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Measurement of dissolved organic nitrogen in a drinking water treatment plant: Size fraction, fate, and relation to water quality parameters

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ABSTRACT

This paper investigates the characteristics of dissolved organic nitrogen (DON) in raw water from the Huangpu River and also in water undergoing treatment in the full-scale Yangshupu drinking water treatment plant (YDWTP) in Shanghai, China. The average DON concentration of the raw water was 0.34 mg/L, which comprised a relatively small portion (~5%) of the mass of total dissolved nitrogen (TDN). The molecular weight (MW) distribution of dissolved organic matter (DOM) was divided into five groups: >30, 10–30, 3–10, 1–3 and <1 kDa using a series of ultrafiltration membranes. Dissolved organic carbon (DOC), UV absorbance at wavelength of 254 nm (UV254) and DON of each MW fraction were analyzed. DON showed a similar fraction distribution as DOC and UV254. The <1 kDa fraction dominated the composition of DON, DOC and UV254 as well as the major N-nitrosodimethylamine formation potential (NDMAFP) in the raw water. However, this DON fraction cannot be effectively removed in the treatment line at the YDWTP including pre-ozonation, clarification and sand filtration processes. The results from linear regression analysis showed that DON is moderately correlated to DOC, UV254 and trihalomethane formation potential (FP), and strongly correlated to haloacetic acids FP and NDMAFP. Therefore, DON could serve as a surrogate parameter to evaluate the reactivity of DOM and disinfection by-products FP.

1. Introduction

Dissolved organic nitrogen (DON) comprises a relatively small portion of the mass of dissolved organic matter (DOM) or total dissolved nitrogen (TDN) in surface waters (Westerhoff and Mash, 2002). However, removal of DON recently has become a potentially critical issue for drinking water treatment and wastewater reuse due to concerns such as the increase in disinfectant/oxidant demand, the formation of disinfection by-products (DBPs) and the occurrence of membrane fouling (Her et al., 2000; Lee et al., 2003). Chlorination and chloramination of DON not only produces regulated DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) but also produces nitrogenous disinfection by-products (N-DBPs) such as nitrosamines, halonitromethanes, and haloacetonitriles (Dotson et al., 2009; Lee et al., 2007; Pehlivanoglu-Mantas and Sedlak, 2008). Toxicity tests have indicated that N-DBPs are far more carcinogenic or mutagenic than some of the regulated DBPs (Plewa et al., 2004; Richardson et al., 2007). Thus, the emerging concerns for N-DBPs have increased the need to understand better the concentrations, structures and reactivity of DON in raw water and its fate in drinking water treatment plants (DWTPs).

During the past decades, many studies have described the occurrence and fate of DON in marine and freshwater ecosystems (McCarthy et al., 1997; Leenheer, 2004). DON is a complex mixture that is primarily composed of amino acids, amino sugars, amides, peptides and heterocyclic-N compounds (e.g. pyrimidine, imidazole, purine and porphyrins) (Fuhrman, 1990; Keil and Kirchman, 1991; Leenheer, 2004). The primary sources of DON include agricultural fertilizers, wastewater discharges, forest litter, and excretion of algae products in eutrophic water (Westerhoff and Mash, 2002). Because there is no direct analytical method for DON quantification, the most commonly used method involves subtracting dissolved inorganic nitrogen (DIN, sum of nitrite, ammonium and nitrate) concentrations from the total dissolved nitrogen (TDN) concentration (Vandenbruwane et al., 2007). However, the accuracy of DON measurements is significantly subject to the cumulative analytical errors of independently measured nitrogen species, especially in the case of high DIN/TDN ratios (Vandenbruwane et al., 2007). Lee and Westerhoff (2005) developed a dialysis pretreatment method to get more accurate DON concentrations for samples with DIN/TDN ratios exceeding 0.6 mg N/mg N. In their work, DON concentrations for water samples from 28 United States (US) DWTPs were analyzed. The average DON concentrations were 0.19 mg

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N/L for raw waters and 0.15 mg N/L for finished waters (Lee et al., 2006). According to public data from the U.S. Geologic Survey National Water Quality Assessment Program (a survey of 23,000 water samples), median DON concentrations in US surface, shallow and deep ground waters were 0.37, 0.24, and 0.18 mg N/L, respectively (Westerhoff and Mash, 2002).

To gain more information on DON characteristics in raw water and wastewater, many separation and classification methods have been developed including separation using XAD resins and membrane isolation, in conjunction with measurements of specific compounds and functional group compositions (Leenheer et al., 2007). Ultrafiltration (UF) was used to determine the size distribution of wastewater-derived DON species (Pehlivanoglu-Mantas and Sedlak, 2008). According to Pehlivanoglu-Mantas and Sedlak (2008), 87% of the DON compounds passed through a 10 kDa ultrafilter (YM10, Millipore Corp.), and 67% of the compounds, which composed most of the precursors of N-nitrosodimethylamine (NDMA), had molecular weights (MWs) less than 1 kDa (YM1, Millipore Corp.). Because NOM contains approximately 30–50% of carbon by weight (Westerhoff and Mash, 2002), most studies focused on analyzing DOC to assess NOM reactivity or its efficient removal during the water treatment processes. There have been no published reports on the fate of DON in the drinking water treatment processes that the authors are aware of, although Lee et al. (2006) demonstrated that DWTPs could remove approximately 20% of DON in raw water, and that adding polymer and ozonation processes could further increase DON removal. Some researchers (Lee et al., 2006; McCarthy et al., 1998; Pehlivanoglu-Mantas and Sedlak, 2008; Richardson et al., 2007) have investigated DON in marine, freshwater ecosystems and wastewater effluents, but a detailed study of the occurrence and treatability of DON in DWTPs is not readily available.

The objectives of this study were to investigate the size fractions of DON, its fate in a DWTP, the relationship between DON and some common water quality parameters, as well as the DBP formation potential (DBPFP). In particular, the research work focused on:

(1) The characteristics of DON in raw water from the Huangpu River, including MW distribution and DBPFPs (trihalomethane formation potential [THMFP], haloacetic acid formation potential [HAAFP], and N-nitrosodimethylamine formation potential [NDMAFP]);
(2) The fate of DON in the Yangshupu DWTP (YDWTP) as well as the shift of its MW distribution after each treatment process;
(3) Correlations between DON and some common water quality parameters such as DOC, UV254, SUVA (UV254/DOC), nitrate, ammonium and DBPFPs.

2. Materials and Methods

2.1. Sampling Plan and Sample Preparation

Samples were collected from the YDWTP, which has a capacity of 1,480,000 CMD (cubic meters per day), supplying approximately one fourth of the drinking water consumed by the 13.8 million residents of Shanghai City. The raw water was delivered upstream of the treatment plant by a 40 km long tunnel from the Huangpu River (30.97° N, 121.30° E), and the characteristics of the raw water were studied and found out to be similar to that in our previous work (Xu et al., 2007). There are seven conventional treatment lines at the YDWTP including coagulation, sedimentation and sand filtration processing lines. An advanced treatment line (320,000 CMD) with pre-ozonation (pre-O_3), high rate clarification, sand filtration, post-O_3 and biologically activated carbon (BAC) filtration was also included in this plant. Samples were taken from the effluent of each process in the advanced treatment line except for post-O_3 and BAC because the last two processes were under engineering reconstruction during the sampling time.

The samples were collected in polypropylene containers, transported to the laboratory on ice, filtered through 0.45 μm membrane filters (Millipore, USA) upon arrival, and then stored at 4 °C in the dark. Samples for DOM fractionation tests were collected on Sep. 15, Oct. 20, and Nov. 4, 2009, respectively, while the samples for the study of the fate of DON and its correlation to water quality parameters and DBPFPs were collected continuously from Apr. to Dec., 2009.

2.2. DOM Fractionation Using UF

DOM in the raw water was fractionated into five groups after filtration using a series of cellulose-derivative UF membranes (Millipore, USA) with MW cut-offs of 30, 10, 5, 3, and 1 kDa, respectively, in dead-end stirred cells (Millipore, USA). The effective surface area of the membrane was 33.2 cm^2. Prior to filtration, Milli-Q water was passed through the membranes to remove any possible leached organics until DOC in the permeate was less than 0.1 mg C/L. High purity nitrogen (99.999%) was used to pressurize the filtration process (~0.15 MPa), and the permeates were collected and stored at 4 °C until analysis. The percentages of DON, DOC and UV254 in each MW fraction were calculated using the method described by Lee and Westerhoff (2006).

2.3. Chemicals and Reagents

Standard solutions of nitrate, nitrite, ammonia and DOC were purchased from the Institute of Environmental Reference Materials (IERM), Ministry of Environmental Protection (China). THMs and HAAs standard solutions were purchased from Dr. Ehrenstorfer (Germany). NDMA standard (99.5%) and NDMA-d6 (used as internal standard) were obtained from Chem Service, Inc. (Westchester, PA, USA) and Cambridge Isotope Laboratories, Inc. (MA, USA), respectively. HPLC-grade methanol, acetonitrile, acetone, n-pentane and methyl tert-butyl ether (MTBE) were obtained from J. T. Baker (USA). Sodium hypochlorite, methanesulfonic acid, ascorbic acid, sulfuric acid, ammonium chloride, potassium dihydrogen phosphate, sodium hydroxide, sodium thiosulfate and ammonium acetate were used as analytical reagents and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All glassware was rinsed with distilled water and dried in an oven at 105 °C for 24 h. Pure water produced from a Milli-Q water purification system (Millipore, USA) was used to prepare all the required reagents.

2.4. Analytical Methods

DON, DOC, UV254, nitrate, ammonium, THMFP, HAAFP and NDMAFP were analyzed for each size fraction of DOM in the raw water effluents obtained from different treatment processes at the YDWTP. DOC and TDN were measured using a Shimadzu TOC-VCSH analyzer with a TNM-1 TN unit (Shimadzu, Japan). Nitrate and nitrite were measured using ion chromatography (Dionex ICS-1000, AS14 column) with a conductivity detector. Nitrite concentrations of all the samples tested in this study were below the method detection limit (MDL, 0.005 mg N/L). Ammonium was quantified using the same ion chromatograph equipped with a Dionex IonPac CS-12A and 20 mM methanesulfonic acid solution as the eluent (flow rate = 1.0 mL/min). Due to the high DIN/TDN ratios (>90%) observed in the raw and treated water samples from the YDWTP, DON was measured after applying the nanofiltration (NF) pretreatment method proposed by the authors in a previous research study (Xu et al., 2010). UV254 was measured at a wavelength of 254 nm (SQ-4802 UV-Vis spectrophotometer, UNICO, Shanghai) using a 1-cm quartz cell.

The THMFP and HAAFP experiments were conducted following the procedure described by Xu et al (2007). THMs and HAAs were analyzed according to the US Environmental Protection Agency-prescribed methods 551.1 and 552.2, respectively. THMs samples