



Molecular characterization of low molecular weight dissolved organic matter in water reclamation processes using Orbitrap mass spectrometry



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ABSTRACT

Reclaimed water has recently become an important water source for urban use, but the composition of dissolved organic matter (DOM) in reclaimed water has rarely been characterized at the compound level because of its complexity. In this study, the transformation and changes in composition of low molecular weight DOM in water reclamation processes, where secondary effluent of the municipal wastewater treatment plant was further treated by biofiltration, ozonation and chlorination, were investigated by “unknown” screening analysis using Orbitrap mass spectrometry (Orbitrap MS). The intense ions were detected over an m/z range from 100 to 450. In total, 2412 formulae with various heteroatoms were assigned, and formulae with carbon (C), hydrogen (H) and oxygen (O) only and C, H, O and sulfur (S) were the most abundant species. During biofiltration, CHO-only compounds with relatively high hydrogen to carbon (H/C) ratio or with saturated structure were preferentially removed, while CHOS compounds were mostly removed. Ozonation induced the greatest changes in DOM composition. CHOS compounds were mostly decreased after ozonation while ozone selectively removed CHO compounds with relatively unsaturated structure and produced compounds that were more saturated and with a higher degree of oxidation. After chlorination, 168 chlorine-containing formulae, chlorinated disinfection by-products (DBPs), were additionally detected. Candidate DBP precursors were determined by tracking chlorinated DBPs formed via electrophilic substitution, half of which were generated during the ozonation.

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1. Introduction

Remarkable increases in water consumption and water pollution have raised concerns about the sustainability of water use in urban cities. Water stress has caused various problems for natural water resources such as instability of water flow in rivers, spring

water drying, groundwater level decline and ecosystem deterioration (Furumai, 2008). Hence, sustainable water use strategies are necessary to ensure long-term water supply with adequate water quality as well as to protect against adverse ecological, economic and social effects. Reclaimed water use is one of the countermeasures towards sustainable water use, and it has been implemented for various applications such as toilet flushing water, river flow maintenance, water front creation, plant irrigation and pavement cooling. The benefits of reclaimed water are not only to secure water supplies while reducing demand for high quality tap water but also to alleviate water pollution by reducing wastewater discharge to natural water resources. Because wastewater increases proportionally with water consumption, reclaimed water should be an abundant and stable water resource.

The quality of reclaimed water is the most important consideration for reuse applications, and dissolved organic matter (DOM) is a central issue. Secondary or tertiary effluents, used as influent streams in water reclamation plants, still contain DOM that is

Abbreviations: BOM, biodegradable organic matter; DATS, dialkyl tetralin sulfonate; DOM, dissolved organic matter; DOC, dissolved organic carbon; DBE, double bond equivalent; DBE-O, double bond equivalent minus oxygen; DBPs, disinfection by-products; EfOM, effluent organic matter; ESI, electrospray ionization; FT-ICR-MS, Fourier-transform ion cyclotron resonance mass spectrometry; H/C, hydrogen to carbon ratio; LAS, linear alkylbenzene sulfonate; LMW, low molecular weight; MS, mass spectrometry; NOM, natural organic matter; Orbitrap MS, Orbitrap mass spectrometry; O/C, oxygen to carbon ratio; SUVA, Specific ultraviolet absorbance; SPC, sulfophenyl carboxylate; SPE, Solid phase extraction; TOC, total organic carbon; TN, total nitrogen.

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refractory to biological treatment and are often referred to as effluent dissolved organic matter (EfOM). EfOM is typically composed of a wide variety of compounds such as natural organic matter (NOM) originating from drinking water, soluble microbial products produced during biological treatment processes and synthetic organic compounds from domestic uses (Shon et al., 2006). During and after the water reclamation process, DOM can cause various problems such as adsorption and deposition of organic foulants in membrane treatment processes (Xu et al., 2010), formation of disinfection by-products (DBPs) by providing precursors, increasing demand for oxidants or disinfectants, and promoting microbial regrowth in distribution systems by providing growth substrates (Acharya et al., 2016; Thayanukul et al., 2013).

To tackle these problems, improved knowledge of DOM in reclaimed water is required. Various characterization and quantification methods have extensively focused on bulk chemical properties such as total and dissolved organic carbon (TOC and DOC), size distribution, fluorescence excitation/emission, functional groups, and spectroscopic properties. However, detailed descriptions at compound level are absent from those methods (Sleighter and Hatcher, 2007; Zhang et al., 2012). An unknown screening (nontargeted screening) by ultrahigh resolution and accurate mass spectrometry can reveal a broad spectrum of a complex mixture and enable characterization of elemental compositions, providing detailed information at the molecular scale. Elemental compositions of DOM can provide useful information to understand reaction pathways, transformations and changes in molecules during treatment processes. Molecular changes of DOM along with drinking water treatment processes have been analyzed by electrospray ionization (ESI) coupled with Fourier transform ion cyclotron resonance (FT-ICR-MS) using unknown screening approach (Gonsior et al., 2014; Lavonen et al., 2013; Zhang et al., 2012). In addition, compositions of EfOM were also evaluated by ESI-FT-ICR-MS (Gonsior et al., 2011; Tseng et al., 2013). Little is currently known about changes in composition and transformation of low molecular weight (LMW)-DOM in further treatment processes of water reclamation plants.

In addition to FT-ICR-MS, a newly developed mass analyzer employing an ion trap in an electrostatic field (Orbitrap) has been developed by Makarov (2000). Coupling of ESI and Orbitrap Fourier-transform mass spectrometry (Orbitrap MS) is a promising technique for unknown screening of complex mixtures of DOM. With internal calibration, mass accuracy less than 2 ppm could be achieved (Krauss et al., 2010; Olsen et al., 2005) enable molecular formula identification for C, H, O and S containing molecules for < 500 Da molecules (Remucal et al., 2012).

In this study, unknown screening by ESI Orbitrap MS was applied to elucidate the molecular composition of LMW-DOM throughout water reclamation processes including secondary effluent, biofiltration, ozonation and chlorination. The transformation/composition changes of LMW-DOM in each treatment process were investigated by comparing compound intensities before and after treatments. Characteristics such as hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios and degree of unsaturation (double bond equivalent; DBE) of molecules were calculated to provide details of how LMW-DOM changed with each of the reclamation processes. In addition, efforts were made to identify DBPs, chlorine-containing formulae additionally formed after chlorination, and their potential precursors to determine the probable origins of those precursors.

2. Materials and methods

2.1. Reclaimed water samples

Water samples were collected from a water reclamation plant receiving secondary effluent from a municipal wastewater treatment plant in Japan in April 2014 and May 2015. The findings and discussion in this study were mainly based on the observations of 2014 samples, and reproducibility was tested on samples taken in 2015 when necessary. The treatment capacity of the plant was 960 m³/d. The treatment processes consisted of biofiltration for removal of remaining biodegradable organic matter (BOM), ozonation for removal of color and odor (4.5 g/m³ of ozone dosage) and chlorination for disinfection. Ceramic filter media was used as the microbial carrier in the biofiltration unit. The reclaimed water was stored in a 2000 m³ storage tank where sodium hypochlorite was added with dosage of 6 mg/L as free chlorine to achieve 1 mg/L of total chlorine concentration before distribution. Reclaimed water was storage for 24 h on average. We sampled the secondary effluent as well as process waters such as biofiltration, ozonation and chlorination waters in pre-combusted glass bottles (6 h, 550 °C). The water samples were immediately transferred to the laboratory within 1.5 h.

TOC and DOC concentrations were measured by TOC-L_{CSH} (Shimadzu, Japan) as a nonpurgeable organic carbon. Total nitrogen (TN) was determined with a TN unit equipped with TOC-L_{CSH}. Residual chlorine and pH were measured on-site using the colorimetric method with a Hach DR/890 colorimeter (Hach, USA) and model multi 3430 (WTW, Germany), respectively. Anion concentrations such as nitrate (NO₃⁻), and chloride (Cl⁻) were evaluated using an ion chromatograph (IC 761, Metrohm, Switzerland) with SI-90 column (Shodex, Japan). Ammonia (NH₄⁺) concentration was evaluated using a spectrophotometric method (Hach DR2800, Hach, USA). UV absorbance at 254 nm was measured using a 1 cm cell (UH3500 Hitachi, Japan) and specific UV-absorbance (SUVA) was calculated by the absorbance value at 254 nm divided by DOC concentration.

2.2. Solid phase extraction (SPE)

Five hundred milliliters of water samples were first filtered with 0.3 μm pre-combusted glass-fiber filters (GF-75, Advantec Toyo, Japan). The filtrates were acidified with high-purity grade hydrochloric acid to pH 2 and passed through an SPE cartridge (Bond Elut PPL, Agilent Technologies, USA) at a flow rate of 20 ml/min. The cartridge contained 1 g of a polystyrene-divinylbenzene modified with a nonpolar surface. It was previously conditioned with methanol (LC-MS grade) and equilibrated with acidified Milli-Q (0.01 M hydrochloric acid) before use. For the elution step, the cartridge was first rinsed with 20 ml of the acidified Milli-Q to eliminate retained salts, after which the retained organic matter was eluted with 10 ml of methanol. A blank sample for SPE (extraction blank) was also prepared with 500 ml Milli-Q water instead of the samples. The extracts were stored at -20 °C in the dark. To calculate DOC recovery in the SPE step, 1 ml of the extract was evaporated to dryness by N₂ gas flow and redissolved in 20 ml of Milli-Q water for TOC measurement.

2.3. Unknown screening analysis

The unknown screening analyses were performed by Orbitrap MS (Exactive, Thermo Scientific, USA). First, the Orbitrap MS was externally calibrated by the calibration solution (Proteomass ESI, Sigma-Aldrich, USA) that covers *m/z* range of 50–2000. Additionally, a hexadecanoic acid peak ([M-H]⁻ = 255.23295) in the

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