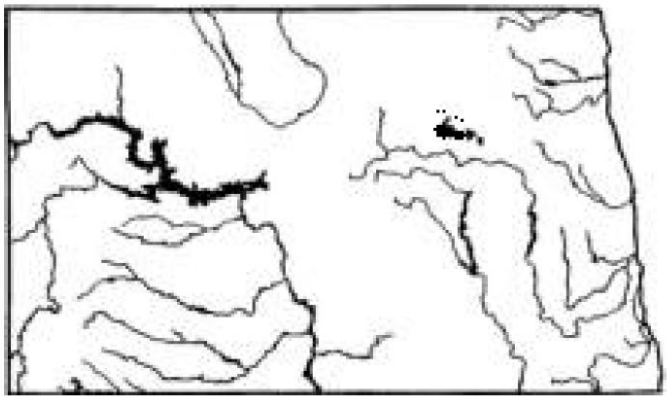

Technical Report No: ND12-03

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ABSTRACT

A comprehensive study to investigate the fate of dissolved organic nitrogen (DON) and biodegradable DON (BDON) through the Fargo Wastewater Treatment Plant (WWTP) was conducted. The Fargo WWTP has a two-stage trickling filter process and discharges treated wastewater to the Red River. The fate of DON and BDON has not been studied for trickling filter WWTPs. Results showed that DON concentrations in the influent and effluent were 27% and 14% of total dissolved nitrogen (TDN). The plant removed about 62% and 72% of the influent DON and BDON mainly by the trickling filters. The final effluent BDON values averaged 1.78 mg/L. BDON was found to be between 51% and 69% of the DON in raw wastewater and after various treatment units. The fate of DON and BDON through the Fargo WWTP was modeled. The BioWin v3.1 model was successfully applied to simulate ammonia, nitrite, nitrate, TDN, DON and BDON concentrations along the treatment train. The maximum growth rates for ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria, and AOB half saturation constant influenced ammonia and nitrate output results. Hydrolysis and ammonification rates influenced all of the nitrogen species in the model output, including BDON. This study provides valuable information on different types of nitrogen particularly BDON and their amounts contributed by the Fargo WWTP to the Red River.

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BACKGROUND

Availability of excess nutrients is known to cause eutrophication of water bodies such as lakes and rivers, which leads to low dissolved oxygen (DO) conditions and eventually makes the water body unsuitable for recreational purposes. Nitrogen is one of the primary nutrients causing low DO conditions, with discharges from wastewater treatment plants (WWTPs) being one of the major contributors. Due to recent advances in treatment processes, WWTPs equipped with nitrification and denitrification processes (biological nutrient removal) are able to achieve more than 95% removal of dissolved inorganic nitrogen (DIN). Most of the WWTPs equipped with these advanced processes discharge effluent total dissolved nitrogen (TDN) of 10 mg/L or less.

Recent studies indicate that a major portion of the wastewater effluent TDN is generally in organic form, dissolved organic nitrogen (DON), ranging from 25% to 80% of the effluent TDN (Pehlivanoglu-Mantas and Sedlak, 2006, Sattayatewa et al., 2009). DON concentration in secondary treated effluent typically ranges from 1 to 5 mg/L as N. Since high DIN removal has been achievable using the best available technologies, the future target for the treatment plants to reach increasingly stringent regulations for receiving water quality protection will be the removal of DON. For impaired receiving waters, the total nitrogen limit for WWTP effluent discharges could be as low as 3 mg/L or less (WERF, 2009).

Although effluent DON is recalcitrant to the current treatment processes, studies showed that about 50% of the effluent DON is bioavailable or biodegradable to algae and/or bacteria in long period incubation tests (2 to 6 weeks) (Murthy et al., 2006; Pehlivanoglu-Mantas and Sedlak, 2006, Khan et al., 2009; Sattayatewa et al., 2009). Bioavailable DON is the portion of DON that can support the growth of algae and/or bacteria (Pehlivanoglu and Sedlak, 2004; Urgun-Demirtras et al., 2008), while biodegradable DON (BDON) is the portion of DON that can be mineralized by an acclimated mixed bacterial culture (Khan et al., 2009). BDON in denitrified effluent from four different WWTPs in Washington, D.C. and Virginia was about 25% to 33% of DON (Murthy et al., 2006). All four plants employ biological nutrient removal suspended growth systems. In batch assays conducted by Sattayatewa et al. (2009), BDON was 57% of the effluent DON for a 4-stage Bardenpho nutrient removal plant.

Due to a long incubation period (28 days) associated with the BDON procedure (Khan et al., 2009), it is not possible for the treatment plants to make timely operational adjustments to efficiently remove DON, which could lead to a possible permit violation. Modeling WWTP processes to predict DON and BDON profiles could be a helpful approach in this case. Limited work has been done on modeling the fate of DON and BDON through wastewater treatment plants. Makinia et al. (2011) attempted to model the fate of particulate organic nitrogen (PON), colloidal organic nitrogen (CON) and DON in an activated sludge wastewater treatment plant. A modified Activated Sludge Model No. 2d (Henze et al., 1999) was used in their study by including these three forms of organic nitrogen. The new model incorporated hydrolysis of PON and CON to DON and ammonification of DON in all three environmental conditions (aerobic, anaerobic, and anoxic).

DESCRIPTION OF THE CRITICAL STATE OR REGIONAL WATER PROBLEM INVESTIGATED

The fate of DON and BDON in WWTPs has gained attention in recent years because of more stringent regulations on total nitrogen concentration in treated wastewater effluent. However, there has been no report on effluent DON and BDON from treatment plants using trickling filters (TFs) since the process is less common in wastewater utilities. The Fargo WWTP relies mainly on a TF process for treating wastewater. The plant employs two sets of TFs in series. The first set of TFs, known as biochemical oxygen demand (BOD) filters, treats mainly carbonaceous BOD materials and reduces ammonia nitrogen (NH_3-N) concentration slightly through the microbial uptake. The second set of TFs converts NH_3-N to nitrate nitrogen (NO_3-N) through nitrification to accommodate the minimal NH_3-N removal in the BOD trickling filters. Currently, there is no regulation on discharge of TDN by the Fargo WWTP, which discharges to the Red River. However, along with the technological improvement, regulatory agencies force wastewater treatment plants to reduce their effluent TDN concentration to certain amount. It is possible that the Fargo WWTP will be regulated on TDN in near future. Therefore, understanding the fate and characteristics of DON and BDON in the Fargo wastewater treatment train is crucial.

SCOPE AND OBJECTIVES

The main scope of this research includes collecting DON and BDON data for a year-round time scale between 08/10/2009 and 08/22/2010 along the Fargo wastewater treatment train. The objectives of the research are as follows:

1. To investigate the fate of DON and BDON through the Fargo wastewater treatment train;
2. To determine BDON degradability (BDON/DON) profile through the treatment train;
3. To determine seasonal effect on DON and BDON profiles through the treatment train; and
4. To apply a computer based model to predict DON and BDON through the treatment train.

MATERIALS AND METHODS

Description of the Fargo WWTP, and sample collection and preparation

The Fargo WWTP has a two-stage tricking filter process with a peak pumping capacity of 29 million gallons per day (MGD) and an average flow of 11-15 MGD. A simplified schematic diagram of the treatment plant is shown in Figure 1. The facility consists of an influent pumping station, screening, grit removal, two pre-aeration channels, seven primary clarifiers, three BOD trickling filters, two intermediate clarifiers, two nitrification trickling filters, one final clarifier, chlorination, and dechlorination units. The plant is not subject to fecal coliform regulations during the winter months; hence the chlorination and dechlorination were not practiced during that period. The treated

wastewater from the plant is discharged continuously by gravity flow to the Red River. However, in emergency situations such as during high river stage or when water quality does not meet North Dakota State discharge standards, the treated water is pumped from the plant to nearby stabilization ponds. The treated water is stored in these ponds until it can be discharged into the Red River.

Grab samples were collected from eight different locations along the treatment train in the plant. Sample identification and collection locations are shown in Figure 1. Sampling was conducted bi-weekly between August 2009 and August 2010. It should be noted that some of the sampling schedules were skipped due to severe weather conditions resulting a total of 18 samples, 8 samples in winter (November to March) and 10 samples in summer (April to October). Three hundred milliliters of each sample was filtered through a 0.2 μm pore size cellulose acetate membrane filter (PALL Co., Port Washington, NY, USA) within an hour after collection and used for determining dissolved nitrogen species (ammonia, nitrite, and nitrate, total nitrogen), DON, and BDON. Samples collected from locations 1 and 2 were filtered through a 1.2 μm pore size glass microfiber filter (Whatman Inc., Kent, UK) before the filtration through the 0.2 μm pore-size filter due to higher solid concentrations.

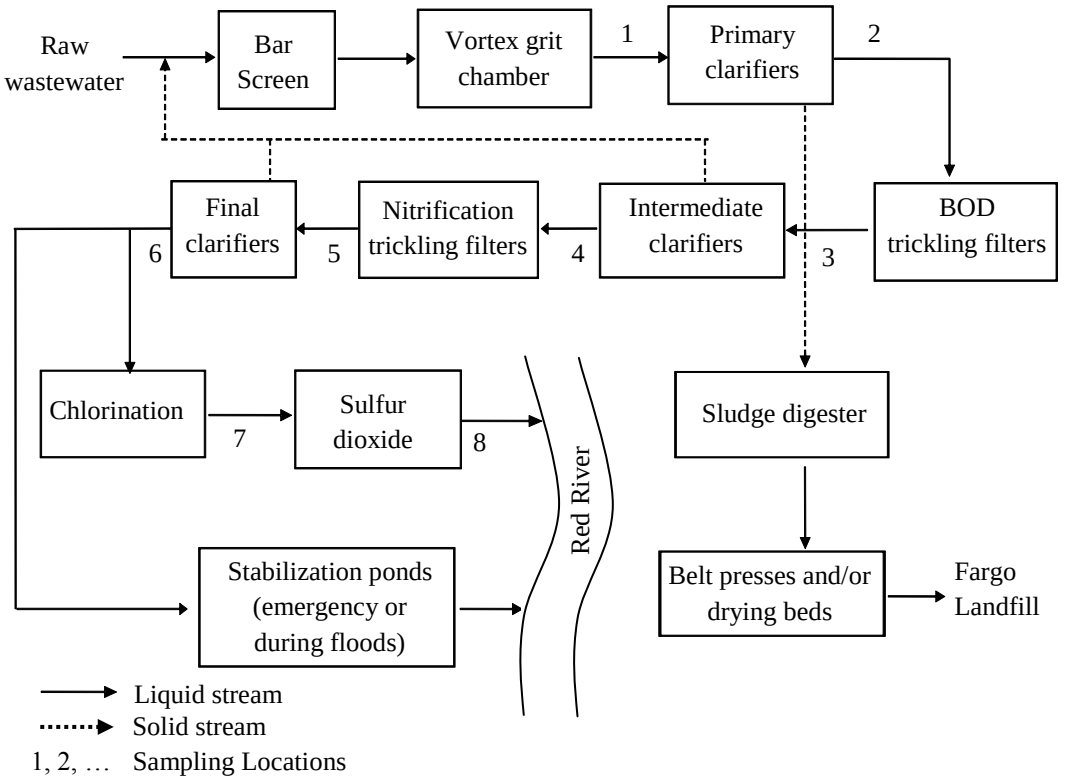

Figure 1. A simplified schematic diagram of the Fargo WWTP.

DON and BDON determination procedures

In this study, the procedure for BDON determination developed by Khan et al. (2009) was followed with slight modifications. A 20-day incubation period and a mixed liquor suspended solids (MLSS) seed were used in the BDON procedure by Khan et al. (2009). However, a 28-day incubation period and a raw wastewater seed were used in this study. The rationale for choosing 28 days for incubation is to further ensure that time was not a limiting factor for ammonification of dissolved organic nitrogen in the sample. MLSS and raw wastewater seeds were experimented with the first few sets of samples and similar results were obtained (data not shown). Raw wastewater seed was chosen to be consistent with the treatment plant that uses it for regular BOD measurement.

The BDON procedure is as follows. All the samples were filtered through a 0.2 µm pore-size cellulose acetate membrane filter (Whatman Inc., Kent, UK) within an hour after collection. A portion of the filtered sample was used for immediate analysis of total nitrogen and inorganic nitrogen species (ammonia, nitrite, and nitrate). DON was determined from the difference between measured TDN and measured DIN species using equation 1. The value was recorded as initial DON (DON_i). Two hundred milliliters of the remaining filtered sample were mixed with 2 mL of acclimated inoculum in a 250 mL amber bottle. Raw wastewater (collected from location 1 in Figure 1) was used as the inoculum. The solution in the bottle was shaken thoroughly to aerate and placed in an incubator in the dark at 20°C for 28 days. During the incubation period, the solution in the bottle was manually shaken to aerate at least once every day to maintain aerobic conditions. A seed control (sample b), which was treated the same way as the samples, was prepared by adding the inoculum to 200 mL of de-ionized distilled water. After 28 days of incubation, all nitrogen species in the supernatant were measured to determine final DON (DON_f). BDON was calculated according to equation 2.

$$DON\ (mg/L\ as\ N) = TDN - DNH_3 - DNO_2 - DNO_3 \quad (1)$$

$$BDON\ (mg/L\ as\ N) = (DON_i - DON_f) - (DON_{bi} - DON_{bf}) \quad (2)$$

Where

DNH_3, DNO_2, and DNO_3 are dissolved ammonia, nitrite and nitrate, respectively;
DON_i and DON_f are DON before and after incubation for samples; and
DON_{bi} and DON_{bf} are DON before and after incubation for control.

Analytical methods

All samples were analyzed in triplicates. The glassware were washed with soap, rinsed with tap water, kept in a 5% v/v hydrochloric acid bath overnight and rinsed with de-ionized water before use.

The salicylate methods (Hach method # 10023 and #10031) were used for ammonia nitrogen measurement. Method # 10023 was used for values ranging between 0.02 and 2.50 mg/L while method # 10031 was applied for values ranging between 0.04 and 50 mg/L. The Test 'N Tube Amver™ test kits and a Hach DR5000 spectrophotometer at 655 nm were used.

The diazotization method (Hach method # 10019) was used for low range nitrite nitrogen measurement (between 0.003 and 0.5 mg/L as NO_2^--N). The Test 'N Tube NitriVer®3 test kits and a Hach DR 5000 spectrophotometer at 507 nm were used. The ferrous sulfate method (Hach method #8153) was used for high range nitrite measurement (between 2.0 and 75 mg/L as NO_2^--N). The NitriVer®2 Nitrite Reagent powder pillows and Hach DR 5000 spectrophotometer at 373 nm were used.

Dissolved nitrate was measured by a second derivative UV spectrophotometric (SDUS) method (APHA et al., 2005). The method was used for nitrate values ranging between 0 and 3.0 mg/L as N. Samples with higher nitrate concentrations were diluted to the measureable range. A Varian Cary 50 UV-V spectrophotometer was used with a quartz cuvette.

TDN was measured by the SDUS method (APHA et al., 2005) after modified persulfate digestion (Sattayatewa and Pagilla, 2008). The method was used for TDN values ranging between 0 and 3.0 mg/L as N. Samples with higher total nitrogen concentrations were diluted to the measureable range. During the digestion, all nitrogen species (dissolved inorganic and organic) in the sample are converted to nitrate.

Statistical analysis

Two-way analysis of variance (ANOVA) using a General Linear Models (GLM) procedure of SAS (version 9.2; SAS Institute, Cary, NC) was conducted to determine the statistical differences in DON and BDON concentrations and BDON degradability (BDON to DON ratio between summer and winter data. In ANOVA, seasons were treated as main plots and treatment processes were treated as subplots, considering sampling dates as replications within each season.

Modeling strategy

BioWin version 3.1 (EnviroSim Associates Ltd., Canada) was used to simulate dissolved organic nitrogen conversion in the Fargo wastewater treatment processes. Influent fractionation was performed using historical plant data. A sensitivity analysis was performed to identify the most influential calibration parameters. The model was calibrated using a dataset obtained in this study. It should be noted that only a steady state calibration was performed.

Model description

The software uses a general activated sludge/anaerobic digestion (ASDM) model (Jones and Takacs, 2004). The ASDM model comprises 50 state variables and 60 process expressions. These expressions are used to describe the biological processes occurring in activated sludge and anaerobic digestion systems, several chemical precipitation reactions, and gas-liquid mass transfer for six gases. BioWin uses a modified 1D biofilm model (Takacs et al., 2007) that is integrated with the ASDM model. Biofilm thickness growth is influenced by attachment and detachment processes.

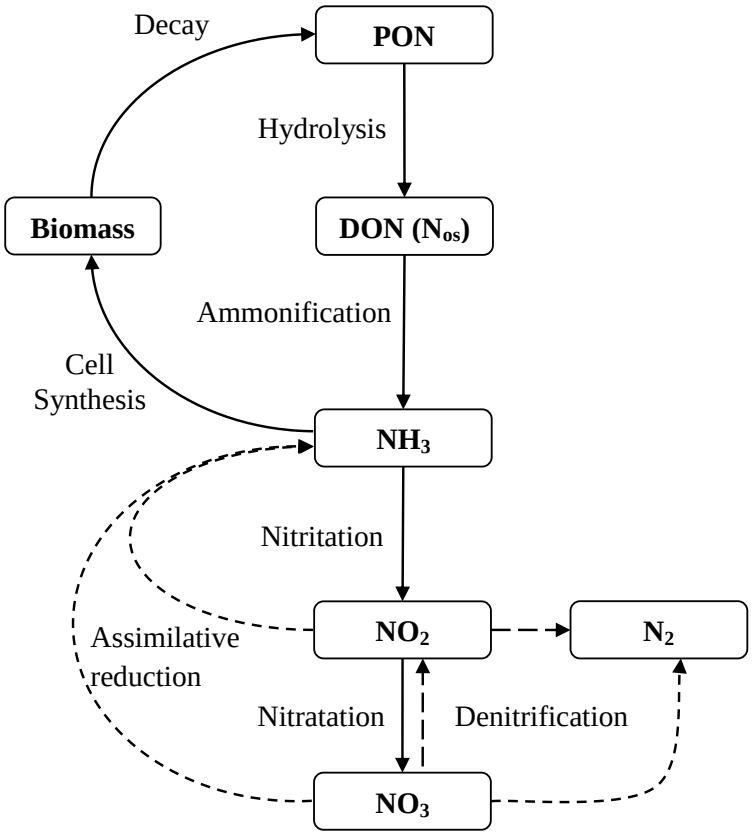

Figure 2. Conceptual nitrogen transformations in the BioWin model.

DON in BioWin is modeled as illustrated in Figure 2. The model includes biomass decay, hydrolysis of PON to DON, and ammonification of DON to ammonia. Both PON and DON have biodegradable and unbiodegradable fractions. The biodegradable (S_{ND}) and unbiodegradable (S_{NI}) fractions of DON in BioWin are assumed to be same as BDON and the difference between DON and BDON (also known as non-biodegradable DON or NBDON). Hydrolysis of biodegradable portion of PON (X_{ND}) and ammonification of DON can be modeled using Monod expressions. The influent NBDON (defined in BioWin nomenclature as soluble unbiodegradable total Kjeldahl nitrogen, F_{nus}) is not removed in any of the treatment processes. It should be noted that the influent NBDON definition is valid because NH_3-N within total Kjeldahl nitrogen (TKN) is considered biodegradable (nitrifiable). BioWin requires two nitrogen species in the influent from the user: TKN and nitrate. The model then estimates the remaining species shown in the schematic in Figure 2 using the influent fractionation information given along with influent data.

Influent fractionation

For accurate process modeling, detailed fractionation data of the influent is required. According to Henze et al. (1987), the influent TKN can be fractionated as shown in Equation 3 below, assuming that no biomass is present in the influent wastewater.

$$TKN = X_{NI} + X_{ND} + S_{NI} + S_{ND} + S_{NH} \quad (3)$$

where, X_{NI} is particulate biodegradable organic nitrogen. More detailed information on the fractions used in BioWin to represent influent TKN components may be found in the software user manual (EnviroSim Associates, 2007). Historical plant sampling data and a plant audit report by Ulteig Engineers, Inc. (Ulteig Engineers, Inc., 2010) were used for influent wastewater characterization and fractionation calculations. BioWin allows user to input soluble, particulate, biodegradable, and unbiodegradable fractions of chemical oxygen demand (COD) and nitrogen species. A selected set of BioWin default fractionation information is summarized in Table 1.

Table1. Steady state model influent data.

Element name	Value
1. Fractionation Data	
F_{bs} - Readily biodegradable (including Acetate) [g COD/g of total COD]	0.16
F_{ac} - Acetate [g COD/g of readily biodegradable COD]	0.15
F_{xsp} - Non-colloidal slowly biodegradable [g COD/g of slowly degradable COD]	0.75
F_{us} - Unbiodegradable soluble [g COD/g of total COD]	0.05
F_{up} - Unbiodegradable particulate [gCOD/g of total COD]	0.13
F_{na} - Ammonia [g NH3-N/g TKN]	0.66
F_{nox} - Particulate organic nitrogen [g N/g Organic N]	0.5
F_{nus} - Soluble unbiodegradable TKN [g N/g TKN]	0.02
F_{upN} - N:COD ratio for unbiodegradable part. COD [g N/g COD]	0.035
2. Annual Average Flow Characteristics	
Flow (MGD)	13
Total COD (mg/L)	721.6
Total Kjeldahl Nitrogen (mg/L)	33.1
Nitrate-N (mg/L)	0.2
Total P (mg/L)	10
Alkalinity (mmol/L)	2.2
Inorganic suspended solids (mg/L)	120
pH	7.35

Model setup, calibration and validation

Daily average flow rates and annual average concentrations for various model inputs were used during the steady state model setup. The constant influent inputs used in the model are summarized in Table 1. The steady state model configuration is presented in Figure 3. Clarifiers were modeled using the modified Vesilind secondary settler model, which simulates a settling tank as a one dimensional settling with multiple layers (minimum of 5). The height of the trickling filters was discretized into four layers in the BioWin model, with each layer representing one quarter of the trickling filter height. This approach has been used successfully elsewhere (Bilyk et al., 2008). Each layer in BOD trickling filter was configured with media having a specific area of 30 ft^2/ft^3 and specific volume of 0.75 ft^2/ft^3. The model was configured using physical characteristics of treatment units obtained from an audit report conducted in 2010 (Ulteig Engineers, Inc., 2010), influent fractionation information (Table 1), and influent characteristics (Table 1). The default BioWin kinetic and stoichiometric parameters were utilized during the initial calibration steps. The model was calibrated by matching the model simulations with averages of long-term intensive monitoring results for BOD, COD, NH_3, NO_2^-, NO_3^-, TDN, DON and BDON (Table 2) for different locations (Figure 1) along the treatment train of the Fargo WWTP.

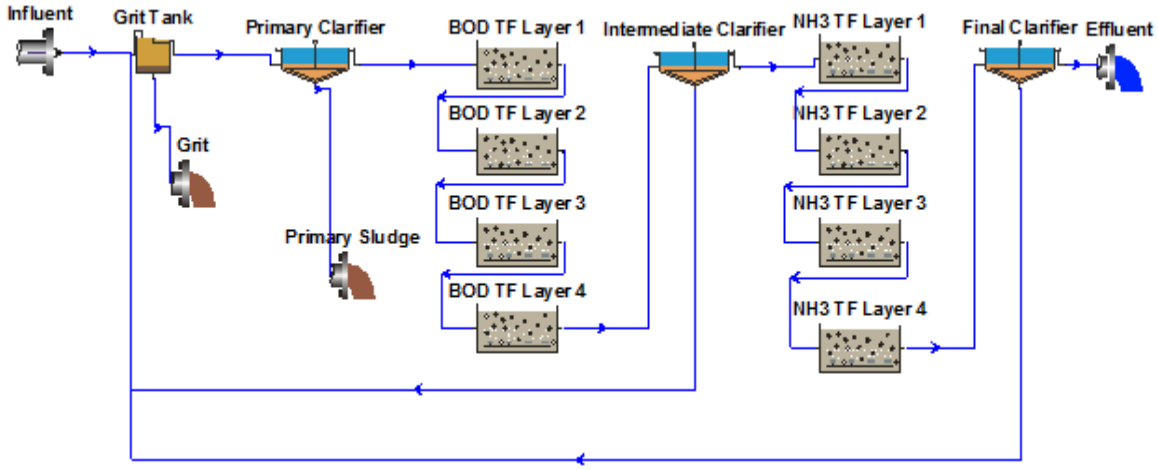

Figure 3. The BioWin steady state model for the City of Fargo WWTP. BOD TF – BOD trickling filters; NH3 TF – nitrification trickling filters.

Table 2. Model input parameters used in sensitivity analysis.

Parameter	Default value	Units
1. Kinetic and stoichiometric parameters		
Kinetic		
Ammonia oxidizing bacteria (AOB)		
Maximum specific growth rate	0.9	day^{-1}
Substrate half saturation	0.7	mg N/L
Nitrite oxidizing bacteria (NOB)		
Maximum specific growth rate	0.7	day^{-1}
Substrate half saturation	0.1	mg N/L
Heterotrophs		
Hydrolysis rate (AS)	2.1	day^{-1}
Hydrolysis half saturation	0.06	
Ammonification rate	0.04	L/(mg N d)
Nitrite oxidizer dissolved oxygen half saturation	0.5	mgO_2/L
Stoichiometric		
N in endogenous residue	0.07	mg N/mg COD
N in biomass (for AOB, NOB, and heterotrophs)	0.07	mg N/mg COD
2. Influent characterization		
Soluble unbiodegradable TKN (F_{nus})	0.02	g N/g TKN
N:COD ratio for unbiodegradable particulate COD (F_{upN})	0.035	g N/g COD
Unbiodegradable soluble (F_{us})	0.05	g COD/g of total COD
Unbiodegradable particulate (F_{up})	0.16	g COD/g of total COD
3. Operating variables		
Dissolved oxygen for the trickling filters	3[£]	mg/L
Combined recycle of settled solids from intermediate and final clarifiers	0.35[£]	million gallons per day
4. Biofilm characteristics		
Thickness	100	µm
Layers	2	

[£]Based on personal communication with plant operators.

Sensitivity analysis

A sensitivity analysis was performed to evaluate the extent to which the parameters used in the model calibration can influence various model outputs. Sensitivity analyses help in identifying those parameters that have little or negligible effect on model outputs, and thus can be left at their default values. Additionally, the analysis helps in identifying the parameters with high sensitivity, for which a small variation in their values causes a large variation in the response predicted by the model. In a linear sensitivity analysis, a relative

change in the model output parameter (y_j) in response to a change in the model input variable (θ_i) can be expressed as:

$$\delta_{i,j} = \left| \frac{\Delta y_j / y_j}{\Delta \theta_i / \theta_i} \right| \quad (4)$$

The influence of a calibration parameter on a model output parameter was interpreted using the following categories: if $\delta_{i,j} < 0.25$, the model is insensitive to the calibration parameter; if $0.25 < \delta_{i,j} < 1$, the calibration parameter is influential; if $1 < \delta_{i,j} < 2$, the calibration parameter is very influential; if $\delta_{i,j} > 2$, the calibration parameter is extremely influential (Peterson et al., 2003).

In the present study, a sensitivity analysis was performed on steady state simulations around BioWin's default parameters. The following parameter categories were considered as input variables (θ_i) in the sensitivity analyses: influent fractionation (*e.g.* biodegradable and soluble fractions), operating variables (*e.g.* recycle and wastage flows), stoichiometric (*e.g.* N and P contents) and kinetic parameters (*e.g.* maximum specific growth rates and half saturation constants), biofilm characteristics (*e.g.* thickness and layers). Additionally, the effect of BioWin switching functions was also included as one of the input variables. Ammonia, nitrite, nitrate, DON (calculated from BioWin outputs: filtered TKN and ammonia), and soluble biodegradable organic nitrogen (or BDON) were chosen as the model output variables (y_j). The analysis was performed by providing a 10% perturbation to the parameters summarized in Table 2.

RESULTS AND DISCUSSION

The profiles of different dissolved nitrogen species (ammonia, nitrite, nitrate, and total nitrogen) along the treatment train of the Fargo WWTP are presented in Figure 4, and DON and BDON profiles are shown in Figure 5. Model calibration results for BOD, COD, ammonia, nitrite, nitrate, TDN, DON and BDON are presented in Figure 6. The data and error bars are based on averages and standard deviations of 18 different samples (from 18 different weeks). Due to weather conditions such as rain and snow, influent nitrogen concentrations fluctuated. In summer, nitrogen concentrations were high since there was minimal dilution involved.

Inorganic nitrogen species and TDN

Ammonia in the influent of the Fargo WWTP was typically around 24 mg/L as N. The plant achieved almost complete ammonia removal through nitrification which occurred in both BOD and nitrification trickling filters (Figure 4a). About 50% of ammonia was removed in the BOD trickling filters, while about 90% of the remaining ammonia was removed in the nitrification trickling filters. All of the ammonia in the samples was nitrified during the BDON incubation except for raw and primary wastewater sample in which there were low amounts of ammonia left (< 1 mg/L).

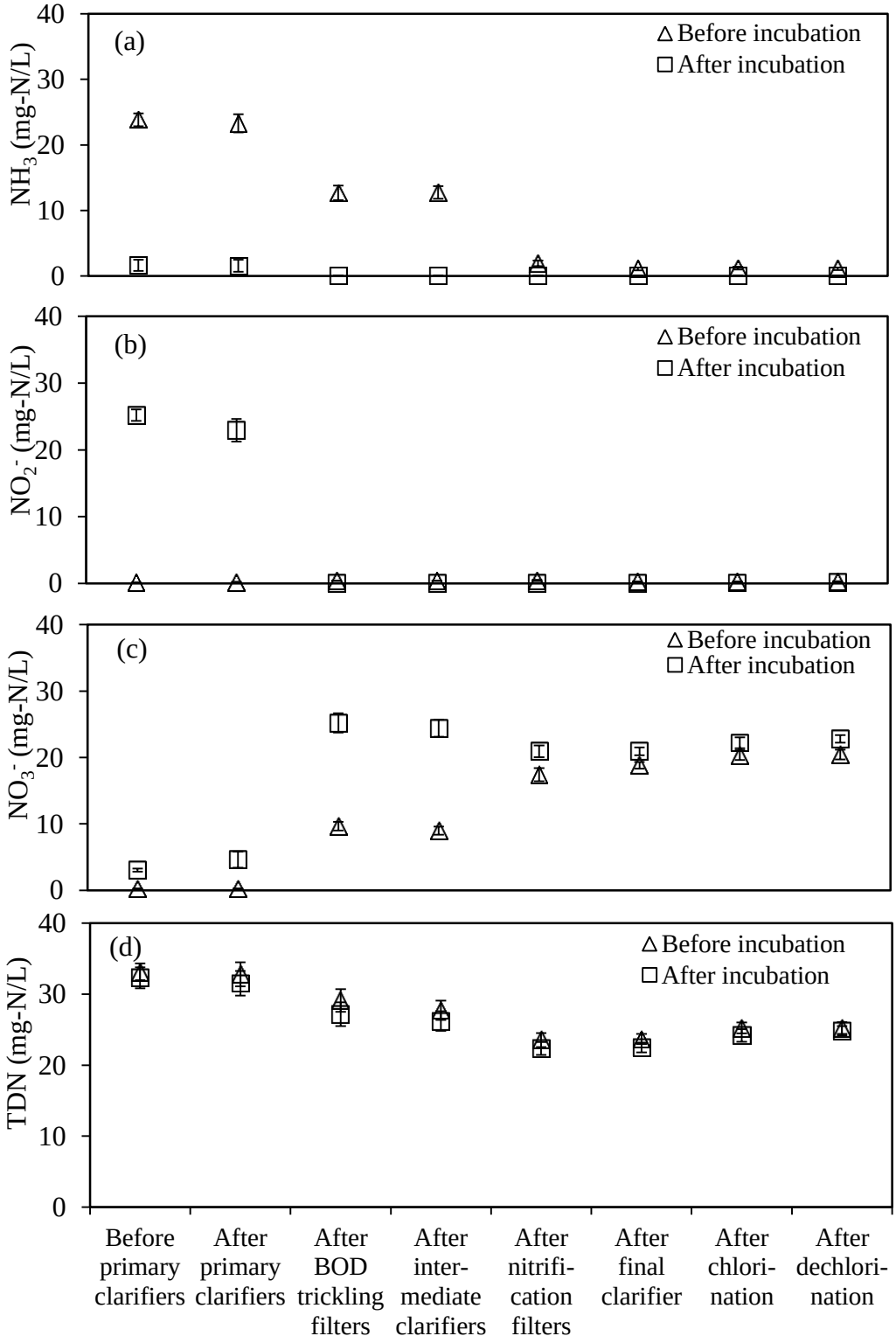

Figure 4. (a) Dissolved ammonia, (b) Dissolved nitrite, (c) Dissolved nitrate and (d) TDN, before and after incubation for samples across the treatment train of the City of Fargo WWTP.

Average nitrite concentration in all the samples was consistently very low (< 0.1 mg/L as N). After the incubation, nitrite in the samples before and after primary clarification was 25.21 and 22.93 mg/L as N, while nitrate at these locations was 3.03 and 4.61 mg/L as N respectively. This was likely due to inadequate DO for nitratation (nitrite conversion to nitrate) during the incubation. However, the last several sets of samples, more frequent manual DO recharging was experimented and almost full nitratation (nitrite < 0.01 mg/L as N) was achieved in these samples after the incubation. Nitrate was usually present in very low concentrations (at an average of 0.20 mg/L as N) in the raw wastewater samples (Figure 4c). However, it was the major portion of DIN after the nitrification filters (93%).

Nitrate nitrogen in almost all of the nitrification trickling filter effluent samples was substantially less than the ammonia nitrogen in the plant influent. An average of 4.50 mg/L as N difference was observed between influent ammonia-N and effluent nitrate-N. Previous studies indicated two possible reasons for this nitrogen loss: assimilation of ammonia by biomass in the trickling filters and/or possible denitrification in the deeper portions of biofilm (Hanaki et al., 1990; Eiroa et al., 2005). Additionally, nitrate may also be used for biomass synthesis in the event of insufficient ammonia (Grady et al., 1999). The third scenario needs not be considered here as there was always sufficient amount of ammonia present in the nitrification trickling filters (> 12 mg/L as N).

Average nitrate values after the incubation in the samples from the remaining locations followed a similar trend as that of before the incubation. The nitrate nitrogen concentrations in the samples after the incubation were however slightly higher than before the incubation. A possible reason for this increase in nitrate concentration could be nitrification of ammonia from two different sources, the residual (untreated) ammonia in the samples and/or the ammonia generated due to ammonification of organic nitrogen during the incubation. Increases of nitrate nitrogen during the incubation ranged from 1.88 to 3.41 mg/L as N, which were higher than ammonia nitrogen in the samples (before incubation). Thus, both ammonia sources discussed should have contributed to the nitrate increases after the incubation. The average TDN in the plant influent was 33.15 mg/L as N while in the effluent was 25.22 mg/L as N. Although the treatment plant was not equipped with nutrient removal processes, it achieved 24% removal of the influent TDN. The removal was observed mainly through the two trickling filters (Figure 4d). The removal of TDN can be explained using the same reasons that were discussed earlier for nitrogen loss in the nitrification trickling filters (assimilation of ammonia by biomass and/or denitrification). The TDN values after the incubation were almost the same and followed the same trend as before the incubation.

Dissolved organic nitrogen

Average DON in the plant influent and effluent were 9.02 and 3.44 mg/L as N, respectively (Figure 5a). The final effluent DON was substantially higher than a typical range of 1.1 mg/L to 2.1 mg/L reported for activated sludge systems with nutrient removal processes (Murthy et al., 2006). However, there has been no data on activated sludge with no nutrient removal process to compare with. The treatment plant removed 62% of the influent DON. Similar to inorganic nitrogen removal, major removal of DON was observed in the biological processes of the plant. The BOD trickling filters removed

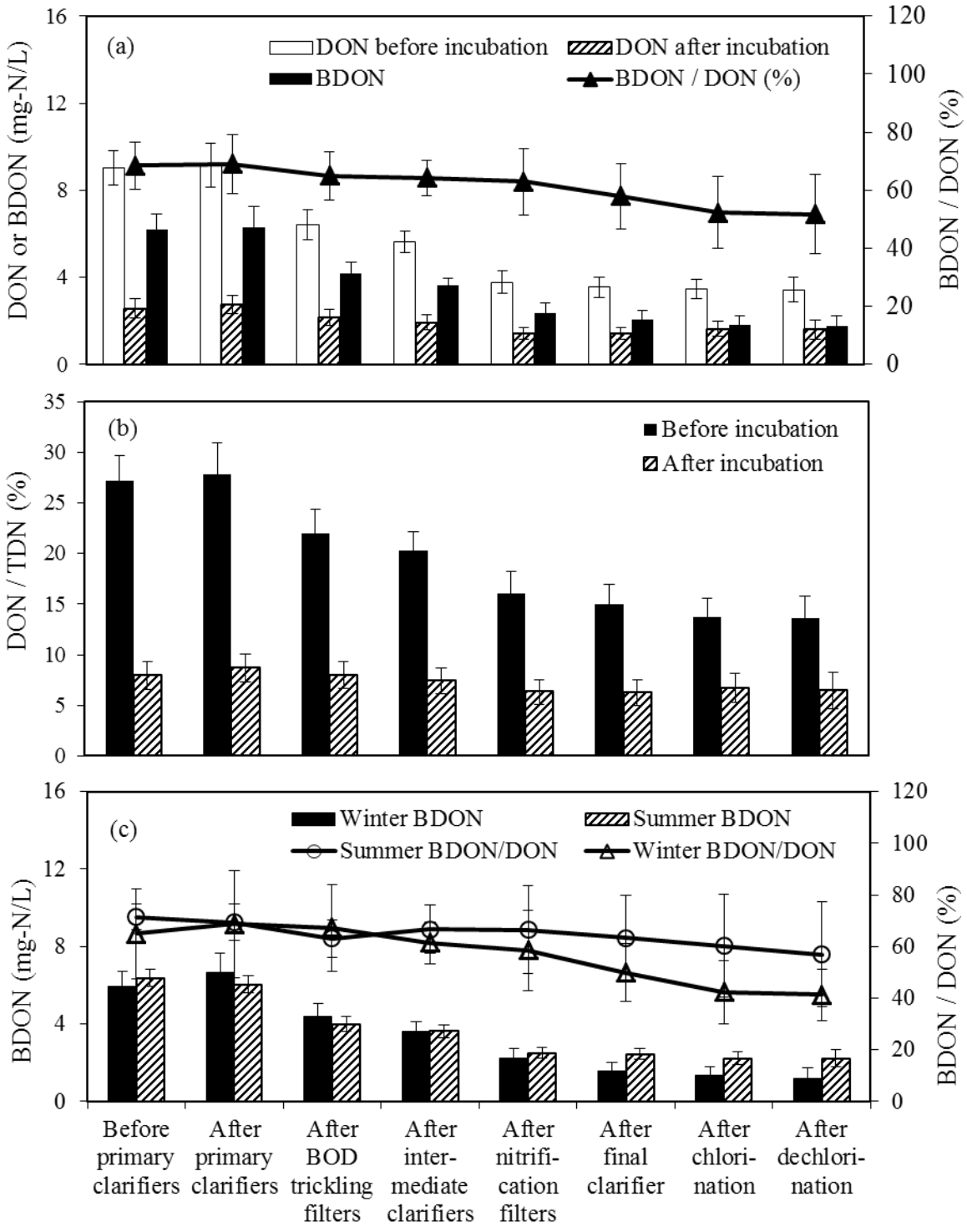

Figure 5. (a) DON before and after incubation, BDON and BDON as a percentage of DON for the entire sampling period, (b) DON as a percentage of TDN before and after incubation for the entire sampling period and (c) BDON and BDON as a percentage of DON during summer and winter months, for samples across the treatment train of the City of Fargo WWTP.

37% of the influent DON while the nitrification trickling filters removed the same percent from the remaining DON. DON fractions of TDN were 27% and 14% in the raw wastewater and in the plant effluent, respectively (Figure 5b).

After the incubation, at least 50% of the DON decreased through ammonification for all the locations (Figures 5a, 5b). The final DON values after the incubation for all the samples from the WWTP were between 1.61 and 2.60 mg/L as N, and their fractions of TDN were between 6.5% and 8% (Figure 5a). This indicates that there was about the same fraction of inert DON (not biodegradable) from each treatment process. Statistical analyses showed that there is no significant difference ($p > 0.05$) on DON concentrations in all the locations of the treatment train between the summer and winter months (data not shown). For the summer months, statistically DON concentrations can be categorized into three groups and within each group there is no significant difference ($p > 0.05$). These three groups are before and after primary clarifiers, after BOD trickling filters and after intermediate clarifiers, and the rest of the sampling locations. The statistical grouping for the winter months is exactly the same as that for the summer months.

Biodegradable dissolved organic nitrogen

The BDON profile had a similar trend as that of the DON profile along the treatment trains (Figure 5a). BDON removal occurred mainly in the trickling filters. BDON in the raw wastewater and plant effluent was 6.18 and 1.78 mg/L respectively corresponding to 72% removal. The BOD trickling filters removed 43% of BDON and the nitrification trickling filters removed 43% of BDON. About 12% removal of BDON was also observed in the chlorination basins. However, the DON concentration did not change after chlorination. Chlorinating DON can form disinfection by-products (DBPs) that contain a nitrogen functional group (Pehlivanoglu-Mantas and Sedlak, 2006; Mitch and Sedlak, 2002). In summer (chlorine disinfection was performed), a portion of BDON could have changed into a form of DON (DBP) that was recalcitrant to biodegradation in the incubation process. The BDON was found to be between 51% and 69% of DON after various treatment units in the plant (Figure 5a). In other words, there was 31% or more of biodegradable DON that was not treated by each of the treatment processes.

The BDON plots for the summer and winter months are presented in Figure 5c. Statistically, BDON concentrations were not different ($p > 0.05$) between the summer and winter months for all locations. During the summer months, the statistical grouping of BDON concentrations from different treatment units is identical to those of DON concentrations as discussed above. For the winter months, the statistical grouping of BDON concentrations (for no significant difference) is as follows: 1) Before primary clarifier to after BOD trickling filters; 2) After BOD tricking filters to after nitrification filters; 3) After nitrification filters to after dechlorination.

Figure 5a presents DON biodegradability of DON (BDON/DON) for the entire year sampling (18 weeks). The biodegradability varied between 52% and 68% for all 8 locations in the treatment train. The final effluent DON was 52% biodegradable which is within a range of previously reported values (Pehlivanoglu-Mantas and Sedlak, 2006, Sattayatewa et al., 2009). The DON biodegradability gradually decreased along the

treatment train which is logical. The ranges of DON biodegradability in the summer and winter months were 57% to 71% and 41% to 65%, respectively. The differences in BDON concentrations between the summer and winter months, although not statistically different ($p > 0.05$), occurred mainly in the last two units of the treatment train. In the summer months, the decrease in BDON/DON was due to a slight decrease in BDON after chlorination (0.23 mg/L as N), while no change occurred in DON. BDON reduction was higher during the winter months since the plant did not employ disinfection in winter. The chlorination and dechlorination basins were simply used as storage tanks, thus providing longer residence time for nitrifiers that did not settle in the secondary clarifiers to continue to remove BDON and eventually DON. This analogy is supported by almost the same magnitude of removal observed for BDON and DON in the final two locations of the plant.

BioWin modeling

Model calibration

During the calibration of the model, unbiodegradable soluble (F_{us}) and unbiodegradable particulate (F_{up}) CODs were adjusted to 0.067 and 0.16 g COD/g of total COD. With the remaining BioWin's default influent fractionation (Table 1), kinetic (except the hydrolysis rate) and stoichiometric parameters, model simulated BOD and COD profiles fairly matched with the measured values (Figure 6a). Hydrolysis rate was changed from a default of 2.1 to 0.5 day^{-1} for the BOD trickling filters and 1.2 day^{-1} for the nitrification trickling filters.

The simulation results for ammonia, nitrite, nitrate, and TDN results are presented in Figure 6b. While the model simulated nitrite and nitrate matched well with the measured values, ammonia values after the BOD trickling filters and intermediate clarifiers were under-predicted by the model. The parameters that were adjusted from their default values in matching ammonia, nitrite, and nitrate were influent fractionation, AOB and NOB kinetic parameters, DO, and boundary layer thickness. Based on the sampling data, ammonia (F_{na}) in the influent fractionation was adjusted to 0.72 g NH_3-N/g TKN. Kinetic parameters for AOB and NOB are summarized in Table 3. DO values between 3 and 5 mg/L were used to match the predicted NH_3, NO_2, and NO_3 with the measured values (Table 3). Higher DO values were provided to the lower layers of the trickling filters (BOD TF Layer 4 and NH3 TF Layer 4 in Figure 3). This type of DO provision in the model was adjusted based on the configuration of the trickling filters. The Fargo WWTP has a natural ventilation system for air flow from the bottom of the filters.

The calibrated boundary layer thickness was 80 µm for the BOD trickling filters and 150 µm for the nitrification trickling filters. Most of the DO was consumed for BOD removal in the BOD trickling filters. The model simulated DO in the lower layers of the biofilm in the BOD trickling filters was less than 0.1 mg/L. The thickness of boundary layer in these trickling filters was kept at 80 µm in order to allow sufficient amounts of DO diffusion into the biofilm and to maintain aerobic conditions required for nitrification. On the contrary, a higher thickness (150 µm) of the boundary layer was needed in the nitrification trickling filters in order to optimize the rates of nitritation and nitratation.

Table 3. Calibrated kinetic, stoichiometric and operational parameters.

Parameter	Default	Value
1. Kinetic		
AOB Max. spec. growth rate [1/d]	0.9	1.2
Substrate (NH4) half sat. [mg N/L]	0.7	0.7
NOB Max. spec. growth rate [1/d]	0.7	1
Substrate (NO2) half sat. [mg N/L]	0.1	0.1
2. Stoichiometric		
AOB Yield [mg COD/mg N]	0.15	0.15
AOB Yield [mg COD/mg N]	0.09	0.09
N in biomass [mg N/mg COD]	0.07	0.07
3. Dissolved oxygen set points (mg/L)		
BOD TF Layer 1		4.0
BOD TF Layer 2		4.0
BOD TF Layer 3		5.0
BOD TF Layer 4		5.0
NH3 TF Layer 1		3.0
NH3 TF Layer 2		3.0
NH3 TF Layer 3		4.0
NH3 TF Layer 4		4.0

Simulation results showed that partial nitrification (accumulation of nitrite) did not occur in any of the BOD or nitrification trickling filter layers (data not presented here). Moreover, the growth of anaerobic ammonia oxidizers was not observed in the simulations. However, the model was able to simulate the loss of dissolved nitrogen, which was observed as the difference between ammonia nitrogen removed and nitrate nitrogen produced after the BOD and nitrification trickling filters in the measured data (Figure 6b). The model simulations predicted this loss of dissolved nitrogen as the production of particulate organic nitrogen.

TDN was calculated from the BioWin simulated TKN, nitrite and nitrate values. Similar to ammonia removal, the model over-predicted the TDN removal in the BOD trickling filters (Figure 6b). Overall, the TDN profile simulated by the model fairly matched with the measured data. DON and BDON profiles are presented in Figure 6c. The simulation results were quite agreeable with the measured data. The calibration parameters used in matching the simulated values for DON and BDON with measured data were influent fractionation parameters and kinetic parameters.

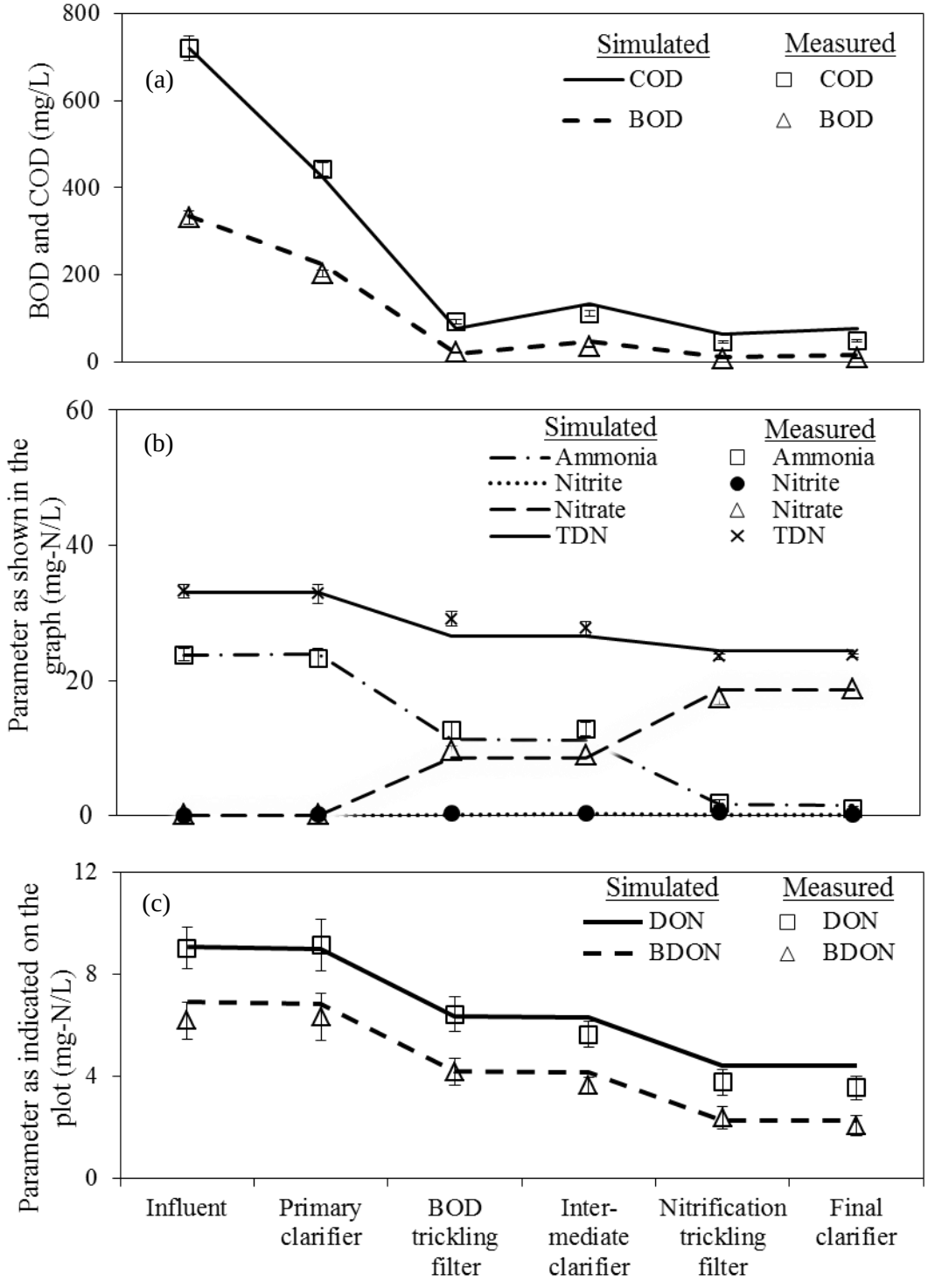

Figure 6. BioWin model simulated versus measured profiles of (a) BOD and COD, (b) Dissolved ammonia, nitrite and nitrate, TDN and (c) DON and BDON data along the treatment train of the City of Fargo WWTP.

The adjusted influent fractionation parameters were particulate organic nitrogen (F_{nox}) to 0.005 g N/g organic N, soluble unbiodegradable TKN (F_{nus}) to 0.065, and N:COD ratio for unbiodegradable particulate COD (F_{upN}) to 0.001. The majority of the measured influent TDN was ammonia and organic nitrogen (> 99%). Hence, the measured TDN value was used as the influent TKN for model simulations. Since the influent TKN was dissolved, F_{nox} and F_{upN} were assumed to be negligible. Measured DON and BDON results showed that an average NBDON (DON - BDON) was 2.15 mg/L, which was about 6.5% of the TDN (or F_{nus} = 0.065).

Hydrolysis rate and ammonification rate for heterotrophs were adjusted to match the simulation results with the measured data; however, the values were different for the BOD and nitrification filters. Calibrated hydrolysis rates were 0.5 day^{-1} for the BOD trickling filters and 1.2 day^{-1} for the nitrification trickling filters, while the calibrated ammonification rates were 0.01 L/mg N-day for the BOD trickling filters and 0.04 L/mg N-day for the nitrification trickling filters. The slower ammonification rates indicate that some of the hydrolyzed organic nitrogen could have been directly used for cell synthesis (Warner, 1956). The measured data (from 28-day incubation) showed a variation in the concentration of NBDON along the treatment processes. The NBDON was 2.57 ± 0.44 mg N/L in the influent and 1.62 ± 0.35 mg N/L in the effluent. However, BioWin simulates NBDON as a constant fraction of the DON, which means that it does not change along the treatment processes.

Sensitivity analysis

Results from the sensitivity analyses on calibrated BioWin model are summarized in Table 4. The values for $\delta_{i,j}$ for model output parameter nitrite (NO_2) and calibration parameter $K_{S,NO2}$ were less than 0.2. Hence, they were not included in Table 4. A large number of calibrating parameters influenced the model output for ammonia, nitrate and DON, while COD, BOD, NBDON, X_{ND} and TDN were influenced by two parameters each.

Although the switching parameters were found to be less influential, they were necessary to match the simulated values of nitrate with those of the measured. The influence category for each calibrating parameter varied depending on the output variable. While the maximum specific growth rate for AOB was found to be extremely influential for ammonia, it was very influential for nitrate. The AOB half saturation constant was found to be very influential for ammonia, but was influential for nitrate. Similarly, hydrolysis rate was extremely influential for BOD, ammonia, nitrate, and particulate biodegradable organic nitrogen, while it was very influential for COD and influential for DON and TDN. Among operational variables, recycle flow rate had influence on ammonia alone, while DO had varying levels of influence on most of the nitrogen species.

Table 4. The values for $\delta_{i,j}$ for the most sensitive parameters of the calibrated BioWin model.

	$\delta_{i,j}$								
Elements	COD	BOD	NH_3	NO_3	DON	BDON	Sol. inert TKN*	Part. bio. org. N**	TDN
$\mu_{max, NH3}$			3.33	1.05					
$K_{S, NH3}$			1.58	0.27					
$\mu_{max, NO3}$			0.48	3.17					
$K_{S, NO3}$				0.16					
Hydrolysis Rate	1.15	4.02	5.77	4.89	0.85	1.46		14.29	0.88
Ammonification Rate			0.48	0.16	0.65	1.10			
NO2 DO half saturation				0.79					
Heterotroph DO half saturation				0.43					
Aerobic denitrifier DO half saturation				0.43					
F_{nus}					0.56				
F_{upN}			0.64		0.54		0.67		
Recycle flow rate	1.15	1.15	1.61						
DO		0.31	4.74		0.71	0.45	1.1	0.62	

*unbiodegradable DON (NBDON)
**Particulate biodegradable organic nitrogen (X_{ND})

CONCLUSIONS

The fate of DON and BDON in the Fargo WWTP was studied. The treatment plant removed 27% of the influent TDN and 62% of the influent DON. The DON fraction of the plant effluent TDN was 14%. The plant removed 72% of BDON and discharged BDON of 1.78 mg/L- N, more than 50% of the effluent DON, into the Red River. The removal of DON and BDON was mainly observed in the BOD and nitrification trickling filters. Seasonal differences in the BDON removal in various treatment units after the BOD trickling filters were observed. Overall, the Fargo WWTP achieved higher BDON removal during the winter months. There was 1.66 mg/L as N of NBDON in the final effluent. This information could be valuable for regulatory agencies when evaluating a limit on TN in the effluent from biological wastewater treatment plants. BioWin v 3.1 was used to simulate inorganic and organic nitrogen species, which include DON and

BDON, through the two-stage trickling filter process. For most of the nitrogen species, the model was able to simulate with generalized kinetic and stoichiometric parameters (without the need to locally specify for each treatment process). Hydrolysis and ammonification rates for heterotrophic bacteria were the only two parameters that differed between the two stages of the trickling filter processes and needed to be adjusted. The model was found be most sensitive to hydrolysis and ammonification rates, and maximum growth rates for AOB and NOB.

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