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Biodegradation and Biotransformation of Wastewater Organics as Precursors of Disinfection Byproducts in Water

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Abstract

Laboratory experiments were carried out to investigate wastewater organics as the precursors of disinfection byproducts (DBPs) in drinking water supply. The focus was on the change in wastewater DBP precursors during biological degradation under simulated natural conditions. The wastewater and its treated secondary effluent were characterized for DBP formation potential (DBPFP) and DBP speciation profile, including trihalomethanes, haloacetic acids, chloral hydrate, and nitrogen-containing DBPs. Several model organic compounds, including humic acid, tannic acid, glucose, starch, glycine, and bovine serum albumin (BSA), were used to represent the different types of organic pollutants in wastewater discharge. The results show that the DBPFP of wastewater decreased after biodegradation, but the remaining organic matter had a greater DBPFP yield with chlorine. Different model organics displayed different changes in DBPFP during biodegradation. The DBPFP remained largely unchanged for the glycine solution, decreased greatly for the tannic acid and BSA solutions, and increased nearly 3-fold for the glucose and starch solutions after 10 d of biodegradation. Meanwhile, the DBPFP yield increased from 3 for glycine to 51 μg DBP mg^{-1} C for its degradation residue, and from 1 for glucose and starch to 87 and 38 μg DBP mg^{-1} C for their organic residues, respectively. Although biodegradation may effectively remove some DBP precursors, biotransformation during the process produces new DBP precursors in the form of soluble microbial products (SMPs). The experimental results reveal that SMPs may be an important source of wastewater-derived DBP precursors in natural waters.

Keywords: Biodegradation; disinfection byproducts (DBPs); DBP precursors; drinking water quality; wastewater organics; water reuse.

1. Introduction

Organic matter in the raw water supply is the primary precursor of disinfection byproducts (DBPs) in finished drinking water. The main organic DBP groups of concern include trihalomethanes (THMs) and haloacetic acids (HAAs) (Singer, 1999; Xie, 2004). It has been found that THMs, some HAA species such as dichloroacetic acid (DCAA), and other chlorinated DBPs are carcinogenic, mutagenic, and teratogenic (Bull, 1993; Koivusalo et al., 1997; Waller et al., 1998; Xie, 2004). Natural organic matter (NOM) is the major reservoir of organic DBP precursors in surface water (Singer, 1999; Chang et al., 2001; Hua and Reckhow, 2007). Numerous studies have been conducted on the characteristics, reactivity, and DBP yield of NOM following water chlorination (Singer, 1999; Xie, 2004).

Due to the worldwide decline of water resources, treated wastewater now represents a growing portion of the water supply. Many surface water bodies, such as rivers, lakes, and reservoirs, are used for both the disposal of treated wastewater and the withdrawal of fresh water for human consumption. The regulations for wastewater disposal were generally developed to protect the quality of the receiving waters and people using such waters for recreational purposes. However, there is limited information about the DBP precursors arising from wastewater discharge. Organic matter in wastewater effluent is likely to contribute to the DBP precursors of the receiving water, resulting in greater DBP formation in drinking water (Galapate et al., 1997; Galapate et al., 1999; Rostad et al., 2000; Chu et al., 2002; Krasner et al., 2009a; Krasner et al., 2009b). Hence, to ensure the safety of the drinking water supply, the problem of wastewater-derived DBP formation needs to be specifically addressed.

Moreover, discharged wastewater organics undergo further biodegradation in the

receiving water under natural conditions. During the biotransformation process, wastewater organics are expected to change in terms of their reactivity with chlorine and their DBP formation characteristics (Chang et al., 2001; Chen et al., 2009). In this experimental study, wastewater organics were characterized for their DBP formation potential (DBPFP) and the resulting DBP speciation in chlorinated water. The process of biological organic degradation was conducted under laboratory conditions, and several model organics, including carbohydrates, proteins, humic acid, tannic acid, and glycine, were used to simulate organic pollutants. The aims of the study were to determine the DBPFP of different types of organic substances in wastewater and the resulting DBP species, and to investigate the changes in the DBP formation behavior of different wastewater organics during the biodegradation process.

2. Materials and Methods

2.1 Wastewater samples

Wastewater samples of raw sewage and secondary effluent were collected from a full-scale municipal biological sewage treatment plant (Stanley Sewage Treatment Works, Hong Kong). The activated sludge process was adopted in the treatment system, which had a sludge age of around 15 d and produced an effluent with a BOD of around 5 mg L^{-1} and a suspended solids (SS) concentration of about 5 mg L^{-1}. The raw sewage influent had a BOD of 130 mg L^{-1}, an SS of about 70 mg L^{-1}, a dissolved organic carbon (DOC) of 40 mg L^{-1}, and a UV absorbance at 254 nm (UV_{254}) of 0.201 cm^{-1}. The secondary effluent had a DOC of 14 mg L^{-1} and a UV_{254} of 0.077 cm^{-1}. The wastewater samples were filtered immediately after

collection through 0.45 μm filter paper to remove any suspended matter, and the filtrates were stored in a refrigerator at 4 °C for later experimental use.

2.2 Model wastewater organic compounds

Six types of model organic chemicals were chosen to simulate the typical organic components found in municipal wastewater. They included humic acid (product no. 2S101H, IHSS Suwannee River Standard, St. Paul, MN, USA), tannic acid (Sigma, St. Louis, NC, USA), glucose (Unichem, Haw River, MO, USA), starch (Riedel-de Haen, Seelze, Hanover, Germany), glycine (BDH, Yorkshire, UK), and bovine serum albumin (BSA) (USB, Cleveland, OH, USA). Humic acid usually results from organic degradation and plant mineralization, and tannic acid is one of the humic precursors in organic degradation. Both types of chemical substances have been found at various levels in wastewater (Dignac et al., 2000). Carbohydrates and proteins are believed to be the two predominant organic groups in wastewater (Dignac et al., 2000; Dignac et al., 2001). In this study, glucose and starch were used to represent the carbohydrate group. Glucose is the simplest carbohydrate molecule, and starch is a polymeric carbohydrate with the molecular structure $(C_6H_{10}O_5)_n$. BSA is a typical protein used in numerous commercial products, and the amino acid glycine (NH_2-CH_2-COOH) is one of the simplest protein degradation products. Each model organic was dissolved in water to make a synthetic wastewater solution sample for the DBP study. The water used for making the organic solutions was ultrapure water produced by the Milli-Q water purification system (Millipore, Billerica, MA, USA). The initial DOC concentrations of the humic acid and tannic acid solutions were set at 3 and 10 mg L^{-1}, respectively, and the

initial DOC concentrations of the other four organic solutions were all 80 mg L^{-1}.

2.3 Organic degradation experiment

The natural degradation of the wastewater organics and the model organic compounds was simulated in a temperature-controlled incubator at 20 °C. The setup and approach of the biodegradation experiment were similar to those used for the conventional BOD test. The biodegradation of the sample solutions was carried out in a batch reactor with an initial water volume of 5 L and placed in a BOD incubator (Velp Scientifica, Usmate, Italy). N, P and trace nutrients were added to the model organic solutions according to the guidelines given by Velp Scientifica for running the BOD test with its incubation setup. The activated sludge from the sewage treatment works was dosed as the seed biomass into the bio-reactors at an initial SS concentration of 2 mg L^{-1}. Aeration was conducted by air pumps to provide oxygen to the water, and the water pH was controlled at about 7 with a phosphate buffer consisting of 8.5 g L^{-1} KH_2PO_4, 33.4 g L^{-1} $Na_2HPO_4 \cdot 7H_2O$, and 21.7 g L^{-1} K_2HPO_4. During the biodegradation experiment, mixed solution samples were collected from a bioreactor after 1, 2, 3, 4, 5, 7, and 10 d. Two duplet samples of 250 mL each were withdrawn each time from a reactor. The samples were filtered through 0.45 μm membranes to remove any suspended solids before the subsequent DBP formation potential tests.

2.4 Determination of the DBPFP

The DBPFP of the wastewater organics was measured for the water samples after different periods of biodegradation. DBP formation tests were carried out on the filtered

water samples upon chlorine disinfection in accordance with the Standard Methods (APHA, 1998). For each DBPFP test, a 100 mL water sample was chlorinated with NaOCl, and the resulting solution incubated for 7 d at pH 7.0±0.2 with a 0.5 M phosphate buffer. The dose of NaOCl was determined such that a free chlorine residue of between 3 and 5 mg L^{-1} in the water would be ensured by the end of the incubation period (APHA, 1998). After chlorination, the samples were sealed without headspace in a container with a Teflon-lined screw cap and incubated in the dark at 25±0.5 °C. Immediately after the 7-d incubation, excess chlorine in the water samples was quenched with 10% Na_2SO_3, and the DBP compounds formed were extracted and measured.

An HP 6890 gas chromatograph (GC) (Agilent, Santa Clara, CA, USA) coupled with an HP electron capture detector was used to analyze the DBP compounds (Li and Chu, 2003). The GC system was equipped with a DB-35MS capillary column (Agilent) with a configuration of 30 m × 0.32 mm and a film thickness of 0.25 µm. An HP 6890 Series automatic liquid sampler was used for the sample injection, and an HP GC ChemStation was used for the data processing. For the liquid-liquid extraction and GC procedure, the samples were analyzed for the following types of DBP compounds: THMs such as chloroform (CF), HAAs such as DCAA and trichloroacetic acid (TCAA), trihaloacetaldehydes such as chloral hydrate (CH), halopropanones such as trichloropropanone (TCP), and nitrogen-containing DBPs (N-DBPs) including haloacetonitriles such as dichloroacetonitrile (DCAN) and trihalonitromethanes such as trichloronitromethane (TCNM).

The method of liquid-liquid extraction and GC analysis for the THMs, trihaloacetaldehydes, halopropanones, and N-DBPs was developed according to EPA Method

551.1 (USEPA, 1995) that had been used by others (Weber et al., 2005; Hua et al., 2006). Methyl tert-butyl ether (MTBE) was used as the solvent for liquid extraction, and the chemicals extracted in the solvent were analyzed by the GC. One µL of the extract solution was introduced into the GC by splitless injection at 200 ºC. The carrier gas was N_2, which was delivered at a constant flow-rate of 0.8 mL min^{-1}. The initial oven temperature was set at 35 ºC and held for 9 min. The temperature was gradually increased first to 40 ºC at a rate of 2 ºC min^{-1}, then to 80 ºC at 20 ºC min^{-1}, then to 160 ºC at a rate of 40 ºC min^{-1}, held for 4 min, and finally to 200 ºC, held for 2 min. The detector temperature was set at 290 ºC for detection of the four THM compounds, trihaloacetaldehydes, halopropanones, and haloacetonitriles and trihalonitromethanes.

The method used to analyze the HAA compounds was developed based on EPA Method 552.3 (USEPA, 2003) with some modifications by others (Xie et al., 2002; Domino et al., 2004). In brief, the HAAs in the water samples were extracted with MTBE. Derivatization was then performed on the extract by adding acidic methanol at a 1:1 (v/v) ratio. One µL of the sample was introduced into the GC by splitless injection at 200 ºC. The carrier N_2 gas was maintained at a flow-rate of 0.9 mL min^{-1}. The temperature program began at 35 ºC for 10 min and increased at a rate of 5 ºC min^{-1} to 70 ºC, where it was held for 10 min, then to 120 ºC for 5 min, then to 135 ºC for 10 min, and finally to 170 ºC, where it was held for 5 min. The detector temperature was 260 ºC for the HAA detection.

2.5 Analytical methods

The SS concentration for the biomass content in a bioreactor during the wastewater

biodegradation process was measured in accordance with the Standard Methods (APHA, 1998). The UV_{254} and DOC of the organic content were measured for each water sample after filtration. UV_{254} has been used as an index of aromatic structures, which are closely related to the DBPFP of a water sample (Reckhow et al., 1990). A UV-visible spectrophotometer (UV/VIS Lambda 12, Perkin Elmer, Waltham, MA, USA) with a 1 cm cuvette cell was used to determine the UV_{254}. The DOC was determined by a TOC analyzer (IL550, Lachat, Loveland, CO, USA) using the catalytic combustion-infrared method.

3. Results and Discussion

3.1 Initial DBP formation characteristics of the wastewater and model organic compounds

Seven DBP species were detected at a significant level in the water samples tested, including CF for the THMs, DCAA and TCAA for the HAAs, CH for the trihaloacetaldehydes, TCP for the halopropanones, DCAN for the haloacetonitriles, and TCNM for the trihalonitromethanes. The last two are both N-DBPs. According to the DBPFP test, the raw wastewater and its secondary effluent and the six model organics – humic acid, tannic acid, glucose, starch, glycine, and BSA – had rather different DBPFP values upon chlorination in terms of the DBPFP yield per unit amount of DOC (Fig. 1a). Humic acid had the highest DBPFP yield at 493 μg mg^{-1} DOC, suggesting a strong DBP formation reactivity with chlorine. The DBPFP yields of tannic acid (365 μg mg^{-1} DOC) and BSA (193 μg mg^{-1} DOC) were comparably lower. The other three model organics – glucose, starch, and glycine – had much lower DBPFP yields with values of 1, 1, and 3 μg mg^{-1} DOC, respectively.

The organic matter in the actual wastewater had a DBPFP yield that was significantly lower than that of humic acid, tannic acid, and BSA but much higher than that of glucose, starch, and glycine. In comparison, the DBPFP yield of the organic in the treated wastewater effluent (47 μg mg^{-1} DOC) was higher than that of the raw wastewater (37 μg mg^{-1} DOC). Sirivedhin and Gray (2005) tested the DBPFP of the secondary wastewater effluent and found a THM yield of around of 23 μg mg^{-1} DOC and a HAA yield of about 21 μg mg^{-1} DOC. While their THM result is comparable to the value obtained for the secondary effluent in the present study, their HAA result is higher than the value of this study, probably due to the different organic composition of the wastewater effluents tested.

The speciation of the DBPs formed also varied among the model organics (Fig. 1b). For humic acid and tannic acid, the important DBPs formed included CF, CH, DCAA, and TCAA. More specifically, for humic acid CF and TCAA were the predominant DBPs, whereas tannic acid had more TCAA and DCAA than CF. For the carbohydrate organics (glucose and starch), CF was the predominant DBP, and no N-DBPs were formed due to the absence of nitrogen in the precursor molecules. In contrast, glycine produced abundant N-DBPs (DCAN and TCNM) due to the high nitrogen content in the precursor. For BSA, HAA species (TCAA and DCAA) were predominant, followed by CF and CH at similar levels of abundance, and then N-DBPs. As for the raw wastewater and its secondary effluent, the DBP speciation profiles were similar and the chlorinated DBPs formed were both dominated by CF, followed by HAAs and CH, which is consistent with the findings of Dotson et al. (2009).

3.2 Organic transformation and DBPFP dynamics during biodegradation

3.2.1 Wastewater influent and effluent

Various changes in organic content and related DBPFP values were observed after 10 d of biodegradation for the actual wastewater samples and most of the model organic solutions (Figs. 2-5). The actual wastewater influent had an initial DOC concentration of 40 mg L^{-1} and a DBPFP of 1466 μg L^{-1}. The wastewater effluent had a much lower DOC of 14 mg L^{-1} and a low DBPFP of 627 μg L^{-1} (Fig. 2). These initial wastewater DBPFP values are comparable to those reported by Chu et al. (2002), with the raw wastewater and its secondary effluent THM formation potentials (THMFP) of around 1000 and 600 μg L^{-1}, respectively.

The DOC of the wastewater influent decreased quickly to 21 mg L^{-1} in the first day of biological incubation, and it then decreased at a relatively slower rate to 11 mg L^{-1} eventually (Fig. 2a). This implies easily-degraded organics in raw wastewater were utilized firstly and refractory ones were degraded gradually thereafter. The UV_{254} decreased at a nearly constant rate (Fig. 2b). Similar to UV_{254}, the total DBPFP of the wastewater influent decreased gradually to 897 μg L^{-1} after the biodegradation (Fig. 2c). However, the mass-based DBPFP yield of the wastewater organic increased from 37 to 81 μg mg^{-1} DOC (Fig. 2d). The increase in DBPFP yield indicates that the organic residues after biodegradation had a higher DBP formation reactivity with chlorine. The DBP speciation of the wastewater influent was dominated by CF, followed by HAAs and CH, throughout the biodegradation process (Fig. 2e).

For the wastewater effluent, its DOC decreased mainly in the first day of biodegradation and showed no further degradation afterward (Fig. 2a). The UV_{254} value also decreased only

at the beginning of the biodegradation incubation (Fig. 2b). Compared to the wastewater influent, the organic in the secondary effluent was much more refractory to biodegradation. The total DBPFP of the effluent decreased from 627 to 495 μg L^{-1} after the biodegradation (Fig. 2c), whereas the DBPFP yield of the residual organic increased from 47 to 82 μg mg^{-1} DOC (Fig. 2d). Similar to the influent results, DBPFP speciation of the secondary effluent was dominated by CF and then HAAs and CH (Fig. 2f). Chen et al. (2009) investigated the fate and transport of effluent organic materials as DBP precursors in an effluent-dominated stream. They also found that the DBP precursor materials could be removed to various degrees along the length of the river.

In general, the results of wastewater biodegradation experiments indicate that biological wastewater treatment can effectively reduce the DBPFP of wastewater, which is essential for the protection of water resources. However, the organic residues after biodegradation become more recalcitrant with a greater mass-based DBPFP yield compared to the organics in raw wastewater.

3.2.2 Humic acid and tannic acid

Humic acid is the main component of NOM that is not considered to be biodegradable. As expected, the humic acid content remained largely constant throughout the biodegradation process in terms of DOC concentration, UV_{254} absorbance, and DBPFP (Fig. 3). The humic acid solution with a DOC of 3 mg L^{-1} had a high DBPFP of 1428 μg L^{-1}. The large DBPFP yield of humic acid is attributed to its abundant aromatic rings, which have been identified as a major DBP-forming molecular structure (Arora et al., 1997; Liang and Singer, 2003; Archer

and Singer, 2006). Humic acid gave rise to the formation of all seven DBP species detected in this study. The DBPFP speciation was dominated by THMs (CF), followed by HAAs (TCAA and DCAA), and then CH, and the speciation profile was not affected by the biodegradation treatment. The DBP formation result is similar to that reported by Reckhow et al. (1990) on NOM, which had an order of DBP abundance of CF ~ TCAA > DCAA (Fig. 3e).

Tannic acid is apparently readily biodegradable, and its degradation was nearly completed in the first 3 days. Tannic acid also contains abundant aromatic rings, as indicated by its high initial UV_{254} value and large DBPFP yield. The tannic acid solution with a DOC of 9 mg L^{-1} had an initial DBPFP as high as 3138 μg L^{-1}. With effective biodegradation, the UV_{254} and DBPFP values of the tannic acid solution decreased greatly after 3 d and remained at a low level thereafter (Fig. 3). The DBPFP was reduced to 500 μg L^{-1} or lower by biodegradation, which was achieved mainly by a decrease in HAA formation potential (TCAA and DCAA). The CH formation potential also decreased to a certain extent, whereas the THMFP (CF) showed little change during the biodegradation process. By the end of the 10-d degradation period, CF became the dominant DBP, followed by TCAA, resulting in a DBPFP profile rather similar to that of humic acid (Fig. 3f). The DBPFP yield of the organics in the tannic acid solution increased slightly during the biodegradation process.

3.2.3 Glucose and starch

Carbohydrates are believed to be the major components of wastewater organics (Dignac et al., 2000). Both of the model carbohydrate organics – glucose and starch – were readily degraded by microorganisms. The DOC of the organic solutions decreased rapidly from a

high level of 80 to around 10 mg L^{-1} after 4 d of biodegradation, and decreased only slightly thereafter (Fig. 4). However, the UV_{254} of the model organic solutions increased during the biodegradation process. The UV_{254} increase suggests a possible biological transformation of the carbohydrates to other organic molecules with an aromatic or double-bonding structure.

In agreement with the low initial UV_{254} values, the DBPFP values of the pure glucose (54 μg L^{-1}) and starch (74 μg L^{-1}) solutions were much lower than those of the other model organic solutions. However, the DBPFP values of the glucose and starch solutions increased considerably during the biodegradation process (Fig. 4). The DBPFP of the glucose solutions first increased more than 15 times to over 800 μg L^{-1} after 2 d of biodegradation and then decreased to a level of between 200 and 300 μg L^{-1}. The DBPFP of the starch solution increased to about 400 μg L^{-1} after 2 d and then decreased to the level of 200-300 μg L^{-1}. For both model waste organics, there was a remarkable peak of DBPFP on day two of biodegradation. The increase in the DBPFP of the model organic solutions is believed to be related to the soluble microbial products (SMPs) produced during the biological process. SMPs are classified as a pool of organic compounds that are released by microorganisms into solution from substrate metabolism and biomass decay (Barker and Stuckey, 1999). SMPs are much more complicated organic compounds than the model carbohydrates, and thus the biotransformation of the model organics to SMPs would apparently increase the DBPFP of the water (Park et al., 2005). Dotson et al. (2009) also reported that SMPs derived from algal and bacterial cultures would result in more formation of DPBs, especially the N-DBPs, during drinking water treatment. In the present study, the final DBPFP yields of the organic residues increased greatly from an initial value of less than 1 μg mg^{-1} DOC to 87 and 38 μg

290 mg^{-1} DOC for the glucose and starch solutions, respectively (Fig. 4).

291 Pure glucose resulted in the formation of only THM (CF), whereas starch produced
292 mainly CF and trace amounts of CH and HAAs (DCAA and TCAA). During biodegradation,
293 the CF and CH formation potentials of the organic solutions increased significantly, and the
294 formation of other DBPs were also observed. Under biodegradation, the CF and CH
295 formation potential in the glucose solution increased to 330 and 280 µg L^{-1}, respectively, on
296 day two, resulting in a dramatic DBPFP increase. A similar trend of CF and CH formation
297 increases were also observed, although to a lesser extent, for the starch solution. The CF and
298 CH formation potential eventually decreased from the peak levels, but other types of DBP
299 species were strongly detected, including N-DBPs in the later phase of biodegradation (Fig.
300 4). Considering that there was no nitrogen in the two model carbohydrates, N-DBP precursors
301 in the solutions can be assumed to contribute to the production of SMPs during the
302 biodegradation process.

303

304 *3.2.4 Glycine and BSA*

305 Both glycine and BSA are biodegradable N-containing organics. BSA was rapidly
306 degraded from 70 to a low level of 6 mg DOC L^{-1} after just 2 d (Fig. 5). For glycine,
307 biodegradation began to take place after 2 d and was completed rapidly in the following 2 d.
308 During the degradation process, UV_{254} decreased for the BSA solution and increased
309 somewhat for the glycine solution.

310 The glycine solution had a moderate initial DBPFP of 176 µg L^{-1}, and contained all seven
311 of the DBP species (Fig. 5). The DBPFP of the glycine solution did not change significantly

through the biodegradation process, despite the substantial organic reduction. The DBPFP yield of the organics in the model solution increased from 3 to 51 μg mg^{-1} DOC. It appears that the SMPs formed during glycine biodegradation had a much higher DBPFP yield than that of glycine. BSA had an extremely high initial DBPFP of 13475 μg L^{-1}, probably due to its abundant aromatic content. The dominant DBP species included HAAs (TCAA and DCAA), THM (CF), and CH. In direct connection to its rapid biodegradation within the first 2 d, the DBPFP of the BSA solution decreased dramatically to less than 1000 μg L^{-1}. Most of the DBPFP reduction was achieved through great decreases in the TCAA, DCAA, CF, and CH formation potential. In comparison, the SMPs in the BSA solution after degradation had a lower DBPFP yield (134 μg mg^{-1} DOC) than pure BSA (193 μg mg^{-1} DOC) (Fig. 5). It would appear that biodegradation can effectively destruct and remove DBP precursors derived from proteins and other similar organics in wastewater.

3.3 Transformation of wastewater-derived DBP precursors during organic degradation

Substantial organic degradation was achieved in the artificial wastewater samples after the 10-d biodegradation for all of the model organics except for humic acid. More importantly, biodegradation led to changes in the DBPFP for most of the model organic solutions (Figs. 2-5). The DBPFP remained largely unchanged for the glycine solution, despite of its great degree of degradation. In contrast, the DBPFP of the tannic acid and BSA solutions decreased significantly as a result of biodegradation. It is interesting to note that the DBPFP increased nearly 3-fold for the starch and glucose solutions after biodegradation. These results indicate that the organic residues after biological degradation of the model organics changed greatly in

terms of DBP formation reactivity. In other words, although the biodegradation process effectively removes some DBP precursors from wastewater, such as tannic acid and proteins, it may also produce new DBP precursors from carbohydrates and other similar organics with a low initial DBPFP, such as starch and glucose.

Microbial activity played an important role in the transformation of wastewater DBP precursors under simulated natural degradation conditions (Chen et al., 2009; Dotson et al., 2009; Krasner et al., 2009b). The organic transformation results and related DBPFP values in this study differed significantly among the different types of wastewater organic compounds. The DBPFP of humic-like organic matter, which is refractory to biodegradation, was not affected by biological treatment. However, for some of the biodegradable organics with a high DBPFP in wastewater, such as tannic acid and BSA, biodegradation may have destroyed the DBP precursors, thereby greatly reducing the DBPFP of the wastewater. For other biodegradable organics with a low DBPFP, such as glucose and starch, the biological process may have increased both the DBPFP of the wastewater and the DBPFP yield of the organic residues. The final DBPFP of wastewater is probably thus attributable to two sources: the humic-like residue of the organics originally present in the wastewater and the SMPs that are formed during the biodegradation process.

The 10-d biological incubation changed the DBP formation characteristics of the organics in the model solutions and wastewater samples. Initially, the DBPFP yields differed remarkably for different organic DBP precursors. After the biodegradation, owing to the production of SMPs, the DBPFP yields of the organic residues in the four readily biodegradable model organic solutions – glucose, starch, glycine, and BSA – became rather

comparable. The resulting DBPFP yield values were similar to those of the wastewater influent and effluent organics and somewhat lower than the DBPFP yields of humic substances in the humic and tannic acid solutions (Fig. 6a).

The importance of SMP production during organic degradation to the formation of DBP precursors in natural waters demands more investigations. In general, biodegradation is beneficial to the removal of organic pollutants and the reduction of the DBPFP of water. However, the SMPs formed during biodegradation may give rise to new DBP precursors. For the biodegradable organics tested in this study, except for BSA, the DBPFP yields of the remaining organic substances after 10 d of degradation in the water samples all increased. In terms of DBP speciation, the final species profiles for the remaining organics became more comparable with each other than the initial DBP species profiles for the model organics. It is apparent that the SMPs produced in the four model organic solutions – glucose, starch, glycine, and BSA – had a similar DBP speciation that was dominated by CF and had a similar level of DCAA and TCAA (Fig. 6b). The comparison suggests that the SMPs, as the final DBP precursors in the model organic solutions after biodegradation, had similar DBP formation characteristics. The resulting DBP species profiles were largely similar to that of wastewater organics, but different from that of pure humic substances which had more TCAA than DCAA (Fig. 6b).

Wastewater organic-derived DBP precursors are greatly related to biological activity and SMP production. The DBPFP of the glucose and starch solutions increased significantly within the first 2 d of biodegradation, which corresponded to a rapid organic degradation (Fig. 7a). It is known that SMPs are produced by microorganisms during substrate metabolism for

microbial growth (Barker and Stuckey, 1999; Cheng and Chi, 2003). Hence, it is likely that SMP production during the early stages of dynamic organic degradation contributed to the large DBPFP increase. A similar trend of rapid organic degradation and N-DBPFP increase was also observed in the glycine solution in the early phase of biodegradation. The final DBPFP of the four model organic solutions with the same initial DOC concentration took the order BSA > glucose > starch > glycine. This is in general agreement with the biomass concentrations in the four bioreactors (Fig. 7b). Such a correlation gives further support for the effect of SMP production during organic degradation and transformation on the formation new DBP precursors.

For actual wastewater, the organic matter consists of different types of organic groups. The DBP formation behavior of the wastewater organic under the natural biodegradation condition should be a combination of the contributions from all of the different organic compounds (Chen et al., 2009; Krasner et al., 2009a; Krasner et al., 2009b), including the model organics tested in this study. Biodegradation of the organic pollutants results in DBPFP reduction, whereas the new DBP precursor production, like SMPs, would give rise to more DBP reactivity with chlorine. Thus, SMPs can be an important source of DBP precursors in water resources. For the complex mixture of organics in wastewater, the present study provides a new insight into the dynamic transformation of wastewater-derived DBP precursors in natural waters receiving wastewater discharge.

4. Conclusions

The DBPFP of the raw wastewater influent and secondary effluent samples decreased after the simulated biological organic degradation process, but the remaining organic matter had a higher potential for DBP formation with chlorine. Different model wastewater organics behaved differently in terms of the change in wastewater DBPFP during organic degradation. The DBPFP of the glycine solution remained largely unchanged, that of the tannic acid and BSA solutions decreased greatly, and that of the glucose and starch solutions increased nearly 3-fold following biodegradation. Thus, although biological organic degradation may effectively remove some DBP precursors from wastewater, the process may also produce new DBP precursors from carbohydrates and other organic pollutants. The DBPFP yield of the organics in the BSA solution decreased from 193 for pure BSA to 134 μg mg^{-1} DOC for the organic residue after the biodegradation process. However, the DBPFP yield of the organics in the glycine solution increased from 3 to 51 μg mg^{-1} DOC for its degradation residue, and the corresponding yield in the glucose and starch solutions increased from 1 to 87 and 38 μg mg^{-1} DOC, respectively, for their organic residues after biodegradation.

The biodegradation of organic pollutants in water produces soluble microbial products, and some SMP materials may become new DBP precursors with a greater DBPFP than the original biodegradable organic compounds. For the DBPs formed from SMPs, THMs were the predominant species, followed by HAAs, chloral hydrate, and then N-containing DBPs. These results indicate that SMPs may be an important source of wastewater-derived DBP precursors in natural waters that receive wastewater discharge. Thus, for the wastewater effluent reused directly or indirectly into any drinking water resources, more stringent discharge standards need to be adopted. In addition, advanced treatment modules with a great

organic removal capability, such as membrane filtration and activated carbon adsorption, may be applied to the wastewater effluent or raw water intake for minimization of the wastewater-derived DBP problems in drinking water supply.

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Figure captions

Fig. 1. (a) Initial DBPFP yield and (b) mass-based DBPFP speciation of the wastewater and model organic solutions: HA – humic acid, TA – tannic acid, Glu – glucose, Star – starch, Gly – glycine, BSA – bovine serum albumin, Inf – wastewater influent, Eff – secondary wastewater effluent.

Fig. 2. (a) DOC, (b) UV_{254} absorbance, (c) DBPFP, and (d) DBPFP yield of the wastewater influent and effluent, and DBPFP species in (e) the wastewater influent and (f) the wastewater effluent during biodegradation.

Fig. 3. (a) DOC, (b) UV_{254} absorbance, (c) DBPFP, and (d) DBPFP yield of the humic acid and tannic acid solutions, and DBPFP species in (e) the humic acid solution and (f) the tannic acid solution during biodegradation.

Fig. 4. (a) DOC, (b) UV_{254} absorbance, (c) DBPFP, and (d) DBPFP yield of the glucose and starch solutions, and DBPFP species in (e) the glucose solution and (f) the starch solution during biodegradation.

Fig. 5. (a) DOC, (b) UV_{254} absorbance, (c) DBPFP, and (d) DBPFP yield of the glycine and BSA solutions, and DBPFP species in (e) the glycine solution and (f) the BSA solution during biodegradation.

Fig. 6. (a) Final DBPFP yield and (b) mass-based DBPFP speciation of the wastewater and model organic solutions after 10 d of biodegradation: HA – humic acid, TA – tannic acid, Glu – glucose, Star – starch, Gly – glycine, BSA – bovine serum albumin, Inf – wastewater influent, Eff – secondary wastewater effluent.

Fig. 7. (a) Biomass concentration during the biodegradation of the glucose and starch solutions, (b) final DBPFP and biomass concentration in the four model organic solutions after biodegradation: Glu – glucose, Star – starch, Gly – glycine, BSA – bovine serum albumin.

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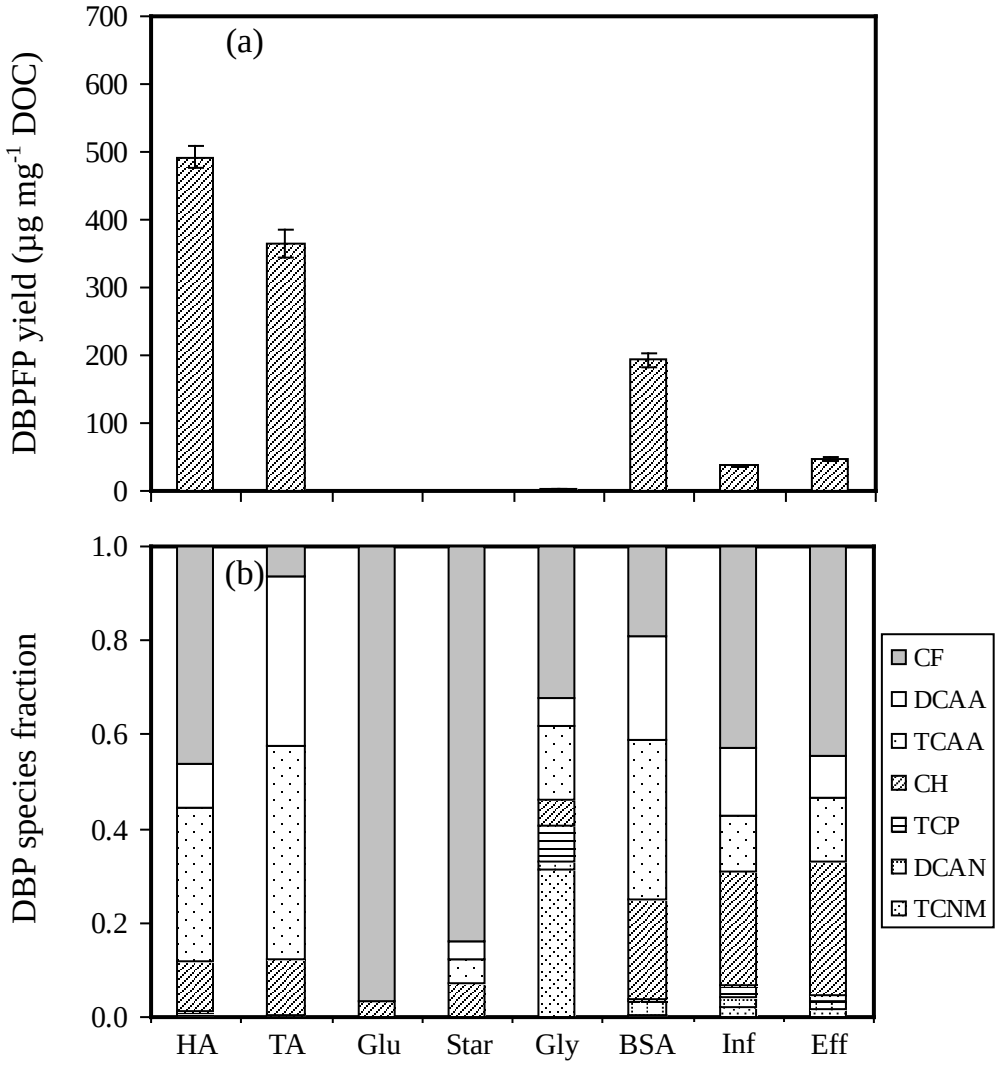

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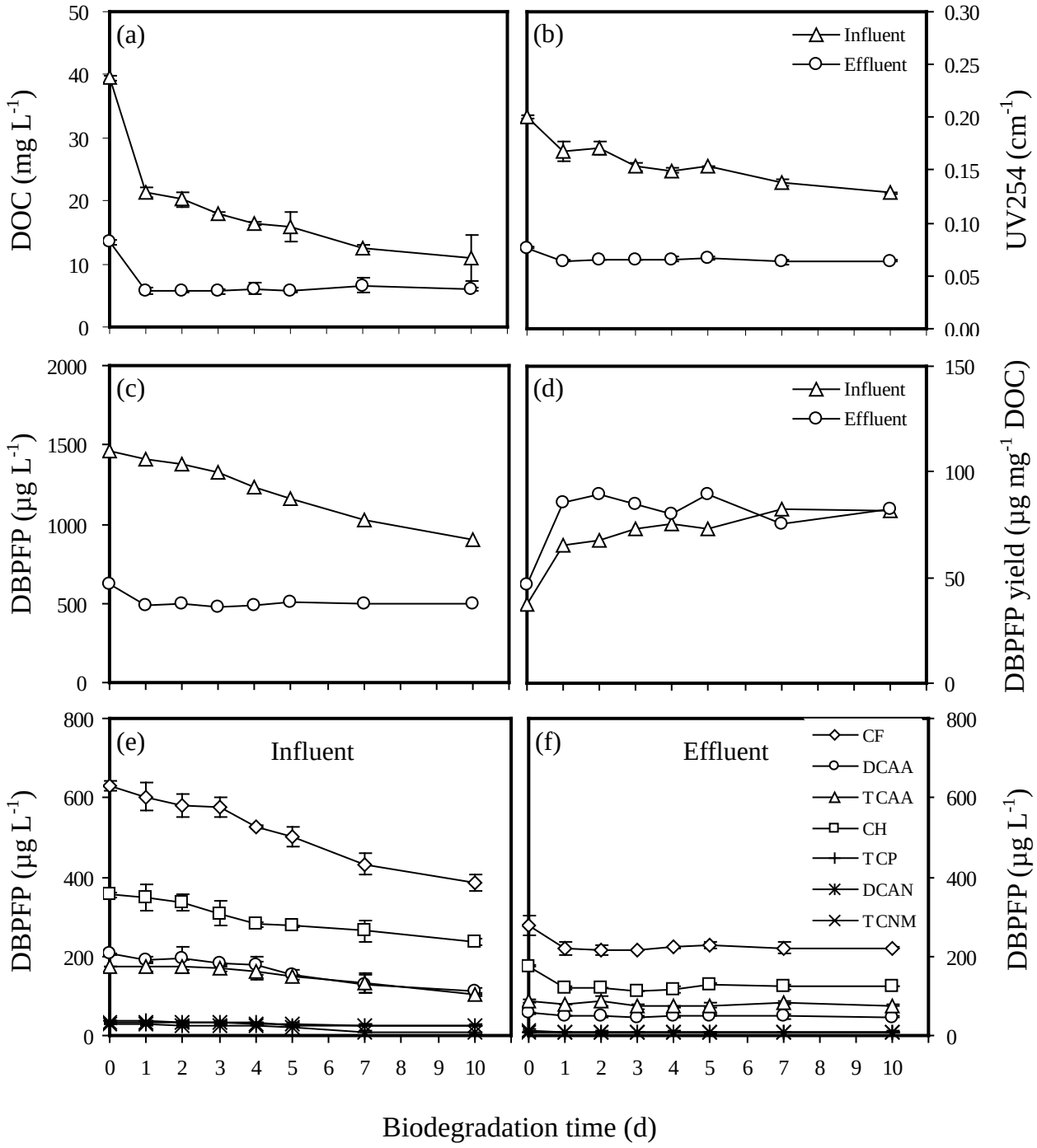

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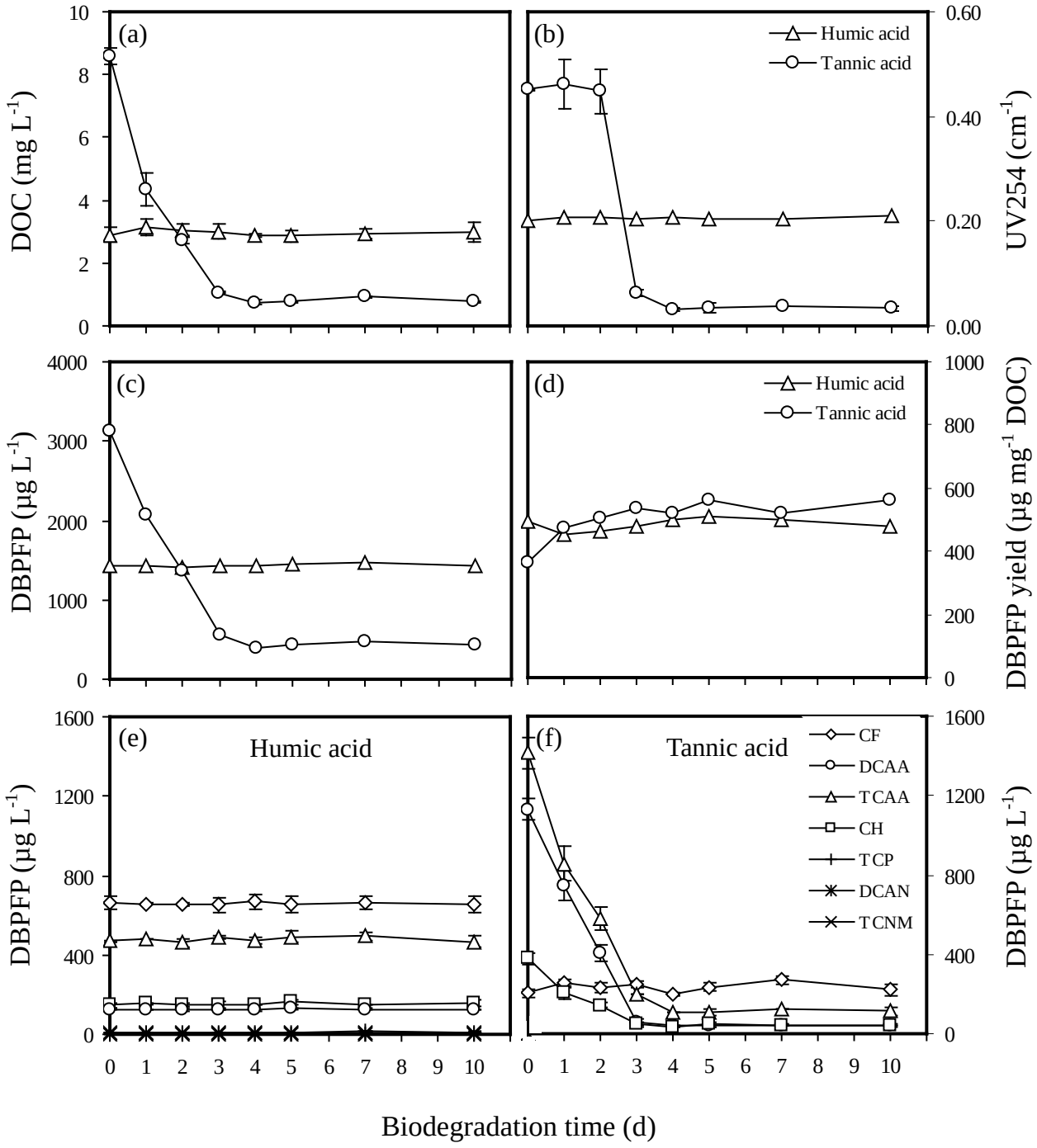

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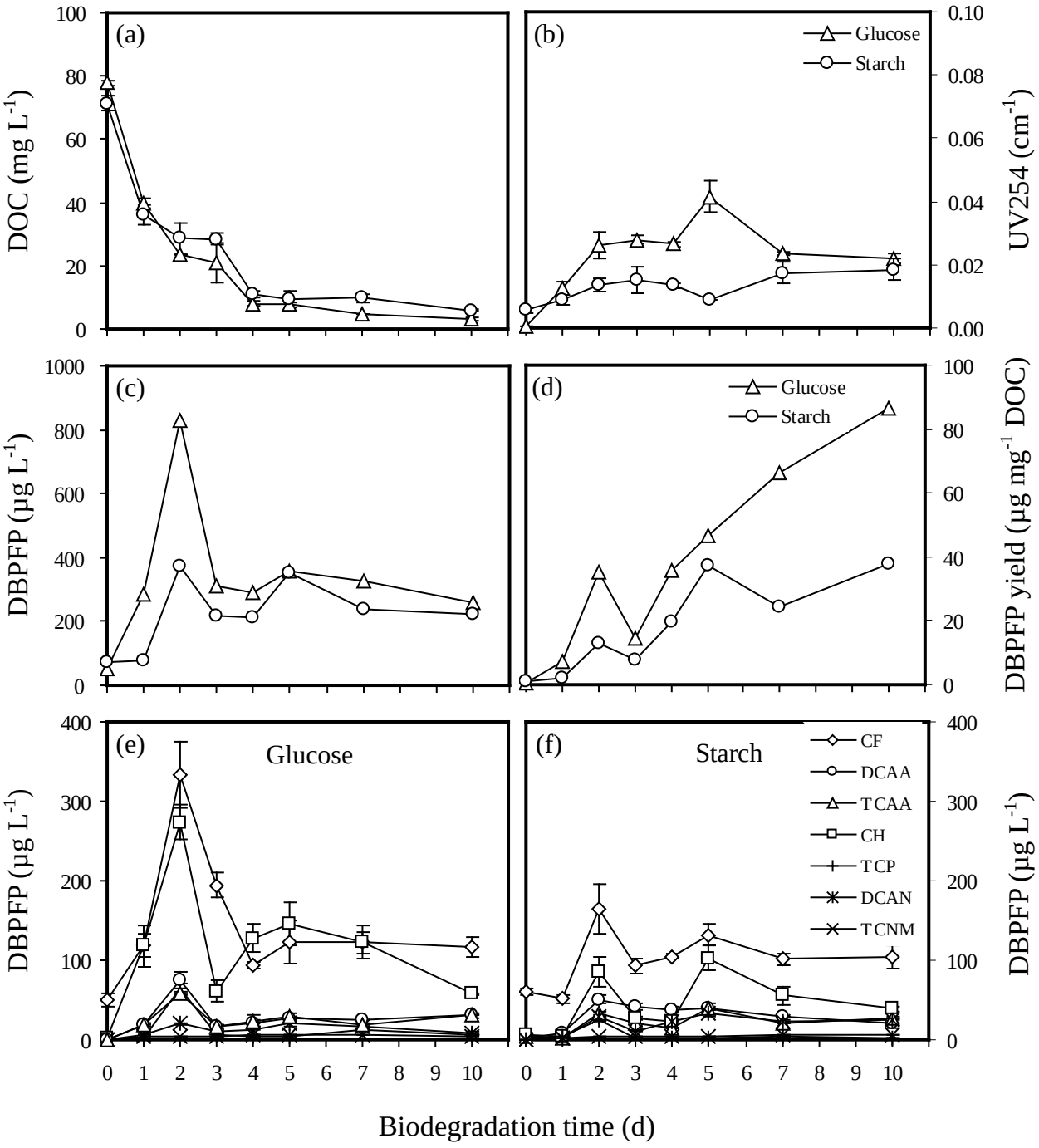

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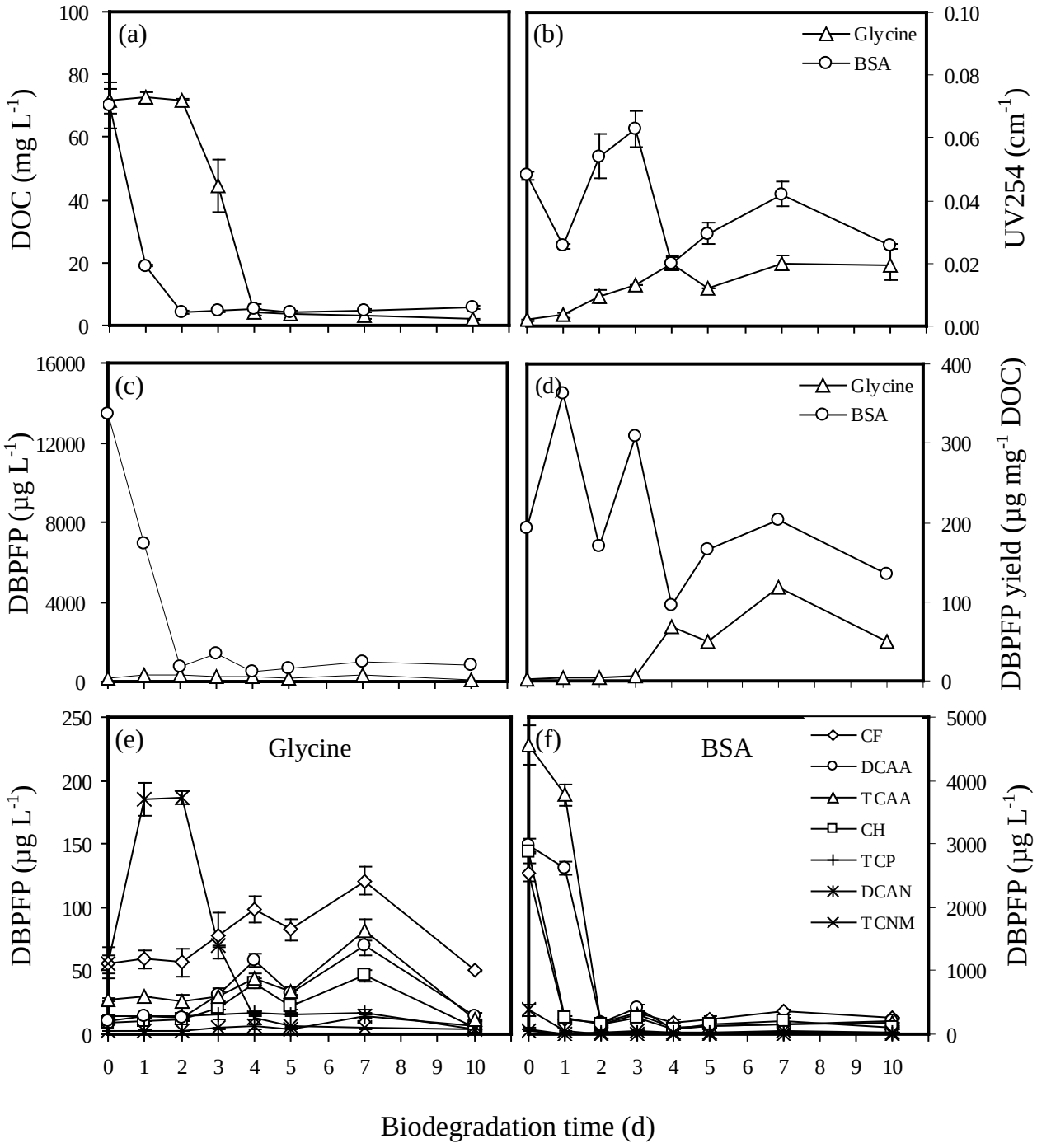

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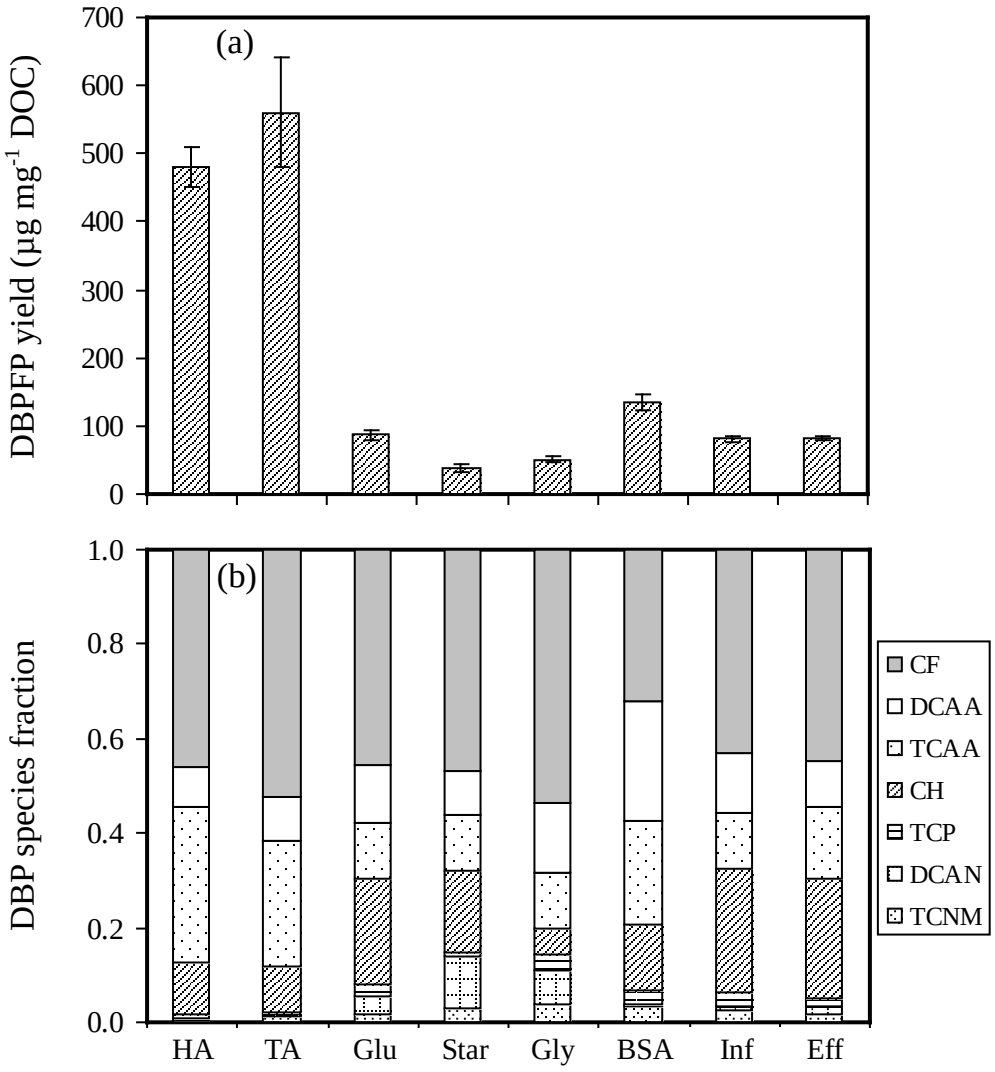

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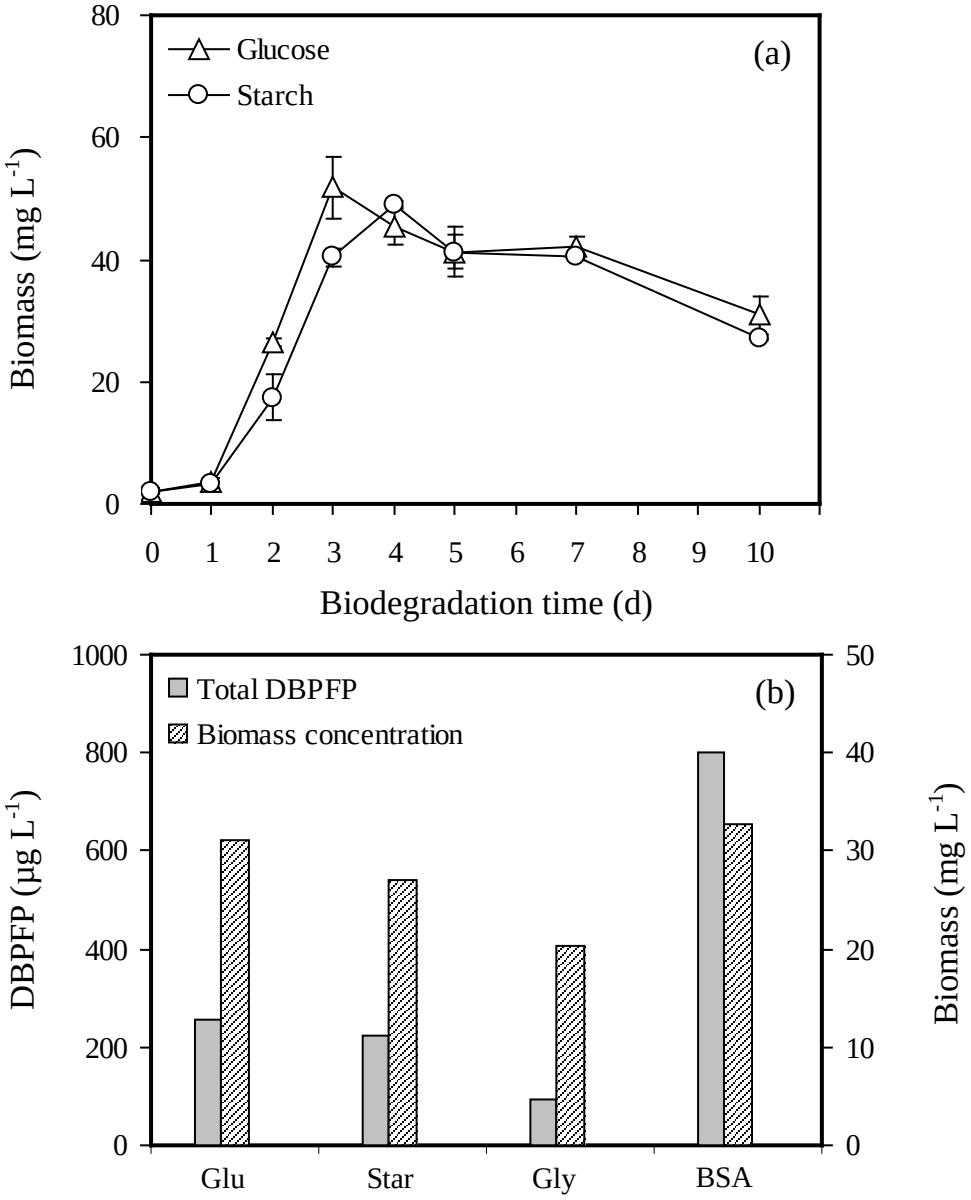

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