an increased stripping of CO_2 due to the longer experiment duration.

The results in Fig. 3 show that the ΔUVA_{254} increased with rising ozone consumption. The correlation results from the reaction of ozone that preferably attacks compounds with electron-rich moieties such as aromatic rings or unsaturated carbon bonds with a high absorption of UV light at 254 nm [5,9]. At ozone consumptions of approximately 0.7 mg/mg O_3/DOC, UVA_{254} decreased by 39–44% for all WWTP effluents, which is in line with values from Sauter et al. [24] and Stapf et al. [10]. Since ΔUVA_{254} has been shown to be a suitable surrogate for OMP abatement [8], the results also demonstrate that typical OMP reductions were reached in the ozonation experiments. Splitting the ozone dose into three partial doses did not affect the UVA_{254} reduction compared to a single ozone dose. Within the investigated range of ozone consumption, the ΔUVA_{254} was independent of bromide concentrations. Higher bromide concentrations, however, might lower the achieved ΔUVA_{254} [36].

The slopes of all graphs decrease with higher ozone consumption, which leads to the assumption that aromatic and unsaturated compounds are already strongly removed at relatively low ozone consumptions, and a further increase of the ozone addition yields lower additional ΔUVA_{254} gains due to the decreasing amount of reaction partners. These findings are confirmed by a study of Chon et al. [6], where the reduction of UVA_{254} was more efficient for O3:DOC ratios below 0.35 mg/mg O_3/DOC. A few studies describe that fast-reacting OMPs such as carbamazepine were effectively removed (more than 80%) at low ozone doses, due to their olefinic or phenolic structure and therefore, high reactivity with ozone [6,37,38].

3.3. *Oxidation of bulk organic carbon*

The LC-OCD results presented in Fig. 4 show the organic carbon composition of all WWTP effluents, where the retention time is related to the size of the molecules [39]. A difference in the resulting organic carbon composition for varying bromide concentrations could not be observed, which is why only the samples with spiked bromide concentrations (1.0–1.1 mg/L) are depicted. The organic carbon composition was similar for all WWTPs, where bigger compounds such as biopolymers were detected first, followed by humics and building blocks, the smaller humic hydrolysates, and lastly low molecular mass (LMM) acids and neutrals [39,40]. Larger compounds, such as biopolymers, could be found in higher concentrations in the effluent of WWTP A, while the effluent of WWTP D showed lower concentrations of humic substances, which represent the major fraction in all native WWTP effluents. Particulate organic carbon (POC) may have been oxidized and subsequently dissolved during ozonation. Since the concentration of humic hydrolysates (building blocks) increased with increasing ozone consumption, it is likely that POC was mostly transformed into building blocks. Consequently, this fraction became available for detection and can be observed in an increase in building blocks and LMM acids [5,41]. Oxidative breakage of bonds might explain the slight decrease of bigger compounds, such as biopolymers, with increasing ozone consumption.

3.4. *Bromate formation during ozonation*

Measurements with IC-CD led to insufficient bromate detection. Consequently, the alternative measurement method LC-MS/MS was used to enable bromate detection in low concentration ranges. Results on bromate formation in Fig. 5 show that most of the bromate concentrations were below the German drinking water limit of 10 μg/L [42]. Solely samples with high bromide concentrations above 1 mg/L treated with high ozone doses above 0.8 mg/mg O_3/DOC resulted in higher bromate concentrations (WWTP A-C). Moreover, bromate formation could only be observed for ozone consumptions above 0.3 mg/mg O_3/DOC and increased with increasing bromide concentration and ozone consumption. For ozone consumptions above 0.6 mg/mg O_3/DOC, bromate concentrations increased more steeply. Multi-stage dosing seemed to reduce bromate formation, especially for higher ozone consumptions. These results confirm that electron-rich dissolved organic

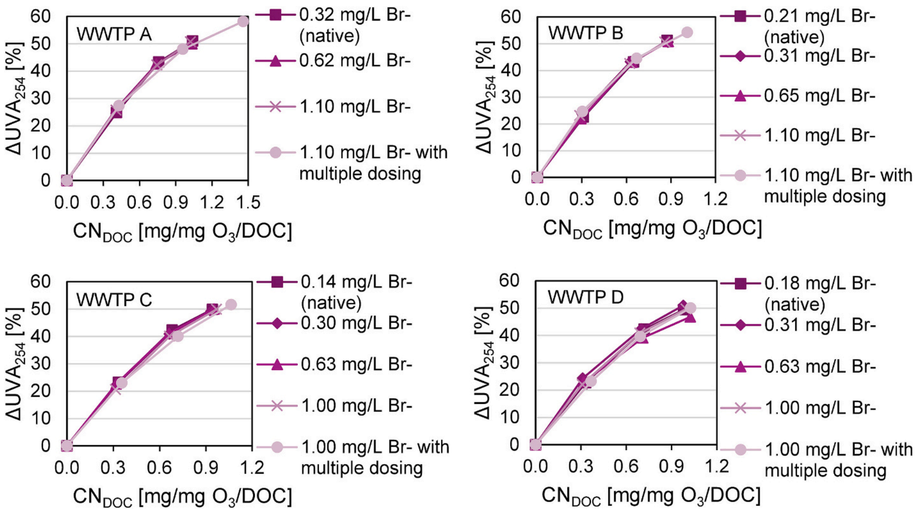

Fig. 3. Reduction of UVA_{254} in all WWTP effluents without (native) and with three different bromide additions prior to ozonation, depending on the specific nitrite-corrected ozone consumption.

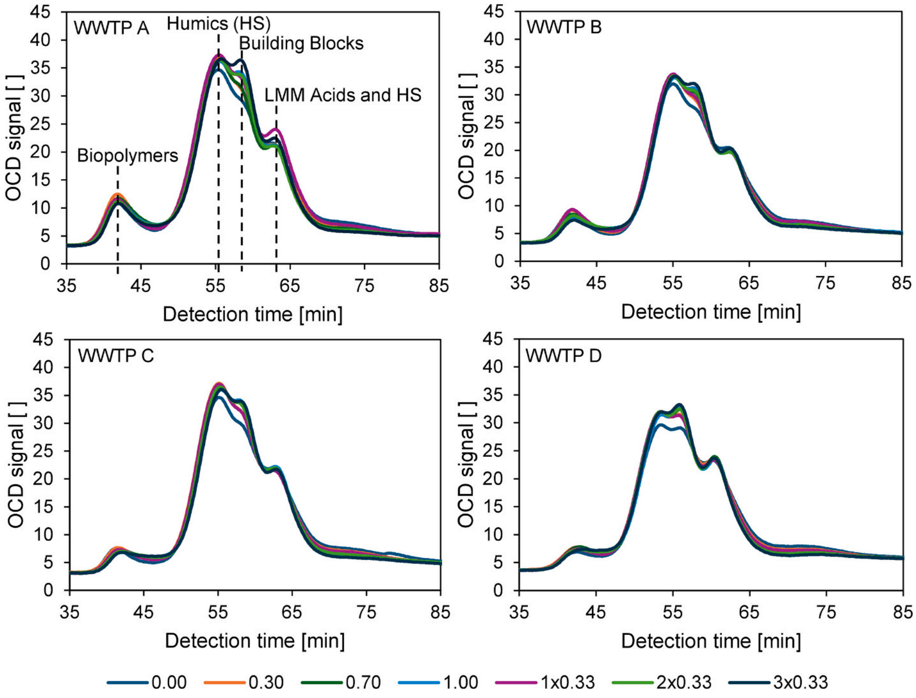

Fig. 4. Organic carbon chromatograms for all WWTP effluents with 1 mg/L spiked bromide. The lines present different ozone consumptions in mg/mg O_3/DOC. Local maxima of organic fractions are presented for WWTP A.

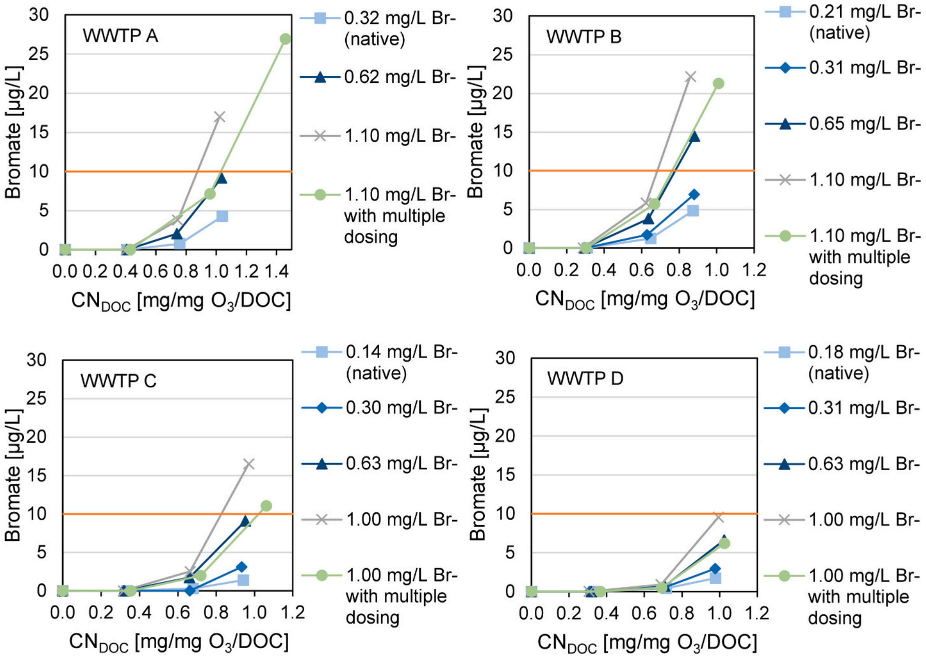

Fig. 5. Bromate concentrations depending on the specific nitrite-corrected ozone consumption and bromide concentration (the orange line represents the German drinking water limit of 10 µg/L).

matter (DOM) moieties are attacked first before enough ozone or OH radicals are available to react with bromide to form bromate [5,43]. For low ozone doses, there are not enough ozone residuals to react with bromide intermediates and therefore, no bromate is formed [6,12,19]. Organic electron-rich compounds are consumed before bromide can react, leading to lower bromate formation.

The relation between ΔUVA_{254} and bromate formation indicates, that higher bromate concentrations could be found for higher ΔUVA_{254} and higher bromide concentration (relation shown in Fig. S5). For UVA_{254} reduction above 40%, bromate formation increased more steeply. Similar results were found in previous studies from Ruffino et al. [36] and Li et al. [44]. Multi-stage dosing of ozone exhibited the same UVA_{254} reduction as single dosing but lower bromate formation for similar total ozone consumptions. The benefit of divided ozone dosage should be considered in the planning stages of ozonation plants while setting target UVA_{254} reduction.

3.5. Interpretation of bromate yields

Fig. 6 depicts the bromide-specific bromate yields for all WWTP effluents depending on the ozone consumption, describing the share of bromate formed from bromide. Bromate yields increased with increasing ozone consumption, more steeply for consumptions above 0.6 mg/mg O_3/DOC. Within the investigated range, the bromide concentration seemed to have a minor influence on the bromate yields. Solely for WWTP C, bromate yields increased slightly with increasing bromide concentrations. The treatment with multiple ozone doses led to lower bromate yields for all WWTPs. This effect was most noticeable at high ozone consumptions, whereas at the target consumption of 0.7 mg/mg O_3/DOC and lower, multi-stage dosing had only a marginal impact on bromate yields. However, for samples with bromide concentration of 1.0–1.1 mg/L and a target ozone consumption of 1 mg/mg O_3/DOC, bromate yields could be reduced by approximately 35–48% with multi-stage dosing compared to one single dose.

Higher bromate yields in the effluent of WWTP B than in other WWTPs might be related to parameters, such as DOM characteristics, pH, carbonates, and nitrite, which affect ozone exposure and therefore bromate formation [3]. Potential scavengers such as DOC or carbonate can influence bromate formation, since they quickly react with OH radicals and in turn decrease the availability of OH radicals to react with organic compounds [25,45]. In waters with high DOC concentrations, fewer OH radicals react with ozone, which results in higher oxidation capacities [25]. Therefore, more ozone might be available to react with bromide intermediates to form bromate. This effect would explain the higher bromate yields for WWTP B (11.4 mg/L DOC for WWTP A, 12.7 mg/L for WWTP B, 11.1 mg/L for WWTP C, 9.9 mg/L for WWTP D). Wang et al. [46] stated on the other hand that bromate formation decreases with higher DOC in drinking water due to fast reactions of natural organic matter with bromide intermediates back to bromide. Hence, the effect of DOC concentration on bromate formation seems to be diverse. In order to evaluate the difference in bromate yields, more experiments are needed regarding the effect of the water matrix on ozone stability and bromate formation.

Nevertheless, differences between the WWTP effluents were minor, and bromate yields were relatively low. For single ozone dosing, WWTP B showed maximum bromate yields of 2.3% mg/mg BrO_3^-/Br^- and 1.4% mol/mol BrO_3^-/Br^- for an ozone consumption of 0.87 mg/mg O_3/DOC. Reported bromate yields are around 8% (in mg/mg BrO_3^-/Br^-) and 5% (in mol/mol BrO_3^-/Br^-) for a specific ozone dose of 0.8 mg/mg O_3/DOC [6,12,20]. Next to the individual water matrix, the experiment setup and reactor configuration of ozonation can influence bromate yields. In semi-batch experiments, less bromate seems to be formed compared to batch experiments, due to higher concentrations of dissolved ozone in batch [10,40]. Moreover, the DOC concentrations of the investigated WWTP effluents are relatively high compared to 4–6 mg/L from other studies dealing with OMP removal [38,47].

Another potential correlation could be found between bromate yield and aromaticity. The SUVA and DOC concentrations of the WWTP effluents without ozone treatment presented in Table 2 show that the SUVA in the effluent of WWTP B was significantly lower, indicating a lower aromaticity. Lower aromaticity means fewer aromatic compounds available for a direct reaction with ozone or a lower reactivity of DOM, which could result in increased reaction of ozone and bromide. Therefore, a lower SUVA in the WWTP effluent might be an indicator for higher bromate yields.

3.6. Prediction of bromate formation

The results depicted in Fig. 7 indicate that an exponential trendline can be assumed to estimate bromate yields during ozonation, based on similar dependencies found in previous studies [12,36,44]. In addition to the correlations mentioned, decrease of fluorescence could also be used for the estimation of bromate yields [36,44].

The commonly used specific ozone consumption did not show a substantial relation with bromate yields (Fig. 7 (a)), caused by the different DOC moieties, such as aromatic compounds in the effluents, which would explain the shifted yields for WWTP B. Even the nitrite-corrected ozone consumption without relation to DOC concentration ($CN_{DOC,total}$) shows higher correlations with bromate yields (Fig. 7 (c)),

Table 2
DOC concentrations and SUVA for all WWTP effluents, measured for samples without ozone treatment.

Parameter	WWTP A	WWTP B	WWTP C	WWTP D
DOC [mg/L]	11.4	12.7	11.1	9.9
SUVA [L/(mg*m)]	2.6	2.0	2.6	2.5

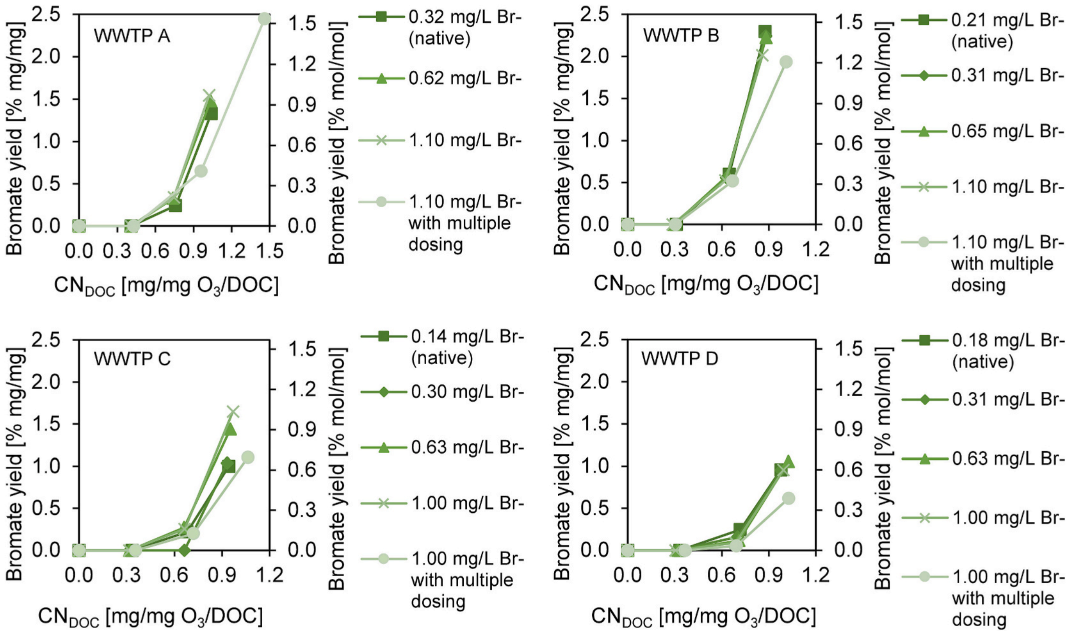

Fig. 6. Bromide-specific bromate yields depending on the nitrite-corrected ozone consumption.

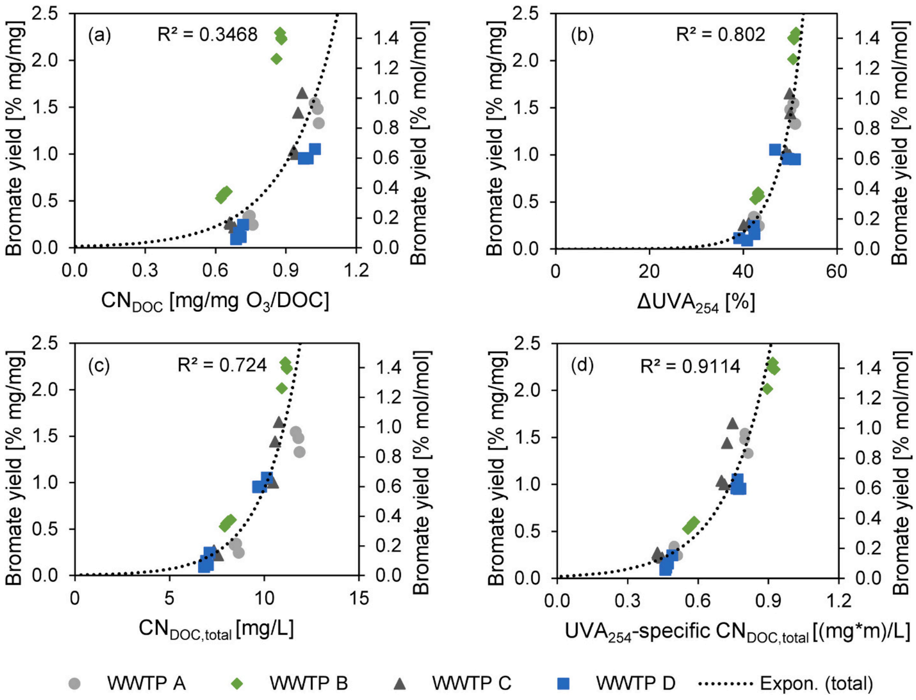

Fig. 7. Relations of relative bromate formation with (a) specific nitrite-corrected ozone consumption, (b) ΔUVA$_{254}$, (c) nitrite-corrected ozone consumption and (d) UVA$_{254}$-specific nitrite-corrected ozone consumption for initial bromide concentrations of 0.14–1.1 mg/L.

indicating that the total DOC concentration might have a lower influence on bromate yields than the individual DOC moieties. The correlation of bromate yields with ΔUVA$_{254}$ is more significant (Fig. 7 (b)), which supports the link of bromate formation with aromatic compounds. The highest coefficient of determination (R^2) with 0.91 could be found for the correlation with the UVA$_{254}$-specific ozone consumption (Fig. 7 (d)). This parameter combines the dependencies of bromate yields on ozone consumption and UV absorption related to aromatic compounds, indicating that this presents the most applicable estimation for WWTP-independent bromate yields.

4. Conclusions

This study investigated the bromate formation potential during ozonation of WWTP effluents, with the following main outcomes:

- Bromate formation directly depends on the initial bromide concentration and ozone consumption. Bromate was only formed at ozone consumptions above 0.3 mg/mg O$_3$/DOC and the concentrations increased more steeply above 0.6 mg/mg O$_3$/DOC.
- Bromate concentrations of all WWTP effluents were below the German drinking water limit of 10 μg/L for an ozone consumption of 0.7 mg/mg O$_3$/DOC. Even a significant increase in bromide concentration does not lead to an exceeding of the drinking water limit.
- Bromate yields increased with rising ozone consumption and were mostly independent of the bromide concentration within the investigated range. The splitting of ozone dose into multiple partial doses revealed a reduction of up to 48% in bromate yields and proved to be an efficient bromate control option, especially for high ozone consumptions.
- The UVA$_{254}$-specific ozone consumption enabled an accurate estimation of WWTP-independent bromate yields. Confirming this relation by further investigation would enhance transferability and could serve as a helpful tool for predictions of bromate formation.

CRediT authorship contribution statement

Hannah Katharina Seibel: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Daniel Sauter:** Writing – review & editing, Supervision, Conceptualization. **Regina Gnirss:** Writing – review & editing, Supervision, Funding acquisition. **Aki Sebastian Ruhl:** Writing – review & editing, Funding acquisition, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2026.110168.

Data availability

Data will be made available on request.

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