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Effects of ozonation pretreatment on natural organic matter and wastewater derived organic matter – Possible implications on the formation of ozonation by-products

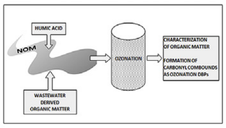
Alexandros Papageorgiou [a, *], Stylianos K. Stylianou [b], Pavlos Kaffes [a], Anastasios I. Zouboulis [b], Dimitra Voutsa [a]

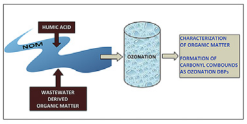
[a] *Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University, 54 124 Thessaloniki, Greece*
[b] *Division of Chemical Technology, Department of Chemistry, Aristotle University, 54 124 Thessaloniki, Greece*

HIGHLIGHTS

- NOM and wastewater organic matter exhibited different spectroscopic patterns.
- Ozonation reduced UV absorbance and fluorescence intensities of organic matter.
- OM from various sources showed different formation yield of carbonyl compounds.
- Wastewater had higher scavenger rates than surface water.

GRAPHICAL ABSTRACT





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ABSTRACT

The aim of this study was to investigate possible implications of natural and wastewater derived organic matter in river water that is subsequently used following treatment for drinking purposes. River water was subjected to lab-scale ozonation experiments under different ozone doses (0.1, 0.4, 0.8, 1.0 and 2.0 mgO_3/mgC) and contact times (1, 3, 5, 8 and 10 min). Mixtures of river water with humic acids or wastewaters (sewage wastewater and secondary effluents) at different proportions were also ozonated. Dissolved organic carbon and biodegradable dissolved organic carbon concentrations as well as spectroscopic characteristics (UV absorbance and fluorescence intensities) of different types of dissolved organic matter and possible changes due to the ozonation treatment are presented. River water, humic substances and wastewater exhibited distinct spectroscopic characteristics that could serve for pollution source tracing. Wastewater impacted surface water results in higher formation of carbonyl compounds. However, the formation yield (μg/mgC) of wastewaters was lower than that of surface water possibly due to different composition of wastewater derived organic matter and the presence of scavengers, which may limit the oxidative efficiency of ozone.

1. Introduction

Ozonation is a process usually employed in water and wastewater treatment for disinfection as well as for oxidation of

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* Corresponding author.
E-mail address: alexpapageorgiou@hotmail.com (A. Papageorgiou).

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micropollutants and natural organic matter. Ozonation can affect the precursors of disinfection by-products (DBPs) and subsequently the formation and the profile of various classes of DBPs. Dissolved organic matter (DOM) is a key parameter that influence the formation of DBPs. DOM is a complex heterogeneous mixture of various organic compounds, highly influenced by its origin, climatic conditions, and biogeochemical cycles of the surrounding environment (Farré et al., 2013; Michael-Kordatou et al., 2015).

Variations regarding the concentration, composition and properties of DOM in surface water are usually observed within the same aquatic system due to rainfall, surface runoff, floods, or droughts (Matilainen et al., 2010). Natural organic matter (NOM) originates from both allochthonous (watershed or terrestrial) and autochthonous (algal, *in situ*) processes. Allochthonous NOM generally exhibits humic character, while autochthonous NOM principally consists of soluble algogenic organic matter (carbohydrates, amino acids etc). Wastewater that reach aquatic environment through discharge/leakages and reuse applications has a significant impact on the concentration and composition of DOM. Due to water shortage, the reuse of wastewater is considered as an important component of sustainable wastewater management practice. Thus, possible implications of wastewater derived organic matter (WWOM) in the biogeochemical cycles, the water quality, the efficiency of downstream treatment facilities, and the formation of DBPs gained special attention lately (Michael-Kordatou et al., 2015; Yu et al., 2015).

Wastewater derived organic matter consists of heterogeneous mixture of organic compounds with diverse structures and varying origins including dissolved natural organic matter, soluble microbial products and trace organic compounds of industrial and residential origin (endocrine disrupting compounds, personal care products, pharmaceuticals etc) along with their transformation products formed during treatment. The composition of WWOM is a reflection of the origin of raw water and of domestic, industrial, and agricultural activities contributing to sewage influent. WWOM also depends on the applied wastewater treatment processes and operating conditions (Michael-Kordatou et al., 2015; Yu et al., 2015). Although wastewater reuse is becoming important due to increasing water shortage, the current knowledge on the potential effects of WWOM to the aquatic environment is limited.

Ozonation usually employed in water and wastewater pretreatment results in the formation of various organic (carbonyl compounds) and inorganic by-products (bromate) (Chon et al., 2015; Papageorgiou et al., 2014). Some carbonyl compounds, such as formaldehyde and acetaldehyde are considered as posing potential risk and are classified as prioritized emerging DBPs in drinking water regarding their potential health impact (Hebert et al., 2010; Richardson et al., 2007). Consequently these emerging DBPs should be monitored in order to assess population exposure. WHO recommended a guideline of 900 μg/L for formaldehyde in drinking water (WHO, 2005). The presence of aldehydes may be responsible for undesirable taste and odor in drinking water. Moreover, since aldehydes represent the major fraction of biodegradable dissolved organic carbon (BDOC), their formation is significant for the biological stability of water in the distribution system or receiving environment. Conventional drinking water treatment processes can effectively remove the carbonyl compounds formed as by-products of ozonation treatment. Papageorgiou et al. (2014) who studied the fate of ozonation by products at a full-scale drinking water treatment plant reported that the carbonyl compounds formed during pre-ozonation and ozonation processes were removed during coagulation/flocculation and filtration through granular activated carbon treatment steps (38 ± 11% and 50 ± 17%, respectively). There are various studies that investigate the behavior of NOM under ozonation in laboratory experiments. However, due to the heterogeneous nature and structural complexity of NOM in reservoirs, its behavior is not yet fully understood. Results cannot be projected to a new system and further research on this field is required covering different case studies. Moreover, the implications of wastewater in surface water is a new issue that gains attention lately.

The aim of this study was to investigate possible implications of natural and wastewater derived organic matter in river water that is subsequently used following treatment for drinking purposes. Therefore, river water as well as mixtures of river water with humic acid and wastewaters were subjected to lab-scale ozonation experiments. This study presents a) the fate of different types of dissolved organic matter due to ozonation regarding changes of dissolved and biodegradable organic carbon (DOC and BDOC) as well as of spectroscopic indices (UV absorbance and fluorescence intensity) and, b) the formation of 14 carbonyl compounds as ozonation by-products.

2. Materials and methods

2.1. Chemicals

The analytical standard containing 14 carbonyl compounds was purchased from Ultra Scientific. The derivatization agent PFBOA (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine) and potassium hydrogen phthalate (KHP) were purchased from Alfa Aesar, Karlsruhe, Germany. Both surrogate standard (2′,4′,5′-trifluoroacetophenone) and internal standard (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. Humic acid (sodium salt), obtained from Sigma & Aldrich Chemical Company. Sodium bisulfite purchased from Sigma & Aldrich. The derivatization agent PFBOA was prepared daily as an aqueous solution (15 mg/mL) in organic free water, while the carbonyl compounds standard solutions was prepared in acetonitrile. Organic free water was provided by the Simplicity UV Ultrapure Water System (Millipore, Molsheim, France).

2.2. Ozonation experiments

Ozonation experiments were employed in water samples containing different types of dissolved organic matter (natural organic matter from river water, humic acids, wastewater derived organic matter). River water was obtained from Aliakmon River and wastewater samples obtained from a sewage treatment plant. Samples were filtered through 0.45 μm and stored at 4 °C.

Ozone stock solution was prepared daily by bubbling ozone gas through a ceramic porous diffuser made of borosilicate glass to ultrapure water until saturation. Ozone-oxygen gas mixture was produced by a laboratory-scale ozone generator (model TOGC2A, Ozonia Triogen). Pure oxygen was used as a feed gas at a pressure of 0.5 bar and a flow rate of 2 L/min. Indigo colorimetric method was used for the determination of ozone concentration in stock solution (APHA et al., 1998). Ozonation experiments carried out in batch mode at ambient conditions (25 ± 0.2 °C, 1 atm). Samples, buffered at $pH = 7 \pm 0.1$, were ozonated by adding small aliquots of O_3 stock solution (23 mgO_3/L) at a final volume sample of 200 ml. Ozone was quenched by sodium bisulfite. The influence of contact time (1–10 min), O_3/DOC ratio (0.1–2.0 mgO_3/mgC) and pH values (1–8) were investigated in duplicated experiments. The difference was usually below 15% for carbonyl compounds and in some cases reached 25% for the experiments in more complex samples, such as