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Fate of NDMA precursors through an MBR-NF pilot plant for urban wastewater reclamation and the effect of changing aeration conditions

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ABSTRACT

The removal of *N*-nitrosodimethylamine (NDMA) formation potential through a membrane bioreactor (MBR) coupled to a nanofiltration (NF) pilot plant that treats urban wastewater is investigated. The results are compared to the fate of the individual NDMA precursors detected: azithromycin, citalopram, erythromycin, clarithromycin, ranitidine, venlafaxine and its metabolite o-desmethylvenlafaxine. Specifically, the effect of dissolved oxygen in the aerobic chamber of the MBR pilot plant on the removal of NDMA formation potential (FP) and individual precursors is studied.

During normal aerobic operation, implying a fully nitrifying system, the MBR was able to reduce NDMA precursors above 94%, however this removal percentage was reduced to values as low as 72% when changing the conditions to minimize nitrification. Removal decreased also for azithromycin (68–59%), citalopram (31–17%), venlafaxine (35–15%) and erythromycin (61–16%) on average during nitrifying *versus* non-nitrifying conditions. The removal of clarithromycin, o-desmethylvenlafaxine and ranitidine could not be correlated with the nitrification inhibition, as it varied greatly during the experiment time. The MBR pilot plant is coupled to a nanofiltration (NF) system and the results on the rejection of both, NDMA FP and individual precursors, through this system was above 90%.

Finally, results obtained for the MBR pilot plant are compared to the percentage of removal by a conventional full scale biological wastewater treatment plant (WWTP) fed with the same influent. During aerobic operation, the removal of NDMA FP by the MBR pilot plant was similar to the full scale WWTP.

1. Introduction

N-nitrosodimethylamine (NDMA) is a disinfection byproduct (DBP) classified as "2B carcinogen - reasonably anticipated to be a human carcinogen" by the United States Environmental Protection Agency (EPA, 2014). It is believed that precursors of NDMA are largely anthropogenic in origin, in contrast to other conventional DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs), where natural organic matter is the main precursor pool (Bond et al., 2011). Therefore, the formation of NDMA is highly relevant to water reclamation or drinking water supplies impacted by wastewater (Schreiber and Mitch, 2006; Zeng et al., 2016).

While THM and HAA precursors are difficult to characterize as different fractions of natural organic matter may generate these DBPs upon disinfection, some particular NDMA precursors might be easier to monitor because, according to the published literature, nitrosamine precursors have a functional group that can release a secondary amine (Choi and Valentine, 2003; Dotson et al., 2009; Krauss et al., 2010; Mitch and Sedlak, 2002). The majority of studies of NDMA formation have concentrated on dimethylamine (DMA) as a precursor, a compound present in human urine and faeces, as well as being a common product of the chemical industry (Krauss et al., 2010; Zeng and Mitch, 2015). However, the conversion of DMA to NDMA by monochloramination is rather inefficient,

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with yields of 0.5% (Sacher et al., 2008). Recent studies focused on the yield of NDMA formed from other individual compounds, including pharmaceuticals (Shen and Andrews, 2011), pesticides (Chen and Young, 2008), cationic polymers and ion exchange resins employed during water treatment (Kohut and Andrews, 2003) as well as other quaternary amines that are used in toiletries (Kemper et al., 2010). Although some precursors may have up to a ~90% molar yield (e.g., tertiary amines containing a β-aromatic ring such as ranitidine) most of them have low molar yields (e.g., ~2%) (Shen and Andrews, 2011). Unfortunately, specific watershed-associated precursors responsible for significant NDMA formation have not yet been identified (Krasner et al., 2013; Shah et al., 2012).

Population increase, particularly in cities, and scarce water resources have raised the demand for use of highly treated municipal wastewater as a supplemental source of potable water. Studying the fate of DBP precursors during secondary effluent treatment is of importance as an increasing number of municipal wastewater treatment plants (WWTPs) are engaged in the practice of potable reuse of treated wastewaters worldwide. NDMA formation in wastewater effluents can vary greatly. As an example, high variability in NDMA concentration and its precursors were reported in the secondary effluent of 7 different WWTPs in U.S.A by Sedlak et al. (2005) with values of up to 29,000 ng/L. On the other hand, Farré et al. (2011a) found concentrations of NDMA precursors between 350 and 1000 ng/L in secondary effluents of 6 WWTPs in South East Queensland (Australia).

Generally, removal of precursors can be achieved easier than the removal of NDMA itself. Previous work has investigated the fate of NDMA precursors through different barriers used for water reclamation such as microfiltration followed by reverse osmosis (Farré et al., 2011a; Fujioka et al., 2013; Sato et al., 2014; Sgroi et al., 2015) and ozone followed by biological carbon filtration (Farré et al., 2011b; Gerrity et al., 2014). Membrane bioreactors (MBR), which combine biological-activated sludge process and membrane filtration, have become more popular in recent years for the treatment of wastewaters, particularly when the conventional activated sludge (CAS) process cannot cope with either composition of wastewater or fluctuations of wastewater flow rate. MBR technology is also used in cases where demand on the quality of effluent exceeds the capability of CAS. Many reports have focused on the removal of pharmaceuticals by MBR (Kimura et al., 2005; Radjenović et al., 2009; Reif et al., 2008). Also, several studies reported that nitrifying conditions in the activated sludge system were responsible for the elimination of pharmaceuticals in wastewater (Batt et al., 2006; Tran et al., 2009), hence it could be hypothesized that this same microbial population would be more effective in removing NDMA formation potential too. In fact, recently, Sgroi and co-authors (2016) observed that NDMA formation upon ozonation during water reclamation was lower in effluents treated for nitrogen removal and by extended biological oxidation. Therefore, they conclude that a complete biological nitrification was a strategic and essential treatment to reduce NDMA formation. Also, several studies (Dytczak et al., 2008; Phan et al., 2014) have investigated the impact of dissolved oxygen (DO) concentration and/or oxidation reduction potential (ORP) conditions on trace organic contaminants. However, a clear consensus has not been reached to date and a focused study that investigates specifically the removal of NDMA formation potential through MBR is still missing in the literature.

This work investigates the removal of NDMA formation potential (FP) as well as individual NDMA precursors by an MBR pilot plant that treats urban wastewater. Specifically, this paper explores how changes of the nitrification performance of the MBR, modified by changing the DO concentration in the aerobic compartment, affect the removal of NDMA formation potential and individual NDMA precursors. The individual precursors investigated include antibiotics and other micropollutants that contain the dimethylamine-moiety responsible for NDMA formation. In particular, we have measured the occurrence and fate of the following compounds: azithromycin, citalopram, clarithromycin, erythromycin, ranitidine, chlorotetracycline, doxycycline, oxytetracycline, roxithromycin, spiramycin, tetracycline, tylosin, and finally venlafaxine and its metabolite o-desmethylvenlafaxine.

Additionally, the investigated MBR effluent is also treated by a nanofiltration (NF) system for water reclamation. Hence, the study also presents the rejection of these individual NDMA precursors by a NF membrane and compares them with up-to-date published literature.

Finally, the effluent from the full scale WWTP, where the MBR pilot plant was located, was also evaluated for NDMA FP and individual precursors and compared to the MBR pilot plant effluent.

2. Methodology

2.1. Chemicals

All chemicals used for the analysis were of analytical grade and commercially available. NDMA (5000 μg/mL in methanol) had a purity of >99.9% and was obtained from Supelco. Deuterated d_6-NDMA was used as internal standard, (Sigma-Aldrich). For the NDMA formation potential test, ammonium chloride (>99.5%, Sigma-Aldrich), sodium hydroxide (ACS, ISO, Reag, Sharlau) and sodium hypochlorite solution (reagent grade, available chlorine ≥4%, Sigma-Aldrich) were used. Potassium dihydrogenphosphate (KH_2PO_4, >99%, Sigma) and disodiumhydrogenphosphate ($Na_2HPO_4 \cdot 2H_2O$, >99%, Sigma) were used to prepare pH buffer solutions. To quench the chloramines, sodium sulphite (>98%, Sigma) was employed. Commercial DPD (*N*,*N*-diethyl-*p*-phenylenediamine) test kits (LCK310, Hach Lange) were used for the analysis of free and total chlorine using a Hach DR2800 spectrophotometer. For solid phase microextraction (SPME), sodium chloride (ACS, ISO, Reag, Sharlau) was used. SPME fibers from Supelco (85 μm CAR/PDMS, Stableflex, 24Ga) were employed.

All individual NDMA precursor standards were of high purity grade (>90%). Venlafaxine, azithromycin, clarithromycin, roxithromycin, spiramycin, ranitidine, tetracycline, oxytetracycline, erythromycin and chlorotetracycline were purchased from Sigma-Aldrich as hydrochloride salts. Doxycycline and tylosin were acquired as hyclate and tartar salt, respectively. Citalopram was obtained as hydrobromide salt. O-desmethylvenlafaxine was purchased from Toronto Research Chemicals. Isotopically labeled compounds, used as internal standards, were venlafaxine-d_6, erythromycin-*N*,*N*-dimethyl-^{13}C, purchased from Sigma–Aldrich. Azithromycin-d_3 and tetracycline-d_6 were purchased from Toronto Research Chemicals. Cimetidine-d_3 and citalopram-d_4 (as hydrobromide) were purchased from CDN isotopes. These internal standards were chosen according to previously published methodologies (Gros et al., 2012, 2013). Both individual stock standard and isotopically labeled internal standard solutions were prepared in methanol at a concentration of 1000 mg/L. After preparation, standards were stored at −20 °C. Special precautions have to be taken for tetracycline and tetracycline-d_6, which have to be stored in the dark, since it has been demonstrated that tetracycline antibiotics are photolabile (Eichhorn and Aga, 2004). Fresh stock antibiotic solutions were prepared monthly due to their limited stability. Stock solutions for the rest of substances were renewed every six months. Working standard solutions, containing all pharmaceuticals, were also prepared in water and were renewed before each analytical run by mixing appropriate amounts of the intermediate solutions. Separate mixtures of isotopically labeled