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PAPER

Disinfection by-product formation potentials in wastewater effluents and their reductions in a wastewater treatment plant

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Disinfection by-product formation potentials (DBPFPs) in wastewater effluents from eight wastewater treatment plants (WWTPs) were investigated. In addition, a WWTP with one primary effluent and two different biological treatment processes was selected for a comparative study. Formation potential tests were carried out to determine the levels of DBP precursors in wastewater. WWTPs that achieved better organic matter removal and nitrification tended to result in lower DBPFPs in effluents. For the WWTP with two processes, haloacetic acid, trihalomethane, and chloral hydrate precursors were predominant DBP precursors in the primary and secondary effluents. The percent reductions of haloacetonitrile and haloketone formation potentials averaged at 96% which was high in comparison to the reductions of other classes of DBPFPs. In addition, biological treatment changed the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The eight plant survey and the comparative analysis of the WWTP with two processes implied that besides nitrification, there may be other confounding factors impacting DBPFPs. Oxic and anoxic conditions, formation and degradation of soluble microbial products had impacts on the DBPFP reductions. This information can be used by water and wastewater professionals to better control wastewater-derived DBPs in downstream potable water supplies.

Introduction

In recent years, increased wastewater discharges pose a serious threat to drinking water supplies.[1,2] As rivers, lakes and groundwater are accepting an increasing amount of treated wastewater, drinking water quality is affected and a notable impact on disinfection byproduct (DBP) precursors was observed.[3] Some DBPs are carcinogenic and have been regulated.[4,5] The removal of DBP precursors in drinking water treatment systems is required under the EPA Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) rule,[6] which specifies the criteria for removing DBP precursors measured as total

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organic carbon (TOC). Although the National Pollutant Discharge Elimination System (NPDES) regulates some trihalomethanes (THMs) (*e.g.* chloroform) in wastewater effluents, currently, there are no regulations on DBP precursor removal by wastewater treatment plants (WWTPs). It is still an important research area because the presence of various chlorine-reacting species such as ammonium, organic carbon, organic nitrogen, and bromide in wastewater effluents can lead to the formation of various DBPs at high levels upon chlorination.[7–12] Sirivedhin and Gray[13] found that wastewater effluent discharge to surface water significantly impacted the quantity and quality of organic materials at various downstream locations. As the public concerns about the water quality grow, downstream water treatment utilities are facing challenges from the DBP precursors in wastewater effluents.

Assessment of DBP precursors can be completed by a formation potential (FP) test,[14–19] which measures the extent of the

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Environmental impact

Wastewater is a source of various disinfection by-product (DBP) precursors. Biological treatment processes in wastewater treatment plants may show different performance in DBP precursor removal, but the levels of DBP precursors and their removal efficiencies have not been investigated. The paper aims to expand our knowledge regarding DBP precursor removal by biological treatment processes. This is an important survey of DBP precursors in treated wastewater as the public concerns about the wastewater-derived DBPs in downstream potable water supplies are increasing.

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organic material in a water or wastewater sample in forming DBPs under a set of controlled conditions and in the presence of excess free chlorine. The DBP precursors in wastewater are generally estimated by analyzing the FPs of the DBPs, including THMs, haloacetic acids (HAAs), oxygenated DBPs and nitrogenous DBPs. Because wastewater organics are substantially different from the natural organic matter in drinking water, the types and amounts of DBPFPs in wastewater can be different from those found in drinking water.[20] Krasner et al.[21] explored the impact of wastewater treatment processes on DBP precursors and concluded a profound impact of nitrification on effluent quality including organic carbon, organic nitrogen, and DBP precursors. Galapate et al.[22] found that the hydraulic retention time (HRT) and mixed liquor suspended solids (MLSS) were two parameters that could affect THM precursors and chemical properties of organic matter in the effluents of an activated sludge process. As WWTPs employ different biological processes, they may result in a wide range of DBP precursors in treated wastewater. Furthermore, the removal efficiencies of DBP precursors during the biodegradation processes remain unclear; therefore, there is a need for a comprehensive study.

In this study, a survey of DBPFPs was conducted on WWTP effluents from systems with different levels of organic removal and nitrification. In addition, the survey focused on a WWTP, which employs two different biological processes to treat the same wastewater influent. The objectives were (1) to compare the levels of DBPFPs in wastewater effluents of different biological treatment processes; and (2) to explore the DBPFP reduction efficiencies by the WWTP with different biological treatment processes. The target species of DBPFPs were chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (BF), chloral hydrate (CH), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), chloropicrin (CP), 1,1-dichloro-2-propanone (DCP), and 1,1,1-trichloro-2-propanone (TCP). Since some of these compounds such as THM and HAA species are regulated in drinking water and wastewater, the research into THMs and HAAs is of particular interest.

Materials and methods

WWTPs surveyed

Eight domestic WWTPs in Pennsylvania, USA were selected for a survey of DBPFPs in treated wastewater. Grab samples of secondary effluents prior to disinfection were collected at these plants. All WWTPs had grit removal and primary treatment. A description of secondary treatment by the WWTPs is presented in Table 1. Due to the different biological treatment processes, the WWTPs produced various effluent qualities as were evaluated by the levels of carbon, nitrogen and DBPFPs. Dissolved organic carbon (DOC) was measured by a Total Organic Carbon Analyzer (O.I. Analytical Model 1010, Texas, United States). Ammonia nitrogen (NH_3-N) was measured by using an ammonium ion-selective probe following the protocols described

Table 1 Description of the eight surveyed WWTPs

WWTP	Capacity ($m^3 s^{-1}$)	Biological treatment processes
#1	0.088	Conventional activated sludge
#2	1.65	Pure oxygen activated sludge
#3	0.092	Trickling filter
#4	0.22	Anoxic–oxic activated sludge
#5	0.096	Conventional activated sludge
#6	0.033	Contact stabilization and extended aeration
#7a[a]	0.088	Oxic–anoxic–oxic activated sludge
#7b[a]	0.088	Trickling filter and activated sludge in tandem
#8	0.26	Anaerobic–anoxic–oxic activated sludge

[a] Plant 7 had two different biological treatment processes.

in Standard Method 4500-NH_3 D.[14] The protocols for DBPFP measurements are described in later sections.

The WWTP

The Pennsylvania State University WWTP (University Park, Pennsylvania, USA), which was listed as Plant #7 in Table 1, was selected as a WWTP for a comparative study. The plant has a treatment capacity of 0.18 $m^3 s^{-1}$. It accepts domestic wastewater from The Pennsylvania State University – University Park campus and a portion of State College Borough, Pennsylvania. The WWTP provides primary treatment, carbonaceous oxidation, nitrification, and denitrification. Wastewater receives preliminary treatment via vortex grit removal and primary treatment with primary clarifiers prior to the secondary treatment. It has two independent process trains to treat the same primary effluent. Approximately, 50% of the flow is treated by a trickling filter and a modified Ludzack–Ettinger activated sludge process (TF/MLE) that operate in tandem while the other 50% is treated by an oxic–anoxic–oxic activated sludge process (ASP). The influent to the TF/MLE side is split between two parallel-operating trickling filters and the anoxic zone of an MLE process. The trickling filter effluent and anoxic zone effluent are combined and enter the aerobic reactors of the MLE process, from which a mixed liquor recycle feeds nitrate to the MLE anoxic zone. The ASP side flow enters an oxic reactor of the activated sludge process, and then it sequentially enters an anoxic zone and a second oxic reactor. Grab samplings of the process trains from eleven sampling points were finished in 2 hours. The eleven sampling points are illustrated in Fig. 1, which included effluents of all secondary treatment units.

Sample preservation and the FP test

Samples collected from the WWTP were chilled at 4 °C and transported to the laboratory immediately. Upon arrival at the laboratory, samples were filtered (0.45 μm) and acidified to pH < 2 by adding a few drops of concentrated sulfuric acid. Samples were then stored at 4 °C until analysis.

The DBPFP test was conducted by applying a chlorine dose of 20 mg L^{-1} to diluted and phosphate-buffered samples (pH 7). The dilution ratio was determined based on the ammonia level to accommodate chlorine demand, as described by Tang et al.,[23] which ensured that free chlorine residuals remained after
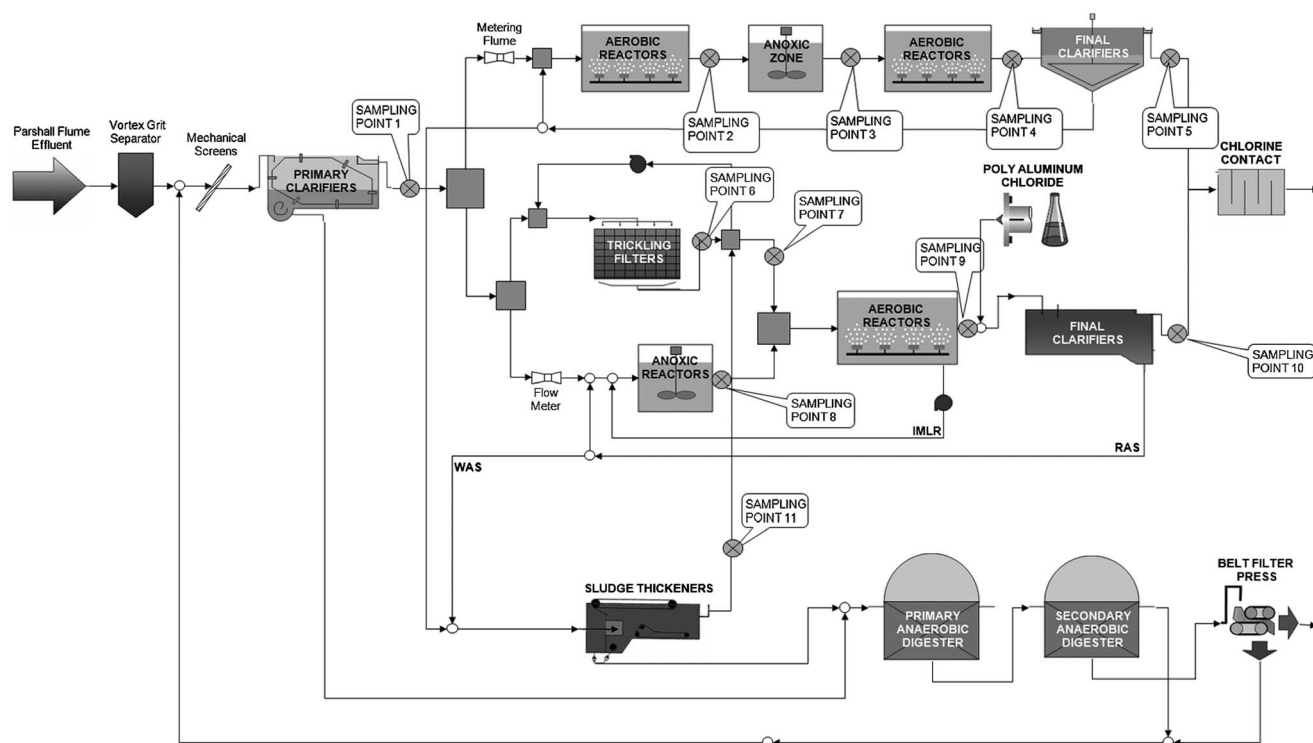
Fig. 1 Flows and sampling points of the WWTP with two processes.

incubation. The incubation was completed at 25 °C in amber glass bottles for 3 days in the absence of light. Then samples were transferred to 40 mL vials containing granular ammonium chloride to quench the free chlorine residuals. The vials were sealed with PTFE-lined screw caps without headspace and stored at 4 °C before extractions.

DBP extractions and measurements

Sample extractions were conducted using modified EPA Methods 552.3 and 551.1. For HAAs, each 30 mL sample was acidified with 1.5 mL concentrated sulfuric acid and extracted with 3 mL of MTBE spiked with 300 μg L^{-1} 1,2-dibromopropane. Approximately 12 g of sodium sulfate was added to enhance the extraction efficiency. Then, 1 mL of the MTBE extract was mixed with 1 mL of 10% sulfuric acid–methanol mix, and incubated for two hours at 50 °C for HAA derivatization. After derivatization, the solution was back-extracted with 4 mL of 10% sodium sulfate solution to remove excess methanol. For other DBPs, each 30 mL sample was treated using the protocols above excluding pre-extraction acidification and post-extraction methylation.

The concentrations of DBPs were determined using gas chromatographs (Hewlett Packard 6890) with electron capture detectors. A DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for HAA analysis. A DB-1 capillary column (30 m × 0.32 mm i.d., 1.0 μm film thickness) was used for the analysis of other DBPs. The temperature ramping programs were as follows: (1) HAAs: initial at 35 °C for 10 minutes, ramp to 75 °C at 5 °C min^{-1} and hold for 15 minutes, a second ramp to 100 °C at 5 °C min^{-1} and hold for 5 minutes,

and a final ramp to 135 °C at 5 °C min^{-1} and hold for 5 minutes; (2) other DBPs: initial at 35 °C for 22 minutes, ramp to 145 °C at 10 °C min^{-1} and hold for 2 minutes. Minimum reporting levels (MRLs) for the DBPs were determined to be 1.0 μg L^{-1}.

Data and statistical analysis

Duplicate samples were analyzed and the average data are presented. The standard deviations were below 10% of the average value. For comparisons of the surveyed WWTPs, statistical methods were implemented using Minitab version 15 (State College, Pennsylvania, USA). The nonparametric Mann–Whitney procedure was used and the level of significance was set to $p < 0.05$.

Results and discussion

Effluents of the eight WWTPs

Carbon and nitrogen levels. The carbon content was evaluated by DOC in this study. The DOC levels of the eight WWTP effluents were in the range of 5.1 and 14.3 mg L^{-1} (Table 2). The NH$_3$–N concentrations were used as a parameter to evaluate the process efficiencies on nitrification. Based on the NH$_3$–N levels, the eight surveyed WWTPs were divided into two categories: five WWTPs (Plants #1, #2, #3, #4, and #5) that had incomplete nitrification with NH$_3$–N greater than 2 mg L^{-1} and three WWTPs (Plants #6, #7a,b, and #8) that had complete nitrification with no detectable NH$_3$–N in their effluents.

Plants #1, #2, #3, #4, and #5, which belong to the category of incomplete nitrification, had relatively high DOC in their effluents. Plants #6 and #7 achieved DOC as low as 5.1 mg L^{-1} and

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Table 2 Effluents of the eight WWTPs

WWTP effluent	DOC [mg L^{-1}]	NH$_3$–N [mg L^{-1}]	HAAFP [μg L^{-1}]	THMFP [μg L^{-1}]	HAA yield [μg per mg C]	THM yield [μg per mg C]
#1	8.9	4.1	400	310	45	35
#2	9.1	3.6	710	280	78	31
#3	8.9	3.2	700	290	79	33
#4	9.5	4.3	630	280	66	29
#5	8.9	4.3	500	250	56	28
#6	5.1	ND^a	320	130	63	25
#7a	7.2	ND^a	350	250	49	35
#7b	6.3	ND^a	300	200	48	32
#8	14.3	ND^a	540	500	38	35

^{a} ND: no detectable. Data presented are average values of duplicate sets.

6.3 mg L^{-1}, respectively, and no detectable NH$_3$–N in their effluents, indicating that the two WWTPs had superior performances on organic matter removal and nitrification. This also implies that while nitrification proceeds to completion, additional organic matter removal could be observed. An exception to this was Plant #8, which had complete nitrification but also showed the highest DOC (14.3 mg L^{-1}) among the eight surveyed WWTPs. This was related with the tertiary membrane system in Plant #8. The membrane treated a portion of the plant's secondary effluent, which rejected 99% of organics and recycled them to the primary effluent. The high DOC observed in the secondary effluent of Plant #8 was likely associated with the return of rejected unbiodegradable organics.

DBPFP levels. For all eight WWTPs, the data showed that their effluents had higher HAAFPs than THMFPs and the ratios of HAAFP and THMFP scattered in a range from 1.1 to 2.5. Bougeard et al.[24] found that the concentrations of THMs correlate well with HAAs in drinking water during an FP test, and they suggested that there is slightly more than 1 mg of HAAs formed for 1 mg of THM formation. However, no correlation could be found between THMs and HAAs in the FP test for the wastewater effluents. In this study, the results indicate that there were more HAA precursors than THM precursors in the wastewater effluents. In addition, the ratios between HAAFP and THMFP were not stable. This was possibly due to the characteristics of wastewater organics. Sirivedhin and Gray[13,20] found that the structural characteristics of wastewater organics differed from the natural organic matter (NOM) found in surface water and they concluded that the structural differences (e.g. phenonic and nitrogen signatures) associated with wastewater organics correspond to the different classes of DBPFPs. The wastewater effluents may have different combinations of aromatic and aliphatic structures, thus showed a non-linear relationship between HAAFP and THMFP.

Plants #6 and #7, which achieved the best organic matter removal and complete nitrification among the eight surveyed plants, also had low DBPFPs including HAAFPs (320 and 300 μg L^{-1}, respectively) and THMFPs (130 and 200 μg L^{-1}, respectively) in their effluents. On the other hand, Plants #1, #2, #3, #4, and #5, which had high organic matter levels and incomplete nitrification, had high DBPFPs. The HAAFPs of these five WWTPs ranged between 400 and 710 μg L^{-1}, and the THMFPs ranged between 250 and 310 μg L^{-1}. The results were partially in agreement with Krasner et al.[21] which concluded a relationship between nitrification and DBPFP. Because of the FP test which ensures high residuals of free chlorine in the wastewater effluent samples after chlorination, this study implied that complete nitrification was related with low DBPFPs in wastewater effluents. An exception to this was still Plant #8, which had extraordinarily high THMFP in its effluent though it achieved complete nitrification. This was likely due to the high concentrations of rejected organics, which were classified as recalcitrant organic matter,[25] from the recycled flow of the tertiary membrane system. The hydrophobic portions of those organics had been related with THM precursors.[22,26–28]

DBP yields. DBP yields normalize the DBPFPs based on the organic matter concentrations.[29] A low DBP yield in wastewater effluent would indicate low reactivity of wastewater organics in forming DBPs. No significant difference of DBP yields was found in effluents between completely nitrified plants and incompletely nitrified plants. The authors also studied the DBP yields of waters containing various levels of humic acid, a component of NOM, and found that the DBP yield was 150 μg per mg C based on the FP test, which was higher than the DBP yields of these wastewater effluents. This was in agreement with Sirivedhin and Gray,[20] which concluded a low reactivity of wastewater organics in forming DBPs.

By investigating the DBPFP levels in effluents of the eight WWTPs, the research data support that a biological treatment process that is able to achieve better organic matter removal and complete nitrification (e.g. Plants #6 and #7) tends to result in lower DBPFPs in the effluent.

The WWTP with two processes

Although all eight WWTPs mainly treat domestic wastewater, it would be difficult to compare their reduction efficiencies on DBPFPs because of their variable influent qualities. It is necessary to investigate a WWTP with different biological treatment processes receiving the same primary effluent.

Primary effluent. The primary effluent with a chemical oxygen demand (COD) of 268 mg L^{-1} and DOC of 52.7 mg L^{-1} was fed into the secondary treatment facilities of the WWTP. Because the NH$_3$–N level was in the 25 mg L^{-1} range, a high dilution ratio (1 : 50) was applied to accommodate a 3-day chlorine demand.[23]

Results of the DBPFP test (Table 3) show that the wastewater prior to biological treatment was high in DBP precursors. HAA, THM and CH precursors were in predominant concentrations. The chlorinated primary effluent had 2000 μg L^{-1} HAAFP, 1080 μg L^{-1} THMFP and 990 μg L^{-1} CHFP. MCAA, MBAA, DBAA, DBCM, BF, DCP, TCAN, BCAN and DBAN were below the MRLs in chlorinated samples during the DBPFP test. The specific ultraviolet absorbance (SUVA) of the primary effluent was 0.89 L mg^{-1} m^{-1}. Because a SUVA lower than 2 L mg^{-1} m^{-1} indicates non-humic organic matter in drinking water systems,[1] the wastewater organics in the primary effluent tended to be non-humic since they were predominantly biodegradable organic matter. The low DBP yield (81 μg per mg C) indicates a low reactivity of these wastewater organics in the primary effluent in forming DBPs during the DBPFP test.

Secondary effluents. Because both the ASP and TF/MLE treated the same primary effluent, the qualities of their secondary effluents can be compared. The SRTs of the ASP and the MLE in the TF/MLE side were 11.9 and 12.3 days, respectively. The long SRTs ensured complete nitrification in both systems. Therefore, NH$_3$–N was not detected in their secondary effluents. However, their carbon removal capabilities were different ($p < 0.05$). The TF/MLE had lower DOC in secondary effluent compared to the ASP, indicating that the TF/MLE was more efficient in organic matter removal.

The two processes also appeared to behave differently on DBPFP reduction efficiencies. The TF/MLE tended to result in lower DBPFPs (710 μg L^{-1}) in secondary effluent in comparison to the ASP (780 μg L^{-1}). However, the difference was not significant ($p > 0.05$). The HANFP and HKFP had the highest reduction efficiencies (averaged at 96%) by both systems compared to the FPs of other DBP species. This was likely due to the properties of the precursors. The HK precursors are primarily small molecules such as ketones which were easily biodegradable.[30] Therefore, greater removal efficiencies could be achieved compared to those more recalcitrant compounds such as HAA precursors and THM precursors.

The DBPFP speciation profile was changed after the secondary treatment. The relevant abundance of two major DBP precursors in wastewater (HAA and THM precursors) was presented by the HAAFP/THMFP ratio. The results demonstrated different ratios before (1.9 : 1 for primary effluent) and after (1.5 : 1 for ASP effluent and 1.4 : 1 for TF/MLE effluent) the secondary treatment. The ratio change by the secondary treatment was significant ($p < 0.05$). This implies that the HAA precursors were likely more associated with those biodegradable organic matters in the primary effluent and thus more HAA precursors were removed by the secondary treatment than THM precursors.

Although the DBPFPs were reduced by both systems, the DBP yields increased from 81 to 102 μg per mg C for the ASP and to 127 μg per mg C for the TF/MLE. The increased DBP yield by the secondary treatment implies a higher reactivity of the wastewater organics in forming DBPs after biological treatment. The increased reactivity was possibly due to the fact that the

Table 3 Primary effluent and secondary effluents of the model WWTP[a]

Parameter	Primary effluent	ASP effluent	TF/MLE effluent	ASP removal efficiency (%)	TF/MLE removal efficiency (%)
MCAAFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
MBAAFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
DCAAFP [μg L^{-1}]	1280	200	180	84	86
TCAAFP [μg L^{-1}]	700	170	150	75	79
BCAAFP [μg L^{-1}]	25	19	21	24	16
DBAAFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
CFFP [μg L^{-1}]	1080	260	250	76	77
BDCMFP [μg L^{-1}]	4	<MRL	<MRL	100	100
DBCMFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
BFFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
CHFP [μg L^{-1}]	990	120	110	88	89
TCANFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
DCANFP [μg L^{-1}]	56	3	2	95	96
BCANFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
DBANFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
DCPFP [μg L^{-1}]	<MRL	<MRL	<MRL	NA	NA
TCPFP [μg L^{-1}]	99	4	4	96	96
CPFP [μg L^{-1}]	18	5	3	72	83
HAAFP [μg L^{-1}]	2000	390	350	80	83
THMFP [μg L^{-1}]	1080	260	250	77	78
HANFP [μg L^{-1}]	56	3	2	95	96
HKFP [μg L^{-1}]	99	4	4	96	96
DBPFP [μg L^{-1}]	4250	780	710	82	83
DOC [mg L^{-1}]	53	7.7	5.6	85	89
DBP yield [μg per mg C]	81	102	127	−26	−58
NH$_3$–N [mg L^{-1}]	23.7	0.0	0.0	100	100
UV$_{254}$ [cm^{-1}]	0.469	0.119	0.095	75	80
SUVA [L mg^{-1} m^{-1}]	0.89	1.55	1.70	−74	−91
HAAFP/THMFP	1.9	1.5	1.4	19	25

[a] MRL: minimum reporting level. NA: not available. Data presented are average values of duplicate sets.

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organic matter that was less associated with DBP precursors (*e.g.* non-humic biodegradable organics) was preferentially removed by the secondary treatment. Therefore, the TF/MLE side, which removed more organic matter, resulted in higher DBP yield than the ASP. The SUVA, which can be used to predict DBP formation in drinking water systems,[31,32] was positively correlated with the change of DBP yield in wastewater, because the SUVA also increased from 0.89 to 1.55 L mg^{-1} m^{-1} for the ASP and to 1.70 L mg^{-1} m^{-1} for the TF/MLE. As the SUVA and DBP yield increased, the effluent organic matter tended to have more-humic constituents relative to the primary effluent.

The reductions of DBPFPs by the WWTP indicate that the TF/MLE was more efficient at DOC removal and tended to have higher DBP precursor removal potential. The secondary treatment reduced higher percentages of HKFP and HANFP than the FPs of other DBP species and affected the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yield and SUVA increased after secondary treatment, indicating that the residual organic matter was less biodegradable and could contain more humic-like constituents.

Implications of the process impact

Nitrification. This research indicates that there is a trend between nitrification and DBPFPs. However, other factors may confound and make contributions to DBPFPs. The impact of nitrification on DBP precursors in treated wastewater was evaluated by Krasner *et al.*[21] Our survey results show that the WWTPs that achieved complete nitrification tended to result in lower HAAFPs (Fig. 2a). However, the trend for the THMFPs may be different, because the range of THMFPs in the effluents of the surveyed WWTPs was 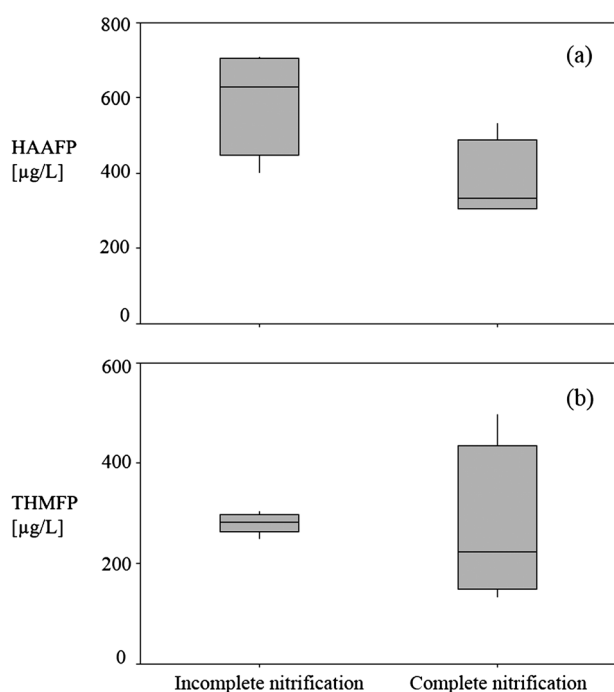relatively wide (Fig. 2b). Since WWTPs normally achieved nitrification by using long SRTs, it is suspected that the SRT may also have impact on the THMFPs, because long SRTs lead to low COD in wastewater effluents. Investigations on the effect of SRT on DBPFP reduction by secondary treatment can be further explored.

Oxic and anoxic conditions. For the model WWTP, the discussion on the DBPFP reduction efficiencies by exploring the start point and end points of secondary treatment presented the effectiveness of the two processes. Furthermore, as each process consisted of one or more reactors, the fate of DBP precursors during the secondary treatment can also be studied. A comparative analysis was conducted by dividing the secondary treatment reactors of the model WWTP into two stages: (1) Stage 1 included the reactors which directly accepted primary effluent. The first oxic tank in the ASP, the trickling filter and the anoxic tank in the TF/MLE were included. These reactors had the primary effluent and recycled flows as influent and their influent organic matter concentrations were relatively high; (2) Stage 2 included the second reactor (the anoxic tank) and the third reactor (the second oxic tank) in the ASP, and the second reactor (the oxic tank) in the TF/MLE. These reactors accepted influents after Stage 1 biological treatment and therefore had relatively low organic matter concentrations. The effects from recycled flows were included by discussing DBP precursor removal in mass per unit influent flow, so that the amount of removed DBP precursors by each reactor can be determined. By defining Stage 1 and Stage 2 reactors, one may obtain some other confounding factors that contribute to DBPFPs.

Comparisons of the Stage 1 reactors showed that the oxic and anoxic conditions of the reactors impacted the DBPFP reduction. The first tank in the ASP and the trickling filter in the TF/MLE side, which were oxic and partially oxic reactors, respectively, reduced more DBPFPs from the primary effluent than the anoxic tank in the TF/MLE (Fig. 3a). The reductions of HAAFP, THMFP, and CHFP were greater than HANFP and HKFP, because the masses of the first three precursors were predominant in the primary effluent. For percent reductions (Fig. 3b), the order of reduction efficiencies were: the first oxic tank in the ASP > the trickling filter in the TF/MLE > the anoxic tank in the TF/MLE. It was speculated that the oxic condition of the first tank in the ASP was favourable for the biodegradation of DBP precursors. The trickling filter in the TF/MLE, which has the combination of oxic and anoxic conditions, had less DBPFP reduction than the first tank in the ASP. The presence of anoxic condition in the trickling filter could be the cause for the inhibition of DBP precursor removal. This may be correlated to the associated electron acceptors, which affect the released energy and the versatility of bacterial uptake of the organics associated with DBP precursors. One could also deduce that due to the anoxic condition, no significant overall DBPFP reduction was observed in the anoxic tank in the TF/MLE. Some DBPFPs (*e.g.* THMFP, HANFP, and HKFP) even showed slight increase after treatment by the anoxic reactor. Although HANFP and HKFP had low concentrations, their reduction percentages (Fig. 3b) were high (82% and 92%, respectively, by the Stage 1's oxic reactor in the ASP). This is in accordance with the previous discussion on the HANFP and HKFP reductions by secondary treatment, because the HAN and HK precursors are readily
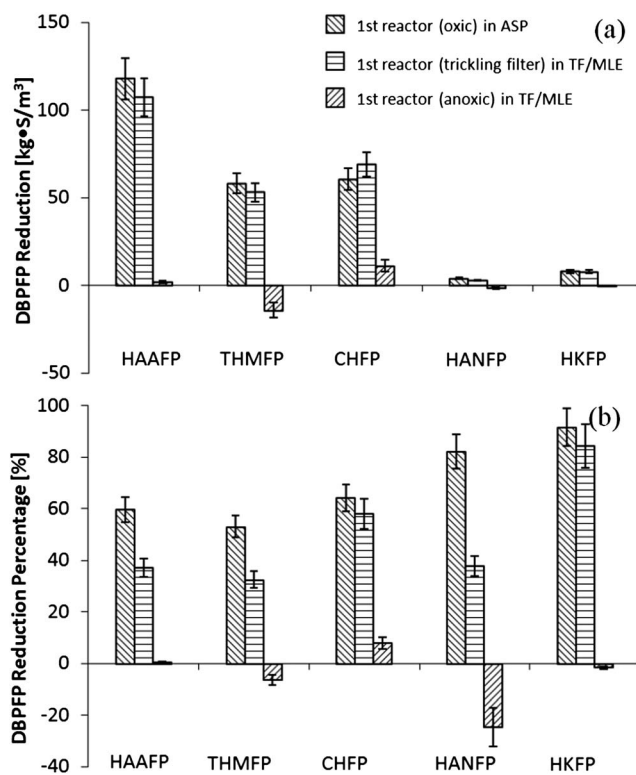

Fig. 2 Correlations between nitrification and DBPFPs including (a) HAAFP and (b) THMFP in treated wastewater.

Fig. 3 (a) DBPFP reductions and (b) DBPFP reduction percentages by the Stage 1 reactors.

Fig. 4 Change of DBP yields by the Stage 2 reactors.

biodegradable compounds and can be easily removed by oxic reactors in secondary treatment.

Soluble microbial products (SMPs). SMPs are intermediates and end products of various metabolic pathways and materials from cell lysis and death.[33] It has been discussed[34] that there are two classes of SMPs: utilization-associated products (UAPs) and biomass-associated products (BAPs). UAPs are the intermediate and end products of biodegradation which can be degraded further. BAPs are formed in part due to cell lysis and they are biodegraded more slowly. SMPs can react with chlorine and are found to be associated with wastewater-derived DBP precursors.[29]

As the Stage 1's two oxic reactors (the first reactor in the ASP and the trickling filter in the TF/MLE) removed the majority of readily biodegradable organics and some recalcitrant organics, the impact of SMPs on DBPFPs became significant in the Stage 2 reactors. The positive bars in Fig. 4 demonstrated that some DBP yields (e.g. the HAA and THM yields) increased significantly by the second oxic tank in the TF/MLE and the third tank (oxic) in the ASP. The increased reactivity in forming DBPs implies that new DBP precursors may have been generated. The generation of new DBP precursors could be attributed to the formation of SMPs. Because BAPs are biodegraded slowly, it is speculated that BAPs are associated with the majority of the remaining DBP precursors (e.g. HAA and THM precursors) in treated wastewater and could be the reason for the DBP yield increase.

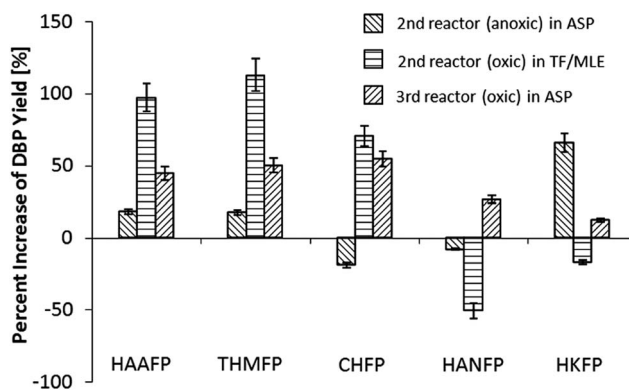The negative bars in Fig. 4, however, demonstrated decreases in some DBP yields (e.g. the CH, HAN and HK yields) after

treatment by the Stage 2 reactors. The decreased reactivity in forming these DBPs indicates that the newly formed precursors from SMPs were further degraded, which was likely due to the UAPs being associated with the HK and HAN precursors. They are intermediate products of biodegradation. In addition, they are readily biodegraded and do not contribute to DBP precursors in the long term view.

Conclusions

The following conclusions were obtained from this study:

(1) There was a relationship between nitrification and DBPFP reduction. WWTPs with better organic matter removal and complete nitrification in secondary treatment tend to result in lower DBPFPs in the effluents.

(2) HAA, THM and CH precursors were predominant in primary effluent and secondary effluents of the WWTP with two processes. Secondary treatment was able to reduce more HKFP and HANFP by percentages than other classes of DBPFPs, and affected the DBPFP speciation profile by lowering the HAAFP/THMFP ratio. The DBP yields and SUVA increased after secondary treatment, indicating that the residual organic matter contained more humic constituents.

(3) The eight plant survey and the comparative analysis of the plant with two processes led to three implications of the process impact: (a) besides the relationship between nitrification and DBPFP removal, there may be other confounding factors (e.g. SRT and COD); (b) oxic and anoxic conditions had an impact on the DBPFP reduction. The oxic condition was more favourable than the anoxic condition on DBPFP reduction; (c) formation and degradation of SMPs had an impact on DBP precursors by changing the DBP yields.

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