

Conversion of organic micropollutants with limited bromate formation

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Conversion of organic micropollutants with limited bromate formation during the Peroxone process in drinking water treatment

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Abstract

Advanced oxidation with O_3/H_2O_2 (peroxone) is conducted on pilot plant scale on pre-treated Meuse river water to investigate the conversion of organic micropollutants (OMPs) and the formation of bromate. Fourteen selected model compounds are dosed to the pre-treated river water on a regular basis to assess the efficiency of the peroxone process and to establish the influence of the water matrix.

The height of the ozone dose is the main factor in the conversion of the model compounds. The conversion of OMPs can be increased by further increasing the ozone dose, however, the ozone dose is limited concerning the bromate formation. The hydrogen peroxide dosage has only a minor effect on the conversion, but it limits the bromate formation effectively. In terms of limited chemical consumption, maximal conversion and adherence to the strict Dutch guideline for bromate in drinking water, a practical full-scale setting is 6 mg L^{-1} hydrogen peroxide and 1.5 mg L^{-1} ozone. During the investigation period, the average conversion of the model compounds was 78.9%.

The conversion of OMPs is higher at higher water temperatures and lower concentrations of DOC and bicarbonate. The bromate formation also is higher at higher water temperature and lower bicarbonate concentration and proportional with the bromide concentration, above a threshold of about $32 \mu\text{g L}^{-1}$ bromide, below which no bromate is formed. The peroxone process can be controlled on basis of the (derived) parameters water temperature, bicarbonate and DOC.

1 Introduction

All over the world surface water is to some extent contaminated with organic micropollutants (OMPs). It is expected that concentrations of OMPs will increase, due to growth and aging of populations and global warming. In areas with a shortage of groundwater, drinking water companies use the available surface water as source for drinking water production. They are more and more aware of the fact that conventional treat-

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ment technologies, such as coagulation, filtration and activated carbon filtration, are not adequate in removing OMPs from the surface water. The combination of the increasing concentrations of OMPs in surface waters and the inadequate removal of the more polar OMPs with conventional treatment processes, necessitate research on an additional barrier against OMPs.

Drinking water company Dunea, in the western part of the Netherlands, recognizes the threat of OMPs in their source the Afgedamde Maas (Enclosed Meuse), a side branch of the Meuse River, although at the moment the drinking water quality still complies fully to the standards of the Dutch Drinking Water Law, including the standards for OMPs. Mainly the managed aquifer recharge (MAR) by dune filtration and the dosing of powdered activated carbon (PAC) are the current barriers against these substances.

Only nonpolar OMPs are well removed by MAR and PAC. Polar OMPs are less well adsorbed and/or converted (Ijpelaar, 2008). OMPs with biological activity, such as pharmaceuticals and pesticides are of concern to drinking water utilities, because of their possible long term effects, the possibility of mixture effects and the sensitivity for customer perception. Pharmaceuticals and pesticides are main contaminants detected structurally in the Dutch Meuse River (Houtman et al., 2010). However, the effect on human health at low concentrations at present is judged negligible (Schriks et al., 2010; Houtman et al., 2014).

Membrane filtration and advanced oxidation (AOP) are the two common technologies to reduce concentrations of OMPs in pretreated surface water. After careful consideration, Dunea chose advanced oxidation as most optimal technique (Abrahamse et al., 2007) and carried out research with these technology. When AOP is installed before MAR, it is expected that this two processes will provide a synergistic hybrid system (Lekkerkerker-Teunissen et al., 2012).

In comparison with other AOP technologies, the O_3/H_2O_2 (or peroxone) process, is known as very energy efficient. The two mechanisms to convert OMPs are direct oxidation by ozone and oxidation by in-situ produced hydroxyl radicals ($\cdot OH$). The reaction rate of direct oxidation depends on the type of compounds, but is relatively slow

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of ozone and increasing the ratio between the hydrogen peroxide and ozone doses (von Gunten, 2003b).

Bromate formation is affected by the varying water matrix parameters pH, water temperature, bromide and bicarbonate. Two other parameters, dissolved organic carbon (DOC) and ammonia, appeared to be not of relevance for the water matrix of the pre-treated enclosed Meuse. According to Croué et al. (1996) and Amy et al. (1993) bromate is formed proportionally when the ratio of ozone dose and DOC is exceeding 0.4 mgO₃/mgC and maximal contact times are applied. The ratio applied in this project is significantly lower than 0.4. The role of ammonia (ammonia can depress the bromate formation) could be neglected, because only in a short period (weeks) the concentration was higher than the detection limit of 0.02 mgNL⁻¹, which is too low for limiting bromate formation.

The goal of this research was to optimise the use of peroxone, restricted by a bromate target value of 0.5 µgL⁻¹, considering the maximum ozone concentration that can be applied, as well as the minimum ozone/hydrogen peroxide ratio and the corresponding conversion of OMPs. The influence of the water matrix, the ozone dose and the hydrogen peroxide concentration on the bromate formation and the conversion of OMPS were investigated in an on-site pilot plant set-up, with batch experiments and long term duration experiments.

2 Materials and methods

2.1 Peroxone process installation

The pilot plant existed of an ozone loop reactor and an ozone generator, from Xylem Wedeco. The loop reactor consisted of sequential injection points, sample points and a degassing contact chamber. A schematic view of the loop reactor is plotted in Fig. 1.

The ozone generator had a capacity between 3.5 and 100 g ozone per hour, produced from oxygen. The minimum dose applicable was 0.7 mgL⁻¹. Hydrogen peroxide

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(10 % stock solution) was dosed in the influent water before it entered the loop reactor. Model compounds were dosed before the dosage of hydrogen peroxide. Directly after each dosing point, a static mixer was installed in the pipe. The water velocity in the loop reactor was 1.44 m s^{-1} at design capacity of $5.0 \text{ m}^3 \text{ h}^{-1}$.

The loop reactor was equipped with a multi ozone dosing system. The ozone was dosed in parts by dividing the gas flow over a number of (maximal 6) injection points (IPs). A static mixer was installed after each injection point. The pressure drop between two IPs was 1.85 mwc at design capacity. The retention time between the injection points was 1.2 s. Between the IPs, sample points (SPs) were installed, see Fig. 2.

The treated water flowed out in a degasser, in which the off gas (oxygen and undissolved ozone) and water were separated. The residence time in this contact chamber was about 25 s. The off gas passed a column in which possible residual ozone was catalytically degraded into oxygen and discharged outside the building by a ventilator. The treated water was collected in a 10 m^3 storage tank and treated by additional AOP before discharge.

The ozone content was measured in the feed gas and in the off gas by an BMT964 ozone analyser. In this way the efficiency of the ozone introduction and reaction is determined. Although six injection points were available in the loop reactor, most of the time only four were used (IPs 3, 4, 5 and 6) to limit pressure drop, by bypassing the first two IPs.

2.2 Influent water

The influent water was pre-treated surface water. The source of this water was a dead-end tributary from the Meuse River. In this tributary, with a residence time of several weeks, coagulation was applied. At the intake the water passed micro-strains (mesh width $35 \mu\text{m}$). Afterwards dual media rapid sand filtration was applied. The quality of the intake of river water varies over the seasons as a result of meteorological, biological and hydrological influences. The main water constituents of the rapid sand filtrate (RSF) are provided in Table 1.

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2.3 Experiments

Regarding the varying matrix of the rapid sand filtrate, investigation over a longer period was required to establish the formation of bromate and conversion of the model compounds. The influence of the varying parameters on the peroxone process was investigated on a regular basis with standard experiments, in which eight hydrogen peroxide/ozone settings were used, see Table 2. In this way, design settings were established to apply the peroxone process.

In addition to the standard experiments, spike experiments were performed to investigate the role of bromide in bromate formation.

2.4 Investigated compounds

A set of 14 compounds were dosed to the RSF to investigate the conversion of model compounds by peroxone, see Table 3.

The model compounds were selected based on their different sensitivity for direct oxidation by ozone and hydroxyl radicals and their representatively for different kind of organic pollutants in river water.

The model compounds were spiked in concentrations from 5 till 30 $\mu\text{g L}^{-1}$, depending on the detection limit of the compound, and at least 95 times the detection limit. The actual concentration of the model compounds was measured before RSF entered the loop reactor. The concentration of DOC was only slightly increased by spiking, by about 0.1 mg CL^{-1} . The DOC concentration of RSF varied over the year from 3.5–5.5 mg CL^{-1} .

2.5 Chemical and physical analyses

The hydrogen peroxide concentration in water was analysed on site with a Hach DRL 2000 spectrophotometer. The measurement is based on the reaction of hydrogen per-

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V_{CPH}). A sample was acidified to a pH of 2–3 with hypochloric acid and the inorganic carbon was subsequently eliminated with purging gas (O_2). The remaining total carbon C was measured and the result is generally referred to as TOC.

UV transmission was measured spectrophotometrically at a wavelength range of 254 nm.

Bromate was analysed using ion exchange chromatography followed by conductivity detection (Dionex IonPac AS9SC). The measured bromate concentration was confirmed using a two point calibrated UV absorption measurement at a wavelength of 200 nm. The reporting limit of bromate was $0.5 \mu\text{gL}^{-1}$, although values higher than the detection limit ($0.1 \mu\text{gL}^{-1}$) were also evaluated to assess the bromate formation, because the reporting limit was equal to the Company standard for bromate.

3 Results and discussion

3.1 Proof of principle

Atrazine was used to investigate the sensitivity for the peroxone process. The conversion increased with the ozone dose, see Fig. 3.

At a dose of 5mgL^{-1} ozone, about 80% of atrazine was converted. By adding 5mgL^{-1} hydrogen peroxide, the conversion reached almost 90%. Increase of the hydrogen peroxide dose above 5mgL^{-1} did not influence the conversion.

The energy consumption necessary to produce 5 g ozone to treat 1m^3 water (resulting in 80% conversion of atrazine) was about 0.045 kWh. To achieve a similar atrazine conversion with a comparable pretreated surface water by applying UV/ H_2O_2 , the energy consumption is at least ten times higher (Lekkerkerker-Teunissen et al., 2013), which demonstrates the energy efficiency of the peroxone process.

Bromate formation also increased with the ozone dose, see Fig. 4. However, by adding hydrogen peroxide, bromate formation was limited and the limitation was more if the ratio peroxide/ozone was higher. This observation is in line with the knowledge

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that bromate formation can be limited by a fast decomposition of ozone and a high ratio between the hydrogen peroxide and ozone doses (von Gunten, 2003b).

From Figs. 3 and 4 can be concluded, that the ozone dose is the main factor in converting atrazine and that the hydrogen peroxide dose is the main factor in limiting the bromate formation. Almost 90 % of atrazine was converted with 5 mgL^{-1} ozone and at least 10 mgL^{-1} hydrogen peroxide, without exceeding the WHO guideline for bromate of $10 \text{ }\mu\text{gL}^{-1}$. However, it is concluded that even 15 mgL^{-1} hydrogen peroxide is not enough to comply with the Company guideline for bromate at an ozone dose of 5 mgL^{-1} .

3.2 Bromate formation

In the period August 2011 up to and including March 2012, every other week peroxone was investigated with standard experiments. The bromate concentrations are shown in Fig. 5. Because the pilot plant settings were similar during the experiments, differences in bromate formation were caused by variations in the water matrix.

As seen before (Knol, 2000), the influent water can contain low background concentrations of bromate. Figure 5 shows the bromate concentrations formed at different ozone/peroxide settings for the standard experiments over the test year. The curves show similar shapes, only the bromate values differs at the same settings. The bromate formation increased with increasing ozone dose and was reduced by increasing the hydrogen peroxide dose at a given ozone dose. Minimum bromate formation occurred in winter season, maximum bromate formation in summer season.

Only the peroxone settings with the high ozone dose of 2.0 mgL^{-1} , with either 6 or 10 mgL^{-1} peroxide, did not comply to the Company bromate guideline (average value of $0.5 \text{ }\mu\text{gL}^{-1}$ with a maximum of $1.0 \text{ }\mu\text{gL}^{-1}$). Minimal dose of 6 mgL^{-1} hydrogen peroxide combined with ozone doses up to 1.0 mgL^{-1} limited the bromate concentration without exception below $0.5 \text{ }\mu\text{gL}^{-1}$. The bromate concentrations at setting 6/1.5 varied over the test period from 0.27 till $0.69 \text{ }\mu\text{gL}^{-1}$, with an average value of $0.41 \text{ }\mu\text{gL}^{-1}$.

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Thus a safe optimal setting concerning the bromate formation was found as 6 mgL⁻¹ hydrogen peroxide and 1.5 mgL⁻¹ ozone.

3.3 Influence water matrix on bromate formation

To appoint the responsible parameter(s) for the variation in bromate concentration, water temperature, bromide, bicarbonate and pH are plotted against bromate of setting 6/2.0 from August 2011 up till and including March 2012, Fig. 6.

The correlations in Fig. 6 are not strong, but certainly trends are visible: the bromate concentration increased with increasing water temperature and bromide concentration and decreasing bicarbonate concentration and pH.

Increase of bromate concentrations with increasing water temperature was expected (Croué et al., 1996; von Gunten, 2003b). Croué reported an increase of 10 % per 10 °C, von Gunten even about 20 % per 10 °C. The variation measured in this study was between 17 and 34 % which was found in line with previous research, regarding the 17 °C temperature difference between the measured minimum and maximum temperature during the standard experiments. A correlation between bromate and bromide was not very obvious, although the dependency of the bromide concentration is known and expected at bromide concentrations higher than 20 µgL⁻¹ (Gottschalk et al., 2010). It is possible that more parameters were involved than bromide alone. The bromate concentration decreased with increasing bicarbonate concentration. Bicarbonate is a known scavenger of hydroxyl radicals, so probably less radicals are available to react with bromide. Decreasing bromate formation with increasing pH is not in line with theory (von Gunten, 2003b). At higher pH, more hypobromite ions are present, which means a higher probability of bromate formation. However, the variation in pH during the standard experiments was small with a bandwidth of 0.19 units (7.81–8.00) and this shift in pH of 0.19 units only increased the hypobromite concentration with approximately 4 %. Probably the influence of the small variation in pH on the bromate formation was marginal and mechanisms with other parameters are most probably preferential.

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To which extent each parameter influenced the bromate formation was difficult to address, because the water matrix changed continuously. For sure, the water temperature and the bicarbonate concentration strengthen each other. With increasing water temperature, the bicarbonate concentration decreased, Fig. 7, both resulting in an increased bromate formation.

For a better insight in the role of bromide in the bromate formation, concerning the forecasted increase in concentration in the Meuse River in global warming scenarios, this parameter is independently changed by spiking in RSF. The actual bromide concentration in RSF of $130 \mu\text{gL}^{-1}$ is increased to 270 and $560 \mu\text{gL}^{-1}$, Fig. 8.

Bromate formation strongly increased with increasing bromide concentration. Concerning the enclosed Meuse, it is therefore of importance to limit industrial spills and discharges of bromide in the main stream of the River Meuse, which are held accountable for about two-thirds of the bromide load in the Meuse (Volz, 2013). Based on the equation in Fig. 8, a provisional bromide threshold of $32 \mu\text{gL}^{-1}$ ($0.24/0.0075$) can be calculated, under which bromate formation is negligible. This value compares to the earlier mentioned $20 \mu\text{gL}^{-1}$ as reported by Gottschalk et al. (2010).

3.4 Conversion of organic micropollutants

The average conversion of the fourteen model compounds at the four different ozone dosages (0.7 to 2.0mgL^{-1}) and at a peroxide concentration of 6mgL^{-1} is shown in Fig. 9. Conversions varied enormously between compounds. Eliminations between less than 10 to over 95 % were observed. Reactivity of organic compounds towards ozone is strongly dependent on the molecular structure of compounds. Electron rich moieties such as aromatic rings and C=C double bonds are main reaction sites at which ozone attacks (Sonntag et al., 2012; Ternes et al., 2002). This structure dependency is clearly reflected in the results of the model compounds.

Lowest conversions were found for the model compounds metformin till diglyme, at the left part of Fig. 9. With the exception of iopromide, these compounds all lack aromatic rings and unsaturated C-C bonds. Their limited conversion is in line with results

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published by Acero et al. (2001) who found that compounds without aromatic and double bond structures, like MTBE, are poorly oxidizable by ozone alone. Iopromide, an X-ray contrast agent, in fact contains one aromatic ring. However, this ring is substituted at all six C positions (a.o. with three iodine atoms) and therefore not easily oxidized.

Higher conversions, between 38 and 68 % at 0.7 mgL^{-1} ozone and between 85 and 99 % at 2.0 mgL^{-1} ozone, were obtained for ibuprofen to phenazone. These five compounds all possess one aromatic ring that is not substituted with halogens at which ozone can attack.

Furosemide, converted for about 95 % at all tested ozone doses, has one aromatic ring in its structure, together with two C=C double bonds. In addition, furosemide has an aromatic amine-N, which also acts as electron rich reaction site for ozone (Lee et al., 2014).

Highest conversions ($\geq 97 \%$) were observed for diclofenac, trimethoprim and carbamazepine, due to the presence of two oxidizable aromatic rings in their structures. For diclofenac and carbamazepine, this is in line with Ternes et al. (2002).

The high conversion of bromacil is surprising regarding the fact that this herbicide does not have aromatic rings in its structure. It however does possess a bromine substituted C=C bond. Bromacil is oxidized directly by the attack of ozone on this C=C bond and the consecutive loss of bromine (Hapeman et al., 1997). This reaction is energetically favorable due to the fact that bromine acts as a very good leaving group and renders the conversion rate of bromacil comparable to that of the easily oxidizable model compounds with aromatic rings.

Besides at a peroxide concentration of 6 mgL^{-1} the conversion of the model compounds was also assessed at 10 mgL^{-1} peroxide. The influence of an increased hydrogen peroxide concentration at the same ozone dose on the conversion was however found to be small. In fact, in all cases the average conversion was equal or lower, with a maximum of 4 % decrease at a dose of 1.5 mgL^{-1} ozone. This is in line with findings published previously for bromacil (Hapeman et al., 1997) and for compounds in hospital waste water effluent (Lee et al., 2014).

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Two mechanisms could have been responsible for this phenomenon. Firstly, decomposition of the ozone will be accelerated at a higher hydrogen peroxide dosage, which is a disadvantage for compounds that are sensitive for direct oxidation by ozone, and, secondly, excessive peroxide itself can act as a scavenger for hydroxyl radicals. Probably both mechanisms play a role, depending on the specific compound.

In general, the conversion of the model compounds was higher with higher ozone dosage. The conversion of the easy oxidizable compounds furosemide, diclophenac, bromocil, trimethoprim and carbamazepine already was maximal at the lowest dosage of 0.7 mgL^{-1} . The conversion of the remaining compounds improved considerably by enhancing the ozone dosage to 2.0 mgL^{-1} . Although from the perspective of micropollutant conversion a dosage of 2 mgL^{-1} would therefore be optimal, the bromate formation at this setting exceeded the Dunea guideline. The setting of 6/1.5 combined acceptable bromate formation with an average conversion of the model compounds of 78.9% (σ 24.8%).

The standard experiments showed that the peroxone process efficiently degrades organic micropollutants with aromatic rings and/or unsaturated C-C bonds in their molecular structures. As many OMPs contain these features, the peroxone process might be a useful technique in the purification of drinking water.

However, it should be noted that the peroxone process, like all advanced oxidation processes, does not provide a full solution for the problem of OMPs in water sources. In the first place, this study showed that the achieved elimination is lower for compounds lacking electron rich moieties that can be oxidized by ozone. Secondly, oxidation by the peroxone process generally leads to the formation of degradation products instead of to full mineralisation of OMPs, e.g. Escher et al. (2009) and Sonntag et al. (2012). Like the OMPs originally present, the generated products may have unwanted toxic properties.

For these reasons, the peroxone process should preferably not be implemented as the only strategy for the removal of OMPs, but in combination with other techniques,

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in this case followed by biological degradation during MAR and adsorption during PAC filtration.

3.5 Influence of the water matrix on OMP conversion

Using the collected data of the standard experiments, the relevant water quality parameters of RSF are plotted against the conversion of the model compounds for which the observed conversion was less than 90 % (Fig. 10).

As expected, the conversion of the model compounds – with the exception of metformin which was hardly converted at all – increased with increasing water temperature and decreasing concentrations of DOC and bicarbonate. The concentrations of bicarbonate and DOC and the water temperature fluctuate seasonally (Fig. 7. All three parameters could be (partly) responsible for the varying conversion of the five model compounds), for sure these three parameters strengthen each other. However, as we did not have test conditions in which only one of the parameters could be varied, it is not possible to distinguish causation and co-correlation.

The fact that bromate formation and OMP conversion appears to be dependent on water temperature, bicarbonate and/or DOC concentration has as practical implication that in summer seasons the ozone dose strictly needs to be limited to 1.5 mgL^{-1} whereas in winter season a higher ozone dose is allowed to achieve the optimum OMP conversion with acceptable bromate formation. In this way the bromate formation and the conversion of OMPs are levelled over the year. Controlling peroxone on basis of the (derived) parameters water temperature, bicarbonate and DOC and monitoring of bromate formation is feasible.

4 Conclusions

The peroxone process efficiently degrades organic micropollutants with aromatic rings and/or unsaturated C-C bonds in their molecular structures. As many OMPs contain

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these features, the peroxone process might be a useful technique in the purification of contaminated surface water. In drinking water treatment the dosage of ozone, and with that the conversion of OMPs, is limited due to the bromate formation. Nevertheless, even in the Netherlands with the most strict guideline for bromate, an average conversion of 14 model compounds of well over 70 % is achieved with 6 mgL⁻¹ hydrogen peroxide and 1.5 mgL⁻¹ ozone. The applied ozone dose is the main factor in the conversion of the model compounds. The hydrogen peroxide dosage has only a minor effect on the conversion, but limits the bromate formation effectively.

The peroxone process can be controlled on basis of the (derived) parameters water temperature, bicarbonate and DOC. Analyses of bromate then can be used to adjust the process.

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Table 1. Minimum, maximum and average values of relevant parameters from RSF.

parameter	unit	minimum	average	maximum
Temperature	°C	1.5	12.3	20.8
pH	–	7.81	7.97	8.11
Ammonia	mg NH ₄ ⁺ L ⁻¹	< 0.02	< 0.02	0.09
DOC	mg L ⁻¹	3.38	4.26	5.26
Bromide	µg L ⁻¹	104	119	136
Bicarbonate	mg L ⁻¹	155	175	204

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Table 2. Settings of the standard experiments.

parameter	unit	settings
Capacity	$\text{m}^3 \text{h}^{-1}$	5.0
Doses peroxide/ozone	$\text{mgL}^{-1}/\text{mgL}^{-1}$	6/0.7; 10/0.7; 6/1.0; 10/1.0; 6/1.5; 10/1.5; 6/2.0; 10/2.0
Dosing ozone points	–	IP 3, 4, 5, 6
Dose rate model compounds solution	$\text{m}^3 \text{h}^{-1}$	0.068

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Table 3. Average concentration of spiked model compounds in RSF.

Compound	Concentration ($\mu\text{g L}^{-1}$)
Diglyme	11.0
Bromacil	10.8
Bentazone	11.9
Atrazine	10.1
Isoproturon	10.2
Ibuprofen	18.8
Metformin	4.1
Carbamazepine	5.7
Metoprolol	5.4
Trimethoprim	5.7
Iopromide	1.8
Phenazone	5.8
Diclofenac	31.5
Furosemide	5.4

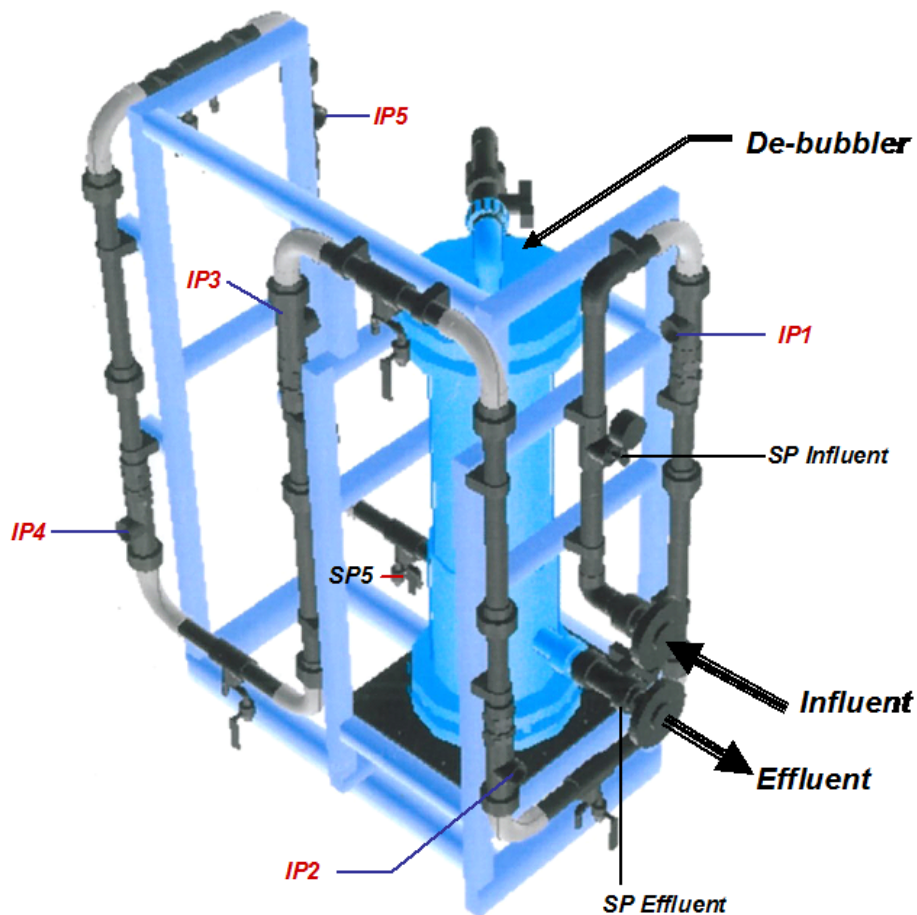


Figure 1. Peroxone loop reactor with injection points (IPs), sample points (SPs) and de-bubbler contact chamber.

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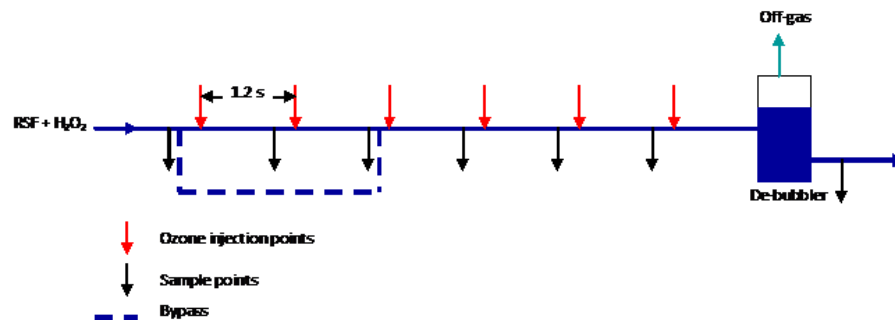


Figure 2. Schematic loop reactor.

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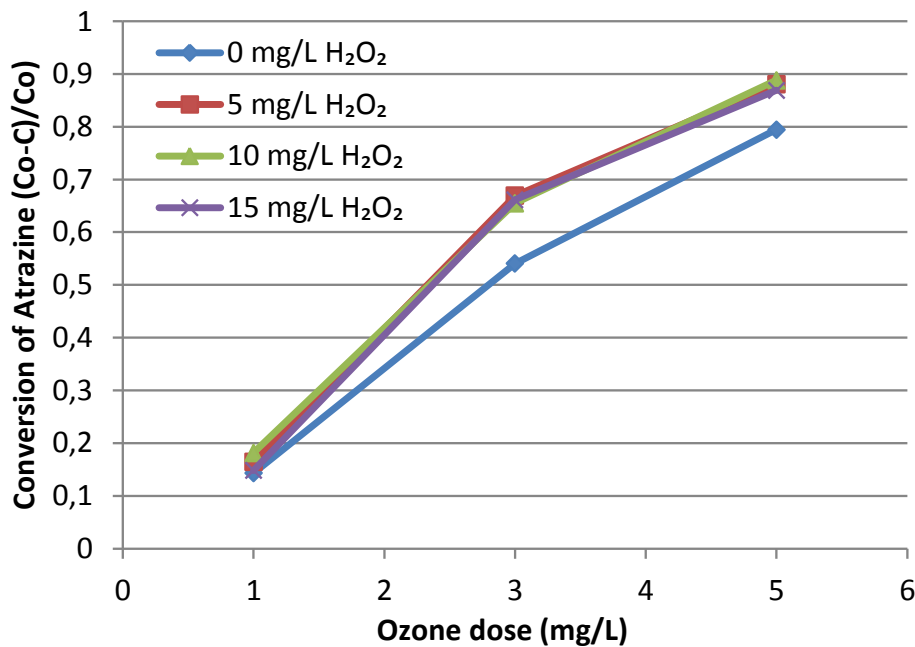


Figure 3. Conversion of atrazine at different settings of the peroxone process.

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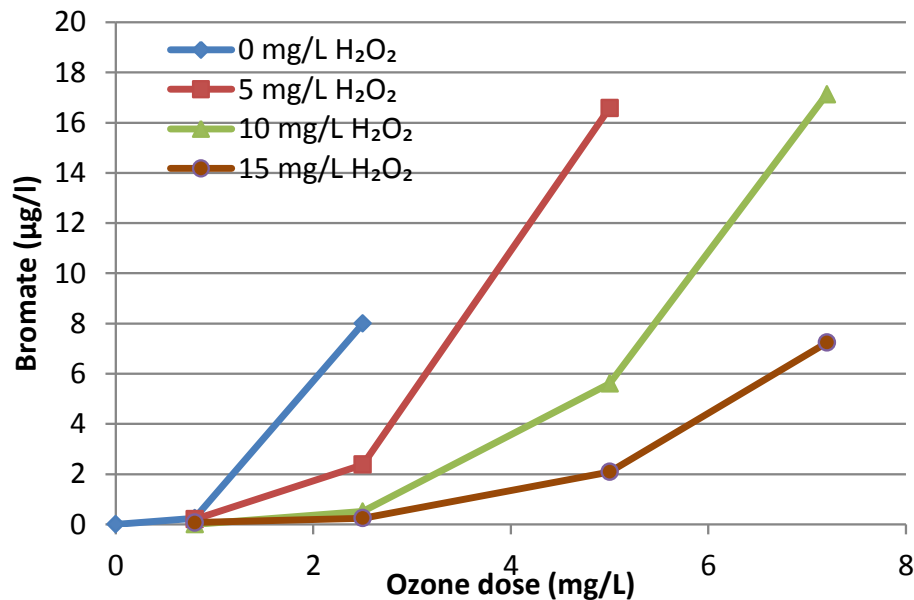
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**Figure 4.** Bromate formation at different settings of the peroxone process.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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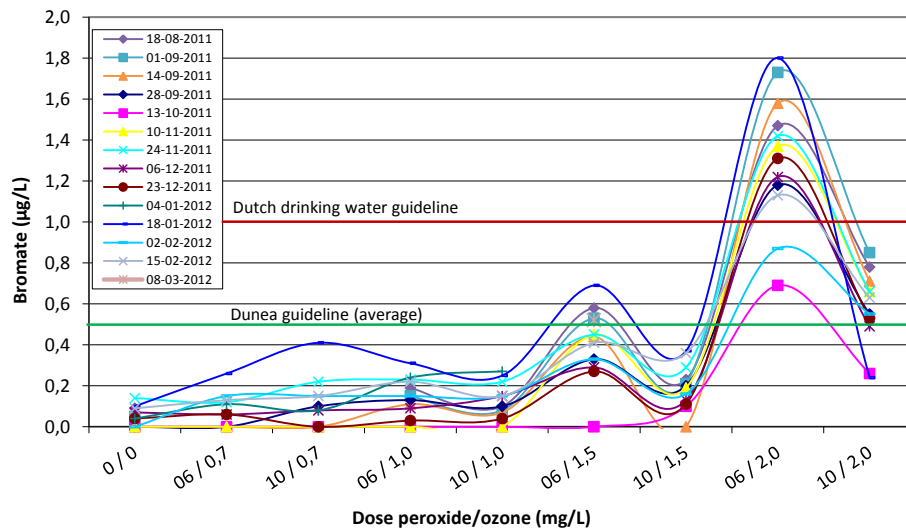


Figure 5. Bromate concentration at standard settings ($n = 14$, August 2011 up to and including March 2012).

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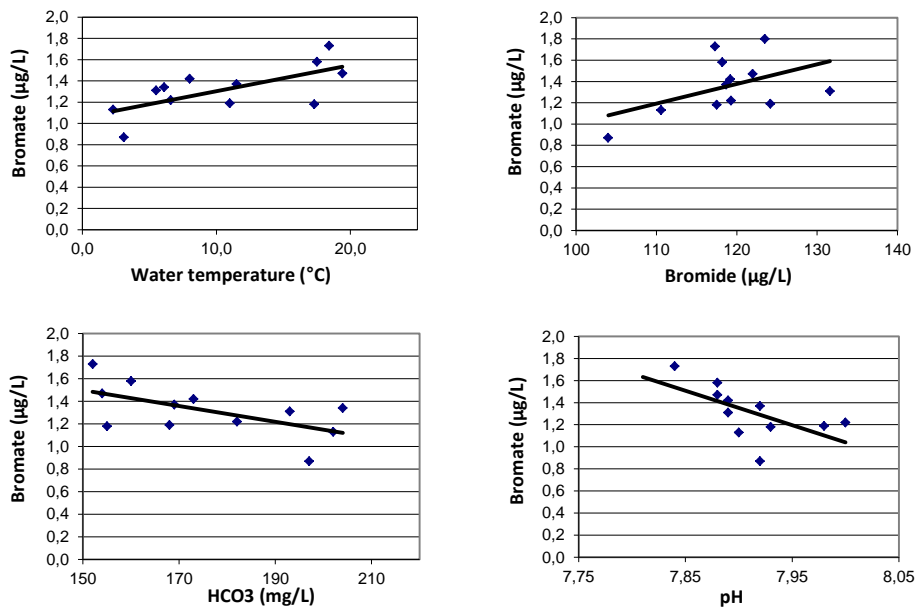
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Figure 6. Water temperature, bromide, bicarbonate and pH vs. bromate concentration.

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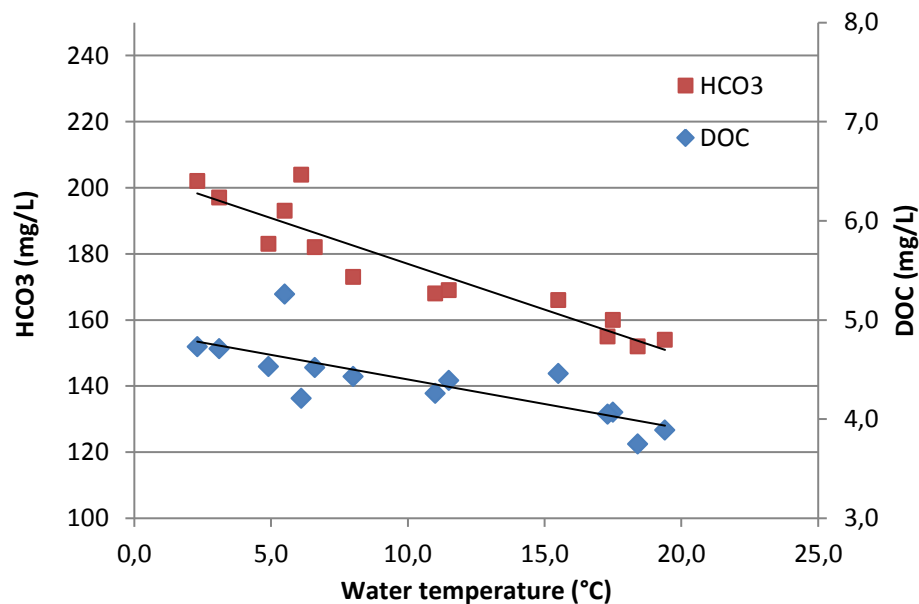


Figure 7. Correlation between water temperature, DOC and bicarbonate concentration.

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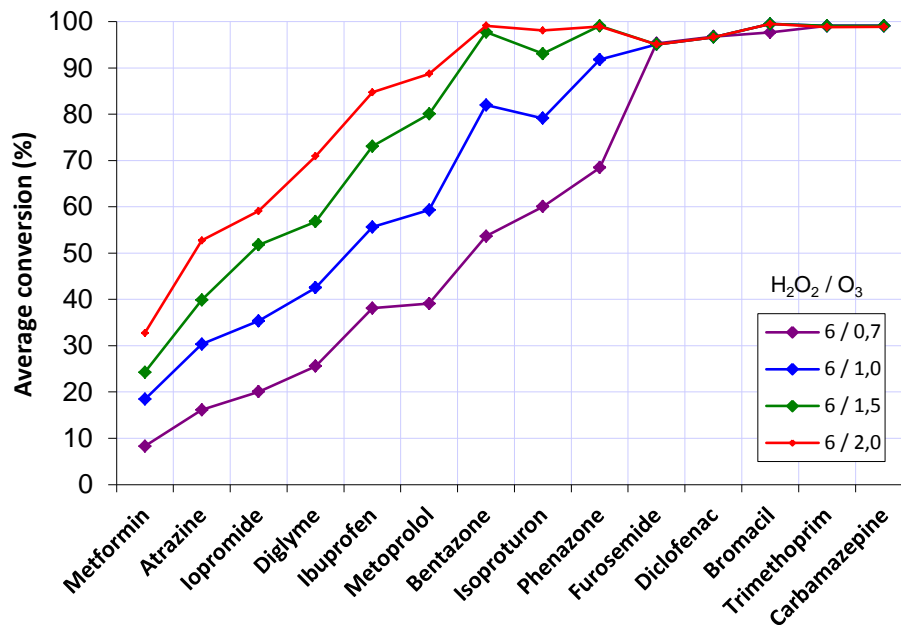


Figure 9. Average ($n = 14$) conversion in percentages of model compounds as function of ozone dosage at a hydrogen peroxide concentration of 6 mg L^{-1} in the period August 2011 till March 2012.

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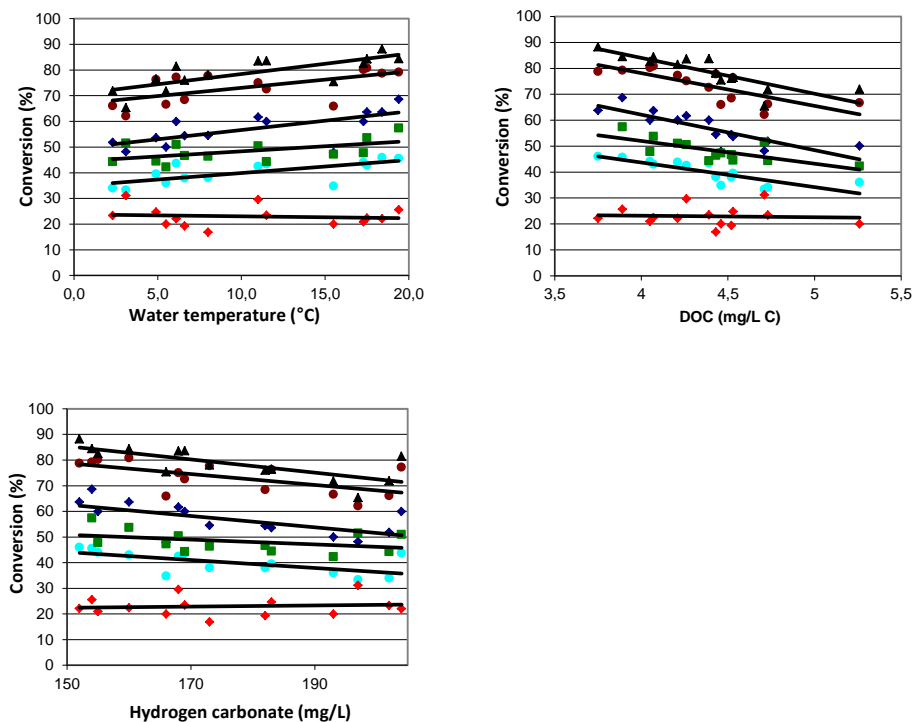


Figure 10. Conversion of compounds vs. water temperature and DOC and bicarbonate concentration (from top to bottom: metoprolol, ibuprofen, dyglime, iopromide, atrazine, metformin).

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