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Formation of assimilable organic carbon during oxidation of natural waters with ozone, chlorine dioxide, chlorine, permanganate, and ferrate

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ABSTRACT

Five oxidants, ozone, chlorine dioxide, chlorine, permanganate, and ferrate were studied with regard to the formation of assimilable organic carbon (AOC) and oxalate in absence and presence of cyanobacteria in lake water matrices. Ozone and ferrate formed significant amounts of AOC, i.e. more than 100 μg/L AOC were formed with 4.6 mg/L ozone and ferrate in water with 3.8 mg/L dissolved organic carbon. In the same water samples chlorine dioxide, chlorine, and permanganate produced no or only limited AOC. When cyanobacterial cells (*Aphanizomenon gracile*) were added to the water, an AOC increase was detected with ozone, permanganate, and ferrate, probably due to cell lysis. This was confirmed by the increase of extracellular geosmin, a substance found in the selected cyanobacterial cells. AOC formation by chlorine and chlorine dioxide was not affected by the presence of the cells. The formation of oxalate upon oxidation was found to be a linear function of the oxidant consumption for all five oxidants. The following molar yields were measured in three different water matrices based on oxidant consumed: 2.4–4.4% for ozone, 1.0–2.8% for chlorine dioxide and chlorine, 1.1–1.2% for ferrate, and 11–16% for permanganate. Furthermore, oxalate was formed in similar concentrations as trihalomethanes during chlorination (yield ~ 1% based on chlorine consumed). Oxalate formation kinetics and stoichiometry did not correspond to the AOC formation. Therefore, oxalate cannot be used as a surrogate for AOC formation during oxidative water treatment.

1. Introduction

Drinking water needs to be delivered to the tap in a hygienically impeccable state. To minimize bacterial regrowth in distribution systems a chemical disinfectant is frequently added, which can lead to the formation of undesired disinfection by-products (Krasner et al., 2006; Richardson et al., 2007). Alternatively, the amount of assimilable organic carbon (AOC) in the water can be reduced to avoid bacterial regrowth through nutrient limitation (van der Kooij, 1992). During drinking water treatment, primary disinfection with chemical oxidants can produce AOC by transforming macromolecular dissolved organic matter (DOM) into smaller molecules, which in turn can be taken up by bacteria more easily (van der Kooij et al., 1989; Hammes et al., 2006). Therefore, oxidative water treatment, e.g. ozonation, is generally followed by a biological

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filtration step to remove AOC (van der Kooij et al., 1989; Lykins et al., 1994; Vahala et al., 1998).

To date many studies concerning AOC production have been performed in full-scale treatment systems under highly variable treatment conditions, which do not allow comparison of different oxidants (Liu et al., 2002; Volk and Le Chevallier, 2002; Polanska et al., 2005; Chen et al., 2007). In the present study five oxidants—ozone (O_3), chlorine dioxide (ClO_2), chlorine (Cl_2 as HOCl), permanganate (MnO_4^-), and ferrate (FeO_4^{2-})—were investigated in the same water matrices with regard to their AOC formation potential and kinetics. Ozone, chlorine dioxide, and chlorine are widely applied in drinking water treatment for oxidation and disinfection purposes, permanganate is used for iron and manganese removal, and ferrate is discussed as a novel oxidant for micropollutant and phosphate removal mainly in wastewater treatment (Lee et al., 2009). These oxidants undergo various reactions with specific functional groups of DOM and as a consequence their stability in water differs significantly. Lee and von Gunten summarized the reactivity of ozone, chlorine dioxide, chlorine, and ferrate (Lee and von Gunten, 2010) and Waldemer and Tratnyek discussed permanganate reactions (Waldemer and Tratnyek, 2006). Briefly, of the five oxidants ozone is known as the most reactive, chlorine dioxide and ferrate mainly react with phenolic compounds, chlorine or hypochlorous acid reacts fast only with amines, and permanganate reacts only slowly with organic compounds, mainly with olefines.

The objective of this study was a comparison of the selected oxidants concerning the extent of their AOC formation from oxidation of DOM in water in absence and presence of bacterial cells. Furthermore, oxalate formation during oxidative treatment was studied as a possible surrogate for AOC and for trihalomethane (THM) formation.

2. Materials and methods

2.1. Water samples

Waters were sampled from three different surface waters. Lake Greifensee (LG) (Switzerland) is a eutrophic lake surrounded by agricultural land. Samples were taken directly at the surface of the lake, 30 m off shore in November 2008 (LGn) and January 2009 (LGj). Lake Zuerich (LZ) (Switzerland) is a mesotrophic lake and samples were taken in April 2009, 30 m below the lake surface around 600 m off shore at the intake pipe for drinking water production. Chriesbach (CB) (Switzerland) is a little creek fed to a considerable part by wastewater treatment plant effluent. Water was sampled in April 2009 at the surface. The pH was 8.0–8.3 for all water samples and the DOC concentration varied between 1.3 and 3.8 mg C/L (supporting information S1). The water samples were filtered through a 0.2 μm filter (regenerated cellulose, Sartorius AG, Goettingen, Germany, rinsed with 1 L of micropure water (NANOpure Diamond™, Barnstead)) and stored at 4 °C in the dark until use (maximum 10 days).

2.2. Oxidant stock solutions

Ozone was applied as aqueous stock solution prepared by sparging an oxygen–ozone gas mixture from an oxygen-fed ozone generator (CMG 3-3, Apaco AG, Switzerland) through ice-cooled water. The ozone concentration of the stock solution was determined spectrophotometrically with $\varepsilon(258\ nm) = 3000\ M^{-1}\ cm^{-1}$ (Elovitz and von Gunten, 1999) and was 1.3–1.5 mM. A chlorine dioxide stock solution was prepared by reaction of chlorite with peroxodisulfate (Hoigné and Bader, 1994b; Huber et al., 2005). The concentration of the stock solution was determined spectrophotometrically with $\varepsilon(358\ nm) = 1200\ M^{-1}\ cm^{-1}$. Sodium hypochlorite (10% active chlorine Riedel-deHaen, Germany) was diluted in micropure water and standardized spectrophotometrically at pH 8.7 with $\varepsilon(292\ nm) = 350\ M^{-1}\ cm^{-1}$ (supporting information section of Lee et al., 2008). Potassium ferrate (K_2FeO_4) was prepared by the method of Thompson and co-workers (Thompson et al., 1951) and had a purity of 88% as Fe (VI) (w/w). Ferrate stock solutions were prepared from solid potassium ferrate in micropure water and used immediately. The stock concentration was measured spectrophotometrically, with $\varepsilon(510\ nm) = 1150\ M^{-1}\ cm^{-1}$ (Lee et al., 2005). A 5 mM permanganate stock solution was prepared in water from solid potassium permanganate and standardized spectrophotometrically with $\varepsilon(525\ nm) = 2430\ M^{-1}\ cm^{-1}$ (supporting information S2).

2.3. Measurement of oxidant consumption and determination of oxidant exposure

Oxidant stock solutions were added to the stirred water samples in a 250 ml Schott bottle equipped with a dispenser system (Hoigné and Bader, 1994a). At various time intervals, the residual oxidant concentration was determined by dispensing aliquots of the sample into a plastic sampling tube containing a buffer and a quenching agent dye that changes color upon oxidation which allowed calculation of the residual oxidant concentration (supporting information S3). For all oxidants, the exposure (ct) was calculated as the integral of the transient oxidant concentration over the reaction time (von Gunten and Hoigné, 1994).

2.4. Measurement of oxidation products

AOC was measured as described elsewhere (Hammes and Egli, 2005). Briefly, all samples were prepared in AOC-free glassware and the water was filtered prior to the experiment (see 2.1). After the experiment the water was partitioned into two AOC-free vials. Cells from a natural microbial community were added and the sample was incubated at 30 °C for three days. The added natural microbial inoculum had been prepared by mixing different water samples (oxidized and untreated LZ, CB, and LG water) and had been stored at 4 °C for several days to weeks. The final cell concentration after regrowth in the actual water sample was determined by staining the cells with SYBR® Green and an addition of 5 mM ethylenediaminetetraacetate and counting the cells by flow cytometry on a PASIII flow cytometer (Partec, Germany). The AOC concentration was calculated assuming a bacterial growth of 10^7 cells per μg assimilable organic carbon (Hammes et al., 2006). The limit of detection was 10 μg/L and the standard error of triplicate incubated samples <10%.

Oxalate was measured after sample filtration through a 0.45 μm nylon syringe filter (BGB Analytik AG, Switzerland)