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Nitrosamines in pilot-scale and full-scale wastewater treatment plants with ozonation

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ABSTRACT

Ozone-based treatment trains offer a sustainable option for potable reuse applications, but nitrosamine formation during ozonation poses a challenge for municipalities seeking to avoid reverse osmosis and high-dose ultraviolet (UV) irradiation. Six nitrosamines were monitored in full-scale and pilot-scale wastewater treatment trains. The primary focus was on eight treatment trains employing ozonation of secondary or tertiary wastewater effluents, but two treatment trains with chlorination or UV disinfection of tertiary wastewater effluent and another with full advanced treatment (i.e., reverse osmosis and advanced oxidation) were also included for comparison. *N*-nitrosodimethylamine (NDMA) and *N*-nitrosomorpholine (NMOR) were the most prevalent nitrosamines in untreated (up to 89 ng/L and 67 ng/L, respectively) and treated wastewater. *N*-nitrosomethylethylamine (NMEA) and *N*-nitrosodiethylamine (NDEA) were detected at one facility each, while *N*-nitrosodipropylamine (NDPrA) and *N*-nitrosodibutylamine (NDBA) were less than their method reporting limits (MRLs) in all samples. Ozone-induced NDMA formation ranging

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Abbreviations: AFU, arbitrary fluorescence unit; AMU, atomic mass unit; AOP, advanced oxidation process; ASPE, automated solid phase extraction; BAC, biological activated carbon; BOD, biochemical oxygen demand; BPR, biological phosphorus removal; CA, California; CAS, conventional activated sludge; CCL3, Contaminant Candidate List 3; CDPH, California Department of Public Health; CEC, contaminant of emerging concern; DN, denitrification; DOC, dissolved organic carbon; DWEL, drinking water equivalent level; EBCT, empty bed contact time; EEM, excitation emission matrix; EfOM, effluent organic matter; EPA, Environmental Protection Agency; GA, Georgia; GF, gravity filtration; IRIS, Integrated Risk Information System; KY, Kentucky; MBR, membrane bioreactor; MDL, method detection limit; MF, microfiltration; MO, Missouri; MRL, method reporting limit; N, nitrification; N/A, not available or not applicable; NDBA, *N*-nitrosodibutylamine; NDEA, *N*-nitrosodiethylamine; NDMA, *N*-nitrosodimethylamine; NDPhA, *N*-nitrosodiphenylamine; NDPrA, *N*-nitrosodipropylamine; NMEA, *N*-nitrosomethylethylamine; NMOR, *N*-nitrosomorpholine; NPIP, *N*-nitrosopiperidine; NPYR, *N*-nitrosopyrrolidine; NV, Nevada; OD, oxidation ditch; PAC, powdered activated carbon; QLD, Queensland; RO, reverse osmosis; RSD, relative standard deviation; SRT, solids retention time; SUVA, specific UV_{254} absorbance; TOC, total organic carbon; TX, Texas; UDMH, unsymmetrical dimethylhydrazine; UF, ultrafiltration; U.S., United States; UV, ultraviolet.

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from <10 to 143 ng/L was observed at all but one site, but the reasons for the variation in formation remain unclear. Activated sludge, biological activated carbon (BAC), and UV photolysis were effective for NDMA mitigation. NMOR was also removed with activated sludge but did not form during ozonation.

1. Introduction

Nitrosamines are disinfection byproducts commonly associated with chloramination (Choi and Valentine, 2002; Mitch et al., 2003a, 2005; Krasner et al., 2013), but recent studies indicate that ozone-induced formation of *N*-nitrosodimethylamine (NDMA) is also a potential problem (Andrzejewski et al., 2008; Oya et al., 2008; Schmidt and Brauch, 2008; Hollender et al., 2009; Kosaka et al., 2009; Yang et al., 2009; Yoon et al., 2011; von Gunten et al., 2010; Nawrocki and Andrzejewski, 2011; Pisarenko et al., 2012; Gerrity et al., 2014). NDMA is also a byproduct of the rubber, dye, tanning, and pesticide industries, and it has been found in groundwater near sites that produce rocket fuel containing unsymmetrical dimethylhydrazine (UDMH) (Mitch et al., 2003b).

In contrast with many contaminants of emerging concern (CECs) (Bull et al., 2011), nitrosamines are relevant to public health even at the ng/L level. For example, the United States (U.S.) Environmental Protection Agency's (EPA) Integrated Risk Information System (IRIS) indicates that NDMA is a probable human carcinogen with an oral slope factor of 51 $(mg/kg\text{-}d)^{-1}$ (EPA, 2012). This corresponds to a drinking water equivalent level (DWEL) of 0.69 ng/L based on an acceptable lifetime risk of 10^{-6}, a body weight of 70 kg, and a drinking water consumption rate of 2 L/d. Other nitrosamines, including *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodipropylamine (NDPrA), *N*-nitrosodibutylamine (NDBA), and *N*-nitrosopyrrolidine (NPYR), have DWELs below 20 ng/L, and the DWEL for *N*-nitrosodiethylamine (NDEA) is even lower than that of NDMA at 0.23 ng/L (EPA, 2012).

These low public health thresholds are particularly problematic for potable reuse systems due to the prevalence of nitrosamines and their precursors in wastewater. In fact, nitrosamines are a significant driver in treatment train selection for potable reuse systems throughout the world (Gerrity et al., 2013, 2014). Nitrosamines are not yet regulated at the federal level in the United States (U.S.), but NDMA, NDEA, NDPrA, NPYR, and *N*-nitrosodiphenylamine (NDPhA) are all listed on the U.S. EPA's Contaminant Candidate List 3 (CCL3) (EPA, 2009). At the state level, the California Department of Public Health (CDPH) has established drinking water notification levels of 10 ng/L for NDMA, NDEA, and NDPrA (CDPH, 2010). The Australian Drinking Water Guidelines specify a value of 100 ng/L for NDMA (NHMRC, 2011), and the Australian Guidelines for Water Recycling specify a more stringent target of 10 ng/L for NDMA and NDEA (EPHC, 2008). Canada has also established a 40 ng/L maximum acceptable concentration for NDMA (Health Canada, 2011). These regulatory agencies face the predicament of balancing public health goals, the industry's current analytical capabilities, and practical limits of treatability. The method reporting limits (MRLs) for NDMA and NDEA exceed their corresponding DWELs, and the MRLs for other nitrosamines provide insufficient sensitivity to allow for lower guidelines or regulatory limits (EPA, 2004; Holady et al., 2012).

The characteristics of nitrosamines also make them a significant environmental and engineering concern. Studies indicate that NDMA is miscible with water and has low sorption potential (Kommineni et al., 2003). This makes NDMA very mobile in the environment and problematic for groundwater replenishment applications. NDMA is also highly resistant to oxidation (Pisarenko et al., 2012) due to its low concentration and relatively low second order rate constants with ozone ($5.3 \times 10^{-2}\ M^{-1}\ s^{-1}$; Lee et al., 2007) and short-lived hydroxyl radicals ($4.6 \times 10^{8}\ M^{-1}\ s^{-1}$; Lee et al., 2007) This recalcitrance is exacerbated by direct formation when ozone reacts with NDMA precursors present in some wastewater matrices. NDMA mitigation is typically achieved with biodegradation (Sharp et al., 2005, 2010; Krauss et al., 2010), reverse osmosis (RO) (Plumlee et al., 2008), or ultraviolet (UV) photolysis (Bolton et al., 2002; Sharpless and Linden, 2003; Lee et al., 2005a, 2005b), although the required UV doses (i.e., generally >100 mJ/cm^2) can be cost prohibitive.

Recent risk assessments indicate that ‘planned’ potable reuse can be more protective of public health than ‘unplanned’ indirect potable reuse or conventional drinking water systems (NRC, 2012). However, pervasive uncertainty in the industry is potentially leading to the overdesign of advanced treatment facilities for potable reuse (Gerrity et al., 2013). A majority of the recently constructed potable reuse facilities employ “full advanced treatment” (CDPH, 2013), which includes RO and an advanced oxidation process (AOP). These systems typically include microfiltration (MF) for pretreatment, chloramination to control biological fouling, and UV/H_2O_2 as the preferred AOP due to the formation of NDMA during chloramination. Treatment trains employing ozone and biological activated carbon (BAC) offer a more sustainable alternative in terms of economic costs and energy consumption (Gerrity et al., 2014), and they are also capable of achieving similar water quality objectives, including CEC mitigation and pathogen inactivation (Reungoat et al., 2010; Gerrity et al., 2011; Reungoat et al., 2012; Gerrity et al., 2014). The combination of ozone and biological sand filtration has also been studied in Europe with respect to CEC mitigation and toxicity (Hollender et al., 2009; Stalter et al., 2010a, b). Several ozone-based potable reuse treatment trains have been operating in the U.S. for years with no documented adverse public health impacts.