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QUATERNARY WASTEWATER TREATMENT

RESEARCH ARTICLE

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Bromides in treated wastewater: limiting the choice of quaternary wastewater treatment technologies for residual micropollutant removal. An Estonian case study

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ABSTRACT

The recent changes in the European Union Wastewater Directive require micropollutant elimination from the effluents of wastewater treatment plants serving at least 150 000 population equivalents, and in some cases even starting from 10 000. While ozonation can degrade micropollutants without secondary wastes, the treated effluent composition must be considered, specifically the concentration of bromide (Br^-). Depending on its amount and oxidant dose, bromide can potentially be oxidised to carcinogenic bromate (BrO_3^-). This research investigates bromide amounts in the effluents of Estonian wastewater treatment plants serving at least 10 000 population equivalents as preliminary work for quaternary wastewater treatment aimed at micropollutant removal.

Introduction

Quaternary treatment for micropollutant removal: legislation

The latest amendments to the EU Wastewater Directive (European Union 2024), which are currently being adopted by legislations, demand that all the wastewater treatment plants (WWTPs) that serve at least 150 000 population equivalents (p.e.) are to adopt quaternary treatment for the elimination of micropollutants. In the EU, there are currently 24 971 operating WWTPs, among which 933 serve at least 150 000 p.e. (Water News Europe 2024). Additionally, WWTPs serving 10 000 p.e. and above may also have to introduce quaternary treatment if their discharge area is considered sensitive to micropollutants, e.g. locations where the dilution rate of the WWTP discharge is low, the discharge goes to water bodies used as drinking water sources, for the growth and production of shellfish, or for bathing purposes. Quaternary treatment is to be fully operational from 2045, with intermediate results expected by 2033.

According to the amendments to the Wastewater Directive, WWTPs must monitor and remove at least 80% of the following micropollutants:

- first category (relatively easily removable compounds): amisulpride, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, and venlafaxine;
- second category (relatively easy to handle compounds): benstriasol, candesartan, irbesartan, and a mixture of 4-methylbensotriasol and 6-bensotriasol.

Micropollutant removal methods

In the literature, numerous technologies, notably Advanced Oxidation Processes (AOPs), are proposed for the elimination of micropollutants, including ozonation (assisted or catalysed), Fenton and Fenton-like systems, adsorption, photocatalytic oxidation, plasma-based treatment methods, and more. While they can degrade literally any kind of pollutants until total mineralisation, that is too costly; combining moderate AOP treatment with biological treatment was shown to efficiently eliminate even the most recalcitrant pollution in a far more sustainable way (Klauson et al. 2015; Klein et al. 2017; Trapido et al. 2017). However, not all of these AOPs are readily

scalable and applicable. Real-life practical applications use technologies that are already operational and have shown multiple proofs of efficiency, narrowing the choice mainly to ozonation and activated carbon adsorption.

Ozonation, both through molecular ozone and radicals, can degrade micropollutants up to complete mineralisation. Due to the relatively high cost of ozone production, partial degradation of the micropollutants into non-toxic and biodegradable by-products is more cost-efficient than outright mineralisation. The ozone dosage choice for the real-life micropollutant removal is more complicated, as the biggest consumer of oxidants is the wastewater matrix. This requires an empirical approach coupled with the measurements of required micropollutants. There are some indications from the authors' previous experience that small doses of ozone, in the range of several mg/L, may degrade micropollutants selectively, without being affected by the general wastewater matrix and without affecting it significantly (Klauson et al. 2019).

Adsorption is an equilibrium mass-transfer process: a higher concentration of a substance dissolved in the aqueous phase results in a higher amount of it adsorbed on the surface of activated carbon. Consequently, micropollutants are a minority of the substances adsorbed by the activated carbon before its surface is filled, and it needs replacement. Spent activated carbon, with its surface laden with concentrated micropollutants and other compounds, becomes a hazardous waste or produces such upon regeneration.

Bromides in wastewater: a possible threat

Bromide (Br^-) in municipal wastewater may originate from several sources, including groundwater with seawater intrusion, relict seawater, surface water bodies fed by groundwater sources, groundwater infiltration into wastewater, and discharges of bromine-disinfected swimming pools or cooling water. These are gaining popularity, as bromine is a more efficient oxidant than chlorine, being simultaneously less irritating (WHO 2018). In the presence of strong oxidants, the bromide ion is prone to stepwise oxidation, terminating in the formation of the carcinogenic bromate anion. In the case of bromide-containing water ozonation, the following reactions take place, both with molecular ozone and OH-radicals (Morrison et al. 2023):

$$Br^- + O_3 \rightarrow BrO^- + O_2, \quad (1)$$

$$BrO^- + H^+ \rightleftarrows HOBr, \quad (2)$$

$$BrO^- + O_3 \rightarrow BrO_2^- + O_2, \quad (3)$$

$$HOBr + O_3 \rightarrow BrO_2^- + O_2 + H^+, \quad (4)$$

$$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2, \quad (5)$$

$$BrO_2^- + O_3 \rightarrow \bullet BrO_2 + \bullet O_3^-, \quad (6)$$

$$2 \bullet BrO_2 \rightleftarrows Br_2O_4, \quad (7)$$

$$Br_2O_4 + H_2O \rightarrow BrO_2^- + BrO_3^- + 2\,H^+, \quad (8)$$

$$Br^- + \bullet OH \rightarrow \bullet Br + OH^-, \quad (9)$$

$$\bullet Br + O_3 \rightarrow \bullet BrO + O_2, \quad (10)$$

$$\bullet BrO + O_3 \rightarrow \bullet BrO_2 + O_2, \quad (11)$$

$$\bullet BrO_2 + \bullet OH \rightarrow BrO_3^- + H^+. \quad (12)$$

Radical reactions (see Eqs (9)–(12)) are known to have a significant role in ozonation only at alkaline pH (e.g. Asgari et al. 2017). At conditions closer to neutral, as expected in the WWTP effluents, their role is marginal, leaving the reactions of molecular ozone as the main pathway. At near-neutral pH, ca 96% of the hypobromite ion formed in reaction (1) exists in water as hypobromous acid (HOBr), as its pK_a is 8.65 (Perrin 1982). This is a potent disinfectant and brominating agent. Its oxidation to bromite (Eq. (3)) is a slow process compared to that of the hypobromite ion, with the second-order rate constants being 0.01 L/(mol × s) for Eq. (4) and 100 L/(mol × s) for Eq. (2), respectively (Morrison et al 2023). While reaction (5) was originally proposed to describe the oxidation of bromite to bromate (Haag and Hoigne 1983), more recent research (Odeh et al. 2004) suggests that the mechanism is somewhat more complex, as described by Eqs (6)–(8). Additionally, the hypobromite anion formed in reaction (1) can undergo reduction by ozone, partially reverting to bromide (Morrison et al. 2023):

$$BrO^- + O_3 \rightarrow Br^- + 2O_2. \quad (13)$$

Moreover, in many places around the world, WWTP effluents are disinfected by chlorine-based chemicals before the discharge. That can be described by the following reaction equations (Mestri et al. 2023):

$$Br^- + HOCl \rightarrow Cl^- + HOBr, \quad (14)$$

$$HOBr + HOCl \rightarrow HBrO_2 + Cl^- + H^+, \quad (15)$$

$$HBrO_2 + HOCl \rightarrow BrO_3^- + Cl^- + 2\,H^+. \quad (16)$$

The maximum level of bromate allowed in drinking water is 10 mg/L (European Union 2020); due to the absence of straightforward guidelines for treated discharged wastewater, this figure could be used as a benchmark in this situation. It has been previously suggested (CWPharma 2020) that potentially unsafe bromide concentrations could be 0.15 mg/L when applying ozone doses above 0.7 mg O_3/mg DOC.

This way, bromides in wastewater impose constraints on the method choices for micropollutant abatement. While ozonation is generally considered to be almost free from side

effects, the presence of bromide requires preliminary studies and process fine-tuning before actual applications. Adsorption, inevitably producing large amounts of concentrated wastes, can be applied in cases where ozonation would seem too risky.

So far, no meaningful bromide removal from water has been shown in the literature. While there have been studies addressing biological, physical, and physico-chemical processes, they largely fail: only reverse osmosis and, to a smaller extent, nanofiltration have provided efficient results (Chowdhury et al. 2022). However, these are not the methods to be applied to the average WWTP effluent. While some studies provided decent to good results for selective ion exchange, these worked well in low-ionic-strength waters, while adding other ionic admixtures present in real-life WWTP effluents lowered bromide removal efficiency drastically (Chowdhury et al. 2022). Consequently, any real-life WWTP treatment aimed at micropollutant removal must face the challenges and restrictions posed by bromides in water.

Estonian groundwater: hydrogeological context

The Republic of Estonia is a country in Northern Europe, situated on the eastern coast of the Baltic Sea. With a population of roughly 1.34 million, Estonia has only two WWTPs serving over 150 000 p.e., namely, in Tallinn, the capital city, and Tartu, the second-largest city. However, some of the municipalities with WWTPs serving at least 10 000 p.e. may also be affected by the micropollutant-connected changes in the EU Wastewater Directive, based on the discharge area risk assessment. Around 2/3 of Estonian drinking water consumption originates from groundwater, the composition of which is strongly affected by the history of the Baltic Sea formation in the geological past. Figure 1 shows the hydrogeological map of Estonia.

Geologically, Estonia is situated on the southern slope of the Baltic Shield, with sedimentary beds inclined southwards by 2–4 m/km, underlain by a porphyritic granite crystalline basement (Karro et al. 2009). The upper part of the basement is partially fractured and contains saline water. The basement is overlain, in turn, by clay minerals from basement granite weathering, Vendian and Cambrian siltstone and sandstone, Silurian and Ordovician limestone, middle-Lower and Middle Devonian siltstone and sandstone, and is finally covered by Quaternary deposits made up mostly of glacial till, glaciolacustrine deposits, and glaciofluvial sand (Karro et al. 2004; Karro et al. 2009). The water-bearing sedimentary rock beds are separated by clay-based aquitards.

In the northernmost part of Estonia, including ca 10% of Tallinn, groundwater from the Cambrian–Vendian aquifers (0.3–2 g/L of the total dissolved solids, TDS) is used; the water-bearing layers are composed of sandstone and are separated by limestone and clay. They are connected to the sea at the bottom of the Gulf of Finland, some 20 km from the shoreline (Karro et al. 2004), making bromide-containing saltwater intrusion a naturally occurring phenomenon. In general, the Cambrian–Vendian aquifer is recharged in Southern Estonia and flows northward at a velocity of 0.0005–0.005 m/d (Karro et al. 2004). This way, the mineral composition of the Cambrian–Vendian groundwater is mainly affected by the water–rock interaction geochemistry (Karro et al. 2004). Additionally, local recharges with modern water take place in buried erosional valleys, formed in the pre-Quaternary interglacial, glacial, and postglacial times. At least 10 larger and around 20 smaller buried valleys have been detected along the Northern Estonian coast (Karro et al. 2004).

At the same time, the Cambrian–Vendian groundwater layer is underlain by more saline water in the fractured crystalline basement, with up to 51–61 mg/L Br^- and up to 5 g/L TDS (Karro et al. 2004). This way, the coastline-related Cambrian–Vendian groundwater wells in the Northern Estonian plain can experience increased salinity due to both seawater intrusion and saline groundwater intrusion, giving bromide levels of up to 4 mg/L. As the Cambrian–Vendian water pumped close to the seashore has a higher Br^-/Cl^- ratio than the seawater from the Gulf of Finland, underlying saltwater levels with an increased bromide content seem to be the main source of elevated bromide concentrations in the northernmost Estonian groundwater (Karro et al. 2004).

The largest city in Northern Estonia, Tallinn, gets around 90% of its water from Lake Ülemiste, situated within the city borders and mainly fed by surface waters from Central Estonia. On the contrary, in other areas of Northern Estonia, around 3/4 of water supply comes from the Cambrian–Vendian aquifer (Karro et al. 2004). In North-Eastern Estonia, due to mining activities, saltwater intrusion into the Cambrian–Vendian aquifers is the most pronounced, resulting in the increased content of salts, including those of barium (up to 6.4 mg/L) (Karro et al. 2009).

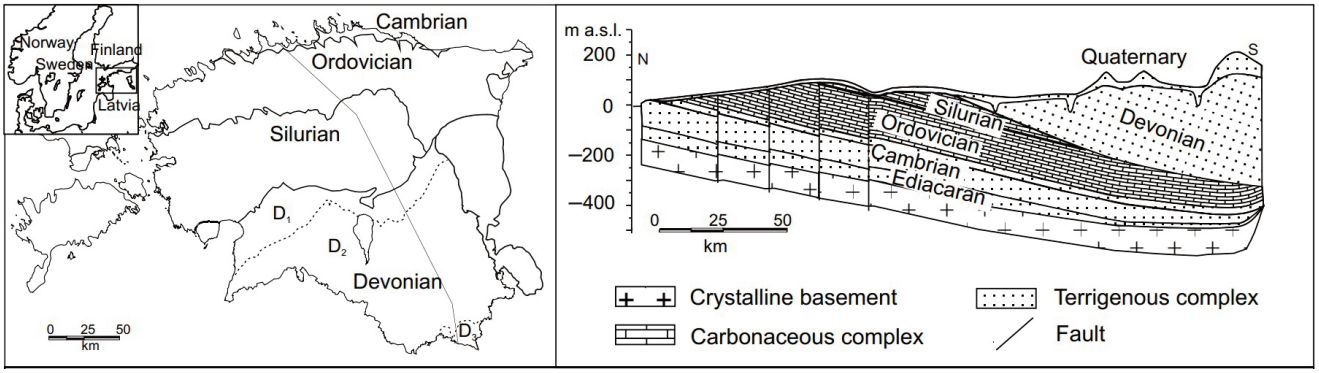

Fig 1. Groundwater map of Estonia (adapted from Karro et al. 2020).

Northern, Western and Central Estonia get their groundwater from the Silurian–Ordovician aquifers, where the water-bearing rock is composed of layers of limestone and dolomite. It consists of interbedded 1–2 m thick carbonaceous zones with lateral water flow, separated by 5–10 m thick fissured zones where water flows vertically (Karro et al. 2009). With the carbonaceous rocks karstified, especially in the upper 30 m (Karro et al. 2009), the aquifer allows rapid refilling of the layer, along with fast contaminant transport. Therefore, Central Estonia with its agricultural lands is a nitrate-sensitive area, where the mainly agricultural pollution, including nitrates and pesticides, ends up in deeper water layers, used as drinking water sources. Groundwater in Western Estonia is known to have pockets of relict seawater: it has elevated concentrations of salts, including above 6 mg/L of F^- and above 2 mg/L of B, together with elevated concentrations of Cl^- and Br^-. The Silurian–Ordovician groundwater has TDS of 0.2–1.5 g/L (Karro et al. 2009).

Southern Estonia uses groundwater from the Devonian aquifers, where the water-bearing rock is again siltstone and sandstone. South-Eastern Estonia is characterised by the availability of relict seawater; in the easternmost part of Southern Estonia, some relict seawater layers have a relatively high mineral content (up to 22 g/L TDS), and brackish mineral water is produced there in Värska. The Middle Devonian water is the most widely used groundwater in Southern Estonia; the water has low salt content (0.2–0.6 g/L TDS), with its characteristic mineral additive being iron, reaching up to 26 mg/L (Karro et al. 2020). The second-largest Estonian city, Tartu, uses both the shallower Devonian and the deeper Silurian–Ordovician wells.

Materials and methods

Sampling was carried out during 2022–2023 in 10 Estonian WWTPs serving 10 000 p.e. or more, with each site sampled twice. Bromide concentrations were measured by a modification of the standard N,N-diethyl-p-phenylenediamine (DPD) method: one droplet of 0.1 N $Na_2S_2O_3$ was added to 50 mL of sample to remove any possible interference from oxidants, with two minutes taken as reduction time. This was followed by 1 mL of 3% H_2O_2. After five-minute oxidation, 10 mL of the obtained solution was taken and measured according to the HACH DPD Method 8016: a sachet of DPD was added to the solution, and the measurement was carried out after one minute of colour development at the wavelength of 530 nm. The calibration made by the authors allowed measurements in the range of 0.01–2.25 mg/L Br^-, with the determination coefficient of $R^2 = 0.907$. The measurement results were double-checked using a bromide-sensitive electrode HI716 by Hanna Instruments (minimal detection practically 0.1 mg/L Br^-). The difference between the two methods was within the limits of analytical precision, while the photocolorimetric method, having greater sensitivity, was employed as the main measurement approach. Additionally, the following parameters were measured: pH, dissolved oxygen, redox potential, electrical conductivity, total phosphorus and nitrogen, ammonium (bromate formation suppressor), nitrites (ozone consumers) and nitrates, suspended solids (ozone consumers, hydraulic load), chemical oxygen demand, total organic carbon, and dissolved organic carbon (main ozone consumer). The measurement parameters were selected to cover the key factors in planning quaternary wastewater treatment.

Results and discussion

Bromides in the analysed WWTP effluent

For the sake of discretion of the companies involved, Fig. 2 shows the results as the average composition of the analysed WWTP effluents. As the analysed WWTPs have different discharge requirements (above 10 000 p.e. and above 100 000 p.e.), the variability in values is noticeable.

The results show an average of 0.12 mg Br^-/L, with a minimum concentration of 0.07 mg Br^-/L and an observed maximum of 0.24 mg Br^-/L. Figure 3 shows the geographic distribution of the results and the concentration ranges. What is interesting to note is that the proximity to the sea, often regarded by default as a source of seawater intrusion and a source of bromides, is not a direct pre-requisite to high bromide content in the WWTP discharge.

Role of nitrogen species

Nitrites present in the WWTP plant effluents show that the nitrification is incomplete. While the detected amounts (average 0.2 mg/L) are not significant in terms of WWTP effluent discharge, they affect quaternary treatment by consuming part of the ozone for the oxidation to nitrates, which at the average effluent pH proceeds via molecular reactions:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2. \quad (17)$$

As shown earlier (CWPharma 2020), the amount of ozone for micropollutant degradation in the presence of nitrites can be calculated as follows:

$$D(O_3) = D_{DOC} \times DOC + 3.43 \times C(NO_2^-), \quad (18)$$

where $D(O_3)$ is the calculated ozone dosage (mg O_3/L), D_{DOC} is the DOC-specific ozone dosage (0.3 to 0.9 mg O_3/(mg DOC)) (CWPharma 2020), DOC is the dissolved organic carbon content in mg/L, and $C(NO_2^-)$ is the concentration of nitrite in the wastewater (mg/L).

Accordingly, for an average Estonian WWTP effluent with a DOC of ca 30 mg/L, the determined amount of nitrite (0.2 mg/L) increases the ozone dosage by 3% to 10%. With an average ozonation energy consumption of 10 kWh/kg O_3 (Sarron et al. 2021) and an average electric energy price of 0.25 EUR/kWh, this may result in additional costs of ca 1500 to 70 000 EUR, depending on the WWTP and the required ozone dosage when using liquefied oxygen (LOX) as the ozone source. When using treated outdoor air to produce oxygen, this additional cost can be in the range of 1700 to 81 000 EUR annually. This highlights the importance of efficient nitrification before micropollutant removal using ozonation.

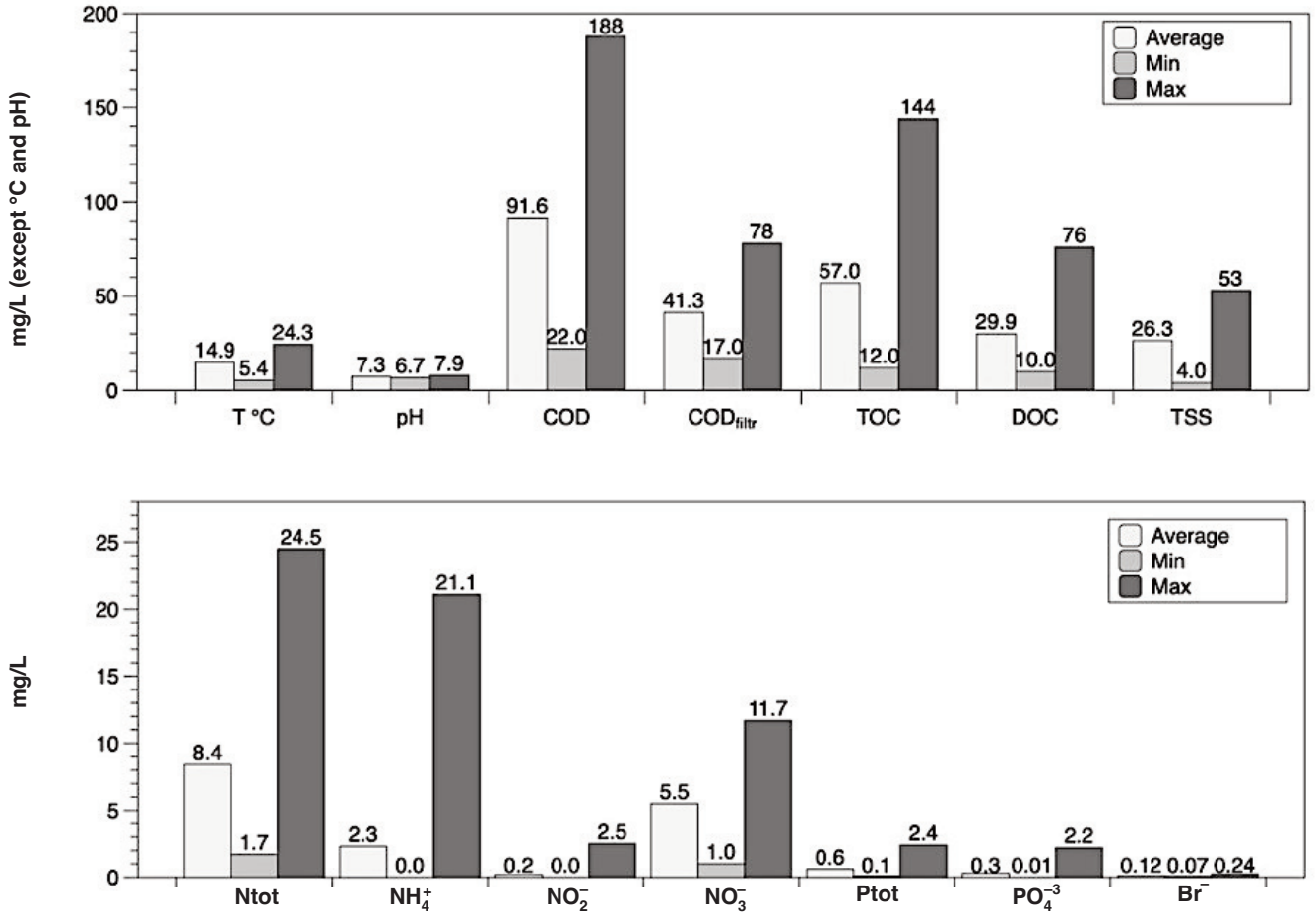

Fig. 2. The average composition of wastewater treatment plant effluents analysed in this study.

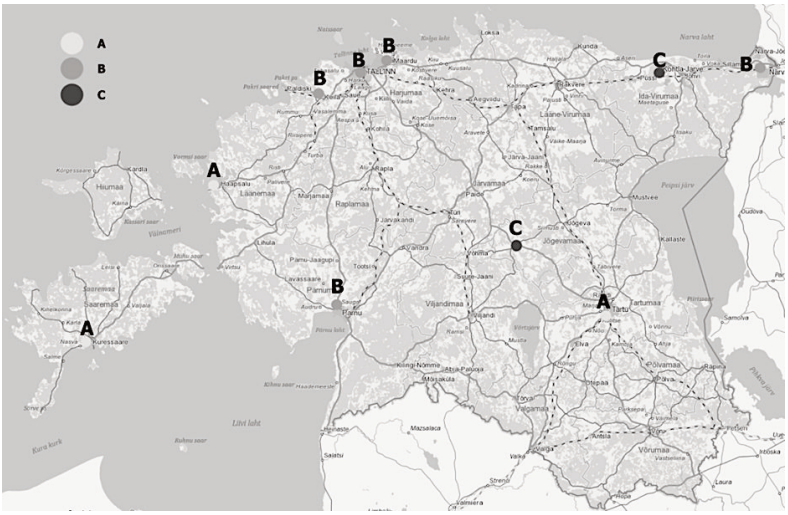

Fig. 3. Geographic distribution and concentrations of Br^- in wastewater plant effluents: <0.1 mg/L Br^- (A), 0.1–0.14 mg/L Br^- (B), and ≥0.15 mg/L Br^- (C). Map source: Land and Spatial Development Board of Estonia.

The presence of ammonium (average detected 2.3 mg/L) in WWTP effluents has more far-reaching effects. During ozonation at the near-neutral WWTP effluent pH = 7.3, reactions of molecular ozone prevail; unlike radicals, molecular ozone cannot oxidise the ammonium ion to a noticeable degree (Hoigne and Bader 1978). When subjecting bromide-containing water to ozonation, excess amounts of NH_4^+ were shown (e.g. Morrison et al. 2023) to supress bromate formation. Hypobromous acid, formed from hypobromite at pH values lower than 8.65, readily reacts with hypobromite to form monobromamine (NH_2Br), as shown in the following equation:

$$HOBr + NH_4^+ \rightarrow NH_2Br + H_2O + H^+. \quad (19)$$

Reaction (19) effectively removes hypobromites and hypobromous acid, considerably hindering their possible oxidation to bromates. It also undergoes ozonation, with

bromide and nitrate ions being the major products, as suggested in the following equation:

$$NH_2Br + 3\,O_3 \rightarrow Br^- + NO_3^- + 3\,O_2 + 2\,H^+. \quad (20)$$

While hypobromous acid reacts with ammonium (Eq. (19)) quickly, then the degradation of monobromamine by ozone (Eq. (20)) is slow. For example, for reaction (19), Morrison et al. (2023) provide a reaction rate constant of 5.5–7.5 × 10^7 L/(mol × s) for ideal conditions, suggesting that it may decrease by up to two orders of magnitude in practice. To compare, the rate constant for reaction (18) is 40 L/(mol × s). Thus, monobromamine forms ca 10 000 times faster than it degrades.

While bromide oxidation reactions are reported as second-order, both ozone and ammonia are present in large excess relative to bromide (with ozone constantly replenished). Consequently, to estimate the ozonation products' concentration, the pseudo-first-order kinetics can be used. Additionally, a continuous stirred-tank reactor (CSTR) model should be applied to continuous-flow ozonation, thus giving the following equation to operate with:

$$C_t = \frac{C_0}{1 + k't}, \quad (21)$$

where k' is the pseudo-first-order reaction rate constant (1/s), t is the reaction time (s), and C_0 is the initial concentration of the respective compound (mol/L).

The pseudo-first-order reaction constant can be obtained by multiplying the second-order rate constant k_2 by the initial concentration of the reagent in excess (ozone or ammonium), e.g.:

$$k' = k_2 \times C_0(O_3). \quad (22)$$

Additionally, the amounts of ozone available for the oxidation reactions, which have moderate reaction rate constants at earlier stages, can be deduced as the difference between the supplied ozone (20 mg O_3/L for the average WWTP effluent) and the ozone consumed by the DOC and the nitrate present in water (see Eq. (17)). For an average ozone dose of 0.6 mg O_3/mg DOC, with DOC = 30 mg/L and 0.2 mg/L NO_2^-, this would result in 18.7 mg O_3/L, making 1.3 mg O_3/L available for bromide oxidation.

The initial oxidation of bromide to hypobromite (Eq. (1)) is reported to have a reaction rate constant of 160 L/(mol × s). Thus, a 30-minute ozonation of 0.15 mg/L of bromide results in the nearly 90% conversion and the formation of ca 0.16 mg/L BrO^-. The hypobromite ion is conjugated with hypobromous acid, having a pK_a = 8.65 (Perrin 1982). The amount of dissociated hypobromous acid at any given pH can be determined as follows:

$$\omega(BrO^-) = 10^{pH - pK_a(HOBr)}. \quad (23)$$

The calculation according to Eq. (23) suggests that, at pH = 7.3, only 4.5% of the formed hypobromite remains in ionic form, while all the rest transforms into hypobromous acid on formation. While this remaining hypobromite can be reduced to bromide, according to Eq. (13), hypobromous acid undergoes fast conversion to monobromamine. Up to 2/3 of the formed monobromamine degrades according to reaction (20), producing nitrates and bromides, while around 0.05 mg/L NH_2Br could be expected to remain in the treated WWTP effluent after a 30-minute ozonation under such conditions. These calculations suggest that, for the average effluent of an Estonian WWTP serving at least 10 000 p.e., ozonation should lead to the formation of monobromamine as opposed to bromate due to the large excess of ammonium.

To compare, the kinetics of stepwise bromide-to-bromate oxidation within 30 minutes of ozonation reaction can be calculated, starting likewise with 0.15 mg/L bromide but without ammonium. There, the formation of bromate can be calculated to ca 0.06 mg/L using the more refined electron-transfer approach (Eqs (6)–(8)). Longer contact times and higher concentrations of both bromide and ozone would allow reaching the dangerous 10 mg BrO_3^-/L threshold, but a 30-minute contact time with average ozone doses seems to rule out that possibility at least in theory. Also, up to 0.15 mg/L hypobromous acid is expected to accumulate. Figure 4 sums up the major reactions taking place in bromide ozonation, both in the absence and in the presence of dissolved ammonium.

It must be noted that with the concentrations of this magnitude, mass transfer will impose additional limitations on the formation of the products; the undertaken analysis results in higher concentrations than could be achieved in reality. This kinetic study was envisioned not to provide

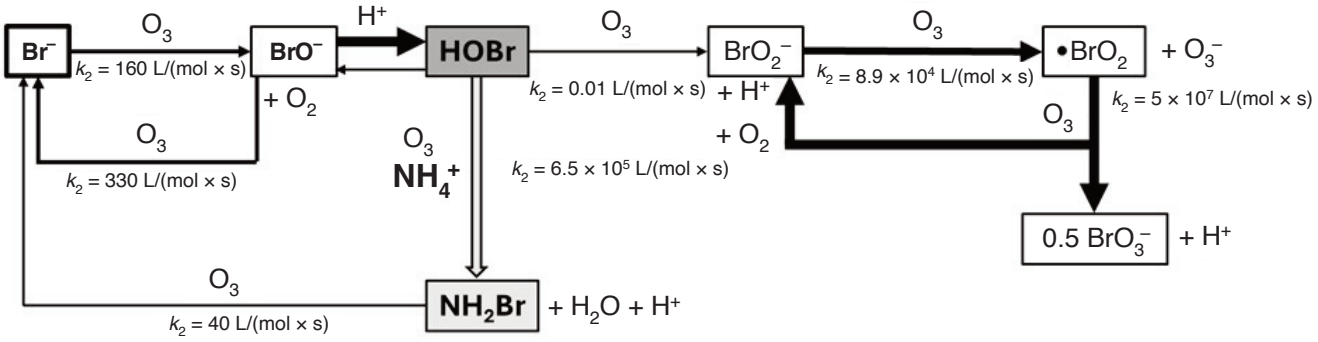

Fig. 4. Major reactions during bromide-containing water ozonation. Arrows reflect the relative reaction rate; major transformation products are in bold. Dark grey background: products obtainable without ammonium, light grey background: products obtainable in the presence of ammonium.

absolute values but as a comparison to provide an insight into the probability of obtaining different bromine-containing products. Mass transfer-induced restrictions would not, however, change the principle qualitative outcomes in terms of obtained products.

Consequently, the average effluent of an Estonian WWTP serving at least 10 000 p.e. is not expected to produce enough bromates on ozonation, with the ammonium present suppressing bromate formation. Instead, monobromamine formation takes place. If the ozonation step is followed by a biofilter, the expected amounts of monobromamine may affect the biofilter performance. The degradation of monobromamine by ozonation alone is time-consuming. In the absence of ammonium, significant formation of bromate would also not be expected according to the kinetic calculations, resulting in the formation and accumulation of hypobromous acid.

To estimate the outcomes of bromide-containing water ozonation in terms of bromide oxidation, one must compare the three distinct products formed: bromate, hypobromous acid, and monobromamine. The direct comparison of the three compounds' aquatic toxicity is not possible, as hypobromous acid and monobromamine are not stable enough to conduct the toxicity tests. Their instability is manifested through reactions forming brominated organics that can be more hazardous than bromate. Consequently, it is highly imperative to consider their reactions with polyaromatic natural organic matter (NOM), which, for the sake of simplicity, we can model here with phenol. Phenol has a pKa value of ca 10 (PubChem 2025), meaning that, at pH = 7.3, it is almost exclusively in molecular form, with only around 0.2% dissociated to the phenolate anion. However, the phenolate anion has a very high reactivity compared to the undissociated molecule, with the $-O^-$ group activating the aromatic cycle through resonance better than the undissociated -OH group: the respective reaction rate can vary by several orders of magnitude in favour of phenolate (Gallard et al. 2003). Once phenolate is reacted, a portion of phenol dissociates to maintain the equilibrium.

In terms of compound toxicity and direct hazards, bromate certainly poses the greatest threat. While bromate is a strong oxidant in theory, the kinetics of organics oxidation by it are very slow, and its bromination ability is the weakest among these three compounds. This is due to high stability of the bromate anion, arising from its tetrahedral shape, resonance stabilisation, and a relatively high number of electrons needed to reduce it. Bromate can react at reasonable rates only with strong reducing agents; these are typically not found in natural waters, including WWTP discharges, but are abundant inside cells (sulfide groups and disulfide bridges in proteins, Fe^{2+}, amino groups in proteins and nucleic acids, etc.), resulting in bromate toxicity and carcinogenicity, as we know it. Consequently, neither NOM in general nor phenol (neither molecule nor the phenolate ion) are affected by bromate as an oxidant or a brominating agent to any noticeable degree.

Hypobromous acid, on the contratry, presents a real danger through the electrophilic substitution reactions it initiates with NOM. HOBr is a strong brominating agent with the respective reaction rates being high, e.g. bromination of phenol proceeds with the apparent reaction rate constant of up to 3.5×10^5 L/(mol × s) (Gallard et al. 2003), taking into account the individual reactions of molecular HOBr and phenol, HOBr and the phenolate ion, hypobromite and the phenolate ions, and the degree of dissociation of HOBr and phenol at pH = 7.3. As an outcome of these reactions, C–Br bonds are created, which easily break and form in different places in photochemical reactions in the environment, leading to the formation of various brominated compounds. During ozonation, the bromination of organic compounds by HOBr creates specific sites for ozone to attack – the carbon atom which had its adjacent hydrogen replaced by bromine, leading to the rupture of aromatic cycles and the production of numerous trihalomethanes (THMs) and other compounds generally referred to as disinfection by-products or DBPs. Many brominated organic compounds, including DBPs, can be considered more dangerous than bromate (Wu et al. 2019).

Finally, in the case of monobromamine, we need to take into consideration its pH-related equilibrium before proceeding with the discussion. An experimentally determined monobromamine pK_a has been reported, due to the compound's relative instability over a wider range, with 6.5 (Johannesson 1960) being perhaps the most cited figure. Taking that into account would mean that, at pH = 7.3, ca 84% of monobromamine is present in the neutral molecular form (see Eq. (23) describing the hypobromite/hypobromous acid pH equilibrium), while the remaining 16% is present as the monobromammonium ion NH_3Br^+, which is a stronger electrophile and therefore more reactive, primarily attacking phenolate anions. Consequently, bromination of phenol at neutral media by monobromamine has the reaction rate of ca 1.3×10^2 L/(mol × s) (Heeb et al. 2017). The rate of phenol bromination by monobromamine is thus three orders of magnitude slower than in the case of HOBr, resulting in the lower formation of brominated organics and bromine-containing DBPs. At the same time, monobromamine degrades by ozone (see Eq. (40)), in addition to undergoing several self-decomposition pathways, producing bromide, gaseous nitrogen, nitrate, nitrogen oxides, etc. (Hu et al. 2021). Consequently, monobromamine reacts relatively slowly and degrades by various mechanisms at a comparable rate, liberating the bromide ion back to the solution. Based on this, the availability of ammonium in the solution appears to summarily shield the bromide anion from any meaningful oxidation that could result in the formation of either directly hazardous bromate or hypobromous acid, which is a precursor to even more hazardous brominated organic compounds, in any meaningful amounts.

These findings allow the authors to suggest that ozonation can in principle be applied to remove micropollutants in the quaternary treatment of WWTP effluents aimed at the abatement of micropollutants, even if the bromide anions are present. However, the amounts of the bromide anions must be firmly estimated, and the availability of ammonium – either deliberately added or remaining from incomplete nitrification – must be assured in order to obtain monobromamine instead of hypobromous acid, the precursor to various brominated

organic compounds. To assure that no bromate is produced in significant amounts, the pH of the treated effluents must be kept below 8, where the role of radical reactions in ozonation is negligible. Any additives that can be used to enhance OH-radical production (H_2O_2, Mn^{2+}, MnO_2, etc.) must likewise be avoided, and no chlorination of the effluent is advised. Additionally, at pH above 8, the alkalinity of water, i.e. carbonates and bicarbonates produced by both organic matter degradation and carbonaceous materials dissolution (Tenno et al. 2018), scavenges hydroxyl radicals, producing enough carbonate radicals. These radicals can oxidise the hypobromite ions at a reaction rate constant of 4.3×10^7 L/(mol × s) (Morrison et al. 2023), enabling the formation of bromates. A further detailed experimental investigation into these matters in the context of Estonian WWTP effluents is currently underway.

Conclusions

The goal of the current research was to map the concentration of bromide (Br^-) in Estonian wastewater treatment plant (WWTP) effluents, identifying areas where the potential use of ozonation for the micropollutant removal in WWTP effluents requires special attention. The results show that among the 10 studied WWTPs throughout Estonia, two measuring sites are clearly above the 0.15 mg/L Br^- threshold suggested by the earlier studies, with another five staying close to it (0.11–0.14 mg/L Br^-). Consequently, for most of the analysed WWTP effluents, the possibility of safely implementing ozonation as the means to remove micropollutants, while backed by kinetic analysis presented in this paper, must still be proven experimentally before undertaken in practice. Moreover, the possible disinfection by chlorination of these effluents would not be advised. An experimental study into this is currently conducted by the authors and is a basis for future publications.

Taking into consideration the composition of an average effluent of Estonian WWTPs serving 10 000 population equivalents or more, the preliminary ozonation conditions (ozone dose 20 mg O_3/L, contact time 30 minutes) suggest that the formation of bromates (BrO_3^-) in significant amounts is not to be expected, based on the available knowledge of reaction kinetics. Instead, monobromamine (NH_2Br) is expected as the main bromine-containing by-product, due to the presence of significant amounts of ammonium in the effluents. In the absence of ammonium, hypobromous acid (HOBr) is the dominant bromine-containing product. This substance is a fast and strong brominating agent, leading to the formation of brominated organics, which is more dangerous than bromate. In comparison, monobromamine seems to be a far more harmless compound, brominating organics ca 1000 times slower than hypobromous acid and degrading simultaneously, with the release of bromide.

The research also results in the general awareness of potential challenges caused by bromide in wastewater, including those arising from the implementation of the latest version of the EU Wastewater Directive. The continuation of this research, which is currently in progress, aims to evaluate the experimental applicability of ozonation as a quaternary treatment technology and to elaborate the working conditions under which ozonation may be considered safe.

Data availability statement

All research data are contained within the article and can be shared upon request from the authors.

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Bromiidid puhastatud reovees: kvaternaarsete reoveepuhastusmeetodite valiku piirangud jääk-mikrosaasteainete eemaldamisel. Eesti juhtumiuuring

Deniss Klauson, Erki Lember ja Jaak Jaaku

Töös uuritakse bromiidide sisaldust vähemalt 10 000 inimekvivalenti teenindavate Eesti reoveepuhastusjaamade heitvees. Bromiididel (Br^-) võib olla oluline roll kvaternaarsete puhastusmeetodite valikul mikrosaasteainete eemaldamiseks heitveest, mida hakkab nõudma peatselt jõustuv uuenenud Euroopa reoveedirektiiv. Nimelt võib bromiide sisaldava vee osoonimisel tekkida kõrvalproduktina ohtlike omadustega bromaate (BrO_3^-); autorite varasemad uuringud on näidanud, et ohtlikuks piiriks võib olla 0,15 mg/L Br^-. Töö käigus tehtud analüüsid näitavad, et ainult 20% reoveepuhastusjaamadest on bromiidide sisaldus heitvees selgelt alla ohtliku piiri, 60% jaamades on see piiripealne ja 20% jaamades märgatavalt suurem. Samas näitab keskmise heitvee koostise põhjal tehtud kineetiline analüüs, et põhilised broomi sisaldavad kõrvalsaadused on pigem monobroomamiin (NH_2Br) ja hüpobroomishape (HOBr). See vajab praktilist kinnitust katselisel viisil, mis kajastub autorite järgnevates publikatsioonides.