

Effects of natural organic matter (NOM) character and removal on ozonation for maximizing disinfection with minimum bromate and AOC formation

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ABSTRACT

The objective of this study was to evaluate the effects of the character and the removal of natural organic matter (NOM) on the formation of assimilable organic carbon (AOC) and bromate during ozone disinfection. Natural waters from two locations with different dissolved organic carbon (DOC) concentrations were tested. In addition, the DOC concentration of one of the natural waters was reduced either by ion exchange (IEX) or by granular activated carbon (GAC) filtration. The resulting four water types were tested in conventional pilot-scale ozone bubble column reactors and in a bench-scale plug flow reactor with dissolved ozone dosing. For the tested waters NOM fractions were determined with size exclusion chromatography using DOC and UVA₂₅₄ detection. As expected, it was observed that for the same ozone dosages the CT is higher when NOM is removed by IEX or GAC compared to the situation without NOM removal. It is concluded that, for the waters tested, removal of the humic compounds with a molecular weight of approximately 1,000 g/mol by using IEX led to less AOC formation and less bromate formation as compared to the removal of humic compounds with a molecular weight of 300–500 g/mol by using GAC.

Key words | AOC, bromate, disinfection, NOM, ozone, SEC-DOC, SUVA

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NOMENCLATURE

AOC	assimilable organic carbon	LMW acids	low molecular weight acids
BB	building blocks (breakdown products of humic substances)	MW	molecular weight
CT	ozone exposure ((mg-O ₃ /l) min)	NOM	natural organic matter
DOC	dissolved organic carbon (mg-C/l)	OCD	organic carbon detection
DOPFR	dissolved ozone plug flow reactor	SEC-DOC	size exclusion chromatography combined with online dissolved organic carbon detection
DPD	diethyl-p-phenylenediamine	SUVA	specific UV absorbance defined as UVA ₂₅₄ divided by DOC concentration ((1/m)/(mg-C/l))
GAC	granular activated carbon	TOC	total organic carbon
HS	humic substances	UVA ₂₅₄	UV absorbance at 254 nm
IEX	ion exchange	UVD	UV absorbance detection
LC-OCD	liquid chromatography combined with online organic carbon detection	Waternet	water cycle company for Amsterdam and surrounding areas
LDN	drinking water treatment plant Leiduin of Waternet		

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WPK	drinking water treatment plant Weesperkarspel of Waternet
c_{O_3}	concentration of ozone in water (mg- O_3 /l)
f_{OCD}	conversion factor for calculation of the DOC concentration from the relative signal response of the OCD chromatogram measured with SEC-DOC (mg-C/l)
f_{UVD}	conversion factor for the calculation of UVA_{254} from the relative signal response of the UVD chromatogram measured with SEC-DOC (1/m)
k_{O_3}	first-order ozone decomposition rate (1/s)
k_{UVA}	UVA_{254} decay rate (1/s)
n_{SP}	number of sampling points
$SUVA_{BB}$	SUVA for building blocks fraction from SEC-DOC ((1/m)/(mg-C/l))
$SUVA_{HS}$	SUVA for humic substances fraction from SEC-DOC (1/m)/(mg-C/l)
$SUVA_{HS+BB}$	SUVA for the humic substances fraction and the building blocks fraction from SEC-DOC together ((1/m)/(mg-C/l))
t	hydraulic residence time (s)
UVA	UVA_{254} in water (1/m)
UVA_0	stable UVA_{254} after completion of the ozonation process (1/m)
Y	yield for ozone consumed per UVA_{254} decrease ((mg- O_3 /l)/(1/m))

INTRODUCTION

In drinking water treatment, ozonation is used for disinfection, oxidation of micro-pollutants, formation of biodegradable organic matter for removal by biological (activated carbon) filtration, and for improvement of color, taste and odor. In bromide-containing waters, the by-product bromate is formed (von Gunten 2003) which is the major constraint to application of ozonation in drinking water treatment. Ozone is an unstable oxidant in water. In general, when ozone is added to natural water, it decomposes in two phases: the initial phase and the second phase (Buffle *et al.* 2006b). The second phase of ozone decomposition (minutes range) follows an empirical first-order rate law, while the initial phase of ozone

decomposition (seconds range) follows higher-order kinetics, indicating that other reaction mechanisms take place (Buffle *et al.* 2006b). The ozone decomposition in the initial phase is mainly due to reactions with natural organic matter (NOM). The objective of this study was to evaluate the effects of the character of NOM and the removal of NOM on CT for disinfection, on the formation of assimilable organic carbon (AOC) as a measure for biodegradable organic matter, and on the formation of bromate during ozonation. With the results of this research it can be determined what amount and which part of the NOM should be removed for maximizing CT with minimum bromate and AOC formation.

NOM is a mixture of a range of organic components that can be quantified by measuring dissolved organic carbon (DOC) concentration and characterized by size, aromaticity and biodegradability. NOM characterization by size is possible with size exclusion chromatography combined with online dissolved organic carbon detection (SEC-DOC, also known as LC-OCD). Characterization of NOM by its aromaticity is done by UV absorbance at 254 nm (UVA_{254}). UVA_{254} is sensitive to the conjugation of three carbon double bonds. In natural waters these are present in NOM as aromatic carbon. The aromaticity per unit of DOC is expressed by the specific UV absorbance (SUVA), which is defined by UVA_{254} expressed as the absorbance per meter of path length (1/m) divided by the DOC concentration (mg-C/l). Croué *et al.* (1999) and Westerhoff *et al.* (1999) observed that SUVA, aromatic carbon content and molecular weight correlate well for NOM isolates. The biodegradable part of NOM can be expressed by assimilable organic carbon (AOC) (van der Kooij *et al.* 1982).

Several studies have been undertaken on the removal of NOM by ion exchange (IEX) and granular activated carbon (GAC) with respect to NOM character. Croué *et al.* (1999) did extensive research on two strong base anion exchange resins (macroporous matrix and gel matrix) and one weak base anion exchange resin. Croué *et al.* (1999) concluded that strong base resins are generally more efficient for the removal of DOC, and the higher the molecular weight of the NOM fraction the lower the affinity with the anion exchange resin. Cornelissen *et al.* (2008) investigated the removal of NOM and specific NOM fractions determined by LC-OCD and fluorescence excitation–emission matrices

of nine anionic exchange resins. [Cornelissen *et al.* \(2008\)](#) observed that removal of specific NOM fractions proved to vary considerably for the different types of IEX resins, ranging from 1% to almost 60%. They concluded that the best-performing IEX resins consisted of the smallest resins and/or those with the highest water content and that the worst-performing IEX resins reflected the highest exchanging capacities and the lowest water contents. [Matilainen *et al.* \(2006\)](#) conducted research on the performance and capacity of NOM removal by three different GAC types. These researchers, using high-performance size exclusion chromatography measurements, concluded that GAC was most effective for DOC fractions with a molecular weight of 1,000–4,000 g/mol and that the removal efficiency for fractions with higher and lower molecular weights was very small. [Chen \(1999\)](#) and [Fettig \(2005\)](#) performed comparison studies between IEX and GAC for NOM removal without a focus on NOM character. [Chen \(1999\)](#) used water with total organic carbon (TOC) concentrations of 0.5–2.2 mg-C/l and [Fettig \(2005\)](#) used water with DOC concentrations of 10.2–42.5 mg-C/l. Both concluded that a strong base anion exchange resin was more effective compared to GAC for the removal of TOC and DOC.

Based on the reactivity of model compounds with ozone, it is known that ozone consumption is influenced by organic carbon structures and functionality. As a result of direct ozone consumption by unsaturated bonds in humic compounds a decrease in UV absorbance occurs during ozonation and, when main chain scissions occur, humic compounds are transformed into smaller organic components ([Langlais *et al.* 1991](#); [Westerhoff *et al.* 1999](#)). From research on physical and chemical properties of NOM isolates [Westerhoff *et al.*](#) found that the ozone decomposition rate parameters correlated best with SUVA. This indicated that a higher SUVA of NOM isolates results in a higher reactivity with ozone.

MATERIALS AND METHODS

Test waters

Natural waters were tested from the drinking water treatment plants Leiduin (LDN) and Weesperkarspel

(WPK) of Waternet (the water cycle company for Amsterdam and surrounding areas), each with a different DOC concentration. In addition, the DOC concentration of the WPK water was reduced by IEX or GAC filtration. At both plants the test water was taken before the ozonation steps. The LDN water before ozonation is Rhine River water treated by coagulation, rapid sand filtration, dune infiltration, aeration and rapid sand filtration. The WPK water before ozonation is seepage water treated by coagulation, self-purification in a lake and rapid sand filtration. For IEX treatment of the WPK water, PWA 958, a strong base anion exchange type 1 resin from Rohm & Haas, was used. PWA 958 is a macroreticular cross-linked acrylic copolymer with an exchange capacity of 0.8 meq/ml (Cl⁻ form) or 4.3 meq/g. For GAC treatment of the WPK water fresh Chemviron F300 was used. The applied empty bed contact time (EBCT) was 15 s for IEX and 5 min for GAC. These EBCTs were sufficient to reduce the DOC concentration by more than 50%.

Installations

Experiments were performed in three different installations:

1. Bench-scale dissolved ozone plug flow reactor (DOPFR). In the DOPFR a small side stream of Milli-Q[®] demineralized water containing dissolved ozone (approximately 10 l/h, with ozone concentrations up to 16 mg-O₃/l) was mixed with a larger main stream consisting of test water (approximately 100 l/h). Subsequently, contact time was created in a plug flow reactor that consisted of a 63.9 m long PTFE tube with an inner diameter of 8 mm with 14 sampling points with contact times ranging from approximately 1.5–120 s ([van der Helm *et al.* 2007](#)). In this installation water from LDN and WPK was treated for determining ozone kinetics.
2. Pilot-plant co-current ozone bubble column (5.10 m height, diameter of 0.10 m with 10 sampling points) followed by a counter current ozone bubble column (4.50 m height, diameter of 0.10 m with 10 sampling points) and two contact columns (4.40 m and 4.20 m height, diameter of 0.39 m with sampling points in the effluent). The flow through the installation was approximately 1 m³/h. In the co-current bubble column, 40% of

the ozone was dosed, and in the counter current bubble column 60% of the ozone was dosed. The water could be treated by either IEX or GAC before entering the ozonation. In this installation water from WPK was treated.

3. Pilot-plant counter current ozone bubble column (5.30 m water height, diameter of 0.22 m with 12 sampling points) followed by three contact columns (5.25 m water height, diameter of 0.22 m with 12 sampling points, 4.9 m water height and 4.7 m water height, both with a diameter of 0.65 m with sampling points in the effluent). The flow through the installation was approximately 5 m³/h. In this installation water from LDN was treated.

Experiments

The water quality parameters for the experiments in the DOPFR and in the bubble column installations at WPK and LDN are presented in Table 1. The ozone dosage in the DOPFR was determined by measuring the ozone concentration in the side stream, the flow of the side stream and the flow of the main stream. The ozone dosage in the bubble column experiments was determined from the applied ozone gas concentration, ozone gas flow and the water flow. Since the transfer efficiency of ozone in the bubble columns was near 100%, based on measurements of the ozone gas concentration of the off-gas, the ozone dosage was regarded as the amount of ozone transferred to water.

Analysis methods

For the DOPFR experiments, ozone was analyzed with the indigo method based on Bader & Hoigné (1982). For the bubble column experiments ozone was analyzed by the DPD (diethyl-*p*-phenylenediamine) method described by Gilbert (1981). Both methods give consistent results (Gilbert

standard procedures (*Standard Methods* 2005). Bromate samples were concentrated on two Ionpac AG9-SC columns and analyzed using a Dionex ICS3000 ion chromatograph, with an anion micro membrane suppressor, UV detection (200 nm) and conductivity meter. Dionex Ionpac AG9-SC and AS9-SC columns were used with a 0.7 mM NaHCO₃ eluent. The minimum detection limit is 0.5 µg-BrO₃⁻/l (Smeenk *et al.* 1994; Orlandini *et al.* 1997). Bromide samples were analyzed using a Dionex DX120 ion chromatograph, with chemical suppressor (12.5 mM H₂SO₄), UV detection (200 nm) and conductivity meter. A Dionex Ionpac AS9-SC column was used with a 0.2 mM NaHCO₃/1.4 mM Na₂CO₃ eluent (Orlandini *et al.* 1997).

NOM characterization was performed by SEC-DOC (also known as LC-OCD) with on-line UVA₂₅₄ detection, described by Huber & Frimmel (1992, 1996). The fractions of interest for this research are the humic substances (HS) fractions (quantified on the basis of Suwannee River Standard Stream humic substances, MW ~ 1,000 g/mol), the building blocks (BB) fraction (humic substances hydrolysates formed from the breakdown of humic substances, MW 300–500 g/mol) and the low molecular weight (LMW) acids fraction. For analysis of the reactivity of NOM with ozone, the SUVA was determined from the SEC-DOC chromatograms for the humic substances fraction, for the building blocks fraction and for the combined fractions of humic substances and building blocks together:

$$\text{SUVA}_{\text{HS}} = \frac{\text{relative signal response UVD}_{\text{at elution time HS peak}} f_{\text{UVD}}}{\text{relative signal response OCD}_{\text{at elution time HS peak}} f_{\text{OCD}}} \quad (1)$$

$$\text{SUVA}_{\text{BB}} = \frac{\text{relative signal response UVD}_{\text{at elution time BB peak}} f_{\text{UVD}}}{\text{relative signal response OCD}_{\text{at elution time BB peak}} f_{\text{OCD}}} \quad (2)$$

$$\text{SUVA}_{\text{HS+BB}} = \frac{(\text{rel.sign.resp.UVD}_{\text{at el.time HS peak}} + \text{rel.sign.resp.UVD}_{\text{at el.time BB peak}}) f_{\text{UVD}}}{(\text{rel.sign.resp.OCD}_{\text{at el.time HS peak}} + \text{rel.sign.resp.OCD}_{\text{at el.time BB peak}}) f_{\text{OCD}}} \quad (3)$$

& Hoigné 1983). AOC was measured in duplicate, applying the simultaneous incubation of strains P17 and NOX (van der Kooij *et al.* 1982). DOC and UVA₂₅₄ expressed as the absorbance per meter of cell length were determined using

where SUVA_{HS} is the SUVA for the humic substances fraction ((1/m)/(mg-C/l)), SUVA_{BB} is the SUVA for the building blocks fraction ((1/m)/(mg-C/l)), SUVA_{HS+BB} is the SUVA for the humic substances fraction and the

Table 1 | Ozone dosages and water quality parameters for: (i) DOPFR experiments; (ii) WPK bubble column experiments at “low” ozone dosages and LDN bubble column experiments; (iii) WPK bubble column experiments at “high” ozone dosages**DOPFR experiments**

Parameter	Unit	WPK water	WPK IEX tr.	WPK GAC tr.	LDN water
O ₃ dosage	mg-O ₃ /l	1.43	1.39	1.48	0.90
UVA ₂₅₄	1/m	15.4	5.6	6.3	6.1
Bromide	μg-Br ⁻ /l	97	99	110	158
DOC	mg-C/l	6.3	3.1	2.8	2.4
SUVA	(1/m)/(mg-C/l)	2.46	1.81	2.25	2.54
SEC-DOC	–	NO	NO	NO	NO
pH	–	7.7	7.8	7.7	7.9
Bicarbonate	mg-HCO ₃ ⁻ /l	208	212	201	200
AOC	μg-C/l	8.3	4.4	3.6	64.0*
Temperature	°C	12.0	12.2	12.5	12.0
O ₃ dosage/DOC	(mg-O ₃ /l)/(mg-C/l)	0.36	0.72	0.84	0.45

WPK bubble column experiments “low” ozone dosages and LDN bubble column experiment

Parameter	Unit	WPK water	WPK water	WPK water	WPK IEX tr.	WPK IEX tr.	WPK GAC tr.	WPK GAC tr.	LDN water
O ₃ dosage	mg-O ₃ /l	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.93
UVA ₂₅₄	1/m	14.4	14.4	14.4	2.5	4.1	1.2	6.0	5.5
Bromide	μg-Br ⁻ /l	99	94	90	–	98	–	–	170
DOC	mg-C/l	6.6	6.0	5.8	1.5	2.7	0.7	2.8	2.5
SUVA	(1/m)/(mg-C/l)	2.18	2.40	2.48	1.67	1.52	1.62	2.14	2.20
SEC-DOC	–	NO	NO	YES	NO	YES	NO	YES	NO
pH	–	7.6	7.6	7.6	7.7	7.6	7.6	7.6	7.9
Bicarbonate	Mg-HCO ₃ ⁻ /l	201	208	202	201	206	203	208	186
AOC	μg-C/l	8.4	8.3	14.0	3.7	6.6	30 [†]	4.9	8.6
Temperature	°C	13.0	12.2	11.0	12.0	10.5	12.2	11.0	12.3
O ₃ dosage/DOC	(mg-O ₃ /l)/(mg-C/l)	0.13	0.14	0.15	0.57	0.31	1.15	0.30	0.37

WPK bubble column experiments “high” ozone dosages

Parameter	Unit	WPK water	WPK water	WPK water	WPK IEX tr.	WPK IEX tr.	WPK IEX tr.	WPK GAC tr.	WPK GAC tr.
O ₃ dosage	mg-O ₃ /l	1.70	1.70	1.70	1.70	1.70	1.70	1.70	1.70
UVA ₂₅₄	1/m	14.2	13.8	14.6	1.4	3.0	3.4	0.3	6.7
Bromide	μg-Br ⁻ /l	92	93	98	–	46	102	–	–
DOC	mg-C/l	5.7	5.5	5.6	1.4	1.8	2.2	0.2	3.3

Table 1 | (continued)
WPK bubble column experiments "high" ozone dosages

Parameter	Unit	WPK water	WPK water	WPK water	WPK water	WPK IEX tr.	WPK IEX tr.	WPK IEX tr.	WPK GAC tr.	WPK GAC tr.
SUVA	(1/m)/(mg-C/l)	2.49	2.51	2.61	1.00	1.67	1.55	1.36	2.03	2.03
SEC-DOC	-	NO	NO	NO	NO	NO	NO	NO	NO	NO
pH	-	7.7	7.7	7.7	7.6	7.6	7.7	7.6	7.6	7.6
Bicarbonate	mg-HCO ₃ ⁻ /l	205	205	210	200	203	203	203	207	207
AOC	µg-C/l	11.0	9.9	8.6	12.0	9.8	13.0	7.5	6.4	6.4
Temperature	°C	15.4	15.2	12.0	15.7	12.0	11.5	15.6	11.6	11.6
O ₃ dosage/DOC	(mg-O ₃ /l)/(mg-C/l)	0.30	0.31	0.30	1.21	0.94	0.77	7.73	0.52	0.52

^aThis value is likely to be a wrong measurement since AOC concentrations for LDN water are between 8 and 13 µg-C/l.

^bThis value is likely to be a wrong measurement since the AOC concentration before treatment with GAC was 10 µg-C/l.

building blocks fraction together ((1/m)/(mg-C/l)), f_{UVD} is the conversion factor for the calculation of UVA₂₅₄ from the relative signal response of the UV absorbance detection (UVD) chromatogram (1/m) and f_{OCD} is the conversion factor for calculating the DOC concentration from the relative signal response of the organic carbon detection (OCD) chromatogram (mg-C/l); f_{UVD} and f_{OCD} are determined from the integrated signal responses of the chromatograms and the measurements of UVA₂₅₄ and DOC in the bypass.

Ozone kinetics and CT calculation

Ozone decomposition consists of an initial phase and a second phase. Buffle *et al.* (2006a) defined the initial phase of ozone decomposition as the decomposition in the first 20 s of contact time ($t < \sim 20$ s) and modeled the initial phase as direct reactions between ozone and some highly reactive moieties of the dissolved organic matter. van der Helm *et al.* (2008) described the initial phase of ozone decomposition as a function of the degradation of UVA₂₅₄ with first-order kinetics, while the second phase was described as first-order kinetics (Hoigné & Bader 1994), resulting in the following equations:

$$\frac{dc_{O_3}}{dt} = -k_{UVA}(UVA - UVA_0)Y - k_{O_3}c_{O_3} \quad (4)$$

$$\frac{d(UVA)}{dt} = -k_{UVA}(UVA - UVA_0) \quad (5)$$

where c_{O_3} is the concentration of ozone in water (mg-O₃/l), t is the hydraulic residence time (s) defined by the reactor volume divided by the water flow, k_{UVA} is the UVA₂₅₄ decay rate (1/s), UVA is the UVA₂₅₄ in water (1/m), UVA_0 is the stable UVA₂₅₄ after completion of the ozonation process (1/m), Y is the yield for ozone consumed per UVA₂₅₄ decrease ((mg-O₃/l)/(1/m)) and k_{O_3} is the first-order ozone decomposition rate (1/s).

The rate constants k_{O_3} and k_{UVA} and the yield Y are calculated from the ozone concentration profiles measured in the DOPFR. In the DOPFR ozone concentrations can be measured for 14 different contact times ranging from approximately 1.5–120 s. For contact times beyond 120 s, batch experiments were performed (van der Helm *et al.* 2007). The CT value (ozone in water concentration

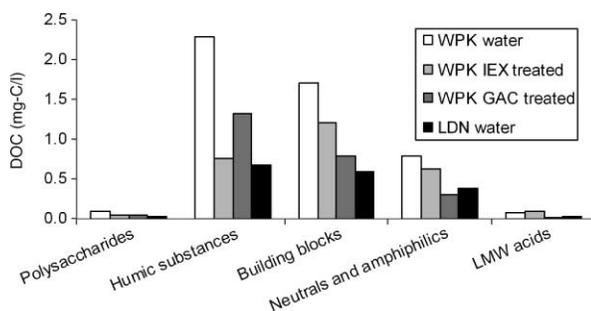


Figure 1 | Concentrations of the DOC fractions of the test waters (polysaccharides MW > 20,000 g/mol; humic substances MW ~ 1,000 g/mol; building blocks MW 300–500 g/mol; neutrals and amphiphilics MW < 350 g/mol).

“C” times contact time “T”) is calculated using

$$CT = \sum_{i=0}^{n_{SP}} \frac{c_{O_3,i} + c_{O_3,i-1}}{2} (t_i/60 - t_{i-1}/60) \quad (6)$$

where CT is the ozone exposure ((mg-O₃/l)*min) and n_{SP} is the number of sampling points. CT values calculated for the bubble column experiments include the contact columns as well as the bubble columns.

RESULTS AND DISCUSSION

NOM characterization of test waters

On all four test waters an SEC-DOC analysis was performed. For these experiments the DOC concentration of the WPK water was 5.8 mg-C/l and the removal with IEX or GAC was around 50%, resulting in 2.7 mg-C/l and 2.8 mg-C/l, respectively. The DOC concentration of the LDN water was 2.4 mg-C/l. In Table 1 the other water quality parameters for the four test waters are shown. The concentrations of the DOC fractions calculated from the OCD chromatogram are shown in Figure 1. DOC recovery by the SEC-DOC measurements was 85–90% for the three

WPK waters and 77% for the LDN water. In the discussion of the experimental results it is assumed that the DOC retained during the SEC-DOC measurements does not consist of the ozone reactive DOC fractions (HS and BB) and thus do not influence bromate and AOC formation.

From Figure 1 it can be observed that the main part of the NOM consists of humic compounds. The polysaccharides and LMW acid concentrations are very low for the tested natural waters. Since the polysaccharides are not ozone reactive, these values are discarded in the discussion. Figure 1 also shows that, for the waters tested, IEX does not remove LMW acids, IEX removes more humic substances than GAC and GAC removes more building blocks and neutrals than IEX.

In Table 2 the UVA₂₅₄, the DOC concentrations and the SUVA values are given for the ozone reactive DOC fractions (HS and BB). It is observed that, even though the IEX-treated WPK water and the GAC-treated WPK water have differences in UVA₂₅₄, DOC concentration and SUVA value for the separate humic substances and building blocks fractions, the summed values (HS + BB) are almost equal.

Effect of ozonation on NOM fractions

In Figure 2 (left), the effect of an ozone dosage of 1.70 mg-O₃/l on NOM is shown for the WPK water, and in Figure 2 (right) the effect of an ozone dosage of 1.04 mg-O₃/l on NOM is shown for the LDN water for different ozone contact times. Only the relevant parts of the OCD and the UVD chromatogram determined by SEC-DOC, as well as the relevant part of the SUVA (relative signal response of the UVD divided by the relative signal response of the OCD) chromatogram, are shown in Figure 2. From the decrease in the UVD chromatograms in Figure 2, it is

Table 2 | UVA₂₅₄, DOC concentrations and SUVA values for the ozone reactive DOC fractions

	UVA ₂₅₄ (1/m)			DOC (mg-C/l)			SUVA ((1/m)/(mg-C/l))		
	HS	BB	HS + BB	HS	BB	HS + BB	HS	BB	HS + BB
WPK water	5.6	3.3	8.9	2.3	1.7	4.0	2.43	1.94	2.23
WPK IEX-treated	1.9	2.0	3.9	0.8	1.2	2.0	2.38	1.67	1.95
WPK GAC-treated	2.8	1.3	4.1	1.3	0.8	2.1	2.15	1.63	1.95
LDN water	1.7	1.1	2.8	0.7	0.6	1.3	2.43	1.83	2.15

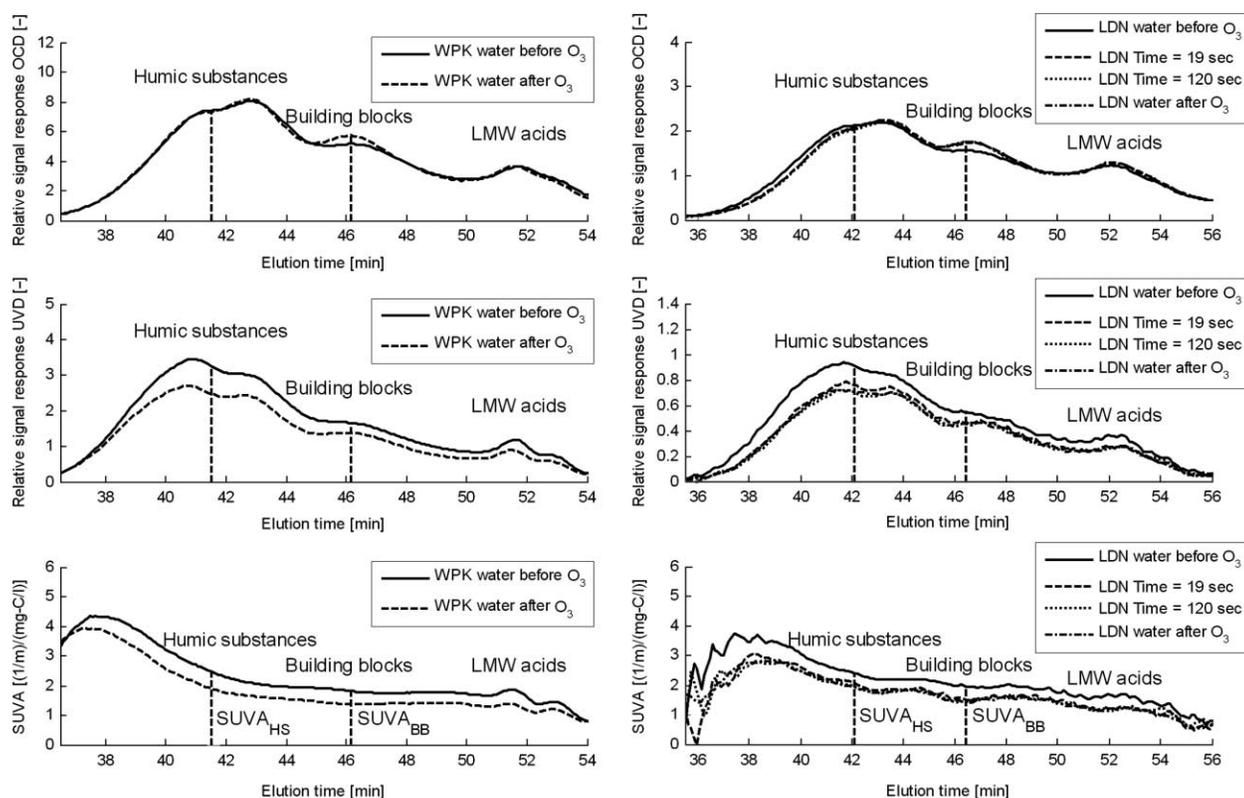


Figure 2 | SEC-DOC chromatograms showing the effect of ozone on NOM: (i) WPK water before and after ozonation (left); (ii) LDN water before ozonation, during ozonation for 19 and 120 s and after ozonation (right); the dotted lines indicate the elution time of the centroids of the humic substances' peak and the building blocks' peak of the OCD chromatogram (top).

suggested that ozone attacks unsaturated bonds in the humic substances and building blocks fractions, which results in smaller organic components since the OCD chromatograms show a small decrease in humic substances accompanied by a small net increase in building blocks and an increase in LMW acids. From Figure 2 (right) it is concluded that the largest part of the change in DOC in the LDN water takes place in the first 20 s of ozone exposure.

In Table 3 the decrease in SUVA due to ozonation is given for the four different test waters. The results shown in Table 3 indicate that the building blocks fraction is more ozone reactive than the humic substances fraction, since the decrease in $SUVA_{BB}$ is larger than the decrease in $SUVA_{HS}$. The IEX-treated WPK water has a higher decrease in $SUVA_{BB}$ than the GAC-treated WPK water. A possible explanation for the difference between GAC and IEX is that GAC may remove more building blocks with aromatic constituents than IEX does. The peak in the SUVA in

Figure 2 appears earlier than the peak in the OCD chromatogram, which indicates that the heaviest part of the humic substances may contain the highest amount of aromatic constituents. The decrease in the UVD chromatogram in the LMW acid region is due to reactions of ozone with building blocks that partly elute at the same time as the LMW acids. Most LMW acids do not absorb UV light at 254 nm and thus do not contribute to a decrease in the UVD chromatogram. The lowest molecular weight acid that does absorb at 254 nm is benzoic acid.

Table 3 | Decrease in SUVA in percentage due to ozonation

	Ozone dosage (mg-O ₃ /l)	ΔSUVA (%)		
		HS	BB	HS + BB
WPK water	0.85	17	23	19
WPK IEX-treated	0.85	18	27	23
WPK GAC-treated	0.85	18	19	19
LDN water	1.04	17	28	23

Effect of NOM character and removal on AOC formation

In Figure 3 the incremental (Δ) AOC formation per unit of DOC, determined in the bubble column experiments for the four different test waters, is plotted against the ozone dosage, including regression lines. For the IEX-treated WPK water, no correlation can be determined because there are only values for one ozone dosage. The regression of the GAC-treated WPK water is based on two measurements and therefore no statistically based conclusions can be drawn from Figure 3. However, the figure shows a trend towards higher Δ AOC concentrations per unit of DOC for the IEX-treated WPK water compared to the GAC-treated WPK water and the WPK water. This trend could be explained by the differences in NOM character. Part of the oxidized humic substances and building blocks are transformed into AOC. From Table 3 it is suggested that the ozone reactivity of building blocks is higher compared to the ozone reactivity of humic substances. From the DOC concentrations shown in Table 2, it can be observed that the IEX-treated WPK water contains relatively more building blocks compared to the GAC-treated WPK water and the WPK water. This suggests that AOC formation from building blocks is higher compared to AOC formation from humic substances. It should be noted that this finding is based on a limited number of test waters and experiments. To further substantiate this finding individual LMW acids such as formic and oxalic acids should also be measured as a function of the ozone dosage.

The LMW acids measured with SEC-DOC are small carboxylic acids, ketones and aldehydes. These small acids are biodegradable organic compounds such as formic acid and acetic acid (Huber & Frimmel 1996). Biodegradable

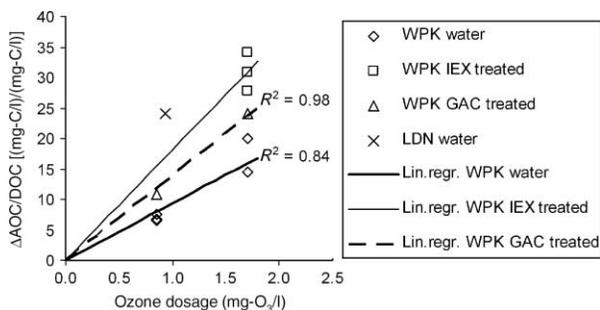


Figure 3 | Effects of ozone on AOC formation per unit of DOC for the different test waters.

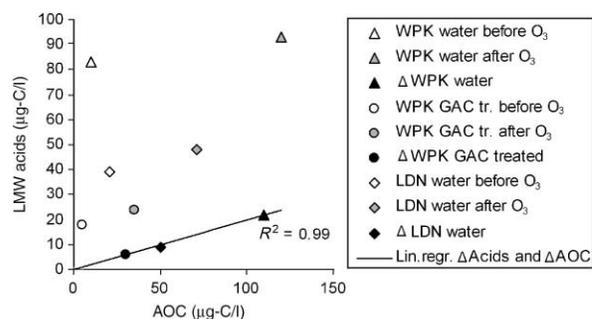


Figure 4 | Absolute values LMW acids versus AOC (white and grey symbols) and Δ LMW acids versus Δ AOC (black symbols) for the WPK water with an ozone dosage of 1.70 mg-O₃/l, for the GAC-treated WPK water with an ozone dosage of 0.85 mg-O₃/l and for the LDN water with an ozone dosage of 1.04 mg-O₃/l.

organic compounds can be measured as AOC so there should be a relation between LMW acids measured with SEC-DOC and the AOC concentration. In Figure 4 LMW acid concentrations from the SEC-DOC measurements are plotted against AOC concentrations for three ozonation experiments. There are three values for each experiment: the influent concentration before ozonation (white symbol), the effluent concentration after ozonation (grey symbol) and the Δ value which is the difference between the effluent and the influent concentration representing the incremental increase due to ozonation (black symbol). Figure 4 shows no correlation between the measured LMW acid concentrations and the measured AOC concentrations (white and grey symbols), but there is a correlation between the increase in the LMW acid concentration and the increase in the AOC concentration due to ozonation.

van der Kooij *et al.* (1989) reported a linear relationship through the origin between the decrease in UVA₂₅₄ and AOC formation during ozonation in Figure 5 (left); this can also be observed for the WPK water (Rietveld *et al.* 2008). However, for the GAC-treated WPK water the correlation is very low and for the WPK water treated by IEX there is no correlation for a linear regression line through the origin. The correlation for the tested waters can be improved when focusing on the decrease in UVA₂₅₄ of the ozone reactive fractions (HS and BB). This is shown in Figure 5 (right) where the AOC formation is plotted against UVA_{HS+BB}. From Figure 5 (right), it is concluded that the lower the SUVA_{HS+BB} before ozonation is, the higher the AOC formation per unit of UVA_{HS+BB} decrease

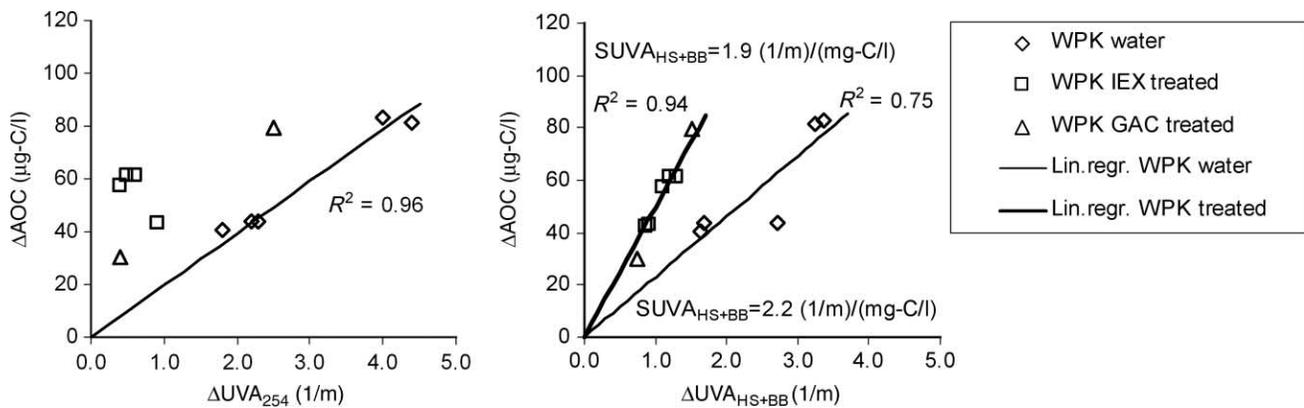


Figure 5 | AOC formation: (i) ΔAOC vs. ΔUVA_{254} (left); (ii) ΔAOC vs. $\Delta\text{UVA}_{\text{HS+BB}}$ (right), for ozone bubble column pilot-plant experiments with the WPK water and the IEX- and GAC-treated WPK water.

due to ozonation. Water types with the same $\text{SUVA}_{\text{HS+BB}}$ before ozonation, such as the IEX- and the GAC-treated WPK water (average $\text{SUVA}_{\text{HS+BB}} = 1.9 \text{ (1/m)/(mg-C/l)}$), have the same AOC formation for the same decrease in $\text{UVA}_{\text{HS+BB}}$ due to ozonation (see Figure 5, right).

Effect of NOM character and removal on the CT value

In Figure 6, the CT values are plotted against the DOC concentrations for different ozone dosages in the bubble column experiments. In the case of the WPK water, the total amount of ozone reacts with DOC and there is no measurable residual ozone for calculating a CT value. For decreasing DOC concentrations, residual ozone and, thus, CT values will first appear for the ozone dosage of $1.70 \text{ mg-O}_3/\text{l}$ and subsequently for the ozone dosage of $0.85 \text{ mg-O}_3/\text{l}$. From Figure 6, it is observed that the relation between the CT value and DOC concentration for the IEX- and GAC-treated WPK water coincide. Thus, the CT value is not influenced by which fraction, i.e. the humic substances fraction or the building blocks fraction, is removed to a greater extent.

From the DOPFR experiments (see Table 1), the initial and second phases of ozone decomposition were determined without interference from ozone gas transfer, in analogy to van der Helm *et al.* (2008). By fitting Equations (4) and (5) to the measured ozone profiles in the DOPFR experiments, the rate constants for fast ozone decomposition in the initial phase, k_{UVA} , and for first-order ozone decomposition in the second phase, k_{O_3} , and the yield Y for

the different test waters were determined. The results of the fits are presented in Table 4, with their respective Pearson R -squared values (R^2).

From Table 4, it can be seen that the first-order ozone decomposition rates k_{O_3} for the IEX- and GAC-treated WPK water are nearly the same, and that the k_{UVA} for the initial phase of ozone decomposition for the GAC-treated WPK water is more than four times greater than for the IEX-treated WPK water. Since the GAC-treated WPK water contains more humic substances and fewer building blocks than the IEX-treated WPK water (see Table 2), this may indicate that humic substances react faster with ozone than building blocks. The Y for the GAC-treated WPK water is higher than for the IEX-treated WPK water: however, the UVA_{254} decrease for the IEX-treated WPK water is higher than that for the GAC-treated WPK water, resulting in an ozone decrease due to initial phase ozone decomposition of $0.94 \text{ mg-O}_3/\text{l}$ and $0.92 \text{ mg-O}_3/\text{l}$ for the IEX- and GAC-treated WPK water, respectively.

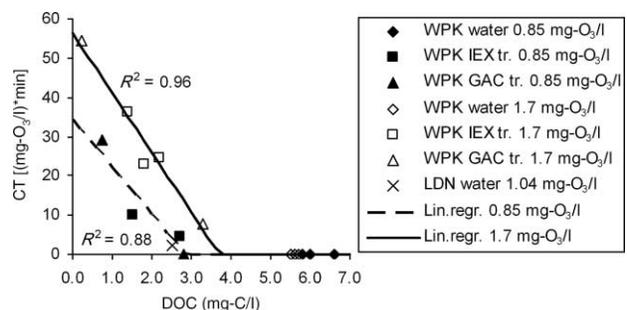


Figure 6 | CT values at different DOC concentrations for the WPK and the LDN pilot-plant bubble column experiments.

Table 4 | Rate coefficients for the initial phase of ozone decomposition (k_{UVA}) and for the second-phase first-order ozone decomposition (k_{O_3}), and the yield factor (Y) determined from DOPFR experiments

	Ozone dosage (mg-O ₃ /l)	Temperature (°C)	DOC influent (mg-C/l)	k_{O_3} (1/s)	k_{UVA} (1/s)	Y ((mg-O ₃ /l)/(1/m))	R^2 (-)
WPK water	1.43	12.0	6.3	0.0687	2.201	0.25	0.99
WPK IEX-treated	1.39	12.2	3.1	0.0025	0.034	0.41	0.97
WPK GAC-treated	1.48	12.5	2.8	0.0027	0.153	0.51	0.99
LDN water	0.90	12.0	2.4	0.0041	0.285	0.16	0.97

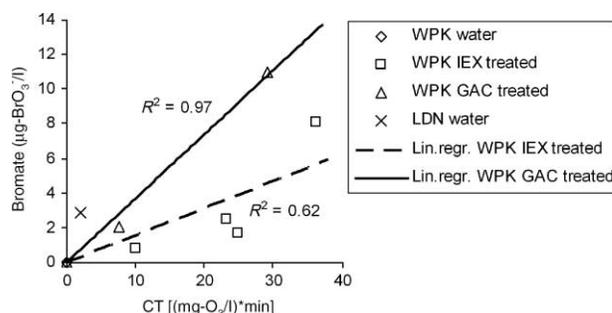
From Figure 6 data it is observed that, for the same DOC concentrations, the CT values for the bubble column experiments with the IEX- and GAC-treated WPK water are the same, even though there are distinct differences in the ozone kinetics due to the difference in the composition of the NOM. The k_{UVA} is more than four times greater for the GAC- than for the IEX-treated WPK water. The observation that the CTs are the same can be explained by the fact that in bubble column experiments the k_{UVA} is not the decisive parameter for the CT value. The main part of initial phase ozone decomposition will take place in the bubble column and therefore will be determined by the gas exchange rate, k_{La} (Lewis & Whitman 1924), between ozone gas and water, which is one or more orders slower than the initial phase ozone decomposition rate. Values found in the literature for the k_{La} of ozone in bubble columns range from 0.0001 1/s to 0.0192 1/s, depending on turbulence and the gas exchange area (Roustan *et al.* 1987, 1996). The decisive parameters for the CT value in bubble column experiments are the amount of ozone consumed during the initial ozone decomposition phase and k_{O_3} . The first parameter determines the ozone concentration at the point where the initial phase shifts to the second ozone decomposition phase, and the second parameter determines the time for this ozone concentration to decrease to zero. Since the differences between both the amount of ozone consumed during the initial phase and k_{O_3} for the IEX- and GAC-treated WPK water are relatively small, the CT values for both waters in bubble column experiments are almost the same for the same DOC concentrations, as seen in Figure 6.

The k_{UVA} that was found for the LDN water on the basis of ozone in water measurements was 0.285 1/s (see Table 4). This means that 99% of ozone decomposition due to reactions with NOM occurs in the first 16 s during the initial phase of ozone decomposition. This is in agreement

with the observation from the SEC-DOC measurements that the largest part of the UVA₂₅₄ decrease for the LDN water took place within the first 20 s, see Figure 2 (right). The observed differences in the k_{UVA} and the k_{O_3} of the untreated WPK water and the LDN water can be explained by the nonlinear relation with the DOC concentration and ozone dosage. Assuming a constant contribution of the ozone decomposition cycle, this can be explained by the various types of sites within NOM that have different reactivity with ozone. For low ozone dosages only the fast-reacting sites consume ozone. When higher ozone dosages are used, the rate of ozone consumption decreases when slowly reacting sites are oxidized as well (Hoigné & Bader 1994; Gallard *et al.* 2003).

Effect of NOM character and removal on bromate formation

In Figure 7, bromate formation is plotted against the CT value for the bubble column experiments. For the WPK water with ozone dosages of 0.85 mg-O₃/l and 1.70 mg-O₃/l, the CT value is zero because of the high concentration of NOM in the water (see Figure 6); accordingly, the bromate formation is zero. Bromate formation for the LDN water is higher than for the WPK water due to higher bromide concentrations of

**Figure 7** | Bromate formation for the bubble column pilot-plant experiments.

around 170 $\mu\text{g-Br/l}$ versus 90–100 $\mu\text{g-Br/l}$ for the WPK water. From the experimental data it can be concluded that the IEX resin does not remove bromide, but bromate formation for the IEX-treated WPK water is lower than for the GAC-treated WPK water. It should be noted that this observation is based on a limited number of data points. The difference in bromate formation between IEX- and GAC-treated water is due to the difference in composition of NOM. Von Gunten (2003) described the reactions of NOM during ozonation that interfere with bromate formation. He distinguished the reaction where the Br atom reacts with NOM to form bromo-organic compounds or bromide and three types of reactions that interfere on the level of HOBr/OBr^- . From the experiments presented it cannot be determined which of the reactions are responsible for the difference.

CONCLUSIONS

In this research natural waters were tested from two locations with different DOC concentrations, both with a relatively high concentration of humic compounds. In addition, the DOC concentration of one of the natural waters was reduced either by IEX or by GAC filtration. This led to different concentrations of the ozone reactive fractions of NOM, being the humic substances fraction (MW $\sim 1,000$ g/mol) and the building blocks fraction (MW 300–500 g/mol) as determined by SEC-DOC. With respect to AOC formation during ozonation, it is concluded from this work that AOC formation per unit of DOC is higher for NOM containing more building blocks than humic substances for the same ozone dosage. As a result of ozonation the LMW acid fraction of NOM, as determined by SEC-DOC, increased, and a correlation was found between the increase in LMW acids and the AOC formation. Also, correlations were found between the AOC increase and the UVA_{254} decrease in the humic substances fraction and the building blocks' fraction together. With respect to the CT value for disinfection during ozonation, it is concluded that removal of humic substances and building blocks leads to a higher CT value for the same ozone dosage. The rate of ozone decomposition in the initial phase of ozone decomposition ($t < \sim 20$ s) is higher for NOM containing more humic substances than building blocks: however, the

CT value is not influenced by which fraction is removed to a greater extent. CT values in bubble column ozone reactors are not determined by the rate of initial ozone decomposition but by the amount of ozone consumed during the initial phase of ozone decomposition and by the first-order ozone decomposition rate in the second phase. With respect to bromate formation during ozonation, it is concluded that bromate formation is possibly higher for NOM containing more humic substances than building blocks. For the waters tested, it is concluded that, when NOM removal is considered before ozone disinfection, a higher removal of the humic substances fraction (MW $\sim 1,000$ g/mol) of NOM is preferred as compared to the removal of the building blocks fraction (300–500 g/mol) of NOM. In the performed experiments this led to less AOC formation, and thus less regrowth and less bromate formation. Therefore, when considering IEX (Rohm & Haas, PWA 958; strong base anion exchange type 1 resin) and GAC filtration (Chemviron, F300) for NOM removal prior to ozonation, IEX is preferred, because from NOM characterization by SEC-DOC, it is concluded that IEX removed more humic substances than GAC filtration. These conclusions are based on the comparison of the SEC-DOC chromatograms, and thus on the relative changes in the SEC-DOC chromatograms. These findings will be used in further research on NOM removal with IEX before ozonation at drinking water treatment plant Weesperkarspel.

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