Quantification and characterization of dissolved organic nitrogen in wastewater effluents by electrodialysis treatment followed by size-exclusion chromatography with nitrogen detection

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ABSTRACT

Dissolved organic nitrogen (DON) can act as a precursor of nitrogenous disinfection byproducts during oxidative water treatment. Quantification and characterization of DON are still challenging for waters with high concentrations of dissolved inorganic nitrogen (DIN, including ammonia, nitrate and nitrite) relative to total dissolved nitrogen (TDN) due to the cumulative analytical errors of independently measured nitrogen species (i.e., $DON = TDN - NO_2^- - NO_3^- - NH_4^+/NH_3$) and interference of DIN species to TDN quantification. In this study, a novel electrodialysis (ED)-based treatment for selective DIN removal was developed and optimized with respect to type of ion-exchange membrane, sample pH, and ED duration. The optimized ED method was then coupled with size-exclusion chromatography with organic carbon, UV, and nitrogen detection (SEC-OCD-ND) for advanced DON analysis in wastewater effluents. Among the tested ion-exchange membranes, the PC-AR anion- and CMT cation-exchange membranes showed the lowest DOC loss (1–7%) during ED treatment of a wastewater effluent at ambient pH (8.0). A good correlation was found between the decrease of the DIN/TDN ratio and conductivity. Therefore, conductivity has been adopted as a convenient way to determine the optimal duration of the ED treatment. In the pH range of 7.0–8.3, ED treatment of various wastewater effluents with the PC-AR/CMT membranes showed that the relative residual conductivity could be reduced to less than 0.50 (DIN removal >90%; DIN/TDN ratio ≤0.60) with lower DOC losses (6%) than the previous dialysis and nanofiltration methods (DOC loss >10%). In addition, the ED method is shorter (0.5 h) than the previous methods (>1–24 h). The relative residual conductivity was further reduced to ∼0.20 (DIN removal >95%; DIN/TDN

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ratio ≤0.35) by increasing the ED duration to 0.7 h (DOC loss = 8%) for analysis by SEC-OCD-ND, which provided new information on distribution and ratio of organic carbon and nitrogen in different molecular weight fractions of effluent organic matter.

1. Introduction

Increasing dissolved organic nitrogen (DON) concentrations in the urban water cycle due to anthropogenic activities (e.g., wastewater discharge, agricultural runoff, etc.) have recently become a growing concern for drinking water treatment and/or municipal wastewater reclamation (Liu et al., 2012; Shah and Mitch, 2012; Westerhoff and Mash, 2002). Nevertheless, it has been difficult to assess the role of DON and often assumed that the behavior of DON is similar to that of dissolved organic matter (DOM) due to its small weight fraction in the DOM ([DON]/[DOM] <5% w/w) (Westerhoff and Mash, 2002). A high DON content may serve as a source of precursors for both halogenated (e.g., haloacetonitrile and halonitromethane) and non-halogenated (e.g., N-nitrosodimethylamine (NDMA)) nitrogenous disinfection byproducts (N-DBPs) formed during disinfection processes, such as chlorination and/or chloramination (Hu et al., 2010; Lee et al., 2007; Pehlivanoglu-Mantas and Sedlak, 2008; Shah and Mitch, 2012; Yang et al., 2010). Nitrogenous DBPs are potentially more mutagenic and carcinogenic than the regulated DBPs (i.e., trihalomethanes and haloacetic acids) (Plewa et al., 2004; Muellner et al., 2007; Richardson et al., 2007). The World Health Organization (WHO) has set a guideline value for NDMA of 100 ng/L in drinking water calculated by a health-based value of NDMA associated with a upper-bound excess lifetime cancer risk of 10^{-5} (WHO, 2006).

A quantification of DON concentrations may help to assess its role in drinking water and/or wastewater (e.g., precursor of DBPs). However, DON concentrations in water samples cannot be measured directly and have to be calculated by subtracting the sum of the concentrations of dissolved inorganic nitrogen (DIN) species (i.e., nitrite, nitrate, and ammonium/ammonia) from the concentration of the total dissolved nitrogen (TDN) (Westerhoff and Mash, 2002):

$$DON = TDN - \sum DIN \tag{1}$$

The high-temperature combustion (HTC) method has been widely used to quantify TDN (Westerhoff and Mash, 2002; Vandenbruwane et al., 2007). Concentrations of DIN can be commonly measured by colorimetric or ion chromatographic methods (Westerhoff and Mash, 2002). However, the accuracy of DON measurements in samples with high DIN/TDN ratios is subject to incomplete oxidations of DIN species by the HTC method and cumulative analytical errors caused by the independent measurement of nitrogen species (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007). It was proposed that the DIN/TDN ratio of samples should not exceed 0.60 to avoid an interference with DIN species for accurate DON measurements and reduce the cumulative analytical variance of DON measurements (Lee and Westerhoff, 2005). Although a few methods, including nanofiltration, catalytic reduction, and dialysis treatment are available to reduce the

DIN/TDN ratios to less than 0.60 for improving the accuracy of DON measurements in surface water and/or drinking water (Ambonguilat et al., 2006; Lee and Westerhoff, 2005; Vandenbruwane et al., 2007; Xu et al., 2010), some of them may not be useful for the practical DON measurements in real samples due to high DOC losses (DOC loss of nanofiltration = 19–24%; DOC loss of catalytic reduction = 30%). Among these, dialysis has been considered as the most attractive option to selectively remove DIN species for accurate DON measurements in drinking and/or surface waters (DIN removal >70%; DON loss <5%; DOC loss = 2%) (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007). However, the dialysis method is problematic for the DON measurements in wastewater effluents since a significant fraction of DOC and DON is removed (DON loss >10%; DOC loss = 10–15%) (Lee and Westerhoff, 2005).

To get more information on DON, in terms of NDMA precursors and formation potential based on molecular weight (MW) fractions, Pehlivanoglu-Mantas and Sedlak (2008) have investigated the reactivity and fate of DON in wastewater effluents using fractionation by ultrafiltration (UF). This method is only applicable to fully nitrified and denitrified wastewater effluents with negligible DIN concentrations. An alternative approach to get comprehensive information on DON characteristics in wastewater effluents is size-exclusion chromatography equipped with organic carbon, UV, and nitrogen detection (SEC-OCD-ND). Unlike the conventional analytical methods (i.e., subtraction methods and UF fractionation), SEC-OCD-ND can not only quantify TDN concentrations but also provide qualitative information on DON fractions (i.e., MW distribution and molar ratio of organic nitrogen to organic carbon (N/C)) (Graeber et al., 2012; Huber et al., 2011). However, the current study found that removal of the DIN species is still necessary due to severe interferences of DIN species on the analysis of DON fractions in wastewater effluents using SEC-OCD-ND.

To overcome these problems, a novel treatment method capable of selectively removing DIN species from wastewater effluents is needed. Electrodialysis (ED) is a well-established method to remove inorganic ions from aqueous solutions (Strathmann, 2004). ED treatment has been applied to fresh water or seawater for DOM isolation (Vetter et al., 2007; Koprivnjak et al., 2006). ED treatment with pulsed electrical currents was also tested for enhanced DOM recovery from seawater (Gurtler et al., 2008). Nevertheless, the ED method has not been applied to wastewater effluent matrices for selective removal of DIN and recovery of effluent organic matter. Furthermore, membrane types, pH of sample and duration of ED operation, which are known as key parameters affecting the performance of ED processes (Kim et al., 2002; Van der Bruggen et al., 2004), should be optimized to enhance the removal efficiency of inorganic ions and minimize the loss of DON. Cation-exchange treatment has been used as a presoftening step to replace magnesium and calcium with

sodium for concentration of DOM by reverse osmosis to reduce the DOM loss by precipitation during NOM fractionation by XAD resins (Leenheer et al., 2000). Cation-exchange treatment can be combined with ED as a method for enhanced DON recovery from wastewater effluents by replacing divalent cations or ammonium by sodium.

In this study, a novel treatment method using ED was developed and optimized for accurate DON measurements in wastewater effluents. We investigated the effect of operating parameters of the ED treatment (i.e., membrane type, pH of sample, and ED duration) on DIN and conductivity removal and DON recovery to assess the criteria of ED treatment for accurate DON measurements in wastewater effluents by the subtraction method (Eq. (1)). In addition, cation-exchange columns were tested as a pre-treatment for ED treatment. The enhanced ED treatment using the cation-exchange was combined with SEC-OCD-ND to characterize DON in wastewater effluents, in terms of MW distribution and N/C ratio.

2. Materials and methods

2.1. ED treatment system and operation

All experiments were performed using a commercial ED system (PCCell GmbH, Heusweiler, Germany) consisting of an ion-exchange membrane stack containing 10 pairs of anion-exchange and cation-exchange membranes (effective surface area of each membrane: 64 cm^2) which is arranged between an anode (i.e., mixed metal oxides (Pt/Ir) coated Ti-stretched metal) and a cathode (i.e., stainless steel), and three reservoirs (each with a 2 L glass cylinder) for the sample, concentrate (5 mM NaCl) and electrolyte solutions (0.25 M Na$_2$SO$_4$), respectively. Prior to use, all the ion-exchange membranes were soaked in deionized (DI) water (NANOpure, Barnstead, Newton, MA, USA) over a few days for removal of membrane-coating materials. Furthermore, the ED system was rinsed thoroughly using DI water during 1 day before and after use and a cleaning with 5% (w/w) NaCl solutions has been regularly conducted to minimize leaching of organic materials from the ion-exchange membranes. Thus, negligible EfOM leaching was found during ED treatments (see Fig. 7 and Fig. S3–S4). The ED system was operated in a batch-recirculation mode and the reservoirs were kept below 20 °C by water cooling (<10 °C) through the surface channel of the reservoirs. The constant voltage/variable current mode, where the voltage remains constant and the current decreases proportionally to the reduction in the conductivity of the samples, was applied to the ED system to minimize organic fouling on the surfaces of the ion-exchange membranes associated with DOC loss which is more pronounced at a higher current density (Lindstrand et al., 2000). The voltage was fixed at 10 V based on previous ED application studies for ion removals (Farrell et al., 2003) and the recommendation of our ED system manufacturer (PCCell GmbH, Heusweiler, Germany). Pulsed ED was generated using a KRDR Digi-Timer (input 12–120 V, ABB Inc., SSAC, New York, USA) to switch the DC power to the ED stack on and off with intervals of 0.6 or 2 s. The interval settings were chosen based on the literature (Gurtler et al., 2008). The same volumes of sample, concentrate and electrolyte solutions were used for each ED treatment (initial volume: 1–2 L). A schematic diagram of the ED system is exhibited in Fig. S1 (Supplementary Information, SI).

2.2. Analytical methods

Concentrations of DOC and total dissolved nitrogen (TDN) in the water samples were measured by a catalytic combustion total organic carbon analyzer (TOC-V$_{CPH}$, HTC at 680 °C, non-dispersive infrared detection, Shimadzu, Kyoto, Japan) equipped with a total nitrogen analyzer (TNM-1, HTC at 720 °C, chemiluminescence detection, Shimadzu, Kyoto, Japan). DOC and TDN were also quantified by a SEC-OCD-ND instrument (DOC-Labor, Karlsruhe, Germany). Ion chromatography (IC; 761 Compact IC, Metrohm, Herisau, Switzerland) equipped with a Metrosep C4 column (Metrohm, Herisau, Switzerland) and a Metrosep A Supp 5 column (Metrohm, Herisau, Switzerland) was used to measure concentrations of anions (i.e., nitrate, chloride and sulfate) and cations (i.e., sodium, potassium, magnesium, and calcium) (injection volume = 20 μL). Concentrations of nitrite and ammonium were measured by colorimetry at 540 nm (DIN EN 26 777, German standard methods) and 655 nm (DIN 38 406, German standard methods), respectively. The method detection limits for TDN (0.012 mgN/L), nitrate (0.001 mgN/L), nitrite (0.0006 mgN/L), and ammonium (0.004 mgN/L) were calculated by multiplying the standard deviation of the replicates for each species by the student's t-value (t-value at 99 % confidence = 2.897 for n-1=8) (United States Environmental Protection Agency (U.S. EPA), 1999). Concentrations of carbonate and bicarbonate were measured as alkalinity using a potentiometric titrator (716 DMS Titrino, Metrohm, Herisau, Switzerland) with 0.1 N hydrochloric acids (pH of the end point = 4.5) and total phosphorus was analyzed using the ascorbic acid method with persulfate digestion and detected at a wavelength of 880 nm (U.S. EPA, 1993). All the samples were filtered by cellulose nitrate membranes (pore size: 0.45 μm, Sartorius Stedim Biotech, Goettingen, Germany).

2.3. Optimization of the ED treatment

Various types of anion-exchange (i.e., PC-AR, PC-Fel, PCAcid60, AMV, and AMT) and cation-exchange membranes (i.e., MT and PC-MV) were tested for DIN removal and DOC recovery during ED treatment of various wastewater effluents depending on the types of ED membranes, pH of sample, ED duration, and operating mode (i.e., with or without pulsed electrical current). DON loss during ED treatment could not be assessed due to the large variations in DON concentrations between raw and treated wastewaters (Lee and Westerhoff, 2005). Therefore, DOC loss was used as an indicator for DON loss during ED treatment assuming that the DON removal is proportional to the DOC removal (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007; Xu et al., 2010). Physicochemical properties of the tested ion-exchange membranes are summarized in Table S1 (SI). A synthetic wastewater (pH = 7.5; conductivity = 730 μS/cm; nitrite = 1.0 mgN/L; nitrate = 10.0 mgN/L; ammonium = 1.0 mgN/L; chloride = 123.0 mg/L; sulfate = 87.0 mg/L; sodium: 80.0 mg/L = potassium = 15.6 mg/L; magnesium = 7.3 mg/L, and calcium = 60.1 mg/L) and a secondary effluent (No 11–12, Table S2, SI) from a pilot plant

(Eawag, Dübendorf, Switzerland) were used to optimize the ED treatment for further experiments. The effects of ED duration on the DIN/TDN ratio, removal of conductivity, DIN, and DOC in wastewater effluents were investigated to elucidate the optimal duration of the ED treatment for efficient DIN removal and low DOC loss. To validate the optimized ED treatment for accurate DON measurements in wastewater effluents, DON concentrations were calculated using the subtraction method (Eq. (1)) for both raw and treated wastewaters.

2.4. Cation-exchange pre-treatment

In the tested ED treatment, the removal rates of ammonium were lower than those of nitrite and nitrate. Therefore, the wastewater samples subject to DON fraction analysis by SEC-OCD-ND were pre-treated by cation-exchange to enhance the removal of ammonium ions (removal efficiency >99%; DOC loss <1%). Two serially connected columns (volume of each column: 7.85 cm^3, Amersham Biosciences, Freiburg, Germany) filled with cation-exchange resins (Dowex Marathon MSC, Sigma–Aldrich, St. Louis, MO, USA) were used. The cation-exchange columns were pre-conditioned with 200 mL of a 100 g/L NaCl solution (i.e., regeneration) and rinsed by 100 mL DI water. The samples were passed through the cation-exchange columns at a flow rate of 10 mL/min and the effluents from the cation-exchange columns were collected after discarding 100 mL of the sample.

2.5. DON fractionation analysis by ED treatment combined with SEC-OCD-ND

SEC-OCD-ND was used to chromatographically separate organic matter according to its MW and charge, and quantify the separated fractions based on organic carbon and nitrogen detection: (i) biopolymers; (ii) humic substances and building blocks, (iii) low MW acids, and (iv) low MW neutrals (Huber et al., 2011). The DON fractions without and with the cation-exchange pre-treatment were compared to identify influences of the pre-treatment on the DON fractionation analysis of

wastewater samples with SEC-OCD-ND. In addition, the optimal ED duration for the accurate DON fractionation analysis by SEC-OCD-ND was evaluated by the relative residual conductivity related to the removal of DIN species and DOC loss.

2.6. Water samples

To compare DON concentrations without and with ED treatment, secondary effluents collected from a pilot WWTP (Eawag, Dübendorf, Switzerland), a full-scale WWTP (Dübendorf, Switzerland), and Lake Greifensee water (Dübendorf, Switzerland) were used. Thirteen water samples from WWTPs (Dübendorf, Switzerland; Regensdorf, Switzerland; Lausanne, Switzerland; Kloten-Opfikon, Switzerland; Beenyup, Australia; Eawag pilot plant, Dübendorf, Switzerland), and Lake Greifensee were used for DON fraction analysis by SEC-OCD-ND without and with ED treatment (No 1–10 and 12–14, Table S2, SI). Water qualities of the tested samples and experimental conditions of each ED treatment are listed in Tables S2 and S3, respectively.

3. Results and discussion

3.1. Influence of ion-exchange membrane type and sample pH on DOC loss

The effects of ion-exchange membrane type on DOC loss were investigated using five kinds of anion-exchange membranes (i.e., PC-AR, PC-Fel, PCAcid60, AMV, and AMT) and two types of cation-exchange membranes (i.e., CMT and PC-MV) with a wastewater effluent sample collected from the Dübendorf WWTP (DDWW-1, No 1, Table S2, SI). As shown in Fig. 1, for a given relative residual conductivity, DOC losses during ED treatment were highly variable depending on the type of membrane and sample pH. The % DOC loss at both ambient pH without acidification (pH = 8.0) and acidic pH adjusted by addition of 6 M HCl (pH = 3.0–3.8) was significant for the
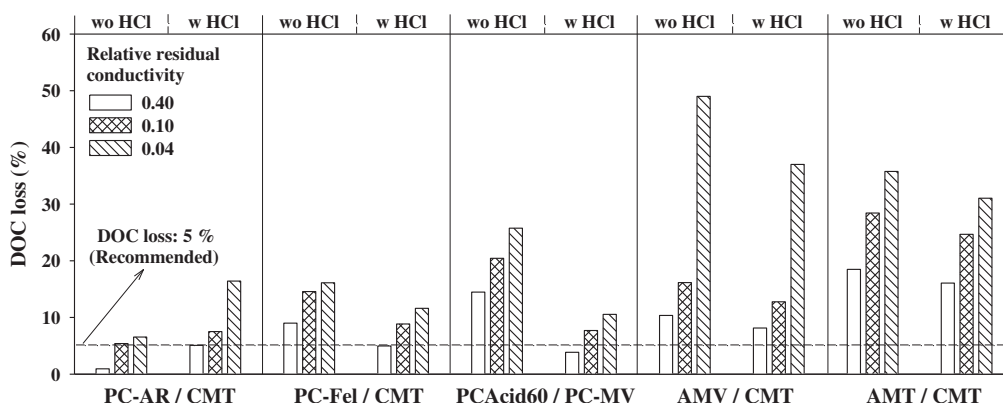

Fig. 1 — Loss of DOC during ED treatment of a wastewater effluent using different types of ion-exchange membranes (see Table S1, SI for further information on the membranes). ED was applied until the residual conductivity of the sample decreased to ~0.4 (left bars), 0.1 (middle bars), and 0.04 (right bars). The nitrate removal was ~90%, >97%, and >99% at the residual conductivity of ~0.4, 0.1, and 0.05, respectively. The effluent samples were treated at an ambient pH of 8 (without HCl) or at acidic pH's of 3.0–3.8 adjusted by 6 M HCl (with HCl). The wastewater effluent (DDWW-1, No 1, Table S2, SI) had an initial DOC of 7.0 mgC/L, pH 8.0, and a conductivity of 1000 μS/cm.

membranes, such as AMV/CMT (ambient pH: 10–21%; acidic pH: 8–16%) and AMT/CMT (ambient pH: 18–36%; acidic pH: 16–31%). Although the % DOC loss for PC-Fel/CMT (5–12%) and PCAcid60/PC-MV (4–11%) at acidic pH was considerably lower than for AMV/CMT and AMT/CMT, a significant DOC loss was found for these membranes at ambient pH (PC-Fel/CMT = 9–16%; PCAcid60/PC-MV = 14–26%). Most of the tested membranes (i.e., PC-Fel/CMT, PCAcid60/PC-MV, AMV/CMT, and AMV/CMT) showed a higher DOC loss at ambient pH (7.4–8.0) presumably due to increasing negative charge of effluent organic matter (EfOM) at higher pH, which can enhance the adsorption of EfOM on the surfaces of anion-exchange membranes (Kim et al., 2002). Among the tested membranes, the lowest % DOC loss (1–7%) was observed for the PC-AR/CMT at ambient pH (7.1–8.3) for the same target relative residual conductivity (0.40–0.04). Based on these findings, PC-AR/CMT has been selected for further experiments to improve the accuracy of DON measurements in wastewater effluents. Pulsed ED treatment was tested using AMT/CMT and PCAcid60/PC-MV to investigate its influence on DOC loss. In contrast to previous research (Gurtler et al., 2008), distinctive differences were not found in DIN removal and DOC loss of the tested wastewater (DDWW-1, No 7 and RDWW-1, No 13, Table S2, SI) without and with the pulsed ED application (data not shown). Therefore, pulsed ED treatment was not further considered in this study.

3.2.　Optimization of ED treatment duration

To optimize the duration of the ED treatment for accurate DON measurements, variations in the DIN/TDN ratio, DON concentrations, DIN removal, and the relative residual conductivity were investigated during ED treatment of a secondary effluent from the Eawag pilot plant (EPPWW, No 12, Table S2, SI) spiked with 0.5 mgN/L nitrite and 0.5 mgN/L ammonium (Fig. 2). A negative DON concentration was initially found for the wastewater without ED treatment. However, the DON concentration significantly increased during ED treatment due to the decreasing interference of nitrate to TDN measurements in the HTC method (Lee and Westerhoff, 2005). Consequently, constant DON concentrations were observed for the tested wastewater with ED treatment when the DIN/TDN ratio was less than 0.60 (ED time = 20 min; relative residual conductivity = 0.47, relative residual DIN concentration = 0.09, and DIN/TDN = 0.53). The cumulative analytical errors from the independent measurements of DIN species were also substantially reduced by ED treatment and they were not significant for the wastewaters with DIN/TDN $\leq$0.60, which is consistent with the results of Lee and Westerhoff (2005). The required ED operating time for accurate DON measurements was only 20 min which is significantly lower compared to dialysis (operating time = 24 h) and nanofiltration (operating time = 1–4 h) (Lee and Westerhoff, 2005; Xu et al., 2010).

The proposed criteria (i.e., DIN/TDN $\leq$0.60) was reported to be critical for accurate DON measurements in wastewater effluents (Lee and Westerhoff, 2005). Nevertheless, it was difficult to evaluate the DIN/TDN ratio in real-time due to the fact that measurements of TDN and DIN species have to be carried out in discrete samples. Thus, changes in the DIN/TDN
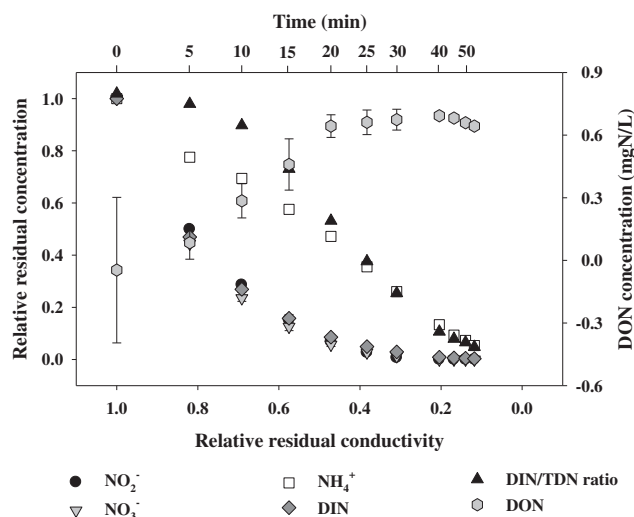

Fig. 2 – Concentration changes of DIN($=NO_2^- + NO_3^- + NH_4^+$), DON, and DIN/TDN ratio as a function of the relative residual conductivity during ED treatment of secondary wastewater effluent. Secondary wastewater effluent (from Eawag pilot plant) contained 6.5 mgC/L as DOC, 0.54 mgN/L as NO_2^-, 8.2 mgN/L as NO_3^-, and 0.62 mgN/L as NH_4^+. The original sample was spiked with 0.5 mgN/L of NO_2^- and NH_4^+ each as the ambient NO_2^- and NH_4^+ concentrations were too low to determine their removal.

ratio during ED treatment were directly correlated to the relative residual conductivity as a surrogate parameter for DIN/TDN ratios (Fig. 3). A lag-phase was observed in the initial decrease of the relative residual conductivity (1.0–0.8). After the lag-phase, the decrease in the DIN/TDN ratio of the secondary effluents was directly proportional to the reduction in the relative residual conductivity (DIN/TDN = 1.62 × (relative residual conductivity) – 0.22, R^2 = 0.99). Based on this finding, it can be postulated that the relative residual conductivity of
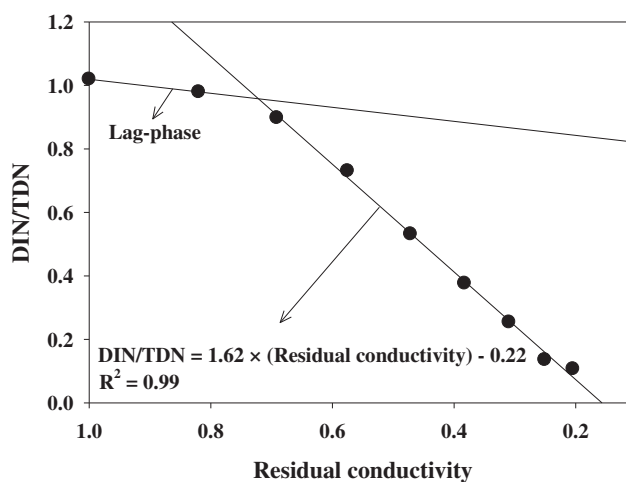

Fig. 3 – Change in DIN/TDN ratios as a function of the relative residual conductivity during ED treatment of a wastewater effluent (EPPWW, No 12, Table S2, SI).

wastewater samples should be reduced to less than 0.50 to meet the proposed DIN/TDN ratio ≤0.60.

DOC losses for a range of relative residual conductivities were investigated using twelve different water samples (No 1, 3—10, and 12—14, Table S2, SI) to validate ED treatment for accurate DON measurements in wastewater effluents (Fig. 4). The DOC losses for a relative residual conductivity of 0.50—0.36 (DIN removal >90%; DIN/TDN ratio ≤0.60) was less than 6%. Approximately 8% of DOC was removed for a relative residual conductivity of 0.34—0.23 (DIN removal >95%; DIN/TDN ratio ≤0.35). The DOC losses for a relative residual conductivity of 0.19—0.04 (DIN removal >99%; DIN/TDN ratio ≤0.01) were higher than 13%. Possible explanations for the DOC losses by ED treatment are adsorption of large MW fractions to the surfaces of the ion-exchange membranes and/ or permeation of small MW fractions through the pores of the membranes (Kim et al., 2002; Gurtler et al., 2008). This is supported by the SEC-OCD analysis of the ED treated wastewater effluents. The DOC losses were found in large MW fractions of humic substances and building blocks (F2) as well as low MW acids and neutrals fractions (F3 and F4) (see Fig. 7 and Fig. S3 − S4). To minimize DOC loss during ED treatment, a relative residual conductivity of 0.50—0.35 can be suggested for the DON measurements by the subtraction method because the ED-treated samples showed a constant DON concentration when their relative residual conductivities were less than 0.50 (see Fig. 2). ED treatment therefore leads to more accurate measurements of DON concentrations in wastewater effluents (DOC loss = 6 ± 3%) compared to dialysis (DOC loss = 10—15%) and nanofiltration (DOC loss = 19—24%) (Lee and Westerhoff, 2005; Xu et al., 2010). However, the proposed relative residual conductivity range (0.50—0.35) for DON measurements was not suitable for determination of DON fractions using SEC-OCD-ND as the remaining DIN species could still contribute significantly to the low MW DON fractions (Fig. S2, SI). In the SEC-OCD-ND analysis, nitrite, nitrate and ammonium are co-eluted with low MW acids and neutrals and can interfere with DON fraction analysis (see Section 3.5). Therefore, a lower relative residual conductivity range is required to avoid overestimation of the low MW DON fractions. Hence, a relative residual conductivity of 0.35—0.20 (ED duration = 0.7 h; DOC loss = 8 ± 4%) was applied to

wastewater effluents for accurate quantification of DON fractions by SEC-OCD-ND.

3.3. Removal behavior of major anions and cations during ED treatment

A synthetic wastewater effluent (pH = 7.5; conductivity = 730 μS/cm; nitrite = 1.0 mgN/L; nitrate = 10.0 mgN/L; ammonium = 1.0 mgN/L; chloride = 123.0 mg/L; sulfate = 87.0 mg/L; sodium: 80.0 mg/ L = potassium = 15.6 mg/L; magnesium = 7.3 mg/L, and calcium = 60.1 mg/L) was used to quantify the removal of major anions and cations during ED treatment (Fig. 5). The DIN species were effectively removed by ED treatment. However, the removal rate of ammonium was lower than for nitrite and nitrate. This finding suggests that an additional pre-treatment (e.g., cation-exchange) has to be applied for wastewater effluents with high concentrations of ammonium. The concentrations of anions and cations decreased during ED treatment but significant differences were found in the removal rates of individual ions. The removal rate of chloride as a monovalent anion was faster than that of sulfate as a divalent anion whereas sodium and potassium as monovalent cations were less efficiently removed compared to magnesium and calcium as divalent cations. For a relative residual conductivity of less than 0.5, sodium and sulfate are found to be the major cation and anion of the ED-treated samples. The removal efficiencies of anions and cations by ED treatment can be influenced by the charge density of the ions, operating conditions (e.g., electric potential and time), and interaction between ions and ion-exchange membranes (Van der Bruggen et al., 2004; Kabay et al., 2006). The removal trends of DIN species (i.e., nitrite, nitrate, and ammonium), anions (i.e., chloride and sulfate) and cations (i.e., sodium, potassium, magnesium, and calcium) in a real wastewater effluent (EPPWW, No 12, Table S2, SI) were similar to those in the synthetic wastewater (Fig. 5). These observations support the assumption that the reduction in DIN species, anions and cations in wastewater effluents correlates to the decrease of the relative residual conductivity.

3.4. Measurements of DON concentrations without and with ED treatment

For comparison of DON concentrations without and with ED treatment, three water samples, secondary effluents from the Eawag pilot plant (EPPWW) and the Dübendorf WWTP (DDWW-3), and Lake Greifensee water (LGW) were analyzed (No 12—14, Table S2, SI). As shown in Fig. 6, prior to the ED treatment, negative or very low DON concentrations were observed for the secondary effluents and the surface water (EPPWW = −0.05 mgN/L; DDWW-3 = 0.19 mgN/L; GLW = 0.15 mgN/L), which was probably due to the influence of the high levels of DIN species (initial DIN/TDN of EPPWW: 1.02; initial DIN/TDN of DDWW-3: 0.97; initial DIN/TDN of GLW: 0.91) to the TDN measurements in the HTC method (Lee and Westerhoff, 2005). The cumulative analytical errors were also significant for the samples without ED treatment (EPPWW = 0.184 mgN/L; DDWW-3 = 0.078 mgN/L; GLW = 0.042 mgN/L). For the suggested relative residual
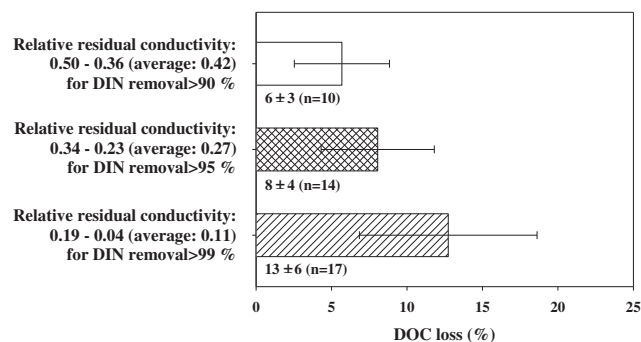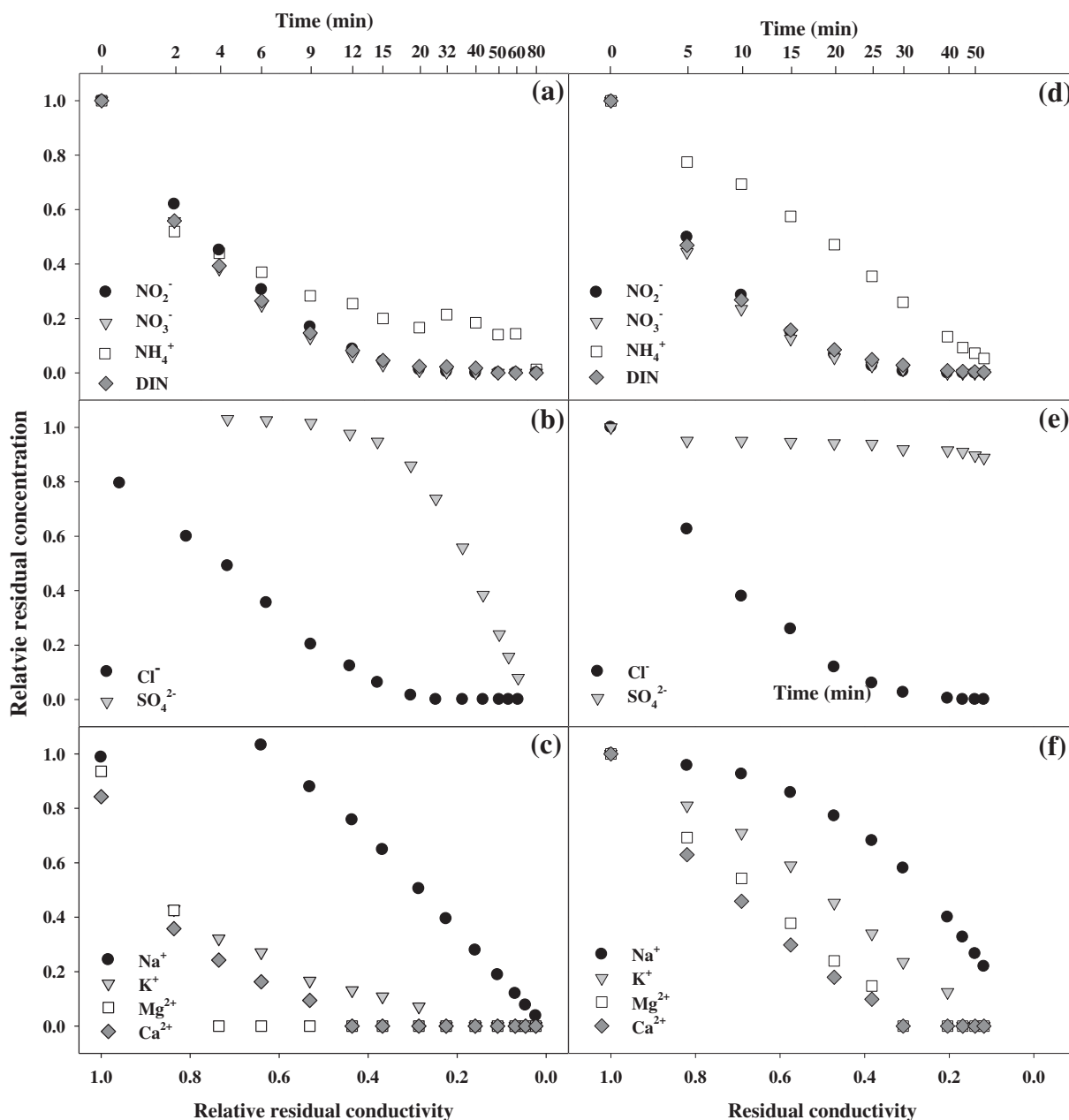

Fig. 4 − DOC losses (%) of secondary effluents during ED treatment as a function of the relative residual conductivity. Investigated samples: No 1, 3—10 and 12—14, Table S2, SI.

Fig. 5 – Removal behavior of dissolved inorganic nitrogen species (DIN=[NO$_2^-$]+[NO$_3^-$]+[NH$_4^+$]), Cl$^-$, SO$_4^{2-}$, Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+} during ED treatment as a function of the relative residual conductivity: (a)–(c) synthetic wastewater and (d)–(f) secondary effluent (from Eawag pilot plant) spiked with 0.5 mgN/L of NO$_2^-$ and NH$_4^+$ each. Composition of the synthetic wastewater effluent: [NO$_2^-$] = 1.0 mgN/L, [NO$_3^-$] = 10 mgN/L, [NH$_4^+$] = 1.0 mgN/L, [Cl$^-$] = 123 mgN/L, [SO$_4^{2-}$] = 87 mgN/L, [Na$^+$] = 80 mgN/L, [K$^+$] = 15.6 mgN/L, [Mg^{2+}] = 7.3 mgN/L, and [Ca^{2+}] = 60 mgN/L. Secondary effluent (EPPWW, No 12, Table S2, SI): [NO$_2^-$] = 0.54 mgN/L, [NO$_3^-$] = 8.2 mgN/L, [NH$_4^+$] = 0.62 mgN/L, [Cl$^-$] = 132 mg/L, [SO$_4^{2-}$] = 42 mg/L, [Na$^+$] = 124 mg/L, [K$^+$] = 12 mg/L, [Mg^{2+}] = 21 mg/L, and [Ca^{2+}] = 105 mg/L.

conductivity (≤0.50), all the samples with ED treatment satisfied the DIN/TDN ratios ≤0.60 and showed constant DON concentrations (EPPWW = 0.64–0.67 mgN/L; DDWW-3 = 0.56–0.58 mgN/L; GLW = 0.26–0.27 mgN/L) with significantly less cumulative analytical error compared to that of the samples without ED treatment (EPPWW = 0.032–0.044 mgN/L; DDWW-3 = 0.005–0.021 mgN/L; GLW = 0.008–0.015 mgN/L). Hence, a relative residual conductivity of 0.50–0.35 is recommended for the DON measurements by the subtraction method to minimize the DOC losses during ED treatment. From these results, it can be concluded that ED treatment facilitates accurate measurements of DON concentrations in both wastewater and surface water samples. The DON concentrations obtained after ED treatment are in accordance with previous studies in which DON concentrations of surface water and secondary effluents were 0.06–0.4 mgN/L and 0.7 to 1.8 mgN/L, respectively (Lee and Westerhoff, 2005; Liu et al., 2012; Pehlivanoglu-Mantas and Sedlak, 2008).
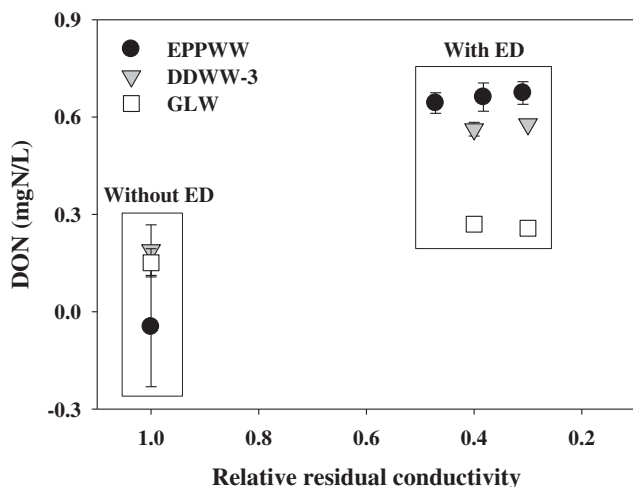
Fig. 6 — DON concentrations in two WWTP effluents (EPPWW and DDWW-3) and one lake water sample (LGW) without and with ED treatment (No 24—26, Table S3, SI). Water quality parameters are provided in Table S2 (No 12—14, SI).

3.5. Comparison of DON fraction analysis using SEC-OCD-ND without and with ED treatment

SEC-OCD-ND chromatograms of secondary effluents from the Dübendorf WWTP (DDWW-2, No 10, Table S2, SI) before and after ED treatment (relative residual conductivity = 0.25) with cation-exchange pre-treatment are compared in Fig. 7. No distinctive differences were found for the OCD and UV chromatograms of the raw and treated wastewater due to selective DIN removal by ED treatment combined with cation-exchange
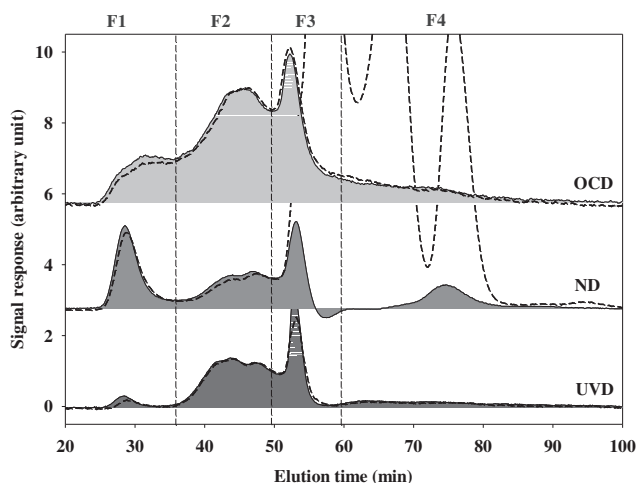

Fig. 7 — SEC-OCD-ND chromatograms of wastewater effluent collected from the Dübendorf WWTP at a relative residual conductivity of 0.25 (DDWW-2, No 21, Table S3, SI). The dashed and filled lines represent signals before and after enhanced ED treatment using cation-exchange pre-treatment (F1: biopolymers; F2: humic substances and building blocks; F3: low MW acids; F4: low MW neutrals).

pre-treatment. The DON fractions of the untreated wastewater effluents could not be accurately determined by SEC-OCD-ND due to the interferences of DIN species on the DON fraction in low MW acids and neutrals (F3 and F4). Their interferences on the ND chromatogram were substantially reduced by ED treatment combined with cation-exchange pre-treatment (Fig. 7). Similar results were observed for the other wastewater samples (No 11 and 14—21, Table S3, SI). Some of those results obtained for LSWW-2 and BYWW are shown in Fig. S3 (SI). Negative ND signals were found for the ED-treated samples at elution time of 55—65 min which is directly after the 'salt boundary peak' (Huber et al., 2011). Due to the lower electrolyte concentration of the ED-treated samples (conductivity <200 μS/cm) compared to the mobile phase (conductivity $= \sim3000$ μS/cm), anionic components in the samples (i.e., salts and low MW acids) elute as a compressed peak ahead of the injected sample water. The negative ND signals could be partially eliminated by preparing the ED-treated samples in the SEC eluent (data not shown). However, this caused a significant reduction of the low MW acids fraction, thus all DON quantifications in this study were performed without adjusting the sample electrolyte concentration.

The effects of cation-exchange pre-treatment on the DON fraction analysis were investigated with DDWW-2. A significant difference was not found in their ND chromatograms without (Fig. S4, SI) and with the cation-exchange pre-treatment (Fig. 7) due to the low ammonium concentration (0.67 mgN/L). This indicates that the cation-exchange pre-treatment is necessary only for wastewater effluents with high ammonium concentrations. As an undesirable side effect, cation-exchange pre-treatment could remove cationic forms of amines, which can play an important role in the formation of N-DBPs (Mitch et al., 2003; Kemper et al., 2010; Shah and Mitch, 2012). Therefore, cation-exchange pre-treatment should be carefully applied for investigations on precursors of N-DBPs.

The results of the DOC and DON fraction analyses using SEC-OCD-ND obtained from the wastewater samples (No 8—10, Table S2, SI) with enhanced ED treatment using cation-exchange (relative residual conductivity = 0.25) are provided in Table 1. Residual DIN also contributed to DON fractions of low MW acids (F3) and neutrals (F4). Based on the peak areas normalized to 0.5 mgN/L, nitrate contributed to 58% to low MW acids and 42% to low MW neutrals, nitrite contributed to 74% to low MW acids and 26% to low MW neutrals, and ammonium contributed to 5% to low MW acids and 95% to low MW neutrals (Fig S5, SI). These contributions were considered for each DON fraction to improve the accuracy of the DON fraction analysis (Table 1). The sum of all the DON fractions quantified by SEC-OCD-ND (DDWW-2 = 0.55 mgN/L; LSWW-2 = 0.49 mgN/L; BYWW = 0.62 mgN/L) was similar to the DON concentrations calculated by the subtraction method (EPPWW = 0.64—0.67 mgN/L; DDWW-3 = 0.56—0.58 mgN/L). This implies that SEC-OCD-ND is a reliable way to measure DON concentrations in wastewater samples. Humic substances and building blocks (MW = 300—1000 Da) were found as major constituents of DOC fractions in the wastewater effluents (DDWW-2 = 44%; LSWW-2 = 48%; BYWW = 53%). Compared to the DOC fractions, a relatively large proportion

Table 1 — Quantification of DOC and DON fractions by SEC-OCD-ND of wastewater effluent samples after ED treatment with cation-exchange pre-treatment (relative residual conductivity = 0.25).

		F1	F2	F3	F4	Total (F1+F2+F3+F4)
DDWW-2	DOC (mgC/L)	0.67	2.00	1.13	0.71	4.52
	%	15	44	25	16	100
	DON (mgN/L)	0.16	0.16	0.13	0.10	0.55
	%	30	30	23	18	100
	N/C molar ratio	0.21	0.07	0.10	0.12	0.10
LSWW-2	DOC (mgC/L)	0.63	2.07	0.97	0.67	4.32
	%	14	48	22	15	100
	DON (mgN/L)	0.14	0.13	0.09	0.13	0.49
	%	28	26	19	27	100
	N/C molar ratio	0.19	0.05	0.08	0.17	0.10
BYWW	DOC (mgC/L)	0.15	3.32	1.67	1.07	6.20
	%	2	53	27	17	100
	DON (mgN/L)	0.06	0.30	0.18	0.08	0.62
	%	10	48	29	12	100
	N/C molar ratio	0.37	0.08	0.09	0.06	0.09

F1: biopolymers; F2: humic substances and building blocks; F3: low MW acids; F4: low MW neutrals.

of the DON fractions is attributed to biopolymers (MW > 10 000 Da) with 10—30% for DON fractions (DDWW-2 = 30% and LSWW-2 = 28%; BYWW = 10%) and 2—15% for DOC fractions (DDWW-2 = 15%; LSWW-2 = 14%; BYWW = 2%) (Table 1). It is evident that EfOM includes a large fraction of DON derived from soluble microbial products produced during biological wastewater treatment (Barker and Stuckey, 1999; Shon et al., 2006; Chon et al., 2012, 2013). High N/C molar ratios of the biopolymers support this observation (DDWW-2 = 0.21; LSWW-2 = 0.19; BYWW = 0.37). A considerable portion of the DON fractions in the wastewater effluents was composed of low MW acids and neutrals (sum of low MW acids and neutrals: DDWW-2 = 41%; LSWW-2 = 36%; BYWW = 40%). This indicates that an accurate quantification of the low MW DON fractions is critical for extending our understanding of occurrence, fate, and reactivity of DON in wastewater effluents. Moreover, an accurate estimation of the N/C molar ratio may be significant for efficient operations of membrane and disinfection processes for wastewater reclamation, in terms of control of membrane fouling and mitigation of DBPs (Amy, 2008; Song et al., 2010; Doston and Westerhoff, 2012).

The DON fractions in wastewater effluents might play an important role in formation of N-DBPs (Shah and Mitch, 2012). However, their characteristics (i.e., occurrence, size, fate and reactivity) in wastewater effluents with high DIN/TDN are still poorly understood due to lack of adequate methods for selective DIN removal from wastewater effluents. A recent study which employed a DON fractionation method with UF found that DON fractions of MW less than 1000 Da were the major precursors of NDMA during chlorination and/or chloramination for municipal wastewater reclamation (Pehlivanoglu-Mantas and Sedlak, 2008). However, the applied method was only suitable for wastewater effluents with low DIN/TDN ratios. Our study demonstrates that the DON fraction analysis by ED treatment combined with SEC-OCD-ND is a feasible method to investigate the MW dependent DON characteristics (e.g., size distribution, amount, and N/C molar ratio) potentially associated with the formation of N-DBPs in wastewater effluents and wastewater impaired drinking waters.

4. Conclusions

Electrodialysis (ED) treatment was investigated as a means for DIN removal, quantification and characterization of DON in surface waters and wastewater effluents with high DIN/TDN ratios. The major findings are:

- The type of ED membranes, pH of sample, ED duration were found to be the major factors related to the selective removal of DIN species from wastewater effluents by ED treatment. Among the tested ion-exchange membranes, the lowest DOC loss during ED treatment of a wastewater effluent was observed for a PC-AR/CMT membrane at ambient pH without acidification (DOC loss = 1—7%).
- A strong correlation has been found between the DIN/TDN ratio and the relative residual conductivity of the water samples (DIN/TDN = 1.62 × (relative residual conductivity) − 0.22, R^2 = 0.99). Thus, variations in the DIN/TDN ratios during ED treatment can be estimated in real time by measuring the sample's relative residual conductivity.
- For the proposed relative residual conductivity of 0.50—0.35, ED treatment allows determination of DON concentrations in wastewater effluents more effectively (DOC loss = 6%; operating time = 0.5 h) compared to dialysis (DOC loss = 10—15%; operating time = 24 h) and nanofiltration methods (DOC loss = 19—24%; operating time = 1—4 h).
- The accurate quantification of DON fractions in wastewater effluents with high DIN/TDN ratios using SEC-OCD-ND after ED treatment (relative residual conductivity = 0.25; DOC loss = 8%) can provide valuable insight into the MW distribution of DON (e.g., biopolymers, humic substances and building blocks, low MW acids, and low MW neutrals), which might play an important role in the formation of N-DBPs during oxidative treatment of wastewater effluents or wastewater impaired drinking waters.
- Pre-treatment by cation-exchange before ED is recommended only for DON quantification of ammonium-rich wastewater effluents due to a potential adsorptive loss of important N-DBP precursors (e.g., cationic amine species).

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.06.019.

REFERENCES

Ambonguilat, S., Gallard, H., Garron, A., Epron, F., Croué, J.P., 2006. Evaluation of the catalytic reduction of nitrate for the determination of dissolved organic nitrogen in natural waters. Water Research 40, 675–682.

Amy, G., 2008. Fundamental understanding of organic matter fouling of membranes. Desalination 231, 44–51.

Barker, D.J., Stuckey, D.C., 1999. A review of soluble microbial products (SMP) in wastewater treatment systems. Water Research 33, 3063–3082.

Chon, K., Kim, S.J., Moon, J., Cho, J., 2012. Combined coagulation-disk filtration process as a pretreatment of ultrafiltration and reverse osmosis membrane for wastewater reclamation: an autopsy study of a pilot plant. Water Research 46, 1803–1816.

Chon, K., Cho, J., Shon, H.K., 2013. Fouling characteristics of a membrane bioreactor and nanofiltration hybrid system for municipal wastewater reclamation. Bioresource Technology 130, 239–247.

Doston, A., Westerhoff, P., 2012. Character and treatment of organic colloids in challenging and impacted drinking water sources. Journal of Environmental Engineering 138, 393–401.

Farrell, S., Hesketh, R.P., Slater, C.S., 2003. Exploring the potential of electrodialysis. Chemical Engineering Education 37, 52–59.

Graeber, D., Gelbrecht, J., Kronvang, B., Guecker, B., Pusch, M.T., Zwirnmann, E., 2012. Technical Note: Comparison between a direct and the standard, indirect method for dissolved organic nitrogen determination in freshwater environments with high dissolved inorganic nitrogen concentrations. Biogeosciences 9, 4873–4884.

Gurtler, B.K., Vetter, T.A., Perdue, E.M., Ingall, E., Koprivnjak, J.F., Pfromm, P.H., 2008. Combining reverse osmosis and pulsed electrical current electrodialysis for improved recovery of dissolved organic matter from seawater. Journal of Membrane Science 323, 328–336.

Hu, J., Song, H., Addison, J.W., Karanfil, T., 2010. Halonitromethane formation potentials in drinking waters. Water Research 44, 105–114.

Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterization of aquatic humic and non-humic matter with size-exclusion chromatography-organic carbon detection-organic nitrogen detection (LC-OCD-OND). Water Research 45, 879–885.

Kabay, N., İpek, Ö., Kahveci, H., Yüksel, M., 2006. Effect of salt combination on separation of monovalent and divalent salts by electrodialysis. Desalination 198, 81–94.

Kemper, J.M., Walse, S.S., Mitch, W.A., 2010. Quaternary amines as nitrosamine precursors: a role for consumer products? Environmental Science & Technology 44, 1224–1231.

Kim, D.H., Moon, S.H., Cho, J., 2002. Investigation of the adsorption and transport of natural organic matter (NOM) in ion-exchange membranes. Desalination 151, 11–20.

Koprivnjak, J.F., Perdue, E.M., Pfromm, P.H., 2006. Coupling reverse osmosis with electrodialysis to isolate natural organic matter from fresh waters. Water Research 40, 3385–3392.

Lee, W., Westerhoff, P., 2005. Dissolved organic nitrogen measurement using dialysis pretreatment. Environmental Science & Technology 39, 879–884.

Lee, W., Westerhoff, P., Croue, J.P., 2007. Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, N-nitrosodimethylamine, and trichloronitromethane. Environmental Science & Technology 41, 5485–5490.

Leenheer, J.A., Croué, J.P., Benjamin, M., Korshin, G.V., Hwang, C.J., Bruchet, A., Aiken, G.R., 2000. In: Barrett, S.E., Krasner, S.W., Amy, G.L. (Eds.), Comprehensive Isolation of Natural Organic Matter from Water for Spectral Characterizations and Reactivity Testing, ACS Symposium Series, vol. 761. American Chemical Society, Washington DC, USA.

Lindstrand, V., Jönsson, A., Sundström, G., 2000. Organic fouling of electrodialysis membranes with and without applied voltage. Desalination 130, 73–84.

Liu, H., Jeong, J., Gray, H., Smith, S., Sedlak, D.L., 2012. Algal uptake of hydrophobic and hydrophilic dissolved organic nitrogen in effluents from biological nutrient removal municipal wastewater treatment system. Environmental Science & Technology 46, 713–721.

Mitch, W.A., Sharp, J.O., Trussell, R.R., Valentine, R.L., Alvarezcohen, L., Sedlak, D.L., 2003. N-nitrosodimethylamine (NDMA) as a drinking water contaminant: a review. Environmental Engineering and Science 20, 389–404.

Muellner, M.G., Wagner, E.D., Mccalla, K., Richardson, S.D., Woo, Y.T., Plewa, M.J., 2007. Haloacetonitriles vs. regulated haloacetic acids: are nitrogen-containing DBPs more toxic? Environmental Science & Technology 41, 645–651.

Pehlivanoglu-Mantas, E., Sedlak, D.L., 2008. Measurement of dissolved organic nitrogen forms in wastewater effluents: concentrations, size distribution and NDMA formation potential. Water Research 42, 3890–3898.

Plewa, M.J., Wagner, E.D., Jazwierska, P., 2004. Halonitromethane drinking water disinfection byproducts: chemical characterization and mammalian cell cytotoxicity and genotoxicity. Environmental Science & Technology 38, 62–68.

Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection byproducts in drinking water: a review and roadmap for research. Mutation Research: Reviews in Mutation Research 636, 178–242.

Shah, A.D., Mitch, W.A., 2012. Halonitroalkanes, halonitriles, haloamides, and N-nitrosamines: a critical review of nitrogenous disinfection by product formation pathways. Environmental Science & Technology 46, 119–131.

Shon, H.K., Vigneswaran, S., Snyder, S.A., 2006. Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. Critical Reviews in Environmental Science and Technology 36, 327–374.

Song, G., Wang, J., Chin, C.A., Westerhoff, P., 2010. Biogenic nanoscale colloids in wastewater effluents. Environmental Science & Technology 44, 8216–8222.

Strathmann, H., 2004. Ion-exchange Membrane Separation Processes. Elsevier, Amsterdam, Netherlands.

U.S. EPA, 1993. Method 365.1: Determination of Phosphorus by Semi-automated Colorimetry (Revision 2.0, August 1993). Office of Research and Development, Cincinnati, Ohio, USA.

U.S. EPA, 1999. Code of Federal Regulations, Title 40, Part 136, Appendix B, Washington, DC, USA.

Van der Bruggen, B., Koninckx, A., Vandecasteele, C., 2004. Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration. Water Research 38, 1347—1353.

Vandenbruwane, J., Neve, S.D., Qualls, R.G., Salomez, J., Hofman, G., 2007. Optimization of dissolved organic nitrogen (DON) measurements in aqueous samples with high inorganic nitrogen concentrations. Science of the Total Environment 386, 103—113.

Vetter, T.A., Perdue, E.M., Ingall, E., Koprivnjak, J.F., Pfromm, P.H., 2007. Combining reverse osmosis and electrodialysis for more complete recovery of dissolved organic matter from seawater. Separation and Purification Technology 56 (383), 38.

Westerhoff, P., Mash, H., 2002. Dissolved organic nitrogen in drinking water supplies: a review. Journal of Water Supply: Research & Technology — Aqua 51, 415—448.

World Health Organization, 2006. N-Nitrosodimethylamine in Drinking Water. Geneva.

Xu, B., Li, D.P., Li, W., Xia, S.J., Lin, Y.L., Hu, C.Y., 2010. Measurements of dissolved organic nitrogen (DON) in water samples with nanofiltration pretreatment. Water Research 44, 5376—5384.

Yang, X., Fan, C., Shang, C., Zhao, Q., 2010. Nitrogenous disinfection byproducts formation and nitrogen origin exploration during chloramination of nitrogenous organic compounds. Water Research 44, 2691—2702.