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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · APRIL 2009

Impact Factor: 5.33 · DOI: 10.1021/es802443t

Article

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Environ. Sci. Technol., **2009**, 43 (8), 2911-2918• DOI: 10.1021/es802443t • Publication Date (Web): 12 March 2009

Environ. Sci. Technol. **2009,** *43,* 2911–2918

Impact of Wastewater Treatment Processes on Organic Carbon, Organic Nitrogen, and DBP Precursors in Effluent Organic Matter

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Received September 3, 2008. Revised manuscript received February 3, 2009. Accepted February 5, 2009.

Unintentional, indirect wastewater reuse often occurs as wastewater treatment plant (WWTP) discharges contaminate receiving waters serving as drinking-water supplies. A survey was conducted at 23 WWTPs that utilized a range of treatment technologies. Samples were analyzed for typical wastewater and drinking-water constituents, chemical characteristics of the dissolved organic matter (DOM), and disinfection byproduct (DBP) precursors present in the effluent organic matter (EfOM). This was the first large-scale assessment of the critical water quality parameters that affect the formation of potential carcinogens during drinking water treatment relative to the discharge of upstream WWTPs. This study considered a large and wide range of variables, including emerging contaminants rarely studied at WWTPs and never before in one study. This paper emphasizes the profound impact of nitrification on many measures of effluent water quality, from the obvious wastewater parameters (e.g., ammonia, biochemical oxygen demand) to the ones specific to downstream drinking water treatment plants (e.g., formation potentials for a diverse group of DBPs of health concern). Complete nitrification reduced the concentration of biodegradable dissolved organic carbon (BDOC) and changed the ratio of BDOC/DOC. Although nitrification reduced ultraviolet absorbance (UVA) at 254 nm, it resulted in an increase in specific UVA (UVA/DOC). This is attributed to preferential removal of the less UV-absorbing (nonhumic) fraction of the DOC during biological treatment. EfOM is composed of hydrophilic and biodegradable DOM, as well as hydrophobic and recalcitrant DOM, whose proportions change with advanced biological treatment. The onset of nitrification yielded lower precursor levels for haloacetic acids and nitrogenous DBPs (haloacetonitriles, *N*-nitrosodimethylamine). However, trihalomethane precursors were relatively unaffected by the level of wastewater treatment. Thus, one design/operations parameter in wastewater treatment, the decision to have a long enough solids retention time to get reliable nitrification, affected much beyond its immediate goal of ammonium oxidation.

Introduction

In addition to intentional water recycling and reclamation programs, indirect unintentional potable reuse of wastewater has often occurred over the past century (*1*), and it will likely increase in the future as upstream wastewater treatment plants (WWTPs) discharge water into rivers or lakes that serve as downstream drinking-water sources. Indirect potable reuse can be defined as occurring in any watershed for a drinking water treatment plant (DWTP) that contains point-source discharges of wastewater; septic tanks adjacent to rivers or impoundments also may alter the quality of the surface water. It is not uncommon to have a substantial portion of the source water for these DWTPs originally derived from the upstream wastewater contribution (*2*). Although attention of late has focused on effluent-derived organic micropollutants such as pharmaceuticals and endocrine disruptors (*3*), WWTPs are also sources of disinfection byproducts (DBPs), if chlorine/chloramine disinfection is practiced, and DBP precursors.

Biological wastewater treatment takes one of two general forms: suspended growth (biofloc) systems (e.g., activated sludge) and attached growth (biofilm) systems (e.g., trickling filters) (*4*). Depending on operational conditions, both can function as partially or completely nitrifying processes. The key operational variable for suspended growth systems is the solids retention time (SRT), whereas for attached growth systems it is the organic-loading rate (e.g., kg BOD/m^3-day) (*4, 5*). When a system is operated at lower SRTs or higher organic-loading rates, the treatment goal is usually biochemical oxygen demand (BOD) removal. Conversely, nitrification occurs at longer SRTs or lower organic-loading rates. The primary goal of nitrification is to transform ammonia and organic nitrogen to nitrate, but increased levels of nitrification usually are accompanied by additional BOD removal. A recent development has been the implementation of membrane bioreactors (MBRs) (*6*), which are conceptually similar to suspended growth systems that use sedimentation for biomass separation, but can be operated at much higher SRTs or mixed liquor suspended solids concentrations. Conventional (biological) wastewater treatment systems are designed and operated to meet BOD and ammonia effluent standards. Advanced biological treatment may include denitrification, where nitrate is converted primarily to nitrogen gas. Advanced wastewater treatment may also include physical/chemical processes that resemble conventional (e.g., coagulation, softening, granular media filtration) or advanced (e.g., granular activated carbon (GAC), membranes) drinking water treatment processes. Moreover, treated wastewater can undergo further renovation by soil

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10.1021/es802443t CCC: $40.75
Published on Web 03/12/2009

aquifer treatment (SAT) at groundwater recharge basins (*7*). The Clean Water Act established the basic structure for regulating discharges of pollutants into the waters of the U.S. The Act requires that discharges of contaminants to surface waters be controlled, and set requirements for water quality standards for surface waters. These standards are specific to designated uses for each of the receiving waters. These uses include aquatic and wildlife, agricultural uses, recreational uses, and drinking water supply. However, these standards typically do not consider many drinking water quality issues, especially emerging ones.

In addition to influent refractory substrates (e.g., natural organic matter [NOM] components such as humic substances from the drinking water source) not assimilated by bacteria during wastewater treatment, effluent organic matter (EfOM) from biological WWTPs is composed of degradation products and soluble microbial products (SMP) (*8*). The characteristics of EfOM and NOM overlap extensively; however, the aromatic moieties present in EfOM are probably of different origin than those of NOM (*9*). SMP are the group of organic compounds that are generated during biological treatment by bacteria as a result of substrate metabolism and biomass decay (*10*). SMP consist of macromolecules and cellular debris with a protein (nitrogen-enriched) and polysaccharide signature (*2, 8, 10*).

WWTPs generally add chlorine or apply ultraviolet (UV) light for final disinfection prior to discharge. Chlorination (oxidation) of amino acids can result in the formation of aldehydes and nitriles, with subsequent or concomitant chlorine substitution to form chloral hydrate (trichloroacetaldehyde) and dichloroacetonitrile, respectively (*11*). EfOM has been shown to be a source of precursors for a wide range of DBPs (trihalomethanes [THMs], haloacetic acids [HAAs], haloacetonitriles [HANs], and nitrosamines) (*2*). THMs are regulated DBPs in finished drinking water in many countries. In addition, HAAs are regulated in U.S. drinking waters. California has notification levels for three nitrosamines (*12*). (Notification levels are health-based advisory levels established for chemicals in drinking water that lack maximum contaminant levels. When chemicals are found at concentrations greater than their notification levels, certain requirements and recommendations apply.) Recent research has suggested that certain nitrogenous DBPs (e.g., HANs) and certain nonregulated carbonaceous DBPs (e.g., haloacetaldehydes) may be of greater health concern than the regulated carbonaceous DBPs (i.e., THMs, HAAs) (*13, 14*). The U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS) database indicates for certain nitrosamines that drinking water concentrations in the low ng/L level are associated with a 10^{-6} lifetime cancer risk (*15*). Some DBPs in WWTP discharges may also be toxic to aquatic organisms (*16*).

The objective of this study was to compare different WWTP processes for the control of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and DBP precursors in EfOM, with a focus on emerging DBPs of health concern. A major issue in addressing effluent-impacted drinking-water sources and wastewater reclamation/reuse is the differences in vocabularies used by wastewater versus drinking-water engineers, particularly with respect to organic matter and nitrogen species. One objective of this research was to reconcile these different vocabularies by assembling a database of corresponding parameters in order to evaluate global and site-specific correlations. Such insight may permit translation of wastewater monitoring data to projected impacts on drinking-water facilities. Moreover, most wastewater studies have examined only selected DBPs and/or their precursors. Thus, in this research, a combination of regulated and emerging DBPs were studied, which included carbonaceous and nitrogenous DBPs, halogenated and nonhalogenated chemicals, and DBPs known to have different precursor sources (e.g., humic substances, amino acids, other types of DON). Furthermore, to facilitate a better understanding of the impact of wastewater treatment processes on DBP precursors, the DOM was characterized, so that EfOM could be differentiated from drinking-water NOM.

Experimental Methods

Survey. A survey was conducted of 23 WWTPs in the U.S. (in the west, southwest, the mountain region, south central, midwest, and northeast). The WWTPs were sampled during a wet/cold season and a dry/warm season; selected WWTPs were sampled once more in a second year. In general, nitrification occurs to a greater degree at most WWTPs in the summer. The WWTPs employed a range of treatment processes: oxidation ditch, aerated lagoon, trickling filter, activated sludge, nitrification/denitrification, SAT, powdered activated carbon (PAC) and GAC, MBR, reverse osmosis (RO), or various combinations. Where possible, one or more WWTPs that served the same community (or geographical region) but used different treatment processes were sampled. Moreover, some WWTPs selected for study operated parallel treatment trains with different treatment processes; they provided a direct comparison of the impact of different biological or physical chemical processes on the parameters under study. For conventional WWTPs, the secondary effluent was sampled prior to chlorination. This sample was then chlorinated in the laboratory under standard/controlled/uniform formation potential (FP) conditions to determine the level of DBP precursors in the treated wastewater. For WWTPs with advanced wastewater treatment processes, samples were collected before and after each major unit process to evaluate their ability to remove DBP precursors. For example, for a WWTP with biological treatment followed by RO membranes, the effluent of the biological treatment process before RO treatment was sampled and analyzed. Results for the biological treatment process before RO treatment were evaluated with that of other WWTPs that used a similar biological treatment process, but did not use RO. For many of the study sites, samples were also collected at DWTPs (e.g., the plant influents) downstream of the WWTP discharges in this study. Although this paper focuses on the WWTPs, results for precursors for *N*-nitrosodimethylamine (NDMA) at the WWTPs are compared to those at the DWTPs.

Analytical Parameters. Survey samples were analyzed for a combination of traditional wastewater and drinking water parameters. Wastewater parameters included 5-day carbonaceous BOD ($CBOD_5$), chemical oxygen demand (COD), and total Kjeldahl nitrogen (TKN). TKN consists of nitrogen in a −3 oxidation state (i.e., amino nitrogen and ammonia). Wastewater parameters also included all inorganic forms of nitrogen: ammonia (NH_3), nitrite (NO_2^-), and nitrate (NO_3^-). All measurements were carried out according to Standard Methods (*17*).

Drinking water parameters focused on DOM. Traditional NOM characterization included DOC, DON, and specific UV absorbance (SUVA), which were performed on samples that had been 0.45-μm filtered (using membrane filters (e.g., polyethersulfone) that were prewashed with organic-free water). DOC and UVA were measured using Standard Methods (*17*), where UVA was determined at 254 nm. The low-level DON method employed dialysis pretreatment to remove dissolved inorganic nitrogen (*18*). Dialysis pretreatment used cellulose ester dialysis tubes with a nominal molecular weight cutoff of 100 Da. Dialysis was conducted for 48 h to separate the DON from the dissolved inorganic nitrogen. SUVA is the ratio of UVA (in m^{-1}) to DOC (in mg/L) and allows classification according to humic (>4 L/mg-m) versus nonhumic NOM (<2 L/mg-m) (*19*). Additional NOM characterizations included XAD resin fractionation (*20*) and

TABLE 1. Criteria for Classifying the Biological Treatment Processes[a]

biological treatment	NH_3	NO_2^- (mg/L as N)	NO_3^-	SRT (days)
no nitrification	>10	<1	<2	<5
partial or poor nitrification	2−10	>1	2−10	
good nitrification	<2	<1	>10	>10
partial denitrification	<2	>1	5−10	>10
good denitrification	<2	<1	<5	>10

[a] Source: reproduced from ref *2*. Copyright 2008. Awwa Research Foundation.

5-day biodegradable dissolved organic carbon ($BDOC_5$) (*21*). In wastewater treatment, organic matter is measured indirectly as oxygen demand (e.g., BOD). BOD is a measure of the biodegradability of the organic matter, expressed in terms of oxygen equivalents. In drinking water treatment, organic matter is measured directly as organic carbon (e.g., DOC). The biodegradable DOC (BDOC) parameter has been developed as a drinking water analog of BOD. The Supporting Information (SI) briefly describes how BDOC was determined in this study. One objective of the research in this project was to reconcile these different vocabularies (e.g., BOD versus BDOC) by assembling a database of corresponding parameters. Amberlite XAD-8 and XAD-4 resins were used to separate the NOM into three operationally defined groups: (1) hydrophobic (HPO), (2) transphilic (TPI), and (3) hydrophilic (HPI) organic matter. More information on the $BDOC_5$ testing and XAD resin fractionation is provided in the SI.

Regulated DBPs (THMs and HAAs) and emerging DBPs that have been or are likely associated with treated wastewater because of elevated DON and dissolved inorganic nitrogen precursors (*11, 22*) were measured before and after laboratory chlorination. The emerging DBPs included HANs, haloacetaldehydes, and NDMA (*22*). In addition to chloral hydrate, dihalogenated and/or brominated analogues of chloral hydrate were measured (*23*). DBP precursors were measured with FP tests using free chlorine for the halogenated DBPs and FP tests using chloramines for NDMA, where the ammonia was added first and then chlorine was added with good mixing (*24*). Details of the analytical methods for the DBPs (*25*−*29*) and the FP test protocols (*24*) are discussed in the SI.

Criteria for Classifying the Level of Wastewater Treatment. Nitrification and denitrification play key roles in determining the quality of EfOM in terms of traditional wastewater parameters. In addition, advanced wastewater treatment processes alter the EfOM. Therefore, we categorize the WWTPs into different treatment types: WWTP with no nitrification, WWTP with partial (or poor) nitrification, WWTP with good nitrification but no denitrification, WWTP with good nitrification and partial denitrification, WWTP with good nitrification and good denitrification, WWTP using the MBR approach, WWTP with PAC or GAC, WWTP with SAT, and WWTP with RO membrane treatment. The SAT category was based on data from WWTPs that did not use RO membranes. Although some RO facilities performed groundwater recharge, there was (in general) an insignificant difference in water quality between the RO product water and the recovered well water.

Table 1 shows quantitative criteria for differentiating among the different levels of biological treatment processes, and each WWTP was classified based on the level of performance that they actually realized during the time of sampling. Particularly important in Table 1 is the guidance for characterizing which biological treatment processes were nitrifying. Three criteria were employed in this priority order: ammonia-nitrogen <2 mg/L, nitrite−nitrogen ≤1 mg/L, and SRT ≥ 10 days. On the other hand, the criteria for determining which systems had no nitrification were ammonia-nitrogen >10 mg/L, nitrite−nitrogen ≤ 1 mg/L, and SRT ≤ 5 days. Systems that met only some of the criteria for both categories were classified as having poor or partial nitrification. For WWTPs with trickling filters, one cannot use the SRT criterion, but the other criteria can classify them as nitrifying or not. WWTPs that achieved good nitrification were further classified according to their level of denitrification (no, partial, or good) based on the concentration of nitrate (>10, >5−10, or <5 mg/L as N, respectively). Because SRT data were not provided by all of the participating WWTPs, most of the focus was on the ammonia, nitrite, and nitrate data.

Statistical Analyses. Some of the parameters were evaluated with parametric statistics (e.g., average, standard deviation) and/or nonparametric statistics (e.g., median, percentiles). The 25−75th percentile represents 50% of the data and is called the interquartile range. In addition to determining the central tendency of a set of values (average ± standard deviation, interquartile range), a *t* test was done to compare different data sets. In this test, a high value means a high similarity or no statistical difference.

Results and Discussion

Water Quality for Each Treatment type. Table 2 shows the median water quality for each treatment type for selected parameters (SI Tables 1−2 show the ranges of water quality for these parameters and the sample counts), whereas Figures 1−3 show box-and-whisker plots for DOC, DON, and SUVA for each treatment type (SI Tables 3−8 show statistical analysis of the data sets in Figures 1−3). As expected, the level of $CBOD_5$ decreased with increasing nitrification, $BDOC_5$ (a drinking-water parameter for biodegradability) decreased in parallel, and the fraction of DOC as $BDOC_5$ was lower. Nitrification also resulted in large step decreases in the concentrations of DOC (Figure 1), DON (Figure 2), and TKN (Table 2 and SI Table 1). Moreover, WWTPs with denitrification (partial or good) or an MBR tended to achieve lower DOC concentrations, as expected, given the necessity of oxidizing an organic electron donor and carbon source to drive denitrification. However, denitrification is not always achieved at MBR facilities (the majority of the MBR samples in this study were collected when denitrification was being achieved).

DON declined substantially at the onset of nitrification (Figure 2). However, denitrification resulted in slightly higher median levels of DON than at the nitrification WWTPs because raw sewage is often passed into denitrification processes to make them anaerobic, and the organic nitrogen can not be oxidized effectively under these conditions. The *t* test analysis (SI Table 6) shows that the DON distribution of the no-nitrification WWTPs was statistically different than that of the other WWTPs, whereas each of the different types of biological treatment (some level of nitrification or denitrification or MBR) were similar to each other (i.e., not statistically different). Moreover, the DON distributions of the advanced treatment processes (SAT or RO) were statistically different than that of the various WWTP types. Alternatively, almost all of the DOC distributions were statistically different from each other except for the partial or poor nitrification and partial denitrification WWTPs (SI Table 4). However, on a central tendency basis (e.g., the interquartile range), the DOC of the no-nitrification WWTPs was different than that of the other WWTP types, whereas the DOC of the WWTPs with different levels of nitrification or denitrification were similar and that of the advanced treatment processes were different (SI Table 3).

Although nitrification substantially reduced the level of UVA (Table 2 and SI Table 2), it resulted in an increase in

TABLE 2. Median[a] Water Quality for Each Treatment Type: Parameters Used in Classifying the Biological Treatment Processes and Some Closely Related Parameters[b,g]

treatment category	TKN (mg/L)	NH_3	NO_2^- (mg/L as N)	NO_3^-	SRT (days)	COD (mg/L)	$CBOD_5$ (mg/L)	$BDOC_5$ (mg/L)	$BDOC_5$/DOC	UVA‡ (cm^{-1})
no nitrification	21.5	20.8	BDL[d]	0.16	1.7	31	9.0	6.8	0.51	0.178
partial or poor nitrification	9.2	6.83	1.68	1.18	5.4	22	5.0	5.2[e]	0.49[e]	0.123
good nitrification	2.2	0.12	BDL	16.5	30	22	1.7	1.2	0.22	0.146
partial denitrification	2.5	0.29	0.50	7.55	5.0	21	4.0	0.8[e]	0.14[e]	0.132
good denitrification	1.4	0.68	0.36	1.14	6.5	20	0.6	NA[f]	NA	0.125
MBR	0.9	1.02	0.03	2.11	15	23	1.0	0.6	0.09	0.108
PAC/GAC	NA	0.10	BDL	2.21	14	6.0	NA	NA	NA	0.043
SAT	NA	0.11	BDL	6.55	NA	3.7	NA	NA	NA	0.022
RO	2.1	1.44	BDL	0.13	NA	2.1	BDL	NA	NA	0.021

[a] Sample counts (n) provided in the SI. [b] DOC data provided in Figure 1. [c] Determined at 254 nm. [d] BDL = Below detection level. [e] Based on one set of samples. [f] NA = Not available. [g] Source: Reproduced from ref *2*. Copyright 2008. Awwa Research Foundation.

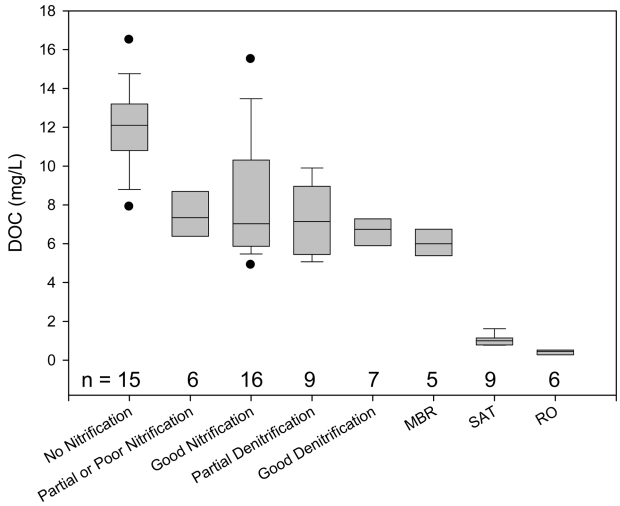

FIGURE 1. Box-and-whisker plot of DOC for each treatment type (PAC/GAC: only two data points, 2.1 and 2.3 mg/L) (top and bottom of box = 75th and 25th percentiles, respectively; top and bottom of whiskers = 90th and 10th percentiles, respectively; line across inside of box = median (50th percentile); and points beyond whiskers = outliers). Reproduced from ref *2*. Copyright 2008 Awwa Research Foundation.

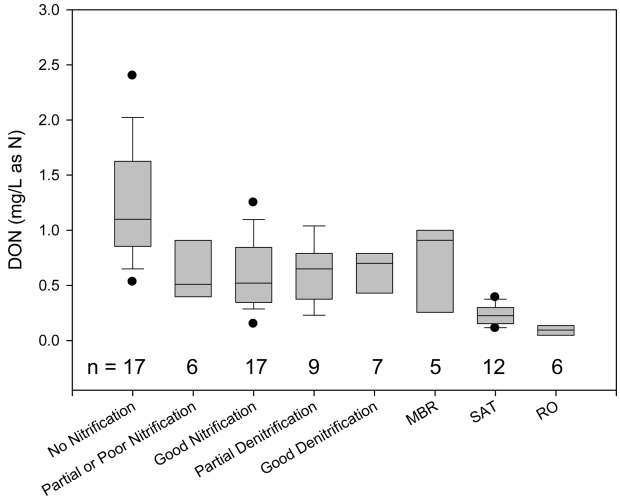

FIGURE 2. Box-and-whisker plot of DON for each treatment type (PAC/GAC: only two data points, 0.27 and 0.29 mg/L). Reproduced from ref *2*. Copyright 2008 Awwa Research Foundation.

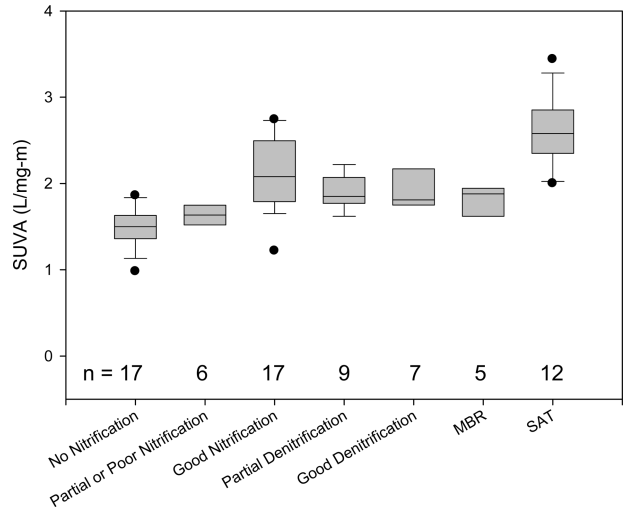

FIGURE 3. Box-and-whisker plot of SUVA (UVA determined at 254 nm) for each treatment type (PAC/GAC: only two data points, 1.76 and 2.12 L/mg-m; RO: not available). Reproduced from ref *2*. Copyright 2008 Awwa Research Foundation.

SUVA (Figure 3), due to the preferential removal of the less UV-absorbing fraction of the DOC (e.g., polysaccharides, proteins) during biological treatment. Based on the interquartile ranges, the SUVA values of the no-nitrification and partial or poor nitrification WWTPs were similar and were different (on a central tendency basis) than that of the WWTPs with good nitrification or denitrification or MBR (SI Table 7). SAT samples exhibited the highest SUVA. Because the UVA levels for SAT samples were low (0.02−0.04 cm^{-1}), these measurements may be less accurate. In other research (*30*), treated wastewater was fractionated into three molecular weight (MW) classes, and the percentage of DOC in each class was compared to the corresponding percentage of UVA. The low-MW material (i.e., <0.5 KDa) was believed to be largely carbohydrates or simple low-MW amino acids; such compounds lack significant UVA at 254 nm.

As an alternative to box-and-whisker plots, the relationship of DOC, DON, or SUVA to the level of ammonia in EfOM was examined (SI Figures 3−5). Although the R^2 values (i.e., 0.38−0.42) of the trend lines are low, the central tendency was that a decrease in ammonia corresponded to a decrease in DOC or DON and an increase in SUVA. For example, the occurrence of high levels of ammonia always corresponded to the presence of low SUVA (i.e., <2.0 L/mg-m) in EfOM. Moderate values of SUVA (i.e., >2.0 L/mg-m) in EfOM were only observed when the concentration of ammonia was low

TABLE 3. Median Water Quality for Each Treatment Type: Other NOM Characterization Parameters[a,d]

treatment category	n[b]	HPO (%)[c]	TPI (%)	HPI (%)	HPO (mg/L)	TPI (mg/L)	HPI (mg/L)
no nitrification	13	37.0	19.2	42.6	4.7	2.3	5.3
partial or poor nitrification	2	40.8	21.4	37.8	3.6	1.9	3.4
good nitrification	10	40.8	22.2	35.7	3.0	1.6	2.8
partial denitrification	2	42.2	22.9	34.8	3.4	1.8	2.8
good denitrification	1	40.3	22.0	37.7	3.0	1.6	2.8
MBR	4	38.4	21.4	38.6	2.5	1.3	2.7
PAC/GAC	2	32.0	19.4	48.6	0.8	0.5	1.2
SAT	4	52.5	20.8	25.8	0.7	0.3	0.4

[a] HPO = Hydrophobic, TPI = transphilic, HPI = hydrophilic. [b] Some treatment category characterizations based on limited (one to two) sets of samples or no data for RO, as the DOC in the latter samples was too low to characterize. [c] The percentages in each row do not add up to 100%, as each value represents the median result for that treatment category for each NOM characteristic. [d] Sourc: reproduced from ref *2*. Copyright 2008. Awwa Research Foundation.

(e.g., <2 mg/L as N). However, low levels of ammonia did not always correspond to moderate values of SUVA.

The over-riding pattern in the current study is that having at least some nitrification—in addition to its impact on certain wastewater parameters—strongly altered the following drinking water parameters: DON, DOC, and UVA. Good nitrification reduced the concentration of $BDOC_5$ and substantially changed the ratio of $BDOC_5$/DOC. Biological treatment—at the WWTP or during soil passage—appears to preferentially remove DOC over UVA (i.e., nonhumic over humic). Low SUVA was observed for WWTPs with no and partial nitrification, whereas WWTPs with good nitrification showed higher SUVA, implying that nitrification probably did not allow for significant biodegradation of the more recalcitrant organic matter, which had high levels of SUVA. Some of the physical/chemical treatment processes (i.e., coagulation, granular media filtration) typically had a minimal impact on most of the parameters in Table 2 and Figures 1−3, whereas lime softening at high pH (i.e., 11.4−11.5) was more effective (Krasner et al. 2008). For example, flocculation/filtration and lime softening/filtration were used in parallel treatment trains at a water reclamation plant to treat EfOM from a no-nitrification WWTP. Because the EfOM has a low SUVA (i.e., 1.2−1.5 L/mg-m), it is expected to be poorly adsorbable. In the flocculation train, there was only an 18−21% removal of the DOC and only a 11−19% reduction in UVA, whereas in the lime softening portion of the plant there was a 22−42% removal of DOC and a 30−33% reduction in UVA. However, the removal of DON in the lime softening process was highly variable (no removal or 60%).

Relationships between Selected Water Quality Parameters. SI Figure 2 shows the relationship between $BDOC_5$ and $CBOD_5$, a drinking water and a wastewater parameter, respectively. On a central tendency basis, the observed $CBOD_5/BDOC_5$ ratio is consistent with having relatively hard-to-biodegrade organic matter comprising much of the EfOM. (See the SI for additional discussion.)

The relationship between $BDOC_5$ and the DOC of the EfOM sources was examined for the same set of data (*2*). As the DOC of the EfOM decreased, the concentration of $BDOC_5$ decreased with a slope of 0.62 g $BDOC_5$/g DOC for the linear regression ($R^2 = 0.87$) (SI Figure 6). The intercept of the linear regression line was large ($BDOC_5$ = zero at a DOC of ~4 mg/L), which also indicates a significant amount of hard-to-biodegrade organic matter. In addition, the relationship of $BDOC_5$ to ammonia in EfOM was examined (SI Figure 7). Although the R^2 (i.e., 0.45) of the regression line was low, the central tendency was for $BDOC_5$ to decrease with decreasing ammonia.

NOM Characterization for Each Treatment Type. Table 3 shows the median NOM polarity characterization for each treatment type (and SI Table 9 show the ranges). (The only treatment type not evaluated with NOM characterization was RO, because there was too little organic matter in the RO permeates for this type of characterization. Nonetheless, RO facilities were fully evaluated for most of the other parameters in this study.) Nitrification reduced the concentration (mg/L amounts) of hydrophobic and transphilic NOM to some extent, but reduced the concentration of hydrophilic NOM considerably. As the concentration of ammonia decreased, the amount of hydrophilic NOM went down (SI Figure 8). Alternatively, for hydrophobic NOM, the decrease was not as substantial (SI Figure 8). Partial or poor nitrification resulted in a 36% decrease (on a median basis) in the hydrophilic NOM compared to without it, whereas there was no obvious change in NOM with degree of nitrification or denitrification (Table 3). At the WWTPs with no nitrification, hydrophilic NOM was generally much greater in concentration than that of the hydrophobic NOM, whereas at the WWTPs with good nitrification, the concentrations of these two fractions of NOM were more similar. These findings suggest that much of the biodegradable EfOM (that which was removed during biological treatment) was in the hydrophilic fraction, whereas the hydrophobic NOM was more recalcitrant. The hydrophobic fraction consists of humic-like NOM which, because of its size and structure, is expected to be more recalcitrant to biodegradation. SI Figure 9 shows the relationship of hydrophobic and hydrophilic NOM to DOC. As the concentration of DOC in EfOM was lowered, the amount of both NOM types was reduced, in particular that of the hydrophilic fraction. SAT resulted in a substantial removal of all types of NOM, where the hydrophilic NOM was preferentially removed compared to the hydrophobic fraction, which resulted in a higher percentage of the NOM being hydrophobic (but this did not result in an increase in hydrophobic NOM per se).

DBP Precursor Levels for Each Treatment Type. Table 4 shows the median levels of DBP precursors for each treatment type (and SI Table 10 shows the ranges for the halogenated DBPs). When the WWTPs were classified by treatment type, the amount of THM precursors was similar (on a central tendency basis) for all of the types of biological treatment, but SAT or RO removed more THM precursors (and that of other DBP classes), due (in part) to the low levels of DOC after these treatment processes. (The data set for PAC/GAC was too small to evaluate fully. The one water reclamation plant in this study that used PAC/GAC may not be representative of other WWTPs with activated carbon. Nonetheless, the removal of DBP precursors at this facility was consistent with the removal of organic matter after PAC/GAC treatment. In addition, the full-scale results were consistent with bench-scale studies with activated carbon that were conducted as another part of this project (Krasner et al., 2008).) SI Figure 10 shows no relationship between THMFP and ammonia. Thus, DOC removed during nitrification was not highly reactive in forming THMs. Moreover, the

TABLE 4. Median Water Quality for Each Treatment Type: DBP[a] Precursors (μg/L of Halogenated DBPFP[b]; ng/L of NDMAFP[c])[f]

treatment category	THMs	HANs	DXAAs	TXAAs	dihaloacetaldehydes	trihaloacetaldehydes	NDMA
no nitrification	259	28.5	155	131	8.6	89.8	878
partial or poor nitrification	237	18.0	121	116	4.7[d]	58.4[d]	341
good nitrification	231	13.0	117	113	4.0	50.4	440
partial denitrification	233	12.0	106	87.9	4.3	58.1	800
good denitrification	255	13.0	103	109	4.6[d]	29.3[d]	302[d]
MBR	220	10.0	114	80.0	3.8	46.4	605
PAC/GAC	103[d]	11.9[d]	53.2[d]	33.7[d]	2.1[d]	16.6[d]	88[d]
SAT	49.5	6.6	18.6	15.1	ND[e]	2.9	ND
RO	9.4	0.3	4.3	1.6	ND	1.8	52

[a] THMs = Trihalomethanes, HANs = haloacetonitriles, DXAAs = dihalogenated acetic acids, TXAAs = trihalogenated acid acids, NDMA = *N*-nitrosodimethylamine. [b] DBPFP test conducted in the presence of chlorine. [c] NDMAFP test conducted in the presence of chloramines. [d] Based on limited (one to three) sets of samples. [e] ND = Not detected. [f] Source: reproduced from ref *2*. Copyright 2008. Awwa Research Foundation.

median THM yields per unit DOC for no-nitrification, partial or poor nitrification, and good nitrification were 0.155, 0.217, and 0.250 μmol of THMFP per mg DOC, respectively, which are consistent with the increase in SUVA upon nitrification (Figure 3). (The yields were examined on a molar basis, as brominated THMs have a higher molecular weight than chlorinated species. For the WWTPs that did not use RO, which can effectively reject bromide, the median level of bromide (and interquartile range) in the EfOMs was 0.19 (0.12−0.24) mg/L. For the WWTPs that did not use RO or PAC/GAC, chloroform was the primary THM species produced [on a molar basis] in the FP tests [median = 70%, interquartile range = 62−77%]. Although the bromide levels were high, the ratios of bromide to DOC were relatively low because of the high DOC in EfOM and the ratio of chlorine to bromide was high in the FP tests, both of which factors disfavor bromine incorporation.) The interquartile ranges for the THM yields for selected treatment types are shown in SI Table 11, which are consistent with the trends based on the median values. Thus, nitrification resulted in an EfOM with less DOC, but more reactivity to form THMs per unit DOC, with a net effect of no significant change in overall THM formation.

In contrast to THMs, even partial or poor nitrification resulted in a significant reduction in precursors for HANs and trihaloacetaldehydes. As discussed above, amino acids are precursors to both chloral hydrate (trichloroacetaldehyde) and dichloroacetonitrile (one of the HANs) (*11*). Thus, biological treatment that included nitrification appeared to remove a portion of the DON that was reactive to form a nitrogenous class of DBPs, as well as nonnitrogenous ones.

HAA precursors were removed with nitrification, although not as much as that of the HANs or trihaloacetaldehydes. Because humic substances are an important source of HAA precursors, the limited degradation of HAA precursors is not surprising.

For NDMA, on a central-tendency basis, achieving some nitrification reduced the level of precursors for this nonhalogenated DBP (Table 4, SI Figure 11, and SI Tables 12−13), similar to the impact of nitrification on DON (Figure 2) or that of the HAN precursors. However, denitrification WWTPs had a higher median and more variable NDMAFP (SI Figure 11). As discussed above, denitrification WWTPs had slightly higher median levels of DON than the nitrification WWTPs. At one WWTP that had two parallel trains, where one train attained partial denitrification and the other did not achieve nitrification, the median NDMAFP for the denitrification train (i.e., 1262 ng/L) was lower than that of the no-nitrification train (1732 ng/L). So, in this site-specific example, the train with advanced biological treatment did result in less NDMA precursors. Based on the *t* test analysis, the distribution of NDMAFPs for no-nitrification WWTPs was statistically different than that of other WWTP types, whereas the distribution of partial or poor nitrification WWTPs was similar to that of the good nitrification or MBR WWTPs (SI Table 13). In a subsequent study (*31*), EfOM from two WWTPs in this study were fractionated and the different NOM isolates were tested for NDMA precursors. Hydrophilic bases were found to have the most NDMA precursors, whereas the hydrophobic fractions had much less. Thus, the preferential removal of the hydrophilic NOM during nitrification (Table 3) is consistent with the removal of NDMA precursors (SI Figure 10). SI Figures 12−14 show the relationships of NDMAFP to ammonia, DON, and hydrophilic NOM in EfOM. Although all of the R^2 values (i.e., 0.25−0.48) are low, the most consistent relationship was with hydrophilic NOM. DON is a heterogeneous mixture of organic compounds, which likely have a wide range of reactivities to form NDMA. Nonetheless, as discussed above, it may be components of the hydrophilic portion of the EfOM that are the more reactive in forming NDMA. The DWTPs in this study had relatively low levels of NDMA precursors in their waters compared to that of the WWTPs (SI Figure 11).

Similar to the trends observed for the common wastewater and NOM parameters, nitrification played a key role in determining the quantity and quality of EfOM character and DBP precursors. Poorly nitrified EfOM was highly composed of hydrophilic and biodegradable DOM, whereas well nitrified EfOM included a similar amount of hydrophobic DOM and a higher proportion of nonbiodegradable DOM. Advanced biological treatment resulted in preferential removal of the less UV-absorbing (hydrophilic) portion of the DOM. In general, nitrification removed precursors for nitrogenous DBPs (e.g., HANs, NDMA)—as well as a nonnitrogenous class of DBPs, trihaloacetaldehyde. Alternatively, THM precursors were found to be relatively recalcitrant to biodegradation, whereas HAA precursors were diminished to some extent with more biological treatment.

Two factors play large and complementary roles in terms of the impact of nitrification. All nitrification processes operate with a relatively long SRT (Table 2). This is needed to ensure stable retention of the nitrifiers. A long SRT means that all bacteria have a slow specific growth rate that allows them to drive the concentration of all organic substrates to low values. A second factor is that nitrifiers release SMP that can be utilized by heterotrophs as an extra substrate supply. The SMP are not normally degraded rapidly, and this means that the long SRT is well matched. In summary, the two factors contribute to selection of slow-growing heterotrophs that are good scavengers of relatively hard-to-biodegrade organic molecules. They are able to degrade all BOD or DOC to low concentrations, and this surely is accentuated for the DBP precursors, which probably are complex and not rapidly degraded, except under conditions that favor scavenging. In

other research carried out as part of this study (*32*), fluorescence excitation−emission matrix measurements and size-exclusion chromatography with DOC detection were conducted on EfOM samples before and after aerobic BDOC testing. Both analytical techniques demonstrated that biodegradation preferentially removed protein-like substances (which would include precursors for HANs and trihaloacetaldehydes). Degradation of DOC in the polysaccharide peak was more complete and faster, whereas humic substances (which would include precursors for THMs) were slowly and incompletely biodegraded. In this study, innovative analytical tools were used to distinguish EfOM from drinking-water NOM within the context of defining a wastewater signature. Moreover, the profound impact of nitrification in so many aspects of effluent water quality is an incredibly important finding. Based on extensive real-world data for a widely diverse group of conventional and emerging parameters, theoretical principles, and a novel binning of the data, a clear message on how to minimize water quality impacts from wastewater discharges is a significant product of this research.

In terms of the impact of treated wastewater discharges to rivers or lakes that serve as drinking-water sources, mixing with surface water will reduce the concentrations of DBPs and their precursors in the receiving water. In order to examine the realistic contribution of treated wastewater to DBPs or DBP precursors in drinking-water supplies, SI Table 14 illustrates the situation for wastewater-derived NDMA precursors. A range of wastewater contributions were examined for the different WWTP types, using median values. This analysis shows that even a few-percent wastewater contribution can substantially increase the level of NDMA precursors in a drinking-water supply. However, this preliminary analysis did not consider any degradation of NDMA precursors in the receiving water or the use of riverbank filtration to remove wastewater-derived contaminants. In field sampling conducted for this study, some rivers downstream of WWTPs were sampled for NDMA precursors (SI Table 15) (*2*). The NDMAFPs in these field cases are consistent with the values calculated based on a simple dilution of treated wastewater with river water.

This study developed information on the simultaneous control of wastewater parameters (e.g., ammonia, TKN, CBOD), NOM (e.g., DOC, DON, UVA, hydrophilic substances, BDOC), and precursors for DBPs (e.g., THMs, HAAs, HANs, haloacetaldehydes, nitrosamines). This information can be used in different watersheds (along with appropriate evaluations of costs) to assess how best to invest public money to upgrade WWTPs and drinking water treatment plants in order to maximize societal benefits while minimizing the health risks posed by wastewater-derived DBPs.

Acknowledgments

We gratefully acknowledge that the Awwa Research Foundation is the joint owner of the technical information upon which this publication is based. We thank the Foundation and the U.S. government, through the U.S. Environmental Protection Agency for its financial, technical, and administrative assistance in funding and managing the project through which this information was discovered. The comments and views detailed herein may not necessarily reflect the views of the Awwa Research Foundation, its officers, directors, affiliates or agents, or the views of the U.S. Federal Government. The project manager was Alice Fulmer. We also acknowledge Zaid K. Chowdhury and Shahnawaz Sinha, of Malcolm Pirnie, Inc., for setting up portions of the full-scale sampling survey. Thanks are given to Metropolitan staff that conducted various analyses in support of this study: Michael J. Sclimenti, Salvador J. Pastor, Russell Chinn, Cordelia J. Hwang, Yingbo C. Guo, Eduardo Garcia-Zayas, Donnie Morquecho, Wing Chow, Rachel M. Kelley, Mary Ann Viernes, Sikha Kundu, Chih Fen Tiffany Lee, Jacob Nikonchuk, Suzanne M. Teague, Xiaoshan Chen, Ching Kuo, Lely Suhady, Robert C. Alvarez, and Jesus Vasquez Jr. Finally, the participating utilities and agencies and their staff are acknowledged for their invaluable assistance and support.

Supporting Information Available

Information on analytical methods; a discussion of the relationship between BOD and BDOC; statistical analysis of water quality data, NOM characterization, and DBP precursors; relationships between selected parameters; impact of WWTP type on NDMA precursors; impact of EfOM on source water NDMAFP for DWTPs; and field examples of impact of EfOM on river water NDMAFP. This material is available free of charge via the Internet at http://pubs.acs.org.

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ES802443T