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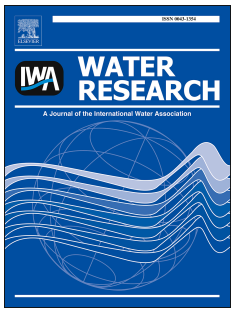

Nitrosamines in Pilot-Scale and Full-Scale Wastewater Treatment Plants with Ozonation

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PII: S0043-1354(14)00454-0

DOI: 10.1016/j.watres.2014.06.025

Reference: WR 10736

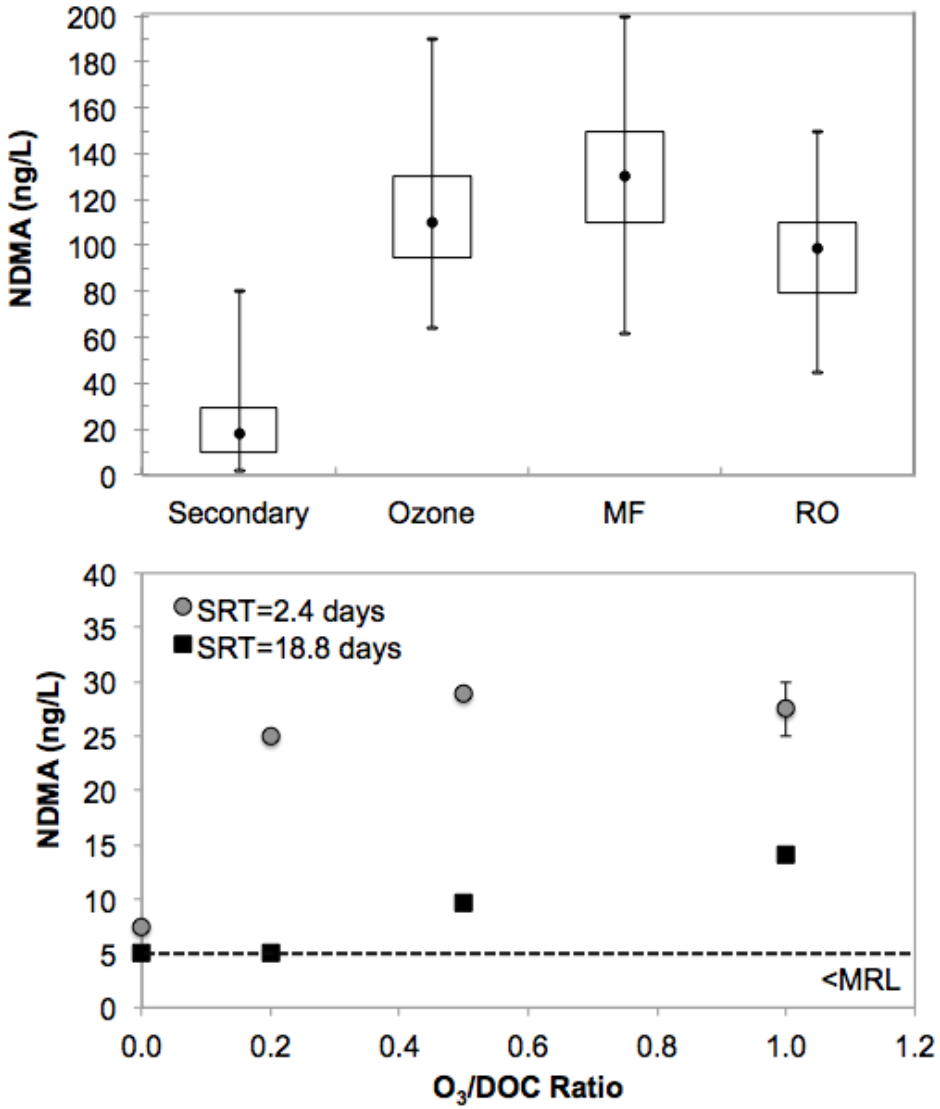
To appear in: *Water Research*

Received Date: 24 March 2014

Revised Date: 13 June 2014

Accepted Date: 16 June 2014

Please cite this article as: Gerrity, D., Pisarenko, A.N., Marti, E., Trenholm, R.A., Gerringer, F., Reungoat, J., Dickenson, E., Nitrosamines in Pilot-Scale and Full-Scale Wastewater Treatment Plants with Ozonation, *Water Research* (2014), doi: 10.1016/j.watres.2014.06.025.


NDMA (ng/L)
200
180
160
140
120
100
80
60
40
20
0
Secondary
Ozone
MF
RO
NDMA (ng/L)
40
35
30
25
20
15
10
5
0
SRT=2.4 days
SRT=18.8 days
<MRL
0.0
0.2
0.4
0.6
0.8
1.0
1.2
O3/DOC Ratio

Nitrosamines in Pilot-Scale and Full-Scale Wastewater Treatment Plants with Ozonation

Running Title: Nitrosamines in Large-Scale Ozone Systems

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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 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.

Keywords: Wastewater, ozone, nitrosamine, N-nitrosodimethylamine (NDMA), potable reuse.

List of 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

88	SRT	Solids retention time
89	SUVA	Specific UV_{254} absorbance
90	TOC	Total organic carbon
91	TX	Texas
92	UDMH	Unsymmetrical dimethylhydrazine
93	UF	Ultrafiltration
94	U.S.	United States
95	UV	Ultraviolet

96

1.0 Introduction

Nitrosamines are disinfection byproducts commonly associated with chloramination (Choi and Valentine, 2002; Mitch et al., 2003a; Mitch et al., 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; Gerrity et al., 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 ($5.3x10^{-2}$ M^{-1} s^{-1}; Lee et al., 2007) and short-lived hydroxyl radicals ($4.6x10^{8}$ 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

143 osmosis (RO) (Plumlee et al., 2008), or ultraviolet (UV) photolysis (Bolton et al., 2002;
144 Sharpless and Linden, 2003; Lee et al., 2005a; Lee et al., 2005b), although the required UV
145 doses (i.e., generally >100 mJ/cm^2) can be cost prohibitive.

146 Recent risk assessments indicate that 'planned' potable reuse can be more protective of
147 public health than 'unplanned' indirect potable reuse or conventional drinking water systems
148 (NRC, 2012). However, pervasive uncertainty in the industry is potentially leading to the
149 overdesign of advanced treatment facilities for potable reuse (Gerrity et al., 2013). A majority of
150 the recently constructed potable reuse facilities employ "full advanced treatment" (CDPH, 2013),
151 which includes RO and an advanced oxidation process (AOP). These systems typically include
152 microfiltration (MF) for pretreatment, chloramination to control biological fouling, and UV/H_2O_2
153 as the preferred AOP due to the formation of NDMA during chloramination. Treatment trains
154 employing ozone and biological activated carbon (BAC) offer a more sustainable alternative in
155 terms of economic costs and energy consumption (Gerrity et al., 2014), and they are also capable
156 of achieving similar water quality objectives, including CEC mitigation and pathogen
157 inactivation (Reungoat et al., 2010; Gerrity et al., 2011; Reungoat et al., 2012; Gerrity et al.,
158 2014). The combination of ozone and biological sand filtration has also been studied in Europe
159 with respect to CEC mitigation and toxicity (Hollender et al., 2009; Stalter et al., 2010a; 2010b).
160 Several ozone-based potable reuse treatment trains have been operating in the U.S. for years with
161 no documented adverse public health impacts.

162 Despite the advantages of implementing ozone in wastewater applications, the potential
163 for nitrosamine formation poses a significant threat to the viability of this technology for future
164 potable reuse systems. NDMA formation in ozone applications is typically low (i.e., <10 ng/L)
165 (Hollender et al., 2009; Zimmerman et al., 2011), but some matrices lead to formation in excess

of 50-100 ng/L (Kosaka et al., 2009; Yoon et al., 2011; Gerrity et al., 2014). Some studies have identified potential precursors (Andrzejewski et al., 2008; Kosaka et al., 2009; von Gunten et al., 2010; Marti et al., 2014), but, in general, little is known regarding the formation pathway and the reasons for the significant variability observed between wastewater matrices. Furthermore, studies often focus on NDMA and fail to address the other nitrosamines that pose similar risks to public health.

The objective of this study was to address these knowledge gaps by monitoring the occurrence of six nitrosamines (NDMA, NMEA, NDEA, NDPrA, *N*-nitrosomorpholine (NMOR), and NDBA) in full-scale and pilot-scale treatment trains with a range of operational conditions. 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 were also included for comparison. This study provides a survey of nitrosamine occurrence and formation and explores the operational conditions that contribute to the observed range in concentrations. This research contributes to the development of nitrosamine mitigation strategies, which will facilitate broad implementation of ozone-based potable reuse treatment trains.

2.0. Materials and Methods

2.1. Study Sites and Sampling Locations

Grab samples were collected from 11 different full-scale or pilot-scale treatment trains in the U.S. and Australia. The study sites, operational conditions, and sampling dates are summarized in Table 1, and more detailed descriptions of the study sites, including treatment train schematics and general water quality information, are provided in the Supplementary

Information (SI). The sampling plan included six full-scale and two pilot-scale systems with ozone, two conventional wastewater treatment plants with chlorination or UV disinfection, and one full advanced treatment facility. Grab samples were collected at various points throughout each treatment train to fully characterize nitrosamine occurrence and formation, but special attention was given to sampling locations before and after secondary treatment, ozonation, and BAC. Several sites employ solids handling processes, including belt filter presses, dewatering centrifuges and/or anaerobic digesters, supplemented with polymer addition. The associated returns flows are often recombined with influent or primary effluent for further treatment, which could impact nitrosamine occurrence and formation. Therefore, digester supernatant was also sampled at one of the sites (Site B).

The facilities encompass a variety of biological treatment conditions with solids retention times (SRTs) ranging from 1.5-36 days. The membrane bioreactor (MBR) at the Site J2 pilot was also operated in multiple modes (i.e., biochemical oxygen demand (BOD) removal with SRT = 2.4 days vs. nitrification/denitrification with SRT = 18.8 days) to evaluate the impacts of biological treatment on downstream NDMA formation during ozonation. The number of ozone application points ranged from one to three, and the ozone to dissolved or total organic carbon ratios (O_3/DOC or O_3/TOC) ranged from 0.2-1.5. The O_3/DOC or O_3/TOC ratio has been identified as a useful parameter for predicting ozone performance with respect to chemical oxidation (Gerrity et al., 2012; Lee et al., 2013) and microbial inactivation (Gerrity et al. 2012; Gamage et al, 2013) in different secondary and tertiary effluents. The Site H and Site J2 pilots were tested at different O_3/TOC or O_3/DOC ratios to determine whether the applied ozone dose was correlated with NDMA formation. Finally, the empty bed contact times (EBCTs) in the BAC processes ranged from 15-18 minutes.

General water quality information was provided by the participating utilities for some samples (see SI). All other nitrosamine and effluent organic matter (EfOM) data were analyzed using the methods described below.

2.2. Target Nitrosamines and Analytical Methods

All chemicals and solvents were purchased from commercial suppliers at 95% purity or higher (details provided in SI Text S12). Nitrosamine samples were collected in 1-L, pre-cleaned, pre-silanized amber glass bottles. Aliquots of sodium azide (1 g/L) and sodium thiosulfate (800 mg/L) were added to bottles prior to sampling for preservation and to quench residual oxidant. After sampling, bottles were kept on ice during transportation or shipping and then stored at 4°C until extraction. Samples were filtered with 90 mm glass microfiber (GF/F) filters (Whatman, GE Healthcare Bio-Sciences, Pittsburgh, PA) and extracted within 14 days of collection.

Nitrosamine analysis was performed with isotope dilution using a modified version of U.S. EPA method 521 (Holady et al., 2012). A detailed description of the method is provided in SI Text S12, and a brief description is provided below. Automated solid phase extraction (ASPE) was performed using a Dionex AutoTrace workstation (Thermo Scientific, Sunnyvale, CA, USA). A Varian (Walnut Creek, CA) CP-3800 Gas Chromatograph with a CP-8400 auto sampler was used for separation, and a Varian 4000 ion trap mass spectrometer was used for analysis in conjunction with multiple reaction monitoring in positive chemical ionization mode. Some of the nitrosamines did not exhibit a second product ion in sufficient abundance for transition confirmation and therefore only have one quantitation transition. Due to thermal degradation upon injection, NDPhA was analyzed as diphenylamine during a preliminary 14-day holding study (see Table S42). MRLs were established at 3 to 5 times the calculated method detection limit (MDL) (n=12). A field blank was collected for each sampling event, extracted, and

analyzed. A laboratory reagent blank was also included in each extract batch. Acceptable average percent recoveries were limited to 70-130%, and acceptable relative standard deviations (RSDs) were limited to 30% for replicate samples. Average percent recoveries and RSDs in reagent water, finished drinking water, surface water, and tertiary wastewater effluent are summarized in Table S44.

The initial target compound list included NDMA, NMEA, NDEA, NDPrA, NMOR, NDBA, NPYR, N-nitrosopiperidine (NPIP), and NDPhA. Primary effluent, secondary effluent, combined ozone influent, and ozone effluent from Site A were collected in October 2011 for preliminary method development. Matrix interference resulted in unreliable quantification for NPYR and NPIP, particularly in the primary effluent, so these compounds were eliminated from the target compound list. A 14-day holding study was then performed on the remaining seven nitrosamines with deionized water and primary effluent from Site J1 (Table S42). Nine samples of each matrix were spiked with 1 μg/L of each nitrosamine. Each sample was preserved with sodium azide (1 g/L) and held at room temperature to simulate a 'worst-case' scenario during shipping. Triplicate samples were analyzed on day 0, day 7, and day 14. Of the seven nitrosamines, only NDPhA showed a consistent decrease in concentration over the 14-day holding period. A 75% decrease in concentration was observed after 7 days, and the concentration was <MRL after 14 days. However, the decrease does not appear to be attributable to biodegradation since it was observed in both matrices.

Based on the matrix effects associated with NPYR and NPIP and the instability of NDPhA, the final target compound list was limited to NDMA, NMEA, NDEA, NDPrA, NMOR, and NDBA. These compounds are summarized along with their corresponding isotopes, precursor and product ions used for quantitation and confirmation, molecular weights, and MRLs

in Table S43. The MRLs in Table S43 apply to all wastewater matrices except primary effluent, for which each MRL was five times higher, and the samples from Site G, which allowed for lower MRLs due to reduced matrix interference. Matrix-specific MRLs are provided in the SI for each site.

2.3. Effluent Organic Matter Characterization

EfOM characterization included TOC or DOC, UV absorbance (220-580 nm), specific UV_{254} absorbance (SUVA), and fluorescence. For the TOC and DOC analyses, samples were collected in glass vials and acidified to pH <3 with hydrochloric acid. Samples with visible suspended solids were filtered in the laboratory through 0.45-µm membranes (GHP Acrodisk, Pall Life Sciences) and reported as DOC; laboratory filtration was also performed prior to the UV-Vis and fluorescence analyses. Samples filtered at pilot-scale or full-scale with membrane filtration were also reported as DOC. A total organic carbon/total nitrogen analyzer (Shimadzu Scientific Instruments, Carlsbad, CA) was used for quantification. Sample absorbance was measured using a Perkin-Elmer Lambda 45 UV-VIS Spectrometer, consistent with Standard Method 5910 B. Excitation emission matrices (EEMs) were created using a QuantaMaster UV-Vis QM4 Steady State Spectrofluorometer (Photon Technology International, Inc., Birmingham, NJ). The spectrofluorometer included a 75-watt, short-arc xenon lamp with an excitation range from 240-1,200 nm. Data processing in MATLAB (MathWorks, Natick, MA) included corrections for blank response, the spectral sensitivity of the lamp, and the inner filter effect. The fluorescence data were also normalized to an average Raman peak area, which was based on excitation at 350 nm and emission from 380-410 nm in deionized water. Regional integration was performed according to published literature (Chen et al., 2003; Gerrity et al., 2011; Stanford et al., 2011) to calculate the regional and total fluorescence intensities in arbitrary fluorescence

281 units (AFU). Integration was based on three regions representing (I) microbial byproducts,
282 proteins, and biopolymers; (II) fulvic-like substances; and (III) humic-like substances. These
283 regions are defined and illustrated in Table S45 and Figure S26, respectively. The EfOM data are
284 referenced throughout the text, but the raw data and figures are provided in the SI.
285

286 **3.0. Results and Discussion**

287 Only six of the original nine nitrosamines were included in the final target compound list.
288 Two of the remaining six nitrosamines (NDPrA and NDBA) were <MRL (100 ng/L in primary
289 effluent and 20 ng/L in other matrices) for all sampling locations at all study sites. With less
290 complex matrices, such as those at Site G, lower reporting limits are possible for these
291 compounds, but in more complex wastewater effluents, it is difficult to evaluate these
292 compounds in the context of their toxicological thresholds and/or regulatory guideline values
293 (e.g., 10 ng/L for NDPrA in California). NMEA was detected in two locations at Site C, and
294 NDEA was detected in two locations at Site E. These compounds were not detected at any other
295 sites.

296 NDMA and NMOR proved to be the most prevalent compounds based on the sample
297 matrices and analytical capabilities in this study. As observed in other studies (Hollender et al.,
298 2009; Zimmerman et al., 2011; Yoon et al., 2011), there was a clear relationship between
299 ozonation and NDMA formation at all but Site C (Figure 1), while NMOR concentrations
300 remained relatively constant or possibly decreased during ozonation (Figure 2). In addition,
301 biodegradation via secondary treatment proved to be an effective mitigation measure for both
302 NDMA (Sites B, D, and E; Figure 1) and NMOR (Sites A and B; Figure 2). Decreases in NDMA
303 concentration after secondary treatment have also been reported in the literature (Sedlak et al.,

2005; Krauss et al., 2010). Biodegradation of NDMA was also observed in two BAC systems (Sites D and F), but BAC did not appear to be effective for NMEA degradation (NMEA only observed at Site C). Site-specific summaries and pilot-scale evaluations of O_3/DOC or O_3/TOC and biological treatment mechanisms are provided below.

3.1 Full-Scale Site A (MO, USA)

Two sets of samples were collected from Train #2 at Site A, which includes conventional activated sludge (SRT = 18-20 days) with nitrification and biological phosphorus removal. The sampling locations included primary influent, primary effluent, secondary effluent, combined ozone influent (combination of biologically treated and filtered wastewater from both trains), and ozone effluent (O_3/DOC = 1.0-1.2). The process stream also includes return flows from solids handling processes supplemented with polymer addition. Detailed descriptions of the treatment trains, sampling locations, and general water quality are provided in Text S1 in the SI.

Based on the EfOM characterization (see SI), the primary and secondary effluents from October 2011 exhibited higher levels of UV absorbance and fluorescence but lower DOC concentrations than the samples from May 2012. The October 2011 secondary effluent also had a higher concentration of NDMA (11 ng/L vs. 7.8 ng/L), but NMOR concentrations were higher for the May 2012 primary (<50 ng/L vs. 58 ng/L) and secondary effluents (12 ng/L vs. 22 ng/L). The high-SRT biological process achieved significant reductions in total nitrogen (TN); EfOM, including a ~50% reduction in total fluorescence; and NMOR (from 58 ng/L to 22 ng/L in May 2012). Similar comparisons of biological treatment efficacy were not possible for NDMA or NMOR in October 2011 because the corresponding concentrations were <MRL.

NMOR remained relatively constant during ozonation, which is consistent with the literature (Hollender et al. 2009; Zimmermann et al. 2011), but ozone-induced formation of

NDMA was observed in both sample events (formation of 14 ng/L and 7.7 ng/L for total concentrations of 26 ng/L and 14 ng/L). NDMA formation may have been higher in the October 2011 sample due to the more complex EfOM, as indicated by the higher UV_{254} absorbance (0.116 cm^{-1} vs. 0.108 cm^{-1}) and fluorescence values (28,782 AFU vs. 23,525 AFU), and/or the greater extent of oxidation, as indicated by differential UV_{254} absorbance (reduction of 49% vs. 39%) and differential total fluorescence (reduction of 84% vs. 76%). Despite the quantifiable increase in NDMA, the change was relatively minor compared to that of other ozonated secondary effluents (i.e., >100 ng/L in Gerrity et al. (2014)). The finished effluent, which is discharged to a nearby surface water, contained NDMA and NMOR concentrations of 14-26 ng/L and <MRL-22 ng/L, respectively.

3.2 Full-Scale Site B (KY, USA)

Preliminary effluent (post-headworks), clarifier effluent (post-oxidation ditch; SRT = N/A; nitrification and partial denitrification), ozone effluent (O_3/TOC = 0.9), and digester supernatant were collected from Site B. Digester supernatant is returned to the process flow prior to biological treatment in the oxidation ditch. Detailed descriptions of the treatment train, sampling locations, and general water quality are provided in Text S2 in the SI.

The oxidation ditch at this facility produces a high quality effluent, as indicated by the low UV_{254} absorbance (0.076 cm^{-1}) and total fluorescence (18,145 AFU) values. Similar to Site A, the biological process reduced the concentrations of NDMA and NMOR from 25 ng/L to <5 ng/L and 67 ng/L to 21 ng/L, respectively. The concentration of NMOR remained relatively constant (20 ng/L) after ozonation, but the concentration of NDMA increased just above the MRL to 5.2 ng/L. The extent of oxidation was consistent with that of Site A, considering the UV_{254} absorbance and total fluorescence decreased by 42% and 78%, respectively. With respect

to solids handling, digester supernatant proved to be a relatively minor contributor of individual nitrosamines in that NMOR was the only compound >MRL (13 ng/L). However, digester supernatant may still contribute precursors responsible for chloramine-induced or ozone-induced nitrosamine formation (Padhye et al., 2011). The finished effluent from this facility, which is discharged to a nearby surface water, contained 5.2 ng/L of NDMA and 20 ng/L of NMOR.

3.3 Full-Scale Site C (TX, USA)

The treatment train at Site C includes primary clarifiers, activated sludge (SRT = 10 days) with nitrification and powdered activated carbon (PAC) addition, secondary clarifiers, denitrification (SRT = 36 days) with methanol addition, tertiary clarifiers, lime addition, recarbonation, sand filtration, ozonation (O_3/TOC = 0.3), and BAC (EBCT = 16 min) prior to direct injection into the local aquifer. Primary effluent, tertiary clarifier effluent, sand filter effluent, ozone effluent, and BAC effluent were collected for analysis. Detailed descriptions of the treatment train, sampling locations, and general water quality are provided in Text S3 in the SI.

NMEA was the only nitrosamine detected at this facility, and the concentrations were 6.3 ng/L and 7.6 ng/L in the ozone effluent and BAC effluent, respectively. Since the NMEA in the ozone effluent was only slightly higher than the MRL and the fact that NMEA was not detected at any other facilities, it is not possible to definitively link its presence to ozone-induced formation. In addition, Site C was the only facility for which NDMA did not exhibit a quantifiable increase during ozonation. This is possibly due to a combination of the low EfOM content of the ozone influent and the relatively low O_3/TOC ratio in comparison to other facilities in this study. The lack of measurable NDMA formation coupled with the low TOC, UV_{254} absorbance, and total fluorescence values (Table S12) indicate that the NDMA precursors

373 may have been removed by the PAC-supplemented biological treatment process. With respect to
374 the BAC process, the persistence of NMEA suggests it might be more biologically recalcitrant
375 than NDMA.

376 **3.4 Full-Scale Site D (GA, USA)**

377 The treatment train at Site D includes primary clarifiers; activated sludge (SRT = 10-12
378 days) with nitrification, denitrification, and biological phosphorus removal; secondary clarifiers;
379 lime addition; recarbonation; parallel ultrafiltration and dual media filtration systems; pre-
380 ozonation (O_3/DOC = 0.2-0.3), BAC (EBCT = 15 min), and post-ozonation (O_3/TOC = 0.2-0.4).
381 Detailed descriptions of the treatment train, sampling locations, and general water quality are
382 provided in Text S4 in the SI.

383 NDMA was the only nitrosamine detected at Site D. The concentration in the primary
384 effluent was 42 ng/L, but the concentration dropped to 6.8 ng/L after secondary treatment, which
385 is consistent with the relatively long SRT and the observed EfOM transformation (i.e., 69%
386 reduction in UV_{254} absorbance and 79% reduction in total fluorescence). However, the NDMA
387 concentration subsequently increased to 9.2 ng/L during ozonation. In comparison to the ~120%
388 increase at Site A, the smaller 56% increase might be attributable to the relatively low O_3/DOC
389 ratio of 0.2-0.3. The downstream BAC process reduced the NDMA concentration to <MRL and
390 presumably removed NDMA precursors as well since the final ozonation step did not yield
391 quantifiable NDMA. Therefore, no nitrosamines were detected in the finished effluent, which is
392 discharged to a nearby surface water for potable reuse applications.

393 **3.5 Full-Scale Site E (GA, USA)**

394 Site E is primarily an industrial wastewater treatment facility that receives denim mill
395 discharge with a pH of 10.5-11. The facility includes preliminary treatment with aeration and pH

adjustment, extended aeration (SRT = N/A), polymer addition, clarification, and ozonation (O_3/DOC = 1.0-1.2). Preliminary effluent, clarifier effluent, and ozone effluent were collected for analysis. Detailed descriptions of the treatment train, sampling locations, and general water quality are provided in Text S5 in the SI.

The EfOM in all samples was highly concentrated (i.e., high DOC concentrations) and complex (i.e., significant aromaticity and fluorophore concentrations). NDMA was detected in the primary effluent at a relatively high level of 89 ng/L, and the concentration only decreased by 19% to 72 ng/L during biological treatment. This is consistent with the relatively poor quality of the clarifier effluent, which still contained 25 mg/L of DOC, a UV_{254} absorbance of 0.376 cm^{-1}, and a total fluorescence of 133,133 AFU. Despite the high ozone dose (O_3 = 28-32 mg/L; O_3/DOC = 1.0-1.2), the UV_{254} absorbance and total fluorescence only decreased by 26% and 58%, respectively. This level of transformation is typically associated with an O_3/TOC or O_3/DOC of 0.25 in secondary effluent (Gerrity et al., 2012), which reflects the complex nature of this particular matrix. Despite the high EfOM concentration and complexity, the NDMA increased by only 18% from 72 ng/L to 85 ng/L. In addition, this was the only site where NDEA was detected; the concentrations were 20 ng/L and 19 ng/L in the clarifier effluent and ozone effluent, respectively. Therefore, the finished effluent, which is discharged to a nearby surface water, contained 85 ng/L of NDMA and 19 ng/L of NDEA.

3.6 Full-Scale Site F (QLD, AUS)

Site F is an advanced treatment facility that receives nitrified secondary effluent (SRT = 16 days) from a nearby wastewater treatment plant. The advanced treatment train includes denitrification with methanol addition, pre-ozonation (O_3 = 2 mg/L; O_3/DOC = 0.2), alum and polymer addition, dissolved air flotation, sand filtration, ozonation (O_3 = 5 mg/L; O_3/TOC = 0.6-

419 0.8), BAC (EBCT = 18 min), and post-ozonation (O_3 = 2 mg/L; O_3/TOC = 0.5) for final
420 disinfection (Reungoat et al., 2010; Reungoat et al., 2012). Primary effluent, secondary effluent,
421 denitrification effluent, pre-ozone effluent, flotation/filtration effluent, ozone effluent, BAC
422 effluent, and post-ozone effluent samples were collected for analysis. Detailed descriptions of the
423 treatment train, sampling locations, and general water quality are provided in Text S6 in the SI.
424 The primary effluent from this facility appeared to be relatively complex based on its
425 high total fluorescence value, although it did not contain any quantifiable nitrosamines. The
426 subsequent reductions in UV_{254} absorbance and total fluorescence were consistent with the
427 biological treatment and ozonation employed at this facility. NDMA was first detected in the
428 pre-ozone effluent at a concentration of 5.4 ng/L. The NDMA remained stable through the sand
429 filters but then increased again to 11 ng/L in the main ozone effluent, thereby indicating that the
430 NDMA precursors had not been consumed by the relatively low pre-ozone dose (O_3/DOC = 0.2).
431 Similar to Site E, the NDMA was <MRL after BAC and the post-ozone step. Therefore, all of the
432 nitrosamines were <MRL in the finished effluent, which is discharged to a nearby surface water.

433 **3.7 Full-Scale Site G (CA, USA)**

434 Site G is a full advanced treatment facility that receives nitrified/denitrified secondary
435 effluent (SRT = 5.5 days) from a nearby wastewater treatment plant. The solids handling
436 processes at the wastewater treatment plant include anaerobic digesters and belt filter presses.
437 The digester supernatant and filtrate are returned upstream of the primary clarifiers for repeated
438 treatment. Polymer is also added at the headworks, primary clarifiers, and belt filter presses. The
439 advanced treatment train includes MF with chloramine addition, RO, UV/H_2O_2, and product
440 water stabilization prior to discharge to spreading grounds or direct injection into the local
441 aquifer. MF influent (post-chloramine), MF effluent, RO permeate, RO concentrate, and

442 UV/H_2O_2 effluent were collected for this study. Detailed descriptions of the treatment train,
443 sampling locations, and general water quality are provided in Text S7 in the SI.
444 Since chloramination is commonly associated with NDMA formation, data from Site G
445 were included in this study as a basis for comparison with the ozone-based treatment trains.
446 Presumably due to chloramination (or possibly combined with background levels), NDMA was
447 detected at 16 ng/L in the MF influent; NMOR was also detected at 6.9 ng/L. Additional
448 chloramine exposure led to an increase in NDMA to 42 ng/L and a NMOR concentration of 7.5
449 ng/L in the MF effluent. RO reduced the NMOR concentration to <MRL and provided a 52%
450 decrease in NDMA, which is consistent with reductions reported in the literature (Plumlee et al.,
451 2008). After UV/H_2O_2, the final concentrations of all nitrosamines were <MRL. However, the
452 RO concentrate contained 100 ng/L of NDMA and 18 ng/L of NMOR.

453 **3.8 Pilot-Scale Site H (CA, USA)**

454 Prior to its recent expansion and upgrade, the full advanced treatment facility at Site H
455 was identical to that of Site G. However, Site H receives non-nitrified secondary effluent (pure
456 oxygen; SRT = 1.5 days), which leads to significant organic fouling of the membranes. To
457 mitigate this issue, Site H recently installed an ozone system upstream of its MF membranes, and
458 they also piloted parallel treatment trains to quantify the net benefits of preozonation on
459 membrane fouling. For this study, samples were collected from the pilot-scale treatment trains
460 composed of MF-RO and ozone-MF-RO; both trains also included sodium hypochlorite addition,
461 which reacted with ambient ammonia to form chloramine immediately upstream of the MF
462 membranes. The O_3/TOC ratios were varied from 0.3-1.5 throughout the six-month test period
463 (from late April 2011 to early November 2011) to evaluate the impact of ozone dose on NDMA

464 formation; the other nitrosamines were not monitored at Site H. Detailed descriptions of the
465 treatment train, sampling locations, and general water quality are provided in Text S8 in the SI.
466 Figure 3 illustrates the range of NDMA concentrations observed over the test period in
467 both trains. The NDMA concentrations in the control train (i.e., MF-RO) are consistent with
468 those from Site G. However, the extremely high level of ozone-induced NDMA formation in the
469 experimental train, which ranged from 30 ng/L to 143 ng/L, is the most significant observation.
470 Although it is significantly higher than other sites in this study, similar levels of ozone-induced
471 NDMA formation have been reported previously (Kosaka et al., 2009; Gerrity et al., 2014). The
472 data for the control versus the experimental train suggests that ozone-induced NDMA formation
473 is more problematic than chloramine-induced NDMA formation for this site, assuming typical
474 oxidant dosing conditions. Additional studies are needed to determine whether the difference in
475 formation is due to differing precursors or kinetics.
476 The reason(s) for this high level of NDMA formation are not entirely clear. The primary
477 distinction between this facility and the other sites in this study is that Site H ozonates non-
478 nitrified secondary effluent that receives limited biological pretreatment (i.e., SRT = 1.5 days)
479 with variable efficacy (i.e., total fluorescence ranges from 123,057 AFU to 239,104 AFU in the
480 secondary effluent). Other facilities employ anaerobic digesters and polymer addition without
481 substantial increases in NDMA, but their more extensive biological pretreatment might be
482 sufficient to mitigate potential precursors in the return flows. However, the site from Gerrity et al.
483 (2014) that exhibited high direct nitrosamine formation (i.e., up to 125 ng/L of NDMA in
484 addition to low levels of NMEA, NDEA, and NDBA) employed extensive biological
485 pretreatment with an SRT of 12 days, nitrification, and partial denitrification. Therefore, the

extent of biological pretreatment is not an absolute indicator of ozone-induced nitrosamine formation potential.

As indicated by the box-and-whisker plots in Figure 3, there was significant temporal variability in the NDMA concentrations over the study period. Figure 4 illustrates the temporal variability in the secondary effluent and ozonated secondary effluent in relation to the corresponding sample dates. Data analyses were performed to evaluate whether EfOM characteristics (Table S28, Figure S17, and Figure S18), secondary effluent NDMA concentrations (Figure S19), or O_3/TOC ratios (Figure 5) could be used to predict ozone-induced NDMA formation. Similar to the O_3/TOC data in Figure 5, none of these parameters exhibited a correlation with NDMA formation. This indicates that more specific precursor compounds that also exhibit temporal variability may be responsible for the high levels of NDMA formation at certain facilities (Hollender et al., 2009). The full-scale version of Site H relies on RO and the photolysis component of its UV/H_2O_2 process to achieve the 10-ng/L notification level established by CDPH for NDMA.

3.9 Full-Scale Site I (NV, USA) and Full-Scale Site J1 (NV, USA)

Sites I and J1 were included in the study as a basis for comparison with the aforementioned ozone-based treatment trains. They are grouped together due to their similar treatment trains, water quality, and geographic location. Both treatment trains include primary clarifiers; activated sludge (SRT = 6-8 days) with nitrification, denitrification, and biological phosphorus removal; secondary clarifiers, and media filtration. Site I includes an advanced treatment train with flocculation, tertiary clarifiers, and UV disinfection or sodium hypochlorite addition, depending on the discharge mechanism (i.e., surface water and a reclaimed water distribution system, respectively). Site J1 uses only sodium hypochlorite addition for final

disinfection. Detailed descriptions of the treatment trains, sampling locations, and general water quality are provided in Text S9 and Text S10 in the SI.

Unlike the facilities with ozonation or chloramination, there was no observable change in nitrosamine concentrations after chlorination or UV treatment at Sites I and J1. This is consistent with the literature on NDMA formation with various oxidants (Lee et al., 2007; Mitch and Sedlak, 2002; Nawrocki and Andrzejewski, 2011; Pehlivanoglu-Mantas et al., 2008). In fact, only NMOR (11 ng/L) was detected in the secondary effluent at both sites; NMOR was also present in the filter effluent (13 ng/L) and chlorinated effluent (11 ng/L) at Site I. If nitrosamines had been present at higher concentrations, the relatively low UV dose used for disinfection at Site I (<100 mJ/cm^2) would have achieved minimal reductions compared to the UV/H_2O_2 systems at the full advanced treatment facilities (>100 mJ/cm^2).

3.10 Pilot-Scale Site J2 (NV, USA)

Similar to the pilot system at Site H, the primary objective of Site J2 was to quantify the net benefits of preozonation on membrane fouling, specifically RO membranes; the results have been published previously (Stanford et al., 2011; Pisarenko et al., 2011; 2012; 2014). Site J2 treats primary effluent from full-scale Site J1 with a pilot-scale MBR and parallel trains composed of RO and ozone-RO. Detailed descriptions of the treatment trains, pilot-scale reactors, sampling locations, and general water quality are provided in Text S11 in the SI.

For the current study, nitrosamine concentrations were monitored in the MBR filtrate and the ozone effluent, and the MBR was operated in multiple modes (i.e., BOD removal with SRT = 2.4 days vs. nitrification/denitrification with SRT = 18.8 days) to evaluate the impacts of varying biological pretreatment on downstream NDMA formation during ozonation. After the MBR had stabilized in each operational mode, the O_3/DOC ratios were varied from 0.2-1.0. It is important

to note that the two MBR modes were sampled several months apart so observed differences in NDMA may be a result of temporal variability of precursor concentrations and/or operational differences.

NDMA and NMOR were the only nitrosamines >MRL at Site J2, and NMOR was only reportable in one sample at 11 ng/L, which is just above the corresponding MRL of 10 ng/L (Table S40). Figure 6 illustrates the ozone-induced formation of NDMA in the MBR filtrate as a function of O_3/DOC ratio. Figure 6 indicates that direct NDMA formation may be a function of ozone dose at O_3/DOC ratios <0.5, but NDMA formation appears to plateau at O_3/DOC ratios >0.5. This relationship with ozone dose was not observed at Site H presumably because of the more variable water quality of the non-nitrified secondary effluent (Table S28 and Figure S17). Furthermore, Figure 6 indicates that extensive biological pretreatment (e.g., nutrient removal with higher SRTs) may lead to reduced NDMA formation during ozonation. The higher NDMA levels in the non-nitrified ozone effluent from Site J2 coupled with the extremely high values in the non-nitrified ozone effluent from Site H indicate that nitrification/denitrification may be a viable mitigation strategy. However, systems with extensive biological pretreatment, including nitrification and denitrification, may still observe exceedingly high levels of NDMA formation during ozonation (Gerrity et al., 2014), presumably due to the presence of precursors with high yields and/or concentrations.

4.0 Conclusion

Nitrosamine formation during ozonation poses a challenge for municipalities seeking to avoid RO and high-dose UV in potable reuse systems. There is limited occurrence data available, particularly for the less common nitrosamines, and the precursors and reaction pathways are not

555 completely understood. This study indicated that NDMA and NMOR are the most prevalent
556 nitrosamines in untreated and treated wastewater. NMEA and NDEA were also detected at two
557 facilities, although one of those facilities receives primarily industrial wastewater. NDPrA and
558 NDBA were <MRL in all samples.

559 NDMA and NMOR were present at concentrations as high as 89 ng/L in the primary
560 effluent at some facilities, but biological treatment achieving full nitrification (i.e., high SRTs)
561 proved to be a relatively effective mitigation measure for these nitrosamines. In the facilities
562 with ozonation, all but one exhibited NDMA formation during ozonation, although the
563 concentrations were generally low for facilities receiving primarily domestic wastewater and
564 employing effective biological pretreatment. However, one facility exhibited NDMA formation
565 exceeding 100 ng/L. The reasons for this anomaly are not entirely clear so additional research
566 into specific precursors and formation pathways is warranted. The other nitrosamines appeared
567 to be unaffected by ozonation. Downstream BAC was also effective in reducing NDMA
568 concentrations to <MRL and eliminating precursors that might form NDMA during final
569 disinfection. As expected, the combination of RO and high-dose UV (i.e., UV/H_2O_2) was also
570 effective in achieving the MRL for all nitrosamines, although significant concentrations were
571 present in the RO concentrate.

572 Therefore, NDMA formation is a potential concern for ozone-based potable reuse
573 treatment trains, but the formation is generally low and can be mitigated with established
574 technologies that would likely be included in those treatment trains regardless of NDMA
575 concerns. However, this issue is a significant concern for certain systems that experience
576 unusually high levels of NDMA formation. Additional research is needed to identify the sources
577 and identities of the precursors at these sites.

Acknowledgements

The authors would like to thank members of the Applied Research & Development Center at the Southern Nevada Water Authority, including Brett Vanderford, Dr. Eric Wert, Dr. Riley Flowers, Dr. Yue Wang, Michael Strileski, Janie Zeigler-Holady, Josephine Chu, David Rexing, and Jennifer Fuel, for all of their efforts during this study. The authors would also like to thank the technology partners, particularly APTwater, Hydranautics, Ozonia, and Pall for their generous contributions to the project. The personnel at the various study sites were also instrumental in the design, scheduling, and implementation of the sampling efforts. This study was made possible through funding from the WateReuse Research Foundation (WRF-08-08, WRF-10-11, and WRF-11-08). The comments and views detailed herein may not necessarily reflect the views of the WateReuse Research Foundation, its officers, directors, employees, affiliates or agents.

Supplementary Information Available

Supplementary Information (SI) is available free of charge via the Internet at (add address). The SI includes detailed treatment train schematics, general water quality information, EfOM characterization, and nitrosamine concentrations for each of the study sites.

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Table 1. Description of treatment trains and operational conditions at study sites

Site	Location	Flow (10^6 m^3/d)	2° Treatment[a]	SRT (days)	3° Treatment[a]	O_3/DOC or O_3/TOC	Sampling Date (MM/DD/YYYY)
A	MO, USA	1.14	CAS; N+BPR+DN	18-20	GF-O_3	1.0-1.2	10/10/2011; 05/01/2012
B	KY, USA	0.37	OD; N+DN	N/A	O_3	0.9	03/06/2012
C	TX, USA	0.45	CAS+PAC; N+DN	10; 36	Lime-GF-O_3-BAC	0.3	10/31/2012
D	GA, USA	1.61	CAS; N+DN+BPR	11	Lime-GF/UF-O_3-BAC-O_3	0.2-0.3; 0.2-0.3	02/01/2012
E	GA, USA	0.21	CAS; N	N/A	O_3	1.0-1.2	04/16/2012
F	QLD, AUS	0.08	CAS; N	16	DN-O_3-GF-O_3-BAC-O_3	0.2; 0.6-0.8; 0.5	05/15/2012
G	CA, USA	2.65	TF+CAS; N+DN	5.5	MF-RO-UV/H_2O_2	N/A[c]	10/10/2011
H	CA, USA	Pilot[b]	CAS	1.5	O_3-MF-RO; MF-RO	0.3-1.5	N/A[c]
I	NV, USA	3.79	CAS; N+DN+BPR	7	GF-UV; GF-NaOCl	N/A[c]	03/28/2012
J1	NV, USA	2.84	TF/CAS; N+DN+BPR	6-8	GF-NaOCl	N/A[c]	03/28/2012
J2	NV, USA	Pilot[b]	MBR; Multiple Modes	2-19[c]	O_3-RO; RO	0.0-1.0	N/A[c]

[a] CAS = conventional activated sludge, MBR = membrane bioreactor, OD = oxidation ditch, TF = trickling filter, N = nitrification, DN = denitrification, BPR = biological phosphorus removal, GF = gravity filtration, BAC = biological activated carbon, PAC = powdered activated carbon, MF = microfiltration, UF = ultrafiltration, RO = reverse osmosis

[b] Both pilot-scale treatment trains operated at 121 m^3/day.

[c] N/A = not available or applicable

Figure 1. Comparison of NDMA concentrations in the primary, secondary, ozone (initial ozonation step only), and BAC effluents from the full-scale and pilot-scale sites. Arrows indicate concentrations less than the corresponding method reporting limit. The data for Site A are based on the results from the second sampling event. Site G was omitted because the secondary effluent sample was influenced by chloramination. The data for pilot-scale Site H are based on averages over the sampling period, and error bars represent ±1 standard deviation. The data for pilot-scale site J2 are based on O_3/DOC = 0.5 in the BOD removal mode.

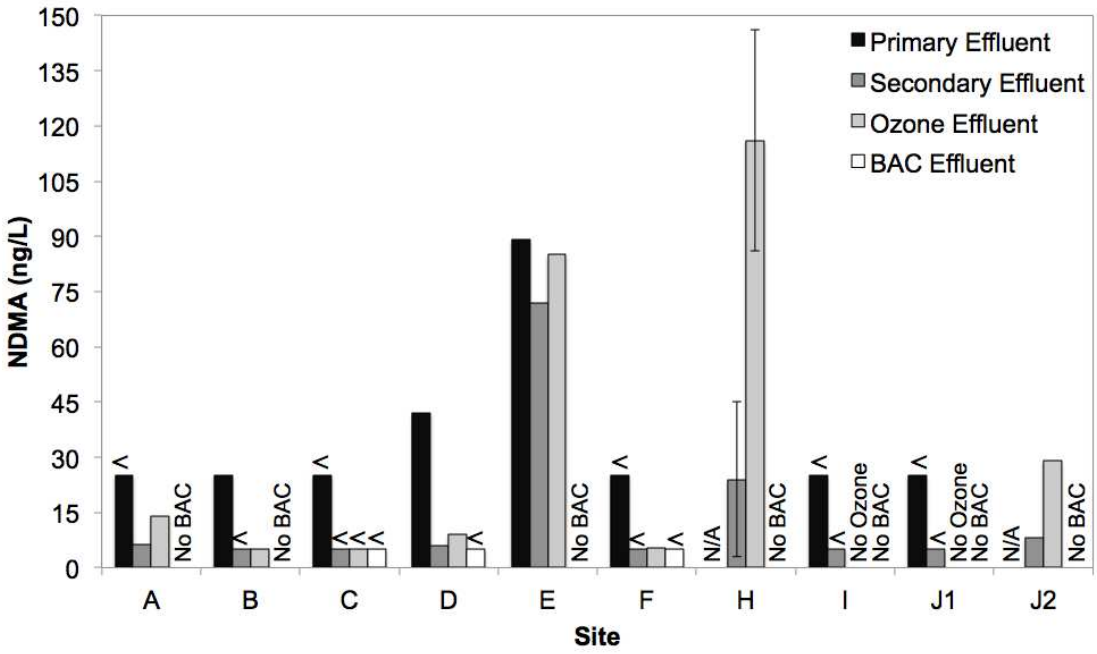


Figure 2. Comparison of NMOR concentrations in the primary, secondary, ozone (initial ozonation step only), and BAC effluents from the full-scale sites. Arrows indicate concentrations less than the corresponding method reporting limit. The data for Site A are based on the results from the second sampling event. Site G was omitted because all of the samples were influenced by chloramination.

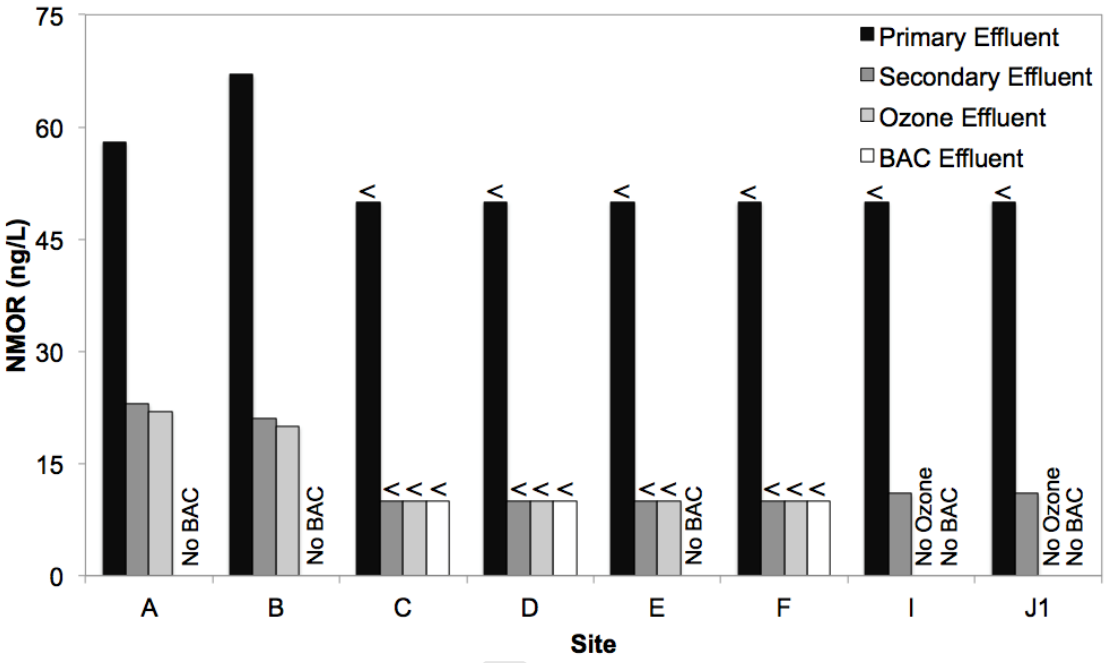


Figure 3. Summary of NDMA concentrations at Site H (CA) (late April 2011 to early November 2011). Dots correspond to median values, boxes correspond to inner quartiles, and whiskers correspond to minimum and maximum values.

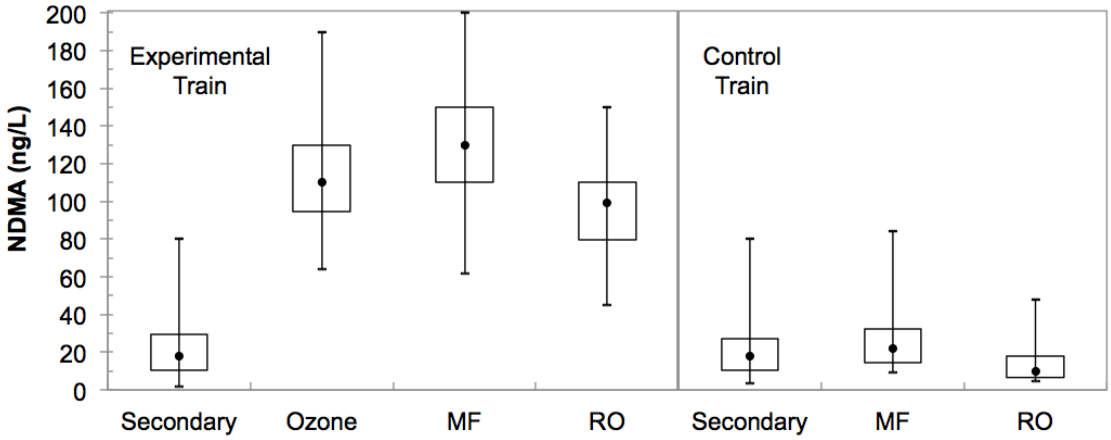


Figure 4. Temporal variability of the NDMA concentrations in the ozonated secondary effluent and non-ozonated secondary effluent at Site H (CA). These data represent samples collected weekly from late April 2011 to early November 2011.

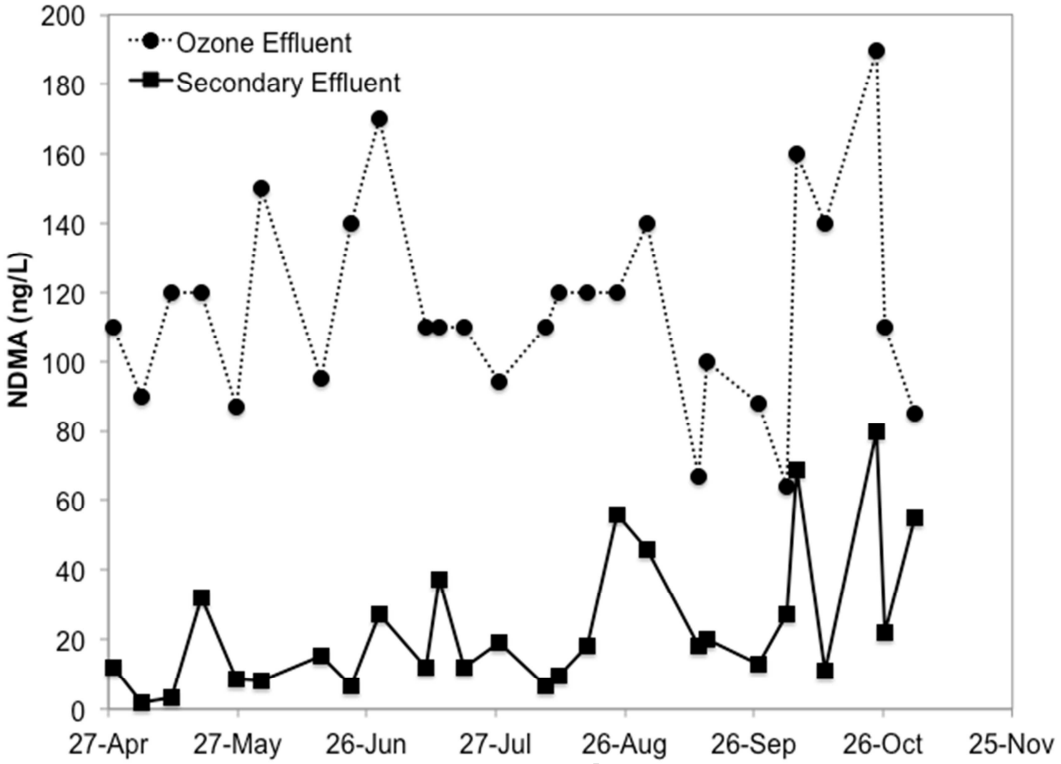


Figure 5. NDMA formation as a function of O_3/TOC ratio at Site H (CA). These data represent samples collected weekly from late April 2011 through early November 2011.

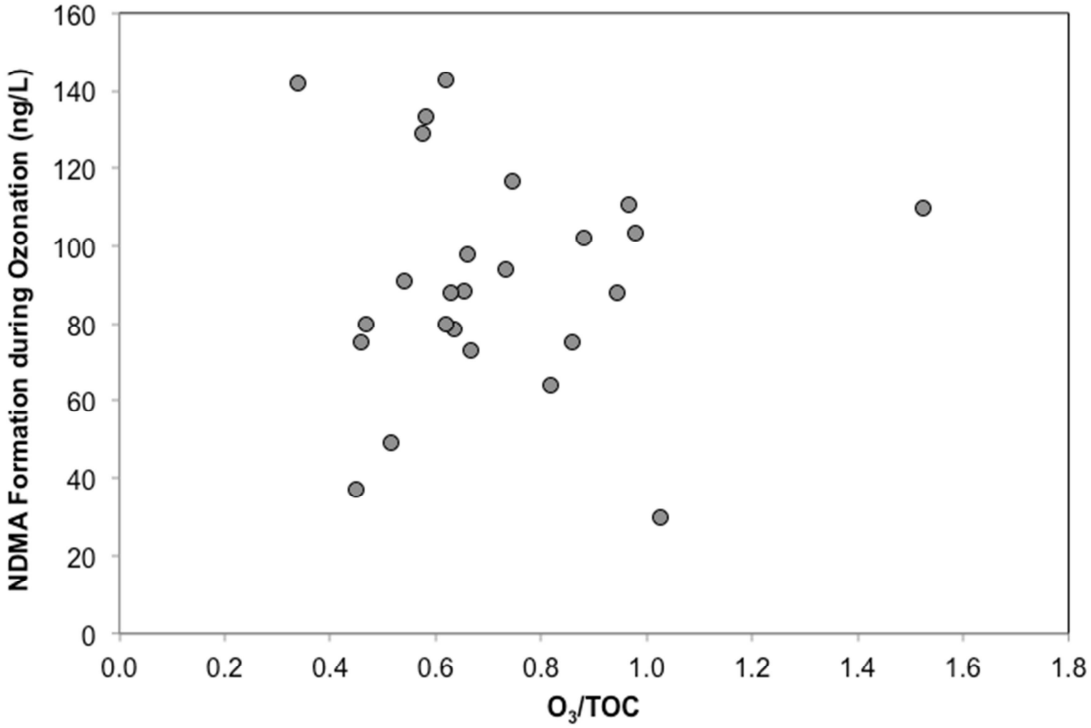
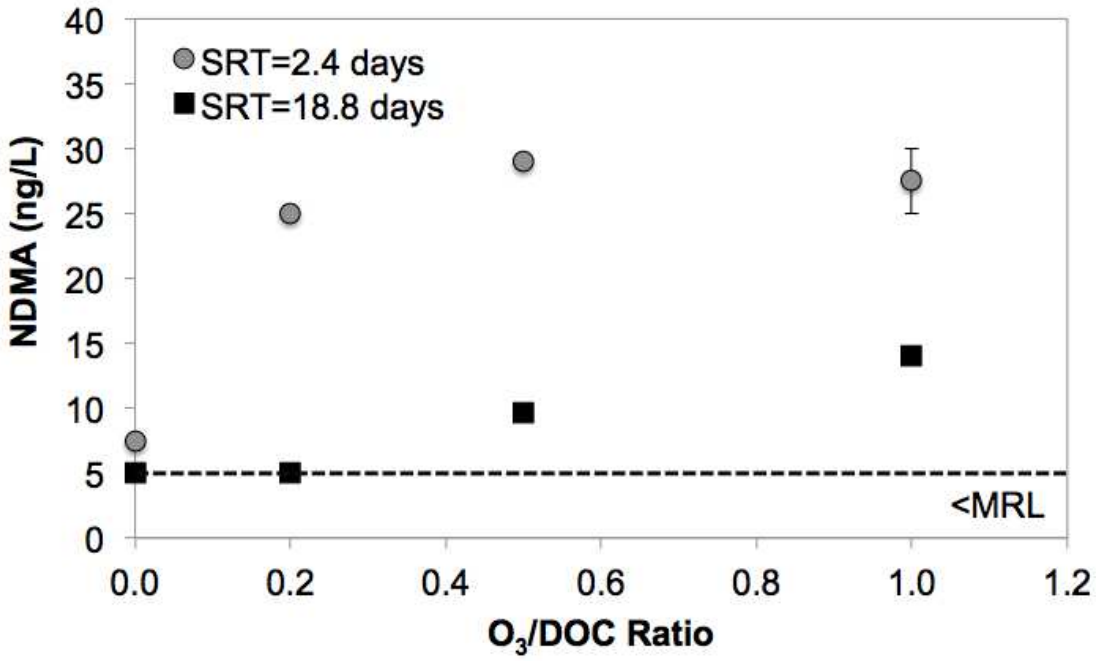


Figure 6. NDMA formation as a function of solids retention time during biological pretreatment and O_3/DOC ratio in the Site J2 pilot. Error bars indicate the minimum and maximum concentrations from duplicate samples.



- NDMA and NMOR were the most prevalent nitrosamines at the 11 study sites
- NMEA and NDEA were detected at one facility each; NDPrA and NDBA were always <MRL
- Ozone-induced NDMA formation ranged from <10 to 143 ng/L
- Ozone-induced NDMA formation was lower in nitrified wastewater and at O_3/DOC <0.5
- Biodegradation was effective for NDMA and NMOR mitigation

Supplementary Information

Nitrosamines in Pilot-Scale and Full-Scale Wastewater Treatment Plants with Ozonation

Running Title: Nitrosamines in Large-Scale Ozone Systems

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List of Abbreviations

AFU	Arbitrary fluorescence units
AOP	Advanced oxidation process
ASPE	Automated solid phase extraction
BAC	Biological activated carbon
BOD	Biochemical oxygen demand
CA	California
COD	Chemical oxygen demand
DCM	Dichloromethane
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EBCT	Empty bed contact time
EEM	Excitation emission matrix
EfOM	Effluent organic matter
EPA	Environmental Protection Agency
GA	Georgia
KY	Kentucky
MBR	Membrane bioreactor
MDL	Method detection limit
MF	Microfiltration
MGD	Million gallons per day
MO	Missouri
MRL	Method reporting limit

MRM	Multiple reaction monitoring
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
NTU	Nephelometric turbidity units
NV	Nevada
PAC	Powdered activated carbon
QLD	Queensland
RO	Reverse osmosis
RSD	Relative standard deviation
SRT	Solids retention time
SUVA	Specific UV_{254} absorbance
TF	Total fluorescence
TKN	Total Kjeldahl Nitrogen
TN	Total nitrogen
TOC	Total organic carbon

TON	Total oxidized nitrogen (i.e., NO_2^- + NO_3^-)
TP	Total phosphorus
TSS	Total suspended solids
TX	Texas
UF	Ultrafiltration
U.S.	United States
UV	Ultraviolet

Text S1. Full-Scale Site A (MO)

The average daily flow at Site A (MO) is approximately 30 million gallons per day (mgd). During wet weather events, excess flows are bypassed to a 43 million gallon holding tank, while peak flows are discharged to nearby surface water after coagulant addition and clarification. During normal flow conditions, wastewater is treated with trash racks, bar screens, aerated grit chambers, primary clarifiers, and parallel biological treatment systems (i.e., Train #1 and Train #2). Train #1 includes alum addition for chemical phosphorus removal, oxygenation tanks (solids retention time (SRT) = 2-3 days), secondary clarifiers, nitrification tanks (SRT = 30+ days), tertiary clarifiers, and denitrifying mixed media filters. Train #2 includes conventional activated sludge (SRT = 18-20 days) with nitrification and biological phosphorus removal, alum addition for chemical phosphorus removal, secondary clarifiers, and sand filters. The parallel flows then recombine prior to ozone disinfection at an average dose of 6 mg/L, which corresponds to an ozone to dissolved organic carbon (O_3/DOC) ratio of approximately 1.0-1.2. The finished effluent is discharged to a nearby surface water. The facility also includes solids handling processes, including anaerobic digesters and dewatering centrifuges with polymer addition. Centrate and digester supernatant are combined with primary effluent for repeated biological treatment. Any residual polymer in the return flow is expected to be degraded biologically, and no additional polymer is used in the clarifiers prior to ozonation. The treatment train is illustrated in Figure S1, and nitrosamine sampling locations are indicated by the colored circles, which are defined in Table S1.

For Site A, preliminary sampling for method development was performed in October 2011, and a second sampling event was conducted in May 2012. The average water quality for the facility is summarized in Table S2. Data characterizing the effluent organic matter (EfOM)

for the October 2011 and May 2012 sampling events are summarized in Tables S3 and S4, respectively. The nitrosamine summaries for the October 2011 and May 2012 sampling events are provided in Tables S5 and S6, respectively.

Table S1. Sampling locations for Site A (MO)

Sample	Description
1	Primary Influent
2	Primary Effluent
3	Secondary Effluent
4	Combined Ozone Influent
5	Ozone Effluent
6	Field Blank

Figure S1. Treatment train schematic and sampling locations for Site A (MO)

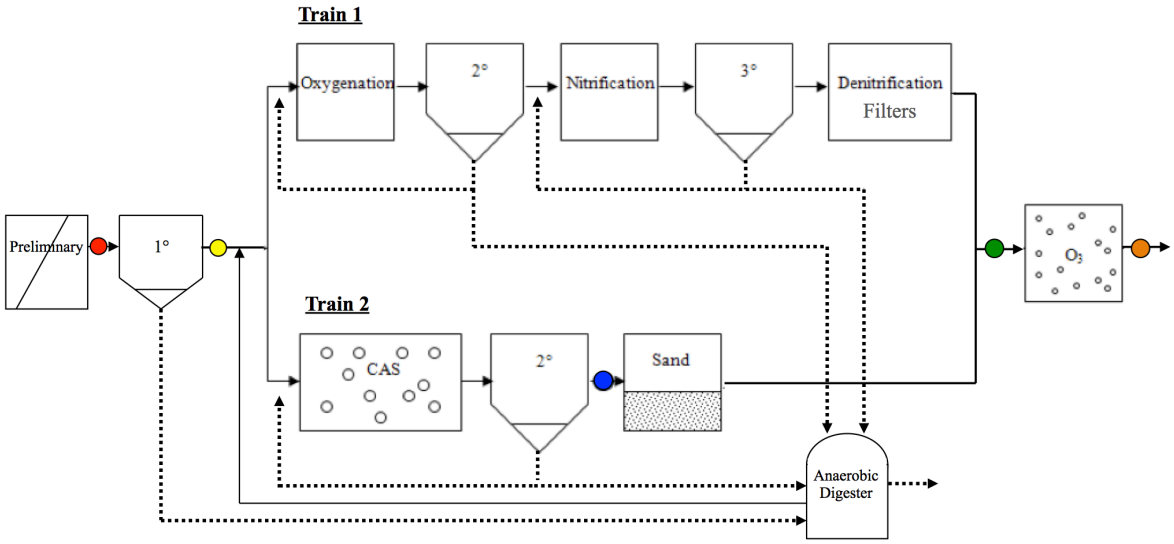


Table S2. Water quality data for Site A (MO) (October 2011)

Parameter	Primary Influent	Primary Effluent	Secondary Effluent (Plant 2)	Combined Ozone Influent	Ozone Effluent
TKN (mg/L)	34.1	N/A	N/A	N/A	< 0.03
NH_3 (mg-N/L)	20.4	20.9	< 0.1	N/A	< 0.1
TN (mg/L)	N/A	25	10	11	12
BOD (mg/L)	N/A	N/A	N/A	N/A	3
TSS (mg/L)	284	200	4	N/A	< 1
pH	7.28	7.48	7.67	N/A	7.87
TP (mg/L)	3.75	N/A	N/A	N/A	0.45

*N/A = Not Available

Table S3. EfOM Characterization Data for Site A (MO) (October 2011)

Parameter	Primary Influent	Primary Effluent	Secondary Effluent (Plant 2)	Combined Ozone Influent	Ozone Effluent	Field Blank
UV_{254} (cm^{-1})	N/A	0.201	0.134	0.116	0.059	< 0.002
UV_{280} (cm^{-1})	N/A	0.148	0.108	0.091	0.039	< 0.002
DOC (mg/L)	N/A	45	5.7	4.9	N/A	N/A
TOC (mg/L	N/A	N/A	N/A	N/A	4.8	< 0.2
SUVA (L/mg-m)	N/A	0.447	2.35	2.37	1.23	N/A
TN (mg/L)	N/A	25	10	11	12	< 0.2
TF (AFU)	N/A	73,516	37,513	28,782	4,546	93
Region 1 (AFU)	N/A	40,786	14,767	10,298	1,269	66
Region 2 (AFU)	N/A	26,081	16,964	13,746	2,398	20
Region 3 (AFU)	N/A	6,649	5,782	4,748	878	7

*N/A = Not Available

Figure S2. Qualitative comparison of EEMs for Site A (MO) (October 2011)

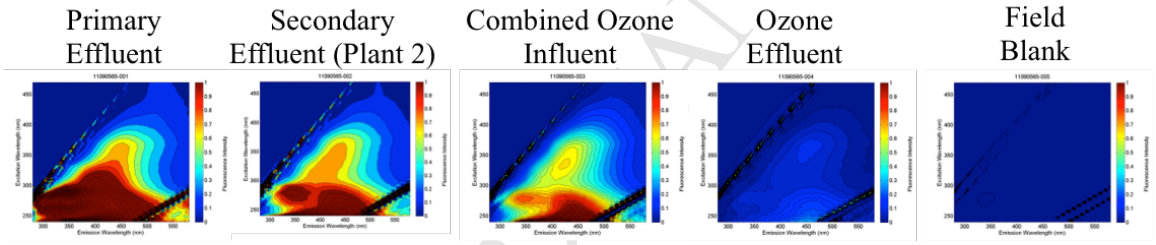


Table S4. EfOM characterization for Site A (MO) (May 2012)

Parameter	Primary Influent	Primary Effluent	Secondary Effluent (Plant 2)	Combined Ozone Influent	Ozone Effluent	Field Blank
UV_{254} (cm^{-1})	0.231	0.210	0.112	0.108	0.066	<0.002
UV_{280} (cm^{-1})	0.172	0.155	0.084	0.081	0.043	< 0.002
DOC (mg/L)	44	19	6.7	5.8	N/A	N/A
TOC (mg/L)	N/A	N/A	N/A	N/A	6.1	0.33
SUVA (L/mg-cm)	0.525	1.11	1.67	1.86	1.08	N/A
TN (mg/L)	19	15	9.3	10	11	< 0.2
TF (AFU)	58,749	53,937	26,185	23,525	5,675	153
Region 1 (AFU)	34,912	30,184	10,509	8,885	1,920	89
Region 2 (AFU)	19,098	18,899	11,813	10,962	2,786	48
Region 3 (AFU)	4,738	4,854	3,862	3,678	969	17

*N/A = Not Applicable

Figure S3. Qualitative comparison of EEMs for Site A (MO) (May 2012)

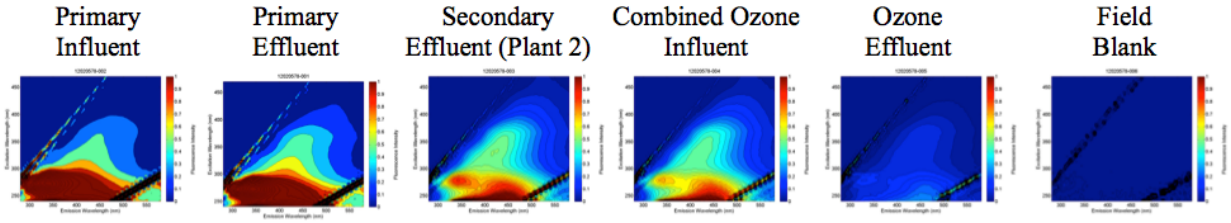


Table S5. Nitrosamines data for Site A (MO) (October 2011)

Nitrosamine	Primary Influent	Primary Effluent	Secondary Effluent (Plant 2)	Combined Ozone Influent	Ozone Effluent	Field Blank
NDMA (ng/L)	N/A	< 25	11	12	26	< 2.5
NMEA (ng/L)	N/A	< 25	< 5.0	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	N/A	< 50	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	N/A	< 100	< 20	< 20	< 20	< 10
NMOR (ng/L)	N/A	< 50	12	12	< 10	< 5.0
NDBA (ng/L)	N/A	< 100	< 20	< 20	< 20	< 10

*N/A = Not Available

Table S6. Nitrosamines data for Site A (MO) (May 2012)

Nitrosamine	Primary Influent	Primary Effluent	Secondary Effluent (Plant 2)	Combined Ozone Influent	Ozone Effluent	Field Blank
NDMA (ng/L)	< 25	< 25	7.8	6.3	14	< 2.5
NMEA (ng/L)	< 25	< 25	< 5.0	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	< 50	< 50	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	< 100	< 100	< 20	< 20	< 20	< 10
NMOR (ng/L)	65	58	22	23	22	< 5.0
NDBA (ng/L)	< 100	< 100	< 20	< 20	< 20	< 10

Text S2. Full-Scale Site B (KY)

The average daily flow at Site B (KY) is 9.9 mgd. The treatment train includes grit removal, an oxidation ditch with nitrification and partial denitrification (SRT = N/A), clarification, and ozone disinfection at an average dose of 3.3 mg/L, which corresponds to an ozone to total organic carbon (O_3/TOC) ratio of approximately 0.9. The final effluent is discharged to a nearby surface water. Solids handling processes include sludge thickening, two-stage anaerobic digesters, and sludge drying beds. Digester supernatant is returned to the process flow prior to biological treatment in the oxidation ditch.

Table S7. Sampling locations for Site B (KY)

Sample	Description
1	Preliminary Effluent
2	Clarifier Effluent
3	Ozone Effluent
4	Digester Supernatant
5	Field Blank

Figure S4. Treatment train schematic and sampling locations for Site B (KY)

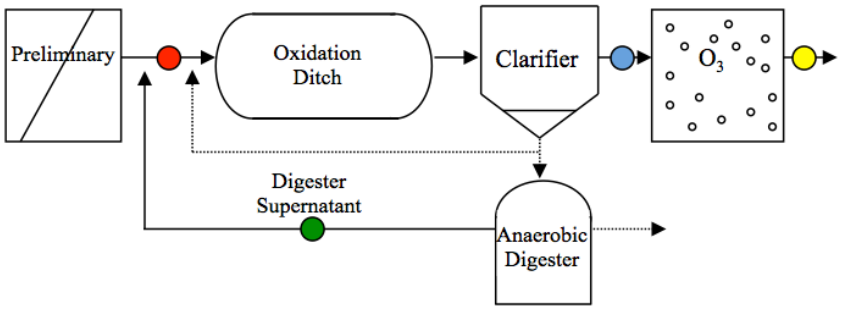


Table S8. Water quality data for Site B (KY) (March 2012)

Parameter	Plant Influent	Preliminary Effluent	Clarifier Effluent	Ozone Effluent	Digester Supernatant
pH	7.00	N/A	N/A	7.68	N/A
NH_3 (mg-N/L)	73	N/A	N/A	0.3	N/A
TN (mg/L)	N/A	18	4.0	4.4	14
TSS (mg/L)	297	N/A	N/A	14.8	N/A
COD (mg/L)	442	N/A	N/A	30	N/A
TP (mg/L)	3.52	N/A	N/A	0.52	N/A
Turbidity (NTU)	N/A	N/A	N/A	3.1	N/A

*N/A = Not Available

Table S9. EfOM characterization for Site B (KY) (March 2012)

Parameter	Preliminary Effluent	Clarifier Effluent	Ozone Effluent	Digester Supernatant	Field Blank
UV_{254} (cm^{-1})	0.195	0.076	0.044	0.767	0.002
UV_{280} (cm^{-1})	0.140	0.057	0.027	0.629	< 0.002
DOC (mg/L)	25	N/A	N/A	30	N/A
TOC (mg/L)	N/A	3.6	3.6	N/A	<0.2
SUVA (L/mg-m)	0.78	2.11	1.22	2.56	N/A
TN (mg/L)	18	4.0	4.4	14	< 0.2
TF (AFU)	58,752	18,145	4,031	296,028	51
Region 1 (AFU)	31,649	4,810	1,105	162,251	16
Region 2 (AFU)	21,661	9,766	2,123	112,372	28
Region 3 (AFU)	5,442	3,570	803	21,405	7

*N/A = Not Applicable

Figure S5. Qualitative comparison of EEMs for Site B (KY) (March 2012)

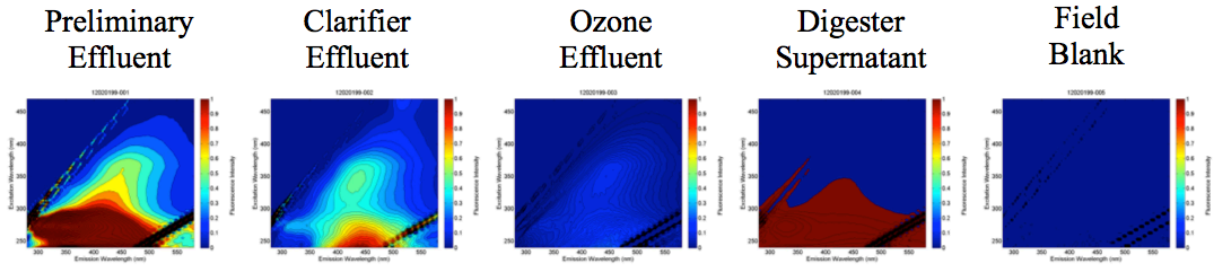


Table S10. Nitrosamines data for Site B (KY) (March 2012)

Nitrosamine	Preliminary Effluent	Clarifier Effluent	Ozone Effluent	Digester Supernatant	Field Blank
NDMA (ng/L)	25	< 5.0	5.2	< 5.0	< 2.5
NMEA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	< 50	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	< 100	< 20	< 20	< 20	< 10
NMOR (ng/L)	67	21	20	13	< 5.0
NDBA (ng/L)	< 100	< 20	< 20	< 20	< 10

Text S3. Full-Scale Site C (TX)

The average daily flow at Site C is approximately 12 mgd. The treatment train includes bar screens, grit removal, primary clarifiers, biological treatment with two-stage activated sludge, lime clarification (pH = 11), two-stage recarbonation (pH = 9.3 then 7.3), sand filtration, ozonation (O_3 = 1.0-1.3 mg/L; O_3/TOC = 0.3), and biological activated carbon (BAC). The first stage of the activated sludge process includes aeration and nitrification (SRT = 10 days), a supplemental powdered activated carbon (PAC) feed, and clarification. The second stage achieves denitrification (SRT = 36 days) with methanol as the carbon source, and the denitrified effluent is clarified again prior to lime addition. The carbon in the BAC process is approximately 10 years old, and the process is operated with a 16-minute empty bed contact time (EBCT). The finished effluent is injected into the local aquifer. Anaerobic digesters are used for processing of primary solids.

Table S11. Sampling locations for Site C (TX)

Sample	Description
1	Primary Effluent
2	Tertiary Clarifier Effluent
3	Filter Effluent
4	Ozone Effluent
5	BAC Effluent
6	Field Blank

Figure S6. Treatment train schematic and sampling locations for Site C (TX)

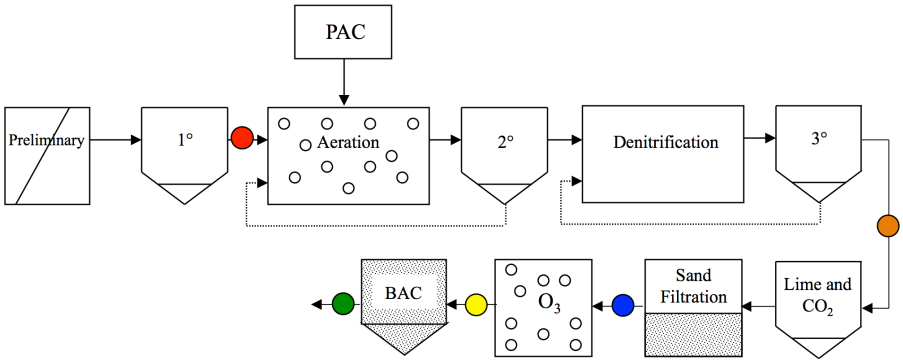


Table S12. EfOM characterization for Site C (TX) (October 2012)

Parameter	Primary Effluent	Tertiary Clarifier Effluent	Sand Filter Effluent	Ozone Effluent	BAC Effluent	Field Blank
UV_{254} (cm^{-1})	0.277	0.103	0.067	0.040	0.035	< 0.002
UV_{280} (cm^{-1})	0.205	0.080	0.051	0.026	0.024	< 0.002
DOC (mg/L)	38	3.6	N/A	N/A	N/A	N/A
TOC (mg/L)	N/A	N/A	3.6	3.1	2.3	< 0.2
SUVA (L/mg-m)	0.73	2.86	1.86	1.29	1.52	N/A
TN (mg/L)	37	2.6	4.5	4.1	4.0	< 0.2
TF (AFU)	108,758	25,489	17,911	N/A	5,015	18
Region 1 (AFU)	66,905	9,111	6,851	N/A	1,729	4
Region 2 (AFU)	33,137	11,842	7,999	N/A	2,415	11
Region 3 (AFU)	8,716	4,536	3,060	N/A	870	2

*N/A = Not Applicable

Figure S7. Qualitative comparison of EEMs for Site C (TX) (October 2012)

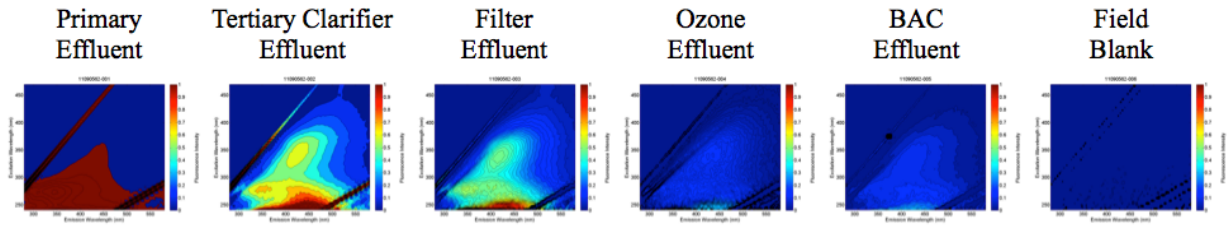


Table S13. Nitrosamines data for Site C (TX) (October 2012)

Nitrosamine	Primary Effluent	Tertiary Clarifier Effluent	Sand Filter Effluent	Ozone Effluent	BAC Effluent	Field Blank
NDMA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 5.0	< 2.5
NMEA (ng/L)	< 25	< 5.0	< 5.0	6.3	7.6	< 2.5
NDEA (ng/L)	< 50	< 10	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 10
NMOR (ng/L)	< 50	< 10	< 10	< 10	< 10	< 5.0
NDBA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 10

Text S4. Full-Scale Site D (GA)

The average daily flow at Site D is 42.5 mgd. The treatment train includes bar screens; grit removal; primary clarifiers; activated sludge (SRT = 11 days) with nitrification, denitrification, and biological phosphorus removal; secondary clarifiers, and lime clarification. The flow is then split between the original train, which employs recarbonation and dual-media filtration, and the new train with strainers and ultrafiltration (UF) membranes. The water recombines for pre-ozonation (O_3 = 1.0-1.5 mg/L; O_3/DOC = 0.2-0.3), BAC, and post-ozonation (O_3 = 1.0-1.5 mg/L; O_3/TOC = 0.2-0.4). The BAC process is operated with a 15-minute EBCT, and the carbon is approximately 6-8 years old. The final effluent is discharged to a nearby surface water. The facility also employs anaerobic digesters and dewatering centrifuges.

Table S14. Sampling locations for Site D (GA)

Sample	Description
1	Primary Effluent
2	Secondary Effluent
3	Pre-ozone Influent
4	Pre-ozone Effluent
5	BAC Effluent
6	Post-ozone Effluent
7	Field Blank

Figure S8. Treatment train schematic and sampling locations for Site D (GA)

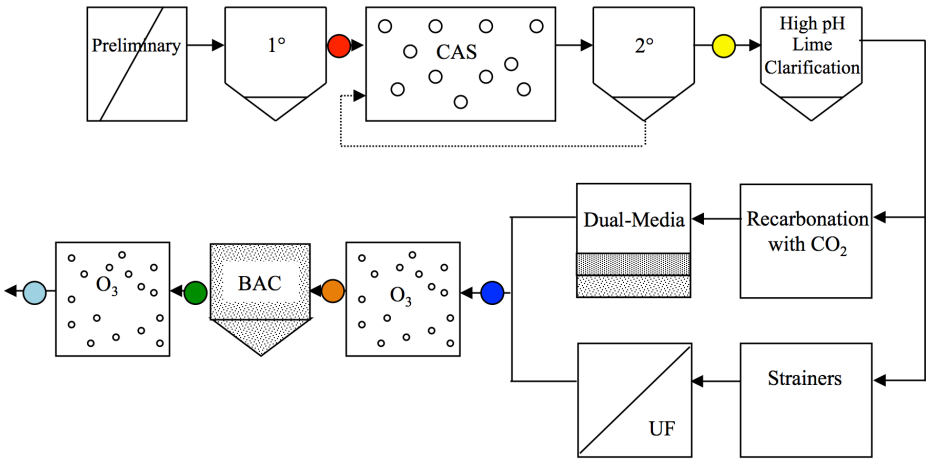


Table S15. EfOM characterization for Site D (GA) (February 2012)

Parameter	Primary Effluent	Secondary Effluent	Pre-ozone Influent	Pre-ozone Effluent	BAC Effluent	Post-ozone Effluent	Field Blank
UV_{254} (cm^{-1})	0.372	0.115	0.107	0.082	0.070	0.047	< 0.002
UV_{280} (cm^{-1})	0.282	0.092	0.084	0.061	0.052	0.032	< 0.002
DOC (mg/L)	42	5.3	5.0	N/A	N/A	N/A	N/A
TOC (mg/L)	N/A	N/A	N/A	5.0	4.1	3.8	< 0.2
SUVA (L/mg-m)	0.886	2.17	2.14	1.64	1.75	1.24	N/A
TN (mg/L)	44	16	15	15	15	15	< 0.2
TF (AFU)	150,942	32,412	30,324	14,356	11,957	3,931	47
Region 1 (AFU)	94,084	11,351	10,590	5,052	4,333	1,436	21
Region 2 (AFU)	46,139	15,133	14,200	6,626	5,420	1,769	18
Region 3 (AFU)	10,719	5,928	5,533	2,678	2,204	725	7

*N/A = Not Applicable

Figure S9. Qualitative comparison of EEMs for Site D (GA) (February 2012)

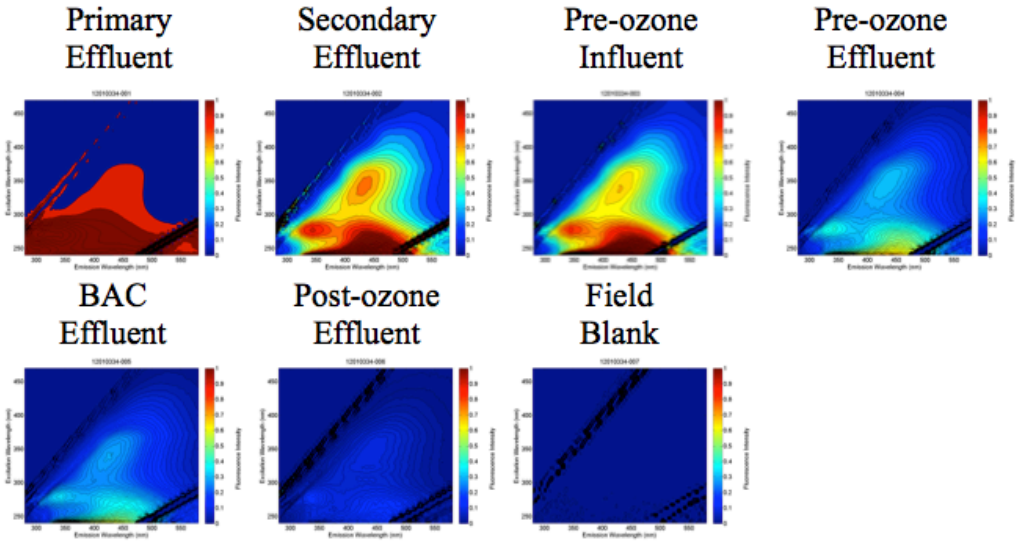


Table S16. Nitrosamines data for Site D (GA) (February 2012)

Nitrosamine	Primary Effluent	Secondary Effluent	Pre-ozone Influent	Pre-ozone Effluent	BAC Effluent	Post-ozone Effluent	Field Blank
NDMA (ng/L)	42	6.8	5.9	9.2	< 5.0	< 5.0	< 5.0
NMEA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
NDEA (ng/L)	< 50	< 10	< 10	< 10	< 10	< 10	< 10
NDPrA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 20	< 20
NMOR (ng/L)	< 50	< 10	< 10	< 10	< 10	< 10	< 10
NDBA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 20	< 20

Text S5. Full-Scale Site E (GA)

The average daily flow at this site is 5.5 mgd, and a large fraction of the incoming wastewater is industrial discharge from a denim mill with a pH of 10.5-11. The treatment train includes preliminary treatment with aeration and pH adjustment to 7.8-8.0 with sulfuric acid, biological treatment with extended aeration (SRT = N/A), polymer addition, clarification, and ozonation (O_3 = 28-32 mg/L; O_3/DOC = 1.0-1.2) for color removal and disinfection. The finished effluent is discharged to a nearby surface water.

Table S17. Sampling locations for Site E (GA)

Sample	Description
1	Preliminary Effluent
2	Clarifier Effluent
3	Ozone Effluent
4	Field Blank

Figure S10. Treatment train schematic and sampling locations for Site E (GA)

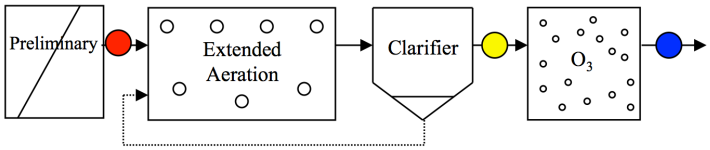


Table S18. Water quality data for Site E (GA) (April 2012)

Parameter	Preliminary Effluent	Ozone Effluent
BOD (mg/L)	311	7.54
TSS (mg/L)	660	6
PO_4 (mg-P/L)	N/A	2.81
TP (mg/L)	N/A	9.56
NH_3 (mg-N/L)	N/A	0.14
TN (mg/L)	47	21
pH	N/A	7.53
DO (mg/L)	N/A	16.25

*N/A = Not Available or Applicable

Table S19. EfOM characterization for Site E (GA) (April 2012)

Parameter	Preliminary Effluent	Clarifier Effluent	Ozone Effluent	Field Blank
UV_{254} (cm^{-1})	1.35	0.376	0.278	< 0.002
UV_{280} (cm^{-1})	0.989	0.313	0.208	< 0.002
DOC (mg/L)	120	25	28	N/A
TOC (mg/L)	N/A	N/A	N/A	< 0.2
SUVA (L/mg-m)	1.13	1.50	0.99	N/A
TN (mg/L)	47	23	21	< 0.2
TF (AFU)	721,172	133,133	56,241	12
Region 1 (AFU)	372,194	51,937	27,015	9
Region 2 (AFU)	306,663	64,438	22,139	3
Region 3 (AFU)	42,314	16,758	7,087	0

*N/A = Not Applicable

Figure S11. Qualitative comparison of EEMs for Site D (GA) (April 2012)

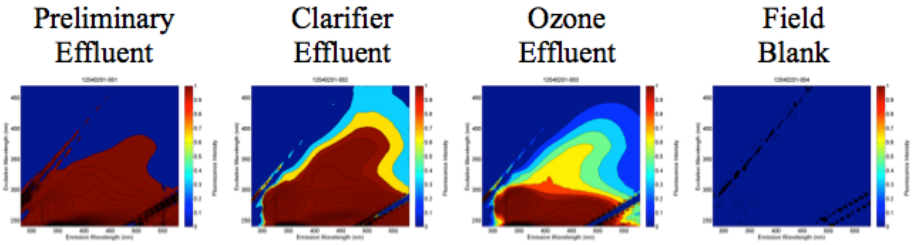


Table S20. Nitrosamines data for Site E (GA) (April 2012)

Nitrosamine	Preliminary Effluent	Clarifier Effluent	Ozone Effluent	Field Blank
NDMA (ng/L)	89	72	85	< 2.5
NMEA (ng/L)	< 25	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	< 50	20	19	< 5.0
NDPrA (ng/L)	< 100	< 20	< 20	< 10
NMOR (ng/L)	< 50	< 10	< 10	< 5.0
NDBA (ng/L)	< 100	< 20	< 20	< 10

Text S6. Full-Scale Site F (QLD)

Site F (QLD) is an advanced treatment facility that receives approximately 2 mgd of nitrified secondary effluent (SRT = 16 days) from a nearby wastewater treatment plant. The advanced treatment train includes denitrification with methanol addition, pre-ozonation (O_3 = 2 mg/L; O_3/DOC = 0.2), alum and polymer addition, dissolved air flotation, sand filtration, ozonation (O_3 = 5 mg/L; O_3/TOC = 0.6-0.8), BAC (EBCT = 18 min), and post-ozonation (O_3 = 2 mg/L; O_3/TOC = 0.5) for final disinfection (Reungoat et al., 2010; Reungoat et al., 2012). The finished effluent is discharged to a nearby surface water.

Table S21. Sampling locations for Site F (QLD)

Sample	Description
1	Primary Effluent
2	Secondary Effluent
3	Denitrification Effluent
4	Pre-Ozone Effluent
5	Flotation/Filtration Effluent
6	Ozone Effluent
7	BAC Effluent
8	Post-Ozone Effluent
9	Field Blank

Figure S12. Treatment train schematic and sampling locations for Site F (QLD)

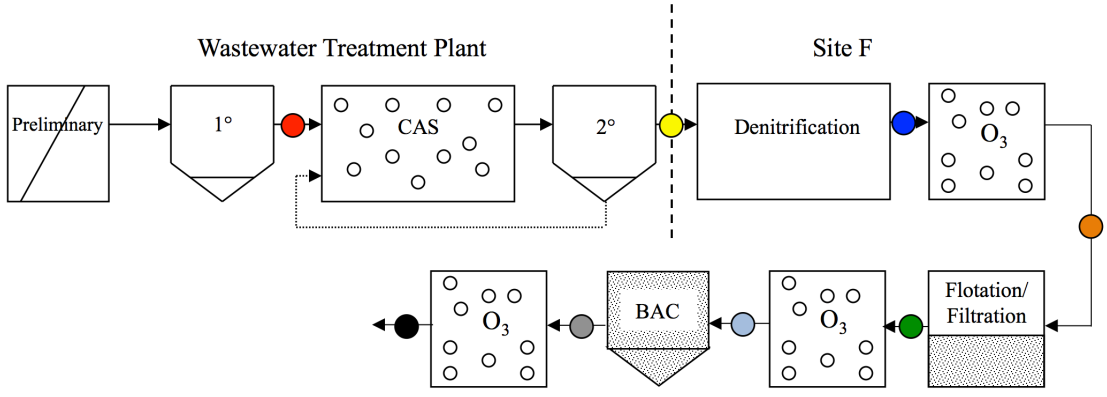


Table S22. EfOM characterization for Site F (QLD) (May 2012)

Parameter	Primary Effluent	Secondary Effluent	Denit. Effluent	Pre-ozone Effluent	Filter Effluent	Ozone Effluent	BAC Effluent	Post-ozone Effluent	Field Blank
UV_{254} (cm^{-1})	0.587	0.221	0.214	0.204	0.131	0.088	0.059	0.046	< 0.002
UV_{280} (cm^{-1})	0.463	0.170	0.162	0.155	0.099	0.061	0.042	0.030	< 0.002
DOC (mg/L)	100	10	9.5	N/A	N/A	N/A	N/A	N/A	N/A
TOC (mg/L)	N/A	N/A	N/A	9.8	6.6	6.0	4.1	4.0	< 0.2
SUVA (L/mg-m)	0.587	2.21	2.25	2.08	1.98	1.47	1.44	1.15	N/A
TN (mg/L)	46	9.5	3.6	3.7	4.0	4.2	4.1	4.2	< 0.2
TF (AFU)	390,541	74,079	74,931	N/A	44,981	18,658	7,735	3,599	226
Region 1 (AFU)	195,545	25,173	26,795	N/A	16,225	7,190	2,629	1,229	145
Region 2 (AFU)	160,613	35,996	35,272	N/A	20,127	8,179	3,597	1,679	67
Region 3 (AFU)	35,383	12,910	12,864	N/A	8,630	3,289	1,508	691	14

*N/A = Not Available or Applicable

Figure S13. Qualitative comparison of EEMs for Site F (QLD) (May 2012)

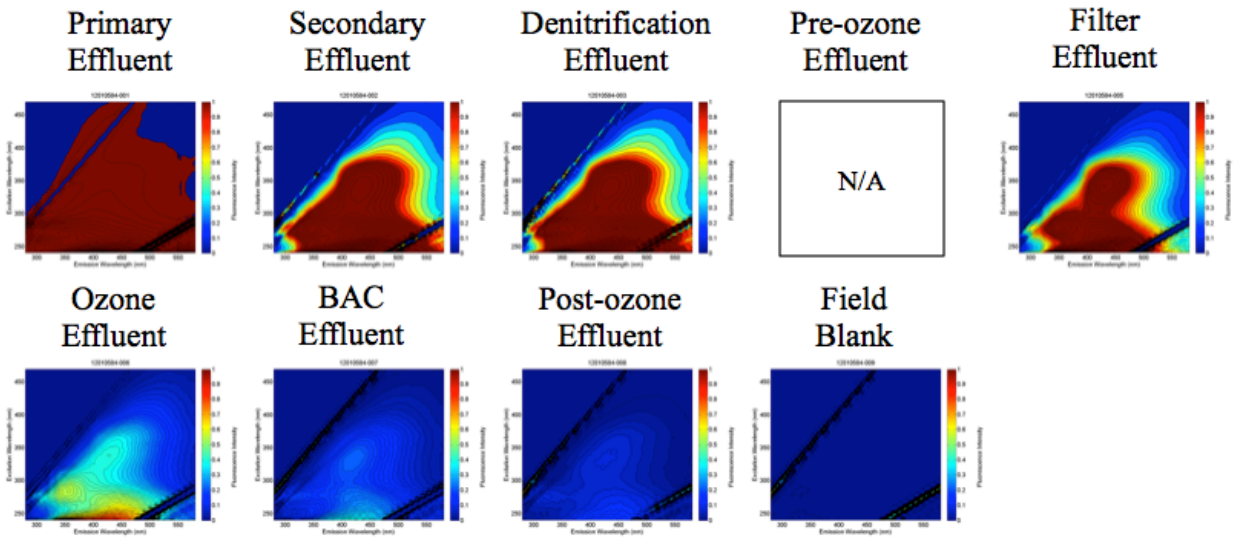


Table S23. Nitrosamines data for Site F (QLD) (May 2012)

Parameter	Primary Effluent	Secondary Effluent	Denit. Effluent	Pre-ozone Effluent	Filter Effluent	Ozone Effluent	BAC Effluent	Post-ozone Effluent	Field Blank
NDMA (ng/L)	< 25	< 5.0	< 5.0	5.4	5.2	11	< 5.0	< 5.0	< 25
NMEA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	< 50	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 10
NMOR (ng/L)	< 50	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 5.0
NDBA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 10

Text S7. Full-Scale Site G (CA)

The average daily flow at Site G is 70 mgd, but it is currently being expanded to accommodate a total flow of 100 mgd. This facility receives nitrified/denitrified secondary effluent (combination of trickling filters and activated sludge; SRT = 5.5 days) from a nearby wastewater treatment plant and provides advanced treatment with microfiltration (MF), reverse osmosis (RO), an advanced oxidation process (AOP) consisting of ultraviolet irradiation and hydrogen peroxide (UV/H_2O_2), and product water stabilization. The finished effluent from Site G is either discharged to spreading basins or directly injected into the groundwater aquifer. The solids handling processes at the wastewater treatment plant include anaerobic digesters and belt filter presses, although the belt filter presses will soon be replaced with dewatering centrifuges. The digester supernatant and filtrate (soon to be centrate) are returned upstream of the primary clarifiers for repeated treatment. Polymer is also added at the headworks, primary clarifiers, and belt filter presses. With respect to this study, the MF influent had been dosed with chloramine upstream of the sampling location so the corresponding nitrosamine concentrations may be a combination of ambient levels and subsequent formation.

Table S24. Sampling locations for Site G (CA)

Sample	Description
1	MF Influent
2	MF Effluent
3	RO Permeate
4	RO Concentrate
5	UV/H_2O_2 Effluent
6	Field Blank

Figure 14. Treatment train schematic and sampling locations for Site G (CA)

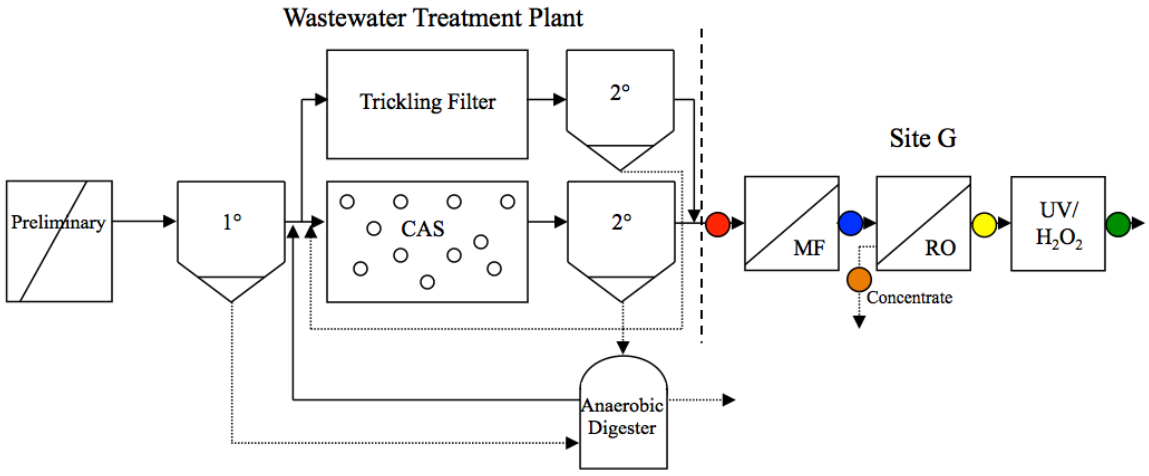


Table S25. EfOM characterization for Site G (CA) (October 2011)

Parameter	MF Influent	MF Effluent	RO Permeate	RO Concentrate	UV/H_2O_2 Effluent	Field Blank
UV_{254} (cm^{-1})	0.153	0.125	0.007	0.696	0.004	< 0.002
UV_{280} (cm^{-1})	0.112	0.087	0.004	0.501	< 0.002	< 0.002
DOC (mg/L)	6.4	N/A	N/A	N/A	N/A	N/A
TOC (mg/L)	N/A	6.0	< 0.2	33	< 0.2	< 0.2
SUVA (L/mg-m)	2.39	2.08	N/A	2.11	N/A	N/A
TN (mg/L)	11	11	1.1	61	1.2	< 0.2
TF (AFU)	33,466	28,739	46	275,877	40	22
Region 1 (AFU)	12,729	9,941	9	100,027	5	4
Region 2 (AFU)	15,310	13,562	40	143,646	33	15
Region 3 (AFU)	5,427	5,236	51	32,204	2	3

*N/A = Not Applicable

Figure S15. Qualitative comparison of EEMs for Site G (CA) (October 2011)

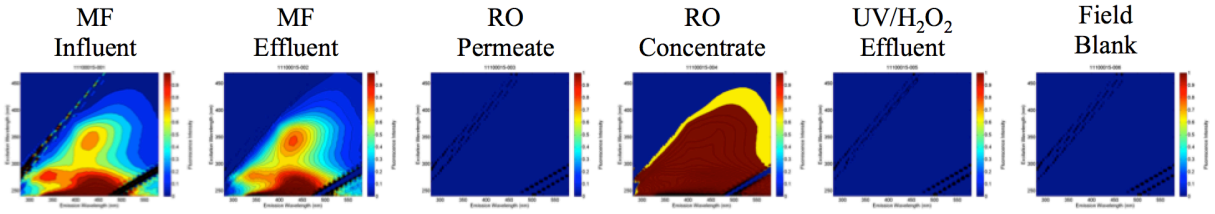


Table S26. Nitrosamines data for Site G (CA) (October 2011)

Nitrosamine	MF Influent	MF Effluent	RO Permeate	RO Concentrate	UV/H_2O_2 Effluent	Field Blank
NDMA (ng/L)	16	42	20	100	< 2.5	< 2.5
NMEA (ng/L)	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
NDEA (ng/L)	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
NDPrA (ng/L)	< 10	< 10	< 10	< 10	< 10	< 10
NMOR (ng/L)	6.9	7.5	< 5.0	18	< 5.0	< 5.0
NDBA (ng/L)	< 10	< 10	< 10	< 10	< 10	< 10

Text S8. Pilot-Scale Site H (CA)

The average daily flow at Site H is approximately 30 mgd, but only 12.5 mgd is treated with full advanced treatment (i.e., RO-UV/H_2O_2). The advanced treatment facility receives non-nitrified secondary effluent (pure oxygen; SRT = 1.5 days) from a nearby wastewater treatment plant. Due to the limited upstream biological treatment, Site H recently upgraded its facility with ozonation to mitigate organic fouling on the MF membranes. The advanced treatment facility now includes ozone, MF, RO, UV/H_2O_2, and product water stabilization prior to direct injection of the finished effluent into the groundwater aquifer. Figure S16 illustrates the original and upgraded full-scale treatment trains. The solids handling processes at the wastewater treatment plant include anaerobic digesters and dewatering centrifuges with polymer addition. The digester supernatant and centrate are combined with the primary effluent for repeated biological treatment.

Prior to the ozone upgrade, Site H operated parallel pilot-scale treatment trains to quantify the net benefits of preozonation on membrane fouling. Both 22-gpm treatment trains included MF (Pall Corp., Port Washington, NY) and RO (Hydranautics, Oceanside, CA), but the experimental treatment train also included upstream ozonation (Ozonia, Leonia, NJ; O_3 = 4.4-11.7 mg/L; O_3/TOC = 0.3-1.5). To control biological fouling, sodium hypochlorite was dosed immediately upstream of the each set of MF membranes to achieve a total chlorine residual of 3-5 mg/L as Cl_2. Recall that the matrix is non-nitrified secondary effluent so residual ammonia is always present. Samples were collected from pilot-scale versions of the treatment processes depicted in Figure S16 to evaluate the potential impacts of ozonation on NDMA in the finished effluent. The sampling locations are summarized in Table S27. Of the target nitrosamines, only NDMA was monitored during the pilot-scale study.

Table S27. Sampling locations for Site H (CA)

Sample	Description
1	Secondary Effluent
2	Ozone Effluent
3	Ozone MF Filtrate
4	Ozone RO Permeate
5	MF Filtrate
6	RO Permeate

Figure S16. Treatment train schematic and sampling locations for Site H (CA)

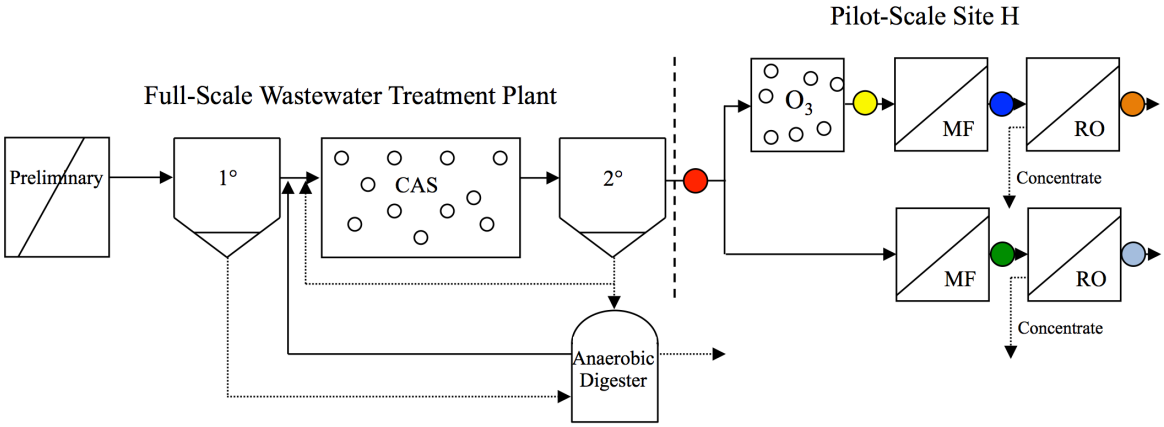


Table S28. EfOM characterization for pilot treatment train at Site H (CA) (July - October 2011)

Parameter	July Secondary Effluent	July Ozone Effluent	August Secondary Effluent	August Ozone Effluent	September Secondary Effluent	September Ozone Effluent	October Secondary Effluent	October Ozone Effluent
UV_{254} (cm^{-1})	0.211	0.138	0.364	0.209	0.192	0.158	0.212	0.162
UV_{280} (cm^{-1})	0.166	0.092	0.295	0.161	0.144	0.120	0.160	0.114
TOC (mg/L)	12.5	N/A	11.5	N/A	12.3	N/A	11.8	N/A
SUVA (L/mg-m)	1.69	N/A	3.17	N/A	1.56	N/A	1.80	N/A
TF (AFU)	142,724	26,376	239,104	26,413	128,806	62,457	123,057	52,219
Region 1 (AFU)	62,355	9,804	101,099	9,509	51,083	27,243	51,439	23,164
Region 2 (AFU)	63,176	12,623	115,245	13,262	59,522	27,050	57,332	23,025
Region 3 (AFU)	17,192	3,949	22,760	3,643	18,171	8,163	14,286	6,030

*N/A = Not Available

Figure S17. Qualitative comparison of EEMs for Site H (CA) (July - October 2011)

Note: The arbitrary fluorescence scale (i.e., AFU) ranges from 0.0 to 5.0 in each of these EEMs. Previous EEMs for other sites ranged from 0.0 to 1.0. Therefore, these samples are more 'concentrated' than they appear.

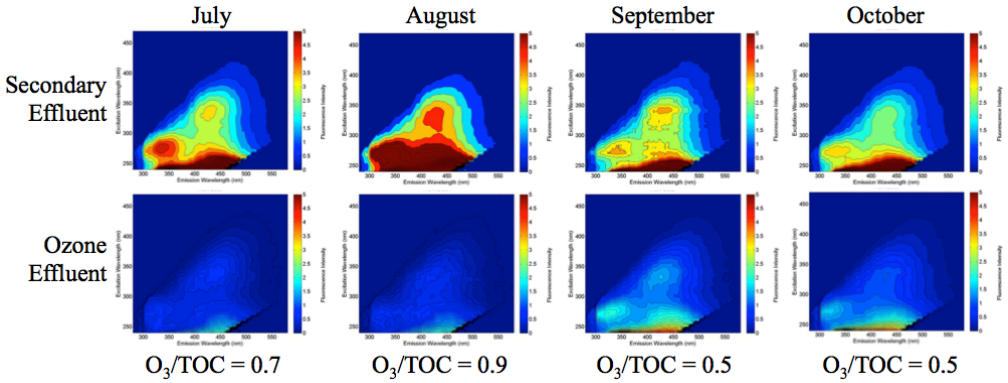


Figure S18. NDMA concentrations at Site H (CA) as a function of influent UV_{254} absorbance. These data represent samples collected weekly from late April 2011 to early November 2011.

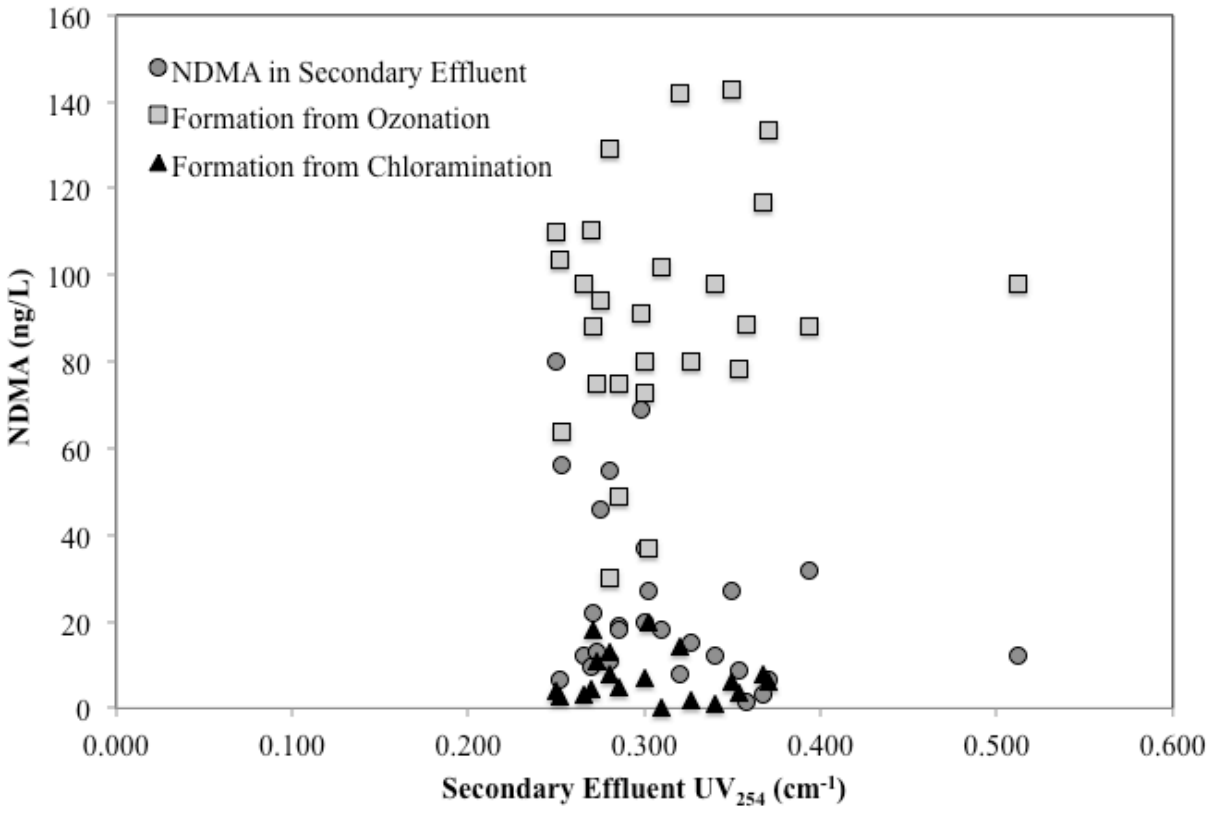
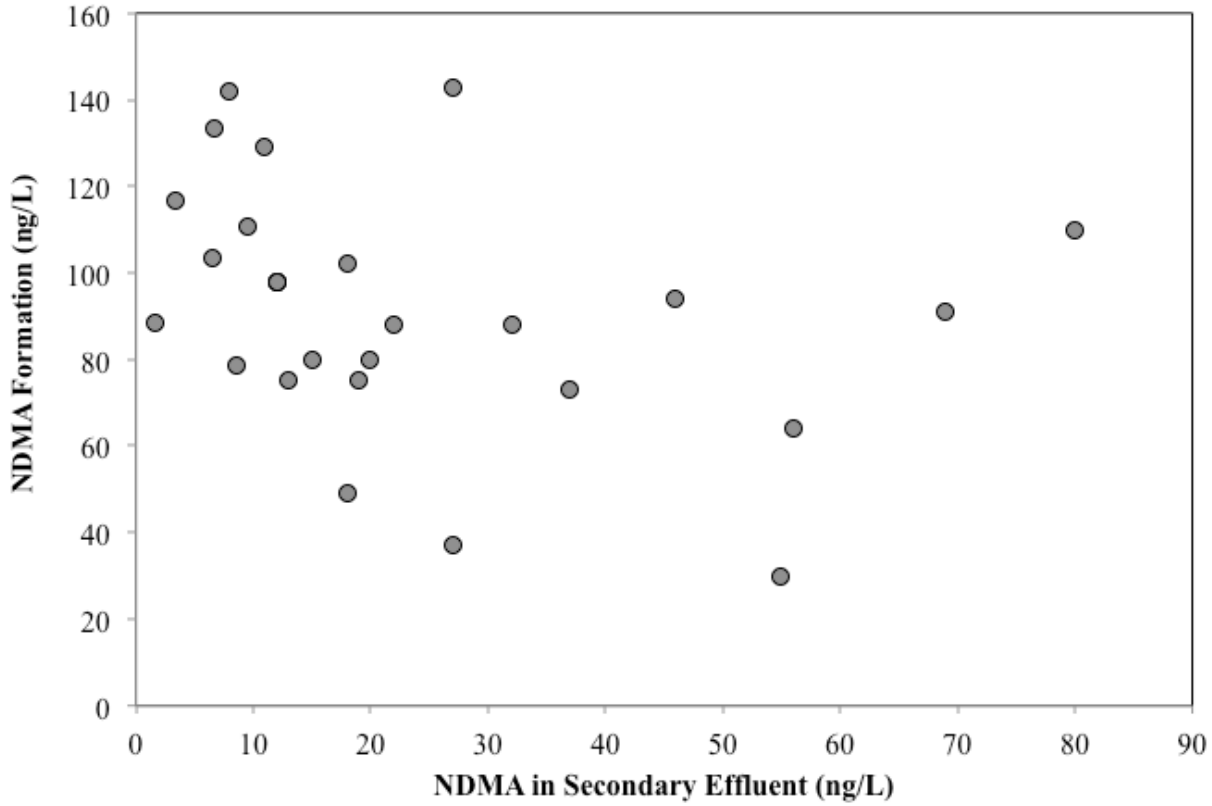


Figure S19. Ozone-induced NDMA formation at Site H (CA) as a function of ambient NDMA. These data represent samples collected weekly from late April 2011 to early November 2011.



Text S9. Full-Scale Site I (NV)

The average daily flow at Site I is 100 mgd. The treatment train includes bar screens; grit removal; ferric chloride and polymer addition; primary clarifiers; activated sludge (SRT = 7 days) with nitrification, denitrification, and biological phosphorus removal; and secondary clarifiers. A portion of the flow is then treated with alum addition, dual-media filters, and UV disinfection (40 mJ/cm^2) prior to discharge to a nearby surface water. The remainder of the flow is treated with alum addition, flocculation, tertiary clarifiers, dual-media filters, and either UV disinfection (40 mJ/cm^2) for surface water discharge or sodium hypochlorite for irrigation applications. Solids handling processes include ferric chloride addition, sludge storage tanks, dissolved air flotation thickeners, and dewatering centrifuges. The centrate is recombined with the primary effluent for repeated biological treatment.

Table S29. Sampling locations for Site I (NV)

Sample	Description
1	Primary Effluent
2	Secondary Effluent
3	Filter Effluent
4	Chlorinated Effluent
5	UV Effluent
6	Field Blank

Figure S20. Treatment train schematic and sampling locations for Site I (NV)

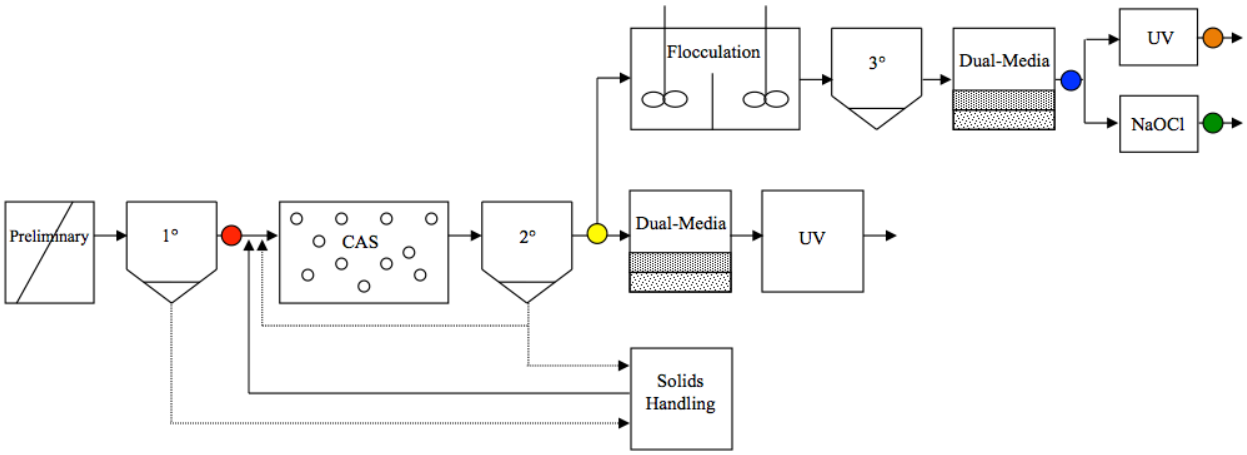


Table S30. Water Quality Data for Site I (NV) (March 2012)

Parameter	Primary Effluent	Secondary Effluent	Chlorinated Effluent	UV Effluent
TSS (mg/L)	106	9	0	0
BOD (mg/L)	196	2	0	0
PO_4 (mg-P/L)	2.33	0.052	0.016	0.014
TP (mg/L)	4.52	0.37	0.058	0.060
NH_3 (mg-N/L)	27	0.05	0	0
TN (mg/L)	30	13	14	13

Table S31. EfOM characterization for Site I (NV) (March 2012)

Parameter	Primary Effluent	Secondary Effluent	Filter Effluent	Chlorinated Effluent	UV Effluent	Field Blank
UV_{254} (cm^{-1})	0.401	0.128	0.118	0.093	0.116	< 0.002
UV_{280} (cm^{-1})	0.307	0.097	0.090	0.061	0.090	< 0.002
DOC (mg/L)	59	7.0	N/A	N/A	N/A	N/A
TOC (mg/L)	N/A	N/A	5.8	5.8	5.8	< 0.2
SUVA (L/mg-m)	0.680	1.83	2.03	1.60	2.00	N/A
TN (mg/L)	30	13	13	14	13	< 0.2
TF (AFU)	140,716	37,039	30,639	11,450	30,537	1,186
Region 1 (AFU)	84,235	14,750	10,661	4,980	10,478	904
Region 2 (AFU)	46,672	16,060	14,403	4,831	14,451	235
Region 3 (AFU)	9,809	6,229	5,575	1,639	5,608	46

*N/A = Not Applicable

Figure S21. Qualitative comparison of EEMs for Site I (NV) (March 2012)

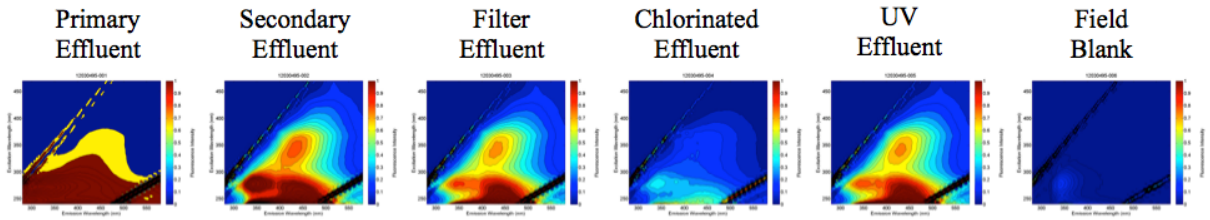


Table S32. Nitrosamines data for Site I (NV)

Nitrosamine	Primary Effluent	Secondary Effluent	Filter Effluent	Chlorinated Effluent	UV Effluent	Field Blank
NDMA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 5.0	< 2.5
NMEA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	< 50	< 10	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 10
NMOR (ng/L)	< 50	11	13	11	< 10	< 5.0
NDBA (ng/L)	< 100	< 20	< 20	< 20	< 20	< 10

Text S10. Full-Scale Site J1 (NV)

The average daily flow at Site J1 is 75 mgd, which is split between two treatment trains. Both treatment trains share bar screens, grit removal, and ferric chloride addition, and then the first treatment train continues with ferric chloride addition, primary clarifiers, trickling filters, secondary clarifiers, activated sludge with nitrification (SRT = 6-8 days), and tertiary clarifiers. After grit removal and ferric chloride addition, the second treatment train continues with primary clarifiers; activated sludge (SRT = 6-8 days) with nitrification, denitrification, and biological phosphorus removal; and secondary clarifiers. The flows then recombine for alum addition, media filtration, and sodium hypochlorite. The finished effluent is either discharged to a nearby surface water or used for irrigation applications. Solids handling processes include gravity thickeners, sludge holding tanks, anaerobic digesters, and dewatering centrifuges. Digester supernatant and centrate are returned to the headworks for repeated treatment.

Table S33. Sampling locations for Site J1 (NV)

Sample	Description
1	Primary Effluent
2	Secondary Effluent
3	Filter Effluent
4	Chlorinated Effluent
5	Field Blank

Figure S22. Treatment train schematic and sampling locations for Site J1 (NV)

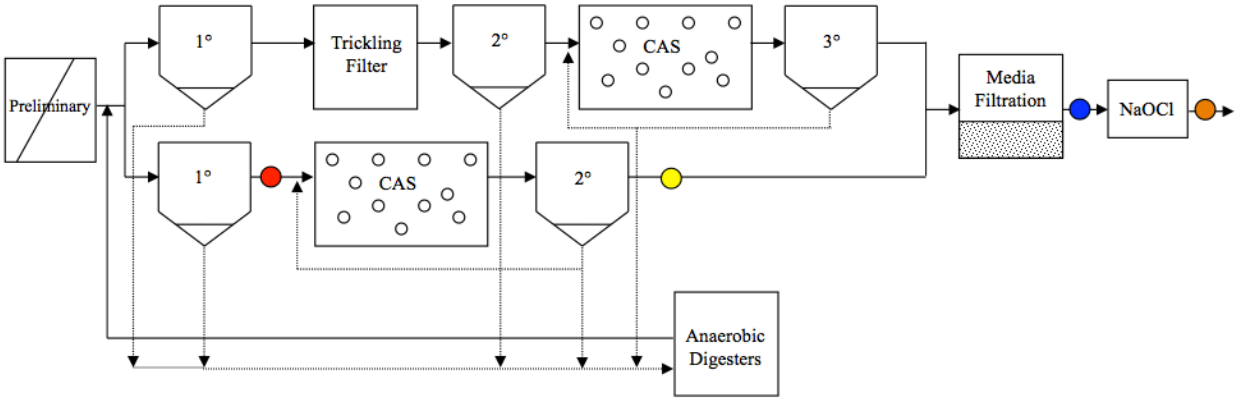


Table S34. Water quality data for Site J1 (NV) (March 2012)

Parameter	Secondary Effluent	Filter Effluent	Chlorinated Effluent
TSS (mg/L)	126	3.6	< 2
BOD (mg/L)	181	6	<2
PO_4 (mg-P/L)	2.37	0.10	0.19
TP (mg/L)	4.17	0.20	0.24
Alkalinity (mg/L $CaCO_3$)	252	111	106
NH_3 (mg-N/L)	N/A	0.3	< 0.1
TON (mg-N/L)	N/A	14.4	22.2
TKN (mg-N/L)	N/A	7.6	1.0
TN (mg/L)	15	22	20

*N/A = Not Applicable

Table S35. EfOM characterization for Site J1 (NV) (March 2012)

Parameter	Primary Effluent	Secondary Effluent	Filter Effluent	Chlorinated Effluent	Field Blank
UV_{254} (cm^{-1})	0.372	0.133	0.134	0.101	< 0.002
UV_{280} (cm^{-1})	0.292	0.099	0.102	0.067	< 0.002
DOC (mg/L)	31	7.7	N/A	N/A	N/A
TOC (mg/L)	N/A	N/A	6.9	6.9	< 0.2
SUVA (L/mg-m)	1.20	1.73	1.94	1.46	N/A
TN (mg/L)	34	15	22	20	< 0.2
TF (AFU)	73,310	20,313	20,324	8,896	99
Region 1 (AFU)	43,629	7,718	7,470	3,937	75
Region 2 (AFU)	24,453	9,124	9,289	3,716	19
Region 3 (AFU)	5,227	3,472	3,565	1,243	5

*N/A = Not Applicable

Figure S23. Qualitative comparison of EEMs for Site J1 (NV) (March 2012)

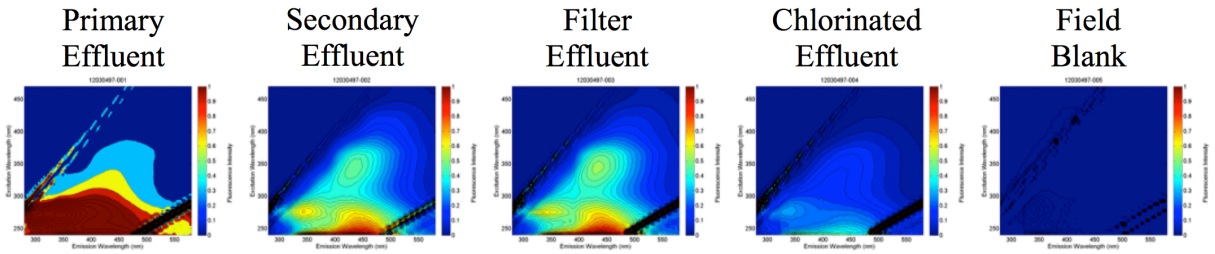


Table S36. Nitrosamines data for Site J1 (NV)

Nitrosamine	Primary Effluent	Secondary Effluent	Filter Effluent	Chlorine Effluent	Field Blank
NDMA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 2.5
NMEA (ng/L)	< 25	< 5.0	< 5.0	< 5.0	< 2.5
NDEA (ng/L)	< 50	< 10	< 10	< 10	< 5.0
NDPrA (ng/L)	< 100	< 20	< 20	< 20	< 10
NMOR (ng/L)	< 50	11	< 10	< 10	< 5.0
NDBA (ng/L)	< 100	< 20	< 20	< 20	< 10

Text S11. Pilot-Scale Site J2 (NV)

Site J2 treated primary effluent from full-scale Site J1 (described earlier) with a 22-gpm pilot-scale membrane bioreactor (MBR; Hydranautics). The MBR was operated at SRTs ranging from 2-20 days to simulate BOD removal and nitrification/denitrification. The MBR filtrate was then split between parallel 10-gpm trains. The control train included RO only (Hydranautics), and the experimental train, which was used to quantify the net benefits of preozonation on membrane fouling, included ozone (HiPOx, APTwater, Pleasant Hill, CA; O_3/DOC = 0.0-1.0) and RO (Hydranautics). For this study, nitrosamine samples were only collected from the MBR filtrate and the ozone effluent, but general water quality data are also provided for the MBR influent in Tables S38.

Table S37. Sampling locations for Site J2 (NV)

Sample	Description
1	MBR Filtrate
2	Ozone Effluent
3	Field Blank

Figure S24. Treatment train schematic and sampling locations for Site J2 (NV)

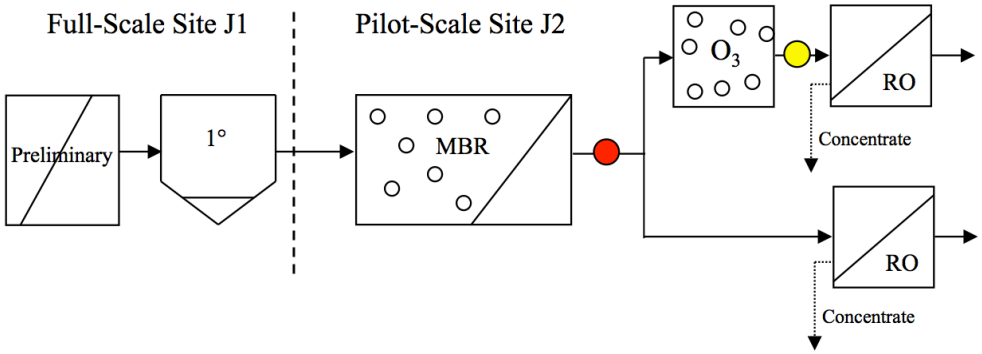


Table S38. Water quality data for Site J2 (NV)

Parameter (units)	MBR Influent[a]	Filtrate SRT=2.4 d	Filtrate SRT=18.8 d	Field Blank
COD (mg/L)	275	54	<20	N/A
BOD (mg /L)	124	<2	<2	N/A
PO_4 (mg/L)	2.32	0.10	0.09	N/A
TP (mg/L)	3.57	0.30	0.12	N/A
NH_3 (mg-N/L)	27	22	2.6	N/A
TON (mg-N/L)	< 0.2	< 0.2	7.8	N/A
TKN (mg-N/L)	35	N/A	3.1	N/A
TN (mg/L)	35	19	13	<0.2

[a] Average values from pilot operation from April 2012 to February 2013

Table S39. EfOM characterization for Site J2 (NV) with SRT = 2.4 days

Parameter (units)	O_3/DOC 0.00	0.20	0.50	1.00	Field Blank
UV_{254} (cm^{-1})	0.108	0.063	0.051	0.044	< 0.002
UV_{280} (cm^{-1})	0.083	0.040	0.030	0.025	< 0.002
DOC (mg/L)	4.7	4.7	4.5	4.3	< 0.2
SUVA (L/mg-m)	2.30	1.34	1.13	1.02	N/A
TN (mg/L)	19	19	19	20	< 0.2
TF (AFU)	9,544	1,855	1,083	691	4.2
Region 1 (AFU)	1,670	269	133	63	0.4
Region 2 (AFU)	3,109	674	402	260	2.3
Region 3 (AFU)	4,765	912	548	368	1.6

Table S40. EfOM characterization for Site J2 (NV) with SRT = 18.8 days

Parameter (units)	O_3/DOC 0.00	0.20	0.50	1.00	Field Blank
UV_{254} (cm^{-1})	0.103	0.091	0.066	0.050	< 0.002
UV_{280} (cm^{-1})	0.078	0.064	0.041	0.030	< 0.002
DOC (mg/L)	5.2	5.2	5.2	6.3	< 0.2
SUVA (L/mg-m)	1.98	1.74	1.26	0.787	N/A
TN (mg/L)	13	15	14	13	< 0.2
TF (AFU)	8,226	4,340	1,858	836	N/A
Region 1 (AFU)	1,500	858	298	103	N/A
Region 2 (AFU)	2,662	1,484	649	295	N/A
Region 3 (AFU)	4,063	1,998	911	439	N/A

Figure S25. Qualitative comparison of EEMs for the MBR filtrate from Site J2 (NV). Each image reflects a different O_3/DOC ratio for an SRT of either 2.4 days (i.e., BOD removal mode) or 18.8 days (i.e., nitrification/denitrification mode).

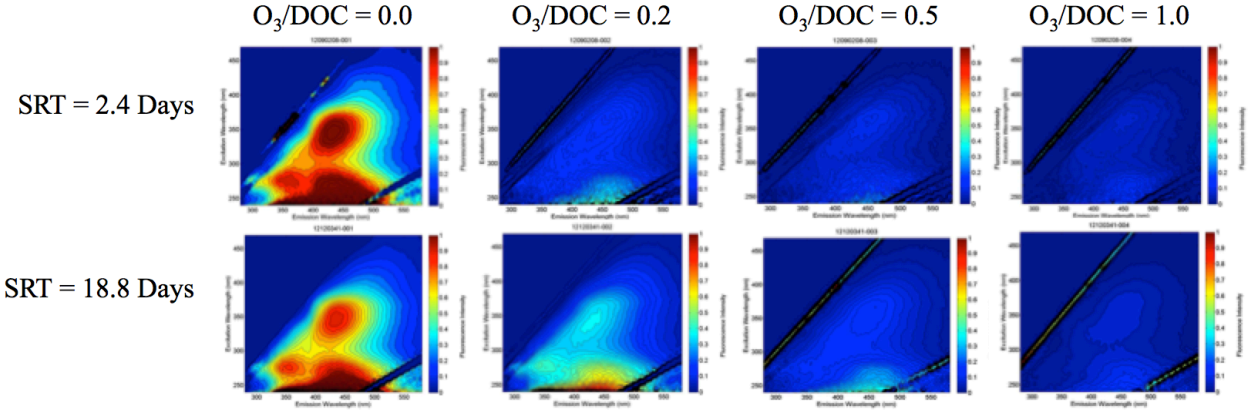


Table S41. Nitrosamines data for Site J2 (NV)

Nitrosamine	SRT = 2.4 days				SRT = 18.8 days			
	O_3/DOC				O_3/DOC			
	0.00	0.20	0.50	1.00	0.00	0.20	0.50	1.00
NDMA (ng/L)	7.4	25	29	28	< 5.0	< 5.0	9.7	14
NMEA (ng/L)	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
NDEA (ng/L)	11	< 10	< 10	< 10	< 10	< 10	< 10	< 10
NDPrA (ng/L)	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
NMOR (ng/L)	< 10	11	< 10	< 10	< 10	< 10	< 10	< 10
NDBA (ng/L)	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20

Text S12. Analytical Methods

Nitrosamine analysis was performed with isotope dilution using a modified version of United States (U.S.) Environmental Protection Agency (EPA) method 521 (Holady et al., 2012). Matrix interference resulted in unreliable quantification for NPYR and NPIP, particularly in primary effluent, and NDPhA proved to be unstable over the 14-day holding period (see Table S42). Therefore, monitoring efforts were limited to NDMA, NMEA, NDEA, NDPrA, NMOR, and NDBA. Corresponding isotopes, precursor and product ions used for quantitation and confirmation, molecular weights, and method reporting limits (MRLs) are summarized in Table S43. Matrix-specific MRLs are also listed in the preceding summary tables.

Table S42. Summary of results from 14-day nitrosamine holding study. Triplicate samples were spiked with approximately 1 µg/L of each target nitrosamine.

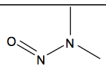
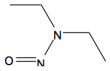
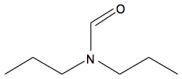
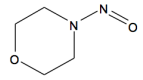
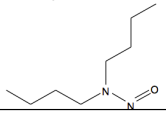
Nitrosamine	Deionized Water			Primary Effluent		
	0 Days	7 Days	14 Days	0 Days	7 Days	14 Days
NDMA	930±20[a]	893±35	937±25	953±31	877±6	897±35
NMEA	983±21	1000±0	997±6	957±38	973±25	953±57
NDEA	1003±87	877±59	957±67	890±20	813±32	830±27
NDPrA	920±10	953±6	1000±100	910±20	870±36	893±179
NMOR	947±76	990±17	930±0	887±29	840±10	860±46
NDBA	1017±144	880±10	900±12	870±105	787±29	810±53
NDPhA	937±47	213±12	<100±0	853±76	233±21	<100±0

[a] ±1 standard deviation based on triplicate spiked samples

Automated solid phase extraction (ASPE) was performed using a Dionex AutoTrace workstation (Thermo Scientific, Sunnyvale, CA, USA). Samples were spiked with 100 µL of isotope mix at 0.5-2.5 mg/L for a final concentration of 100-500 µg/L in the final extract. Pre-packed activated carbon cartridges (Resprep 521, Restek, Bellefonte, PA, USA) were sequentially conditioned with 5 mL of dichloromethane (DCM), 5 mL of methanol, and 10 mL of reagent grade water with flow rates of 15 mL/min. Samples were loaded at a rate of 15 mL/min. Cartridges were rinsed with 5 mL of reagent grade water with a flow rate of 20 mL/min

and dried for 10 min with nitrogen gas. Analytes were eluted with 10 mL of DCM into 15 mL conical vials (Dionex) with a flow rate of 5 mL/min. Extracts were evaporated under nitrogen gas to approximately 2 mL. Water was then removed from the DCM extracts by passing the 2 mL extract through a DryDisk separation membrane (Horizon Technology, Salem, NH, USA). The DCM extract was collected and concentrated to a final volume of 500 µL with nitrogen gas, resulting in a 1:2000 concentration factor.

Table S43. Target nitrosamines and corresponding isotopes.

Nitrosamine	CAS#	Structure	Isotope	MW (amu)	Precursor Ion (m/z)	Product Ion (m/z)	MRL[b] (ng/L)
N-nitrosodimethylamine (NDMA)	62-75-9		NDMA-d_6	74	75	47 (44, 43, 58) [a]	5.0
N-nitrosomethylethylamine (NMEA)	10595-95-6		NMEA-d_3	88	89	61 (47)	5.0
N-nitrosodiethylamine (NDEA)	55-18-5		NDEA-d_{10}	102	103	75	10
N-nitrosodipropylamine (NDPrA)	621-64-7		NDPrA-d_{14}	130	131	89	20
N-nitrosomorpholine (NMOR)	59-89-2		NMOR-d_8	116	117	86 (87)	10
N-nitrosodibutylamine (NDBA)	924-16-3		NDBA-d_{18}	158	159	103	20

[a] ( ) – confirmation product ions
[b] MRL for all matrices except primary effluent (5x higher for each nitrosamine) and Site G (lower MRLs due to reduced matrix interference; see site-specific summaries in SI)

A Varian (Walnut Creek, CA) CP-3800 Gas Chromatograph with a CP-8400 auto sampler was used for all analyses. The injector (Varian 1177) was operated in splitless mode with a Siltek™ deactivated glass liner (Restek, Bellefonte, PA) and set at a temperature of 200°C. Analytes were separated on a 30 m x 0.32 mm ID x 1.4 µm DB624 column (J & W, Agilent, Palo Alto, CA) using a 1.4 mL/min helium flow with an initial pressure pulse of 35 psi for 0.85

min. The temperature program was as follows: 35°C, hold for 1.0 min; 35-120°C at 5°C/min; 120-145°C at 3°C/min; 145-250°C at 35°C/min, hold for 4.64 min. An injection volume of 2 µL was used for all analyses. The transfer line was set at 240°C.

Analysis was performed using a Varian 4000 ion trap mass spectrometer (Walnut Creek, CA). All analyses were performed using multiple reaction monitoring (MRM) in positive chemical ionization mode using liquid methanol. Some of the nitrosamines did not exhibit a second product ion in sufficient abundance for transition confirmation and therefore only have one quantitation transition. Due to thermal degradation upon injection, NDPhA was analyzed as diphenylamine during the 14-day holding study. MRLs were established at 3 to 5 times the calculated method detection limit (MDL) (n=12). A field blank was collected for each sampling event, extracted, and analyzed. A laboratory reagent blank was also included in each extract batch. Acceptable average percent recoveries were limited to 70-130%, and acceptable relative standard deviations (RSDs) were limited to 30% for replicate samples. Average percent recoveries and RSDs in reagent water, finished drinking water, surface water, and tertiary wastewater effluent are summarized in Table S44.

Table S44. Average recovery and relative standard deviations (RSDs) for target nitrosamines (spiked at 25 ng/L) in various water matrices (n=6).

Nitrosamine	Reagent Water		Drinking Water		Surface Water		Tertiary Wastewater	
	Average %	RSD %	Average %	RSD %	Average %	RSD %	Average %	RSD %
NDMA	114	4.0	117	3.2	117	0.9	136	2.1
NMEA	99	3.1	98	1.5	101	2.1	99	2.8
NDEA	98	6.2	104	6.2	97	5.0	101	5.7
NDPrA	109	10	82	9.9	105	7.3	78	10
NMOR	107	7.2	100	6.8	101	4.6	109	9.8
NDBA	105	6.8	98	9.1	95	7.7	47	5.7
NDPhA[1]	84	6.1	87	5.9	89	2.8	105	4.9

[1] Eliminated from target compound list after 14-day holding study

Trace analysis grade methanol and DCM were obtained from Burdick and Jackson (Muskegon, MI, USA). Sodium azide was purchased from Fisher Chemicals (Fisher Scientific, Fair Lawn, NJ, USA), and sodium thiosulfate was purchased from EM Science (Merck KGaA, Darnstadt, Germany). Reagent grade water was prepared by using a Milli-Q Gradient water purification system (Millipore, Billerica, MA, USA). Nitrosamine standards were purchased from Ultra Scientific (Kingstown, RI, USA), whereas isotopically labeled nitrosamines were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Working stock solutions of nitrosamines and isotopically labeled nitrosamines were made in DCM. Appropriate dilutions were made in methanol for ASPE spiking solutions (i.e., nitrosamine spike mix and isotopically labeled standards). Calibration standards (minimum of seven ranging from 1.0 to 500 µg/L) were made in DCM and were replaced every three months. All stock solutions, ASPE spiking solutions, and calibration standards were stored at -20 °C.

The quantification of subtle differences in the EEMs involved the use of the FRI method (Chen et al., 2003), which was modified and described previously (Gerrity et al., 2011; Stanford et al., 2011). The FRI concept uses specific regions of the EEM to identify (and quantify) specific organic matter fractions. The EEM integration included three regions representing (I) microbial byproducts, proteins, and biopolymers; (II) fulvic-like substances; and (III) humic-like substances. These regions are defined in Table S45 and illustrated in Figure 26.

Table S45. Fluorescence region definitions

Region	Excitation/Emission Range	Description
I	$EX_{240-300}/Em_{280-390}$	Microbial byproducts, proteins, biopolymers
II	$EX_{240-300}/Em_{390-580}$	Fulvic-like compounds
III	$EX_{300-470}/Em_{317-580}$	Humic-like compounds

Figure S26. Illustration of fluorescence regions