

Prediction of the disinfection and oxidation efficiency of full-scale ozone reactors

Hervé Gallard, U. von Gunten and H. P. Kaiser

ABSTRACT

The efficiency of a two-step ozonation with regard to disinfection and oxidation of micropollutants was assessed for a river-water treatment plant (Limmat River, Zürich, Switzerland). The assessment was based on laboratory experiments to estimate transient ozone and OH radical concentrations coupled with hydraulic modelling of the ozone reactors. The laboratory experiments were performed for various temperatures, ozone dosages and pretreatments to mimic the full-scale treatment. The hydraulics were determined by a conservative tracer test. The kinetic data for disinfection and oxidation were taken from the literature. The inactivation of microorganisms (*Cryptosporidium parvum* oocysts, *Bacillus subtilis* spores, *Giardia lamblia* cysts and polio virus) was more critical at low temperature (5°C) than at high temperature (20°C). For *Cryptosporidium parvum* oocysts it was calculated to be less than 1 log for the two ozonation steps, and an overall ozone dose of 1.5 mg/l (5°C). For the same microorganism it was >3.5-log inactivation at 20°C. For other microorganisms, the calculated inactivation was ≥ 2 log (5°C) with *B. subtilis* spores being the most resistant. The oxidation of micropollutants was much less affected by variations in the temperature. The fraction of oxidation increased in the following order: between 15 and 25% of tetrachloroethene, 15 and 25% of methyl tertiary butyl ether, 30 and 40% of atrazine, 80 and 90% of p-xylene and between 97 and 100% of trimethylbenzene were oxidized. For the oxidation of methyl tertiary butyl ether, the formation of degradation products was modelled in the pre-ozonation step. For all investigated treatment conditions the overall bromate formation was ≤ 2.5 µg/l.

Key words | disinfection, modelling of ozone contactors, oxidation kinetics, ozonation, micropollutants

INTRODUCTION

In Switzerland, the quality of drinking water is regulated by the food law and several food-related ordinances. The same legal requirements are applicable to drinking water and other foodstuff. Drinking water has to meet the legal requirements at any time and producers are liable for drinking water related health problems. To meet these requirements 'Good Manufacturing Practice', which includes validation of the water treatment processes, is indispensable. The starting point of a validation process is the identification and quantification of health risks and critical treatment steps, better known under the term of 'Hazard Analysis and Critical Control Points' (HACCP).

Important hazards in raw water for drinking water production are pathogenic microorganisms and toxic micropollutants. Therefore, a validation study should include the assessment of the reduction of the risk associated with microorganisms and micropollutants during water treatment.

In many waterworks in Switzerland, ozonation is a critical treatment step (Kaiser *et al.*, 2000). Therefore, an ozonation step has to be quantified with regard to microorganisms and micropollutants for disinfection and oxidation efficiency. To achieve this goal, a kinetic approach is necessary. The following approach consists

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of four principal steps proposed by von Gunten *et al.* (1997, 1999) and can be summarized as follows:

- Laboratory-scale experiments to determine the ozone decay kinetics and the R_{ct} values (ratio between OH radical ($^{\circ}\text{OH}$) and ozone exposures) (Elovitz & von Gunten, 1999).
- Determination of the rate constants for the oxidation of micropollutants by ozone and OH radicals and for the inactivation of microorganisms by ozone.
- Characterization of the hydraulics of the ozonation chamber with a conservative tracer.
- Coupling of the reactor hydraulics with chemical kinetics.

The R_{ct} parameter, the ratio of the $^{\circ}\text{OH}$ -exposure to the O_3 -exposure, is determined by using an OH radical probe compound to measure the transient steady-state concentration of $^{\circ}\text{OH}$. Since R_{ct} is constant over a wide range of the ozonation, R_{ct} corresponds directly to the ratio of the concentrations of $^{\circ}\text{OH}$ and O_3 . Therefore, the degradation of a micropollutant via O_3 and $^{\circ}\text{OH}$ reaction pathways can be predicted by the O_3 reaction kinetics and R_{ct} as long as the corresponding rate constants for its reaction with O_3 and $^{\circ}\text{OH}$ are known (Elovitz & von Gunten, 1999).

Based on this approach, ozone profiles, formation of chlorate from chlorine and the oxidation of micropollutants were correctly predicted in a full-scale ozonation system of a lake-water treatment plant of Zürich (von Gunten *et al.*, 1999). Because the ozone profile in the reactor of this study is known, the disinfection efficiency can also be assessed. Disinfection has become a major issue again since it was observed that protozoa are difficult to inactivate with conventional disinfectants such as chlorine. The inactivation of bacteria, viruses and protozoa can be calculated by the Chick–Watson equation (Chick, 1908; Watson, 1908; Rennecker *et al.*, 1999):

$$\ln \frac{N}{N_0} = -k_i ct \quad (1)$$

where N and N_0 are the volumetric concentrations of microorganisms at time t and at the initial time t_0 , respectively, and c is the concentration of the disinfectant.

The rate constant k_i can be used for the calculation of the disinfection efficiency in full-scale systems. However, there are several limitations to the Chick–Watson approach for disinfection (Masschelein, 2000). The population of microorganisms in natural water is not homogenous, and several strains coexist with various resistances towards a disinfectant. In addition, disinfection efficiency can be measured by a determination of loss of viability (inactivation) or loss of infectivity. Therefore, the inactivation rate constant may vary according to the method applied, and the calculation of disinfection in a full-scale water treatment plant is subject to many approximations. Despite these facts and a lack of other simpler models, the present approach for a quantitative estimation of disinfection efficiency is very useful. Although the calculated relative inactivation N/N_0 may not be the exact value, the order of magnitude for the inactivation of microorganisms with varying resistances towards ozone is shown. To exemplify this, in the present study, *Cryptosporidium parvum* oocysts (*C. parvum*), *Giardia lamblia* cysts (*G. lamblia*) and *Bacillus subtilis* spores (*B. subtilis*) a microorganism with similar inactivation properties, were used for model calculations.

The water treatment plant used for our previous study was characterized by a constant raw water quality and, therefore, by constant treatment conditions (von Gunten *et al.*, 1999). In the present study, we have selected a water treatment plant in the city of Zürich (Switzerland) treating river water. The quality of the raw water shows important seasonal variations that modify the conditions of treatment. Therefore, in the first part of the study, laboratory scale experiments were performed to show the impact of water quality and treatment conditions on ozone consumption. In the second part, calibration of the full-scale ozonation reactors was performed for various temperatures and ozone dosages.

MATERIALS AND METHODS

Laboratory experiments

Experimental material and procedures were described previously in detail (Elovitz & von Gunten, 1999).

Concentrated ozone solutions were prepared daily by bubbling ozone-containing oxygen gas through a flask of ice-cooled double-distilled water. Ozonation was initiated by adding an aliquot of the concentrated stock solution into a pH-buffered (borate 10 mM) natural water solution containing *p*-chlorobenzoic acid (pCBA = 0.5 μM) as a probe compound to measure the transient OH radical concentration. At various time intervals, samples were withdrawn with a dispenser system and the reaction was quenched by an indigo solution (Hoigné & Bader, 1981). Samples were analysed for ozone with the indigo method (Hoigné & Bader, 1981) and for pCBA by reverse-phase HPLC (55/45 methanol/10 mM H_3PO_4 buffer eluent, 1 ml/min and UV detection at 234 nm). Bromate concentrations were determined using ion chromatography followed by a post-column reaction (Sahli & von Gunten, 1999).

Water types

The ozone decay experiments were performed with Swiss waters from River Limmat, Lake Zürich and two springs at pH 8.0. All natural waters were filtered with 0.45 μm filters. Experiments were conducted at various temperatures (5–30°C) and for varying ozone dosages (0.5–2 mg/l). Temperature and pH of the River Limmat water show considerable seasonal variations. Temperature varies between 5 and 20°C and the pH between 7.5 and 8.5. The DOC content at 1.2–1.5 mg/l is more or less stable throughout the year but shows a large variation in the UV-absorbance at 254 nm of 1.8 to 4 absorption units per metre (AU m^{-1}). The alkalinity varies between 1.9–2.9 mM HCO_3^- .

Lake Zürich water was taken from a depth of 32 m in Lake Zürich. Lake Zürich is an oligotrophic lake with a constant water quality throughout the year at a depth of 32 m. Lake Zürich water has a low DOC (approximately 1.3 mg/l) and a relatively low alkalinity (2.6 mM HCO_3^-). The UV-absorbance is about 3.2 extinction units per metre at 254 nm. At the raw water intake of the Lake Zürich water treatment plant, temperature varies between 4 and 8°C and the pH between 7.6 and 8.1.

The two spring waters were from Weihermattquelle (DOC 0.5 mg/l, pH 7.3, alkalinity 5.2 mM HCO_3^- ,

temperature 11.7°C) and Eisetquelle (DOC 1.5 mg/l, pH 7.6, alkalinity 4.0 mM HCO_3^- , temperature 10.6°C). Weihermattquelle water is characterized by a very low DOC content and low UV-absorbance of 0.97 units per metre. UV-absorbance of Eisetquelle is much higher and equal to 4.5 AU m^{-1} . The kinetics of the ozone decrease of both waters were measured at $10 \pm 1^\circ\text{C}$.

River Limmat water treatment plant

Full-scale experiments were performed with the ozonation reactors of the Zürich river-water treatment plant. The water treatment plant consists of pre-oxidation with a chlorine/chlorine dioxide mixture, sedimentation, pre-ozonation, flocculation with iron chloride, rapid sand filtration, intermediate ozonation and BAC filtration. Pre-oxidation is mainly used to protect the installation against mussels and algae bloom. After the sedimentation step the raw water turbidity of occasionally >100 NTU is reduced to <10 NTU. The two ozonation steps are critical for disinfection of the river water but also for the oxidation of NOM and potential micropollutants. In the BAC filtration, dissolved residual ozone is reduced and organic material is adsorbed and biologically degraded. Finally, the finished water is used for artificial recharge of groundwater. Table 1 shows the basic characteristics of the two identical ozone reactors involved in this study. The design of the two ozone reactors is shown in Figure 1.

The hydraulic properties of the ozone reactors were established by a conservative tracer. A solution of sodium chloride was dosed to the reactors for about 2 h. The conductivity was measured at the sampling points P1 to P5 in the pre-ozonation reactor, and at the inlet and outlet of the intermediate ozonation reactor. The measured breakthrough curves were fitted by the AQUASIM (Reichert, 1994) computer program as a series of plug flow (PF) and completely stirred tank reactors (CSTR) (von Gunten *et al.*, 1997, 1999). Ozone concentrations were determined continuously with instruments from EIT[®] and Orbisphere[®]. Calibration of this equipment was performed with the indigo method (Hoigné & Bader, 1981). Turbidity and pH were measured continuously with standard equipment.

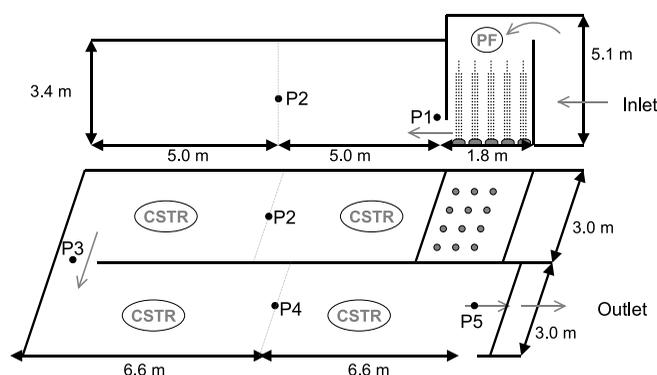
Table 1 | Characteristics of the ozone reactors

	Pre-/intermediate ozonation reactor
Volume of ozone transfer compartment (m ³)	28
Volume of 1st contact compartment (m ³)	102
Volume of 2nd contact compartment (m ³)	139
Water flow (m ³ /h)	625
Hydraulic retention time t_H (min)	23
t_{10} n. (US EPA, 1989) (min)	18 (78% of t_H)
Mean ozone residual at P5 (20°C) (mg/l)	0.2/0.3
ct (20°C) (US EPA, 1989)	3.6/5.4
Mean ozone residual at P5 (5°C) (mg/l)	0.3/0.35
ct (5°C) (US EPA, 1989)	5.4/6.3
Mean flow rate in ozone transfer chamber (m/min)	1.9
Mean flow rate at P1 (inlet 1st contact chamber) (m/min)	5.0
Flow rate at P3 (inlet 2nd contact chamber) (m/min)	3.0

RESULTS AND DISCUSSION

Ozonation in laboratory experiments

Ozone consumption was followed in a batch reactor for various ozone dosages and varying temperatures for two Limmat River water samples. For each experiment, the R_{ct} value, the ratio between OH radical and ozone exposures, was determined to predict the behaviour of micropollutants in the ozonation chambers. Pseudo first-order rate constants, values of R_{ct} and the extent of the fast ozone consumption are given in Table 2 for various temperatures (5–30°C) and ozone doses (0.5–2 mg/l). Rate constants (k_{O_3}) vary between $2.6 \times 10^{-4} \text{ s}^{-1}$ and $1.6 \times 10^{-2} \text{ s}^{-1}$, corresponding to R_{ct} values of 1.9×10^{-9}

**Figure 1** | Design of pre- and intermediate ozonation reactors in the River Limmat water treatment plant, Zürich. Hypothetical reactors for modelling: PF=plug flow reactor and CSTR=completely stirred tank reactor.

and 1.1×10^{-7} , respectively. The fast ozone consumption makes up between 20 and 70% of the initial ozone dose.

Effect of ozone dosage

Figure 2 shows the first-order representation of the ozone decrease for three ozone dosages ($T = 20^\circ\text{C}$). This empirical method can be applied to characterize the ozone decrease during ozonation processes. The ozone decay can be plotted with a linear plot only after the fast ozone consumption (measured at $t_o + 1$ min). The pseudo first-order rate constants vary between $1.0 \times 10^{-3} \text{ s}^{-1}$ for $[\text{O}_3]_o = 2 \text{ mg/l}$ ($t_{1/2} = 11$ min, No. 1, Table 2) and $5.6 \times 10^{-3} \text{ s}^{-1}$ for $[\text{O}_3]_o = 0.5 \text{ mg/l}$ ($t_{1/2} = 2$ min, No. 3, Table 2). The percentage of the fast ozone consumption increases from 32% to 52% when the initial ozone concentration decreases from 2.0 mg/l to 0.5 mg/l. Assuming a constant contribution of the O_3 decomposition cycle, these results can be explained with various types of sites within the NOM, with differing reactivity with ozone. For low ozone dosages such as 0.5 mg/l, ozone is only consumed by the fast-reacting sites. When higher ozone dosages are applied, the rate of ozone consumption decreases since slowly-reacting sites are oxidized as well.

Effect of temperature

To predict the effect of temperature on the ozone decrease in River Limmat water, the kinetics of ozone consumption

Table 2 | Kinetic data for the ozone consumption in River Limmat water at pH 8.0

No.	Ozone dose (mg/l)	Pretreatments ^a	Abs 254 nm ^b (5 cm cell)	T (°C)	k_{O_3} (s ⁻¹)	R_{ct}	Fast ozone consumption (%)/ μ M
1	2	No	0.129	20	1.0×10^{-5}	9.8×10^{-9}	32/13.5
2	1	No	0.129	20	2.5×10^{-5}	2.7×10^{-8}	38/8.0
3	0.5	No	0.129	20	5.6×10^{-5}	4.3×10^{-8}	52/5.4
4	1	No	0.129	5	8.6×10^{-4}	6.2×10^{-9}	34/7.1
5	1	No	0.129	13	1.4×10^{-5}	1.2×10^{-8}	35/7.3
6	1	No	0.129	30	6.2×10^{-5}	5.7×10^{-8}	56/11.8
7	2	No	0.129	5	2.6×10^{-4}	1.9×10^{-9}	24/10.0
8	2	No	0.129	30	2.8×10^{-5}	3.0×10^{-8}	36/15.0
9	0.5	5 μ M O ₃	0.098	20	3.7×10^{-5}	3.0×10^{-8}	43/4.6
10	2	5 μ M O ₃	0.098	20	9.6×10^{-4}	8.9×10^{-9}	25/10.5
11	0.5	10 μ M O ₃	0.085	20	3.1×10^{-5}	2.2×10^{-8}	39/4.2
12	2	10 μ M O ₃	0.085	20	1.0×10^{-5}	8.0×10^{-9}	23/9.7
13	2	40 μ M O ₃	0.054	20	6.5×10^{-4}	6.6×10^{-9}	20/8.4
14	0.5	40 μ M O ₃	0.054	20	1.2×10^{-5}	1.3×10^{-8}	31/3.3
15	2	No	0.170	20	2.2×10^{-5}	1.5×10^{-8}	43/18.0
16	1	No	0.170	20	4.6×10^{-5}	3.8×10^{-8}	50/10.4
17	0.5	No	0.170	20	1.6×10^{-2}	1.1×10^{-7}	70/7.6
18	1	10 μ M ClO ₂	0.151	20	4.3×10^{-5}	2.5×10^{-8}	61/12.5
19	1	10 μ M HOCl	0.144	20	4.0×10^{-5}	2.6×10^{-8}	43/8.9
20	1	10 μ M O ₃	0.109	20	2.8×10^{-5}	2.0×10^{-8}	36/8.1
21	1	21 μ M O ₃	0.085	20	1.7×10^{-5}	1.1×10^{-8}	28/5.8
22	2	21 μ M O ₃	0.085	20	1.2×10^{-5}	9.7×10^{-9}	34/13.9
23	1	42 μ M O ₃	0.066	20	1.5×10^{-5}	1.0×10^{-8}	26/5.4
24	2	42 μ M O ₃	0.066	20	1.1×10^{-5}	1.1×10^{-8}	24/2.3

Nos 1 to 14: Limmat River water sampled after pre-oxidation with 0.35 mg/l Cl₂/0.1 mg/l ClO₂ in River Limmat water treatment plant.

Nos 15–24: River Limmat water sampled before pre-oxidation.

^aPretreatments conducted in the laboratory in batch reactor.

^bUV absorbance measured before the ozone kinetics.

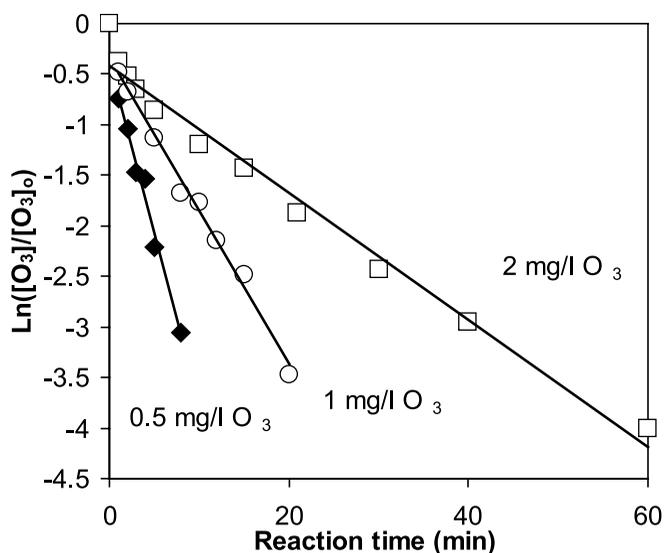


Figure 2 | First-order representation of the ozone consumption of River Limmat water at pH 8 for three different ozone dosages (20°C).

were performed at 5, 13, 20 and 30°C for ozone dosages of 1 and 2 mg/l (Nos 1, 2, 4–8 in Table 2). The apparent activation energies of k_{O_3} were 57 kJ mol^{-1} and 64 kJ mol^{-1} for ozone dosages of 1 and 2 mg/l, respectively. A similar value of 67 kJ mol^{-1} was determined for Lake Zürich water and for an ozone dose of 0.5 mg/l (Elovitz *et al.*, 2000). Therefore, an Arrhenius type equation can be applied with the same apparent activation energy for various ozone dosages.

Effect of pre-oxidation

In the Limmat water treatment plant, the ozonation follows a pre-oxidation in which chlorine or a mixture of chlorine and chlorine dioxide is used. Moreover, the ozonation is performed in two successive ozone reactors (pre- and intermediate ozonation). To predict the effect of pre-oxidation on ozone consumption, Limmat raw water and Limmat water sampled after pre-oxidation in the water treatment plant (dose of 0.35 mg/l Cl_2 and 0.1 mg/l ClO_2) were pretreated with chlorine, chlorine dioxide and ozone before the kinetics of the ozone decrease were measured. Both types of water were pretreated in laboratory scale reactors at pH 8.0 with various concentrations of oxidants as shown in Table 2. Three initial ozone

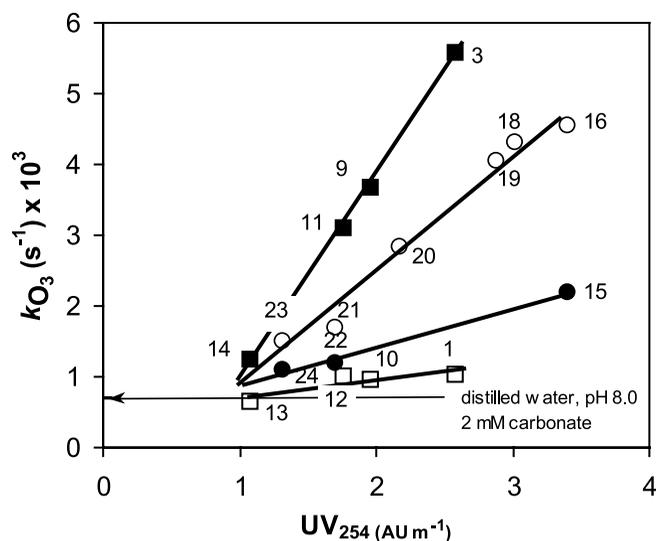


Figure 3 | Effect of oxidative pretreatment (HOCl , ClO_2 , O_3) on UV_{254} absorbance and apparent pseudo first-order rate constants (numbers correspond to numbers in Table 2; ozone dosages: 0.5 mg/l (■), 1 mg/l (○), 2 mg/l (□), circles and squares represent two different samples, 22°C; alkalinity = 2 mM).

concentrations (0.5, 1.0 and 2.0 mg/l) were used for ozone kinetics. The effect of pretreatments on NOM was followed by measuring the UV absorbance at 254 nm (see Table 2). Figure 3 shows the plot of the pseudo first-order rate constant (k_{O_3}) as a function of the initial UV_{254} . It shows that the k_{O_3} is linearly correlated with the initial UV absorbance and that the linear regression depends on the ozone dosage.

For an ozone dosage of 1 mg/l, the rate constant for the decrease of ozone in pre-oxidized water was $2.5 \times 10^{-3} \text{ s}^{-1}$ (No. 2, Table 2) and increased to $4.6 \times 10^{-3} \text{ s}^{-1}$ (No. 16, Table 2) for raw River Limmat water. Furthermore, all pre-oxidations carried out in the laboratory lead to a reduction of both UV_{254} and k_{O_3} . The effect is most prominent for pretreatment with ozone because similar sites are already oxidized. All the linear correlations shown in Figure 3 converge to the same point. The ordinate value of this point corresponds to the first-order rate constant of the ozone decrease at pH 8.0 ($k_{O_3} = 6.5 \times 10^{-4} \text{ s}^{-1}$ for 2 mM carbonate solution at room temperature). The abscissa value represents the UV_{254} absorbance of refractory sites (1 AU m^{-1}) present in River Limmat water samples. In summary, the UV_{254}

absorbance can be used to predict the rate constant for the ozone decomposition for a given ozone dosage. Similar correlations were observed for the R_{ct} values (results not shown).

Figure 4 shows the R_{ct} values as a function of the k_{O_3} values for various types of water (raw and pretreated River Limmat waters of Table 2, Lake Zürich water and two spring waters), temperatures (5–30°C), ozone dosages (0.5–2 mg/l) at pH 8.0. Results show that R_{ct} increases with increasing k_{O_3} and that a reasonable linear correlation exists between R_{ct} and k_{O_3} ($R_{ct} = 8.0 (\pm 0.5) \times 10^{-6} \times k_{O_3}$; $r^2 = 0.903$; $n = 25$). A correlation with a similar slope was also obtained for River Sihl water (Elovitz *et al.*, 2000). Both the correlations between k_{O_3} and UV_{254} , and k_{O_3} and R_{ct} are helpful tools to limit the number of calibration experiments that are needed to model and optimize ozonation processes.

Full-scale experiments on the River Limmat water treatment plant, Zürich

Effect of pre-oxidation on ozone stability and bromate formation

The effect of pre-oxidation of the River Limmat water on ozone stability and bromate formation was investigated. In the River Limmat water, bromide concentrations are in the range of 7 µg/l (0.09 µM) to 10 µg/l (0.12 µM), which is very low. The mean water temperature during these investigations was 6.5°C. Bromate concentrations between 1.0 and 2.5 µg/l (8–20 nM) were found after the intermediate ozonation with ozone doses of 1.5 and 1.0 mg/l for the pre-ozonation step, and 0.5 mg/l for the intermediate ozonation. These values are far below the drinking water standards of 10 µg/l for bromate (European Community, 1998). For five ozone doses, the ozone residual and the bromate concentration were measured at the end of the pre-ozonation reactor without pre-oxidation and with a pre-oxidation (dose 0.35 mg/l (4.93 µM) Cl_2 /0.1 mg/l (1.48 µM) ClO_2). Figure 5 shows that both ozone residual and bromate concentrations increased with increasing ozone dosages and that all data can be well fitted with a logarithmic regression curve. Results also show that both parameters were significantly

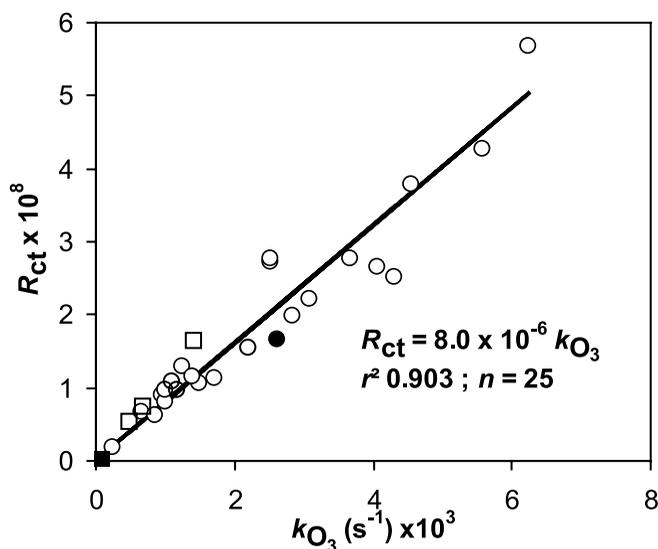


Figure 4 | R_{ct} vs secondary pseudo first-order rate constant of the ozone decay for Limmat river water (○), Lake Zürich water (□) Weihermattquelle spring water (■) and Eisetquelle spring water (●) (7.5 < pH < 8.0; 5°C < T < 30°C; 0.5 mg/l < $[O_3]_0$ < 2 mg/l).

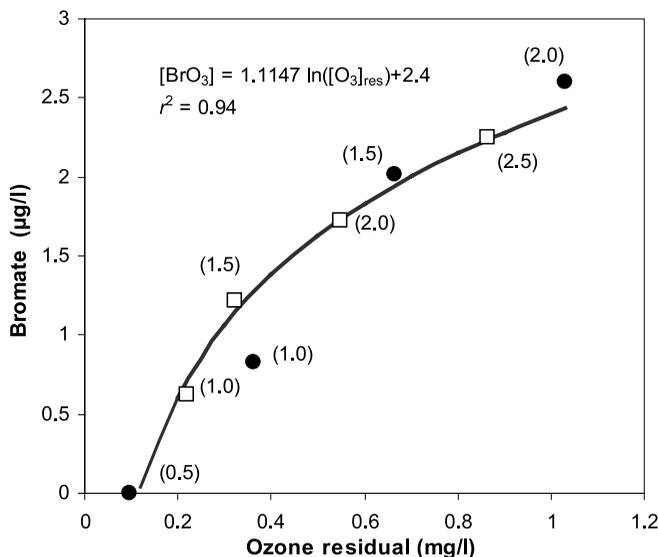


Figure 5 | Effect of pre-oxidation and ozone doses (0.5–2.5 mg/l) on both ozone residual and bromate formation after the pre-ozonation reactor of the River Limmat water treatment plant (●: with pre-oxidation (0.35 mg/l Cl_2 /0.1 mg/l ClO_2); □ without pre-oxidation). Mean water temperature 6.5°C.

higher with pre-oxidation for the same ozone dose. For an ozone dose of 0.5 mg/l, the bromate concentration was always below the detection limit (0.1 µg/l; Sahli & von Gunten, 1999).

For an ozone dosage of 2 mg/l, the ozone residual was 1 mg/l with pre-oxidation and 0.55 mg/l without pre-oxidation. The corresponding bromate concentration was 2.6 µg/l and 1.7 µg/l, respectively. These results are in agreement with those obtained in laboratory-scale experiments where the stability of ozone was significantly enhanced by pre-oxidation with chlorine and/or chlorine dioxide (Nos 16, 18 and 19, Table 2). Because bromate formation is directly proportional to the ozone exposure (ozone *ct*) (von Gunten & Hoigné, 1994), its higher formation in the case of pre-oxidation can be explained by the higher ozone exposure and the formation of HOBr. The oxidation of bromide to HOBr during pre-oxidation and the fast reaction of HOBr with organic matter seems to have no effect on bromate formation because both data sets, with or without pre-oxidation, can be described by the same curve.

Modelling of the ozone decomposition

Prior to modelling the ozone profile, the hydraulics of the ozone reactors were characterized using a conservative tracer. A good agreement between the experimental data and the hydraulic model was obtained using a plug flow reactor with diffusion for the ozone transfer compartment, and two completely stirred tank reactors for the first and second contact compartments, both with a high back flow rate.

For the experiments with pre-oxidation, ozone residual concentrations were measured at the different sampling points in the first ozonation reactor for each ozone dose (0.5, 1.0, 1.5 and 2.0 mg/l). In parallel, rate constants were directly determined in laboratory-scale experiments at 5°C for the ozone doses of 1 and 2 mg/l (Nos 4 and 7, Table 2). For an ozone dose of 0.5 mg/l, a rate constant equal to $1.8 \times 10^{-3} \text{ s}^{-1}$ at 5°C was calculated using the rate constant determined at 20°C (No. 3, Table 2) and a mean activation energy of 60 kJ/mol. For the ozone dose of 1.5 mg/l, a rate constant of $4.9 \times 10^{-4} \text{ s}^{-1}$ was extrapolated by plotting k_{O_3} vs O_3 dose for ozone doses of 0.5 mg/l, 1.0 mg/l (No. 4, Table 2) and 2.0 mg/l (No. 7, Table 2).

The rate constants for the ozone decomposition were used to calculate the ozone residual concentrations in the

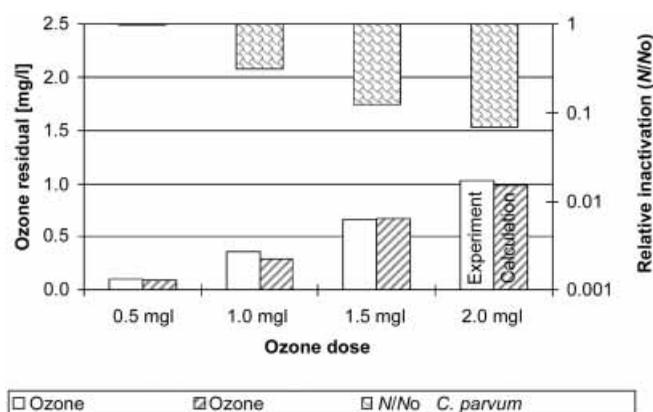


Figure 6 | Experimental and modelled ozone residual concentrations at P5 for different ozone doses (0.5–2 mg/l) and the corresponding modelled inactivation of *C. parvum* at 5°C and pH 8, in the pre-ozonation of the River Limmat water treatment plant, Zürich.

first ozonation reactor at the sampling points P1 to P5 (Figure 1) with the AQUASIM model (Reichert, 1994). Figure 6 shows a comparison of measured and modelled ozone concentrations at P5 for four different ozone doses. The model calculations and the measurements are in good agreement. A good correlation between experimental data and model calculations was also found at the other sampling points (results not presented). It was concluded from these experiments that the ozone concentration in the reactor could be well simulated by model calculations with AQUASIM. However, this is only true for a specific sampling day with defined water characteristics.

To further expand our predictions, two extreme situations were modelled: a typical winter (5°C) and a summer situation (20°C). During winter, a typical ozone dose for the pre-ozonation is about 1 mg/l. A rate constant of $8.65 \times 10^{-4} \text{ s}^{-1}$ and a fast initial ozone consumption of 34% (No. 4, Table 2) were used in the model calculations. The modelled ozone concentrations were 0.5 mg/l and 0.3 mg/l at P3 and P5, respectively, and are in agreement with values usually found in the treatment plant.

During summer, the ozone dose for the first ozonation is about 2 mg/l. A rate constant of $1.0 \times 10^{-3} \text{ s}^{-1}$ and fast ozone consumption of 32% (No. 1, Table 2) were used in the calculations. Calculated ozone concentrations of 0.5 and 0.2 mg/l at P3 and P5 were close to the values measured in the ozone reactor.

For the intermediate ozonation reactor, a constant dose of 0.5 mg/l ozone is applied throughout the year. The measured ozone concentrations at point P5 are about 0.35 and 0.3 mg/l in winter and summer, respectively. For a water with a low UV absorbance of 1 AU m⁻¹ (0.05 in 5 cm-cell) as expected in the intermediate ozonation step, a rate constant of 1.2 × 10⁻³ s⁻¹ was determined at 20°C (No. 14, Table 2). For the same water, a rate constant of 6 × 10⁻⁴ s⁻¹ at 5°C was calculated using an activation energy of 60 kJ/mol and the rate constant measured at 20°C (No. 14, Table 2). Introducing these two rate constants into the model, the calculated ozone concentrations were significantly below the measured values. During the second ozonation step, ozone has an unexpectedly high stability. With the rate constants fitted from full-scale data by the AQUASIM model, ozone decay rate constants of 2.0 × 10⁻⁴ s⁻¹ and 4.0 × 10⁻⁴ s⁻¹ were found at 5 and 20°C, respectively. An improved description of the ozone profile in the ozone contactor is possible with these values. Therefore, the modelling of the inactivation of

pathogens and the degradation of micropollutants is based on this approach.

Modelling of the inactivation of pathogens

The pathogens of main concern are currently *C. parvum* and *G. lamblia*. These protozoan microorganisms require a relatively high ozone exposure for inactivation. In addition to the pathogenic microorganisms, *B. subtilis* was used as a non-pathogenic indicator microorganism for the inactivation of *C. parvum* (Driedger *et al.*, 2000). *Bacillus subtilis* mimics the inactivation of *C. parvum* quite well at temperatures >15°C and is therefore included in this study for comparative purposes. The inactivation of these microorganisms occurs with a lag-phase followed by a first-order decrease. To account for this characteristic in the calculation of the relative inactivations (N/N_o), the delayed Chick–Watson expression proposed by Rennecker *et al.* (1999) was applied:

$$\frac{N}{N_o} = \begin{cases} 1 & \text{if } ct \leq ct_{lag} = \frac{1}{k_i} \ln \left(\frac{N_1}{N_o} \right) \\ \frac{N_1}{N_o} \exp(-k_i ct) = \exp(-k_i \{ct - ct_{lag}\}) & \text{if } ct > ct_{lag} = \frac{1}{k_i} \ln \left(\frac{N_1}{N_o} \right) \end{cases} \quad (2)$$

In Equation 2, k_i is the post lag-phase inactivation rate constant in 1/(mg · min) and N_1/N_o is the intercept with the ordinate axis resulting from extrapolation of the pseudo first-order line.

For the River Limmat water, the disinfection efficiency was calculated using the kinetic data given in Table 3. For *C. parvum* and *B. subtilis*, the calculations are based on kinetic inactivation studies (Hunt & Marinas, 1999; Driedger *et al.*, 2000, 2001). For viruses and *G. lamblia*, estimates of the rate constants were based on a database of the US Environmental Protection Agency (1989).

In the model calculations, a lag phase of $ct = 4.3$ mg · min/l for *C. parvum* and of 10 mg · min/l for *B. subtilis* were considered in the first ozonation step at 5°C. For the intermediate ozonation step, we assumed that oocysts and spores were already damaged by the pre-ozonation. Therefore, no lag phase was used in the model

calculations. Driedger *et al.* (2000) has shown that the lag phase is reduced by pre-treatment with chlorine.

Figure 7a and b shows the calculated relative inactivation of microorganisms in the pre-ozonation and intermediate ozonation reactor, respectively, at 5°C. Figure 7a shows that, because of its important lag phase at 5°C, there is no inactivation of *B. subtilis* in the pre-ozonation reactor. The relative inactivation of *C. parvum* oocysts is less than 1 log. In the intermediate ozonation reactor, inactivation of *B. subtilis* is more important than for *C. parvum* because there is no lag phase and the inactivation rate constant is higher for *B. subtilis*. In the first and intermediate ozonation reactors, >3 and >4-log inactivation of *G. lamblia* and enteric viruses are achieved, respectively.

Similar calculations were performed at 20°C using data from Table 3 with an ozone dose of 2 mg/l. At 20°C, the lag phase ct is 0.8 mg · min/l for *C. parvum* and 2.9 mg · min/l for *B. subtilis*. Figure 8 summarizes the

Table 3 | Kinetic data for the inactivation of bacteria, viruses and protozoa by ozone

Microorganism	T (°C)	Inactivation rate constant		Ea (kJ/mol)	ct _{lag} (mg · min)/l	Reference
		k _i (l/(mg · min))	Inactivation rate constant k _i (M ⁻¹ s ⁻¹)			
<i>C. parvum</i> oocysts	20	0.84	6.7 × 10 ²	81.2	0.8	Driedger <i>et al.</i> (2000)
<i>C. parvum</i> oocysts	5	0.16	1.3 × 10 ²	81.2	4.3	Driedger <i>et al.</i> (2000)
<i>B. subtilis</i> spores	20	2.9	2.3 × 10 ³	42.1	2.9	Driedger <i>et al.</i> (2001)
<i>B. subtilis</i> spores	5	0.97	7.8 × 10 ²	42.1	10	Driedger <i>et al.</i> (2001)
<i>G. lamblia</i> *	20	9.6	7.7 × 10 ³	47.7	0	US EPA (1989)
<i>G. lamblia</i> *	5	3.6	2.9 × 10 ³	47.7	0	US EPA (1989)
Enteric viruses (polio virus)*	20	18	1.4 × 10 ⁴	47.7	0	US EPA (1989)
Enteric viruses (polio virus)*	5	7.7	6.2 × 10 ³	47.7	0	US EPA (1989)

*Rough estimation of kinetic parameters using the Chick–Watson Equation (1) where $\ln(N/N_0) = -k_i \times ct$.

total inactivation (pre- and intermediate ozonation) of microorganisms at 5 and 20°C. Depending on the microorganisms, the inactivation for a given ozone dose in winter is lower by about 1 to 5 log units than in summer. At 5°C, there is only 1-log inactivation of *C. parvum* whereas for *G. lamblia* and viruses, the inactivation is higher than 7-log.

It is a good principle in water treatment to achieve equal safety levels (i.e. relative inactivation of microorganisms by ozone) throughout the year. Figure 8 shows that with an ozone dose of 1 mg/l in winter and 2 mg/l in summer a much lower inactivation is obtained in winter for *C. parvum* and other microorganisms. A higher ozone dose is required at low temperatures to obtain equal inactivation. In Figure 6 the model calculations for the inactivation of *C. parvum* are depicted for ozone doses between 0.5 and 2.0 mg/l. At an ozone dose of 2 mg/l, a five-times higher inactivation is achieved compared to an ozone dose of 1 mg/l. An ozone dose of 2 mg/l in winter, as well as in summer, improves relative inactivation and therefore drinking water safety. This leads to significantly higher ozone residuals after the contact compartment. Consequently, the common use of a constant ozone

residual throughout the seasons does not appear to be a good practice for ozone disinfection.

Modelling the oxidation of micropollutants

The degradation of micropollutants can be calculated knowing the ozone and OH radical concentrations in a particular water, based on the R_{ct} concept (von Gunten *et al.*, 1999). Using the ozone decay of a typical summer day (20°C) and a typical winter day (5°C), the degradation of five potential micropollutants was calculated. The selected micropollutants were tetrachloroethene (TCE), atrazine, 1,3,5-trimethylbenzene (TMB), p-xylene and methyl tertiary butyl ether (MTBE). Their second-order rate constants with ozone and OH-radical are given in Table 4.

Figure 9 shows the calculated relative degradation of these micropollutants in the ozonation reactors (pre- and intermediate ozonation) for a typical winter (5°C) and a summer situation (20°C). The ozone dosages for pre- and intermediate ozonation were 1 and 0.5 mg/l for winter, and 2 and 0.5 mg/l for summer. Methyl tertiary butyl ether and tetrachloroethene showed quite similar behaviour and the smallest degree of degradation, which was in the

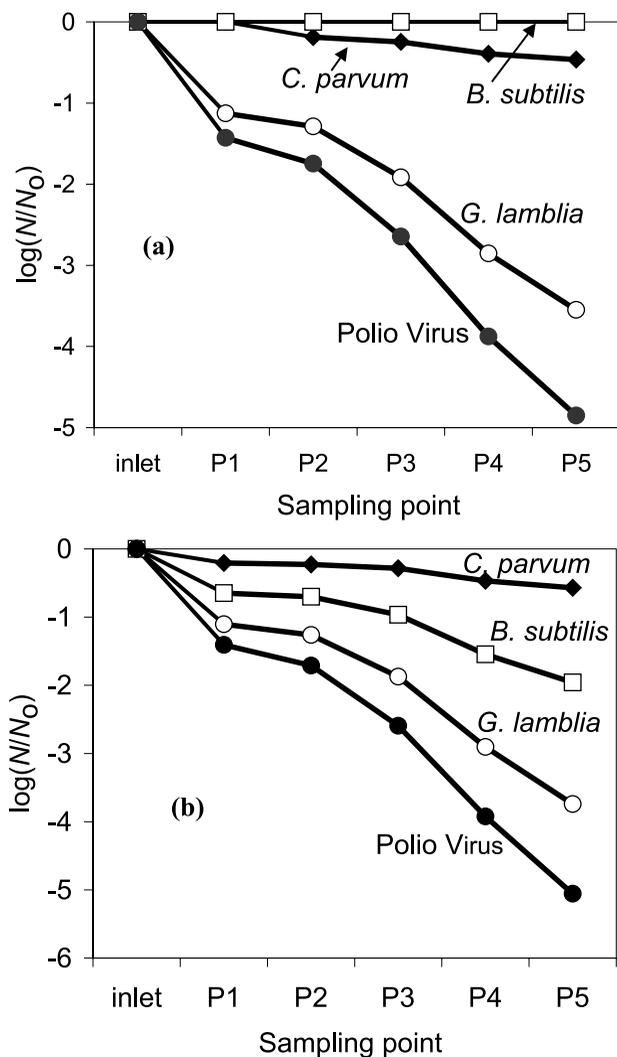


Figure 7 | Modelled relative inactivation of microorganisms during the pre- and intermediate ozonation at 5°C and pH 8 (River Limmat water treatment plant, Zürich). (a) Pre-ozonation (ozone dose 1 mg/l), (b) intermediate ozonation (ozone dose 0.5 mg/l).

range of 15 to 25%. Both compounds do not react with ozone (Table 4) and have the lowest rate constants for the reaction with OH radicals. The degree of oxidation of atrazine was in the range of 30–40% whereas the degree of oxidation of 1,3,5-trimethylbenzene and p-xylene was much higher (>80%). This observation can be explained by the higher rate constants for these compounds (TMB, p-xylene) for the reaction with ozone. For both compounds the oxidation by ozone is the dominant process.

In the case of poorly oxidizable compounds such as MTBE and TCE, degradation products have to be expected. As an example, the oxidation of MTBE and the formation of degradation products were calculated for the pre-ozonation reactor of the River Limmat water treatment plant and are shown in Figure 10. A further oxidation in the intermediate ozonation can be neglected because of the higher ozone stability, which leads to limited oxidation by OH radicals as the only oxidation pathway for MTBE (Table 4). The calculated degree of oxidation of MTBE in the pre-ozonation reactor is approximately 20%. The degradation products were calculated based on the relative rate constants leading to these products which have been determined in a previous study (Acero *et al.*, 2001). The example in Figure 10 shows that it is not only possible to predict the degree of oxidation of a compound but also the formation of degradation products. However, this is only possible if the corresponding kinetics are known. The most important products are tertiary butyl formate (TBF), 2-methoxy-2-methyl propionaldehyde (MMP), acetone (AC), tertiary butyl alcohol (TBA) and methyl acetate (MA). Some of these products are biodegradable and will be eliminated in a biological filtration step which follows ozonation. However, the tertiary products in particular are difficult to degrade and will persist in the drinking water.

CONCLUSIONS

The two ozonation steps of the River Limmat water treatment plant were validated with respect to disinfection and oxidation. The validation is based on several levels:

- In laboratory-scale experiments the ozone decomposition kinetics were determined, together with the ratio R_{ct} of the concentrations of OH radicals and ozone for the whole range of expected seasonal variations (concentration of natural organic matter and temperature). In addition, the effect of ozone dose was tested. It was shown that for a certain water there is a linear correlation between

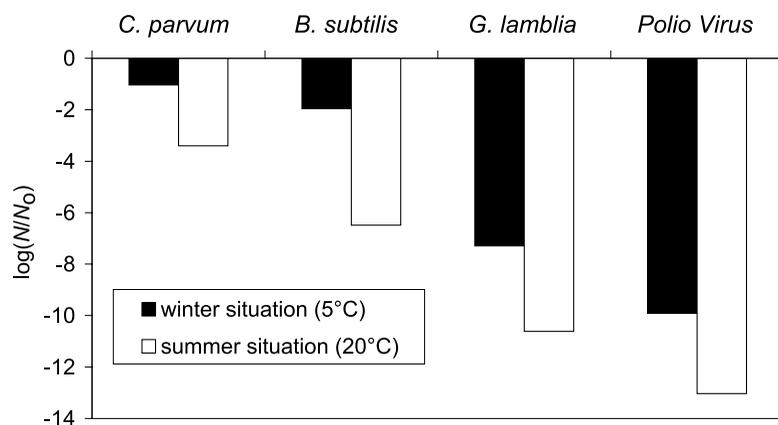


Figure 8 | Limmat River water treatment plant, Zürich: model calculations for the total relative inactivation of microorganisms after pre- and intermediate ozonation for a winter (5°C) and summer (20°C) situation at pH 8. Winter: pre-ozonation 1 mg/l, intermediate ozonation 0.5 mg/l; summer: pre-ozonation 2 mg/l, intermediate ozonation 0.5 mg/l.

Table 4 | Kinetic data for the reaction of organic compounds with ozone and OH radical

Micropollutant	Rate constant with O ₃ at 20°C (M ⁻¹ s ⁻¹)	Activation energy, E _a (kJ/mol)	Rate constant with O ₃ at 5°C (M ⁻¹ s ⁻¹)	Rate constant with °OH at 5–20°C (M ⁻¹ s ⁻¹)
Tetrachlorethene	0.1	40	0.04	2.3 × 10 ⁹
Atrazine	7.0	37	4.0	3.0 × 10 ⁹
1,3,5-trimethylbenzene	400	40	170	6.4 × 10 ⁹
p-xylene	140	40	58	7.0 × 10 ⁹
Methyl tertiary butyl ether	0.14	—	—	1.9 × 10 ⁹

Sources: Hoigné & Bader (1983); Buxton et al. (1998); Acero et al. (2000, 2001).

the first-order rate constant for the ozone decomposition and the R_{ct} (ratio of concentration of OH radicals and ozone) which allows a significant reduction of the number of measurements.

- The hydraulics of the two ozonation reactors were determined by a tracer test and modelled with AQUASIM. Furthermore, the hydraulics were coupled with the ozone and OH radical characteristics, which allows prediction of the extent of disinfection and oxidation.
- It could be calculated that the two ozonation steps (1 mg/l ozone and 0.5 mg/l ozone) yield an overall inactivation for *C. parvum* oocysts of 1-log (5°C) or

3-log (20°C); for *B. subtilis* spores 2-log (5°C) or >6-log (20°C); for *G. lamblia* >7-log (5°C) or >10-log (20°C); and for polio virus >9-log (5 and 20°C). The lower temperature reflects winter conditions, whereas the higher temperatures indicate summer conditions.

- Chemical compounds showed a less pronounced effect of temperature, however, seasonal variation in the ozone dosage affects the degree of oxidation. The percentage oxidation increased in the order: 15–25% of tetrachloroethene, 15–25% of methyl tertiary butyl ether, 30–40% of atrazine, 80–90% of p-xylene and 97–100% of trimethylbenzene.

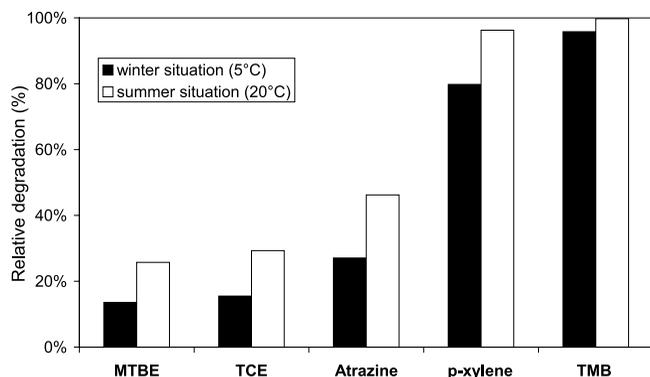


Figure 9 | Relative degradation of micropollutants in the ozonation reactors (pre- and intermediate ozonation) of the River Limmat water treatment plant, Zürich, at pH 8. Winter (5°C): pre-ozonation 1 mg/l, intermediate ozonation 0.5 mg/l; summer (20°C): pre-ozonation 2 mg/l, intermediate ozonation 0.5 mg/l. MTBE: methyl tertiary butyl ether, TCE: tetrachloroethene, TMB: 1,3,5-trimethylbenzene.

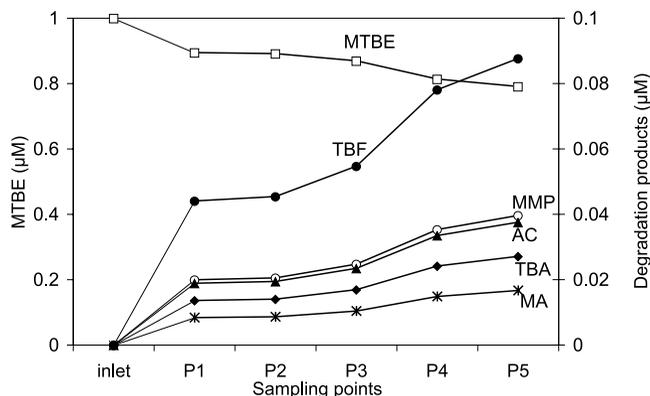


Figure 10 | Oxidation of MTBE (methyl tertiary butyl ether) and formation of degradation products during pre-ozonation in the River Limmat water treatment plant, Zürich at pH 8 and 20°C (ozone dose 2 mg/l). TBF: tertiary butyl formate; MMP: 2-methoxy-2-methyl propionaldehyde; AC: acetone; TBA: tertiary butyl alcohol; MA: methyl acetate.

- Bromate formation was $\leq 2.5 \mu\text{g/l}$ for all treatment conditions. This is mainly due to the low bromide levels in the raw water ($\leq 10 \mu\text{g/l}$).

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