Nitrogen speciation in wastewater treatment plant influents and effluents—the US and Polish case studies

K. R. Pagilla, K. Czerwionka, M. Urgun-Demirtas and J. Makinia

ABSTRACT

The fate of N species, particularly dissolved organic nitrogen (DON), through process trains of a wastewater treatment plant (WWTP) was investigated. In this study, three fully nitrifying plants in Illinois, USA and biological nutrient removal (BNR) plants in northern Poland were sampled for N characterization in the primary and secondary effluents as a function of the particle size distribution. The correlations between dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations were examined. The key findings are that DON becomes significant portion (about 20%) of the effluent N, reaching up to 50% of effluent total N in one of the Polish plants. The DON constituted 56–95% of total ON (TON) in the secondary effluents, whereas in the Polish plants the DON contribution was substantially lower (19–62%) and in one case (Gdansk WWTP) colloidal ON was the dominating fraction (62% of TON). The DOC to DON ratio in the US plants is significantly lower than that in the receiving waters indicating potential for deterioration of receiving water quality. In Polish plants, the influent and effluent C:N ratios are similar, but not in the US plants.

Key words | colloidal, dissolved, organic nitrogen, speciation, wastewater

K. R. Pagilla
M. Urgun-Demirtas
Department of Civil,
Architectural and Environmental Engineering,
Illinois Institute of Technology,
3201 S. Dearborn St,
Chicago, IL 60616,
USA
E-mail: *pagilla@iit.edu*

K. Czerwionka
J. Makinia
Faculty of Civil and Environmental Engineering,
Gdansk University of Technology,
ul. Narutowicza 11/12,
80-952 Gdansk,
Poland
E-mail: *jmakinia@pg.gda.pl*

INTRODUCTION

Most of the influent total nitrogen (TN) in wastewater treatment plants (WWTPs) can successfully be removed by nitrification and denitrification. In contrast, the dissolved organic N (DON) portion which has not been converted into inorganic N forms is very difficult to remove from the wastewater. Most of the WWTPs have hardly considered DON removal in their existing processes because it constituted a small fraction of the effluent TN limit. However, for WWTPs facing stringent effluent TN regulations, the fraction of DON in the effluent becomes critical. In fact, effluent DON can make up a large part in low TN effluent plants. For example, DON constitutes 85% of TN in the effluent of Truckee Meadows Water Reclamation Facility (Nevada, USA) (Pehlivanoglu & Sedlak 2004) and 40% of TN in the Broadneck WWTP (Maryland, USA) (Pagilla *et al.* 2006).

Release of DON into the receiving waters along with phosphorus and organic carbon may have adverse effects on the water quality, such as eutrophication (Seitzinger & Sanders 1997). The DON fraction that passes through the plant into the effluent is potentially not bioavailable or biodegradable in the biological processes of WWTPs and hence DON bioavailability and biodegradability in the receiving waters may also be questionable. However, the DON produced in post-nitrification biological processes in a WWTP as soluble microbial products could be potentially bioavailable for bacterial and/or algal assimilation in the receiving waters. The bioavailability and environmental fate of effluent N released into the receiving waters are not only related to the residual N concentration in the treated effluent, but also to its speciation.

The effluent DON has been found to be a heterogeneous mixture of organic compounds which are mainly high molecular weight compounds, originated from unchanged or partially changed influent organic compounds, and by-products from microbial metabolism (soluble microbial products (SMP)) (Namour & Müller 1998; Baker & Stuckey 1999; Dignac *et al.* 2000). The dissolved organic matter (DOM) in

doi: 10.2166/wst.2008.213

biological process effluents, composed of soluble organic carbon and nitrogen, may have microbial origin rather than the original organic substrates (Boero *et al.* 1996), hence it is important to understand the transformation of N species in wastewater treatment facilities. Very few studies have been conducted on DON and DOM characterization in municipal wastewater treatment effluents. The identification and measurement of DON and dissolved organic carbon (DOC) species can be very difficult because of complexity and diversity of these compounds, unknown chemical structure of majority of these compounds, and limited techniques to quantify them.

In this research, DON and colloidal organic nitrogen (CON) concentrations in the influent and effluents of various plants with varying wastewater characteristics, size and process configuration have been investigated to understand the fate of DON through conventional secondary treatment plants' (US) and biological nutrient removal plants' (Poland) treatment trains.

METHODS

Studied plants

The studies were conducted independently at three fully nitrifying plants in the state of Illinois (USA) and four biological nutrient removal (BNR) plants in northern Poland. The basic characteristics of all the facilities are presented in Table 1. The daily average samples of primary and secondary effluents were collected for nitrogen and carbon characterization. The samples in the Illinois plants were collected during five sampling events during the period of April 2005 to August 2005. In Poland, the plants were sampled three times between November, 2006 and February, 2007.

Laboratory analyses

The quantification of organic N was based on filtration of primary or secondary effluent sample through a series of filters to determine concentrations of CON and DON fractions, as well as to analyze in detail the CON fractions. The samples were filtered through membrane filters of different pore sizes including 0.1, 0.22, 0.3, 0.45 and 1.2 μm pore size Millipore nitrocellulose filters (Billerica, MA) and then, the filtrate was analyzed for TN, NH_4-N, NO_3-N, NO_2-N and total Kjeldahl nitrogen (TKN). The procedures were adapted by Hach Chemical Company (Hach, Loveland, CO) and Dr Lange GmbH (Germany) for the US and Polish studies, respectively, and followed the *Standard Methods* (APHA 1992). The DON concentration was estimated from the difference between TN and the summation of NH_4-N, NO_3-N and NO_2-N concentrations. In the US part of the study, total carbon (TC) and inorganic carbon (IC) concentrations in the samples were measured by Dohrman DC80 TOC analyzer (Rosemount Analytical Inc., CA, USA). Total organic carbon (TOC) was calculated as the difference between TC and IC. In the Polish part of the study, TOC was not measured and alternatively COD was determined by Xion 500 spectrophotometer (Dr Lange GmbH, Germany).

RESULTS AND DISCUSSION

Influent and effluent wastewater characterization in the studied WWTPs

Table 2 shows the primary nitrogen and carbon forms in the samples of primary and secondary effluents filtered through a 0.45 μm pore size filter, which is conventionally used to

Table 1 | Basic characteristics of the studied WWTPs

WWTP	Flow rate $m^3\,d^{-1}$	Configuration of bioreactor	Nitrogen limits
Stickney (USA)	4,500,000	Conventional	2.5/4.0 mg NH_4-N dm^{-3} (seasonal)
Hinsdale (USA)	76,000	Conventional	1.5/2.1 mg NH_4-N dm^{-3} (seasonal)
Elmhurst (USA)	45,000	Conventional	2.3/4.6 mg NH_4-N dm^{-3} (seasonal)
Gdynia (Poland)	56,000	JHB	10 mg TN m^{-3}
Gdansk (Poland)	81,000	MUCT	10 mg TN m^{-3}
Elblag (Poland)	36,000	Pre-denitrification	10 mg TN m^{-3}
Slupsk (Poland)	19,000	UCT	10 mg TN m^{-3}

Table 2 | Nitrogen and carbon speciation in the studied WWTPs

WWTP		TN g/m³	NH_4-N % of TN	NO_x-N % of TN	TON % of TN	DON g/m³	% of TN	TC* g/m³	DOC† % of TC
Stickney (USA)	Prim. eff.	29.7	77	2	21	5.4	18.3	86.0	40
	Sec. eff.	11.3	2	72	26	1.7	14.9	36.6	24
Hinsdale (USA)	Prim. eff.	20.7	79	6	15	1.4	6.6	90.6	23
	Sec. Eff.	19.9	4	75	21	3.6	18.2	40.7	13
Elmhurst (USA)	Prim. eff.	34.1	86	6	8	2.4	6.9	84.2	32
	Sec. eff.	22.5	1	90	9	2.0	8.9	29.0	9
Gdynia (Poland)	Prim. eff.	80.0	55.2	0.2	44.6	6.7	8.3	813.3	22
	Sec. Eff.	17.1	26.8	53.0	20.2	2.4	14.1	39.4	79
Gdansk (Poland)	Prim. eff.	79.2	64.7	0.3	34.9	8.6	11.0	564.0	30
	Sec. Eff.	9.7	1.7	78.3	20.1	1.3	13.0	39.2	83
Elblag (Poland)	Prim. eff.	56.7	52.5	0.5	47.0	11.8	20.8	825.0	20
	Sec. Eff.	10.1	3.0	47.3	49.7	2.7	27.1	51.9	76
Slupsk (Poland)	Prim. eff.	61.7	60.1	0.2	39.7	13.0	21.3	488.0	37
	Sec. eff.	8.3	1.6	78.6	19.8	1.3	15.6	24.8	81

*COD in the Polish WWTPs.
†DCOD in the Polish WWTPs.

determine soluble (or dissolved) components in wastewater. In Table 3, a detailed fractionation of organic N is presented including "true" DON (<0.1 μm), CON (0.1–1.2 μm) and particulate organic nitrogen (PON) (>1.2 μm).

Detailed N and C speciation in Illinois plants

Table 2 shows the nitrogen and carbon forms in samples filtered through 0.45 μm pore size filter, which are used to determine soluble or dissolved components of parameters. The fractions of DON in the primary and secondary effluents ranged from 8 to 21% and 9 to 26% of TN, respectively. The DON fraction of TN in the primary effluent was lower than that in the secondary effluent of Stickney and Hinsdale unlike Elmhurst WWTPs because of the differences in the secondary treatment processes between those plants. The DOC fraction of TC in the primary and secondary effluents ranged from 23 to 40% and 9 to 24%, respectively.

In Stickney WWTP primary effluent, the CON was about 10% of TON and the remaining was 95% DON (Figure 1(a)). This could be due to large sewer collection system that can solubilize the CON in the wastewater being treated by the Stickney WRP. However, CON constitutes 57% of TON in

Table 3 | Organic N fractions (dissolved, colloidal and particulate) in the studied WWTPs

WWTP (USA)		DON	CON + PON (% of TON)	WWTP (Poland)		DON	CON (% of TON)	PON
Stickney	Prim. eff.	89	11	Gdynia	Prim. eff.	6.9	25.5	67.6
	Sec. eff.	56	44		Sec. eff.	46.2	27.0	26.8
Hinsdale	Prim. eff.	43	57	Gdansk	Prim. eff.	5.5	42.7	51.7
	Sec. eff.	86	14		Sec. eff.	19.4	62.4	18.2
Elmhurst	Prim. eff.	84	16	Elblag	Prim. eff.	40.6	11.7	47.7
	Sec. eff.	95	5		Sec. eff.	40.5	35.0	24.5
				Slupsk	Prim. eff.	39.6	17.8	42.6
					Sec. eff.	62.1	20.9	17.0

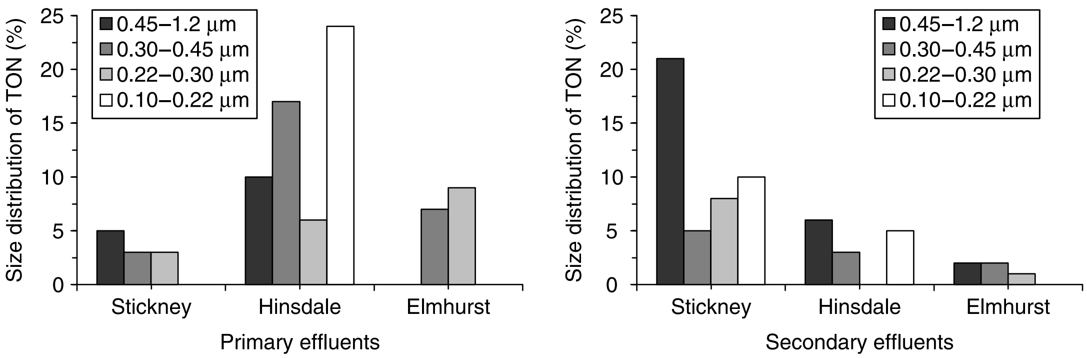

Figure 1 | Size distribution of TON in the primary and secondary effluents of Illinois WWTPs.

the primary effluent of Hinsdale, and all size fractions of CON were present. In the primary effluent of Elmhurst WWTP, the particle size of the CON ranges from 0.22 to 0.45 μm and constitutes 16% of total ON filtered through 1.2 μm pore size filter. The secondary effluent of Stickney effluent includes 44% CON, 21% of within the 0.45 to 1.2 μm size range, 5% of within the 0.3–0.45 μm, 8% of within 0.22–0.3 μm, and 10% of within the 0.1–0.22 μm size range (Figure 1(b)). It implies that the larger particle size CON (0.45–1.2 μm) fraction is significant higher (21% versus 5%) in the secondary effluent compared to the primary effluent at Stickney and could be associated with cellular components formed due to cell lysis in the biological process. The CON fraction constitutes 14 and 5% of TON in the secondary effluents of Hinsdale and Elmhurst WWTPs, respectively, and more importantly no significant increase in the larger size fraction is seen. This indicates that the fraction of CON was very small with respect to DON in the effluent of these plants. This could be due to the coagulants used in the secondary clarifiers to enhance activated sludge settleability. This observation has an important implication for nutrient removal plants employing chemical precipitants in the secondary treatment process either to enhance activated sludge settleability or for chemical P removal in reducing TON in the effluents. The observation could also be supportive of the membrane filtration or membrane bioreactor applications for achieving lower TN effluents.

The size distribution of TOC filtered through 1.2 μm filter paper in the primary and secondary effluents is shown in Figure 2 (a) and (b). Similar to the size distribution of TON, 78–93% and 65–87% of TOC filtered through 1.2 μm filter paper was found to be DOC in the primary and secondary effluents of all WWTPs, respectively. A similar result was found by Levine *et al.* (1985). They reported that 63–70% of the TOC was associated with particles less than 1.2 μm in the primary effluents of some US plants. However, there were no distinct signature patterns between the TOC profiles of either primary or secondary effluents in Stickney and Hinsdale plants. A larger COC fraction for all size ranges was found in the primary and secondary effluents of

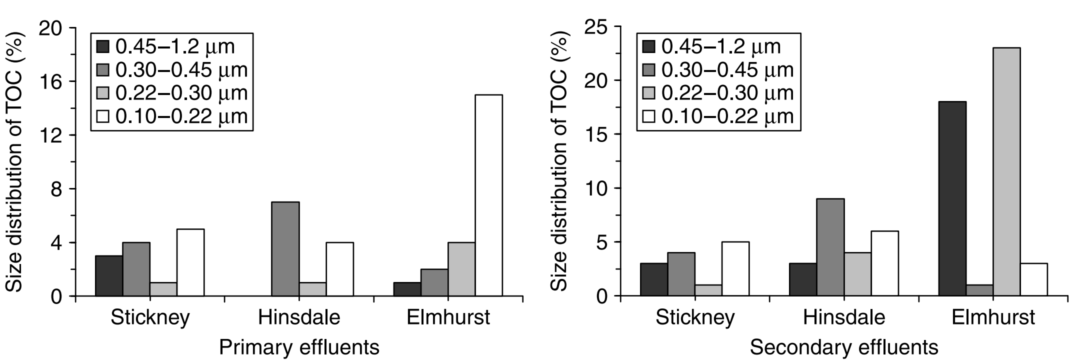

Figure 2 | Size distribution of TOC in the primary and secondary effluents of Illinois WWTPs.

Elmhurst WWTP, compared to the other two plants. It indicates that the hydrolysis of the colloidal particles in the influent wastewater of Elmhurst WWTP might be lower than that in other WWTPs. In the secondary effluent of this WWTP, the highest fraction of COC was found in the size range of 0.22 to 0.33 μm (23% of TOC) and in the size range of 0.45 to 1.2 μm (18% of TOC), indicating variations from the CON patterns seen in Figure 1(b).

To assess the impact of DON release from the Illinois WWTPs on the receiving water quality, DOC to DON ratio in the effluents of these plants was determined. The DOC:DON ratio decreases through the treatment of processes of these plants as expected because nitrification takes place after carbonaceous removal. The DOC:DON ratio ranges from 5.4 to 10.1 in the primary effluents and 1.1 to 3.2 in the secondary effluents of WWTPs. The DOC:DON ratios for Illinois WWTPs (3) (nitrification only) (average = 2.2) are significantly lower than the reported C:N ratios (ranging from 4 to 30) in the receiving waters (Hopkinson *et al.* 1993). The DOC:DON ratios of both N removal and ammonia removal plants suggest that they are significantly lower than the receiving waters and hence, DON from wastewater treatment plant effluents may significantly deteriorate the receiving water quality. For example, low effluent DOC:DON ratio of 1.2 for Stickney WRP could adversely affect the water quality in the Chicago River because the effluent constitutes about 30 to 50% of the Chicago River flow. It has been reported that lower C:N ratios of 5 to 11 can adversely affect receiving waters; this issue warrants further investigation on receiving water quality deterioration due to release of treated effluents with low C:N ratio.

Detailed N and C speciation in Polish plants

The effluent TN concentrations in the studied plants remained close to the Polish limit of 10 mg N dm^{-3} for large WWTPs (>100,000 PE). In one plant (Elblag), the dominant form of N was TON contributing to nearly 50% of TN, whereas NO_X-N was the major component of TN in the other three WWTPs (Table 2). In Gdynia WWTP, seasonal perturbations with the nitrification process were observed in the winter (for $T < 12°C$). This resulted in the increase of NH_4-N contribution to TN up to 26.8% and this value was several times higher compared to the other studied plants (1.6–3.0% of TN). The average TON/TN ratios in the secondary effluents were approximately 0.2 excluding Elblag WWTP, where this ratio was as high as 0.5. In the primary effluents, the average TON/TN ratios varied within a smaller range (0.35–0.47).

When a 0.45 μm pore size filter was used to determine dissolved components, DON constituted 8.3–21.3% and 13.0–27.1% of TN in the primary effluents and secondary effluents, respectively. An increase in the DON contribution in the secondary effluents was observed in three plants excluding Slupsk WWTP, where the decrease resulted not only from relative low concentrations of DON (1.3 mg N dm^{-3} on average) but also due to very high concentrations of this fraction in the primary effluent (the highest values among the studied plants).

The analysis of different species of organic N (DON, CON and PON) was based on the fractionation presented in Table 3. In the primary effluents, the highest contribution (42.6–67.7% of TON) originated from PON. In Gdansk WWTP, CON contributed considerably to TON (42.7%), and the highest contribution (40% of CON) was by the fraction ranging from 0.45 to 1.2 μm. In the other plants, the contribution of CON varied from 11.7 to 25.5% of TON and the dominant fraction (40–66% of CON) originated again from the range 0.45–1.2 μm. Only in Slupsk WWTP, the dominant fraction (46% of CON) is the smallest pore (0.1–0.22 μm). The detailed distribution of CON fractions is illustrated in Figure 3. As high as 39.6 and 40.6% of TON in the primary effluents were in the form of DON in the Slupsk and Elblag WWTPs, respectively.

A significant increase in the contribution of DON was observed in the secondary effluents. Apart from the Gdansk WWTP, DON is the dominant fraction of organic nitrogen ranging from 40.5 to 62.1% of TON. In Gdansk WWTP, a significant contribution of CON (62.4% of TON) was observed again with a dominant fraction in the range 0.1–0.22 μm. In the other WWTP plants, CON constituted 20.9–35.0% of TON. It should be noted that a minor contribution (<2%) of one of the CON fractions was observed in each of the studied plants. The fraction in the range 0.3–0.45 μm was not found in Gdynia and Elblag WWTPs, whereas the fraction in the range 0.22–0.3 μm was not found in Gdansk and Slupsk WWTPs.

With regard to the COD distribution in the primary effluents (Figure 4), the dominant fraction originated from

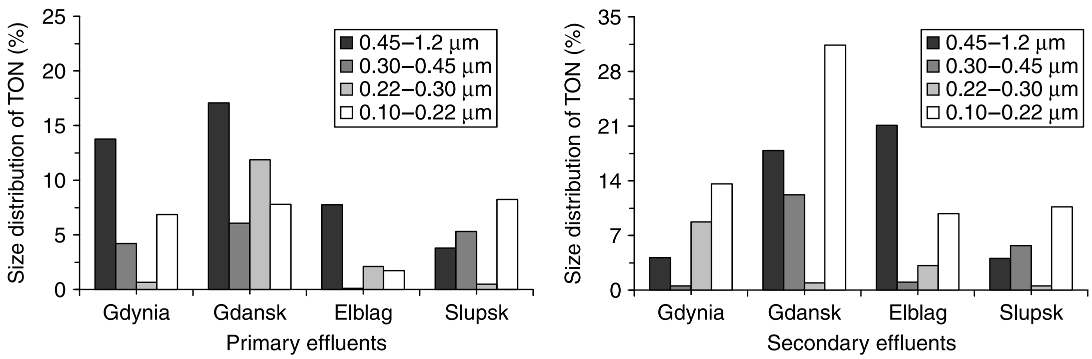

Figure 3 | Size distribution of TON in the primary and secondary effluents of Polish WWTPs.

particulate organic compounds (>1.2 μm), which constituted 61–75% of COD. In the secondary effluents, the greatest fraction (67–73% of total COD) was composed of dissolved compounds (<0.1 μm). The colloidal fraction contribution varied in the range 3.3–12.4% and 9.8–17.3% of COD in the primary effluent and secondary effluents, respectively.

The DCOD/DON ratios in the primary effluents ranged from 37.5 (Slupsk WWTP) to 12.3 (Gdynia WWTP). For the secondary effluents, these ratios were lower ranging from 16.5 (Gdynia WWTP) to 30.7 (Gdansk WWTP). The DOC:DON ratios in primary and secondary effluents of Illinois WWTPs are not significantly different like the Polish plants.

Potentials for removing different effluent N fractions

Although DON characteristics have not been well known until now, DON can be classified by its molecular weight (MW). The DON compound group with <1000 Da MW are urea, amino acids, DNA, peptides and various synthetic compounds (N-containing pesticides and pharmaceuticals). The DON group with MW ranging from 10^3 to 10^6 Da is composed of fulvic acids, which are complex aromatic compounds that are soluble at all pH ranges, and some proteins. High molecular weight DONs include humic substances, which are insoluble at pH 2 and consist of aromatic ring structures linked with functional side groups such as cyclic nitrogen groups, carboxylic and phenolic acids, and peptide chains, and large proteins.

Biological treatment, such as the activated sludge process, has been thought effective in removing low MW DON, while high MW DON is considered refractory to this kind of treatment (Gulyas *et al.* 1995; Dignac *et al.* 2000). The popular method for removing high MW DON species from the wastewater is chemical oxidation process. The chemical oxidation process breaks high MW DON to low MW compounds that are more biodegradable or bioavailable. Various chemical oxidation processes have been examined for removing high MW organic compounds, for example,

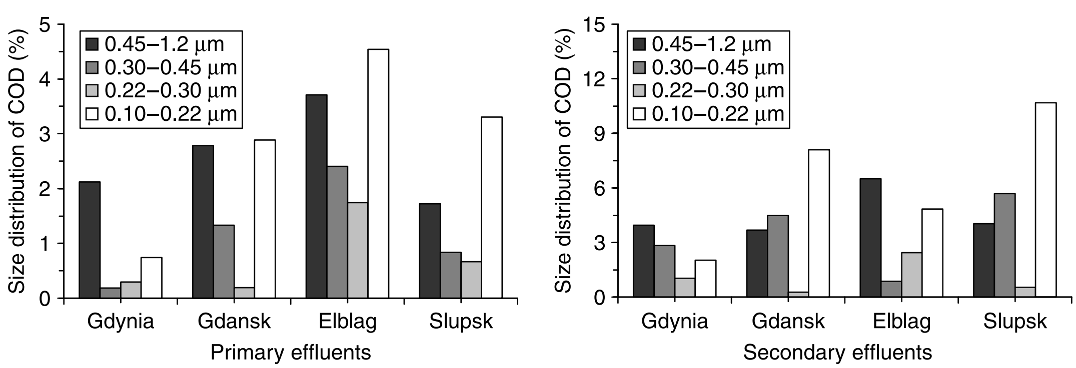

Figure 4 | Size distributions of COD in the primary and secondary effluents of Polish WWTPs.

ozonation, UV radiation (Wenzel *et al.* 1999), hydrogen peroxide (Beschkov *et al.* 1997), and Fenton process (Chou *et al.* 1999). However, these processes are usually used for removal of high MW organics in industrial wastewater, not in municipal wastewater, due to high costs. The ability of newer filtration technologies such as microfiltration being used in membrane bioreactors to remove the colloidal fractions ($<0.45\,\mu$m) in the sub-micrometre particle size range is unknown.

CONCLUSIONS

(1) The high variation in DON ranging from 9 to 50% of TN in the treated effluents places challenges to achieving low effluent TN values in the plants. However, the information gathered on organic N speciation in US and Polish WWTP effluents is very valuable to show the importance of residual N fractions that are not efficiently removed by the current N removal processes, and also to demonstrate the fate of DON through the plant appears to be specifically dependent on the site and plant.

(2) In the Illinois plants, the DON constituted 56–95% of TON in the secondary effluents, whereas in the Polish plants the DON contribution was substantially lower (19–62%). In one case (Gdansk WWTP), the CON was the dominating fraction (62% of TON).

(3) The impact of DON release from the WWTPs on the receiving water quality could be roughly estimated by DOC/DON ratio which remains in the range 1.1–3.2 for Illinois plants. In the Polish plants, the DCOD/DON ratios in the primary effluents varied within the range 12.3–37.5 compared to a similar range of 16.5–30.7 for the secondary effluents. These data do not confirm the trends observed in the Illinois WWTPs with respect to differences between primary and secondary effluent DOC:DON ratios.

ACKNOWLEDGEMENTS

The Polish part of this research has been financially supported by the Norwegian Financial Mechanism under the grant no. PL0085-PIP-00151-E-V1. The US part of the research has been funded by the Water Environment Research Foundation under the project, 01-CTS-1a.

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