



Reductions of dissolved organic matter and disinfection by-product precursors in full-scale wastewater treatment plants in winter



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HIGHLIGHTS

- Total removal efficiency of DOC, UV-254, THMFP, and HAAFP was higher than 50% in WWTPs.
- Biological treatment was the predominant process responsible for the removal of DOC, THMFP, and HAAFP.
- BAF and SCAS processes achieved better DOM removal because of higher biomass concentration.
- HPO-N and HPI were removed to a higher degree via biological treatment than the other fractions.
- Humic-like fluorescent compounds were not readily eliminated during the biological treatment.

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ABSTRACT

The reductions of dissolved organic matter (DOM) and disinfection byproduct precursors in four full-scale wastewater treatment plants (WWTPs) (Liaoning Province, China) where different biological treatment processes were employed in winter were investigated. The total removal efficiencies of dissolved organic carbon (DOC), ultraviolet light at 254 nm (UV-254), trihalomethane formation potential (THMFP), and haloacetic acid formation potential (HAAFP) were in the range of 70.3–76.0%, 49.6–57.3%, 54.4–65.0%, and 53.7–63.8% in the four WWTPs, respectively. The biological treatment was the predominant process responsible for the removal of DOC, THMFP, and HAAFP in WWTPs. Differences in the reduction of UV-254 were not significant ($p > 0.05$) among biochemical reaction pool, secondary sedimentation tank, and disinfection tank. Biological aerated filter and suspended carrier activated sludge processes achieved higher DOM removal than the conventional active sludge and anaerobic–anoxic–oxic processes. Hydrophobic neutral and hydrophilic fraction were removed to a higher degree through biological treatment than the other three DOM fractions. HAAFP removal was more efficient than THMFP reduction during biological treatment. During primary treatment, fluorescent materials in secondary sedimentation tanks were preferentially removed, as compared to the bulk DOM. Humic-like fluorescent compounds were not readily eliminated during biological treatment. The fluorescent materials were more susceptible to chlorine than nonfluorescent compounds.

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1. Introduction

Dissolved organic matter (DOM) includes various organic compounds, which consist of aromatic, aliphatic, phenolic, and quinolic functional groups with varying molecular sizes and properties (Chen et al., 2003a, b). DOM plays important roles in the interaction and transport of many toxic organic or inorganic chemicals

throughout the environment (Zhang et al., 2008). DOM also acts as an important precursor of disinfection byproducts (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), and enables microorganisms to grow in the treatment unit or distribution system (Kim and Yu, 2005).

The widespread use of wastewater treatment plants (WWTPs) has the potential to yield a considerable amount of organic matter such as proteins, polysaccharides, and humic substances, acids, and neutral compounds. Treated wastewater is commonly discharged into rivers, lakes, estuaries, and oceans, and thus, it can be an important source of DOM in the receiving waters (Yang et al., 2014).

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Therefore, understanding the fate and removal of DOM in wastewater treatment processes is of great interest to plant design engineers and environmental scientists alike. Some studies investigated the occurrence of DOM and/or DBPs in WWTP effluents. Imai et al. (2002) evaluated the characteristics of DOM in WWTP effluent by comparing DOM fraction distributions, ultraviolet absorption properties, and molecular size distributions. Krasner et al. (2009a) determined the occurrence of DBPs in WWTPs and examined the effect of well-nitrified versus poorly nitrified effluent organic matter (EfOM) on disinfection byproduct (DBP) occurrence. Krasner et al. (2009b) compared different WWTP processes for the control of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and DBP precursors in EfOM. However, the majority of the research studies were focused on WWTP discharges. Wei et al. (2012) examined the removal and transformation of DOM during a full-scale anoxic/oxic (A/O) WWTP in summer and winter. Removal efficiency of organic micropollutants in WWTPs is often highly dependent on the biological treatment, and it has been indicated that the biological treatment design can affect the overall micropollutant removal (Behera et al., 2011; Luo et al., 2014). However, there remains a lack of sufficient information on the occurrence and fate of DOM and DBP precursors in different treatment units of WWTPs, which use various types of biological treatment processes.

The goal of the present work was to investigate the reductions of DOM and DBP precursors in four full-scale WWTPs in winter. Different biological treatment technologies were used in the four WWTPs: conventional active sludge (CAS) process for WWTP A, biological aerated filter (BAF) for WWTP B, suspended carrier activated sludge (SCAS) process for WWTP C, and anaerobic–anoxic–oxic (A²O) process for WWTP D. The CAS process is one of the most commonly used technologies in municipal and industrial wastewater treatment, because it is cost effective and straightforward (Zhang et al., 2017). The A²O process is a sequential process that uses anaerobic, anoxic, and oxic reactors. Currently, the A²O process is the most widely used for biological nutrient removal because of its cost effectiveness and high efficiency (Fang et al., 2016). BAF was developed on the basis of biological filters in Europe in the late 1980s and then widely applied worldwide as novel, flexible, and effective bioreactors (Wu et al., 2015). A BAF is a fixed-film biosystem with a small footprint that uses filter media with a high specific surface area and porosity. The filter can promote in-growth biofilms for wastewater treatment (Bao et al., 2016). BAF has the advantages of higher biomass and organic loadings, stronger environmental shock resistance, and less sludge production (Ye and Ni, 2002). The SCAS process is based on the use of plastic carriers with density a little lighter than that of water in which microorganisms form biofilms. Because of air agitation, the carriers are mobilized in suspension of aeration tanks during oxygenation (Wei and Han, 2011). The SCAS process has been successfully used as the favored biological treatment technique during the past two decades, owing to compactness, flexibility, and high-quality effluent production (Wei and Han, 2011). The four types of biological sewage treatment processes are employed on a large scale in China (Wang et al., 2011; Wei and Han, 2011), thereby making them worthy of intensive study. The specific objectives of the present study are as follows: (1) examining the removal of DOM and its fractions isolated by the XAD-8/XAD-4 resin method within different treatment units; (2) investigating the effectiveness of different treatment units for the removal of THM and HAA precursors; and (3) evaluating the impact of different treatment units on the spectroscopic properties of DOM. Such knowledge would be helpful in establishing an optimal treatment strategy for the control of DOM and DBP precursors in WWTPs in cold areas.

2. Materials and methods

2.1. Sample collection

Four municipal WWTPs (WWTP A to WWTP D) in Liaoning Province, China, were chosen for this study. Basic information and process flow charts of the four WWTPs are shown in Table 1 and Fig. 1. Wastewater samples included influents, primary sedimentation tank effluents, biochemical reaction pool (i.e., aeration tank in WWTP A, BAF in WWTP B, aeration tank filled with suspended carrier in WWTP C, and aerobic tank in WWTP D) effluents, secondary sedimentation tank effluents, and disinfection tank effluents. In addition, the V-filter effluents in WWTP D were also sampled. The sampling points are shown in Fig. 1. The general water quality characteristics of influents of the four WWTPs are shown in Table 1. The wastewater samples were collected biweekly in two winters, from December 2013 to February 2014 and from December 2014 to February 2015. Daily-composite samples were obtained by mixing 500 mL sample volumes collected every hour during 24 h. Water samples were collected in acetone-rinsed amber glass bottles with polytetrafluoroethylene (PTFE)-lined caps. To eliminate the variations in wastewater, all the samples were obtained when the plants ran normally. The ambient temperature during the sampling ranged from −24.4–2.1 °C, and there was no snow during the sampling.

2.2. DOM fractionation

DOM in wastewater samples was fractionated into five classes: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N), and hydrophilic fraction (HPI), by using the XAD-8/XAD-4 resin chromatography (Chow et al., 2006). The isolation methods were described in detail by Xue et al. (2009). The recovery rate of the DOC ranged from 93% to 102% in the fraction and isolation procedures in this study.

2.3. Analysis

All wastewater samples were filtered using a 0.45- μm cellulose nitrate membrane filter and stored at 4 °C prior to analysis. DOC was analyzed on a Shimadzu TOC-5000 Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan). Ultraviolet light at 254 nm (UV-254) was measured with a Cary 50 ultraviolet–visible (UV/VIS) spectrophotometer (Varian, Palo Alto, California, USA) at 254 nm using a 1-cm pathlength quartz cell. The instrument was zeroed using Milli-Q water as a blank. Specific ultraviolet light absorbance (SUVA) was calculated as $(\text{UV-254}/\text{DOC}) \times 100$.

Trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) measurements were performed according to the Standard Method 5710B. The chlorine dosage for each water sample was determined such that a final residual chlorine of 3–5 mg L^{−1} remained in the sample after the 7 d of incubation at 25 °C. All samples were adjusted to a pH of 7 ± 0.2 using sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH). The neutralized solution was then buffered with a phosphate solution prior to incubation in amber bottles at 25 ± 2 °C for 7 d. At the end of the incubation period, samples were dechlorinated using sodium sulfite (Na₂SO₃). THMs were extracted using methyl-tert butyl ether (MTBE) from the chlorinated samples using a modified EPA method 551.1. Five species of HAAs, i.e., monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA), were analyzed in accordance with the EPA method 552.2. MTBE was used as the sole extracting solvent. The concentrations of THMs and HAAs were measured using a gas chromatograph (CP-3800)

Table 1
Information and water quality parameters of influents of the four WWTPs studied.

WWTPs	Location (city)	Treatment capacity of plant ($\times 10^4 \text{ m}^3 \text{ d}^{-1}$)	Industrial/domestic	Biological treatment processes employed	Disinfectant/Dose (mg L^{-1} as Cl_2)	HRT (h)	SRT (d)	Water quality parameters of influents					
								COD (mg L^{-1})	BOD (mg L^{-1})	$\text{NH}_3\text{-N}$ (mg L^{-1})	SS (mg L^{-1})	pH T ($^\circ\text{C}$)	
A	Shenyang	40	66: 34	CAS	Liquid chlorine/10.0	6	8	339.1	102.8	19.9	185.5	7.1	10.8
B	Shenyang	40	45: 55	BAF	Liquid chlorine/8.0	1	–	396.0	160.7	54.0	240.0	6.7	12.2
C	Shenyang	20	93: 7	SCAS	Liquid chlorine/6.0	4.5	5	319.0	104.5	29.6	166.0	7.2	11.1
D	Jinzhou	20	30: 70	A^2/O	Liquid chlorine/7.5	19	25	415.7	137.3	36.6	213.9	7.4	12.3

with an electron capture detector (ECD) (GC/ECD, CP-3,800, Varian, Palo Alto, California, USA). The chlorine residuals in disinfection tank effluent samples were determined using the DPD ferrous titrimetric method.

Fluorescence spectra were collected using a Cary Eclipse spectrofluorometer (Varian, Palo Alto, California, USA), which uses a Xe excitation source. Filtered water samples were diluted to 5 mg L^{-1} of DOC with 0.01 M potassium chloride (KCl) and acidified to pH 3 with hydrochloric acid (HCl) to minimize complexation of metals with DOC (Drewes et al., 2006). The slits were set to 5 nm for both excitation and emission, and the scan speed was set to 1000 nm min^{-1} . A 1-cm pathlength quartz cell was used. To obtain the excitation–emission matrix (EEM) profiles, excitation wavelengths were incremented from 220 to 400 nm at 5-nm steps; for each excitation wavelength, the emission was detected from 300 to 510 nm at 1-nm steps. Blank sample (0.01 M KCl at pH 3) fluorescence was subtracted from all spectra.

3. Results and discussion

3.1. Reductions of DOM and its fractions

As shown in Fig. 2, DOC in WWTP A, WWTP B, WWTP C, and WWTP D influents was 33.0 , 29.9 , 32.9 , and 36.8 mg L^{-1} ,

respectively. The DOC in effluents of WWTP A, WWTP B, WWTP C, and WWTP D was 9.8 , 7.2 , 8.3 , and 9.1 mg L^{-1} , respectively. Therefore, the total removal efficiency of DOM was 70.3% , 76.0% , 74.7% , and 75.2% in WWTP A, WWTP B, WWTP C, and WWTP D, respectively.

All the four WWTPs employed primary and secondary treatment processes. In addition, WWTP D also employed advanced wastewater treatment (inclined tube sedimentation tank + folded-plate flocculating tank + V-filter). The removal efficiency of DOM ranged from 11.9% to 14.8% in primary treatment (screen + aerated grit chamber/grit chamber + primary sedimentation tank) in the four WWTPs. Organics were removed mainly by sorption on primary sludge, as distribution of a compound on the organic (lipophilic) layer is the predominant way of sorption (Temes et al., 2004). The primary treatment was responsible for $16.4\text{--}19.5\%$ of the total removal achieved in the WWTPs. In secondary treatment, pollutants were subjected to various processes, including dispersion, dilution, partition, biodegradation, and abiotic transformation (Jelic et al., 2011; Luo et al., 2014). Biodegradation/biotransformation and sorption are the two major removal mechanisms during biological treatment (Verlicchi et al., 2012). DOM was effectively removed during biological treatment with removal efficiency of 57.9% , 71.5% , 66.1% , and 60.3% in WWTP A, WWTP B, WWTP C, and WWTP D, respectively. The results suggest that the biological

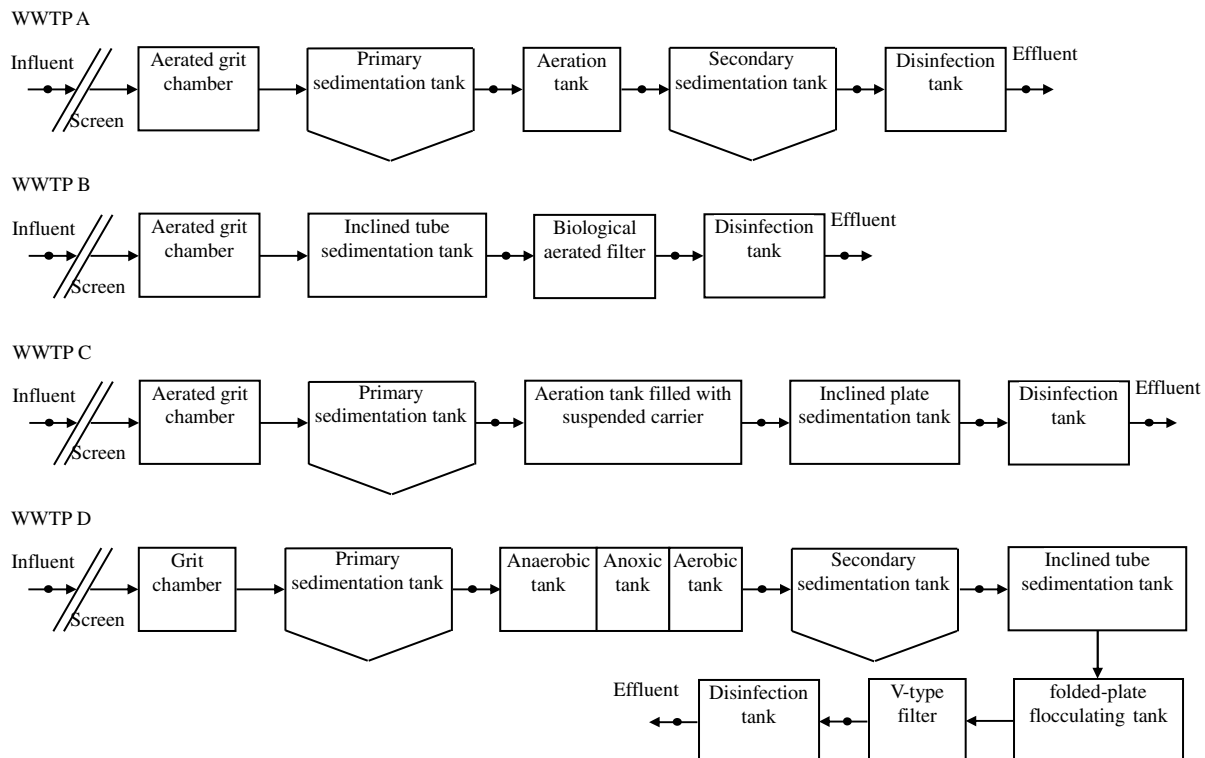


Fig. 1. Schematic diagram of the treatment processes in the four WWTPs and the sampling site location. The black dot represents the sampling location.

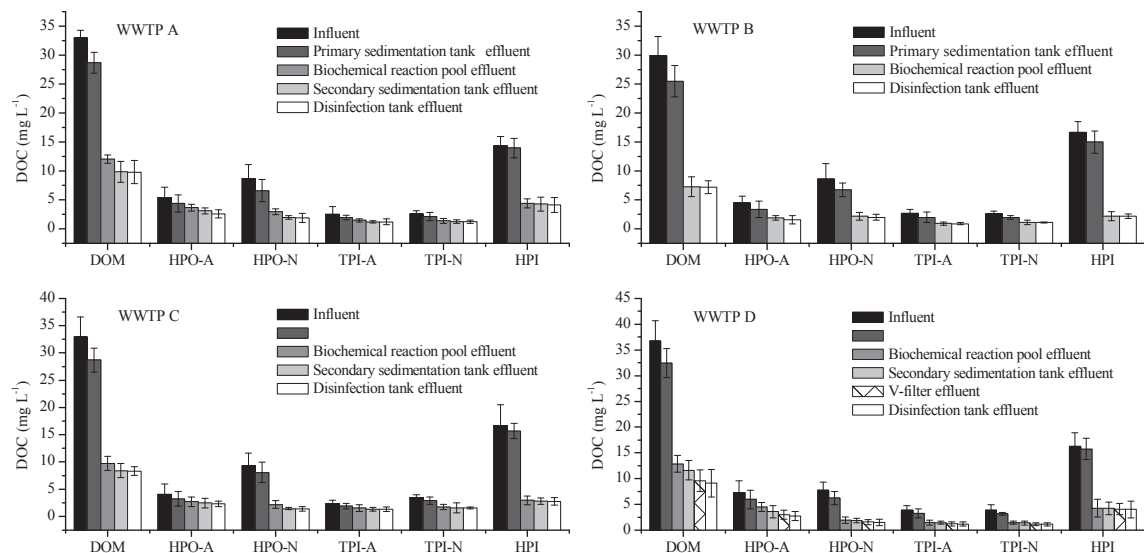


Fig. 2. DOC concentration for DOM and its fractions in influents and different treatment unit effluents of the four WWTPs.

treatment was the predominant process responsible for DOM removal in WWTPs. Biological wastewater treatment techniques can normally be classified as either suspended or attached growth processes (Luo et al., 2014). CAS and A²/O processes belong to suspended processes, while BAF and SCAS processes belong to attached growth processes. The fate of micropollutants in WWTPs is under the control or influence of “internal factors” and “external factors.” Internal factors are micropollutant related, including the characteristics of micropollutants (e.g. biodegradability and volatility). External factors are WWTP specific, which are linked to the treatment conditions of wastewater treatment processes and the nature of wastewater (pH and temperature) (Luo et al., 2014). Westerhoff and Pinney (2000) conducted biological dissolved organic carbon tests to assess the biodegradable nature of DOC. They found that nonaromatic DOM was preferentially biodegraded. The SUVA values for biochemical reaction pool influents of WWTP A, WWTP B, WWTP C, and WWTP D were 0.73, 0.52, 0.39, and 0.36 L m⁻¹ mg⁻¹ (Fig. 3), respectively, which suggested that DOM in biochemical reaction pool influents of WWTP C and WWTP D seemed to be more readily biodegraded than that of WWTP A and WWTP B. pH and temperature for biochemical reaction pool influents of the four WWTPs were in the range of 6.9–7.3 and 10.6–11.9 °C, respectively. These data indicate that the pH values were very close to each other; the same result was observed for temperature. Therefore, both pH and temperature might have no significant effect on the differences in DOM removal by biological treatment processes in the four WWTPs. Sludge retention time (SRT) controls the size and diversity of a microbial community. Enhanced elimination of micropollutants can be achieved if the treatment processes have extended SRT (Luo et al., 2014). Clara et al. (2005) suggested that the SRT allowing nitrogen removal (nitrification and denitrification) above 10 d can enhance the elimination of some biodegradable compounds. Hydraulic retention time (HRT) is the amount of time that allows for biodegradation and sorption. The micropollutants having slow/intermediate kinetics will experience less effective biodegradation at shorter HRT or increasing loading rates (Fernandez-Fontaina et al., 2012). The better DOM removal by the A²/O process employed in WWTP D might be because of the lower contents of aromatic structures in DOM and the longer SRT and HRT of the process as compared to those of the CAS process employed in WWTP A. Although with low

SUVA and long SRT and HRT, the A²/O process employed in WWTP D achieved lower DOM removal than those by the BAF process employed in WWTP B and the SCAS process employed in WWTP C. The results demonstrated that attached growth treatment processes had a greater potential for DOM removal than suspended growth processes. The BAF and SCAS processes involve attached growth on inert carriers fixed and mobilized in suspension of biochemical reaction pools, respectively (Wang et al., 2011; Wei and Han, 2011). The inert carriers for attached growth placed in biochemical reaction pools in WWTP B and WWTP C were circular ceramsites with particle size of 3–6 mm and hollow and cylindrical plastic products with diameter and length of 44 and 38 mm, respectively (Wang et al., 2011; Wei and Han, 2011). Microorganisms grew on carrier surface to form biofilm. Thus, the BAF and SCAS processes offered higher biomass concentrations and more effective biodegradation than those by the CAS and A²/O processes (Guo et al., 2012; Luo et al., 2014). In addition to biodegradation, ceramsites and biofilm attached to ceramsites removed DOM from wastewater by filtration and adsorption in biochemical reaction pools in WWTP B. The carriers with density of slightly less than 1000 kg m⁻³ and surface area of as high as 380 m² m⁻³ were suspended in biochemical reaction pools in WWTP C and flowed with water and air flow, which enhanced the mass transfer processes (Wei and Han, 2011). These also improved DOM reduction in biochemical reaction pools in WWTP B and WWTP C. The biological treatment processes accounted for 70.6–77.1% of the total removal achieved in the WWTPs. The additional 2.2–9.7% of the total removal was observed in secondary sedimentation tanks in WWTP A, WWTP C, and WWTP D. In addition, the advanced wastewater treatment accounted for 8.9% of the total removal in WWTP D. There was little change in DOC after disinfection process in all the four WWTPs.

The primary treatment could remove HPO-A, HPO-N, TPI-A, and TPI-N moderately with removal efficiencies ranging from 13.3% to 26.6% in the four WWTPs. In comparison with the other four fractions, HPI was removed to a lesser degree (2.7–9.9%) during primary treatment.

Except HPO-A in WWTP A and WWTP B, which was removed to a slightly higher degree through primary treatment as compared to that by biological treatment, all DOM fractions exhibited a higher reduction through biological treatment than all the other treatment

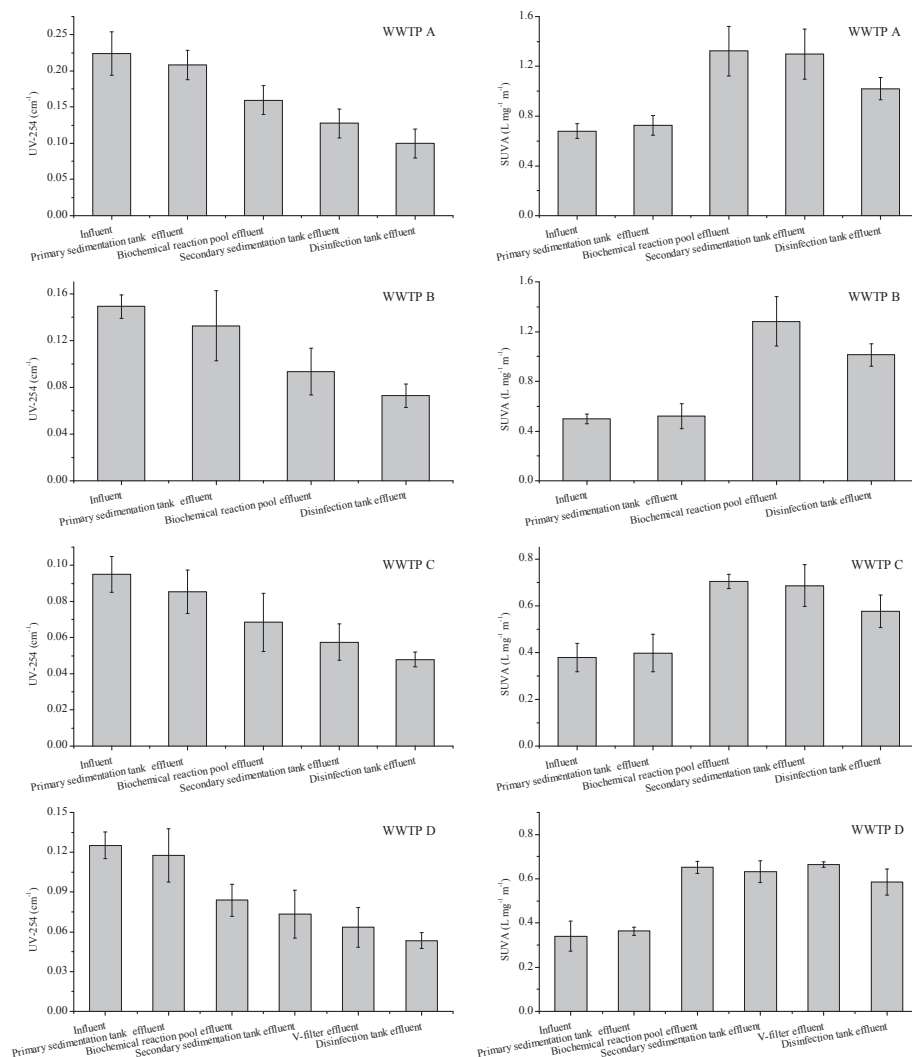


Fig. 3. UV-254 and SUVA for DOM in influents and different treatment unit effluents of the four WWTPs.

progresses, suggesting that the biodegradation was the predominant removal mechanism for DOM fractions in WWTPs. The DOM fractions exhibited a common general relationship with respect to the reduction through biological treatment in WWTP A, WWTP C, and WWTP D: HPO-N (55.5–73.1%) and HPI (68.7–85.5%) > TPI-A (20.2–54.8%) and TPI-N (35.7–55.1%) > HPO-A (16.7–24.9%) ($p < 0.05$). With regard to WWTP B, HPO-N and HPI also showed significantly higher removal through biological treatment (68.0% and 85.5% for HPO-N and HPI, respectively) than the other three fractions ($p < 0.05$). However, the removal of HPO-A through biological treatment (44.8%) was not different from that of TPI-A (53.6%) and TPI-N (43.5%) ($p > 0.05$). Differences in the removal of HPO-N, TPI-A, TPI-N, and HPI through biological treatment were not significant ($p > 0.05$) among the four WWTPs. However, HPO-A exhibited significantly higher reduction through biological treatment in WWTP B than in the other three WWTPs ($p < 0.05$), which suggested that the BAF process employed in WWTP B was much more efficient in the removal of HPO-A than the other biological treatment processes employed in the other three WWTPs. The highest removal efficiency of HPO-N, TPI-A, TPI-N, and HPI through biological treatment was observed in the SCAS process employed in WWTP C, the BAF process employed in WWTP B, the A²/O process employed in WWTP D, and the BAF process employed in WWTP B, respectively.

HPO-A was removed by 9.3–21.4%, HPO-N by 10.9–34.1%, TPI-A by 8.8–16.6%, TPI-N by 9.8–12.6%, and HPI by 0.9–6.6% in secondary sedimentation tanks in WWTP A, WWTP C, and WWTP D. On the one hand, the removal of HPO-A, HPO-N, TPI-A, and TPI-N was not significantly different from each other ($p > 0.05$), which, on the other hand, was significantly higher than that of HPI ($p < 0.05$) in the three WWTPs. The phenomena were also found during advanced wastewater treatment in WWTP D, where HPO-A, HPO-N, TPI-A, TPI-N, and HPI were removed by 15.7%, 15.7%, 14.1%, 18.0%, and 4.3%, respectively.

Chlorination resulted in relatively obvious changes in HPO-A characteristics, as indicated by the DOC decrease of 5.3–17.7% in HPO-A. However, DOC changes of less than 3.8% for the other four fractions were found in disinfection tanks, which suggested that chlorination had little effect on their polarity (hydrophobic/hydrophilic) and acid/neutral properties.

3.2. Reductions of UV-254

UV-254 is mainly caused by electron-rich sites such as aromatic functional groups and double-bonded C groups in the DOM molecule (Fuentes et al., 2006; Tipping et al., 2009). SUVA is obtained by dividing the UV-254 with its DOC, which represents the aromaticity of the DOM samples (Weishaar et al., 2003). As shown in Fig. 3,

SUVA for the influents of WWTP A, WWTP B, WWTP C, and WWTP D had an average of 0.68, 0.50, 0.37, and 0.34 L mg⁻¹ m⁻¹, respectively, suggesting that the influents of WWTP A and WWTP B contained a relatively high amount of aromatic structures, while the influents of WWTP C and WWTP D were rich in aliphatic carbon. WWTP A, WWTP B, WWTP C, and WWTP D reduced UV-254 by 55.4%, 51.2%, 49.6%, and 57.3%, yielding effluent UV-254 values of 0.100, 0.073, 0.048, and 0.053 cm⁻¹, respectively.

A reduction of 5.9–11.0% in UV-254 through primary treatment was observed in the four WWTPs. It was also found that the primary treatment led to a lower reduction of UV-254 than that of DOC, thereby resulting in an increased SUVA value, in each WWTP. It was reported that the primary treatment using aerated grit chamber could cause significant increase in phenolic compounds, which are generally characterized by high SUVA values, because the compounds originally attached to the grits could be peeled off due to the air agitation in grit chamber (Nie et al., 2012). The removal efficiency of UV-254 via biological treatment in the four WWTPs could be ranked as follows: the BAF process employed in WWTP B (29.7%) > the A²/O process employed in WWTP D (26.5%) > the CAS process employed in WWTP A (23.3%) > the SCAS process employed in WWTP C (20.0%). The reduction of UV-254 through biological treatment was significantly lower than that of DOC. Thus, biodegradation seemed to preferentially remove nonaromatic components and resulted in a substantial increase in SUVA (>79%) during biological treatment. The reduction of UV-254 in secondary

sedimentation tanks ranged from 11.9% to 15.8% in the four WWTPs, which was higher than the corresponding DOC reduction. As a result, SUVA slightly decreased in secondary sedimentation tanks. The preferential removal of nonaromatic components as compared to the bulk DOM represented by DOC was found during advanced wastewater treatment in WWTP D, as indicated by an increase of 11.8% in SUVA. Chlorine disinfection caused decreases of 15.8–21.9% in UV-254, which were significantly higher than those in DOC. It was reported that chlorine attacks DOM predominantly at the activated aromatic sites or conjugated double bonds, which absorb ultraviolet (UV) light effectively at the wavelengths of 250–280 nm, and that chlorination led to a decrease in UV-254 value of the DOM as a result of alteration and destruction of these sites (Li et al., 2000; Ates et al., 2007). Differences in the reduction of UV-254 were not significant ($p > 0.05$) among the biochemical reaction pools, secondary sedimentation tanks, and disinfection tanks in the four WWTPs.

3.3. Reductions of THMFP and HAAFP

THMFP and HAAFP are often the terms employed to indicate the amount of THMs and HAAs that could be produced during the chlorination process and could indirectly represent the amount of THM and HAA precursors in water samples (Iriarte-Velasco et al., 2007; Wu et al., 2013; Ma et al., 2014). As shown in Figs. 4 and 5, the total removal efficiencies of THMFP and HAAFP ranged from

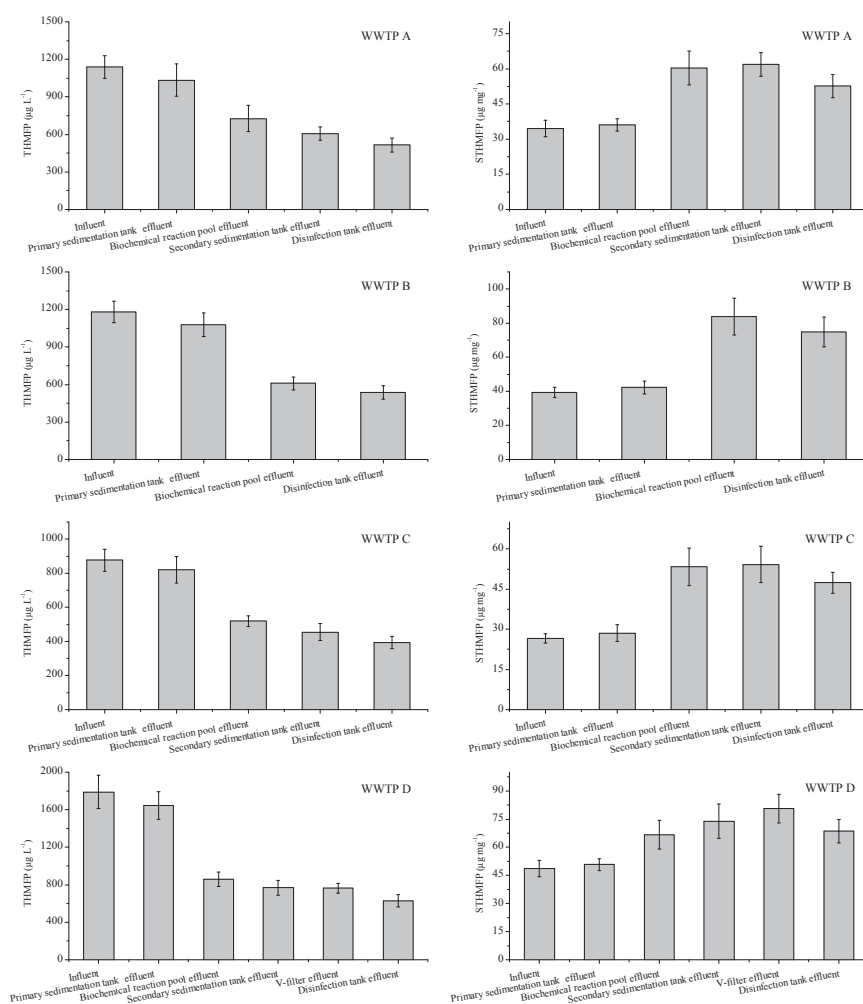


Fig. 4. THMFP and STHMFP for DOM in influents and different treatment unit effluents of the four WWTPs.

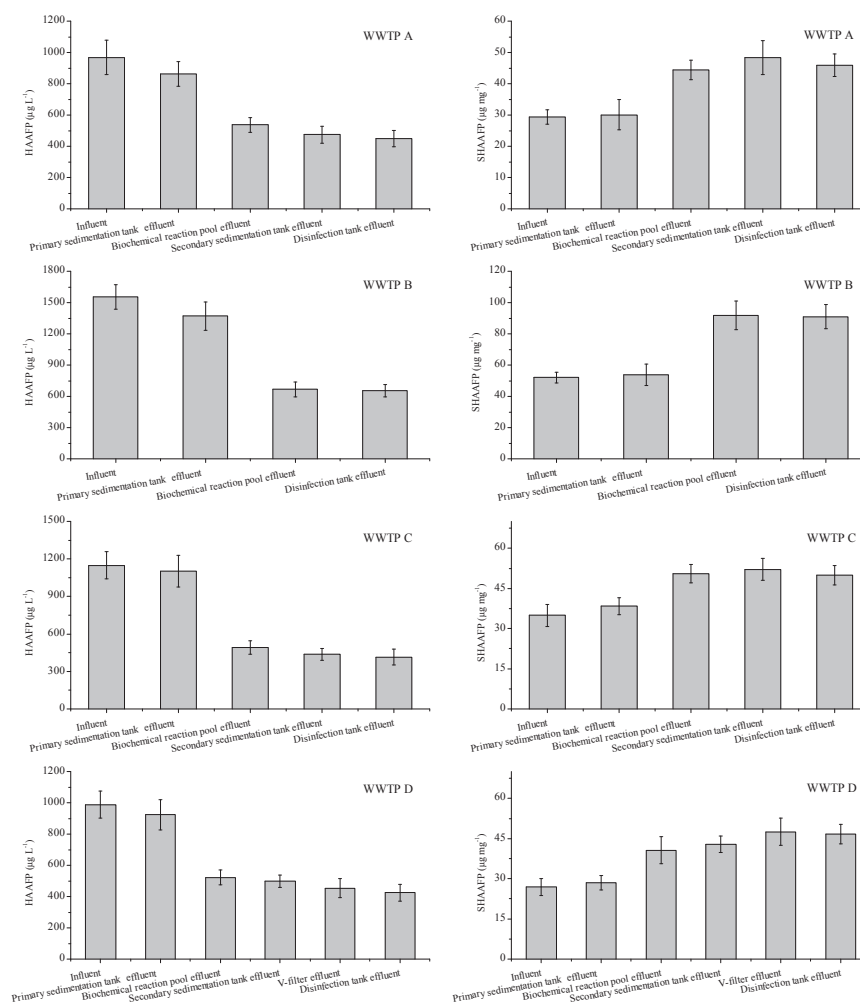


Fig. 5. HAAFP and SHAAFP for DOM in influents and different treatment unit effluents of the four WWTPs.

54.4% to 65.0% and from 53.7% to 63.8%, respectively, in the four WWTPs. THMFP and HAAFP were removed to a similar extent during primary treatment in the four WWTPs, with removal efficiencies of 6.4–9.1% and 4.1–11.0%, respectively. The biological treatment accounted for 49.7–73.0% and 62.7–83.2% of the total removal achieved in the four WWTPs, which indicated that biodegradation was the major removal mechanism for THM and HAA precursors. It was also found that the removal efficiency of HAAFP during biological treatment was higher than that of THMFP in each WWTP, suggesting that HAAFP removal was more efficient than THMFP removal during biological treatment. On the contrary, THMFP was removed to a slightly higher degree than HAAFP in secondary sedimentation tanks in the four WWTPs and during advanced wastewater treatment in WWTP D. An obvious decrease of 10.9–15.1% in THMFP was observed in the disinfection tanks, while chlorine disinfection seemed to have a minor effect on HAAFP with a decrease of 2.0–6.1%, which suggested that chlorine preferentially reacted with THM precursors in the disinfection tanks where the dosage of chlorine was not enough to make chlorine react with all the THM and HAA precursors.

In comparison with THM and HAA values for the WWTP effluents disinfected with free chlorine (Krasner et al., 2009a), THM and HAA levels of disinfection tank effluents in this study were relatively low, in the range of 12.2–29.0 and 26.9–44.7 $\mu\text{g L}^{-1}$, respectively. The chlorine residual results indicated that there was

almost no free chlorine present in the disinfection tank effluents of the four WWTPs. To achieve breakpoint chlorination, a chlorine dose of 7.6–10.0 mg L^{-1} as Cl_2 is required for each 1.0 mg L^{-1} of $\text{NH}_3\text{-N}$ (Krasner et al., 2009a). The four WWTPs exhibited $\text{NH}_3\text{-N}$ concentrations of 2.2–12.4 mg L^{-1} in the effluents and had chlorine doses of 6.0–10.0 mg L^{-1} as Cl_2 (Table 1), respectively, resulting in $\text{Cl}_2/\text{NH}_3\text{-N}$ ratios of 0.81–3.64 mg mg^{-1} . Therefore, the presence of a high amount of ammonia resulted in the formation of combined chlorine (chloramines) when chlorine was added. The presence of chloramines during the disinfection process probably reduced the formation of most of the halogenated DBPs because chloramines are much less reactive with humic substances to form THMs and HAAs than free chlorine (Krasner et al., 2009a).

Because THMFP is dependent on DOC concentration, the reactivity of DOC is also reported in terms of specific THMFP (STHMFP), that is, micrograms of THMFP formed per milligram of DOC precursor material in the water ($\mu\text{g mg}^{-1}$). Similarly, specific HAAFP (SHAAFP) represents the reactivity of DOC toward chlorine and formation of HAAs. Both STHMFP and SHAAFP increased not only after primary treatment but also after biological treatment, indicating that the reductions of THM and HAA precursors were lower than those of the bulk DOM represented by DOC. Increased STHMFP and SHAAFP were also found in the secondary sedimentation tanks in WWTP A, WWTP B, and WWTP D. On the contrary, chlorine disinfection seemed to have a greater impact on THM and HAA

precursors than on the bulk DOM, as indicated by the decrease in both STHMFP and SHAAFP after disinfection. STHMFP did not follow similar trends in secondary sedimentation tanks in the four WWTPs, nor did SHAAFP. The results suggested that the removal priority of THM and HAA precursors versus the bulk DOM in secondary sedimentation tanks was WWTP specific.

3.4. Reductions of fluorescence materials

The EEM spectra of DOM within different units in the four WWTPs are shown in Fig. 6. Fluorescence EEM provides an overall view of the fluorescent properties of DOM in a selected spectral range, and it has been employed to identify the fluorescent compounds in DOM (Hur et al., 2007; Xue et al., 2016). In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to aromatic protein-like compounds. Peaks at intermediate excitation wavelengths (250–280 nm) and shorter emission wavelength (<380 nm) are related to soluble microbial byproduct-like (SMP-like) materials. Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics. Peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Chen et al., 2003a, b; Drewes et al., 2006; Baker et al., 2007). Traditionally, fulvic acid- and humic acid-like peaks have been associated with humic-like substances, and aromatic protein-like and SMP-like peaks have been recognized as belonging to protein-like fluorescence (Chen et al., 2003a, b; Sierra et al., 2005).

As shown in Fig. 6, the EEM spectra of DOM in influents of both WWTP A and WWTP D were dominated by aromatic protein- and SMP-like fluorescence peaks, with the aromatic protein-like peak exhibiting the highest intensity. In addition, a humic acid-like peak was also observed, although it looked more like a shoulder peak in the two spectra. The WWTP B influent DOM was characterized as containing aromatic protein-, humic acid-, and fulvic acid-like fluorescent compounds. The EEM spectrum of the WWTP C

influent DOM was characterized by well-defined aromatic protein- and fulvic acid-like fluorescence peaks with approximately equal intensity and also showed a relatively weak humic acid-like peak. The aromatic protein-like peak was the strongest peak in the spectra of DOM in influents of WWTP A, WWTP B, and WWTP D, while it showed a slightly lower intensity than the fulvic acid-like peak in the WWTP C influent DOM spectrum. Therefore, the WWTP C influent DOM was more humic-like and less protein-like in the fluorescence characteristics than DOM in influents of the other three WWTPs.

As all EEM spectra were obtained for water samples with a DOC concentration of 5.0 mg L^{-1} , an increase in fluorescence intensity was an indication of increased relative content of fluorescent materials in DOM, and vice versa. As shown in Fig. 6, there was little change in the fluorescence characteristics of DOM after primary treatment, with the most notable difference being the decrease in the intensity of all peaks present in the spectra of DOM in influents of all the four WWTPs, indicating that the fluorescent materials were preferentially removed during primary treatment, as compared to the bulk DOM.

As shown in Fig. 6, the aromatic protein- and SMP-like peaks became very weak shoulder peaks in the spectrum of DOM in the aeration tank in WWTP A, suggesting that protein-like fluorescent materials were effectively removed during the CAS process. However, the substantially increased intensity of humic acid- and fulvic acid-like peaks might indicate the ineffective removal of humic acid- and fulvic acid-like fluorescent materials as compared to that of the bulk DOM, during the CAS process in WWTP A. A significant increase in the intensity of humic acid- and fulvic acid-like peaks after biological treatment was also observed in WWTP B, WWTP C, and WWTP D. However, the intensity of aromatic protein-like peak decreased in the BAF in WWTP B but increased in the aeration tank in WWTP C. These results suggested that humic-like fluorescent compounds were not readily eliminated through biodegradation, while the reduction of protein-like fluorescent materials during biological treatment was generally WWTP specific and/or process specific. The intensity of humic acid- and fulvic acid-like peaks



Fig. 6. Fluorescence spectra for DOM in influents and different treatment unit effluents of the four WWTPs.

decreased by 8.0–48.1% in secondary sedimentation tanks in WWTP A, WWTP C, and WWTP D. Similarly, the intensity of aromatic protein-like peak decreased in secondary sedimentation tanks in WWTP C. Thus, the fluorescent materials seemed to be preferentially removed in secondary sedimentation tanks, as compared to nonfluorescent compounds. The preferential reduction of fulvic acid-like fluorescent materials during advanced wastewater treatment in WWTP D was indicated by the further decrease in the intensity of fulvic acid-like peak. The fluorescent materials might react with chlorine more readily than nonfluorescent compounds, as illustrated by the decrease in fluorescence intensity of all fluorescent peaks after chlorination. Note that the changes in the humic acid-like peak in disinfection tanks in each WWTP were less distinct as compared to those in the corresponding fulvic acid-like peak. This led to hypothesize that fulvic acid-like fluorescent materials were more susceptible to chlorine than humic acid-like fluorescent compounds.

4. Conclusions

The goal of this study was to investigate the reductions of DOM and DBP precursors in full-scale WWTPs in winter. The following conclusions are drawn on the basis of the experimental results:

- (1) The total DOC removal efficiency of higher than 70% was observed in the four WWTPs. The biodegradation was the predominant removal mechanism for DOM and its fractions in WWTPs. BAF and SCAS processes achieved higher DOM removal than CAS and A²/O processes.
- (2) The total removal efficiency of UV-254 ranged from 49.6% to 57.3% in the four WWTPs. Differences in the reduction of UV-254 were not significant ($p > 0.05$) among biochemical reaction pools, secondary sedimentation tanks, and disinfection tanks.
- (3) The total removal efficiencies of THMFP and HAAFP were in the range of 54.4–65.0% and 53.7–63.8%, respectively, in the four WWTPs. The biodegradation seemed to be the major removal mechanism for THM and HAA precursors.
- (4) Fluorescent materials were preferentially removed during primary treatment and in secondary sedimentation tanks, as compared to the bulk DOM. Humic-like fluorescent compounds were not readily eliminated through biodegradation.

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References

- Ates, Nuray, Kitis, M., Yetis, U., 2007. Formation of chlorination by-products in waters with low SUVA-correlations with SUVA and differential UV spectroscopy. *Water Res.* 41, 4139–4148.
- Baker, A., Elliott, S., Lead, J.R., 2007. Effects of filtration and pH perturbation on freshwater organic matter fluorescence. *Chemosphere* 67, 2035–2043.
- Bao, T., Chen, T.H., Tan, J.W.M.L., Zhu, D., Chen, D., Xi, Y.F., 2016. Synthesis and performance of iron oxide-based porous ceramsite in a biological aerated filter for the simultaneous removal of nitrogen and phosphorus from domestic wastewater. *Sep. Purif. Technol.* 167, 154–162.
- Behera, S.K., Kim, H., Oh, J.E., Park, H.S., 2011. Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plant of the largest industrial city of Korea. *Sci. Total Environ.* 409, 4351–4360.
- Chen, J., LeBoeuf, E.J., Dai, S., Gu, B., 2003a. Fluorescence spectroscopic studies of natural organic matter fractions. *Chemosphere* 50, 639–647.
- Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003b. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* 37, 5701–5710.
- Chow, A., Guo, F., Gao, S., Breuer, R.S., 2006. Size and XAD fractionations of trihalomethane precursors from soils. *Chemosphere* 62, 1636–1646.
- Clara, M., Kreuzinger, N., Strenn, B., Gans, O., Kroiss, H., 2005. The solids retention time—a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Res.* 39, 97–106.
- Drewes, J.E., Quanrud, D.M., Amy, G.L., Westerhoff, P.K., 2006. Character of organic matter in soil-aquifer treatment systems. *J. Environ. Eng.* 132, 1447–1458.
- Fang, F., Qiao, L.L., Cao, J.S., Li, Y., Xie, W.M., Sheng, G.P., Yu, H.Q., 2016. Quantitative evaluation of A²O and reversed A²O processes for biological municipal wastewater treatment using a projection pursuit method. *Sep. Purif. Technol.* 166, 164–170.
- Fernandez-Fontaina, E., Omil, F., Lema, J.M., Carballa, M., 2012. Influence of nitrifying conditions on the biodegradation and sorption of emerging micropollutants. *Water Res.* 46, 5434–5444.
- Fuentes, M., González-Gaitano, G., García-Mina, J.M., 2006. The usefulness of UV-visible and fluorescence spectroscopies to study the chemical nature of humic substances from soils and composts. *Org. Geochem* 37, 1949–1959.
- Guo, W., Ngo, H.H., Vigneswaran, S., 2012. Enhancement of membrane processes with attached growth media (Chapter 20). In: Zhang, T.C., Surampalli, R.Y., Vigneswaran, S., Tyagi, R.D., Ong, S.L., Kao, C.M. (Eds.), *Membrane Technology and Environmental Applications*. American Society of Civil Engineers, Virginia, pp. 603–634.
- Hur, J., Jung, N.C., Shin, J.K., 2007. Spectroscopic distribution of dissolved organic matter in a dam reservoir impacted by turbid storm runoff. *Environ. Monit. Assess.* 133, 53–67.
- Imai, A., Fukushima, T., Matsushige, K., Kim, Y.H., Choi, K., 2002. Characterization of dissolved organic matter in effluents from wastewater treatment plants. *Water Res.* 36, 859–870.
- Iriarte-Velasco, U., Álvarez-Urriarte, J.I., González-Velasco, J.R., 2007. Removal and structural changes in natural organic matter in a Spanish water treatment plant using nascent chlorine. *Sep. Purif. Technol.* 57, 152–160.
- Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., Barcelo, D., 2011. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. *Water Res.* 45, 1165–1176.
- Kim, H.C., Yu, M.J., 2005. Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. *Water Res.* 39, 4779–4789.
- Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B.E., Amy, G., 2009a. Occurrence of disinfection byproducts in United States wastewater treatment plant effluents. *Environ. Sci. Technol.* 43, 8320–8325.
- Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B.E., Nam, S.N., Amy, G., 2009b. Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter. *Environ. Sci. Technol.* 43, 2911–2918.
- Li, C.W., Benjamin, M.M., Korshin, G.V., 2000. Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. *Environ. Sci. Technol.* 34, 2570–2575.
- Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* 473–474C, 619–641.
- Ma, D.F., Gao, B.Y., Wang, Y., Yue, Q.Y., Li, Q., 2014. Impacts of powdered activated carbon addition on trihalomethane formation reactivity of dissolved organic matter in membrane bioreactor effluent. *Chemosphere* 117, 338–344.
- Nie, Y., Qiang, Z., Zhang, H., Ben, W., 2012. Fate and seasonal variation of endocrine-disrupting chemicals in a sewage treatment plant with A/A/O process. *Sep. Purif. Technol.* 84, 9–15.
- Sierra, M.M.D., Giovanela, M., Parlanti, E., Soriano-Sierra, E.J., 2005. Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques. *Chemosphere* 58, 715–733.
- Temes, T.A., Joss, A., Siegrist, H., 2004. Scrutinizing pharmaceuticals and personal care products in wastewater treatment. *Environ. Sci. Technol.* 38, 392A–399A.
- Tipping, E., Corbishley, H.T., Koprivnjak, J.F., Lapworth, D.J., Miller, M.P., Vincent, C.D., Hamilton-Taylor, J., 2009. Quantification of natural DOM from UV absorption at two wavelengths. *Environ. Chem.* 6, 472–476.
- Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment—a review. *Sci. Total Environ.* 429, 123–155.
- Wang, J., Liu, Y., Jiang, S.Z., Bai, Y., Hu, X.M., 2011. Study on change rules of SS on concentration in back washing of BAF. *China Water Wastewater* 27, 99–102.
- Wei, A.S., Han, L.Z., 2011. Application of flocced biochemical process in treating municipal sewage. *Environ. Prot. Sci.* 37, 23–26.
- Wei, L.L., Wang, K., Zhao, Q.L., Xie, C.M., 2012. Characterization and transformation of dissolved organic matter in a full-scale wastewater treatment plant in Harbin, China. *Desalin. Water Treat.* 46, 295–303.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* 37, 4702–4708.
- Westerhoff, P., Pinney, M., 2000. Dissolved organic carbon transformations during laboratory-scale groundwater recharge using lagoon-treated wastewater. *Waste Manage.* 20, 75–83.

- Wu, M.N., Wang, X.C., Ma, X., 2013. Characteristics of THMFP increase in secondary effluent and its potential toxicity. *J. Hazard. M.* 261, 325–331.
- Wu, S.Q., Qi, Y.F., Yue, Q.Y., Gao, B.Y., Gao, Y., Fan, C.Z., He, S.B., 2015. Preparation of ceramic filler from reusing sewage sludge and application in biological aerated filter for soy protein secondary wastewater treatment. *J. Hazard. M.* 283, 608–616.
- Xue, S., Zhao, Q.L., Wei, L.L., Ren, N.Q., 2009. Behavior and characteristics of dissolved organic matter during column studies of soil aquifer treatment. *Water Res.* 43, 499–507.
- Xue, S., Wang, C., Zhang, Z.H., Song, Y.T., 2016. Photodegradation of dissolved organic matter in ice under solar irradiation. *Chemosphere* 144, 816–826.
- Yang, X., Meng, F., Huang, G., Sun, L., Lin, Z., 2014. Sunlight-induced changes in chromophores and fluorophores of wastewater-derived organic matter in receiving waters-The role of salinity. *Water Res.* 62, 281–292.
- Ye, Z.F., Ni, J.N., 2002. Performance comparison between the immobilized and the dissociated microorganisms in wastewater treatment. *J. Basic Sci. Eng.* 10, 325–331.
- Zhang, T., Lu, J., Ma, J., Qiang, Z., 2008. Fluorescence spectroscopic characterization of DOM fractions isolated from a filtered river water after ozonation and catalytic ozonation. *Chemosphere* 71, 911–921.
- Zhang, X.Y., Zheng, S.K., Xiao, X.Z., Wang, L., Yin, Y.J., 2017. Simultaneous nitrification/denitrification and stable sludge/water separation achieved in a conventional activated sludge process with severe filamentous bulking. *Bioresour. Technol.* 226, 267–271.