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Characteristics and fate of organic nitrogen in municipal biological nutrient removal wastewater treatment plants

K. Czerwionka[1], J. Makinia[1]*, K.R. Pagilla[2], H.D. Stensel[3]

[1] Faculty of Civil and Environmental Engineering, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdansk, POLAND (E-mail: kczer@pg.gda.pl, jmakinia@pg.gda.pl), tel. +48 58 347-19-54, fax +48 58 347-24-21

[2] Department of Civil, Architectural and Environmental Engineering, Illinois Institute of Technology, USA (E-mail: pagilla@iit.edu)

[3] Department of Civil and Environmental Engineering, University of Washington, Seattle, USA (E-mail: stensel@u.washington.edu)

ABSTRACT

The aim of this study was to investigate the occurrence and fate of colloidal and dissolved organic nitrogen (CON and DON) across biological nutrient removal (BNR) activated sludge bioreactors. Primary and secondary effluent total nitrogen (TN) measurements and component fractionation, CON and DON concentration profiles across BNR bioreactors, and laboratory batch experiments with the process mixed liquor were carried out at several full-scale BNR plants in northern Poland. The organic nitrogen (ON) components were divided into high CON, low CON, and DON based on sequential filtration through 1.2, 0.45 and 0.1 μm pore size filters. The average influent $DON_{0.1\mu m}$ (<0.1 μm) concentrations ranged from 1.1 g N/m^3 to 3.9 g N/m^3 and accounted for only 4-13% of total organic nitrogen. In the effluents, however, this contribution increased to 12-45% (the $DON_{0.1\mu m}$ concentrations varied in a narrow range of 0.5-1.3 g N/m^3). Conversions of ON inside the bioreactors were investigated in more detail in two largest plants, i.e. Gdansk (565,000 PE) and Gdynia (516,000 PE). Inside the two studied bioreactors, the largest reductions of the colloidal fraction were found to occur in the anaerobic and anoxic compartments, whereas an

* Corresponding author

increase of $DON_{0.1\mu m}$ concentrations was observed under aerobic conditions in the last compartment. Batch experiments with the process mixed liquor confirmed that $DON_{0.1\mu m}$ was explicitly produced in the aerobic phase and significant amounts of ON were converted in the anoxic phase of the experiments.

KEYWORDS

Activated sludge; biological nutrient removal; colloidal organic nitrogen; CON; dissolved organic nitrogen; DON; nitrogen fractionation; nitrogen removal

INTRODUCTION

Biological nitrogen removal (BNR) activated sludge processes are commonly used in municipal wastewater treatment plants (WWTPs) around the world to produce effluents with total nitrogen (TN) concentrations below 10 g N/m^3. Effluent TN includes total inorganic nitrogen (NH_4-N + NO_3-N + NO_2-N) and total organic nitrogen (TON), which is the sum of dissolved organic nitrogen (DON), particulate organic nitrogen (PON), and colloidal organic nitrogen (CON). Biological nitrogen removal involves transformations and removal of inorganic nitrogen (NH_4-N and NO_X-N) by biomass synthesis and sludge wasting, and nitrification (NH_4-N oxidation to NO_2-N and NO_3-N) and denitrification of NO_3-N and/or NO_2-N to nitrogen gas. Solid-liquid separation processes, including final clarifiers, sand filters, and membrane filters remove organic nitrogen (ON) contained in suspended solids (as PON) and removable colloidal solids (as CON). Inorganic nitrogen is of primary concern for effluent goals for TN of less than 10 g N/m^3. With stricter effluent TN permit limits becoming more common in the United States (less than 3.0 g N/m^3), and in some cases in Europe and Japan, the contribution of effluent ON, mainly as DON and CON, has become more important and may account for 30-50% of the effluent TN (WERF, 2008). Observed effluent DON contributions vary widely in municipal BNR WWTPs with reported $DON_{0.45\mu m}$ concentrations (defined by the fraction passing through 0.45 µm pore-size filters) ranging from <2% to as high as 85% of the effluent TN (Pagilla et al., 2006; 2008; Pehlivanoglu and Sedlak, 2004; WERF, 2008).

Because of the importance of effluent ON in BNR WWTPs addressing low effluent TN concentration goals, understanding the fate of ON in the influent wastewater and across the activated sludge process is of great interest. Influent TN primarily consists of ammonia/ammonium (NH_4-N) and ON plus none or little in the oxidized inorganic forms. Similar to effluent ON, the influent ON may also be characterized as the sum of PON, DON and CON. Traditionally, a 0.45 µm pore-size filter has been used to separate the DON (referred further to as $DON_{0.45\mu m}$) from

PON in analytical measurements. However, in the work of Makinia et al. (2011), three different pore-size filters were used to separate the ON into PON, CON, and DON fractions. Each physical fraction was further divided into biodegradable and non-biodegradable sub-fractions. This approach resulted in accurate modeling of ON conversions in activated sludge bioreactors (Makinia et al., 2011).

So far, very little has been done on the fate and characteristics of effluent DON in WWTPs since the early pioneering work of Parkin and McCarty (1981a,b,c), which followed DON in untreated and treated wastewater, and considered sources of DON in the activated sludge effluents, including production during biological treatment. From bench-scale tests they found the lowest effluent DON concentrations at aeration times of 6-9 hours, which corresponded to a 6-10 day aerobic solids retention time (SRT) at the studied WWTP (Palo Alto, California (USA)). Bratby et al. (2008) noted that DON concentration increases through biological treatment, and on the contrary, biological processes in activated sludge systems were identified as a potential method of DON removal (O'Shaughnessy et al., 2006; Pagilla et al., 2006). Factors influencing DON treatment efficiency include SRT, temperature, reactor hydraulics and plant perturbations. Sharp et al. (2009) found that SRT and temperature may impact both PON and $DON_{0.45\mu m}$ fraction and concentration of effluent DON for a specific plant, but were not the only factors. Studies in several WWTPs in the US and Poland revealed that the effluent concentrations of CON and DON were relatively stable regardless of the influent TN concentrations and process configurations (Pagilla et al., 2008; Sattayatewa et al., 2009b; Sattayatewa et al., 2010). Dignac et al. (2000a) found that the BNR processes can be efficient in removing low molecular weight (LMW) organic matter and DON compounds such as urea, amino acids, and proteins. In contrast, the high molecular weight (HMW) DON is considered to be inert in biological treatment (Gulyas et al., 1995; Dignac et al., 2000a; Pehlivanoglu-Mantas and Sedlak, 2008; WERF, 2008).

Present knowledge on the characteristics and behavior of CON and DON is still limited and insufficient to estimate BNR process effluent ON concentrations as a function of plant design and influent ON concentration and characteristics. The fate of ON has not been specifically studied in BNR processes and important research questions include (WERF, 2008):

- where DON and CON is removed or produced in BNR processes?
- what is the effect of BNR process design and configuration (anaerobic and anoxic contact) on effluent DON and CON?

This paper reports on the results of studies at full-scale BNR WWTPs to address these questions under the Polish conditions which are characterized by very strong municipal wastewater (e.g. TN concentrations are 2-4 times higher compared to the USA). The study evaluated influent wastewater nitrogen characteristics and the fate of nitrogen species across BNR activated sludge bioreactors at eight full-scale WWTPs in northern Poland. Batch experiments were also done at some plants to further investigate nitrogen transformations within different BNR process conditions.

MATERIALS AND METHODS

Description of WWTPs

All of the WWTPs in the study were designed and operated for both nitrogen and phosphorus removal and varied in size and activated sludge process configurations (Table 1). The effluent TN concentration goal for the four largest facilities, with greater than 100,000 population equivalents (PE), is at the most stringent European Union (EU) standard of 10 g N/m^3. The effluent TN concentration goal for the other plants is 15 g N/m^3. Design configurations for enhanced biological phosphorus removal (EBPR) are used in all of the facilities except the Elblag WWTP, which has an anoxic-aerobic activated sludge process (MLE) and ferric addition in the primary treatment step for phosphorus removal. The EBPR process configurations are the University of Cape Town (UCT), modified UCT (MUCT), Johannesburg (JHB) and anaerobic-anoxic-aerobic (A_2/O). All the plants were operated over a range of SRTs due to significant seasonal activated sludge temperature fluctuations from 10-22 ºC.

Table 1

In addition to the primary and secondary effluent ON fractionations, conversions of ON and organic carbon (OC) in BNR activated sludge process steps were investigated in more detail at the two largest plants, Gdansk and Gdynia WWTPs. Process schematics for these plants and the sampling locations are illustrated in Figure 1. More detailed characteristics of those plants can be found elsewhere (Makinia et al., 2006).

Figure 1

WWTP measurements

Influent-effluent analysis. Primary and secondary effluent 24-hour, flow-proportional composite samples were collected during ten sampling events between March, 2007 and December, 2008 and analyzed for ON and OC fractions. The ON and OC fractions were based on pore-size filter separation and defined as particulate (>1.2 µm), "high" colloidal (>0.45 and <1.2 µm), "low" colloidal (>0.10 and <0.45 µm), and dissolved (<0.1 µm). For ON, these are defined as PON, high CON, low CON, and $DON_{0.1\mu m}$, respectively. In addition, between January and March, 2009, three additional measurement series were carried out with the Gdansk and Gdynia WWTPs secondary effluent 24-hour composite samples by sequential filtration through 0.1 and 0.015 µm filters to evaluate the effect of ultrafiltration on ON and OC removal.

ON and OC concentration profiles across BNR bioreactors. Conversions of non-particulate ON and OC fractions across the Gdansk and Gdynia WWTPs bioreactors were investigated by 5 measurement campaigns between November, 2008 and July, 2009. Average colloidal and dissolved ON and OC concentrations in the bioreactors were based on three grab samples (8 AM, 11 AM and 2 PM) at the inlet and outlet from the anaerobic, anoxic and aerobic compartments. Sampling point locations at both plants are shown in Figure 1.

Bench-scale experiments

Bench-scale experiments to evaluate the fate of ON and OC under anaerobic, anoxic, and aerobic conditions were carried out with settled wastewater and return activated sludge (RAS) seed from the Gdansk WWTP (5 tests) and Gdynia WWTP (6 tests) during the same time period as the concentration profile measurements. The experimental apparatus consisted of two parallel 4.0 dm^3-batch reactors with electrodes for a continuous monitoring of pH, ORP, temperature and dissolved oxygen (DO) and computer control system to maintain DO concentration and temperature around set points. This system also controlled a cyclic measurement of oxygen uptake rate (OUR) in small chambers connected to the main units. During the batch experiments, both reactors were operated in a 3-step sequence of anaerobic (2 h), anoxic (4 h, after addition of KNO_3) and aerobic (6 h) conditions.

To observe the fate of only the dissolved ON and OC and the effect of PON and CON on effluent DON concentration, reactor 1 (R1) was fed settled wastewater and reactor 2 (R2) was fed pretreated settled wastewater with only DON and dissolved OC constituents (Figure 2). The rapid coagulation-flocculation method by Mamais et al. (1993) based on $Zn(OH)_2$ precipitation at pH = 10.5 was used to remove particulate and colloidal ON and OC. After removing the colloids and particulates by settling, the pH was adjusted to its original value by adding 6M HCl. The RAS seed was diluted to obtain mixed liquor suspended solids (MLSS) concentration at approx. 2.5-3 kg/m^3 in the reactors. The actual MLSS concentrations were measured at the beginning and end of the experiment. A heating/cooling system was set to maintain the batch reactor temperature equal to the actual (current) process temperature in the full-scale bioreactors. After adding the RAS and feed wastewater to the reactors, the mixers were turned on at 180 rpm. Samples of 100-150 cm^3 were withdrawn at the time intervals shown in Figure 2, filtered under vacuum pressure on 1.2 µm pore-size filter and then analyzed. The "basic" set of lab analyses comprised NH_4-N, NO_2-N, NO_3-N, COD and PO_4-P measurements, whereas the "full" set of lab analyses included additional TN and total organic carbon (TOC) measurements in 1.2, 0.45 and 0.1 µm pore size filtrates. At the beginning of the anoxic phase (2 hour), potassium nitrate (KNO_3) was added in order to raise the initial concentration of NO_3-N by 20 g N/m^3. At the beginning of the aerobic phase (6 hour), the aeration system was turned on and the DO set point was controlled at 6 g O_2/m^3.

Figure 2

Analytical methods

The samples were sequentially filtered through membrane filters of different pore sizes including 1.2, 0.45 and 0.1 µm pore-size nitrocellulose filters (Billerica MA, USA). The effect of ultrafiltration was investigated with 0.015 µm pore-size polycarbon filters (Whatman, Kent, UK).

The TOC and TN concentrations were determined using a TOC analyzer (TOC-V_{CSH}) coupled with a TN module (TNM-1) (SHIMADZU Corporation, Kyoto, Japan). Catalytic thermal decomposition/chemiluminescence methods, conformed to the American Society for Test Method's (ASTM) D5176 procedure, are adopted for TN measurement. Samples containing nitrogen are introduced into an oxygen-rich combustion tube with platinum catalyst at a temperature of 720 °C. Bound nitrogen is then converted to nitrogen monoxide (NO), further oxidized to nitrite (NO_2^-) in the presence of ozone, and is then detected by a chemiluminescence detector. TN concentrations in the range of 0.1 to 4000 g/m^3 can be measured.

The concentrations of inorganic N forms (NH_4-N, NO_3-N and NO_2-N) were determined using

Xion 500 spectrophotometer (Dr Lange GmbH, Berlin, Germany). The analytical procedures, which were adopted by Dr Lange, followed the Standard Methods (APHA, 1992). The $DON_{0.1\mu m}$ and $DON_{0.45\mu m}$ concentrations were calculated as a difference between TN after filtration on the appropriate pore size filter (i.e. 0.1 µm and 0.45 µm) and the sum of inorganic N (NH_4-N, NO_3-N and NO_2-N) fractions. The CON concentrations were calculated as a difference between TN after filtration on the 1.2 µm pore size filter and the sum of $DON_{0.1\mu m}$ and inorganic N fractions.

RESULTS AND DISCUSSION

ON characteristics in primary and secondary effluent

The TON accounted for 24-45% of the TN in primary effluent composite samples from 7 of the studied WWTPs (excluding the smallest plant, Koscierzyna WWTP) and the average primary effluent TON concentrations in those plants ranged from 15.5 g N/m^3 (Elblag WWTP) to 35.0 g N/m^3 (Tczew WWTP) (Table 1). For Koscierzyna WWTP, the average primary effluent TON concentration and TON/TN ratio were much higher, i.e. 61.0 g N/m^3 and 57%, respectively. The detailed fractionation of primary and secondary effluent ON (including $DON_{0.1\mu m}$, low and high CON and PON) is presented in Figure 3. The primary effluent PON fraction (PON/TON) was above 50% for all the WWTPs, with the highest at Koscierzyna WWTP (78%), at 60-70% for 3 WWTPs (Gdansk, Gdynia and Tczew), and near 50% for the remaining four WWTPs (Elblag, Slupsk, Lebork and Kartuzy). For the latter, the colloidal fraction (0.1-1.2 µm) of the TON was very significant (36-44%), whereas it ranged from 17 to 34% for the other WWTPs. The average $DON_{0.1\mu m}$ concentrations accounted for only 4-13% of TON and ranged from 1.1 g N/m^3 (Elblag WWTP) to 3.9 g N/m^3 (Lebork WWTP).

Figure 3

The average secondary effluent TN concentrations in the WWTPs ranged from 6.5 to 14.1 g N/m^3. In all the plants, the concentrations of NH_4-N were low (<1.3 g N/m^3) and the dominating form of N was NO_X-N (47-73%). The TON portion constituted 23-35% of the effluent TN, and ranged from 1.9 g N/m^3 (Tczew WWTP) to 4.3 g N/m^3 (Koscierzyna WWTP). The average contributions of $DON_{0.1\mu m}$, CON and PON varied within the ranges of 12-45% (0.5-1.3 g N/m^3), 35-44% (0.7-1.9 g N/m^3) and 20-43% (0.4-1.9 g N/m^3), respectively. The $DON_{0.1\mu m}$ and CON concentrations were reduced to a different extent compared to the primary effluent, i.e. on average 56 and 88%, respectively. As a consequence, the average $DON_{0.1\mu m}$/CON ratio increased from 0.24 in the primary effluent to 0.85 in the secondary effluent. The secondary effluent $DON_{0.1\mu m}$ concentrations were not (or poorly) correlated to any ON form in the primary effluent (the highest correlation, R^2 = 0.29, was found with respect to the primary effluent CON concentration). In contrast, a good correlation (R^2 = 0.55) was found between the secondary effluent $DON_{0.45\mu m}$ concentrations and primary effluent CON.

Ultrafiltration (0.015 μm) after 0.10 μm filtration of the Gdansk and Gdynia WWTP effluents resulted in similar and relatively small amounts of $DON_{0.10\mu m}$ and dissolved organic carbon ($DOC_{0.10\mu m}$) removal. The average reductions in $DON_{0.10\mu m}$ and $DOC_{0.10\mu m}$ at both plants were 10-13% and 2-3%, respectively (Table 2). Thus, it can be assumed that the 0.10 μm filtration provides a reasonable approximation of the DON. The DON consists of both low and high molecular weight (LMW and HMW) compounds as shown by Pehlivanoglu-Mantas and Sedlak (2008) for which almost all of a secondary effluent DON passed through a 10 kDa filter (0.005 μm). About half of the DON passed through a 1 kDa filter and represents LMW substances, which may include free and combined amino acids and synthetic organics. Nitrogen may also be present in humic acids at the 3-10 kDa size and higher molecular weight range. In the earliest studies on the characteristics of DON in secondary effluents, Keller et al. (1978) and Parkin and McCarty (1981c) reported the percentage of LMW nitrogen compounds (<1.8 kDa) in the range of 50-66%. Bratby et al. (2008) also noted a dominance of LMW DON from a previous study, in which 78% of a secondary effluent DON was at a molecular size of 1.0 kDa or less.

Table 2

The average primary and secondary effluent TOC concentrations varied from 125-320 g C/m^3 and 9.4-17.8 g C/m^3, respectively (detailed data not shown). Biological treatment consistently increased the DON/DOC ratio of the wastewater for both conventional (0.45 µm pore size) solids separation filtration and the 0.1 µm pore size approaching the true dissolved filtrate (Figure 4). In general, the smaller pore size filtrate had a higher ON/OC ratio suggesting that the colloids in the pore size range of 0.45-0.1 µm contain proportionally higher amounts of ON than OC. A similar switch of the DON/DOC ratio was also found by Dignac et al. (2000b) in a conventional activated sludge pilot plant treating municipal wastewater (SRT = 10 d). The elemental analysis after electrodialysis (ED) revealed that the ON/OC atomic ratio increased from 0.07 (influent wastewater) to 0.12 (ozonated sludge) and 0.14 (conventional sludge). Lower degradation rates for ON would increase the secondary effluent DON/DOC ratio, as observed the full scale facilities evaluated here, which agrees with Parkin and McCarty (1981a) reporting that the observed degradation rate of $DON_{0.45µm}$ in raw wastewater was less than 50% of the degradation rate of dissolved COD. The authors attributed this change to the presence of heterocyclic nitrogen compounds, such as nucleic acid bases, which can yield high N/COD ratios. Westerhoff and Mash (2002) noted that the DON/DOC ratios are >0.1 in receiving waters affected by wastewater discharges, agricultural activity or high algae productivity, whereas the DON/DOC ratios are <0.025 in receiving waters not affected by WWTP effluents or other sources of N pollution.

Figure 4

The effluent ON concentrations observed in the northern Poland WWTPs are within the range reported for municipal WWTPs in the USA Chesapeake Bay region, where very stringent effluent TN limits of 3 g N/m^3 have been set to help control eutrophication. This study's WWTP data and

USA effluent DON data (WERF, 2008; Sattatayewa et al., 2009b) were plotted in Figure 5 to show the probability distributions of the DON concentrations. WERF (2008) summarized the reported effluent DON data from 32 BNR facilities across the USA and found that effluent DON concentrations (without defining the filter pore-sizes used at each plant) varied in the range of 0.1-2.8 g N/m^3 with the 50 and 90 percentile values of 1.2 and 2.1 g N/m^3, respectively. The same figure also presents the distribution of effluent DON data from a recent study (Sattatayewa et al., 2009b) for 7 US BNR plants. The average $DON_{0.45\mu m}$ concentrations in three samples collected at each plant ranged from 0.6 to 1.4 g N/m^3 and the 50 and 90 percentile values were 0.9 and 1.7 g N/m^3, which is significantly lower in comparison with the results of the 32 plants presented by WERF (2008). It should be noted that at two WWTPs (Blue Plains, DC and Stamford, CT), also included in the review of WERF (2008), the $DON_{0.45\mu m}$ concentrations found by Sattatayewa et al. (2009b) were lower by 0.6 and 0.9 g N/m^3, respectively. For comparison, very similar values of the 50 and 90 percentiles, i.e. 0.9 and 1.3 g N/m^3, were obtained for the Polish plants but with respect to the $DON_{0.1\mu m}$ concentrations.

Figure 5

Similar ranges of ON concentration were also reported for other US WWTPs. In the study of Pehlivanoglu-Mantas and Sedlak (2008), the $DON_{0.2\mu m}$ concentration (in the samples passed through 0.2 μm pore-size filters) ranged from 0.7 to 2.1 g N/m^3 in the effluents from three WWTPs (conventional and N removal activated sludge processes, and a biofilm system). A very similar range (0.5-2.0 g N/m^3) was reported by Sattayatewa et al. (2010) in four BNR plants regardless of the effluent TN concentrations (<5 to 14 g N/m^3). At another three WWTPs (conventional and N removal activate sludge processes), Westgate and Park (2010) found the effluent TON concentrations in the range of 0.9-1.7 g N/m^3 (7-29% of TN) at very low effluent VSS concentrations (1.3-6.1 g/m^3).

The effluent DON consists of compounds which are difficult to remove or produced during biological treatment (Pehlivanoglu-Mantas and Sedlak, 2008). Despite the variety of ON-containing compounds detected in municipal WWTP effluents, most of the compounds could not be identified with available methods. The authors estimated the contributions of some groups of the compounds as: 1) 10-20% - dissolved free and combined amino acids (these compounds are most likely produced during biological treatment since amino acids and proteins are readily biodegradable), 2) <5% ethylenediaminetetraacetic acid (EDTA), and 3) 10% - humic substances originating from the drinking water sources.

A relatively low amino acid fraction in municipal WWTP effluent DON of only about 10% was also noted by Parkin and McCarty (1981c) and Dignac et al. (2000a). Furthermore, Dignac et al. (2000a) concluded that some of the difficulties in identifying DON with common analytical methods may be due to the presence of complex structures, which are concentrated during the biological treatment as a result of the resistance to microbial degradation. Parkin and McCarty (1981c) suggested that a combination of nucleic acid degradation products, nucleic acid bases, and heterocyclic nitrogen compounds could account for up to 25% of the effluent $DON_{0.45\mu m}$. Westgate and Park (2010) found a strong correlation between protein-N and ON concentrations in the effluent wastewater. The protein-N constituted a substantial fraction (approximately 60%) of effluent ON. However, the authors admitted that this value may be overestimated due to two potential sources of the errors: (1) humic substances that are present in effluents can interfere with the Lowry protein measurement, (2) inaccuracy of the ON determination by subtracting inorganic forms from the TN. It should also be noted that the analysis was performed on non-filtered samples (see above)).

Fate of DON/CON in activated sludge bioreactors

Measurement of DON/CON concentration profiles inside bioreactors. Examples (fall and spring measurement series) of $DON_{0.1\mu m}$ and CON profiles in the full-scale bioreactors at the Gdansk and Gdynia WWTPs are presented in Figure 6. During the measurements, the sum of CON and $DON_{0.1\mu m}$ concentrations in the bioreactor effluent remained in a narrow range, i.e. 1.9-2.3 g N/m^3 (Gdansk WWTP) and 2.1-2.4 g N/m^3 (Gdynia WWTP). For comparison, the corresponding average concentrations during the comprehensive survey were 1.7 g N/m^3 (standard deviation 0.32 g N/m^3) and 2.2 g N/m^3 (standard deviation 0.86 g N/m^3) at the Gdansk and Gdynia WWTPs, respectively.

At the Gdansk plant, the primary effluent $DON_{0.1\mu m}$ concentrations ranged from 1.1 to 2.2 g N/m^3 and these values are comparable to the results of the comprehensive survey (average concentration 1.8 g N/m^3, standard deviation 2.42 g N/m^3). For modeling N conversions in that plant, Makinia et al. (2011) assumed that only 10% of the primary effluent DON (<0.2 g N/m^3) and CON (>1.0 g N/m^3) was non-biodegradable, which ultimately accounted for approximately 50% of the sum of effluent DON and CON concentrations. For comparison, Parkin and McCarty (1981a) estimated that under optimal conditions (SRT = 6-10 d), inert substances from the influent wastewater represented 60-80% of the effluent $DON_{0.45\mu m}$, whereas the remaining portion was produced during activated sludge treatment by the biomass.

Low concentrations of $DON_{0.1\mu m}$ were observed in all the sampling points along the MUCT bioreactor. A minor increase in the last (aerobic) compartment was compensated by a reduction of the "low" (0.1-0.45 µm) colloidal subfraction. The effluent $DON_{0.1\mu m}$ concentrations ranged from 0.3-1.1 g N/m^3, which is relatively low when compared to the results of the comprehensive survey (average concentration 1.2 g N/m^3, standard deviation 0.71 g N/m^3). The largest reductions of both colloidal subfractions were found to occur in the anaerobic and anoxic compartments, which is substantially affected by influent dilution and by the recirculated mixed liquor. In the anaerobic compartment, the concentrations of "low" (0.1-0.45 µm) and "high" (0.45-1.2 µm) colloidal subfractions decreased by 2.7-3.0 g N/m^3 and 2.1-2.5 g N/m^3, respectively. In the anoxic compartment, the corresponding maximum reductions were 0.8-1.0 g N/m^3 and 1.9-2.0 g N/m^3.

At the Gdynia plant, relatively high primary effluent $DON_{0.1\mu m}$ concentrations (2.4-3.5 g N/m^3) were observed in comparison with the results of the comprehensive survey (average concentration 2.2 g N/m^3, standard deviation 1.00 g N/m^3). The $DON_{0.1\mu m}$ concentrations decreased to 0.6-0.9 and 0.3-0.7 g N/m^3, respectively, in the anaerobic and anoxic compartment. However, similar to the Gdansk WWTP, an increase in $DON_{0.1\mu m}$ concentration and decrease in the “low” CON subfraction were observed under aerobic conditions in the last compartment. The highest reductions of the “low” and “high” CON subfractions were observed in the anaerobic compartment (by 3.2-4.3 g N/m^3) and anoxic compartment (by 1.7-2.4 g N/m^3), respectively.

With regard to colloidal and dissolved OC, the dominant primary effluent fraction (75-80%) at both plants was DOC, which is very similar to the results of the comprehensive survey (see above). The DOC concentrations primarily decreased in the anaerobic compartment (by 50-70%), whereas the DOC reduction in the entire bioreactors reached 75-85%. The colloidal fraction was reduced in the anaerobic compartment and then stabilized. After that, no significant transformations between the two colloidal subfractions (“low” and “high”) were observed.

Figure 6

Sattayatewa et al. (2009a) carried out similar measurements of ON concentration profiles in a full-scale 4-stage Bardenpho bioreactor. The primary effluent $DON_{0.45\mu m}$ concentrations were low, ranging from 0.84 to 1.37 g N/m^3 with the average value 1.11 g N/m^3. The results showed ON release in the primary anoxic compartment and no ON release in the first aerobic compartment of the activated sludge process. With regard to the DON concentrations determined in the samples after pretreatment using the coagulation-flocculation method of Mamais et al. (1993) (DON_{ff}), a decreasing trend was observed along the treatment train until the first anoxic compartment and then remained stable in the last three compartments (first aerobic/second anoxic/second aerobic). In the bioreactor effluent, $DON_{0.45\mu m}$ and DON_{ff} were essentially identical. In the follow-up study (Sattayatewa et al., 2010), however, the effluent $DON_{ff}/DON_{0.45\mu m}$ in four BNR bioreactors ranged from 0.76 to 0.95 suggesting a significant contribution of the "low" CON subfraction to the effluent ON.

Determination of DON/CON behavior in bench-scale experiments. The average CON and $DON_{0.1\mu m}$ concentrations (±standard deviations) for all the experiments are summarized in Table 3, and Figure 7 illustrates an example of the behavior of CON and $DON_{0.1\mu m}$ profiles measured at the Gdansk and Gdynia WWTPs plants during the summer testing. In all the cases, $DON_{0.1\mu m}$ was explicitly produced in the aerobic compartment of the anaerobic/anoxic/aerobic process. For the Gdansk batch tests, the $DON_{0.1\mu m}$ concentration increases ranged from 0.6-1.9 (average 0.9) g N/m^3 when fed pre-settled wastewater influent (reactor 1) and ranged from 0.2-1.3 (average 0.7) g N/m^3 when fed coagulated-flocculated wastewater influent (reactor 2). Corresponding results for the Gdynia WWTP were concentration increases of 0.3-1.1 (average 0.5) g N/m^3 (reactor 1) and 0.4-1.6 (average 0.8) g N/m^3 (reactor 2), respectively. These findings are in accordance with the observations in the full-scale activated sludge process in which $DON_{0.1\mu m}$ concentrations also increased in the aerobic compartment. Furthermore, in order to evaluate if the increase under aerobic conditions was statistically significant, unpaired t-tests with unequal variances were performed on two data sets ($DON_{0.1\mu m}$ concentrations at the end of anoxic and aerobic period/zone). The calculated p-value, which is the probability of observing equal concentrations for these sampling points, varied at both studied plants in the range of 0.008-0.009 and 0.05-0.09, respectively, for the batch tests and full-scale measurements. Such low p-values, especially for the batch tests, suggest that the examined increase was statistically significant.

It should also be noted that the behavior of inorganic N forms (NH_4-N, NO_3-N, NO_2-N) was similar in the batch tests with the process mixed liquor from both WWTPs (Makinia et al., 2009). However, complete nitrification could not be achieved due to high initial NH_4-N concentrations ranging from 35 to 40 g N/m^3, and NO_2-N accumulated to a peak concentration of approximately 9 g N/m^3 in one test at the Gdansk WWTP. During the other tests, the peak NO_2-N concentrations ranged from 2 to 4 g N/m^3. In contrast, no NO_2-N accumulation was observed during the measurements either in the aerobic compartments of the full-scale bioreactors or in the secondary effluents during routine samplings by the plant operators.

In contrast to the full-scale measurements, the CON profile behaviors in the anaerobic and anoxic phases were different for the two WWTPs. During the Gdansk WWTP batch experiment, an apparent production of DON from CON hydrolysis occurred in the anoxic phase. This finding was derived based on the observation that lower amounts of CON were utilized and higher amounts of DON were produced in reactor 2 (containing exclusively the soluble fraction) compared to reactor 1 (containing all the fractions). These results are consistent with the full-scale measurements at that plant. On the other hand, the batch test CON behavior was the opposite in the Gdynia batch tests, with only a slight decrease in CON (reactor 1) or increase (reactor 2) (Table 3).

Table 3

Figure 7

Until now, the only laboratory experiments evaluating the behavior of ON in activated sludge were reported by Parkin and McCarty (1981b,c). Parkin and McCarty (1981c) carried out a series of eight aeration batch tests (up to 72 h) and the average ultimate $DON_{0.45\mu m}$ concentration was 1.4 (±0.46) g N/m^3. Based on the N mass balance, the authors estimated that 52% of it was recalcitrant (resistant to biological transformations) from the influent wastewater sources, 19% was produced from biomass endogenous decay in the activated sludge process (this portion is a function of the biomass concentration and SRT, 16% was in equilibrium between that sorbed to biomass and that in the liquid (this portion is independent of the biomass concentration and temperature, but dependent on cultural characteristics) and about 13% could be further degraded. Furthermore, the authors noted that increasing the activated sludge SRT could either degrade further influent $DON_{0.45µm}$ or it could also raise $DON_{0.45µm}$ via biomass endogenous respiration. The compounds released during biomass decay were defined as "poorly biodegradable". Furthermore, Parkin and McCarty (1981b) observed peak $DON_{0.45µm}$ concentrations (0.1 to 0.6 g N/m^3) during the initial 6 hours of aeration batch tests regardless of initial substrate, MLSS and NH_4-N concentrations, and a substrate type. The authors attributed that excretion of DON to concentration gradients, starvation conditions, addition of exogenous substrate, and changes in phase and rate of growth. Excreted $DON_{0.45µm}$ was subsequently utilized by the microorganisms, leading to a minimum $DON_{0.45µm}$ concentration after 4 to 8 hours. Starvation conditions then prevailed, and a gradual increase in $DON_{0.45µm}$ concentration occurred due to microorganism decay. This finding is consistent with the observations of the bench-scale experiments at the Gdansk and Gdynia WWTPs where minimum $DON_{0.1µm}$ concentrations were observed at the end of the anoxic phase (after 6 hours from the beginning of the experiment).

CONCLUSIONS

From this study in the 8 BNR WWTPs, the following conclusions can be derived:

- The average primary effluent $DON_{0.1µm}$ concentrations ranged from 1.1 g N/m^3 to 3.9 g N/m^3 and $DON_{0.1µm}$ accounted for only 4-13% of TON concentrations which varied in a wide range from 15.5 to 61 g N/m^3. The fraction of $DON_{0.1µm}$ increased to 12-45% of the effluent TON following BNR activated sludge treatment, but the average secondary effluent $DON_{0.1\mu m}$ concentrations ranged from only 0.5 to 1.3 g N/m^3 which implies the biodegradability of a major portion of the primary effluent $DON_{0.1\mu m}$.

- The relatively narrow range of secondary effluent $DON_{0.1\mu m}$ concentrations was observed despite high variations in the size of the studied plants (37,000-565,000 PE), biological process configuration employed (UCT, MUCT, JHB, A_2/O, MLE) and operating parameters (SRT = 9-34 d). Furthermore, the secondary effluent $DON_{0.1\mu m}$ concentrations were not (or poorly) correlated to any ON form in the primary effluent (the highest correlation, $R^2 = 0.29$, was found with respect to the primary effluent CON concentration). In contrast, a good correlation ($R^2 = 0.55$) was found between the secondary effluent $DON_{0.45\mu m}$ concentrations and primary effluent CON.
- The secondary effluent CON fraction accounted for 43 to 78% of the non-particulate ON (<1.2 μm) with the remainder as $DON_{0.1\mu m}$. Ultrafiltration with 0.015 μm pore size filters had only a minor effect on further reductions of the effluent $DON_{0.1\mu m}$.
- The largest reductions of the CON fractions were found to occur in the anaerobic and anoxic compartments of the studied bioreactors, whereas an increase of $DON_{0.1\mu m}$ concentrations was observed in the aerobic compartment. During batch experiments with process mixed liquor and primary effluent wastewater, $DON_{0.1\mu m}$ was consistently produced in the aerobic phase.

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Seattle.

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Table 1. BNR WWTPs configuration, average flowrate, SRTs, and plant influent and effluent TN concentrations for 2007-2008 (based on the routine operating data)

Facility	Size	Average flowrate	SRT	Bioreactor configuration	Average TN (2007-08)	
					Influent	Effluent
	PE	m^3/d	d		gN/m^3	gN/m^3
Gdansk	565,000	81,000	21-31	MUCT	81.2	11.6
Gdynia	516,000	56,000	14-27	JHB	82.5	12.9
Elblag	181,000	36,000	15-22	MLE	66.9	5.6
Slupsk	180,000	19,000	18-29	UCT	73.9	8.4
Tczew	70,000	8,900	19-34	A_2/O	84.5	6.8
Lebork	56,000	7,200	18-25	JHB	80.7	10.9
Kartuzy	47,000	3,200	9-24	UCT	97.9	14.0
Koscierzyna	37,000	3,200	12-29	JHB	113.0	10.3

Table 2. DON and DOC before and after0.10 um filtration and ultrafiltration of the secondary effluents at the Gdansk and Gdynia WWTPs

Sample	Unit	Test 1	Test 2	Test 3	**Average**
Gdansk WWTP					
DON (<0.1 μm)	g N/m^3	1.88	2.10	1.99	**1.99**
DON_{UF} (<0.015 μm)	g N/m^3	1.77	2.04	1.59	**1.80**
DOC (<0.1 μm)	g C/m^3	17.0	17.5	10.2	**14.9**
DOC_{UF} (<0.015 μm)	g C/m^3	16.6	17.2	9.4	**14.4**
Gdynia WWTP					
Sample	Unit	Test 1	Test 2	Test 3	**Average**
DON (<0.1 μm)	g N/m^3	1.52	1.63	1.05	**1.40**
DON_{UF} (<0.015 μm)	g N/m^3	1.26	1.39	1.00	**1.22**
DOC (<0.1 μm)	g C/m^3	16.0	10.7	9.9	**12.2**
DOC_{UF} (<0.015 μm)	g C/m^3	15.8	10.4	9.6	**11.9**

Table 3. Average CON and DON concentrations during the 3-phase anaerobic/anoxic/aerobic batch experiments at the Gdansk and Gdynia WWTPs

Gdansk (average ± standard deviations from 5 experiments) (T = 12.8-16.8 ºC, MLVSS = 1.17-3.04 kg/m^3)						
	Reactor 1 (without pretreatment)			Reactor 2 (with pretreatment)		
Sample	DON	CON	Total	DON	CON	Total
Start	0.6 ± 0.21	3.3 ± 1.34	3.9 ± 1.53	0.6 ± 0.56	2.1 ± 0.84	2.7 ± 1.20
Anaerobic	0.8 ± 0.52	3.3 ± 1.04	4.1 ± 1.43	0.8 ± 0.42	2.1 ± 0.84	2.9 ± 1.15
Anoxic	0.7 ± 0.33	2 ± 0.33	2.7 ± 0.50	0.2 ± 0.08	2.1 ± 0.88	2.3 ± 0.91
Aerobic	1.6 ± 0.55	2.1 ± 0.76	3.7 ± 0.38	0.9 ± 0.42	1.7 ± 1.00	2.6 ± 0.82
Gdynia – (average ± standard deviations from 6 experiments) (T = 13.1-17.9 ºC, MLVSS = 1.21-2.57 kg/m^3)						
	Reactor 1 (without pretreatment)			Reactor 2 (with pretreatment)		
Sample	DON	CON	Total	DON	CON	Total
Start	0.8 ± 0.38	2.4 ± 0.84	3.2 ± 1.00	0.7 ± 0.32	1.8 ± 0.93	2.5 ± 0.78
Anaerobic	0.8 ± 0.45	2.1 ± 0.77	2.9 ± 1.03	0.9 ± 0.51	1.8 ± 0.56	2.7 ± 0.90
Anoxic	0.6 ± 0.28	1.9 ± 0.8	2.5 ± 1.03	0.6 ± 0.17	2.3 ± 1.17	2.9 ± 1.12
Aerobic	1.1 ± 0.58	2.2 ± 0.62	3.3 ± 1.12	1.4 ± 0.70	2.4 ± 1.18	3.8 ± 1.38

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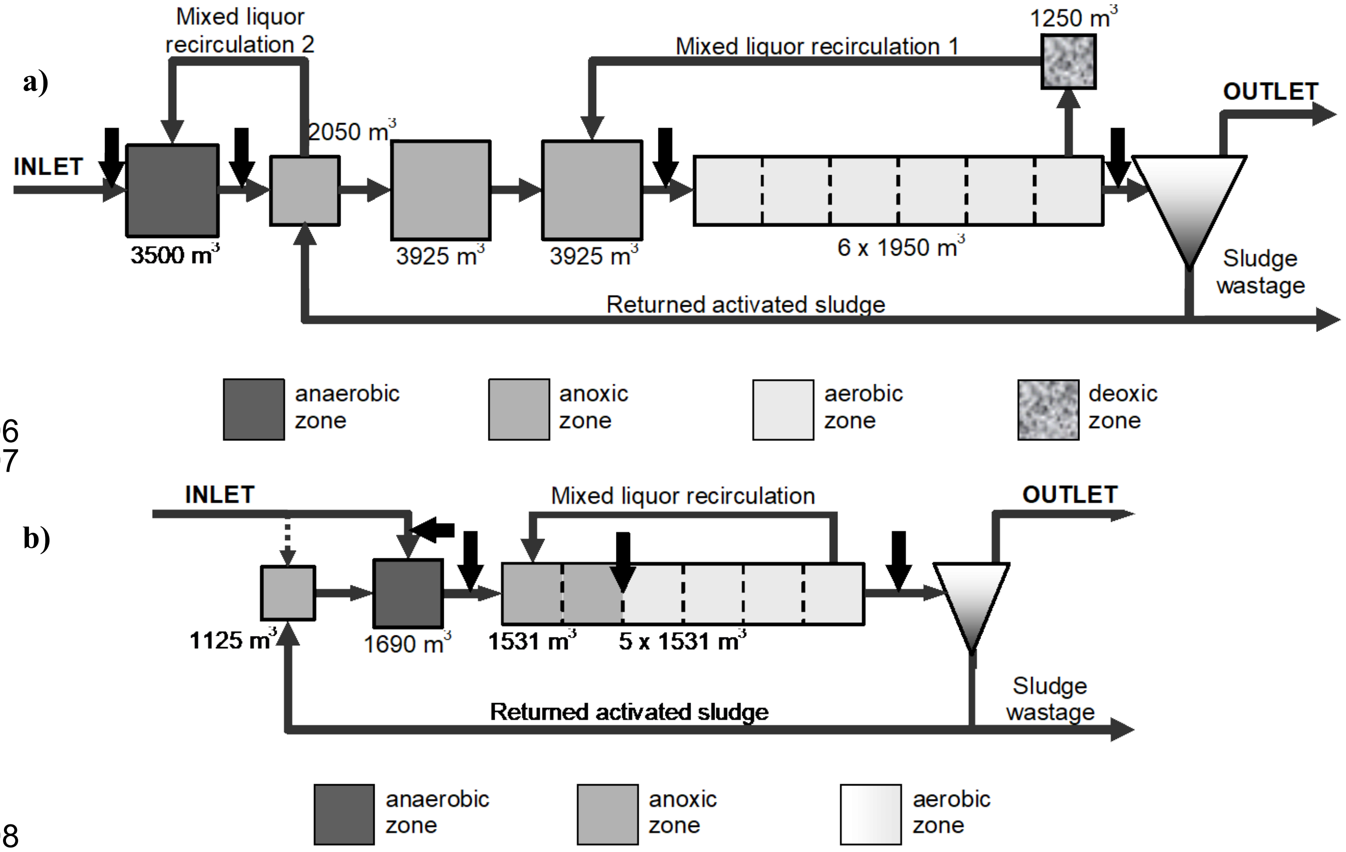

Figure 1. Schematic of BNR system bioreactor compartments: (a) Gdansk MUCT process, (b) Gdynia JHB process (black arrows show sampling locations)

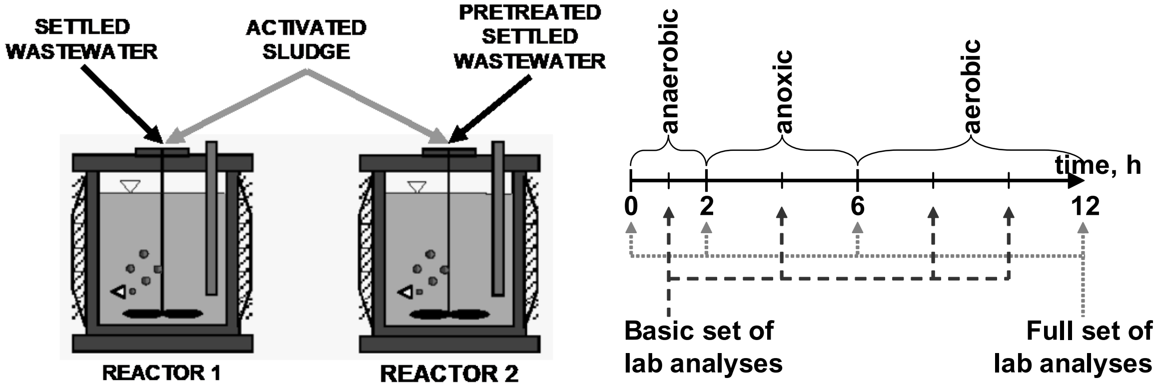

Figure 2. Feed source, operating sequence, and analyses for experiments with two parallel batch reactors (parameters measured in the basic and full sets are described in the text)

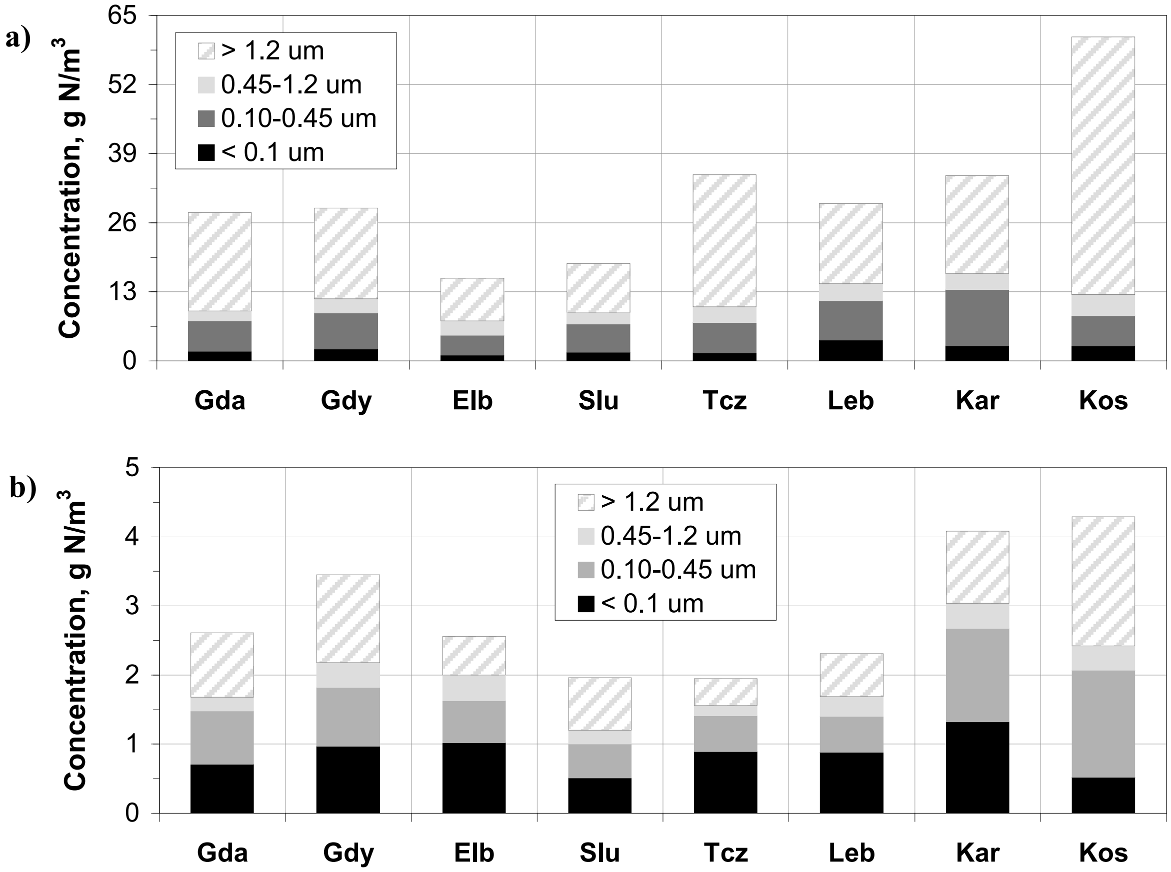

Figure 3. Primary and secondary effluent ON fractions in the 8 studied BNR WWTPs

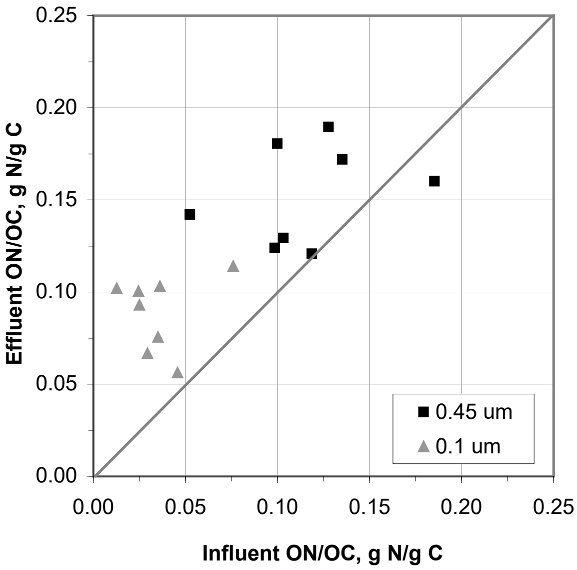

Figure 4. Effluent DON/DOC vs. influent DON/DOC in the 8 studied BNR WWTPs based on filtration through 0.45 μm and 0.1 μm pore-size filters

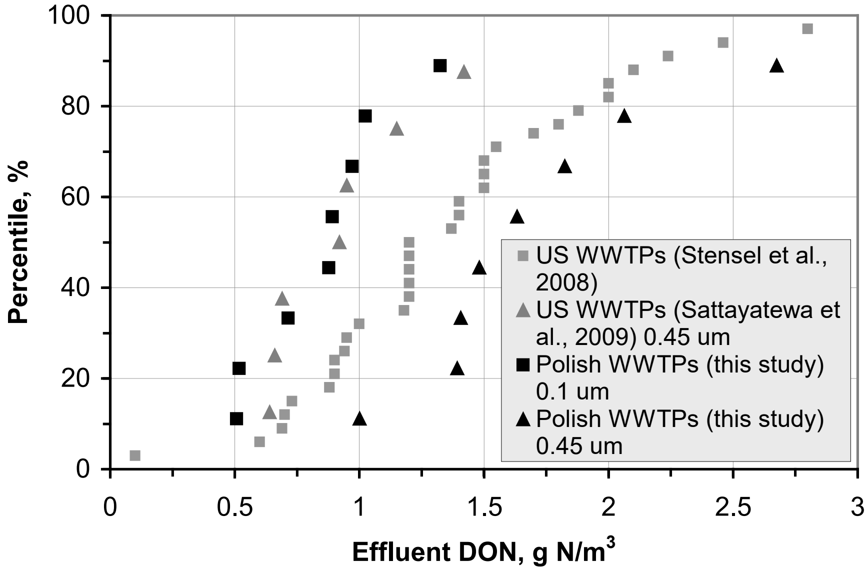

Figure 5. Probability distributions of secondary effluent DON concentrations

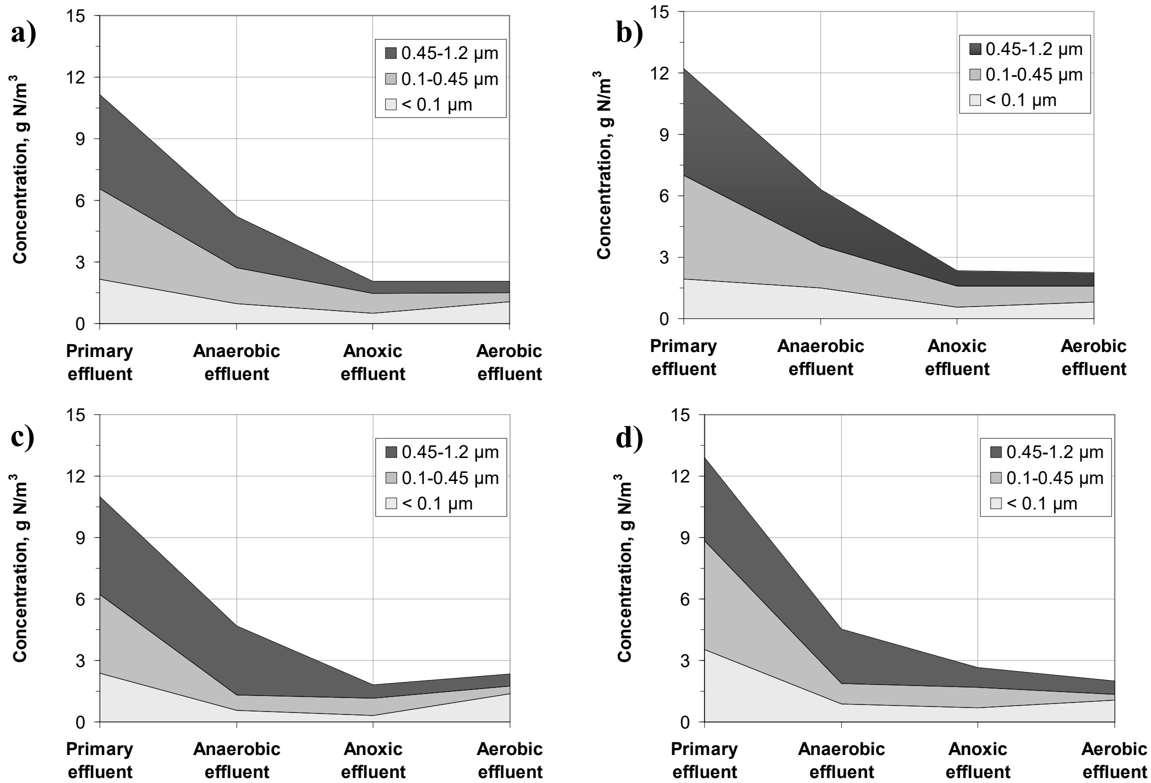

Figure 6. Average concentration profiles of DON and CON in the full-scale bioreactors (fall and spring study sessions) at the Gdansk WWTP (a-b) and the Gdynia WWTP (c-d)

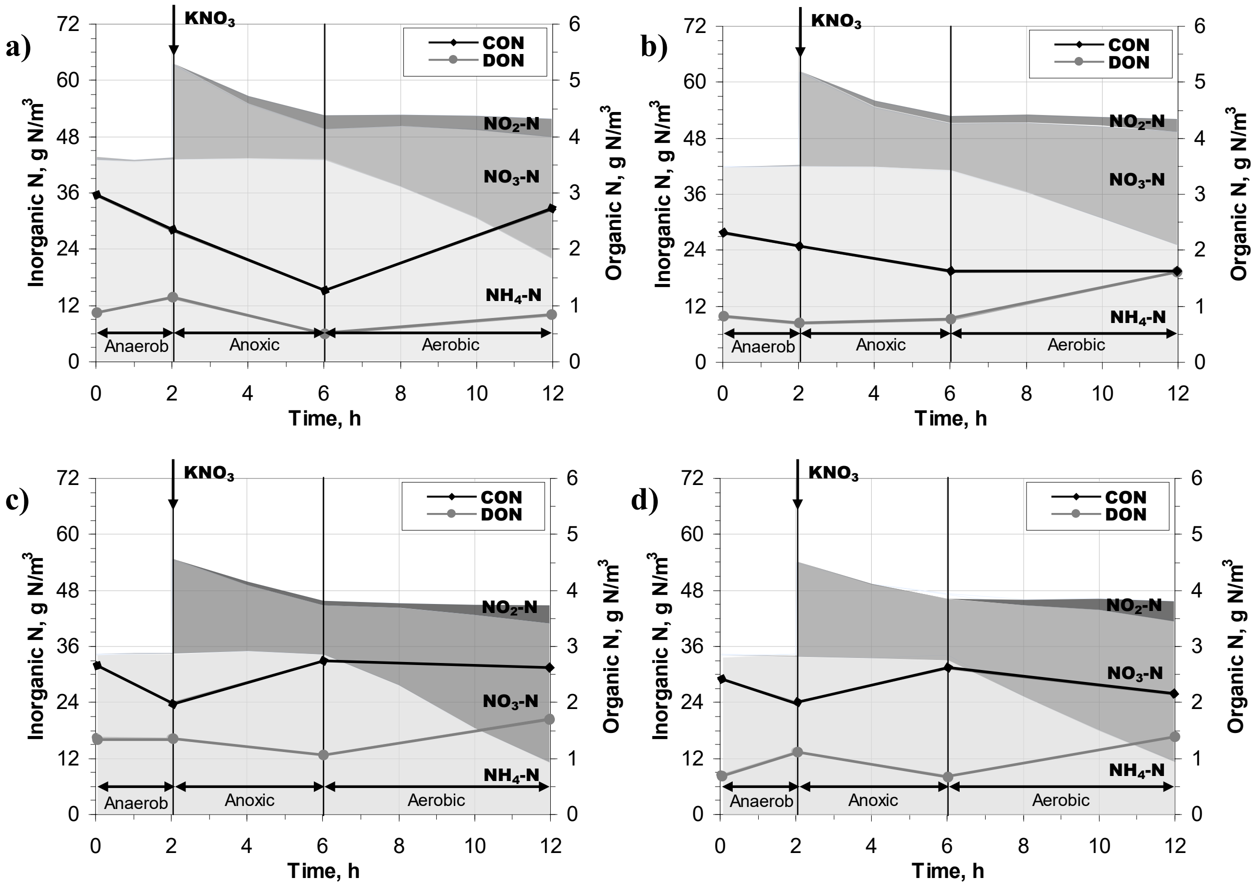

Figure 7. Behavior of nitrogen compounds during 3-phase batch tests with the full-scale process biomass from the Gdansk WWTP: (a) settled wastewater, (b) settled wastewater after coagulation-flocculation, and the Gdynia WWTP: (c) settled wastewater, (d) settled wastewater after coagulation-flocculation