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Occurrence and treatment of wastewater-derived organic nitrogen

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ABSTRACT

Dissolved organic nitrogen (DON) derived from wastewater effluent can participate in reactions that lead to formation of nitrogenous chlorination by-products, membrane fouling, eutrophication, and nitrification issues, so management of DON is important for both wastewater reuse applications and nutrient-sensitive watersheds that receive discharges from treated wastewater. This study documents DON occurrence in full-scale water/wastewater (W/WW) treatment plant effluents and assesses the removal of wastewater-derived DON by several processes (biodegradation, coagulation, softening, and powdered activated carbon [PAC] adsorption) used for advanced treatment in wastewater reuse applications. After varying levels of wastewater treatment, the dominant aqueous nitrogenous species shifts from ammonia to nitrate after aerobic processes and nitrate to DON in tertiary treatment effluents. The fraction of DON in total dissolved nitrogen (TDN) accounts for at most 52% in tertiary treated effluents (median = 13%) and 54% in surface waters impacted by upstream wastewater discharges (median = 31%). The 5-day biodegradability/bioavailability of DON (39%) was higher, on average, than that of dissolved organic carbon (DOC, 26%); however, upon chlorination, the DON removal (3%) decreased significantly. Alum coagulation (with ≥8 mg/L alum per mg/L DOC) and lime softening (with pH 11.3–11.5) removed <25% of DON and DOC without selectivity. PAC adsorption preferentially removed more DOC than DON by 10% on average. The results provided herein hence shed light on approaches for reducing organic nitrogen content in treated wastewater.

1. Introduction

Reclaimed, recycled, and reused wastewaters are now perceived as a valuable alternative water supply in some arid areas to meet the demands of growing population and industrial development. In 2004, the United States Environmental Protection Agency (USEPA) upgraded its "Guidelines for Water Reuse" (EPA/625/R-04/108) to promote wastewater reuse for urban, industrial, agricultural, and even potable purposes. However, concerns about possible adverse effects of compounds persisting in treated wastewater may hinder potable reuse practices (Servais et al., 1999). These constituents of health concern include but are not limited to pharmaceuticals (Heberer, 2002), endocrine-disrupting compounds (Snyder

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et al., 2001), and disinfection by-products (DBPs) (Krasner et al., 2009). Earlier studies also found that dissolved organic nitrogen (DON) in water and wastewater has several adverse implications, including that it serves as a precursor of nitrogenous DBPs (Lee et al., 2007; Krasner et al., 2009); alters the speciation of carbonaceous DBPs (Hureiki et al., 1994); and supports microbial survival and growth, which may cause membrane fouling (Her et al., 2004), eutrophication (Pehlivanoglu and Selak, 2004), and nitrification issues (Zhang et al., 2009). Systematic evaluation of the occurrence and control of DON is therefore important to enable better decisions for wastewater reuse practices and receiving water protections.

The occurrence and treatment of organic nitrogen in algae-impacted drinking water supplies can shed light, potentially, on DON removal in wastewater effluents. Studies in DON is present in drinking water supplies at levels typically less than 0.3 mg-N/L, although some highly eutrophic surface waters contain up to 10 mg-N/L (Westerhoff and Mash, 2002; Lee and Westerhoff, 2006; Pehlivanoglu-Mantas and Sedlak, 2006; Dotson et al., 2008; Dotson and Westerhoff, 2009). The composition of DON in these water supplies is not well known, but can include small amounts of free (FAAs) and combined (CAAs) amino acids, which consist of FAAs, hydrolyzable proteins and polypeptides. For example, a survey of several algal-influenced drinking water supplies found that, on average, FAAs and CAAs accounted for 0.5% and 15% of DON, respectively, with the other portion of DON remaining unclassified (Dotson and Westerhoff, 2009). In treated wastewater effluent, DON can account up to 2.5 mg/L-N in activated sludge effluent. FAAs account for 0.1–2% of DON and CAAs composed less than 13% of DON (Burleson et al., 1980; Parkin and McCarty, 1981; Dignac et al., 2000). Fractionation of organic matter from reservoirs and wastewaters concluded that colloidal, basic and neutral organic matter fractions were nitrogen enriched relative to acidic fractions; a significant portion of DON is present in the colloidal fraction of poorly nitrified effluents (e.g., trickling filters); and a portion of the acidic fractions (proteins) were more nitrogen enriched from the terpenoid acid fractions (Leenheer et al., 2007). Such fractionation provides a framework for potential DON treatment.

Coagulation of surface waters appears not to selectively remove nitrogen containing organic matter. Enhanced coagulation during drinking water treatment removed equal or slight lower amounts of DON (35%) as compared to dissolved organic carbon (DOC) (Lee and Westerhoff, 2006), and this value was on average 30% in algae-influenced waters (Dotson and Westerhoff, 2009). DON from raw wastewater was biodegradable (50–60%) in during activated sludge treatment, and advanced treatment of treated effluents achieved 72% DON removal using high levels of powdered activated carbon (PAC) dosage, or 33–56% removal by the use of cation exchange resins targeting to basic organic matter fractions (Parkin and McCarty, 1981). Even for low TN effluents (TN = 4–5 mg/L), which represent well-nitrified and denitrified waters, algae and bacteria can utilize 18–61% of the DON (Urgun-Demirtas et al., 2008). While advanced treatment of wastewaters have not historically considered DON removal as a major goal, it may be increasingly important because of the reasons mentioned above.

Current analytical methods for DON have been developed for surface waters (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007) but may require further refinement to deal with wastewater samples which often contain much higher levels of dissolved inorganic nitrogen (DIN). The two most commonly-used DON analysis methods involve: 1) subtracting ammonia from total Kjeldahl nitrogen (TKN) or 2) subtracting DIN, which includes ammonia, nitrite, and nitrate, from total dissolved nitrogen (TDN). Waters with low ammonia (e.g., well-nitrified or denitrified waters) often contain TKN levels at or below common detection limits, between 0.5 and 2 mg-N/L, and thus are often not sensitive enough for wastewater effluents intended for reuse. For the second method, the accuracy of the DON measurement relies strongly on the accuracies of the methods used to determine the amount of each DIN species and also is dependent on the fraction of DIN in TDN. It was reported that when DIN/TDN is higher than 0.6, the variance in DIN measurements can be greater than actual DON levels (Lee and Westerhoff, 2005). Therefore, addition of a dialysis pretreatment step was recommended to remove DIN prior to determination of DON. Dialysis pretreatment decreased DIN levels in the sample while not allowing larger DON molecules to permeate through the dialysis membrane, thus reducing the DIN/TDN ratio and facilitating accurate DON (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007). Wastewater effluent is high in DIN (typically >5 mg/L) which results in elevated DIN/TDN ratios (typically >0.9). Consequently, wastewater effluents often require greater DIN removal during pretreatment to obtain reliable DON values.

This study had two aims: 1) the occurrence of DON in the United States at various types of full-scale water/wastewater (W/WW) treatment plants, focusing on its relative magnitudes with TDN and DOC; and 2) DON treatment by certain commonly-used W/WW treatment processes, including biodegradation, coagulation, softening, and PAC adsorption, especially the factors affecting DON further treatment. It was hypothesized that DON contributes to a significant portion of the TDN in highly-treated wastewater effluent and that commonly employed advanced reuse processes can reduce DON levels. Evidence to support the aims were obtained from both field and laboratory tests, including a USA nationwide survey for full-scale plants, a series of bench-scale experiments, and two monitoring events of an effluent-dominated stream.

2. Materials and methods

2.1. *Survey of plants*

A survey examined 32 full-scale W/WW treatment plants utilizing a wide variety of treatment technologies across the USA, which are described in detail elsewhere (Krasner et al., 2008). The samples included 100 effluent samples from 23 wastewater treatment plants (WWTPs) using aerated lagoon, activated sludge, biofilter, nitrification, denitrification, membrane bioreactor, reverse osmosis, softening, PAC, or sand filtration processes; 30 samples from 9 drinking water treatment plants (DWTPs) equipped with conventional

Table 1 – Qualities of effluents for biodegradation tests.

Parameters	Unit	Effluent from AL	Effluent from AS	Effluent from ND	Effluent from MBR
pH	unitless	7.98	7.93	8.05	7.88
DOC	mg/L-C	12.85	17.97	12.21	7.16
DON	mg/L-N	1.21	1.49	1.56	0.69
TDN	mg/L-N	30.45	14.96	9.39	7.59
NH_4^+	mg/L-N	28.14	11.2	0.09	3.21
NO_2^-	mg/L-N	BDL	BDL	BDL	BDL
NO_3^-	mg/L-N	0.11	0.12	7.33	2.28
UVA	cm^{-1}	0.192	0.169	0.15	0.207
SUVA	L/mg-m	1.49	0.94	1.23	2.89

AL: aerated lagoon, AS: activated sludge, ND: nitrification and denitrification, MBR: membrane bioreactor, BDL: below detection limit.

coagulation, filtration, softening, ozonation, and chlorination processes; and 21 samples from 10 monitoring wells downstream of WWTPs with varying levels of soil aquifer treatments. The water quality differed significantly in terms of DOC (0.2–23 mg/L), DON (0.03–2.44 mg/L) concentrations, and ultraviolet absorbance at 254 nm wavelength (UVA_{254}, 0.01–1.3 cm^{-1}); more details regarding the sampling sites, seasons, and the geological variations were archived in the project report (Krasner et al., 2008).

2.2. *Monitoring of effluent-dominated river*

The Santa Cruz River, AZ served as an effluent-dominated stream for the study of DON fate and transport under natural conditions (Chen et al., 2009), and potentially represents DON transformations which could occur between upstream WWTP discharges and downstream DWTP intakes in other river systems. During dry periods, the Santa Cruz River (SCR) in Arizona (USA) consists entirely of wastewater effluent discharged from the Nogales International Wastewater Treatment Plant (NIWWTP). The contents of conservative ions, including chloride and sulfate, varied by less than 10% over 14 miles, confirming that the stream had no significant inflow from unexpected sources. The samples were collected in two seasons: in summer (June 1–3, 2004) and in winter (February 2, 2005). During the summer event, water was collected three times per day for three days at each of five sites over 14.3 miles (~23 km) along the river; during the winter event, each site was sampled only once. The NIWWTP treated approximately 10 million gallons per day of domestic wastewater during the study and employed aerated lagoon treatment. Our previous work showed that over a 14-mile reach below the NIWWTP there was a decrease in organic matter (DOC and DON) along with a shift from ammonia to nitrite and nitrate, indicating active biological mechanisms within the stream (Chen et al., 2009).

3. Bench-scale experiments

3.1. *Biodegradation*

Laboratory biodegradation experiments were carried using biologically active sand (BAS) reactors. The bioreactor protocol was adopted from an earlier study (Allgeier et al., 1996) in which fine sand (Mesh #50) was acclimated with return activated sludge for more than two months. The feed sludge was obtained from a full-scale WWTP at a point immediately after nitrification and denitrification treatment but prior to the settling tank. After acclimation, each 1-L amber bioreactor was fed with 100 mL of BAS and 400 mL of target effluent. The bioreactors were kept in the dark at room temperature (~20 °C) with continuous stirring, and supernatants were collected 1, 3, and 5 days after the start of the experiment. Dissolved oxygen concentrations were higher than 3 mg/L during the experiment period.

The study employed four representative WWTP effluents to evaluate the effect of biological pretreatment methods on DON further biodegradability (Table 1). One effluent was obtained at the effluent of NIWWTP (named AL sample); one effluent was collected from an effluent of conventional AS treatment (named AS sample); another effluent named ND was retrieved from an effluent with nitrification and denitrification treatment (note: the target plant was different from the one at which the BAS feed sludge was collected); and the fourth effluent was obtained from an effluent after membrane bioreactor treatment (named MBR sample). The influence of chlorination on changes in organic matter biodegradability was also evaluated by dosing the same effluents with free chlorine (Cl_2:DOC = 3:1 in weight basis) at room temperature (20° C) and buffered pH (8.2). For effluents AL and AS, chloramine residuals were found after three days; for effluents ND and MBR, free chlorine was maintained for 24 h; all tests were followed by quenching of residual disinfectants via sodium sulfite.

3.2. *Physical/chemical treatment processes*

The experimental methods used for coagulation, softening, and powdered activated carbon adsorption treatment have been described elsewhere (Westerhoff et al., 2005) and also in the Supplementary Information (SI). The target waters came from four sources (Table 2): one effluent was obtained from NIWWTP behind the aerated lagoon (AL sample); one sample was an AS treatment effluent from a full-scale WWTP (AS sample); the third sample was a nitrified/denitrified effluent (ND sample); and a fourth sample was an artificial soluble microbial product (SMP) generated by a 20-gallon activated sludge (AS) reactor, which was acclimated by glucose and inorganic nutrients (ammonia, iron, etc) to produce SMPs without other refractory organics present in full-scale wastewater effluents (Krasner et al., 2008).

Table 2 – Qualities of effluents for coagulation, softening, and PAC adsorption tests.

Parameters	Units	Sample from AL	Sample from AS	Sample from ND	Sample from Lab-AS
pH	unitless	7.7	7.0	7.3	7.3
DOC	mg/L	12.95	10.95	10.41	3.90
DON	mg/L-N	1.47	1.28	2.44	0.68
TDN	mg/L-N	25.33	20.78	11.80	25.86
NH_4^+	mg/L-N	25.60	BDL	0.35	1.06
NO_2^-	mg/L-N	2.09	0.60	0.78	BDL
NO_3^-	mg/L-N	0.16	20.17	8.23	24.14
UVA	cm^{-1}	0.157	0.264	0.173	0.075
SUVA	L/mg-m	1.21	2.41	1.66	1.91

AL: aerated lagoon, AS: activated sludge, ND: nitrification and denitrification, Lab-AS: laboratory-generated activated sludge, BDL: below detection limit.

3.3. *Analytical methods*

All samples were filtered using 0.45-μm filters (polyethersulfone, GE Osmonics) prior to chemical analysis. DOC was detected by the catalytic combustion method at 720 °C using an organic carbon analyzer (TOC-V_{CSH}, Shimadzu Scientific Instruments). TDN was analyzed by a coupled TOC-V_{CSH} and nitrogen analyzer (TNM-1, Shimadzu Scientific Instruments) without acidification pretreatment of the samples, which intended to retain volatile nitrogen species, such as nitrous acid (pK_a = 3.25, Henry's law constant = 2.45×10^{-2} atm-m^3/mole), and to achieve a high N recovery. Ammonia was measured via the salicylate method by a continuous-flow wet chemistry analyzer (TrAAcs 800 Autoanalyzer, Bran-Luebbe). Nitrite and nitrate were analyzed by Dionex DX-120 ion chromatography. UVA_{254} was measured by a spectrophotometer (Shimadzu). Methods of other miscellaneous parameters (chloride, sulfate, pH, temperature, free chlorine, chloramine, oxygen, etc) were documented elsewhere (Krasner et al., 2008). The DON values reported here are based on the differential method using TDN minus DIN (Equation (1)) after dialysis pretreatment (Lee and Westerhoff, 2005).

$$DON = TDN - DIN = TDN - NO_3^- - NO_2^- - NH_4^+ \quad (1)$$

Due to the characteristic high DIN level (typically >5 mg/L) and DIN fraction in TDN (typically >90%, or DON/TDN <10%) in wastewater effluent, the dialysis period was extended to 48 h (versus 24 h for drinking water) to increase the separation degree of DIN from DON and minimize the subtraction-magnified error. The three analytical methods for computing DON, TDN–DIN with dialysis versus TDN–DIN without dialysis versus TKN–NH_4 without dialysis, were compared in the SI.

4. Results and discussion

4.1. *Survey of biologically treated effluent*

4.1.1. *Sample classification*

Typical wastewater effluent organic matter (EfOM) consists of refractory natural organic matter (NOM) originating from drinking water (Fox et al., 2001), soluble microbial products produced by bacteria and algae growth and decay (Rittmann et al., 1987), and synthetic organic chemicals of anthropogenic heritage (Daughton and Ternes, 1999). DOC and DON are two measures of EfOM. The performance of biological treatment processes in WWTPs is determined by many factors, such as sludge retention time, aeration intensity, organic loading, and mixed liquor concentration (Rittmann and McCarty, 2001). It is possible that a plant equipped with extended aeration facilities does not achieve complete nitrification as intended, and a plant that claims to use a conventional aeration using an activated sludge process may achieve partial denitrification too. Evidence existed that nitrification and denitrification can occur simultaneously (Rittmann and Langeland, 1985; Bertanza, 1997). Therefore, to better reflect the degrees of biological treatment in various types of processes, WWTP samples were classified into three groups according to the inorganic nitrogen concentration and speciation: 1) if TDN >5 mg/L-N and $NH_4^+ > NO_x^-$, the sample was binned as non-nitrified (NN); 2) if TDN > 5 mg/L-N but $NH_4^+ > NO_x^-$, the sample was classified as well-nitrified (WN); and 3) if TDN < 5 mg/L-N, the sample was considered a tertiary treatment effluent (TE) that had undergone denitrification or beyond (e.g., membrane filtration, PAC, ozonation, etc). For samples collected outside of WWTPs, the waters were categorized as soil aquifer treated (SAT) samples; wastewater-affected DWTP influents (DWI) samples, and DWTP effluents (DWE) samples.

4.1.2. *DON, DIN, and TDN*

Fig. 1 summarizes the levels of TDN, ammonia, nitrite, nitrate, and DON in several types of waters. The median TDN values of wastewater effluents were 24, 13, 2.8, 4.5 mg-N/L for NN, WN, TE, and SAT samples, respectively. NN samples contained the highest concentrations of ammonia (median = 21.3 mg/L; average = 20.7 mg/L) and negligible nitrate (median = 0.3 mg/L; average = 0.75 mg/L), whereas WN effluents contained the highest nitrate concentrations (median = 10.0 mg/L; average = 11.7 mg/L) and the least ammonia amounts (median = 0.3; average = 0.8 mg/L). TDN and nitrate concentrations in SAT samples were higher than those in TE samples, because some effluents were not tertiary treated prior to recharge. Due to the dilution effect of surface water and

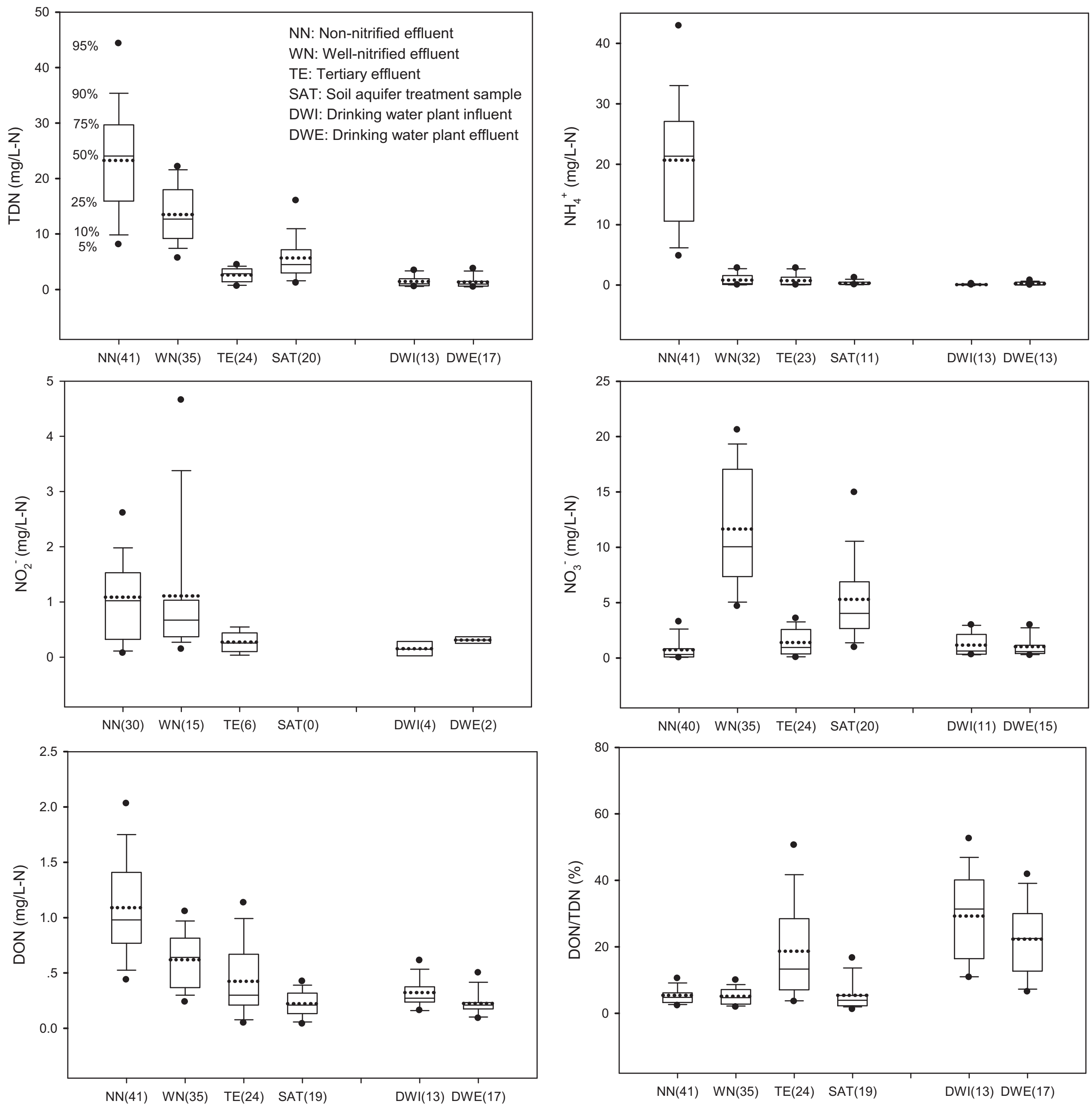

Fig. 1 – Occurrences of nitrogen species in full-scale water/wastewater treatment plants (note: numbers of detectable samples are shown in brackets; dotted lines represent average values).

multiple transformation mechanisms (e.g., biodegradation, photolysis, and hydrolysis) in the watershed, the TDN and nitrate contents in the intake sites of DWTP were lowered to less than 4 mg/L. DWI samples had a lower median TDN of 1.0 mg/L (average = 1.44 mg/L). Nitrite occurred in most NN samples (median = 1.0; average = 1.1 mg/L; 30 of 42 samples contained detectable nitrite) but rarely in SAT, DWI and DWE samples.

The percentage of DON in TDN ranged from <1% to 54% with a median of 6.0% (average = 10.8%) for all samples collected; DIN/TDN ratios varied from 0.36 to >0.99. The percentages of DON in TDN were small (median = 4.7%, average = 5.3%) for NN and WN samples, but reached up to 52% for TE samples (median = 13.3%; average = 18.7%). This result was in line with earlier findings that DON can dominate the TDN of nitrification–denitrification effluent (Pehlivanoglu-Mantas and Sedlak, 2006). NN and WN samples contained high DIN/TDN ratios (median = 0.94, average = 0.89), which justified the need for extended dialysis pretreatment to achieve accurate DON measurements. The percentage of DON in TDN for DWI and DWE (highest = 54%, median = 24.2%, average = 25.3%) were much higher than those in WWTP effluents, showing DON to be an important or even a dominant portion of the nitrogen in wastewater-impacted drinking water supplies. The percentages decreased from DWI(median = 31.4%, average = 29.3%) to

DWE (median = 22.55%, average = 22.3%), suggesting that in most DWTPs, DON was more subject to treatment than DIN by most physical and chemical treatment processes used within drinking water treatment plants. Overall, the dominant nitrogen species in NN effluents was ammonia, in WN effluents was nitrate/nitrite, and in TE effluents and DWTP samples was DON (SI Fig. 2).

4.1.3. *DON and DOC*

Fig. 2 presents the DOC and UVA levels. DOC concentrations ranged from 0.2 to 24 mg-C/L, and the median DOC values of wastewater effluents were 10.5, 6.5, 3.1, 1.1 mg-C/L for NN, WN, TE, and SAT samples, respectively. The change in the DOC:DON ratio is an indicator of the removal selectivity of treatment processes: increase in DOC:DON ratio means that DON is preferentially removed while decrease in DOC:DON ratio means that DOC is preferentially removed. The median ratios of DOC to DON were increased from non-nitrified (NN) samples (median = 9.8 mg-C/mg-N; average = 12.5 mg-C/mg-N) to well-nitrified (WN) samples (median = 13.8 mg-C/mg-N; average = 14.7 mg-C/mg-N), implying that DON was more biodegraded than DOC under aerobic biodegradation processes. The DOC:DON ratios, however, decreased from samples in WN to those in TE and SAT, which means that DON was not preferentially removed during the tertiary treatment processes or may due to an input of DON from the release of soluble microbial products during biomass decay (Rittmann and McCarty, 2001). In general, the median DOC:DON ratio ranged from 8 to 11 mg-C/mg-N in WWTP effluents, significantly below the ratios (median = 19 mg-C/mg-N) of natural waters (Lee and Westerhoff, 2006; Dotson et al., 2008), but close to the samples (median = 12.6 mg-C/mg-N) influenced by algal activity or WWTP discharges (Dotson and Westerhoff, 2009).

UVA_{254} is an indicator of the hydrophobicity and aromatic content of organic matter. Specific UVA (SUVA), calculated as UVA_{254} per unit of DOC, is a parameter allowing classification of humic (e.g., >4 L/mg-m) and non-humic matter (e.g., <2 L/mg-m) (Edzwald and Van Benschoten, 1990). SUVA was lower in NN (median = 1.5 L/mg-m, average = 1.5 L/mg-m) than in WN samples (median = 1.8 L/mg-m, average = 1.9 L/mg-m) (Fig. 2), which indicates that aerobic biodegradation favors removal of non-UVA_{254} absorbing organic matter. In contrast, DWTP facilities tended to remove more UV-absorbing materials than DOC. As a result, SUVA in DWI samples (median = 1.8 L/mg-m, average = 2.6 L/mg-m) was greater than that in effluent samples (median = 1.2, average = 1.8 L/mg-m).

4.2. *Transformations in DON in natural systems*

Increasingly, natural systems are viewed as potential "treatment systems" or "natural buffers". Similar to the results of treatment in WWTPs, the organic matter concentrations in

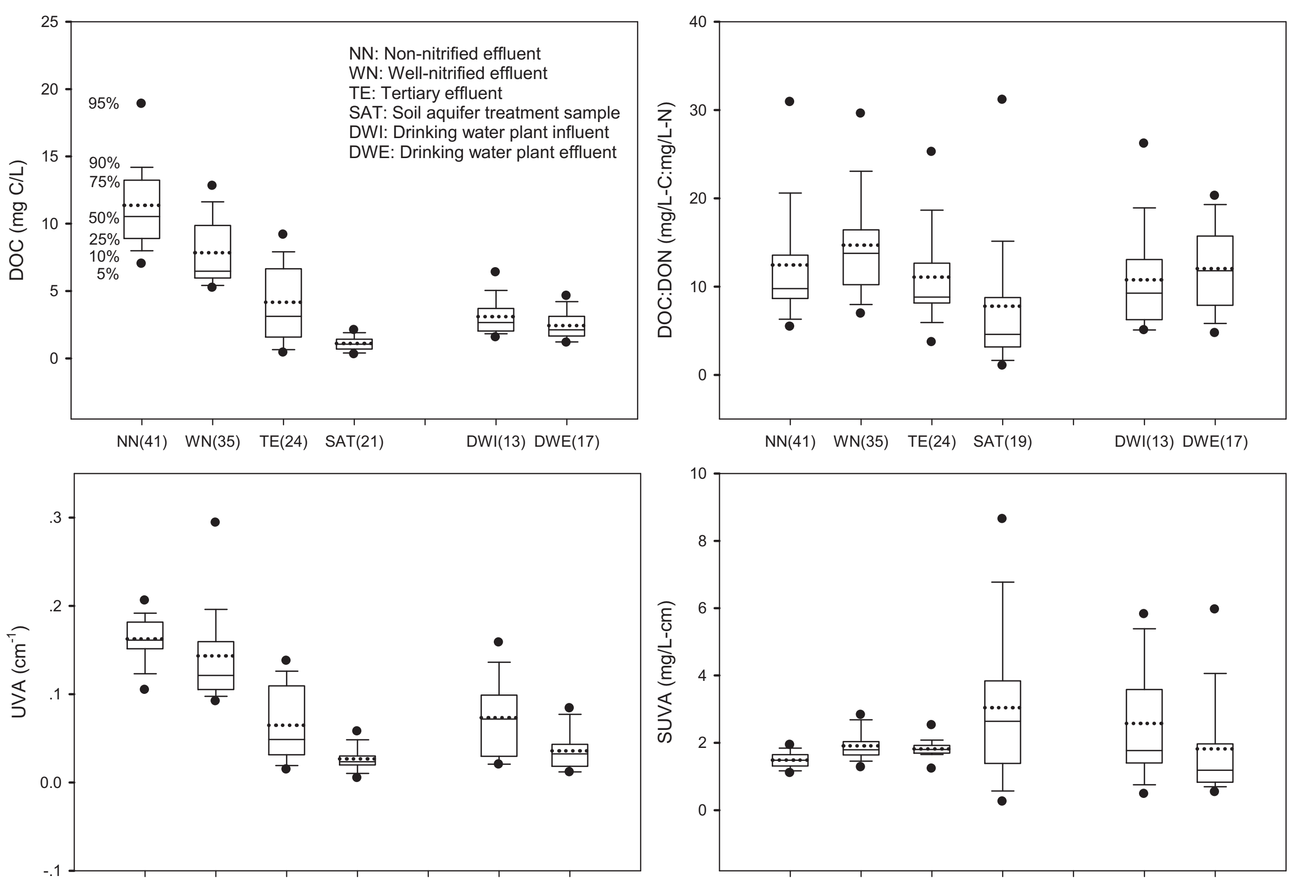

Fig. 2 – Water quality changes in full-scale water/wastewater treatment plants (note: numbers of detectable samples are shown in brackets; dotted lines represent average values).

the SCR decreased constantly along the length of the river (Fig. 3). In summer, only 17% of DON and 37% of DOC was removed within the 14.3-mile river length. In winter, however, the DON concentration was reduced by 35% and DOC by only 27%. The reduced DOC removal in winter (median ambient water temperature = 14° C) relative to in summer (median temperature = 29° C) could be related to reduced microbial activity at water lower temperatures (Rittmann and McCarty, 2001). However, the elevated DON biodegradability in winter was unexpected. After investigating the processes used in the NIWWTP, we found that free chlorine (average dose = 3.9 mg/l Cl_2) was applied in summer but not in winter. The treatment plant discontinued the chlorination process during winter because of the low risks of human contact with wastewater. It was speculated that the chlorination pretreatment altered the biodegradability of DON. This was further investigated in laboratory biodegradation tests (see below). Reductions of 10%–20% in UVA values were observed along the river reach, but these were less than the observed reductions in DOC, leading to rising SUVA values along the river length. The observation that SUVA increases with extended biological treatment here, and with NN and WN samples above, is consistent with the framework that biodegradation favors non-aromatic carbon structures which tend to have low UVA_{254} (e.g., carbohydrates).

5. Laboratory testing on wastewater effluents for organic nitrogen removal

5.1. *Biodegradation*

Biodegradation of DON and DOC in four effluents was studied with and without chlorination pretreatment (Fig. 4). The average percentage reduction in DON or DOC over the five-day test occurred in the following rank-order: DON without chlorination had the highest removal (39%) > DOC without

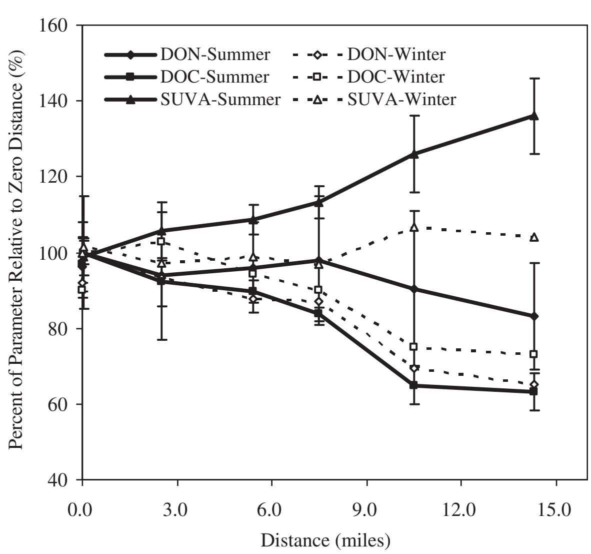

Fig. 3 – Water quality changes in an effluent-dominated river (Santa Cruz River) during two seasons (note: data points are average values; error bars indicate standard deviations of multiple samples).

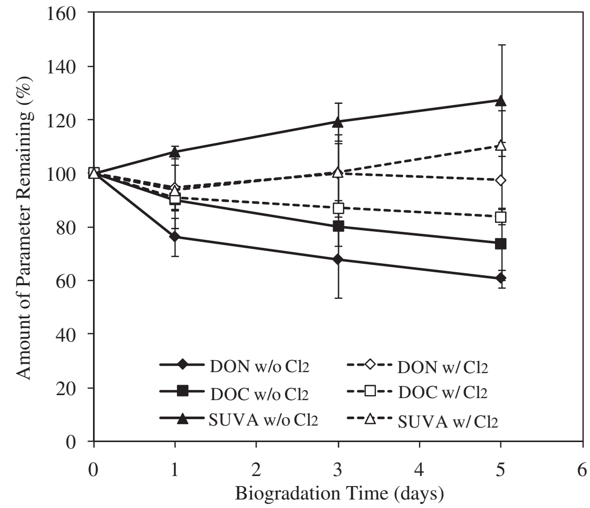

Fig. 4 – Water quality changes during biodegradation of effluents with (w/) and without (w/o) chlorination pretreatment (note: data points are average values; error bars indicate standard deviations of multiple samples).

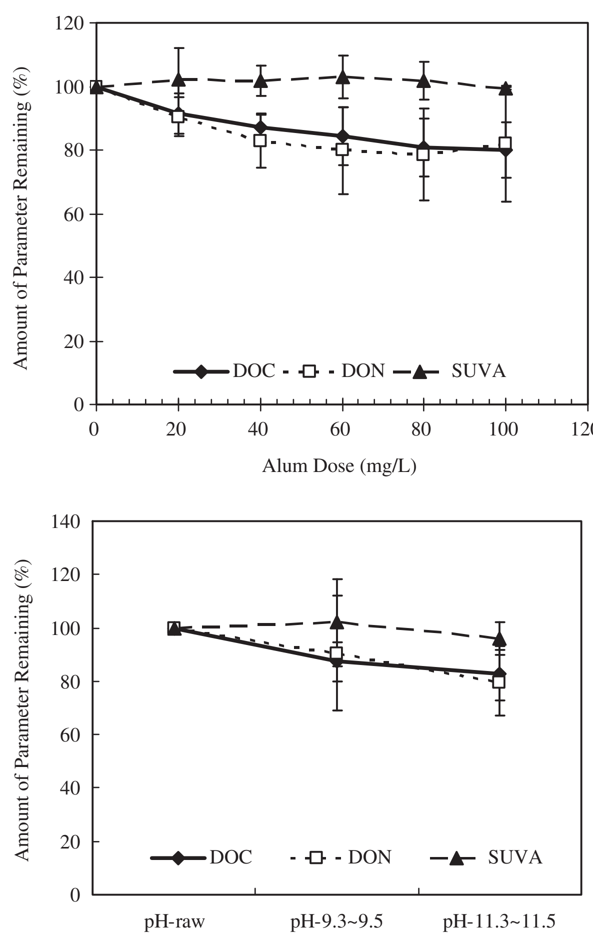

Fig. 5 – Effects of alum coagulation (top) and lime softening (bottom) processes on water quality changes in wastewater effluents (note: data points are average values; error bars indicate standard deviations of multiple samples).

chlorination (26%) > DOC with chlorination (16%) > DON with chlorination (3%). The observation that chlorination decreases DOC and DON biodegradation in the five-day tests is consistent with the reduced degradation observed within the Santa Cruz River (above). Chlorination has many potential impacts on wastewater effluents. One of the effects of Chlorination is to oxidize organic matter into lower molecular weight organic matter with higher carboxylic acid content (Westerhoff et al., 2004; Swietlik et al., 2009). However, the dominant cause may be the fact that chlorination oxidizes proteins and amino acids to organic chloramines, some of which are relatively stable and have disinfecting capabilities (Donnermair and Blatchley, 2003), so that chlorine substituted organics are more difficult to aerobically degrade than non-substituted analogs.

Biological pretreatment levels affected DOC and DON biodegradability as well (SI Fig. 3). In the absence of disinfectant, the activated sludge effluent had the highest DON (43%) and DOC (46%) removals, whereas the membrane bioreactor effluent had the smallest reductions (DON = 34%; DOC = 8%) with 5 day tests. In all cases, <10 percent of UVA_{254} was removed in all effluents, much lower than DOC and DON removals, resulting in increases in SUVA (27% in summer, 10% in winter). The observation of rising SUVA values is in line with the observations of the full-scale survey and effluent-dominated river.

5.2. Alum coagulation and lime softening

For wastewater effluents, DON removal efficiencies were nearly equal to or slightly greater than those of DOC during alum coagulation and lime softening tests (Fig. 5), which is consistent with data from drinking water treatment plants (Lee and Westerhoff, 2006; Dotson and Westerhoff, 2009). Dosages of 8 mg/L alum per mg/L DOC or lime softening at pH of 11.3–11.5 resulted in <25% removals of DON and DOC, indicating it is difficult to remove organic matter in these low SUVA waters. This is consistent with the premise behind the Enhanced Coagulation concept of the USEPA Disinfection/Disinfection Byproduct rule where waters with SUVA <2 L/mg-m can be exempt from the mandate to remove organic carbon through coagulation. SUVA itself changed little during treatment, varying by <10%, exhibiting no selectivity for UVA and non-UVA absorbing matter.

For the nine full-scale wastewater-impacted DWTPs surveyed in this study, similar results were observed although it is a combined effect of coagulation/softening, filtration, chlorination, etc. The median removals of DON and DOC from plant influent to effluent were 23% and 21%, respectively. A full-scale wastewater recycling plant was equipped with lime softening and sand filtration processes. For two sampling seasons, the average removals of DOC (11%) and DON (17%) at pH of 9.5 in this plant also fell within the range of those achieved in the bench-scale tests.

5.3. PAC adsorption

DOC concentrations decreased with increasing PAC dosages (SI Fig. 4). DOC removals were greater than DON removals by 10% on average. The percentage of UVA removal was much greater than both DOC and DON removals. Consequently, the SUVA values decreased considerably (>50%). To further quantify and

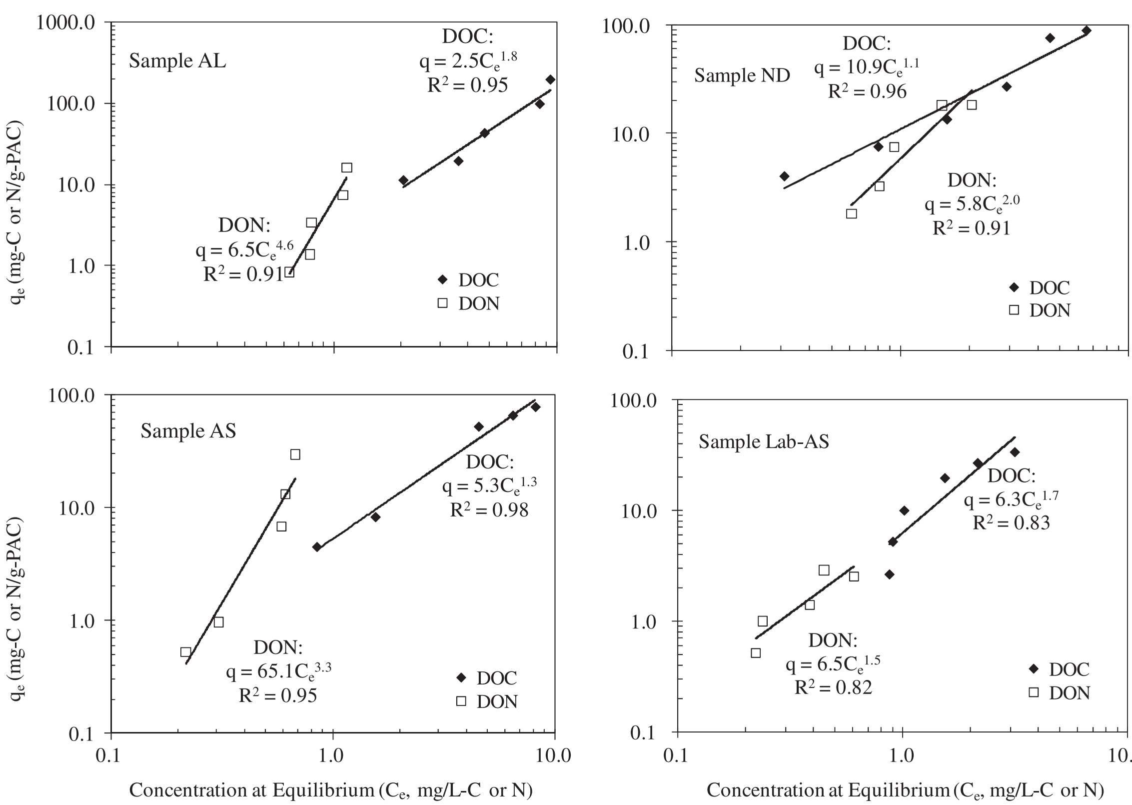

Fig. 6 – Freundlich isotherms of DOC and DON in equilibrium with PAC. AL: aerated lagoon, AS: activated sludge, ND: nitrification and denitrification, Lab-AS: laboratory-generated activated sludge.

compare the dose-dependent removal of DOC and DON, data were fit by Freundlich adsorption isotherms (Fig. 6). For DOC, the adsorption capacity (K) ranged from 2.5 to 11 (mg-C or N/g) [L/mg-PAC]$^{1/n}$, and the adsorption intensity (1/n) ranged from 1.1 to 1.8. In comparison, K (from 5.8 to 65 (mg-C or N/g)[L/mg-PAC]$^{1/n}$;) and 1/(1/n: from 1.5 to 4.6) values for DON were more variable than Freundlich parameters for DOC across the different waters tested. This could indicate greater variability in organic nitrogen composition among water sources, because organic nitrogen is part of larger and more complex organic matter, or greater competition between nitrogen enriched and nitrogen deficient organic matter fractions. All 1/n values were greater than unity, indicating unfavorable adsorption trends with continued loading to the PAC.

$$q_e = K \cdot C_e^{1/n} \tag{2}$$

where C_e is the equilibrium concentration after experiment (mg/L); q_e is the adsorbed amount of organic matter per gram of PAC at equilibrium (mg-C or N/g-PAC)and K and n are the Freundlich constants characteristic of the system. K is the adsorption capacity factor (mg-C or N/g)[L/mg-PAC]$^{1/n}$, and n is the intensity factor (unitless).

The $1/n$ values of DON and DOC decreased from the AL sample to the AS sample to the ND sample, indicating biological treatment removes non-adsorbing organic matter fractions and the efficiency of PAC improves with increased levels of biological activity, as indicated by better removal of dissolved inorganic nitrogen. Biodegradation processes tend to remove hydrophilic substances, leaving behind more hydrophobic organic matter, which happens to be more absorbable to PAC than hydrophilic organic matter (Karanfil, 2006).

6. Summary and conclusions

Based on the studies of full-scale plants, an effluent-dominated river, and bench-scale tests, our dataset provides important insights into the occurrence and treatment of dissolved organic nitrogen. The DON fractions in TDN were low (<10%) for most wastewater effluents, which justified the need for a longer dialysis pretreatment time to obtain accurate DON detection. The DON fractions in TDN were as high as 52% (median = 13%) in tertiary treated effluents and 54% (median = 31%) in wastewater-affected waters, indicating that DON can sometimes be a considerable or dominant part of TDN.

Removal of DON from wastewater effluents via coagulation and softening processes, as part of reuse planning or protection of the environment, can be difficult. Because wastewater effluents have low SUVA values (<2 L/mg-m), they exhibit poor DON adsorption onto alum floc (coagulation) or calcium carbonate solids (lime softening). Likewise, DON exhibits low adsorption capacities onto activated carbon. In-situ biological treatment using soil systems or rivers does seem to remove part of the DON. Chlorination appears quite detrimental to the efficiency of these natural systems, possibly due to the formation of organic chloramines. Thus, as direct or unintentional potable reuse of wastewater for drinking water expands, the focus for controlling DON should focus at improved removal at WWTPs.

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