Tracking the reactivity of ozonation towards effluent organic matters from WWTP using two-dimensional correlation spectra

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ABSTRACT

The characteristics of effluent organic matter (EfOM) from a wastewater treatment plant (WWTP) during ozonation were investigated using excitation and emission matrix (EEM) spectra, Fourier transform infrared spectroscopy (FT-IR) and high-performance size exclusion chromatography (HPSEC) at different ozone dosages. The selectivity of ozonation towards different constituents and functional groups was analysed using two-dimensional correlation spectra (2D-COS) probed by FT-IR, synchronous fluorescence spectra and HPSEC. The results indicated that ozonation can destroy aromatic structures of EfOM and change its molecular weight distribution (MWD). According to 2D-COS analysis, microbial humic-like substances were preferentially removed, and then the protein-like fractions. Terrestrial humic-like components exhibited inactivity towards ozonation compared with the above two fractions. Protein-like substances with small molecular weight were preferentially reacted during ozonation based on 2D-COS probed by HPSEC. In addition, the selectivity of ozone towards different functional groups of EfOM exhibited the following sequence: phenolic and alcoholic C–O groups > aromatic structures containing C=C double bonds > aliphatic C–H. X-ray photoelectron spectroscopy (XPS) further elucidated the preferential reaction of aromatic structures in EfOM during ozonation.

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Introduction

Advanced treatment and comprehensive utilization of urban wastewater have become effective approaches to alleviating the shortage of water resources in arid regions and reducing the pollution of aquatic environments. The slowly biodegradable or recalcitrant organic matter (i.e. natural organic matter, soluble microbial products, persistent organic matters, trace pollutants) remaining in wastewater treatment plant (WWTP) effluents has drawn extensive attention due to its potential risk to human and environmental health, and its adverse effects on subsequent treatment processes (Shon et al., 2006; Hubner et al., 2015). In such cases, based on its high oxidation potential, ozone is widely utilized in tertiary water treatment for the degradation of refractory and toxic organic pollutants (Peña et al., 2003; Broséus et al., 2009; Gong et al., 2008; Tang et al., 2014). During ozonation, organic contaminants were oxidized through either direct reactions with molecular ozone or through indirect reactions with hydroxyl radicals, a powerful and non-selectively oxidant produced by ozone decomposition (Cai and Lin, 2016; Westerhoff et al., 1999; Yong and Lin, 2016). Nevertheless, according to Cai and Lin (2016), the direct reactions between ozone molecular and effluent organic matter (EfOM) fractions dominated the ozone–EfOM
reactions when the pH was 7.4–7.5. Chen et al. (2017), also reported that EfOM degradation was dominated by ozone rather than hydroxyl radicals during ozonation at pH 7.7, because the exposure level of ozone was 10th higher than that of hydroxyl radicals.

In recent years, studies on the reactivity characteristics of ozone with EfOM have mainly focused on removal efficiency. A number of studies have been done on the effects of ozone oxidation on organic matters from wastewater treatment effluent. Results from these demonstrated that ozonation was effective in removing ultraviolet-absorbing organic substances, with UV254 reduction reaching as much as 60%. However, the removal of dissolved organic carbon (DOC) was only around 20%, which was attributed to the selective reaction during ozonation (Gong et al., 2008; Qi et al., 2018; Tang et al., 2014; Phungsi et al., 2016; Jin et al., 2016). This implied that the chemical structures and fractions of organic matter varied during ozonation. Furthermore, this was verified by the variation of fractions and chemical structures of dissolved organic matter during ozonation (Westerhoff et al., 1999; Świetlik et al., 2004; Audenaert et al., 2012; Tang et al., 2014). In addition, many researches have been carried out on the effect of ozonation on subsequent treatment processes (Jeong et al., 2014; Qian et al., 2013; Liu et al., 2011; Bose and Reckhow, 2007). Jin et al. (2012) studied the reaction kinetics of micropollutants during ozonation. The general reactivity of micropollutant structure with ozone was indirectly revealed through time-consuming analysis methods. Nevertheless, up to now, there has been limited systematic research related to the reaction characteristics, and in particular, to the selectivity of ozonation towards components of EfOM.

Two-dimensional correlation spectra (2D-COS), as developed by Noda (1993), can be applied to resolve overlapped peaks by distributing the spectral intensity trends along a second dimension with the data set collected, as a function of a perturbation (e.g. time, temperature, concentration) (Noda, 1993; Dluhy et al., 2006). More importantly, it can also provide information about the relative direction and sequential order of structural variations in response to the perturbation (Jia et al., 2009; Chen et al., 2015; Phong and Hur, 2016). Previous studies have demonstrated many successful applications of 2D-COS for exploring the heterogeneous distribution of metal binding sites within dissolved organic matter (DOM) using fluorescence spectroscopy and/or Fourier transform infrared (FT-IR) spectroscopy (Hur et al., 2011; Chen et al., 2015; Wei et al., 2016; Huang et al., 2017; Jin et al., 2017). Furthermore, in several studies, the interactions between organic structures and nanoparticles were investigated (Chen et al., 2014). In addition, in some studies, chromatograms were also applied to 2D-COS analysis (Mecozzi et al., 2014; Simon and Felinger, 2015). In the work using chromatograms, the incorporation of size exclusion chromatography (SEC) in 2D-COS was very limited. Only Lee and Hur (2017) utilized this method to reveal the continuous and heterogeneous presence of copper binding characteristics within bulk humic substances (HS) with respect to molecular weight (MW). Few studies have been related to the selectivity of ozonation towards EfOM using 2D-COS.

The main object of this study was to reveal the reactivity of ozone towards EfOM from WWTP. The characteristics of EfOM during ozonation were investigated using excitation and emission matrix (EEM) spectra, FT-IR and high-performance size exclusion chromatography (HPSEC) at different ozone dosages. Furthermore, 2D-COS was applied to analyse the selectivity of ozone with different components of EfOM probed by FT-IR, synchronic fluorescence spectra and HPSEC. In addition, X-ray photoelectron spectroscopy (XPS) was conducted to further elucidate and verify the selectivity of ozonation.

1. Materials and methods

1.1. WWTP and water samples

The water used in this study was collected before the disinfection step after the sedimentation tank in a municipal WWTP in Xi’an, China. The WWTP consists of a biological Anaerobic–Anoxic–Oxic treatment process that treats mainly domestic wastewater. The effluent of the WWTP typically has the following characteristics: 44.1 ± 4.2 mg/L COD, 12.4 ± 1.9 mg/L total nitrogen, 0.27 ± 0.11 mg/L total phosphorus and pH 7.26 ± 0.19. The water samples were filtrated through a 0.45 μm filter (Shanghai Xinya, China) for the removal of particles before ozonation.

1.2. Ozonation experiment

The ozonation experiment was carried out based on the methods described in our previous study (Jin et al., 2016). The ozone dosage was determined according to Kasprzyk-Hordern et al. (2006) and Galapate et al. (2001). The reacted ozone dosage in this study was determined by the difference between pre-determined in-gas amount of ozone and off-gas ozone trapped by the 20% KI solution. The reacted dosage of the ozone was adjusted using the reaction time. The ozonation experiments were performed in triplicate and the results are presented as mean values with standard deviations. In this study, three different ozone dosages were applied: 0.45 ± 0.06, 0.98 ± 0.09 and 2.15 ± 0.14 mg O3/mg DOC.

1.3. Analytical methods

1.3.1. Measurement of DOC, colour and UV absorbance

DOC was measured using a Shimadzu TOC-VPCH analyser with infrared detection. The DOC analyser was calibrated with potassium hydrogen phthalate standard solutions before each run. All of the samples were passed through a 0.45 μm filter, acidified with H2SO4 and purged with nitrogen to remove inorganic carbon before measurement. The colour content of samples was measured as proposed by Faniang and Xiantao (2006). UV254 was measured at 254 nm using a UV–VIS spectrophotometer (UV-2102C UNIC™, China) with 1 cm path length quartz cells. All analyses were performed in triplicate for all of the measurements of DOC, colour and UV254.

1.3.2. Fluorescence excitation–emission matrix analysis

Fluorescence measurements were conducted using a spectrofluorometer (FP-6500, Jasco, Japan) with a 150 W xenon lamp. The analyses were performed at ambient temperature. A 1 cm quartz cuvette with four optical windows was used for the
analyses. Emission scans were performed from 280 to 550 nm with 5 nm steps, while excitation wavelengths were measured from 220 to 480 nm with 2 nm intervals. The slit widths for excitation and emission were 5 nm. The detector was set to high sensitivity and the scanning speed was kept at 2000 nm/min.

1.3.3. Molecular weight distribution analysis
The characterization of the apparent molecular weight distribution (MWD) of the EfOM was performed using SEC coupled with a fluorescence detector. The detection wavelengths were Ex/Em 350/440 nm and Ex/Em 225/340 nm for humic-like substances and protein-like substances, respectively. The high-performance liquid chromatography (HPLC) system was a Shimadzu LC-2010AHF with a Zenix SEC-100 column (Sepax Technologies, USA). The injection volume was 10 µL and the column temperature was 30°C. The mobile phase was 150 mmol/L phosphate buffer solution (PBS) with a pH of 7.0 ± 0.1, and the flow rate was 0.8 mL/min. Polyethylene glycol (PEG) and bull serum albumin (BSA) were used for the humic-like and protein-like apparent molecular weight (AMW) calibration, respectively.

1.3.4. FT-IR analysis
A mixture of 0.5 mg lyophilized sample and 50 mg KBr was ground and then compressed. The samples were analysed using a FT-IR spectrometer (Model Nicolet 6700, Thermo Fisher Scientific) covering a frequency range of 4000–500 cm⁻¹.

1.3.5. The 2D-COS analysis
In 2D-COS, the system is placed under the influence of some external perturbation, which induces changes in the spectral features. Such spectral variations, traditionally referred to in this field as dynamic spectra, are observed for a specific interval of data collection to detect, deviations from the reference state, and then are subjected to a cross correlation analysis. Either a computational method based on the Fourier transform or a Hilbert transform is used to generate a pair of correlation intensity maps (i.e. synchronous and asynchronous correlation spectra) (Noda, 2012). The synchronous map shows correlations between all spectral bands changing in the experiment and whether they increase or decrease relative to each other. The asynchronous correlation map relates wavenumbers that change at different rates, and it also contains information on the sequence of the events taking place (Domínguez-Vidal et al., 2006).

In this study, ozone was used as the external perturbation to induce structural changes in the organic matter from the WWTP effluent, and a set of ozone dosage-synchronous fluorescence, MWD and FT-IR spectra were collected. All calculations were performed using 2D Shige software (Kwansei-Gakuin University, Japan). Synchronous and asynchronous spectra were plotted using Matlab 2012b software. More detailed description of the mathematical procedures associated with 2D-COS was presented in Supplementary data (Text S1).

1.3.6. X-ray photoelectron spectroscopy analysis
X-ray photoelectron spectroscopy was used to determine the ratio of different carbon species (aromatic carbon, aliphatic carbon, ketonic carbon and carboxylic carbon) in the EfOM fractions. The water samples were dried at 50°C to complete dryness before XPS analyses. The XPS analyses were performed with an X-ray photoelectron spectrometer (K-Alpha, Thermo Fisher Scientific, UK). The detailed operational conditions were the same as described by Jin et al., 2016.

2. Results and discussions

2.1. Characteristics of ozonation interaction with EFOM

2.1.1. Effect of ozonation on EFOM fluorescence characteristics
The water quality of the WWTP effluent upon different ozone dosages is shown in Appendix A Table S1. Fig. 1 shows the EEM spectra of the EFOM upon different ozone dosages. Two apparent EEM peaks at Ex/Em 220/340 nm (Peak A) and Ex/Em 350/440 nm (Peak B) were observed for the raw water from WWTP effluent. The peaks at Ex/Em 300–380/400–450 nm correspond to humic-like structures, classified as Type C according to Coble (1996) and Leenheer (2009). In addition, the peaks at Ex/Em 220–250/320–370 nm are attributable to tyrosine-like (Type B) constituents, which represent protein-like substances in general. With the addition of ozone, the intensity of Peak A and Peak B fluorophores decreased significantly. Ozonation can change the structures of fluorescent EfOM at low ozone dosage (0.45 mg O₃/mg DOC). As the ozone dosages increased to 0.98 mg O₃/mg DOC, Peak A vanished. It can be inferred that protein-type fluorescence was thoroughly destroyed during ozonation at this ozone dosage. Moreover, the intensity of Peak B further decreased at the same ozone dosage. The previous study of Zhang et al. (2008) showed that ozonation decreased the intensity of Type C fluorophores by about 50%–70% at the ozone dosage of 1 mg O₃/mg DOC. According to Uyguner and Bekbolet (2005), the intensity decrease indicates the depletion of aromatic structures and the increase in electron withdrawing groups in aromatic compounds. In addition, ozonation shifted both the excitation and emission wavelengths of humic-like substances (Peak B) to shorter wavelengths (blue-shift) as the ozone dosages increased to 2.15 mg O₃/mg DOC. Similar trends were observed by Korshin et al. (1999) who studied the influence of chlorination on hydrophobic acids of humic substances in surface water. Chlorination shifted the emission band towards lower wavelengths and decreased specific ultraviolet absorbance (SUVA) at 254 nm (Korshin et al., 1999). According to Coble (1996), the blue-shift was caused by a reduction in the degree of the π-electron systems at high ozone dosages, such as a decrease in the number of aromatic rings, reduction of conjugated bonds in a chain structure, or conversion of a linear ring system to a non-linear system. In addition, the changes in synchronous fluorescence spectra of EfOM upon the different ozone dosages are shown in Appendix A Fig. S1.

2.1.2. Molecular weight distribution of EFOM during ozonation
The molecular weight distribution of EfOM during ozonation was determined using HPLC coupled with a fluorescence detector. The EEM spectra shown in Fig. 1 at detection
wavelengths Ex/Em 350/440 nm and Ex/Em 220/340 nm, allowed observation of the MWD variation of humic-like substances and protein-like substances in EfOM with increasing ozone dosage. As shown in Fig. 2, the molecular weight distribution of humic-like substances was mainly 100–5000 Da. With increased ozone dosage, ozonation showed little effect on the molecular weight distribution of humic-like substances in the EfOM except for a decrease in the fluorescence intensity. The protein-like substances exhibited a wide molecular weight distribution (0.001–200 kDa). As the ozone dosage increase to 0.98 mg O₃/mg DOC, the intensity of the small molecular weight protein-like substances decreased significantly. Only a slight decrease could be observed in the intensity of the large molecular weight protein-like substances. This implied that smaller molecular weight protein-like substances were preferentially reacted during ozonation, which can be attributed to the thorough depletion of conjugated bonds or aromatic rings in this fraction (Jin et al., 2016).

2.1.3. FT-IR spectroscopic analysis of EfOM during ozonation

The FT-IR results of EfOM at different ozone dosages are shown in Fig. 3. The dominant infrared spectral information of the raw water occurred in the range 1650–800 cm⁻¹. The peak around 1610 cm⁻¹ was attributed to aromatic structures containing C=C double bonds (Xue et al., 2009). Around 1350 cm⁻¹, there was a relatively strong peak indicating C–H deformation of C–H₂ groups (Qi et al., 2018). The peak around 1050 cm⁻¹ was associated with C–O bonds (Bosch et al., 2006). This indicated that some kinds of alcohols, ethers and carbohydrates were present in the WWTP effluent. A peak observed at 870 cm⁻¹ was attributed to aromatic C–H structures (Chang et al., 2002). With increasing ozone dosage, the peak intensity of the bands diminished remarkably, indicating that ozonation could change the structure of organic matter. Nevertheless, the one-dimensional FT-IR spectra failed to reveal the dynamics of the structural transformation of EfOM during ozonation. To specify the selectivity of ozone for each observed EfOM functional group, and to judge the reaction sequence of the EfOM fractions with ozone, it was necessary to use 2D-COS to analyse synchronous fluorescence, HPSEC and FT-IR.

2.2. Characteristics of ozone selectivity towards fractions of EfOM

2.2.1. 2D-COS analysis of synchronous fluorescence

2D-COS is capable of resolving overlapped peaks by extending spectra along the second dimension, as well as of providing information about the relative directions and sequential orders of structural variations (Chen et al., 2015).
shows the 2D-COS map for the synchronous fluorescence spectra of EfOM during ozonation. The synchronous maps exhibited three prominent auto-peaks on the diagonal at 220, 320, and 360 nm. The peak at 220 nm was attributed to protein-like fractions. In addition, the humic-like fractions were divided into two components (320 and 360 nm), which were assigned to microbial humic-like substances and terrestrial humic-like components, respectively (Carstea et al., 2014; Phong and Hur, 2016). The intensities of the peaks decreased in the order 360, 320, and 220 nm, indicating that the fluorescence of humic-like fractions was more sensitive to ozonation, while the fluorescence of protein-like fractions was relatively stable. Furthermore, all the cross-peaks were positive, indicating that the spectral changes proceeded in the same direction as the increase of the ozone dosage. This result is consistent with that in Fig. 1, which shows that the fluorophore intensities of fluorescent EfOM were decreased during ozonation.

The asynchronous map elucidates the sequential changes of fluorescence fractions with the addition of ozone. The cross-peaks of 220/320, 220/360 and 320/360 are shown in the asynchronous maps (Fig. 4b), and their signs are given in Appendix A Table S2. By comparing the signs of the cross-peaks...
in the synchronous and asynchronous maps, information about EfOM fraction degradation order during ozonation was determined (320 nm > 220 nm > 360 nm according to Noda’s rule). This result indicated that the degradation order of EfOM fluorescence components during ozonation was: microbial humic-like substances > protein-like fractions > terrestrial humic-like components. The results of this study are consistent with the early studies from Liu et al. (2016) who also revealed that microbial humic-like substances exhibited the highest reactivity towards ozonation through fluorescence spectra coupled with parallel factor analysis (PARAFAC).

2.2.2. 2D-COS analysis of molecular weight
As discussed above, the MWD of humic-like substances was mainly 100–5000 Da, which can hardly be affected by ozonation. Therefore, the 2D-COS spectra only exhibited one obvious auto-peak (Appendix A Fig. S2). In contrast with humic-like substances, more information can be obtained from 2D-COS analysis of protein-like substances due to their wider molecular weight distribution.

Fig. 5a showed four auto-peaks centred at 0.05, 0.2, 0.5 and 93 kDa. The intensity of the peak at 50 Da was especially strong, indicating that smaller molecular weight protein-like substances were more susceptible to ozonation. This result was consistent with that in Fig. 2, which shows that protein-like substances with molecular weight < 1 kDa are completely decomposed when the ozone dosage is > 0.98 mg O₃/mg DOC. In addition, all the cross-peaks in Fig. 5a are positive, indicating that the detected protein-like substances were reacted in the same direction during ozonation. Furthermore, six cross-peaks centred at ν₁/ν₂ of 93/0.5, 93/0.2, 93/0.05, 0.5/0.2, 0.5/0.05 and 0.2/0.05 kDa can be observed on the asynchronous map (Fig. 5b), and the sign of each cross-peak is presented in Appendix A Table S3. Based on Noda’s rule, the reaction order of different molecular weight protein-like substances during ozonation is: 200 Da > 500 Da > 50 Da > 93

Fig. 4 – Synchronous (a) and asynchronous (b) 2D correlation maps generated from the synchronous fluorescence spectra of EfOM at different ozone dosages.

Fig. 5 – Synchronous (a) and asynchronous (b) 2D correlation maps generated from molecular weight distribution chromatograms of protein-like substances in the EfOM at different ozone dosages.
kDa. It can be inferred that ozone preferentially reacted with protein-like substances of smaller molecular weight. This result is consistent with that in a previous study (Jin et al., 2016), which reported that ozone preferentially reacts with fluorophores in the smaller molecular size protein-like substances in EfOM. Gonzales et al. (2012) also reported that the fractions of EfOM with AMW < 10 kDa had a faster ozone decay rate than the large molecular weight fractions, indicating that components with smaller molecular weight had higher reactivity with ozone.

2.2.3. 2D-COS analysis of FT-IR

To clarify more completely the transformation characteristics of each EfOM functional group with increasing ozone dosage, 2D-COS analysis of FT-IR was performed and the results are displayed in Fig. 6 and Table S4. The synchronous maps (Fig. 6a) exhibited three prominent auto-peaks on the diagonal at 1610, 1350, and 1050 cm\(^{-1}\). The auto-peaks were assigned to aromatic structures containing C=C double bonds, aliphatic C-H, and phenolic and alcoholic C-O bonds, respectively. The band at 1050 cm\(^{-1}\) was shown to vary most significantly, followed by the band at 1610 cm\(^{-1}\). The smallest variation was observed for the band at 1350 cm\(^{-1}\). The results of this study are consistent with the results of Westerhoff et al. (2005), who reported that ozone oxidized steroids containing phenolic moieties more efficiently than it did those without aromatic or phenolic moieties. Moreover, Jin et al. (2012) indicated that the order of reactivity of ozone with organic matter was activated aromatic ring compounds (i.e. phenolic compounds and aniline derivatives) > anisole derivative compounds (i.e. polycyclic aromatic hydrocarbons) > deactivated aromatic ring compounds (i.e. phthalate, halosubstituted compounds) > saturated aliphatic compounds. Thus, it could be concluded that ozone reacted with EfOM containing phenolic and alcoholic functional groups more efficiently than those without aromatic or phenolic structures. Aromatic and phenolic structures are deprotonated species which exhibited fast reaction with electrophilic ozone. Furthermore, as shown in Fig. 6a, the signs of the cross-peaks in the synchronous map are all positive, indicating that each EfOM functional group change proceeded in the same direction during ozonation. Considering the SUVA reduction in Appendix A Table S1, this result implies that unsaturated and aromatic organics in EfOM are degraded during ozonation. Accordingly, it is believed that each EfOM functional group observed in Fig. 6a was diminished during ozonation. In addition, Tang et al. (2014), who used the secondary effluent collected from an inverted anaerobic-anoxic-oxic (AAO) system, revealed that aliphatic C-H bonds increased after reaction between ozone and DOM. According to Qi et al. (2018), the content of aliphatic structures for hydrophobic fractions in EfOM was significantly reduced with increasing reaction time, but for hydrophilic fractions, ozonation obviously increased the relative contents of C-H bonds. Therefore, the discrepancy observed between our study and others is most likely caused by different characteristics of the raw water.

As shown in Fig. 6b, three cross-peaks centred at \(\nu_1/\nu_2\) of 1050/1350, 1050/1610 and 1350/1610 nm were identified. The detailed assignments of the bands and signs of the cross-peaks in the asynchronous map are presented in Appendix A Table S4. Using the sequential order rules, it can be concluded that the structural change sequence of EfOM functional groups during ozonation follows the order phenolic and alcoholic C-O bond > aromatic structure containing C=C double bonds > aliphatic C-H. As was previously reported, ozone preferentially removed organic compounds with relatively unsaturated structure (Phungsai et al., 2016). Qi et al. (2018) also stated that ozone preferentially reacted with oxygen functional groups such as aldehyde. According to Galapate et al. (2001), the reactivity of ozone is highly dependent on the electron density. Electron-donating groups like \(-\text{OH}\) could enhance the reactivity of aromatic rings to ozone (Galapate et al., 2001). Beltrán (2004) reported that, aromatic compounds were made susceptible to electrophilic substitution reactions by an electrophilic agent, such as ozone. Thus, compared with aliphatic C-H, aromatic structures were preferentially attacked by ozone.

![Fig. 6](https://example.com/fig6.png)  
**Fig. 6** – Synchronous (a) and asynchronous (b) 2D correlation maps generated from the FT-IR of EfOM at different ozone dosages.
response to ozonation, followed by the protein-like fractions, then by terrestrial humic-like components. According to the 2D-HPSEC-COS, small molecular weight protein-like substances were preferentially reacted during ozonation. Furthermore, the variation sequence of EfOM functional groups during ozonation occurred in the order: phenolic and alcoholic C–O bond > aromatic structure containing C=C double bonds > aliphatic C–H. During ozonation, high ratios of aromatic carbon in the raw water were lowered via addition reactions of double bonds or electrophilic attacks on aromatic rings. This produced a large amount of saturated compounds causing considerable increase of aliphatic carbon.

2.3. Chemical structure variation of the EfOM during ozonation

XPS analysis results of EfOM before and after ozonation were obtained for better understanding of the effect of ozonation on the structure of the EfOM. Afterwards, the ratio of total carbon was obtained by analysing the results through XPSpeak software for Gaussian fitting, as illustrated in Fig. 7. The C1s high resolution spectra are shown in Appendix A Fig. S3. According to Monteil-Rivera et al. (2000) and Lin et al. (2014), the four types of chemical binding signals shown in Appendix A Fig. S3 could be assigned to aromatic carbon (C=C), aliphatic carbon (C–C), ketonic carbon (C=O) and carboxylic carbon (O–C=O). As shown in Fig. 7, with increased ozone dosage, the ratios of aromatic carbon decrease sharply. This is in accordance with high UV254 removal after ozonation (Appendix A Table S1). Nevertheless, an opposite trend is observed for aliphatic carbon. This can be attributed to the transformation of organic compounds containing unsaturated structures to those with saturated structures (Phungsai et al., 2016). Moreover, only a very slight variation is observed in ketonic carbon (C=O) and carboxylic carbon (O–C=O). As shown in Fig. 7, with increased ozone dosage, the ratios of aromatic carbon decrease sharply. This is in accordance with high UV254 removal after ozonation (Appendix A Table S1). Nevertheless, an opposite trend is observed for aliphatic carbon. This can be attributed to the transformation of organic compounds containing unsaturated structures to those with saturated structures. As shown in Fig. 7, with increased ozone dosage, the ratios of aromatic carbon decrease sharply. This is in accordance with high UV254 removal after ozonation (Appendix A Table S1). Nevertheless, an opposite trend is observed for aliphatic carbon. This can be attributed to the transformation of organic compounds containing unsaturated structures to those with saturated structures.

Fig. 7 – Carbon species in the EfOM at different ozone dosages.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.05.012.

REFERENCES


3. Conclusions

In this study, the reaction characteristics and selectivity of ozonation towards fractions within EfOM are investigated by the application of EEM, HPSEC, FT-IR and 2D-COS analysis. The microbial humic-like substances gave the fastest


