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Measurement of dissolved organic nitrogen forms in wastewater effluents: Concentrations, size distribution and NDMA formation potential

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ABSTRACT

Dissolved organic nitrogen (DON), which may act as a nutrient and a disinfection by-product precursor, accounts for most of the dissolved nitrogen in nitrified–denitrified wastewater effluents. To gain insight into the behavior of wastewater-derived DON in engineered and natural systems, samples from treatment plants employing a range of different processes were characterized by several different methods. Dissolved free and combined amino acids accounted for the majority of the identifiable DON. Combined amino acids typically accounted for less than 10–20% of the wastewater-derived DON. Other organic-nitrogen containing species such as EDTA and humic substances from the water source only accounted for a few percent of the remaining DON. The remaining DON mainly consisted of hydrophilic, low-molecular weight compounds, capable of passing through a 1 kDa ultrafilter. This fraction of the DON also contained most of the precursors of *N*-nitrosodimethylamine (NDMA). The chemical properties of wastewater-derived DON pose challenges to designers of wastewater treatment plants because most physical and chemical treatment processes will not remove low-molecular weight, hydrophilic compounds.

1. Introduction

The increasing use of nitrification–denitrification processes for municipal wastewater treatment leads to the presence of dissolved organic nitrogen as the main form of nitrogen in the wastewater effluent. Wastewater-derived DON may simulate algal growth (Pehlivanoglu and Sedlak, 2004) or act as precursor for the carcinogenic disinfection by-product N-nitrosodimethylamine (NDMA, Mitch and Sedlak, 2002, 2004; Pehlivanoglu-Mantas and Sedlak, 2006a; Lee et al., 2007). As a result of these concerns, methods for characterizing the structure and properties of wastewater-derived DON are needed.

In WWTPs that do not practice nitrification–denitrification, the measurement of DON is usually problematic due to the nature of the available analytical methods. In all of the available methods for quantifying dissolved organic nitrogen as a bulk parameter, DON is determined by subtraction of the sum of the inorganic nitrogen species from total dissolved nitrogen. Because the concentration of the inorganic nitrogen species often is considerably higher than that of the organic nitrogen species, DON measurements are subject to substantial error. Although dialysis pretreatment to remove inorganic nitrogen species may be useful for the measurement of DON in drinking waters, the method may not be useful for DON measurement in wastewater due to matrix effects (Lee and

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Westerhoff, 2005). These problems have often discouraged researchers studying wastewater treatment processes from measuring DON and as a result, little is known about the nature and behavior of DON in wastewater treatment plants. The limited available information often is based on an assumed relationship between DON and other collective organic parameters, such as dissolved organic carbon (DOC) and chemical oxygen demand (COD, Manka et al., 1974; Confer et al., 1995). Using COD or DOC as surrogates for DON assumes that the behavior of organic nitrogen compounds in wastewater treatment plants is identical to that of other organic compounds. The validity of this assumption is questionable.

As an alternative to measuring DON as a bulk parameter in wastewater, researchers have quantified specific organic-nitrogen containing compounds such as dissolved free and combined amino acids (DFAA and DCAA), low-molecular weight amines (e.g., dimethylamine (DMA)), chelating agents (e.g., nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA), Table 1). Despite the variety of organic nitrogen-containing compounds detected in municipal wastewater effluent, the sum of the specific compounds normally accounts for less than 10% of the DON in wastewater effluent, leaving most of the wastewater-derived DON unidentified. In addition to the above-mentioned hydrophilic substances, a fraction of the wastewater-derived organic nitrogen can be classified as hydrophobic substances. Nitrogen bound to functional groups of humic substances (Zang et al., 2000) is an example of the hydrophobic fraction of wastewater-derived DON.

To further characterize the unidentifiable wastewater-derived DON, a few researchers have attempted to measure the molecular weight distribution of DON using size exclusion chromatography and other characterization techniques. Results of these studies indicate that the low-molecular fraction (MW < 1800) accounts for between 58 and 66% of DON of the wastewater effluent (Keller et al., 1978; Parkin and McCarty, 1981). However, these measurements have not been made in conjunction with measurements of specific compounds or disinfection by-products.

In this paper, we measure DON and specific organic nitrogen compounds, such as free and combined amino acids and EDTA, in samples from different parts of municipal wastewater treatment plants to assess the effect of biological treatment on DON and its components. In addition, the molecular weight distribution of dissolved organic nitrogen compounds as determined by ultrafiltration and the affinity of those compounds for various synthetic solid-phase extraction resins are measured to provide a better understanding of the nature and behavior of the unidentified fraction of DON. Finally, the concentrations of organic-nitrogen containing NDMA precursors are measured in several fractions of wastewater-derived DON to characterize the DON compounds responsible for NDMA formation.

Table 1 – Typical concentration of DON compounds detected in municipal wastewater effluent, expressed on the basis of nitrogen content

DON compound	Concentration (μM N)	Reference
Dissolved organic nitrogen	75–150	Parkin and McCarty (1981), Qasim (1999)
Dissolved free amino acids (DFAA)	0.04–2	Burleson et al. (1980), Confer et al. (1995), Grohmann et al. (1998)
Dissolved combined amino acids (DCAA)	1–19	Scully et al. (1988), Confer et al. (1995), Grohmann et al. (1998)
Dimethylamine (DMA)	0.3–5.1	Hwang et al. (1995), Abalos et al. (1999), Mitch and Sedlak (2004)
Ethylenediaminetetraacetic acid (EDTA)	0.1–0.5	Kari and Giger (1996), Nowack et al. (1996), Bedsworth and Sedlak (1999)
Nitrilotriacetic acid (NTA)	0.1–0.5	Alder et al. (1997), Bucheli-Witschel and Egli (2001)
Caffeine	0.1–0.2	Siegener and Chen (2002), Buerge et al. (2003)
N-containing pharmaceuticals	<0.001	Hirsch et al. (1996), Ternes (1998)

2. Materials and methods

All chemicals used in the experiments were of analytical grade and were purchased from either Fisher Scientific or Sigma–Aldrich. All glassware used in the experiments were rinsed with NanoPure water (Barnstead) and baked at 450 °C for 4 h prior to use. Samples were collected from three municipal wastewater treatment plants and the locations where samples were collected are listed below.

The Dublin/San Ramon wastewater treatment plant (DSR WWTP) is located in Dublin, CA and has an average dry weather flow of 0.5 m^3/s (11.5 MGD). The treatment plant is a secondary activated sludge plant where the treated effluent is chlorinated and dechlorinated before discharge into San Francisco Bay. The Truckee Meadows Water Reclamation facility (TMWRF) is a 1.24 m^3/s (28.4 MGD) treatment plant located in Reno, NV. The TMWRF consists of an activated sludge unit with separate nitrification and denitrification tanks. The effluent of the TMWRF is chlorinated and dechlorinated prior to discharge into the Truckee River. The Mt. View wastewater treatment plant (Mt. View WWTP) receives a flow of 0.1 m^3/s (1.8 MGD) during dry weather. The treatment plant has a trickling filter followed by a nitrification biotower. The treated effluent is disinfected using an ultraviolet light system prior to discharge into a system of engineered treatment wetlands.

At all three wastewater treatment plants, grab samples of wastewater were collected in Teflon-lined polypropylene containers and were filtered either on site or were kept on ice until filtration, which always occurred within 24 h. The wastewater was filtered through 0.2-μm cartridge filters (Millipore Corp.) with a peristaltic pump fitted with Teflon tubing. Due to the