



# Formation of aldehydes and carboxylic acids in ozonated surface water and wastewater: A clear relationship with fluorescence changes



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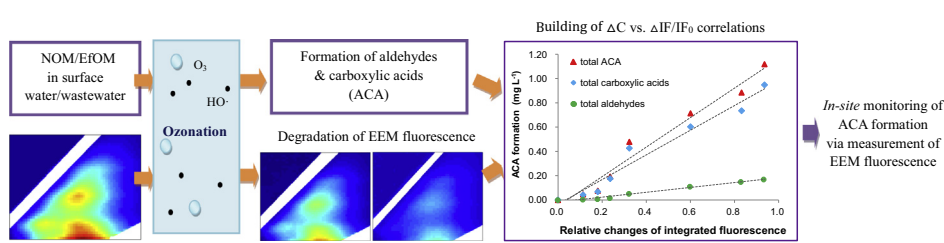
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## HIGHLIGHTS

- Aldehydes and carboxylic acids (ACA) formed in ozonated water and wastewater were studied.
- Changes of fluorescence were correlated with HO<sup>•</sup> exposures and ACA concentrations.
- Online fluorescence monitoring can be used to estimate the generation of ACA species.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study examined the formation of aldehydes and carboxylic acids in ozonated surface water and municipal wastewater secondary effluent and addressed correlations between the generation of these compounds and concurrent changes of the fluorescence of natural/effluent organic matter (NOM/EfOM) substrates. Ozonation was effective in removing fluorophores in all excitation/emission matrix (EEM) regions, with those operationally assigned to humic- and protein-like species showing relatively higher reactivity than fulvic-like species. Examination of HO<sup>•</sup> exposures and attendant changes of fluorescence-based parameters allows establishing strong linear relationships between formation of the aldehydes and carboxylic acids and the relative changes of integrated fluorescence ( $\Delta IF/IF_0$ ). This demonstrates the feasibility of surrogate monitoring of the formation of biodegradable ozonation by-products via online measurements of water/wastewater EEM fluorescence.

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## 1. Introduction

Ozonation is a very effective treatment method to degrade many trace-level organic contaminants and practically all pathogens in drinking water or wastewater effluent (Gerrity and Snyder, 2011). However, several classes of by-products form in the process. These by-products include bromate (Wert et al., 2008; Zimmermann et al., 2011) and a number of aldehydes and carboxylic acids (referred henceforth as ACA) (Dąbrowska et al.,

2005; Huang et al., 2005). These ACA compounds and other groups of low-molecular-weight disinfection by-products (DBPs, <300 Da) formed upon the oxidation of natural organic matter (NOM) or effluent organic matter (EfOM) that is present in drinking water and wastewater, respectively may be significant for several reasons. Some aldehydes (e.g., formaldehyde, acetaldehyde, glyoxal and methylglyoxal) are toxic and had been classified as known carcinogens or suspected carcinogens (Richardson et al., 2007; McGwin et al., 2009). They may also be responsible for the undesirable odor in the treated waters because of their very low odor detection thresholds, e.g., 4.0  $\mu\text{g L}^{-1}$  for acetaldehyde (Dąbrowska and Nawrocki, 2013). Additionally, because ACA species are major

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contributors to assimilable organic carbon (AOC) that is most readily consumed by microorganisms (Griffini et al., 1999), their formation has important consequences for the biological stability of the treated waters in the distribution networks or the receiving environment, especially in the cases of with long residence times or at high DOC concentrations (Raczyk-Stanislawiak et al., 2004). Therefore, online monitoring of these by-products from ozonation as well as comparison of their formation from NOM and EfOM is practically important and beneficial for the optimization of operations of water/wastewater treatment facilities and achievement of biologically stable quality of treated waters.

It is our assertion that these needs can be addressed by means of *in-situ* monitoring of changes of the spectroscopic properties of NOM or EfOM. Both UV absorbance and fluorescence are efficient in examining the engagement and transformation of NOM/EfOM in virtually any reaction pertinent to water treatment (Spencer et al., 2007; Hudson et al., 2008). Compared with absorbance, use of fluorescence offers several advantages such as increased sensitivity (Skoog et al., 2004) and ability to ascertain the presence of different classes of fluorescing compounds whose contributions to absorbance spectra may be impossible to deconvolute (Stedmon and Markager, 2005). Three-dimensional excitation–emission matrix (EEM) has several well resolved structures which can be used to provide, potentially in real time, fingerprint information about distinct NOM/EfOM fluorophores and their interactions with oxidants or halogenating agents (Świetlik and Sikorska, 2004; Roccaro et al., 2009). Given the complexity of EEM data, several alternative methods have been developed ranging from conventional peak-picking, regional integration to multivariate data analysis such as parallel factor method (PARAFAC) (Chen et al., 2003; Hudson et al., 2007; Ishii and Boyer, 2012), yet a uniformly applicable standard approach for correcting, processing and interpreting EEM data is still being explored (Murphy et al., 2010). Prior research has demonstrated that the generation of products of NOM/EfOM oxidation by ozone is correlated with the changes of surrogate absorbance- and fluorescence-parameters that reflect the reactivity of NOM/EfOM (Korshin et al., 1999; Hur et al., 2006; Baker et al., 2008; Snyder et al., 2012; Audenaert et al., 2013). Most of these parameters were developed using absorbance or fluorescence emission intensity at selected wavelengths. For instance, our studies (Liu et al., 2012) have found strong correlation between the formation of several aldehydes and the relative changes of UV absorbance at 254 nm (quantified as  $\Delta A/A_{254}^0$ ) of ozonated wastewater. However, such correlations have not been explored in detail with an extensive range of ACA by-products in samples of different properties, and particularly in the use of three-dimensional fluorescence spectroscopy of the treated waters.

Because ozone dosage and contact time that define hydroxyl radical ( $\text{HO}^\cdot$ ) exposures have been found to have direct influence on ACA formation (Tripathi et al., 2011), ozonation of a wastewater was carried out in two types of experiments with either varying ozone doses for a certain time of reaction or varying ozonation times at a fixed ozone dosage. Relevant  $\text{HO}^\cdot$  exposures were calculated by determining the removal of spiked radical probe compound *p*CBA. By investigating the  $\text{HO}^\cdot$  exposures, resultant ACA formation and attendant fluorescence changes, this study was able to find unambiguous relationships between the formation of these species and the developed fluorescence-change-based parameters. For comparison purposes, results of similar experiments with a typical surface water were also included in this study to examine whether correlations observed for the formation of ACA by-products for this environmental matrix differ from those of wastewater. Ultimately, the present study is expected to allow establishing an efficient and practically useful approach for real-time monitoring of DBPs of interest.

## 2. Materials and methods

### 2.1. Reagents

Standards of selected aldehydes and carboxylic acids, PFBHA for GC derivatization, hexane and LC/MS-grade methanol, acetonitrile and ammonium acetate were purchased from Sigma–Aldrich (Saint Louis, MO, USA).  $\text{Na}_2\text{SO}_3$ , NaOH and indigo were purchased from JT Baker (Phillipsburg, NJ, USA). Ultrapure water was produced by the Milli Q apparatus (Millipore, USA).

### 2.2. Samples

Natural surface water and wastewater secondary effluent were collected from Lake Washington (47°37'0"N, 122°15'53"W) and West Point municipal wastewater treatment plant (WWTP) in Seattle, WA, respectively. Wastewater effluent was sampled before its disinfection as shown in Fig. S1 in the Supplementary material, SM section. The samples were transported to the laboratory in pre-cleaned polypropylene containers, 0.45  $\mu\text{m}$  vacuum-filtered using a hydrophilic polypropylene filter and stored at 4 °C. Initial DOC concentrations were 1.6 and 7.8  $\text{mg L}^{-1}$  for the tested surface water and wastewater, respectively. Upon use, samples were spiked with *p*CBA (*para*-chlorobenzoic acid) to a level of ca. 78  $\mu\text{g L}^{-1}$  (Rosenfeldt and Linden, 2007).

### 2.3. Ozonation

Ozone was generated with an AC 2000 series ozone generator with Mini Hicon ozone analyzer (IN USA Incorporated, Norwood, MA, USA) using oxygen source. Oxygen flow and voltage of the generator were optimized to obtain an average concentration of 50–60  $\text{mg L}^{-1}$  in ozone stock solution. Ozone concentration was determined by the standard 4500- $\text{O}_3$  indigo colorimetric method (Eaton et al., 1995).

To elucidate the role of the reaction conditions of ozone application on ACA formation and the extent of the resultant fluorescence change, experiments were carried out in two types: (1) by varying ozone doses with a series of initial concentrations from 0.00 to 5.00  $\text{mg L}^{-1}$  at 30 min contact time (no residual ozone remained in the samples at that time). Reaction started by injecting defined volumes of ozone stock solution to 60 mL samples; and (2) by varying times of exposure of 1.0 L water/wastewater sample to a continuous flow of gaseous ozone (with equivalent concentration at a steady state of 1.5  $\text{mg L}^{-1}$ ). At different times within 0–30 min of ozonation, 60 mL samples were collected into flasks that were added in advance with sodium sulfite (10  $\text{g L}^{-1}$ ) in order to quench the residual ozone immediately after sampling.

### 2.4. Aldehyde and carboxylic acid analysis

Sixteen compounds that include eight aldehydes and eight carboxylic acids were chosen as target oxidation by-products for determination. Since aldehydes can undergo degradation, the samples were processed immediately after the ozonation experiments. A list of the detected ACA species in the ozonated samples with their basic properties and detection limits is shown in Table 1.

All analyses were done in triplicates. Analyses of aldehydes (formaldehyde, glycolaldehyde, acetaldehyde, propionaldehyde, heptaldehyde, octaldehyde, benzaldehyde and nonaldehyde) were carried out in accord with Method 6252 “Disinfection By-Products: Aldehydes” (Eaton et al., 1995). Briefly, aldehydes were derivatized to corresponding oximes by *o*-(2, 3, 4, 5, 6-pentafluorobenzyl)-hydroxylamine (PFBHA). The obtained oximes were extracted with hexane and analyzed using a GC-2010 Shimadzu gas

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