Fate of Organic Nitrogen in Four Biological Nutrient Removal Wastewater Treatment Plants

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ABSTRACT: This study investigated the fate of nitrogen species, especially organic nitrogen, along the mainstream wastewater treatment processes in four biological nutrient removal (BNR) wastewater treatment plants (WWTPs). It was found that the dissolved organic nitrogen (DON) fraction was as high as 47% of soluble nitrogen (SN) in the low-SN effluent plant, which limited the plant's capability to remove nitrogen to very low levels. A lower DON fraction was observed in high-SN effluent plants. Effluent DON concentrations from the four plants ranged from 0.5 to 2 mg N/L and did not vary significantly, even though there was a large variation in the influent organic nitrogen concentrations. Size fractionation of organic nitrogen by serial filtration through 1.2-, 0.45-, and 0.22-μm pore-sized membrane filters and the flocculation-and-filtration with zinc sulfate ($ZnSO_4$) method was investigated. The maximum colloidal organic nitrogen (CON) fractions found were 68 and 45% in the primary effluent and final effluent, respectively. The experimental results showed that effluents after filtration through the 0.45-μm pore-sized filter contain significant colloidal fractions; hence, the constituents, including organic nitrogen, are not truly dissolved. A high CON fraction was observed in wastewater influents and was less significant in effluents. The flocculation and filtration method removed the colloidal fraction; therefore, the true DON fraction can be determined. *Water Environ. Res.*, **82,** 2306 (2010).

KEYWORDS: colloidal organic nitrogen, dissolved organic nitrogen, biological nutrient removal, low effluent nitrogen.
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Introduction

Effluent organic nitrogen (EON) has become a key concern for wastewater treatment plants (WWTPs) achieving very low total nitrogen (TN) levels (TN < 3 mg N/L) (Pagilla et al., 2006). Most biological nutrient removal (BNR) plants successfully remove inorganic nitrogen, but a significant fraction of organic nitrogen (ON) still remains in the effluent. Although many plants report EON data from routine monitoring, the data have not provided a clear understanding about the fate of organic nitrogen through the treatment train of a WWTP. Additionally, the EON data reported based on total Kjeldahl nitrogen (TKN) measurement and inorganic nitrogen species are not accurate enough to determine the organic nitrogen fractions at low total nitrogen levels. Therefore, this study was conducted to determine the EON fractions and also the fate of nitrogen species through the treatment trains of four BNR WWTPs in the United States.

Nitrogen species transformation in the wastewater treatment process train is key to the understanding of the fate and occurrence of dissolved organic nitrogen (DON), which is a majority fraction when nitrogen is treated to very low levels (<3 mg N/L). Effluent organic nitrogen consists of particulate organic nitrogen (PON), colloidal organic nitrogen (CON), and DON. Most of influent PON fraction is removed in a primary clarifier during the primary treatment process and the remaining is removed in the biological process. The fate of CON and DON through the wastewater treatment processes is unclear. The CON and DON become a significant fraction of the total nitrogen in the final effluent of some plants. The most recent study found that CON constituted up to 62% of the effluent total nitrogen in some plants, and DON could range from 56 to 95% of the total nitrogen in secondary effluents (Pagilla et al., 2008). APHA et al. (2005) defined the "dissolved solids" as the portion of solids that pass through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. Therefore, there is no standard to separate between particulate and dissolved fractions. A 0.45-μm nominal pore size filter is conventionally used to separate dissolved and particulate fractions (Pagilla et al., 2008).

Further size characterization of the dissolved fraction of wastewater organic matter based on the molecular weight of the compounds recently was investigated. Guo et al. (2003) characterized natural organic matter (NOM) by using size and molecular weight into particulate (POM > 0.45 μm), colloidal (COM, 1 kDa to 0.45μm), and dissolved (DOM < 1kDa) fractions based on the size of the filter through which each fraction passes. Organic matter size fractionation attributed to size and molecular weight also was investigated by Shon et al. (2006). They reported that dissolved organic carbon passing though a 0.45-μm filter, whose molecular weight equivalent is smaller than 10^9 Dalton, mainly was composed of cell fragments and macromolecules. The major macromolecules are the polysaccharides, proteins, lipids, nucleic acids, and NOM. Natural dissolved organic compounds have sizes ranging from low-molecular-weight (LMW) compounds, such as amino acids and urea, to high-molecular-weight (HMW) compounds, collectively called *humic substances*. The fraction of POM found in wastewater measured as suspended solids includes organic matter, protozoa, algae, bacterial floc and single cells, and microbial waste products.

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The EON is a combination of influent NOM organic nitrogen, recalcitrant influent synthetic organic matter organic nitrogen, and microbially generated organic nitrogen in the biological process (Nam and Amy, 2008; Pehlivanoglu and Sedlak, 2006b). It was found that humic substances originating from drinking water sources likely account for approximately 10% of wastewater-derived DON (Pehlivanoglu-Mantas and Sedlak, 2006a). It was found that the microbial-origin chemical oxygen demand (COD) was degraded biologically by up to 90% (Gaudy and Blachly, 1985). Namkung and Rittmann (1986) reported that the effluent soluble organic compounds contained approximately 85% soluble microbial products in their experimental studies.

The fate of organic matter in a WWTP—specifically organic nitrogen—is a function of the treatment processes/operations used in the treatment train. Solids (particulate and colloidal) removal, hydrolysis of solids, assimilation, and oxidation/reduction of inorganic nitrogen in the treatment processes/operations results in total nitrogen removal in a WWTP. However, the occurrence of organic nitrogen in forms that cannot be removed in the treatment train and organic nitrogen formed in the treatment processes is collectively responsible for the EON. The EON may be amenable to removal by either the existing processes in a WWTP through their optimization/modification and/or by tertiary treatment processes, such as microfiltration, enhanced coagulation/flocculation, and others that are used for achieving other effluent quality objectives. For example, effluents that are discharged to sensitive water bodies or reused are typically treated by those tertiary treatment processes to remove phosphorus, microorganisms, and residual organic matter. The same could be investigated carefully for EON removal also. The fraction of the EON that is not removable practicably and does not have an effect on the receiving water environment typically is the so-called *non-biodegradable* and/or *non-bioavailable EON* (Urgun-Demirtas et al., 2008). Therefore, it is critical to investigate the fate of organic nitrogen in advanced treatment processes in existing WWTPs to determine the feasibility of reducing EON practicably.

It has been known that coagulation and flocculation can remove colloids from water or wastewater successfully. Moreover, coagulation and flocculation generally are implemented in WWTPs as a phosphorous removal method and to enhance particle removal in a secondary settling tank. Hence, coagulation and flocculation/precipitation may be advantageous in EON removal also. This could be a key to enhance nitrogen removal in very stringent effluent total nitrogen permit plants. Therefore, fractionation of EON, in both influent and effluent, and fate of those fractions through the treatment train needs to be investigated. Specifically, BNR plants that have been successfully removing total nitrogen to low levels need to be investigated for additional EON removal.

The objectives of this study were to investigate the occurrence and fate of organic nitrogen in the four BNR WWTPs with varying BNR configurations, influent characteristics and operating conditions; and to determine the DON and CON fractions and their fate/transformations during treatment. In addition, nitrogen species (reduced and oxidized nitrogen species) composition in the wastewater treatment processes was investigated, as the wastewater is treated during primary, secondary, and tertiary treatment of WWTPs with varying configurations.

Materials and Methods

Wastewater samples were collected along the treatment processes from selected WWTPs, including Parkway (Maryland), Neuse River (North Carolina), Nansemond (Virginia), and South Durham (North Carolina). The 24-hour composite samples collected were relayed to the hydraulic retention time (HRT) of each process and filtered through 1.2-μm filters before shipping them overnight to the laboratory. Plant operating conditions and routine influent characterization were documented for each day of sampling. As soon as the samples were delivered to the laboratory, they were separated in two portions. The first portion was filtered serially through 1.2-, 0.45-, and 0.22-μm pore-sized filters, and the second portion was flocculated using zinc sulfate ($ZnSO_4$) and filtered using 0.45-μm pore-sized filters (flocculation-and-filtration [FF] method) (Mamais et al., 1993). The samples were analyzed for nitrogen and carbon species, with concurrent size fractionation by microfiltration.

The measured parameters were soluble nitrogen (SN), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), COD, soluble carbon, and soluble inorganic carbon. Soluble nitrogen was measured by the second-derivative UV spectrophotometric (SDUS) method following persulfate digestion optimized for low total nitrogen measurements (APHA et al., 2005; Sattayatewa and Pagilla, 2008). Nitrate (NO_3^-) was measured by the SDUS method (APHA et al., 2005). Nitrite (NO_2^-) was measured by diazotization (Hach method 10019, Hach Company, Loveland, Colorado), and ammonium (NH_4^+) was measured by the salicylate method (Hach method 10023). The COD measurement was according to Hach method 435. Soluble total carbon and soluble inorganic carbon were measured by a Dohrmann DC-190 TC/IC analyzer (Dohrmann, Cincinnati, Ohio).

The calculations and definitions of the nitrogen fraction and species are as follows. A subscript under the organic nitrogen parameter indicates the filter pore size. For example, $ON_{1.2}$ represents the organic nitrogen in filtrate from 1.2-μm pore-sized filter ($ON_{1.2}$ = CON + DON). The DON in flocculated and filtered samples represents "true" DON or FFDON. The CON concentration was calculated from the difference between $ON_{1.2}$ and FFDON (CON = $ON_{1.2}$ − FFDON). The CON fraction was calculated by dividing the CON concentration by the $ON_{1.2}$ concentration. The DON is the organic nitrogen passing through the 0.45-μm pore-sized filter, as currently practiced in WWTPs. Soluble nitrogen includes dissolved inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$), FFDON, and CON (SN = FFDON + CON + $NH_4^+ + NO_3^- + NO_2^-$). Therefore, the term *soluble nitrogen* in this study is a combination of colloids and dissolved nitrogen fractions. Because particles were removed upon sample collection at the WWTP, the term *total nitrogen* is not an appropriate notation to describe the total nitrogen content in the samples. Each wastewater sample was analyzed on a triplicate basis.

The sampling campaign was conducted between January and August 2008, and sampling dates were selected randomly, depending on the accessibility to each plant. Table 1 shows the summary of plant information and their respective BNR configurations. The mainstream process configuration schematics are shown in Figure 1. The composite samples were collected at the influent end, final effluent, and within the treatment processes. Three sampling events were conducted for each plant on 3 different days. Composite samples provide more representative sampling of heterogeneous matrices, in which the concentration of the analytes of interest may vary over short periods of time and/or space, and hence were selected for this study.

Table 1—Plant Information of the Studied WWTPs.

Plant	BNR technology	Design flow (m^3/d)	Coagulant added	Filter	Nitrogen limit (mg N/L)	Disinfection	Sludge stabilization
S. Durham	5-stage Bardenpho	76 000	Alum (April to October)	Dual media	5.5	UV	Anaerobic digestion
Nansemond	3-stage VIP	114 000	$FeCl_3$*	Not applicable	8	Chlorination	Anaerobic digestion
Neuse River	4-stage Bardenpho	230 000	Not applicable	Deep bed monomedia sand	Not applicable	UV	Chemical
Parkway	4-stage Bardenpho	28 000	PACl	Not applicable	7.0	Chlorination Hypochlorite	Chemical (lime)

* Only when needed.

Studied Wastewater Treatment Plants

Parkway. Parkway uses a 4-stage Bardenpho process for carbon, nitrogen, and phosphorus removal. The average influent flowrate was approximately 22 500 m^3/d. There are two significant industrial discharges to the Parkway service area at the flowrate of 675 m^3/d or 3% of the daily total flow.

The influent soluble nitrogen was approximately 25 mg N/L during the three sampling events. Ammonium was the predominant nitrogen species (63 to 92% of the influent soluble nitrogen) in the raw wastewater. Wastewater characteristics, including influent soluble nitrogen, influent suspended solids, 5-day biochemical oxygen demand (BOD_5), influent DON, and BOD_5/TN ratio, are shown in Table 2. The Parkway WWTP receives a continuous flow of alum sludge (285 m^3/d) from the Patuxent water treatment plant (WTP) (Laurel, Maryland) discharged to the sewers. As a result, a high influent suspended solids concentration (measured by the plant) was observed from the three sampling dates (Table 2). This alum sludge increased the suspended solids significantly and was removed mostly in the primary clarifiers.

Neuse River. The Neuse River WWTP has a design capacity of 227 000 m^3/d. It is an advanced wastewater treatment facility serving the City of Raleigh, North Carolina. A total of 21 industrial users contribute to the wastewater flow to the Neuse River WWTP. The industrial contribution is approximately 3 to 4% (7200 m^3/d) of the total influent flow, and approximately 44% of the industrial flow is from food-processing products.

A four-stage BNR process is used for secondary treatment with internal mixed-liquor recirculation and returned activated sludge recycle. During our sampling period, the daily average flow was approximately 150 000 m^3/d. Wastewater characteristics of the Neuse River WWTP are summarized in Table 2. The ammonium concentration was up to 85% of soluble nitrogen, and organic nitrogen was 15% of soluble nitrogen in the influent samples. Nitrate and nitrite concentration in the influent were less than 0.05 mg N/L. The organic nitrogen concentration in the influent was approximately 1 mg N/L in one sampling event and approximately 5.5 mg N/L for the other two.

Nansemond. Nansemond WWTP is located in Suffolk, Virginia. The daily average flow is approximately 63 000 m^3/d. The Nansemond WWTP receives the largest industrial contribution of the four plants in this study. The Nansemond WWTP uses a 3-stage VIP process as the secondary treatment process. Ferric chloride is used as a coagulant/flocculant for phosphorus removal and is mixed in-line with the mixed liquor before it reaches the secondary clarifiers. Nansemond WWTP currently uses gaseous chlorine and sulfur dioxide (anhydrous) for chlorination/dechlorination. Sodium bisulfite also is added to the final effluent to remove any remaining chlorine before discharge. Advanced

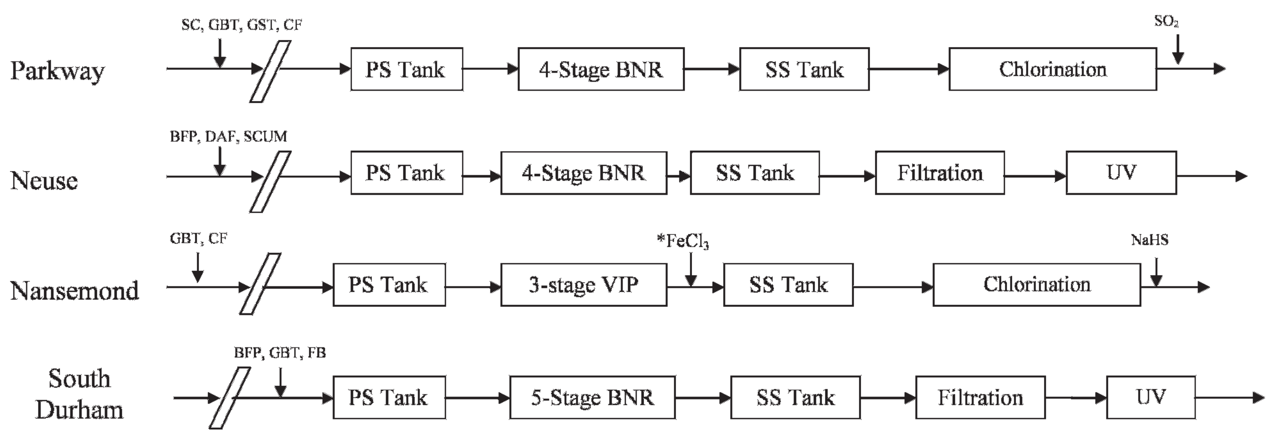

Figure 1—Wastewater treatment process schematic diagrams of the studied WWTPs. (SC = scum concentrator filtrate, GBT = gravity belt thickener filtrate, GST = gravity settling tank filtrate, CF = centrifuge filtrate, BFP = belt filter press filtrate, DAF = dissolved air flotation filtrate, and FB = filter backwash).*$FeCl_3$ is intermittently added for phosphorus removal.

Table 2—Influent wastewater characteristics of the plants.

	Influent soluble nitrogen (mg N/L)	BOD_5 (mg/L)	Influent suspended solids (mg/L)	Influent DON (mg N/L)	BOD_5/TN ratio
Parkway	25	187 to 218	317 to 578	2.0 to 10.0	8
Neuse River	35	235 to 250	205 to 308	1 to 5.5	7
Nansemond	35	230 to 234	150 to 178	2.0 to 4.0	6.5
S. Durham	25 to 42	210 to 260	175 to 183	1.5 to 6	7

anaerobic digestion, the two-phase acid–gas process, is used to treat solids before disposing to the off-site facilities. The influent soluble nitrogen concentration was approximately 35 mg N/L, with 85 to 90% as the ammonium concentration. The organic nitrogen concentration was between 2 and 4 mg N/L. Nitrate and nitrite were not detected in the influent. The summary of influent wastewater characteristics is shown in Table 2.

South Durham. The South Durham wastewater treatment facility is located in Durham, North Carolina. The treatment facility is capable of treating up to 76 000 m^3/d. The average flow during the three sampling events was 34 000 m^3/d. South Durham receives an average industrial contribution from industrial users. A 5-stage BNR process is used for biological treatment (for both nitrogen and phosphorus removal) of wastewater. Dual media filters are used to remove particles from the secondary effluent. UV disinfection is used as tertiary treatment before discharging the effluent to the environment. Influent soluble nitrogen varied between 25 and 42 mg N/L. Influent ammonium content is up to 88% of soluble nitrogen. The organic nitrogen concentration varied between 1.5 and 6 mg N/L. Similar to the other plants, nitrate and nitrite were not detected in the influent. The summary of influent wastewater characteristics is shown in Table 2.

Results and Discussion

Dissolved Organic Nitrogen and Colloidal Organic Nitrogen in Primary Effluent and Final Effluent. Sampling dates, operating conditions, and summary results of the DON and CON concentrations in primary effluents and final effluents are shown in Table 3. The results illustrated the colloidal fraction in both primary effluent and final effluent samples. It was found that a high variation of the primary effluent $ON_{1.2}$ concentration was observed within a plant on different days. This variation could be related to the collection system characteristics and residence time of the wastewater in the collection systems. For example, primary effluent $ON_{1.2}$ in South Durham varied from 1.1 mg N/L to as high as 6.4 mg N/L. High variations in $ON_{1.2}$ in primary effluent also were observed in the Neuse River, Parkway, and South Durham wastewater samples. In some samples, CON was the majority fraction of primary effluent $ON_{1.2}$. It was as high as 68% in a sample taken from Nansemond and 67% in a sample from Parkway. A similar finding was reported by Pagilla et al. (2008), who found that 62% of organic nitrogen was CON. The results from the four plants showed that the primary effluent $ON_{1.2}$ ranged from 0.7 to 6.9 mg N/L. The CON/$ON_{1.2}$ fraction varied within the three sampling dates. A possible reason for the high CON fraction in the Parkway primary effluent was the solids from the Patuxent water treatment in the Parkway influent. It can be hypothesized that a high influent organic nitrogen concentration reflects a short residence time of the wastewater in the collection system. The nitrogen present in fresh wastewater is primarily in proteins and urea. Decomposition by bacteria readily changes the organic nitrogen form to ammonia. Wastewater from the four plants had different NH_4^+/SN ratios on different days. The age of wastewater is indicated by the relative amount of ammonia that is present (Metcalf & Eddy, 2003). A high variation of influent wastewater characteristics also was reported by Pagilla et al. (2008) in the samples from 3 fully nitrified WWTPs in Illinois and 4 BNR plants in Poland. The fractions of DON in primary effluents ranged from 2 to 21% and 13 to 27% of total nitrogen in the Illinois and Polish plants, respectively.

Even though a high fluctuation in $ON_{1.2}$ concentration was found in the primary effluent samples, the effluent organic

Table 3—Summary results of plant operating conditions and organic nitrogen concentrations in primary effluent of the studied plants.

							PE ON			Effluent ON		
Plant	Sample dates	Effluent SN (mg N/L)	Temp (°C)	SRT (days)	Flow (m^3/d)	MLSS (mg/L)	1.2 μm (mg N/L)	ON/SN (%)	CON (%)	1.2 μm (mg N/L)	ON/SN (%)	CON (%)
Parkway	3/10/2008	3	14.4	25.3	23 400	3500	4.04	15.8	66.8	0.68	33.8	41
	4/21/2008		18.3	12.3	29 900	3700	6.89	32.7	10	0.93	38	29
	6/3/2008		20.5	8.38	22 400	2935	1.72	7.2	43.6	0.63	46.7	2
Neuse River	3/25/2008	3	18	23.8	149 000	4449	4.26	14.7	34.7	0.71	33.3	1
	5/9/2008		21	17.7	151 000	3271	1.16	4.1	29.3	0.84	43.1	8.3
	6/5/2008		23.7	21.8	150 000	3208	5.89	15.8	45.3	1.36	36.3	6.6
Nansemond	4/9/2008	12	18	14.3	63 200	2540	2.64	6.7	33.3	1.41	11.3	45
	5/21/2008		17	15.4	63 500	2600	3.49	10.1	55.9	0.94	7.3	4
	6/17/2008		26	14.9	62 500	2380	0.74	2	67.6	1.34	10.6	17.5
S. Durham	1/29/2008	12	16	16.4	N/A	N/A	6.42	16.7	39	0.74	5	6.2
	3/6/2008		17	16.9	35 100	2900	1.08	4.1	26.6	1.92	17	26.6
	6/7/2008		23	16	34 400	3110	3.74	10.2	46.6	1.17	15.7	6

nitrogen concentration was less than 2.0 mg N/L in most of the plants and more consistent among the three sampling events. Effluent $ON_{1.2}$ concentrations varied between 0.5 and 2 mg N/L, regardless of the types of biological reactor. The $ON_{1.2}$ concentration decreased significantly during the primary treatment process in the Parkway samples, by approximately 30%. This could be the result of the removal of colloids and DON by excess polyaluminum chloride in the sludge from the Paluxent water treatment plant. A large fraction of organic nitrogen decreased within the secondary treatment process. It can be hypothesized that labile organic nitrogen was oxidized by biological activity in the secondary treatment process, and refractory organic nitrogen was a main fraction of the effluent organic nitrogen.

It was found that CON in final effluent was lower than in the primary effluent. The South Durham and Neuse River WWTPs used filtration in tertiary treatment, and could be expected to have low colloids in the final effluent. The results showed that colloids were present in a lower amount in the samples from the Neuse River. This could be because the Neuse River WWTP uses a biologically active filter for tertiary treatment, and this could be advantageous in CON removal. The Neuse River had a CON fraction less than 8% of the effluent $ON_{1.2}$. The results from South Durham showed a 27% CON fraction on one sampling date, while the other two were approximately 6%.

A high $ON_{1.2}$/SN ratio was observed in low or very low total nitrogen effluents. For instance, $ON_{1.2}$ was as high as 47% of the soluble nitrogen in the effluent from Parkway (soluble nitrogen = approximately 3 to 4 mg N/L) and ranged from 33 to 43% in the Neuse River effluents (soluble nitrogen = approximately 4 to 5 mg N/L). Pagilla et al. (2008) reported a DON/TN ratio of approximately 20% in Illinois WWTPs in full nitrification plants and reached 50% in BNR Polish WWTPs. A similar finding was reported by Pagilla et al. (2006) and Pehlivanoglu and Sedlak (2004)—a DON/TN ratio of 85% in a WWTP achieving an effluent total nitrogen concentration of 2 mg N/L. The results from this study showed that a high effluent total nitrogen concentration did not cause a high effluent DON, and vice versa.

Most WWTPs report nitrogen in terms of TKN, which is a combination of ammonium and organic nitrogen. In domestic wastewater, approximately 60% of the nitrogen is in ammonium form, and 40% of nitrogen is in organic form (WEF, 2005). In this study, ammonium and organic nitrogen were measured separately to obtain better understanding of nitrogen species in WWTPs. The results showed that the ON/NH_4^+-N ratio varies among sampling events within each plant (data not show). The organic nitrogen concentration is inversely related to the amount of ammonium in the influent. Nitrogen transformations could be occurring in the wastewater collection system, and water usage characteristics influence the wastewater composition received at the WWTP. The transformation processes include ammonification of organic nitrogen and hydrolysis of urea (WEF, 2005). Even when influent was sampled from the same WWTP, high variation of influent organic nitrogen was observed. The difference among sampling events may be influenced by a number of factors, including water usage, type of collection system, infiltration and inflow, variation of flow and loads, season, and weather. The sampling campaigns were between January and August 2008 and were selected randomly among the 4 plants. Different sampling dates over a long period of time may affect wastewater characteristics also.

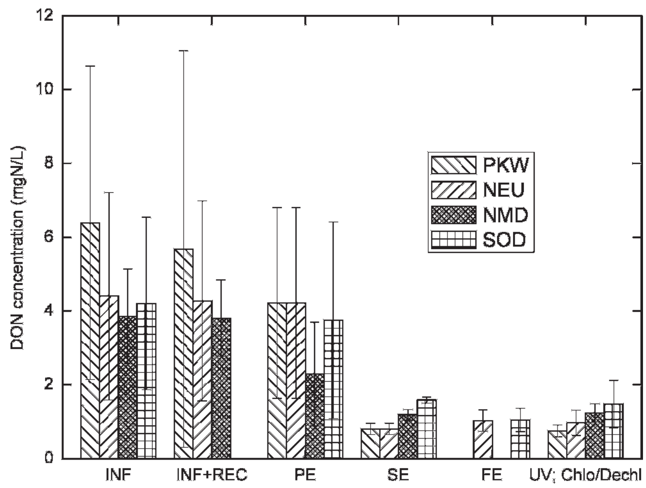

Figure 2—Average $ON_{1.2}$ profiles from four WTTPs along the mainstream treatment (PKW = 4-stage BNR, NEU = 4-stage BNR, NMD = 3-stage VIP, and SOD = 5-stage BNR).

Organic Nitrogen Concentrations Along the Mainstream Treatment. The fate of organic nitrogen and fractionation was investigated with collected samples of influent, primary effluent, secondary effluent, filter effluent, and final effluent (after UV or chlorine disinfection). Those samples were filtered serially though different filter pore sizes, as previously discussed in the Materials and Methods section. Average $ON_{1.2}$ concentration profiles along mainstream treatment within four WWTPs are shown in Figure 2. The letters INF, INF + REC, PE, SE, FE, and FNE represent influent, influent mixed with recycle flow, primary effluent, secondary effluent, filtered effluent, and final effluent, respectively. Each bar in the graph represents the average organic nitrogen concentration in each plant. The legend in the graph represents the four WWTPs (PKW = Parkway, NEU = Neuse, NMD = Nansemond, and SOD = South Durham), and the error bars represent 1 standard deviation of triplicate measurements.

As can be seen from Figure 2, the average influent $ON_{1.2}$ from the four plants was approximately 4 mg N/L and decreased to less than 2 mg N/L in the effluent. The results showed that the four WWTPs produced different levels of effluent soluble nitrogen, but $ON_{1.2}$ in the effluent was approximately the same magnitude. Tertiary treatment did not reduce the organic nitrogen in the effluent. To obtain a better understanding of organic nitrogen removal, influent organic nitrogen from each plant was normalized to 100%, and the organic nitrogen content along the treatment stream was calculated as a fraction of influent organic nitrogen (Figure 3). Approximately 20% of influent organic nitrogen decreased after primary treatment, and approximately 20% of influent organic nitrogen content remained in the final effluent. The results agree with the previous observations and hypothesis on the solubilization of organic nitrogen during treatment. Approximately 60 to 80% of organic nitrogen were removed in the treatment processes. The fate of CON through the treatment process was similar to the fate of $ON_{1.2}$. Figure 4 shows the normalized CON fraction by averaging the colloidal fraction from three sampling events and normalizing the influent CON to 100%. The CON removal in primary treatment ranged from 10 to 30% of the initial concentration. The majority of CON removal was found in the biological reactor, ranging from 30 to 60%. The CON decreased

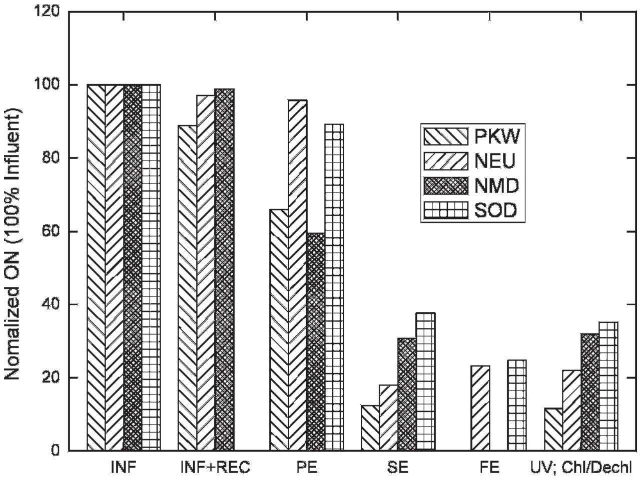

Figure 3—Normalized organic nitrogen levels based on concentrations in the four WWTPs along the mainstream treatment (PKW = 4-stage BNR, NEU = 4-stage BNR, NMD = 3-stage VIP, and SOD = 5-stage BNR).

along the primary treatment and also within biological reactor. Approximately 10 to 20% of the influent CON left the WWTPs in the effluents, even though those WWTPs use different biological technologies and achieve different effluent soluble nitrogen levels.

In addition, all nitrogen species were monitored through treatment processes, and the results are shown in Figure 5. It was found that there was very little or no nitrate and nitrite in the influent samples. The influent soluble nitrogen concentration ranged from 30 to 40 mg N/L. Ammonium was the dominant species and was approximately 80 to 90% of the soluble nitrogen. The soluble nitrogen concentration in the primary treatment processes fluctuated slightly. This could be because the samples were composited for 24 hours. From Figure 5, the important findings can be listed as follows:

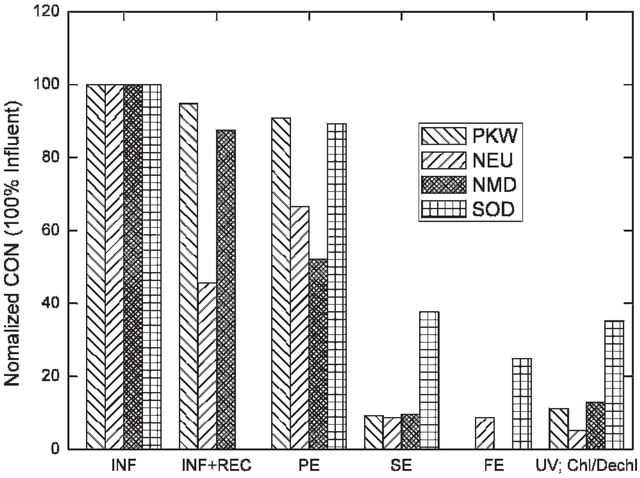

Figure 4—Normalized CON levels in the 4 WWTPs along the mainstream treatment (PKW = 4-stage BNR, NEU = 4-stage BNR, NMD = 3-stage VIP, and SOD = 5-stage BNR).

(1) Organic nitrogen, CON, and ammonium were the majority nitrogen fractions in the wastewater influent samples;
(2) Organic nitrogen and nitrate were the majority nitrogen fractions in the wastewater effluent samples;
(3) CON and organic nitrogen deceased during the treatment processes; and
(4) The organic nitrogen fraction was significant at low effluent soluble nitrogen levels.

In the 12 influent samples from the four plants, the DON/SN ratio ranged from 6 to 40, 2 to 19, 8 to 14, and 5 to 19% in the Parkway, Neuse River, Nansemond, and South Durham plants, respectively. The most variable plant was the Parkway WWTP, which comprised up to 40% of the influent nitrogen as organic nitrogen. In the case of a high influent organic nitrogen concentration, the results show that the organic nitrogen concentration decreased both during the primary and along the advanced treatment processes. The reduction in concentrations in the primary treatment could be the result of dilution from filter backwash recycles and thickener supernatants or biological ammonification when wastewater was exposed to treatment conditions in the preliminary and primary treatment processes. High variations of the influent DON/TN ratio also were reported by Pagilla et al. (2008).

Ammonium removal was observed mainly in the biological process. The results showed that the Parkway and Neuse River WWTPs removed ammonium to very low concentrations. Nitrate concentrations were present at very low concentrations in the effluent of these plants. It was found that complete nitrification was achieved in Nansemond, because there was no ammonium in the effluent, but the same is not true for South Durham. Ammonium was present in the effluent at a concentration of 1 to 2 mg N/L. Generally, the ammonium concentration increased in the primary treatment process, with a corresponding decrease in organic nitrogen. The similarity was found in all four plants. In low-soluble-nitrogen effluents, organic nitrogen seems to be the majority of nitrogen species and can reach up to 50% of the effluent soluble nitrogen. The percentage is smaller in high-soluble-nitrogen effluent. However, it was noticed that, even though organic nitrogen was present in a lower fraction in the high total nitrogen effluent, the concentration was in the same magnitude as the low-total-nitrogen effluent (up to 2 mg N/L). The Parkway and Neuse River WWTPs achieved low to very low effluent soluble nitrogen concentrations. One observation was that these two plants were provided with an additional carbon source during the biological treatment processes. This carbon source was used as a supplemental electron donor for denitrification. Plants producing low soluble nitrogen also were producing low effluent $ON_{1.2}$, but the $ON_{1.2}$/SN ratio was more significant.

The effect of solids retention time (SRT) on the $ON_{1.2}$/SN ratio was investigated. Figure 6 shows the relationship between the SRT and $ON_{1.2}$/SN ratio. The lines illustrated that effluent soluble nitrogen levels decreased with the increasing SRT in the Parkway, Neuse River, and Nansemond plants. This was not the case in the South Durham samples. However, the number of results generated during this study is not enough to have a statistically significant fit to the linear regression. The SRT should be maintained at an optimal level to obtain a low organic nitrogen level (Barker and Stuckey, 1999). Manipulation of the SRT could be a solution to minimize the high $ON_{1.2}$ /SN ratio in the plants producing very low nitrogen levels.

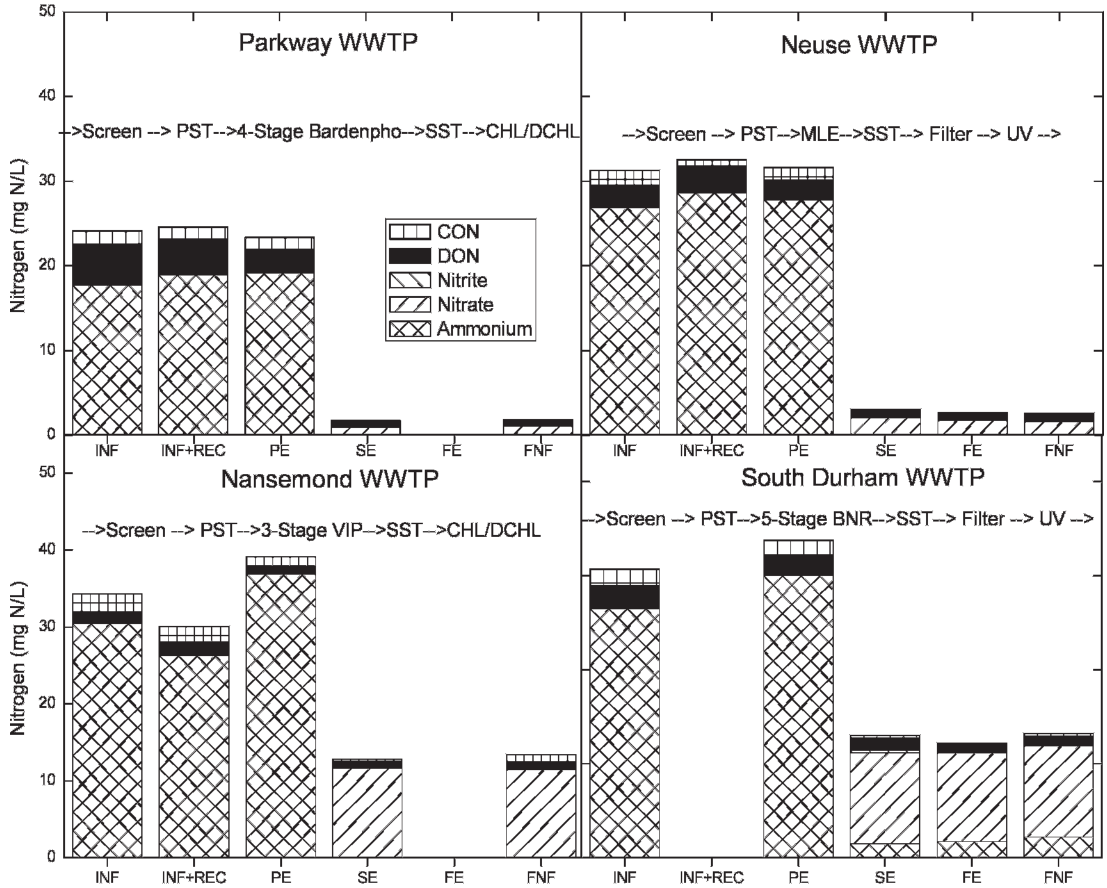

Figure 5—Summary nitrogen species concentrations in the studied WWTPs.

Organic nitrogen size fractionation found that significant CON was found in wastewater influents. The difference between $ON_{1.2}$ and FFDON was calculated as the CON concentration. Generally, particles that pass through 0.1 μm are considered to be truly soluble. However, filtration with very small nominal pore size filters is not practical and is an energy-intensive process. Colloids have a size range between 0.1 and 1.2 μm, based on filtration through filters of those pore sizes. The retentate on a 1.2-μm pore-size filter is considered to be particulate solids. Serial filtration with 1.2-, 0.45-, and 0.22-μm pore-size filters showed the fraction of CON that was removed during filtration. Figure 7 is an example of organic nitrogen size fractionation by filtration in the Neuse River Samples. The figure is composed of three stacked graphs representing three different sampling dates. Each bar represents the organic nitrogen concentration of different organic nitrogen fractions from serial filtration of samples. Statistical analysis (*t*-test) of results on the organic nitrogen concentration can be summarized as follows:

- $ON_{1.2}$ concentration was always the larger value.;
- $ON_{0.45}$ (or commonly referred to as DON) and $ON_{0.22}$ concentrations were different in some cases, and the FFDON concentration was always less than $ON_{1.2}$; and
- $ON_{0.22}$ was not more than FFDON in all of the cases, showing that filtration through a 0.22-μm pore-size filter could be substituted for FFDON to determine the true DON.

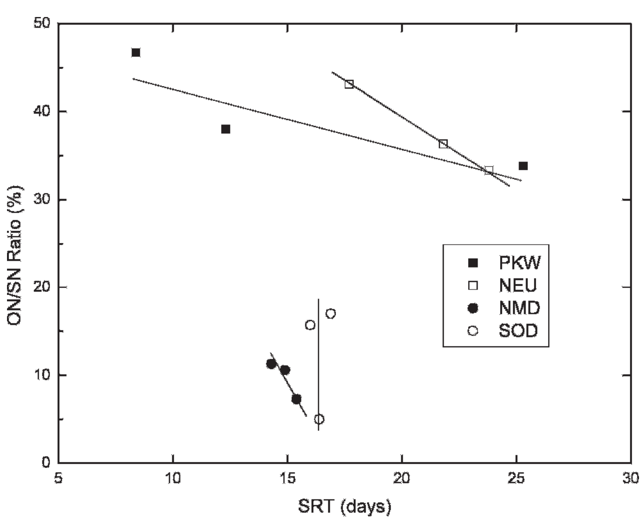

Figure 6—Relationship between $ON_{1.2}$/SN ratio (percent) and SRT (days) in the studied plants.

When considering conventional filter size, the average effluent $ON_{0.45}$ or DON concentration was slightly different among WWTPs. The average DON concentrations in final effluents were 0.69 ± 0.18, 0.95 ± 0.33, 1.05 ± 0.35, and 1.42 ± 0.23 mg N/L

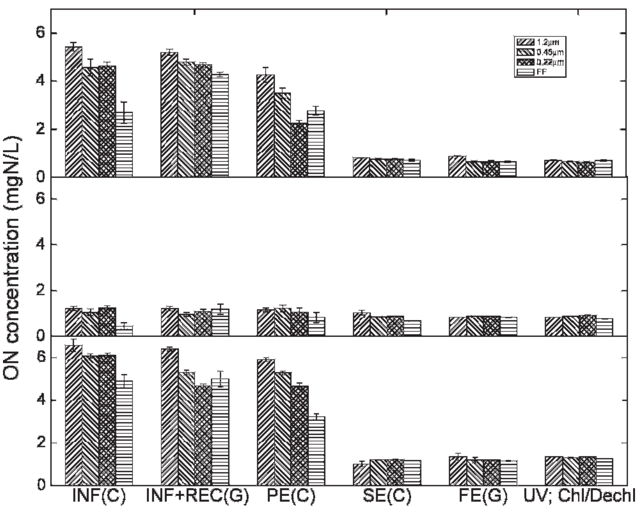

Figure 7—Neuse River organic nitrogen profile from different sampling dates (each of the three stacked graphs is from one sampling date).

in the Parkway, Neuse, Nansemond, and South Durham plants, respectively. The results showed low variation of effluent DON concentration among the three sampling events; hence, the variations in influent organic nitrogen did not influence the effluent DON concentration.

Colloidal removal by a 0.45-µm nominal pore-size microfilter and flocculation-and-filtration method were compared, and the results are shown in Tables 4 and 5. The truly dissolved organic nitrogen fraction can be obtained from the flocculation-and-filtration sample. It was found that filtration with a 0.45-µm nominal pore-size filter contains some colloidal fraction. Flocculation-and-filtration samples were analyzed and measured for chemical oxygen demand (FFCOD), dissolved organic carbon (FFDOC), and FFDON. The flocculation-and-filtration method removed up to 51% of CON, 43% of colloidal COD (CCOD), and 47% of colloidal organic carbon (OC) in the influent samples. Colloidal removal was lower in the effluent samples. The flocculation-and-filtration method shows significant removal of CON. The CON removal was 36 to 51% and 13 to 25% for influents and final effluents, respectively (Tables 4 and 5). A significant fraction of CCOD was observed in the samples when the samples were filtered through a 0.45-µm pore-size filter and was able to be removed by flocculation (Tables 4 and 5). Colloid removal by the flocculation-and-filtration method was within the removal range observed by Lee and Westerhoff (2006). Their study showed that 5 to 40% of DOC and DON were removed, depending on coagulant dosage. The DOC removal was slightly higher than that of DON, but the trends were comparable. At an aluminium sulfate concentration of 5 mg/mg DOC, the cationic polymer addition enhanced DON removal by 15 to 20%. These results show that physical–chemical treatment, such as coagulation/flocculation and filtration, is able to minimize CON in the effluent. The percent CON removal varies, depending on the CON fraction in the untreated samples.

The effect of tertiary treatment on the EON concentration was investigated during these sampling events from the four plants. During tertiary treatment, various treatment processes, such as filtration, chlorination, and UV disinfection are used. Because the samples were composited and the sampling time interval was relayed to the HRT for each process, the samples did not ideally illustrate the treatment effects in a continuous-flow plant. The organic nitrogen concentrations before and after tertiary treatment were not statistically different (results not shown). Typically, removal of organic and inorganic colloidal and suspended solids is supposed to be accomplished by filtration (Metcalf & Eddy, 2003). To better understand tertiary treatment effects, studies should be conducted at laboratory-scale and in a controlled environment. The observation that the organic nitrogen concentration remains at the same level after chlorination could be attributed to the fact that chlorination only transforms dissolved organic matter and does not eliminate it. It is well-known that wastewater-derived organic nitrogen serves as a disinfection byproducts precursor during disinfection with chlorine (Mitch and Sedlak, 2004; Pehlivanoglu-Mantas and Sedlak, 2006a; Schreiber and Mitch, 2006) and hence could be of concern.

The DON concentration in the effluent after passing through the UV disinfection in the South Durham and Neuse River plants was not significantly different. It is generally thought that most of the complex organic nitrogen can be oxidized by hydroxide radicals (Chou et al., 1999) in advanced oxidation involving UV; however, the oxidation of organic matter requires a longer detention time and more UV intensity than that provided by the effluent disinfection UV systems in WWTPs. Hence, the results obtained from the South Durham and Neuse River plants are consistent with this fact. There were several studies on DON removal with advanced oxidation processes in the literature. A combination of several methods can give higher treatment efficiency compared with individual methods (Li et al., 2006; Takeda and Fujiwara,

Table 4—Average calculated organic nitrogen fraction ratios for Parkway and Neuse River WWTPs.

	Parkway				Neuse River			
	Influent		Effluent		Influent		Effluent	
Parameters	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
$FFDON/ON_{0.45}$	0.82	0.07	0.83	0.06	0.58	0.33	0.95	0.06
$(ON_{1.2}\text{-}FFDON)/ON_{1.2}$	0.28	0.12	0.17	0.14	0.47	0.20	0.06	0.03
$FFCOD/COD_{0.45}$	0.68	0.11	0.87	0.11	0.64	0.11	0.73	0.07
$FFDOC/OC_{0.45}$	0.72	0.08	0.80	0.14	0.72	0.16	0.52	0.14

Table 5—Average calculated organic nitrogen fraction ratios for Nansemond and South Durham WWTPs.

	Nansemond				South Durham			
	Influent		Effluent		Influent		Effluent	
Parameters	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
$FFDON/ON_{0.45}$	0.49	0.17	0.76	0.21	0.53	0.43	0.88	0.13
$(ON_{1.2}\text{-}FFDON)/ON_{1.2}$	0.58	0.14	0.27	0.22	0.30	0.10	0.19	0.12
$FFCOD/COD_{0.45}$	0.76	0.04	0.73	0.07	0.57	0.01	0.74	0.11
$FFDOC/OC_{0.45}$	0.73	0.07	0.52	0.14	0.53	0.15	0.72	0.07

1996). Dwyer et al. (2008) found that advanced oxidation by UV and hydrogen peroxide (H_2O_2) possibly could reduce 50% of the DON at an optimum H_2O_2 dosage. If and when WWTPs are required to remove or reduce trace and emerging organic contaminants from the effluents, it would be prudent to investigate these advanced oxidation processes for DON removal also.

Conclusions

Based on the results from this study, $ON_{1.2}$ concentrations in the influents varied considerably for each plant over the three sampling events. However, there was low variation of effluent $ON_{1.2}$ concentrations for each plant over the sampling dates. High soluble nitrogen effluent (soluble nitrogen = approximately 14 mg N/L) contained less DON fraction; however, the magnitude was approximately in the same range (0.5 to 2.0 mg N/L) as the low-soluble-nitrogen effluents (<5 mg N/L). The CON concentration decreased along both primary and secondary treatment processes. The experimental results showed that effluents after filtration through a 0.45-µm pore-sized filter contained significant colloidal fractions; hence, the constituents, including organic nitrogen, were not truly dissolved. In high-CON-concentration effluents, CON removal could lower the effluent total nitrogen concentration by approximately 0.5 to 1.0 mg N/L (up to 30% of effluent soluble nitrogen = 3 mg N/L), but the same is not applicable for low-CON effluents. The fate of organic nitrogen in the plant depended considerably on the plant configuration and operating conditions. The majority of organic nitrogen removal occurred in the biological treatment process of all four BNR plants studied. Plants with a longer process SRT produced a low effluent ON/SN ratio. However, the optimum relationship between SRT and effluent organic nitrogen levels should be investigated further. Organic nitrogen removal is not significant across filtration and disinfection (UV or chlorination) in the treatment train of all four plants. Additionally, it was found that the FFDON method, which is similar to the FFCOD method, could be used to obtain a very good indicator of ‘‘true’’ DON in the effluent that escapes in the effluent.

Credits

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