WATER RESEARCH 42 (2008) 347–355

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N-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC–MS/MS

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ARTICLE INFO

Article history:
Received 30 January 2007
Received in revised form
27 June 2007
Accepted 18 July 2007
Available online 26 July 2007

Keywords:
Nitrosamines
NDMA
LC–MS/MS
Reverse osmosis
Advanced treatment

ABSTRACT

N-nitrosodimethylamine (NDMA) is a probable human carcinogen found in ng/l concentrations in chlorinated and chloraminated water. A method was developed for the determination of ng/l levels of NDMA using liquid chromatography–tandem mass spectrometry (LC–MS/MS) preceded by sample concentration via solid-phase extraction with activated charcoal. Recoveries were greater than 90% and allowed a method reporting limit as low as 2 ng/l. Using this method, the removal of NDMA was determined for the Interim Water Purification Facility (IWPF), an advanced wastewater treatment facility operated by the Orange County Water District (OCWD) in Southern California. The facility treats effluent from an activated sludge treatment plant with microfiltration (MF), reverse osmosis (RO), and an ultraviolet-hydrogen peroxide advanced oxidation process (UV-AOP). Six nitrosamines were surveyed: NDMA, N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), N-nitrosopiperidine (NPip), and N-nitrosopyrrolidine (NPyr). Only NDMA was detected and at all treatment steps in the IWPF, with influent concentrations ranging from 20 to 59 ng/l. Removals for RO and UV ranged from 24% to 56% and 43% to 66%, respectively. Overall, 69 ± 7% of the original NDMA concentration was removed from the product water across the advanced treatment process and, in combination with blending, the final concentration did not exceed the California drinking water notification level of 10 ng/l. NDMA removal data are consistent with findings reviewed for other advanced treatment facilities and laboratory studies.

1. Introduction

N-nitrosodimethylamine (NDMA) is one of several N-nitrosamines classified as probable human carcinogens by the US Environmental Protection Agency (US EPA, 1993). NDMA received much attention as a potential drinking water contaminant after its 1998 detection in California drinking water wells (up to 3 μg/l) due to contamination from unsymmetrical dimethylhydrazine (UDMH)-based rocket fuel. Subsequent monitoring led to the discovery that NDMA was also a disinfection byproduct arising from the chlorination and chloramination of drinking water and wastewater (CA DHS, 2006). More potent than the trihalomethanes, NDMA concentrations of 20–100 ng/l typically result from the chlorination of wastewater effluent (Mitch et al., 2003). In 2002, the California Department of Health Services established a 10 ng/l

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doi:10.1016/j.watres.2007.07.022

notification level (action level) in drinking water (CA DHS, 2006).

The indirect reuse of highly treated municipal wastewater is being increasingly considered as an alternative water source for domestic and ecological applications. Consequently, the performance of secondary and advanced water treatment schemes with regard to their mitigation of potential contaminants like NDMA is an area of active research. In addition to NDMA, the EPA has listed five other nitrosamines on the Unregulated Contaminant Monitoring Rule 2 (UCMR 2) to be monitored from 2008 to 2010 (US EPA, 2006). These probable human carcinogens have been found in soil, air, plants, food, and water (Fine et al., 1977; US EPA, 2007).

A recent study found that secondary wastewater treatment achieves variable NDMA removals ranging from 0% to 75% (Sedlak et al., 2005); consequently, NDMA must be mitigated at the source or during advanced treatment. While reverse osmosis (RO) has been found to significantly remove salts, emerging contaminants (>99% for pharmaceuticals), and other compounds (Reinhard et al., 1986; Reinhard et al., 2003), the rejection of NDMA by RO is relatively low (Mitch et al., 2003), necessitating additional removal technologies such as UV treatment to meet regulatory limits. UV irradiation is the most commonly applied treatment for NDMA and has been used for drinking water, wastewater, and industrial effluents. However, it is estimated that the dose required for an order of magnitude reduction in NDMA is 10 times that for equivalent virus removal in a drinking water system, highlighting the expense of such an approach for adequate treatment (Mitch et al., 2003). While a variety of UV photolysis studies under different laboratory conditions show NDMA half-lives on the order of minutes (Ho et al., 1996; Stefan and Bolton, 2002; Sharpless and Linden, 2003), there are fewer reports for online UV treatment systems, in which other factors like path length, lamp choice, and light screening may play a role (Sharpless and Linden, 2003). In one such report from an Ohsweken drinking water plant in Ontario, Canada, NDMA was discovered in the water above the Ontario limit of 9 ng/l. Laboratory, pilot tests, and finally full-scale implementation of UV irradiation removed NDMA to below detectable levels (Jobb et al., 1994).

For the detection of NDMA in wastewater and drinking water, some existing methods are based on continuous liquid–liquid extraction followed by gas chromatography (Raksit and Johri, 2001; Mitch et al., 2003; Richardson, 2003). These methods are labor intensive, require large volumes of toxic solvents, and achieve low recoveries. Grebel et al. (2006) recently developed a solid-phase microextraction method for NDMA and other nitrosamines, which requires a conveniently short analysis time but does not achieve detection limits in the 1–10 ng/l range required for drinking water. While some methods utilizing solid-phase extraction (SPE) have achieved recoveries of only 30–60% (Mitch et al., 2003), other techniques show >80% recovery and generally rely on gas chromatography coupled to mass spectrometry (GC–MS) (Ontario Ministry of the Environment, 2003; Charrois et al., 2004) or tandem mass spectrometry (GC–MS/MS) (Munch and Bassett, 2004). Recently, Zhao et al. (2006) developed a method for nitrosamine analysis using liquid chromatography–tandem mass spectrometry (LC–MS/MS), also coupled to SPE for sample concentration.

The objectives of the present study were to assess NDMA removal efficiencies during microfiltration (MF), RO, and UV treatment at an advanced wastewater treatment facility, and to develop a simple SPE–LC–MS/MS technique for analysis of NDMA and other nitrosamines given in Table 1. The method combines the extraction efficiency of SPE with the convenience and selectivity of LC–MS/MS detection. The selectivity of the technique is due to the detection of multiple specific mass spectral fragmentations ("transitions") (Budde, 2001). Findings are compared to literature reports of both laboratory and treatment plant data in an effort to provide a useful summary of NDMA removal via advanced wastewater treatment processes, with particular emphasis on rejection data for RO.

2. Experimental

2.1. Materials

Chemicals, sources, and purities were as follows: methanol and acetonitrile, HPLC grade from Fisher Scientific (Fair Lawn, NJ, USA); acetone UltimAR from Mallinckrodt Chemicals (Phillipsburg, NJ, USA); neutralized activated charcoal from Sigma (St. Louis, MO, USA); NDMA, *N*-nitrosopiperidine (NPip), *N*-nitrosodiethylamine (NDEA), and *N*-nitrosodi-*n*-propylamine (NDPA) from Supelco (Bellefonte, PA, USA); *N*-nitrosomethylethylamine (NMEA) and *N*-nitrosodi-*n*-butylamine (NDBA) from Ultra Scientific (North Kingstown, RI, USA); *N*-nitrosopyrrolidine (NPyr) from Aldrich (St. Louis, MO, USA), and NDMA-d6 99.8% from CDN isotopes (Pointe-Claire, Canada). Glass fiber filters were obtained from Whatman (Florham Park, NJ, USA). Teflon 1/8″ tubing, weights, tube adaptors, and a 16-port vacuum manifold for performing SPE sample loading were purchased from Supelco. Extract-Clean SPE 8 ml cartridges, frits, and syringe adapters (for connecting SPE cartridges in-series) and the SPE vacuum manifold were purchased from Alltech (Deerfield, IL, USA). Strata Phenyl SPE cartridges were from Phenomenex (Torrance, CA, USA). Milli-Q water was generated using a Synergy 185 Millipore with Simpak2 purifying system (Billerica, MA, USA).

2.2. Site description and sample collection

Water samples were obtained from different stages throughout the IWPF (Fig. 1), also known as Interim Water Factory 21, a now-decommissioned advanced wastewater treatment plant operated by the OCWD in Southern California. This facility reclaimed effluent from the Orange County Sanitation District (OCSD) secondary sludge plant to potable standards for injection into a coastal aquifer as a hydraulic seawater barrier. Advanced treatment at the IWPF included the following: disinfection by chlorination, MF (Siemens), RO (Hydranautics ESPA2 composite polyamide membranes), and an ultraviolet-hydrogen peroxide advanced oxidation (UV-AOP; Trojan Technologies UVPhox) system of six reactors each equipped with 72 low-pressure, high-intensity UV