



Occurrence and fate of ozonation by-products at a full-scale drinking water treatment plant



A. Papageorgiou^{a,*}, D. Voutsas^{a,*}, N. Papadakis^b

^a Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University of Thessaloniki, 511 24 Thessaloniki, Greece

^b Medical School, Aristotle University of Thessaloniki, 511 24 Thessaloniki, Greece

HIGHLIGHTS

- Fate of ozonation by-products at DWTP
- For, Ace Gly and MGly are the dominant compounds.
- The post-ozonation filtration processes effectively remove ozonation DBPs.
- Seasonal changes in DOC reactivity

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ABSTRACT

The occurrence and fate of carbonyl compounds as ozonation by-products at a full scale drinking water treatment plant (DWTP) were studied for one year. Raw water and samples after the main treatment processes (pre-ozonation, coagulation/flocculation, sand filtration, main ozonation, filtration through granular activated carbon and chlorination) were collected on a monthly basis. Pre-ozonation led to the formation of carbonyl compounds at concentrations of $67.3 \pm 43.3 \mu\text{g/l}$ as sum of 14 carbonyl compounds whereas lower concentrations were determined after the main ozonation process, $32.8 \pm 22.3 \mu\text{g/l}$. The dominant compounds were formaldehyde, acetaldehyde, glyoxal and methyl glyoxal contributing to 65% of total carbonyl content. The DOC reactivity in formation of carbonyl compounds varied through the year exhibiting the higher values in spring. Coagulation/flocculation and sand filtration significantly removed (64–80%) the carbonyl compounds formed at the pre-ozonation step. The removal efficiency of filtration through granular activated carbon showed great variation ranging from 15 to 62%. Finally, the concentrations of carbonyl compounds in finished water were low, close to detection limits, revealing the efficiency of DWTP in the removal of this class of ozonation by-products.

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1. Introduction

Ozonation has been applied for drinking water treatment for more than 100 years. Beginning in Nice, France in 1906, it has been continuously used since then, causing Nice to be called the birthplace of ozonation in drinking water treatment (Le Pauloué and Langlais, 1999). The use of ozone in water treatment increased rapidly after the first evidence of the formation of chlorination by-products with adverse health effects (Bellar and Lichtenberg, 1974; Rook, 1974), where the need of an alternative and effective disinfectant became obvious. Therefore, ozonation has emerged as an effective practical alternative and/or complementary to chlorination treatment process (Finch et al., 1997; Joret et al., 1997).

Ozone, exhibits excellent disinfection efficiency and high oxidation potential. Therefore, effective microbiological disinfection can be achieved with lower concentration in shorter contact time compared to other disinfectants, such as chlorine, chlorine dioxide and monochloramine (von Sonntag and von Gunten, 2012a). Also, ozone can oxidize both taste and odor compounds, organic micropollutants, iron and manganese (Qi et al., 2013; Rodríguez et al., 2008; Seo et al., 2010; Srinivasan and Sorial, 2011; von Gunten, 2003; Yuan et al., 2013). Ozone in water treatment enhances the efficiency of the coagulation/flocculation process and also oxidizes the organic compounds to more biodegradable forms that can be removed by biological filtration (Matilainen et al., 2010). Moreover, ozonation generally reduces the formation potential of hazardous chlorination by-products, such as THMs and HAAs, by oxidizing their precursor compounds (Hua and Reckhow, 2013; Li et al., 2008; Rodríguez et al., 2012).

Carbonyl compounds, carboxylic acids and keto-acids are formed during ozonation of surface water as by-products of the reaction between ozone and natural organic matter (NOM) (Can and Gurol,

* Corresponding authors. Tel.: +30 2310997858; fax: +30 8310997747.

E-mail addresses: apapage@chem.auth.gr (A. Papageorgiou), dvoutsas@chem.auth.gr (D. Voutsas).

2003; Griffini et al., 1999; Jurado-Sánchez et al., 2014; Weinberg et al., 1993; Westerhoff et al., 1999). It has been reported that carbonyl compounds along with carboxylic acids represent about 30% of the ozonation by-products (Richardson, 2003). Although the exact mechanism of their formation is not clearly established, it has been reported that ozone cleaves larger organic molecules into smaller ones, reacts with unsaturated aliphatic chain compounds or aromatic groups of NOM to produce carbonyl compounds (Glaze, 1987; Weinberg, 1999). Their formation depends on several factors, such as ozone dosage, pH, temperature and alkalinity of water and above all the concentration and chemical profile of NOM (Nawrocki and Kalkowska, 1998; Schechter and Singer, 1995).

There is concern regarding the occurrence of carbonyl compounds due to their possible adverse health effects. Formaldehyde is classified as carcinogenic to humans and acetaldehyde as possible carcinogenic to humans (I.A.R.C., 1999, 2012). However, this refers mainly to exposure through inhalation, whereas the weight of evidence indicates that they are not carcinogenic by the oral route (Lippmann, 2009; Richardson et al., 2007; WHO, 2011). Also, formaldehyde occurs in drinking water at concentrations well below those of health concern and eventually no guideline value is established (WHO, 2005, 2011). In addition, acetaldehyde, formaldehyde, glyoxal and methyl glyoxal in water have been recognized as possible mutagenic compounds (Matsuda et al., 1992; Richardson et al., 2007).

Several studies investigated the formation of carbonyl compounds under ozonation and their removal at lab scale. The results vary substantially and sometimes are contradictory reflecting the range of impacting factors including raw water and DOC characteristics as well as operational conditions (Hammes et al., 2006; Huang et al., 2005; Karnik et al., 2005; Melin and Ødegaard, 2000; Nawrocki et al., 2003). For this reason it is difficult to expand these results to field studies. Considering that NOM, as precursor of carbonyl compounds formed during ozonation, is highly variable in terms of concentration and its characteristics even for the same system, studies on the fate of ozonation by-products during water treatment become increasingly important. However, there is limited information regarding the fate of these compounds under the conditions occurred in water treatment plants (Hammes et al., 2006).

The aim of this study was to investigate the occurrence and fate of ozonation by-products and especially carbonyl compounds in a full scale water treatment plant. Particularly, the concentrations of 14 carbonyl compounds were studied for one year at eight sampling points along DWTP: at the entrance (raw water) and after the main treatment processes (pre-ozonation, coagulation/flocculation, sand filtration, ozonation, filtration through granular activated carbon, chlorination) of the waterworks for a period of one year. The contribution of each treatment process in formation and removal of ozonation by-products is discussed. Moreover, seasonal variation of the concentrations of carbonyl compounds and DOC reactivity as well as the possible relationships with main physicochemical characteristics of raw water and technical parameters are presented.

2. Materials and methods

2.1. Chemicals

The analytical standard containing 14 carbonyl compounds (formaldehyde, acetaldehyde, propanal, butanal, pentanal, hexanal, cyclohexanone, heptanal, octanal, benzaldehyde, nonanal, decanal, glyoxal and methyl glyoxal) was purchased from Ultra Scientific. The derivatization agent O-(2,3,4,5,6-pentafluoro-benzyl)hydroxylamine (PFBOA) and potassium hydrogen phthalate (KHP) were purchased from Alfa Aesar, Karlsruhe, Germany. Both surrogate (2',4',5'-trifluoroacetophenone) and internal standards (1,2-dibromopropane) were purchased from Chem Service (West Chester, PA, USA). HPLC grade n-hexane (Chem-Lab, Belgium) was used as a solvent for the liquid–liquid extraction.

Copper (II) sulfate pentahydrate (Sigma-Aldrich, Germany) and ammonium chloride (Chem-Lab, Belgium) were the preservatives.

The PFBOA was prepared daily as an aqueous solution (15 mg/ml) in organic free water, while the carbonyl compound standard solutions were prepared in acetonitrile. Organic free water was provided by the Simplicity UV Ultrapure Water System (Millipore, Molsheim, France).

2.2. Description of DWTP-sample collection

Sampling was conducted at the drinking water treatment plant (DWTP) of Company of Water Supply and Sewerage, Thessaloniki, Northern Greece. The raw water is abstracted from the Aliakmonas River. Aliakmonas River is the longest Greek river with a total length of nearly 310 km and mean flow rate of 42 m³/s. It originates from northwestern Greece and after traversing a basin of about 5600 km² discharges into the Thermaikos Gulf. Point pollution sources (urban and industrial effluents) and non-point pollution sources along its route may affect the water quality; however their impact is considered relatively low (Arditsoglou and Voutsas, 2010; Simeonov et al., 2003; Voutsas et al., 2001).

A schematic presentation of various treatment steps at this plant is shown in Fig. 1. The plant is an eight stage treatment system that involves pre-ozonation (PO), pH adjustment, coagulation/flocculation (CF), sand filtration (SF), main ozonation (OZ), granular activated carbon filtration (GAC), chlorination (CL) and final pH adjustment. The DWTP provides 150,000 m³ of potable water per day.

Water samples were collected monthly from eight sampling points along the DWTP, including raw water (RW) and water samples after each treatment step (Fig. 1). Ten sampling campaigns were conducted during the period March 2012–February 2013. Samples were collected in amber glass 40 ml vials with PTFE-lined screw caps. Prior to sampling, 15 mg of copper (II) sulfate pentahydrate was added to each vial to inhibit bacteriological decay of carbonyl compounds. Also, ammonium chloride (15 mg) was added in order to react with the free chlorine to form monochloramine and retard the formation of additional carbonyl compounds. The target analytes were extracted from the samples on the same day of collection and the extracts were stored at <4 °C away from light. Samples were analyzed by GC/ECD within the next two days.

All glassware used was scrupulously cleaned by detergent, hot water, and organic-free water and finally heated at 200 °C for at least 6 h. After cleaning, glassware was stored in a clean environment to prevent any accumulation of dust or other contaminants.

2.3. Analysis of carbonyl compounds

The EPA 556 method was employed for the determination of carbonyl compounds in water samples (EPA, 1998). This method includes derivatization of carbonyl compounds and analytical determination by GC/ECD. Briefly, potassium hydrogen phthalate was added in the water sample to adjust pH = 4. Then 2',4',5'-trifluoroacetophenone was added as surrogate standard. The carbonyl compounds were derivatized with PFBOA at 35 °C for 2 h. Drops of concentrated sulfuric acid were added to complete the derivatization reaction. Then 1,2-dibromopropane was added as internal standard. The oxime derivatives were first subjected to a purification step with sulfuric acid at 0.2 N and finally extracted with n-hexane.

The extracts were analyzed by gas chromatography using a Trace GC Ultra (Thermo Scientific) equipped with ⁶³Ni electron capture detector (ECD). For the separation an Rtx-5MS fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, Restek, Bellefonte, PA, USA) was used. Helium (1 ml/min) was the carrier gas and nitrogen (30 ml/min) the detector make-up gas. The oven temperature program was as follows: 50 °C for 1 min, increased at 4 °C/min to 220 °C, increased at 20 °C/min to 250 °C hold at 250 °C for 10 min. The

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