

Supporting Information

N-Nitrosodimethylamine Formation upon Ozonation and Identification of Precursors Source in a Municipal Wastewater Treatment Plant

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Text (4)

Figure (6)

Text S1. Materials. All purchased solvents (methanol, methylene chloride) were HPLC grade or superior, obtained from Fisher Scientific and used without further purification. Tert-Butyl alcohol (TBA) (ACS reagent grade, Sigma-Aldrich) was used as $\cdot\text{OH}$ radicals scavenger. Potassium indigotrisulfonate, N,N-dimethylformamide, dimethylamine hydrochloride, sodium hydroxide, sodium phosphate monobasic monohydrate, sodium phosphate dibasic heptahydrate, phosphoric acid (ACS reagent grade, ≥ 85 wt. % in H_2O) and hydrogen peroxide (50 wt. % in H_2O) were purchased at $>98\%$ purity from Sigma-Aldrich. Sodium sulfate anhydrous (Granular, ACS reagent grade), hydrochloric acid, ammonium chloride and sodium thiosulfate crystalline ($> 99\%$ purity) were obtained from Fisher Scientific. 1000 mg/L Br^- in water, prepared with high purity NaBr and water was purchased from Sigma-Aldrich. N-Nitrosodimethylamine (*d6*, 98%) from Cambridge Isotope Laboratories (Andover, MA) was used as a surrogate, N-Nitroso-Di-N-Propylamine (*d14*, 98%) from Cambridge Isotope Laboratories (Andover, MA) was used as an internal standard, and nitrosamine mix from Supelco (Bellafonte, PA) was used as the standard for NDMA analysis. Whatman (Clifton, NJ) glass microfiber filters grade GF/F (0.7 μm pore size) were used for filtering.

Text S2. Wastewater treatment plant. The investigated wastewater treatment plant (WWTP) serves about four million people and treats wastewater characterized by about 90% from domestic discharges. Industrial sources are few and include textile factories and carpet dye operations. The unchlorinated final effluent is in part discharged to the ocean and in part sent to a down-

stream wastewater reclamation plant (WWRP) that through advanced technologies is able to produce water of quality necessary for indirect potable reuse. The plant scheme consists of preliminary treatments, primary sedimentation and secondary treatment where high-purity-oxygen is directly bubbled into the activated sludge reactor having a sludge retention time of 1.5 days (Figure S1). Sludge from the secondary treatment is transferred to the waste activated sludge (WAS) thickening centrifuges. Primary sludge (PS) and thickened WAS (TWAS) are pumped together to the anaerobic digesters operating under thermophilic condition at about 53°C with direct steam injection for stabilization and solids reduction and with a sludge retention time of about 15 days. Finally, the digested sludge is pumped to the dewatering centrifuges. Supernatant from dewatering centrifuges and WAS thickening centrifuges are sent back to the head of the plant. Dewatered biosolids are trucked offsite for use through a diversified management plan utilizing 100% beneficial use. The cationic polymer Mannich is used as a chemical conditioning agent for WAS thickening centrifuges and digested sludge dewatering. The daily usage is approximately 757 cubic meters of diluted polymer with 0.22% of active ingredient (3% is the active ingredient percentage in the undiluted polymer emulsion). An anionic polyacrylamide polymer is used in primary treatment to aid coagulation. The daily usage is 280 cubic meters of 3% active ingredient solution, diluted to 0.03% before injection.

Text S3. Ozonation. Ozone gas generated from pure oxygen using an ozone generator (Wedeco, Modular 4 HC series, Herford, Germany) was introduced into a glass reaction vessel containing the sample by a ceramic diffuser. Mixing was accomplished by a magnetic stirrer. The ozonation conditions were as follows: sample volume, 1 L; ozone concentration in feed gas, 12 mg/L; ozone gas flow rate, 1 L/min; temperature, 20 °C. Two glass reaction vessels were set in parallel, one was filled with sample and the other one with DI water. Initially, ozone gas was bubbled into

the glass jar with DI water in order to set the desired ozonation condition, then the ozone feed gas was deviated to the jar containing the sample by a switch valve. Ozone feed gas concentration and ozone off-gas concentration were measured by two pressure and temperature compensated ozone analyzers with UV quartz cells. The scheme of the utilized ozone system is shown in Figure S2. Over the whole experiments, ozone concentration data of the feed gas and off gas were recorded every 30 seconds by a data logger and the applied ozone dose was calculated by mass balance (eq. 1):

$$\text{ozone dose} = \frac{Q_{gas} \cdot t \cdot (\beta_{feed\ gas} - \beta_{off\ gas})}{V} \quad (1)$$

where Q_{gas} is the gas flow, t is the time, $\beta_{feed\ gas}$ and $\beta_{off\ gas}$ are the ozone concentration in the feed gas and in the off gas, respectively, and V is the sample volume. The total applied ozone dose was calculated in a cumulative way summing the doses transferred in each 30 seconds interval.

Text S4. Analytical Methods. The NDMA extraction was performed using a modified version of EPA Method 521¹. Briefly, analytes and the surrogate analyte were extracted by passing a 0.5-L water sample through a solid phase extraction (SPE) cartridge containing 2 g of 80-120 mesh coconut charcoal (UCT Enviroclean 521). The organic compounds were eluted from the solid phase with 12 mL of methylene chloride. Residual water was removed from the extracts by passing through five grams anhydrous sodium sulfate. Eluent was then concentrated under a gentle stream of nitrogen to 1.0 ml and the internal standard was added. Analysis of NDMA was performed on an Agilent 7000 Triple Quadrupole GC/MS-MS. The sample components were separated, identified, and measured by injecting 5 μ L of the concentrated extract onto the fused silica capillary column of the GC/MS-MS system equipped with Gerstel autosampler, and operated in the chemical ionization (CI) mode with ammonia as the reagent gas. Identification and quantita-

tion were performed in the MS-MS mode with a resulting method reporting limit in ultrapure water of less than 1 ng/L.

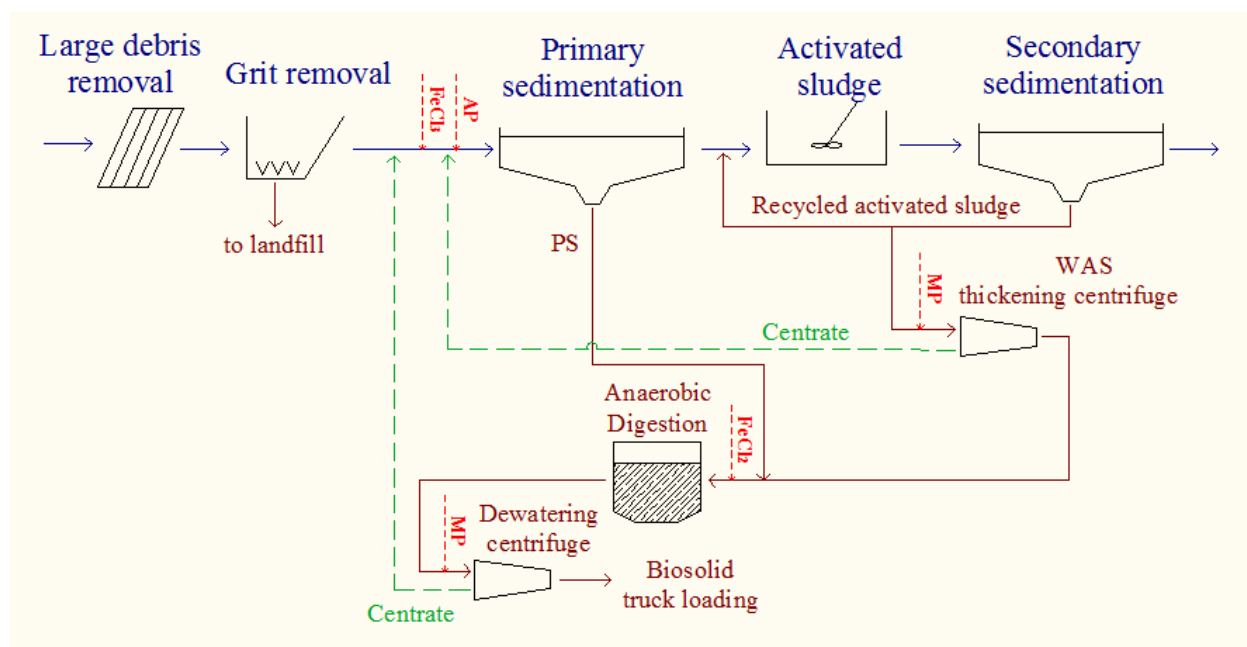


Figure S1. Scheme of the investigated WWTP. MP, Mannich polymer; AP, anionic polymer; FeCl_2 , Ferrous chloride; FeCl_3 , Ferric chloride; PS, primary sludge; WAS, waste activated sludge

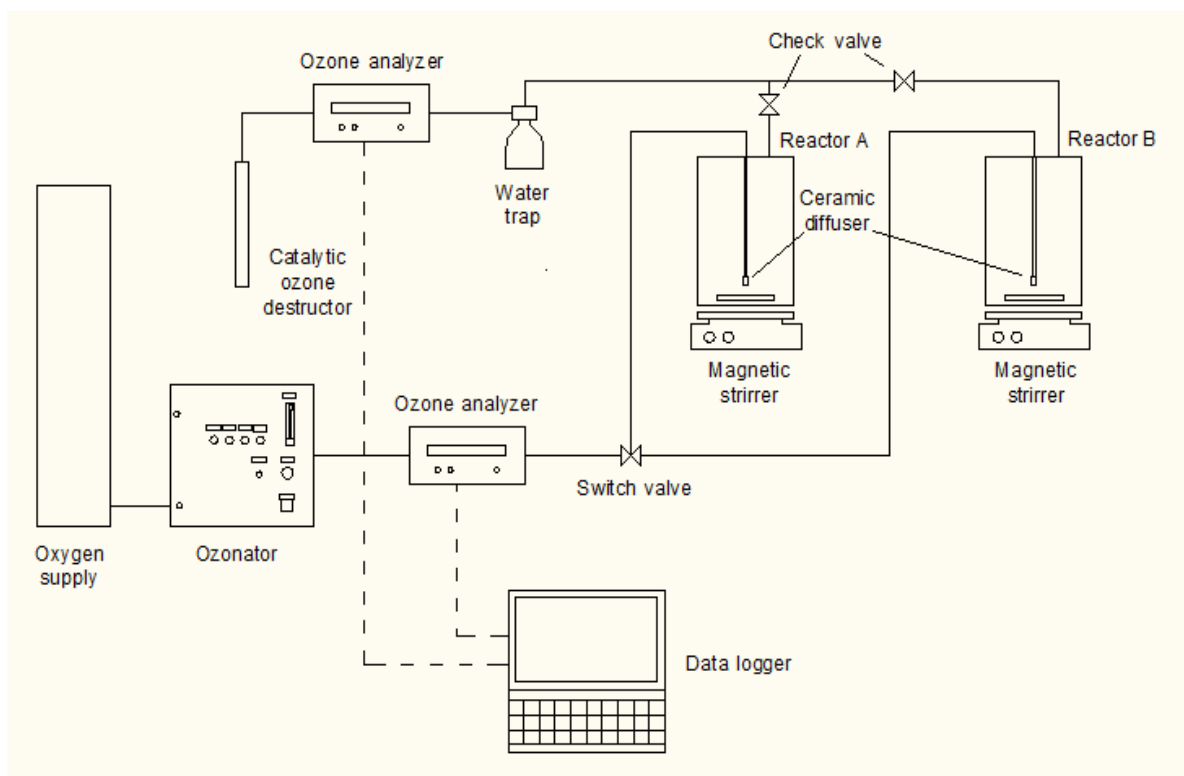


Figure S2. Lab-scale apparatus used for semi-batch ozonation

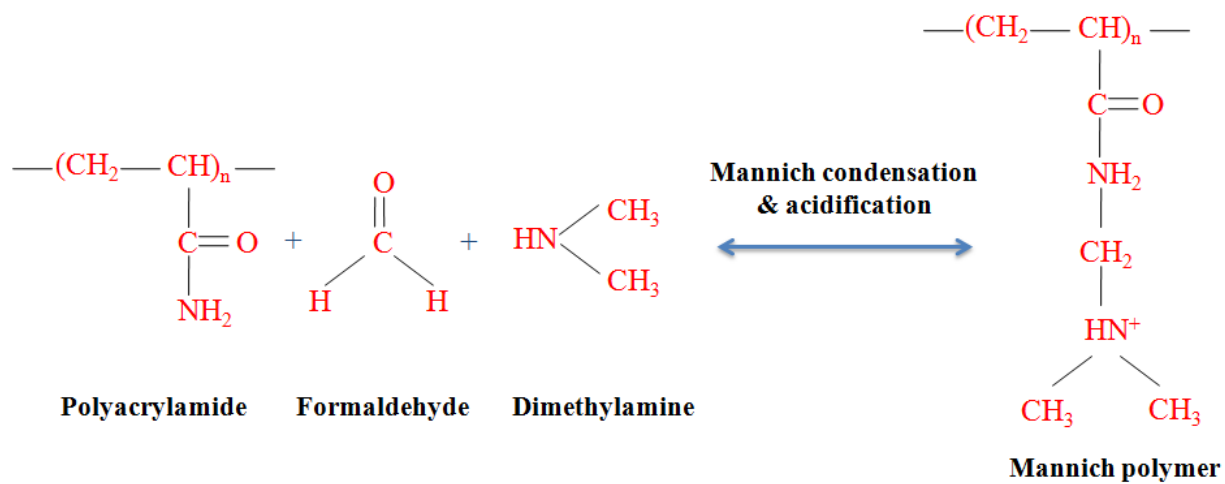


Figure S3. Synthesis of Mannich polymer

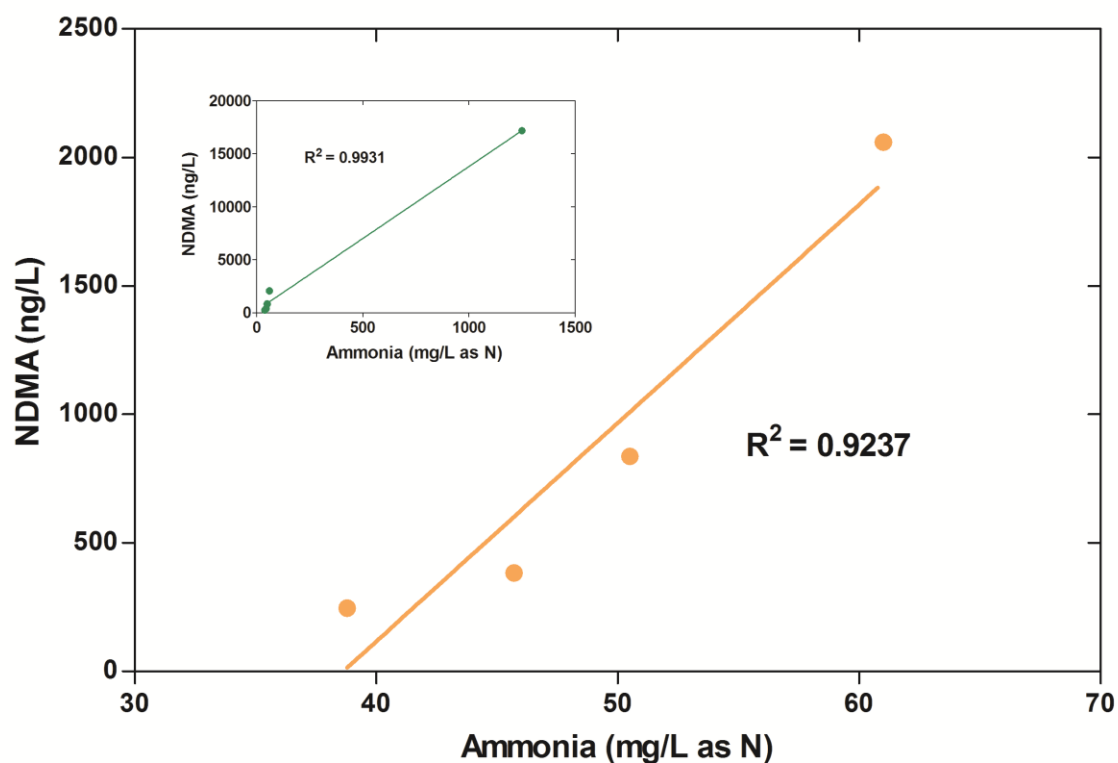


Figure S4. Correlation between NDMA formation by ozonation and ammonia concentration in primary influent, primary effluent, secondary effluent and WAS thickening recycle stream at the studied WWTP. Inset shows the correlation obtained by also including the data from the dewatering centrate sample (though biased by very high concentration of ammonia).

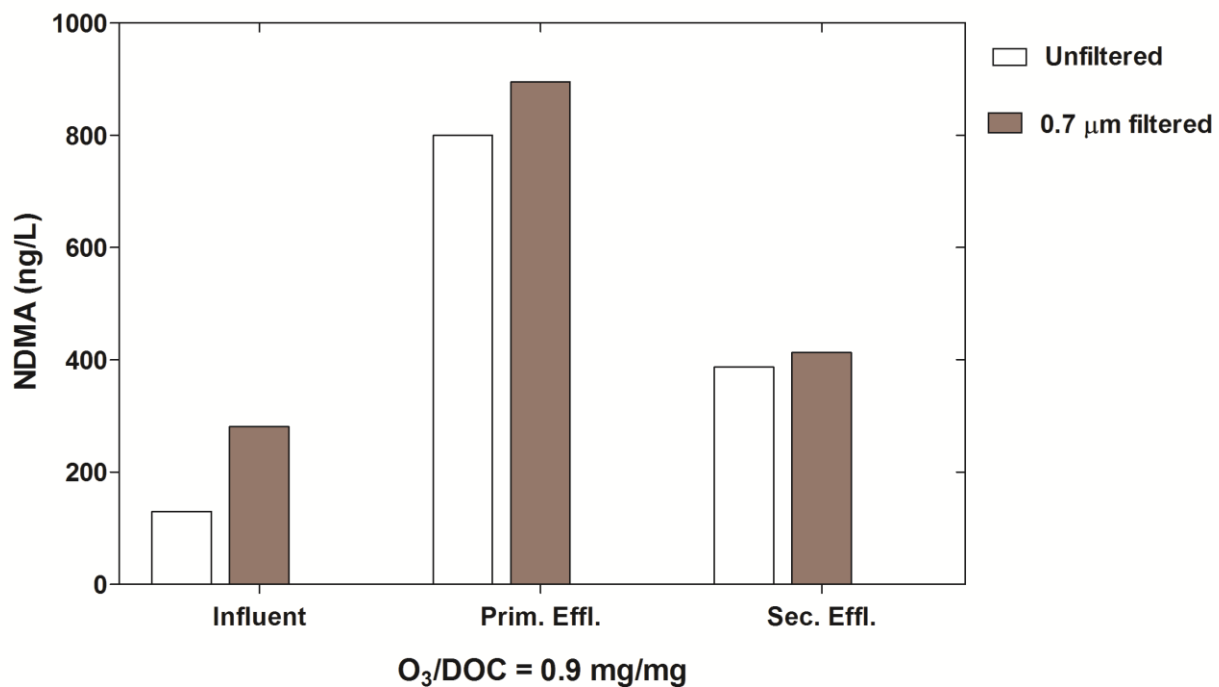


Figure S5. NDMA formation upon ozonation of 0.7 µm filtered and unfiltered samples. Influent, primary influent; Prim. Effl., primary effluent; Sec. Effl., secondary effluent. Average of triplicate analysis is reported for filtered samples. Ozone doses were normalized to the dissolved organic carbon concentration (O₃/DOC)

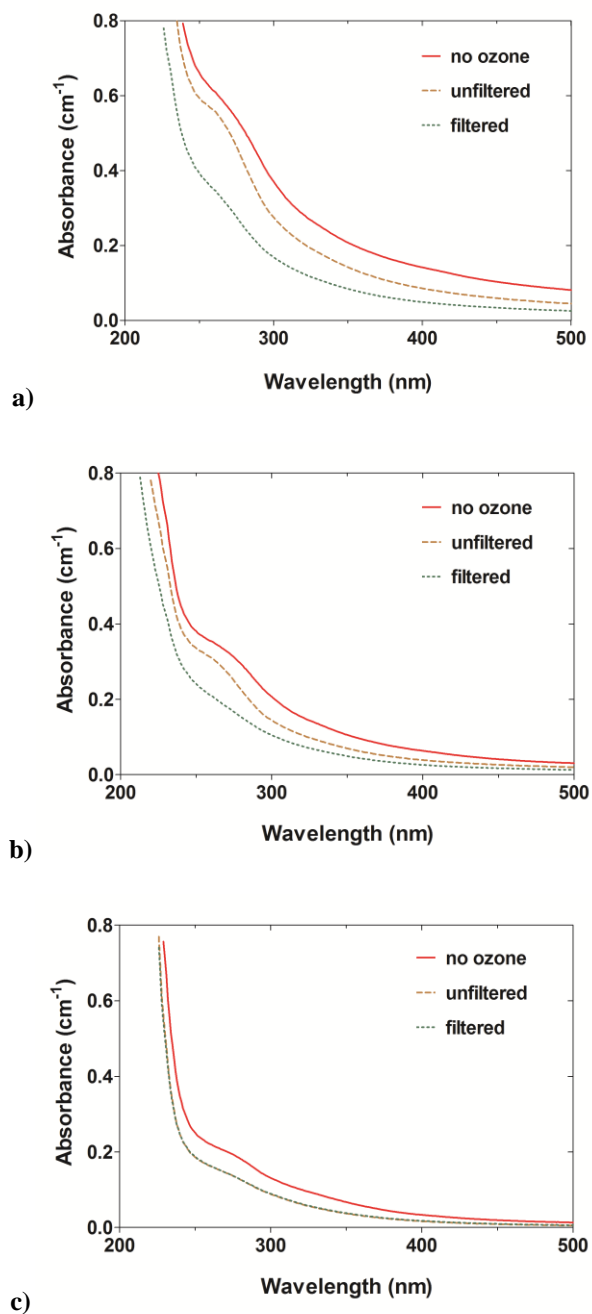


Figure S6. UV absorbance spectra of (a) primary influent, (b) primary effluent and (c) secondary effluent at the investigated WWTP. No ozone, no ozonated samples; unfiltered, sample ozonated without previous filtration; filtered, sample ozonated after 0.7 μm filtration. Ozonation was performed according to $\text{O}_3/\text{DOC} = 0.9 \text{ mg/mg}$

Literature cited

1. Munch, J.W.; Basset, M.V. Determination of Nitrosamines in Drinking Water by Solid Phase. Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS). U.S. Environmental Protection Agency **2004**, Method 521.