



Fate of bisphenol A, perfluorooctanoic acid and perfluorooctanesulfonate in two different types of sewage treatment works in Hong Kong



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HIGHLIGHTS

- Wastewater treatment processes (WTP) were not effective in removing PFOA/PFOS.
- Majority of PFOA, PFOS and BPA presented in the effluent rather than in the sludge.
- Substantial amount of PFOA/S and BPA discharged into the Victoria Harbor, Hong Kong.

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ABSTRACT

This study aimed at investigating the removal efficiencies of perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) and bisphenol A (BPA) of two major sewage treatment works in Hong Kong: Stonecutters Island STW (SCISTW) which adopts chemically enhanced primary treatment (CEPT) process and Sha Tin STW (STSTW) which employs biological treatment. Liquid portion (LP) and particulate matter (PM) of liquid sewage samples and sludge samples were collected and followed by liquid chromatograph system. It was found that BPA ($44.6 \pm 35.1\%$) generally achieved higher TRE than the two other chemicals (PFOS ($-18.8 \pm 34.8\%$) and PFOA ($-104 \pm 86.8\%$)) in STSTW ($p < 0.05$). Most of the PFOA, PFOS and BPA was discharged through final effluent (PFOA: $95.6 \pm 1.00\%$ and $94.5 \pm 3.13\%$; PFOS: $77.7 \pm 1.48\%$ and $72.6 \pm 6.07\%$; BPA: $99.2 \pm 0.950\%$ and $92.8 \pm 7.25\%$, respectively) rather than stored in the sludge/cake (PFOA: $4.45 \pm 1.00\%$ and $5.47 \pm 3.13\%$, PFOS: $22.3 \pm 1.48\%$ and $27.4 \pm 6.07\%$, BPA: $0.844 \pm 0.950\%$ and $7.20 \pm 7.25\%$, respectively). After the sewage purification process, the two STW released considerable amounts of PFOA, PFOS and BPA in the final effluent (PFOA: 0.638 ± 0.227 kg/year; PFOS: 0.409 ± 0.126 kg/year; BPA: 10.4 ± 3.83 kg/year in STSTW; PFOA: 3.08 ± 1.415 kg/year; PFOS: 2.13 ± 0.452 kg/year; BPA: 714 ± 768 kg/year in SCISTW) and in the sludge (PFOA: 0.0360 ± 0.0250 kg/year; PFOS: 0.149 ± 0.00100 kg/year; BPA: 1.09 ± 1.47 kg/year in STSTW; PFOA: 0.139 ± 0.0670 kg/year; PFOS: 0.606 ± 0.0780 kg/year; BPA: 3.05 ± 3.95 kg/year in SCISTW). This study may help to provide crucial information for further development of municipal sewage system in treating synthetic emerging chemicals.

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1. Introduction

Perfluorooctanoate (PFOA; $C_8F_{15}O_2H$), Perfluorooctane sulfonate (PFOS; $C_8F_{17}SO_3$) and Bisphenol A (BPA; $(CH_3)_2C(C_6H_4OH)_2$) are contaminants of emerging concern (CECs) not commonly monitored in the environment, which impose adverse effects on the

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environment, biota and human due to their extensive uses as raw materials or additives in daily products (MDH, 2005; Rochester, 2013; Vrijheid et al., 2016).

PFOA and PFOS are synthesized perfluorinated compounds (PFCs) widely used in industry due to their unique and extraordinary chemical properties. The fluorinated structures and functional groups ($-\text{SO}_3^-$ and $-\text{COO}^-$) synchronize the hydrophobic and hydrophilicity properties of the chemicals (Fujii et al., 2012). This renders PFOA and PFOS excellent surface treatment chemicals and surfactants, commonly applied as a water repellent or stain-resistant agent in carpets, leathers, textiles, paper packaging, and coating additives (US EPA, 2016). One of the well-known products containing PFOA is Teflon[®] used as a non-stick coating surface for cookware (ACS, 2017). PFOS can even be found in aqueous fire-fighting foam (Suja et al., 2009).

PFOA and PFOS are highly persistent in the environment which is attributed to the high-energy carbon-fluorine (C–F) bonds (Giesy and Kannan, 2002; Chirikona et al., 2015). Therefore, they have high thermal and chemical stability and usually regarded as persistent organic pollutants (POPs), which are extremely recalcitrant and highly resistant to degradation and can bioaccumulate in organism body for a long period of time (Giesy and Kannan, 2002; Xiao et al., 2015; Vrijheid et al., 2016).

BPA (4, 4'-dihydroxy-2, 2-diphenylpropane) is also a synthetic compound having two phenol functional groups connected with two methyl groups. It is moderately water soluble and having a low volatility (Huang et al., 2012). BPA is an industrial chemical, with a large volume of production (Careghini et al., 2015; Corrales et al., 2015). It was commonly used as a color developer in thermal paper, which mostly found as consumer receipts. In addition, the production of polycarbonate plastic and epoxy resins requires BPA as a starting substance and additive (Pivnenko et al., 2015). Therefore, BPA can be added as polycarbonate plastic and epoxy resins in many consumer products such as food storage containers, electronic equipment, baby bottles, mugs and digital media (Huang et al., 2012).

Due to the substantial use of PFOA and PFOS in food packaging materials and cookware, ingestion is usually believed to be a major human exposure pathway of these perfluoroalkyl and poly-fluoroalkyl substances (PFAS) (ATSDR, 2017). BPA shares similar exposure pathways as PFOA and PFOS. Majority of human exposures to BPA originates from food and beverage containers (OEHHHA, 2009). Furthermore, the exhaust gas emission from the manufacturing process and open burning of BPA containing plastics waste would emit BPA to air (Huang et al., 2012). Individuals can also be exposed to PFOA, PFOS and BPA through inhalation and dermal contact of the surfaces treated with these chemicals (e.g. thermal paper and furniture surface) (Careghini et al., 2015; Seachrist et al., 2016; ATSDR, 2017).

PFOA, PFOS and BPA may bring along potential health impacts to human and the wildlife via bioaccumulation and biomagnification through food chains. PFOA and PFOS are not readily metabolized and excreted upon absorption into human and animal bodies (Olsen et al., 2007; Liu et al., 2017). They would be mainly accumulated in serum, liver and kidney with a half-life of 3.8 years and 5.4 years, respectively, on average (Olsen et al., 2007; Liu et al., 2017). Bioaccumulation and biomagnification of PFOA and PFOS may take place and cause adverse impacts to liver, immunization system, neural system and even reproduction system (Pan et al., 2016; Liu et al., 2017). In addition, BPA is a well-known endocrine disruptor, especially to the vulnerable groups like fetus, baby and children (Careghini et al., 2015). It was suggested that human embryogenesis and neonatal development may probably be affected by BPA through disruption or inhibition of thyroid hormone pathways (Heimeier and Shi, 2010). Cardiovascular disease

and hypertension were also recorded in some cases of BPA exposure in human (Rochester, 2013). Therefore, there is an urgent need to investigate the fates of PFOA, POFA and BPA in the sewage treatment facilities and estimate subsequent release of these chemicals in the natural water bodies nearby.

There is a wide range of sources of PFOA, PFOS and BPA in our daily life, applications in domestic products have a significant contribution to the ubiquitous presence of these chemicals in the environment, especially their discharges into natural water bodies through municipal drainage system which were not designed specifically for treating these emerging chemicals (Buttiglieri and Knepper, 2007). PFOA, PFOS and BPA may enter the water bodies through surface water runoff and treated wastewater effluent especially without proper wastewater treatment (Liu et al., 2017). These chemicals would be released to the environment and eventually reach the sewage treatment facilities during the manufacturing process, application and disposal of the products (Huang et al., 2012; ATSDR, 2015). A few studies have been conducted investigating the capabilities of conventional sewage treatment facilities in removing PFOA, PFOS and BPA (Li et al., 2010; Wang et al., 2010; Arvaniti et al., 2012). In general, results showed that the sewage treatment works (STWs) were able to remove these chemicals to a limited extent (e.g. the total removal rates of PFOA and PFOS were –28% and 7%, respectively, in a secondary treatment plant in Athens, Greece) (Arvaniti et al., 2012). Nevertheless, information about the fate of these chemicals in conventional STWs is limited. In addition, the removal potential of chemically enhanced primary treatment (CEPT) system was not evaluated in the previous studies. Therefore, the present study will provide critical information in these aspects.

The release of PFOA, PFOS and BPA from municipal wastewater treatment system is one of the dominant sources of discharge into the water environments and thus this study aimed at investigating the removal rates of these chemicals from wastewater in two of the major wastewater treatment facilities in Hong Kong. It is hypothesized that the Stonecutter Island Sewage Treatment Works (SCISTW) with CEPT and Shatin Sewage Treatment Works (STSTW) with secondary biological treatment vary in removal efficiencies of PFOA, PFOS and BPA due to the use of different wastewater treatment technologies. It is also expected that the primary and secondary treatments in STSTW would vary in their removal performance. The removal mechanisms of PFAS (PFOA and PFOS) and BPA are also diverse attributing to their different chemical characteristics. Therefore, this study is aimed at investigating: (1) the capabilities of the two sewage treatment works (SCISTW and STSTW) in the removal of PFOA, PFOS and BPA; (2) the fates of PFOA, PFOS and BPA in different treatment stages in the two sewage treatment works; and (3) the removal mechanisms of these chemicals by various sewage treatment technologies adopted in the STWs.

2. Materials and methods

2.1. Description of sampling site

Sha Tin Sewage Treatment Works (STSTW) and Stonecutters Island Sewage Treatment Works (SCISTW) are two sewage treatment works (STWs) in Hong Kong, providing sewage treatment service to different districts (DSD, 2009a,b). STSTW is a secondary (biological) sewage treatment work that located next to the estuary of Shing Mun River and providing service to Ma On Shan and Shatin Districts since 1982. Being the largest secondary sewage treatment works in Hong Kong, STSTW is able to treat a maximum 0.34 million m³ of sewage/day, but currently receiving 0.25 million m³ sewage from the mentioned districts by around 600,000 people

every day (DSD, 2009a). On the other hand, SCISTW is a compacted sewage treatment works for treating 1.7 million m³ of sewage/day generally from Kowloon and Northeast Hong Kong Island by using chemically enhanced primary treatment (CEPT) to Kowloon and Northeast Hong Kong Island. SCISTW processes higher treatment capacity and occupies less land area than STSTW (SCISTW:10 ha and STSTW:28 ha), and in fact the treatment capacity in SCISTW was planned to further increase to 2.4 million m³/day for meeting the future need of the Harbour Area Treatment Scheme (HATS) (DSD, 2009b).

2.2. Sample collections

Different sewage and sludge samples were collected once a week during the 5 weeks between November 2011 and February 2012 for both STSTW and SCISTW, from various locations in each STW.

2.2.1. STSTW

- (1) Degrittied crude sewage (CS) after preliminary treatment was taken at the inlet of primary sedimentation tank;
- (2) Primary effluent (PE) from primary sedimentation tank was collected at the outlet of the tank;
- (3) Final effluent (FE) discharged from final sedimentation tank was taken at the effluent pump before entering the UV disinfection unit;
- (4) Dewatered sludge/cake sample was collected from 3 skips in the sludge treatment facility after centrifuge dewatering process;
- (5) Activated sludge/mixed liquor (ML) derived from the secondary treatment tank was taken from the bioreactors.

2.2.2. SCISTW

- (1) Degrittied crude sewage (CS) was collected as a mixture of multiple grabs before the chemical enhance primary treatment (CEPT) process;
- (2) Final effluent (FE) was collected from multiple grabs before the disinfection, chlorination process;
- (3) Dewatered sludge/cake was collected as a mixture of multiple grabs from 3 centrifuges in the sludge treatment facility.

All the sewage samples (CS, PE and FE) were stored by using amber glass bottles which were pre-cleared and solved rinsed, with Teflon caps. The sludge/cake samples were wrapped with aluminum foil which was prebaked at 450 °C, and placed in polypropylene plastic bag. Both sewage and sludge samples were kept in ice boxes during transportation from the sampling sites to the laboratory.

2.3. Determination of total suspended solid (TSS) and volatile suspended solids (VSS) of liquid samples

0.45 µm glass fiber filters (Whatman, Maidstone, England) in filtration unit were weighed before applying to separate the well mixed liquid samples (CS, PE and FE) into liquid portion (LP) and particulate matter (PM). The used glass fiber filters with PM were then placed into an oven for drying at 105 °C to determine the TSS (g/L) and percentage of moisture of the PM. The weight loss of the used filters at 105 °C due to the evaporation of moisture and the TSS g/L was obtained by calculating the net weight of PM on the filters. Therefore, both moisture and TSS g/L results were obtained. The filters were heat at 550 °C in a furnace for determining the VSS

content g/L which was the weight loss of the filters between 105 °C and 550 °C (APHA et al., 2012). The dried sludge samples were also analyzed based on the weight loss between 105 °C and 550 °C to determine the organic matter content (APHA et al., 2012).

2.4. Determination of PFOS and PFOA

2.4.1. Sewage liquid sample extraction

Filtered samples were extracted using Oasis® WAX cartridges (ISO 25101). The cartridges were preconditioned by passage of 4 mL of 0.1% NH₄OH in methanol, followed by methanol and Milli-Q water. Surrogate standards purchased from Wellington Laboratories Inc, Canada were added prior to the solid-phase extraction (SPE) extraction. Samples were passed through the pre-conditioned cartridges. The cartridges were washed with 25 mM ammonium acetate buffer. Before elution, the water remaining in the cartridges was removed by centrifugation at 3000 rpm for 2 min. The target analytes were eluted into two fractions by methanol and 0.1% NH₄OH in methanol, respectively. The two fractions were then concentrated to 0.5 mL, under a gentle stream of high-purity nitrogen. If particulates/suspension appeared in the final solution, samples were centrifuged at 3000 rpm for 2 min before being transferred to vials for instrumental analysis.

2.4.2. Sludge and particulate matter extraction

Sludge and particulate matter samples were extracted using the method described by Powley et al. (2005) and Ahrens et al. (2009). Dried samples were extracted in 100 mM sodium hydroxide (8:2; MeOH: Milli-Q water) and ultra-sonicated for 30 min. Methanol was added to the mixture and ultra-sonicated for 30 min. Surrogate standards purchased from Wellington Laboratories Inc, Canada were added prior to the extraction. The mixture was separated by centrifugation at 4000 rpm for 15 min. The supernatant was then transferred and collected into a 100 mL round bottom flask. The extraction was repeated twice. All extracts were combined in the same flask. The extracts were used for further ENVI-Carb and SPE cleanup. The Supelclean™ ENVI-Carb™ cartridge was preconditioned by passing through three times 2 mL of methanol. After sample loading, the sample was further eluted by passing through five times 1 mL of methanol. The extracts were concentrated to 1 mL, under a gentle stream of nitrogen after ENVI-Carb cleanup. Concentrated sample extracts were diluted in 125 mL of Milli-Q water and subjected to Oasis® WAX cartridge for further SPE cleanup, following the same procedures for sewage clean up.

2.4.3. Instrumental analysis

Separation of the target analytes was performed using an Agilent 1290 Infinity ultra-performance liquid chromatograph (LC) (Agilent, Palo Alto, CA, USA), interfaced with a 3200 QTRAP mass spectrometer (MS) (AB Sciex, Foster City, CA, USA). Significant interference from standard LC systems and mobile phase has been commonly encountered during ultra-trace quantification of PFCs, preventive measures were therefore carried out when performing the analysis. A 10-µL aliquot of the extract at a ratio of 1:1 MeOH and Milli-Q water was injected onto a C18 column, Agilent Zorbax Eclipse Plus C18 (2.1 mm i.d. × 50 mm length, 1.8 µm; Agilent, Palo Alto, CA, USA). A gradient mobile phase of 2 mM ammonium acetate in Milli-Q water/methanol 95:5 (solvent A) and 2 mM ammonium acetate in methanol (solvent B) was used. At a flow rate of 0.3 mL/min, the gradient condition in a sequence of 10% solvent B was increased to 85% at 5 min, 100% at 9 min, and converted to original conditions. Target compounds were detected using multiple reaction monitoring (MRM), in negative ion electrospray mode to provide sufficient sensitivity and selectivity.

2.4.4. Quality control and quality assurance

The concentrations of target PFCs were quantified using an external calibration curve. The calibration curve was based on a PFC concentration series (0.1, 0.25, 0.500, 1, 2, 5, 10, 25 ng/mL), and the deviation of every point from the regression line was less than 20% from its theoretical value. The standard calibration curve exhibited a strong linearity (correlation coefficients > 0.99). The linearity and repeatability of these calibration curves were confirmed prior to each set of determinations. To check the stability of the instrument, a quality control standard was injected after every 10 sample injections. If the concentrations of the quality control standards were not measured within $\pm 20\%$ of their corresponding theoretical values, then a new calibration curve was prepared. In addition, surrogate standards purchased from Wellington Laboratories Inc, Canada and matrix spike recovery tests were used to examine the matrix effects of the samples. The surrogate standards purchased from Wellington Laboratories Inc, Canada were used as a reference to check for negative effects (i.e., matrix effect or ion suppression). The recovery efficiencies for PFOA/PFOS were $86.2 \pm 9.20\%$ for liquid samples (CS, PM and FE) and $80.9 \pm 8.62\%$ for solid samples (cake and PM).

2.5. Determination of BPA

2.5.1. Sewage liquid sample extraction

Sewage samples were passed through glass-fiber filters (GFFs), with GFFs baked at 450 °C for 8 h before use. All plastic ware and polypropylene tubes were thoroughly rinsed with methanol before use. One liter of filtered sample was extracted by solid-phase extraction (SPE) C18 or Oasis HLB, based on Method 1694 (US EPA, 2007), with slight modifications. The cartridges were conditioned using methanol and distilled water. 1% methanol was added to all samples. Surrogates purchased from Sigma-Aldrich were spiked just prior to extraction unless otherwise stated. The samples were loaded in the cartridges, at a flow rate between 5 and 10 mL/min. The cartridges were then washed with distilled water, and dried for 15 min using a vacuum. 10 mL of methanol was used for elution and the extract was concentrated to 0.2 mL, using a gentle nitrogen stream prior to liquid chromatography tandem-mass spectrometry (LC/MS/MS) analysis.

2.5.2. Sludge and particulate matter extraction

Labeled standards purchased from Sigma-Aldrich, USA were added to the samples before the extraction. Freeze-dried sludge and particulate samples were extracted by ultra sonication, with a 20 mL of mixture of methanol and acetone (1:1) for 10 min. After extraction for three times, the extracts were combined and centrifuged for 5 min at 4000 rpm, concentrated to dryness by rotary evaporation, and diluted in 2 mL of methanol and acetone (1:1) plus 18 mL of Mille-Q water. The extracts were then purified by SPE C-18 cartridges, which were conditioned with acetonitrile, methanol and Mille-Q water. After loading the sample, the cartridges were washed with 3 mL of Mille-Q water, dried, and further eluted with 8 mL of acetonitrile. The eluates were then evaporated to dryness, using a stream of nitrogen and finally reconstituted in 0.2 mL of methanol for subsequent LC/MS/MS analysis.

2.5.3. Instrumental analysis

Instrumental analysis of BPA followed the method described by Gándara et al. (1993, 1998), Losada et al. (1993). It is quantified using ultra high-performance liquid chromatography (UHPLC) coupled with ABSciex 3200 Qtrap or ABSciex 5500 Qtrap electro spray triple-quadrupole mass spectrometer (ESI-MS/MS). Chromatographic separation was performed using an Agilent Zorbax Eclipse Plus C18 (2.1 mm i.d. \times 50 mm length, 1.8 μ m; Agilent, Palo

Alto, CA, USA). Gradient LC conditions were adopted for separation and quantification of BPA in samples. Briefly, mobile phases were A: Mille water and B: acetonitrile (CAN) at a ratio 65:35 (v/v) and at a flow rate of 0.3 mL/min, then it was proceeded to 100% B ($t = 6$ min), held for 2 min ($t = 8$ min), reverted to initial condition of 65:35 and re-equilibrated for 4 min ($t = 12$ min). The injection volume was 2 μ L, with the column temperature maintained at 25 °C throughout the chromatography. The MS/MS was operated in the negative and positive ESI mode for BPA. In order to achieve greater sensitivity, analyses were detected in a Multiple Reaction Monitoring (MRM) mode. The ionization source parameters were as follows: ion spray voltage, $-4500/5500$; source temperature, 480 °C; GS1, 40 and GS2, 50. Standards of native and labeled standards purchased from Sigma-Aldrich, USA used for calibration were both prepared in methanol. Isotope dilution quantitation was used to determine the level of BPA. A five-point calibration curve (1, 2, 5, 10 and 20 ppb) was prepared for determination. If the sample concentration was out of the calibration range, the extract was either concentrated or diluted further, before detection.

2.5.4. Quality control and quality assurance

For each set of samples, a procedural blank (solvent) was processed. The variation of analytic concentrations between duplicate samples was proposed to be less than 20%. For testing the recovery of BPA, known amounts of standards purchased from Sigma-Aldrich, USA were added into solid sample or sewage liquid sample before extraction. These enriched samples were extracted and analyzed with the method described above. Unsliced "blank" sample was also analyzed to determine the possible presence of contamination. The recovery efficiencies for BPA were $85.0 \pm 1.99\%$ for liquid samples (CS, PM and FE) and $68.4 \pm 1.26\%$ for solid samples (cake and PM).

2.6. Operation data, flow process and flow analysis of STSTW and SCISTW

The operation data included average daily sewage flow (m^3/day), average daily cake (kg/day), total solids (TS, g/L) in cake and total suspended solids (TSS, g/L) in different stages of sewage treatment (crude sewage (CS), primary effluent (PE) and final effluent (FE)) were provided by the Drainage Services Department (DSD) and is listed in Table S1 (Supplementary information). In addition, the analytical data for PFOS, PFOA and BPA was presented in ng/L for liquid sample (CS, PE and FE) and in ng/g dry wt. for solid samples (dewatered sludge and particulate matter of ML, CS, PE and FE). The data of solid samples was then re-evaluated by using the operation data of STSTW and SCISTW, which provided by DSD for finding the distribution profiles and removal efficiencies of PFOS, PFOA and BPA during the sewage flow process.

2.7. Equations

Equations and descriptions for calculations of total removal efficiencies (TRE (%)), removal efficiencies by primary treatment (RE-PT (%)) and removal efficiencies by secondary treatment (RE-ST (%)), distribution coefficient and mass loading (MLD) of PFOA, PFOS and BPA by STWs are listed in Table S2 and Supplementary information.

2.8. Data analysis

The collected quantitative data was analyzed by statistical software SPSS 16.0 (SPSS of Windows, version 16.0; SPSS Inc., Chicago, IL, USA). The Shapiro-Wilk test was also applied in the data analysis process for checking the normality of the data. The

significance of the differences between the samples was identified by Student *T*-test and which set at $p < 0.05$ and two-tailed for normal distribution data and the abnormal distribution data was analysis by Mann–Whitney *U* test. The partition coefficients of PFOS, PFOA and BPA concentration in particulate matter to liquid phase were determined by using Spearman correlation coefficients. All the data was presented as means \pm standard deviation.

3. Results and discussion

3.1. Removal efficiencies of PFOA, PFOS and BPA in STSTW and SCISTW

The influent concentrations of PFOA (SCISTW: 4.62 ± 1.80 ng/L; STSTW: 4.11 ± 1.32 ng/L) and PFOS (SCISTW: 4.51 ± 0.65 ng/L; STSTW: 4.32 ± 0.120 ng/L) were prominently lower than those reported in other studies (e.g. PFOA: 12.4 ± 0.370 ng/L and PFOS: 11.4 ± 0.63 ng/L in Guangzhou, China) (Table 1). Undoubtedly, the rapidly growing demand of these chemicals in mainland China was a critical contributing factor to this observable difference (Huang et al., 2012; Liu et al., 2017). On the other hand, the concentration of BPA in the influent from STSTW (309 ± 169 ng/L) was comparable to the levels generated by different studies (e.g. 542 ± 275 ng/L in Germany and 1250 ± 1380 ng/L in Shenzhen, China), while the level found in SCISTW (2880 ± 2870 ng/L) was significantly higher (Table 1). This was probably due to the different sources of municipal wastewater received by SCISTW and STSTW (DSD, 2009a,b). SCISTW serves the populations (3.5 million) in Kowloon and Northeast Hong Kong Island, with relatively higher industrial activities including printing industry (newspaper, poster and other thermal printing) and plastic and metal processing (polyform) industries (Planning Department, 2015; HKABC, 2016), while STSTW mainly collects wastewater from Shatin and Ma On Shan Districts where population (0.6 million) and industrial activities are relatively lower and less frequent (DSD, 2009a,b; Lands Department, 2017). Consequently, less PFOA, PFOS and BPA are flushed into the municipal sewage system in STSTW.

The average total removal efficiencies (TRE) of BPA, PFOA and PFOS are shown in Fig. 1. BPA generally achieved higher TRE than the two other chemicals (PFOA and PFOS) in STSTW ($p < 0.05$), while no significant removal rate could be observed in SCISTW ($p > 0.05$). In SCISTW, the TRE of BPA was $25.5 \pm 31.9\%$, while PFOS and PFOA were $5.47 \pm 6.49\%$ and $-30.5 \pm 32.1\%$ respectively. In STSTW, the TRE of BPA was $44.6 \pm 35.1\%$, while PFOS was $-18.8 \pm 34.8\%$ and PFOA was $-104 \pm 86.8\%$. The biodegradation of PFOS and PFOA precursors result in the higher final concentrations of PFOS and PFOA, leading to the negative value of TRE. In contrast, biodegradation is unlikely to occur to form BPA (Dorn et al., 1987; Yu et al., 2009). However, the two STWs did not register significant difference in the removal capabilities in all chemicals ($p > 0.05$) (Fig. 1).

The two STWs demonstrated similar TREs of BPA though they were adopting different types of treatment technologies (STSTW: secondary biological treatment; SCISTW: chemical enhance primary treatment) (Fig. 1). This finding disagreed with the previous studies, which suggested that biodegradation is the predominated mechanism of BPA removal, and hence higher removal efficiency was found in biological treatment process (Staples et al., 1998; Wang et al., 2010). One of the reasons for explaining our results is sorption of BPA onto the organic solid due to the moderate hydrophobicity of BPA ($K_{ow} = 3.32$) (Stasinakis et al., 2013; US EPA, 2015a,b). Furthermore, the concentrations of BPA and organic particles in influent were higher than the following treatment steps, and thus facilitated the occurrence of sorption (Staples et al., 1998; Stasinakis et al., 2013). Therefore, the TRE of BPA in CEPT was

comparable to that in secondary biological treatment (Fig. 1).

The mean TRE of BPA in this study ($44.6 \pm 35.1\%$ in STSTW) was slightly lower than those obtained from the other studies (secondary treatment), ranging from 53.0 to 88.5% (Table 1). It could be explained by the variation in operational conditions (e.g. hydraulic retention time, mixed liquor suspended solids concentration and chemical oxygen demand) between STSTW and the STWs investigated in these studies. For example, there was a significant positive correlation between hydraulic retention time (correlation coefficient: $0.6-0.7$; $p < 0.05$) and the TRE of BPA in the study conducted by Guerra et al. (2015).

The TRE of PFOA in STSTW and SCISTW (i.e. $-104\% \pm 86.8\%$ and $-30.5\% \pm 32.1\%$ respectively) were negative, which indicated the concentration of PFOA in effluent was higher than in influent (Fig. 1). The average TRE of PFOS in STSTW also showed a negative percentage which was $-18.8\% \pm 34.8\%$, while the average TRE of PFOS in SCISTW was positive. It may be due to the fact that the biological treatment process in STSTW was able to break down the precursors of PFOS, leading to negative values of TRE in STSTW compared with those in SCISTW (Yu et al., 2009), but the performance of this sewage treatment plant was still not satisfactory (i.e. $5.47 \pm 6.49\%$), when comparing with the results of other studies (Table 1).

The TRE of PFOS varied among different STWs in the world, ranging from $-99.1-97.7\%$, and the results in this study (5.47 ± 6.49 and $-18.8 \pm 34.8\%$) fell within this range (Table 1). Previous studies in China and other countries around the world also coincided with our results that negative TREs of PFOA and PFOS were observed (Table 1). The average TRE of PFOA achieved a similar result ($-104 \pm 86.8\%$) in the studies of Ma and Shih (2010) (-100%) and Arvaniti et al. (2012) (-71.4%) (Ma and Shih, 2010; Arvaniti et al., 2012). It was suggested that the biodegradation of their precursors was carried out in the biological treatment process (i.e. activated sludge process). The precursors of included *N*-alkyl substituted perfluorooctane sulfonamides, perfluorooctane sulfonamides and perfluorooctane sulfonamide substances (FOSAMs), perfluorooctanesulfonate precursors (PreFOS), *N*-methyl perfluorooctanesulfonamidoacetate (MeFOSAA), *N*-ethyl perfluorooctanesulfonamidoacetate (EtFOSAA), perfluorooctanesulfonamidoacetate (FOSAA), diethyl perfluorooctanesulfonamidoethanol (EtFOSE)-based polyfluoroalkyl phosphate ester (di-SAMPAP) etc. (Martin et al., 2010; Benskin et al., 2012; Yeung et al., 2013). Meanwhile, 8:2 or 10:2 fluorotelomer alcohols (FTOH), Polyfluoroalkyl Phosphoric Acid (PAPs) and polyfluorinated iodides (PFIs) can be biodegraded into PFOA (Houtz and Sedlak, 2012; Vierke et al., 2012). These precursors are commonly present in industrial processed and customer products such as paper, insecticide and food packaging, and can readily reach the two STWs through municipal drainage system. They would be readily transformed into PFOA and PFOS via biodegradation from their precursors (Ma and Shih, 2010; Pan et al., 2016). Moreover, PFOA and PFOS contain high energy covalent bonding between C–F bonds (i.e. ~ 466 kJ/mol), and thus they are terminal biodegradation end-products (Mattsson et al., 2015; Khalil et al., 2016; Pan et al., 2016), which could be hardly degraded into other species via bacteria metabolism in the secondary treatment (Prevedouros et al., 2006; Hu et al., 2011). As a result, their concentrations in the effluent drastically increased.

In the present study, there was no significant difference in removal rates of BPA, PFOS and PFOA in primary (30.9 ± 29.4 , $-14.8 \pm 20.5\%$ and $8.21 \pm 10.9\%$, respectively) and secondary ($5.67 \pm 67.2\%$, $-2.42 \pm 12.0\%$ and $-129 \pm 120\%$, respectively) treatments of STSTW ($p > 0.05$) (Fig. 2). It was anticipated that primary and secondary treatments might result in different TREs due to the varied sorption activities, biological process and

Table 1

Comparisons of influent (ng/L), effluent (ng/L), sludge (ng/g) and total removal efficiencies (TRF) (%) of PFOA, PFOS and BPA in STSTW and SCISTW in Hong Kong and STWs in other countries.

Location & WTP ^a	Sewage source	Treatment methods	Sewage sample	Perfluorooctanoate (PFOA)	Perfluorooctane sulfonate (PFOS)	Bisphenol A (BPA)	Reference
Hong Kong, China SCISTW	Municipal	Chemically enhanced primary	Influent	4.62 ± 1.80	4.51 ± 0.65	2880 ± 2870	Present study
			Effluent	6.11 ± 2.80	4.29 ± 0.91	1430 ± 1550	
			Sludge	1.80 ± 0.937 [0.276 ± 0.133]	10.5 ± 8.22 [1.22 ± 0.16]	155 ± 162 [5.96 ± 7.64]	
			TRE	-30.5 ± 32.1%	5.47 ± 6.49%	25.5 ± 31.9%	
Hong Kong, China STSTW	Municipal	Secondary	Influent	4.11 ± 1.32	4.32 ± 0.12	309 ± 169	Present study
			Effluent	8.04 ± 2.86	5.15 ± 1.65	131 ± 47.7	
			Sludge	2.67 ± 1.30 [0.453 ± 0.308]	10.7 ± 5.71 [1.88 ± 0.0345]	142 ± 165 [13.7 ± 18.3]	
			TRE	-104 ± 86.8%	-18.8 ± 34.8%	44.6 ± 35.1%	
Hong Kong, China (n = 2)	Municipal	Secondary	Influent	ND	39.7 ± 14.5	–	Ma and Shih, 2010
			Effluent	4.10	23.9 ± 6.90	–	
			Sludge	2.20 ± 0.85	83.0 ± 106	–	
			TRE	-100% ^b	39.7% ± 42.3%	–	
Hong Kong, China (n = 1)	Municipal	Primary	Sludge (Apr)	ND	3.10 ± 25.0	–	Ma and Shih, 2010
			Sludge (Dec)	ND	69.4 ± 10.0	–	
Guangzhou, China (n = 2)	Mainly Domestic	Secondary	Influent	3.39 ± 0.49	6.98	–	Pan et al., 2016
			Effluent	3.99 ± 0.0800	4.41	–	
			Sludge	1.20 ± 0.560	23.9	–	
			TRE	-18.8% ± 14.8%	37.7% ± 17.7%	–	
Guangzhou, China (n = 1)	Industrial and Domestic	Secondary	Influent	12.4 ± 0.370	11.4 ± 0.630	–	Pan et al., 2016
			Effluent	12.7 ± 0.640	22.7 ± 2.26	–	
			Sludge	1.48 ± 0.0100	37.5 ± 1.05	–	
			TRE	-2.42%	-99.1%	–	
Athens, Greece (n = 1)	80% Domestic 20% Industrial	Secondary	Influent	16.5 (10.2–20.7)	13.4 (2.40–26.3)	–	Arvaniti et al., 2012
			Effluent	21.1 (12.7–34.0)	12.5 (5.20–21.0)	–	
			Sludge	4.00 (<LOD - 19.4)	6.70 (1.80–16.7)	–	
			TRE	-28.0%	7.00%	–	
Mytilene, Greece (n = 1)	100% Domestic	Secondary	Influent	4.20 (<LOD-6.30)	3.50 (1.00–6.30)	–	Arvaniti et al., 2012
			Effluent	7.20 (<LOD-12.7)	0.0800 (<LOD-0.45)	–	
			Sludge	2.10 (<LOD - 4.10)	1.90 (0.58–3.80)	–	
			TRE	-71.4%	97.7%	–	
Taiwan (n = 2)	Domestic & Commercial	Secondary	Influent	20.6 ± 4.24	196 ± 29.5	–	Lin et al., 2010
			Effluent	22.4 ± 4.31	214 ± 72.1	–	
			TRE	-8.64 ± 1.44%	-7.56 ± 20.6%	–	
Denmark (n = 4)	Municipal		Influent	16.4 ± 3.68	5.60 ± 1.75	–	Bossi et al., 2008
			Effluent	12.3 ± 7.09	5.48 ± 2.76	–	
			TRE	17.0 ± 57.0%	8.00 ± 34.0%	–	
Shanghai, China (n = 1)	93% Domestic 7% Industrial	Secondary	Waste Activated sludge	71.6	30.1	–	Li et al., 2010
Shanghai, China (n = 1)	100% Domestic	Primary	Primary sludge	37.3	31.2	–	Li et al., 2010
Shanghai, China (n = 1)	65% domestic 35% industrial	Secondary	Activated sludge	15.9	135	–	Li et al., 2010
Xiamen, China (n = 1)	100% Domestic	Secondary	Influent	–	–	345 (189–590)	Sun et al., 2017
			Effluent	–	–	116 (16.8–544)	
			Sludge	–	–	145 (72.5–577)	
			TRE	–	–	66.4%	
Germany	60% Domestic 40% Hospitals & Industrial	Secondary	Influent	–	–	542 ± 275	Körner et al., 2000
			Effluent	–	–	162 ± 35.0	
			TRE	–	–	70.0%	
Shenzhen, China (n = 2)	Municipal	Secondary	Influent	–	–	1250 ± 1380	Wang et al., 2010
			Effluent	–	–	153 ± 169	
			TRE	–	–	87.5 ± 0.710%	

Remarks:

The influent and effluent of PFOA, PFOS and BPA were presented in ng/L, the sludge of PFOA, PFOS and BPA were presented in ng/g dw.

WTP: wastewater treatment plant (the location and naming were according to the original reports).

ND.: not detected.

TRE: total removal efficiency.

LOD: limit of detection.

LOQ: limit of qualification.

(): represent the range of PFOA, PFOS or BPA.

n: is the number of wastewater treatment plant selected and summarized from the other research.

[]: represent the concentration of PFOS, PFOS and BPA in the unit of ng/L.

^a The selected wastewater treatment plants were having similar characteristic to STSTW or SCISTW such as flow rate, sewage source and/or treatment methods.

^b If the influence concentration was not detected (N.D.) and the effluence is higher than the LOD, the total removal efficiency was assumed as -100%.

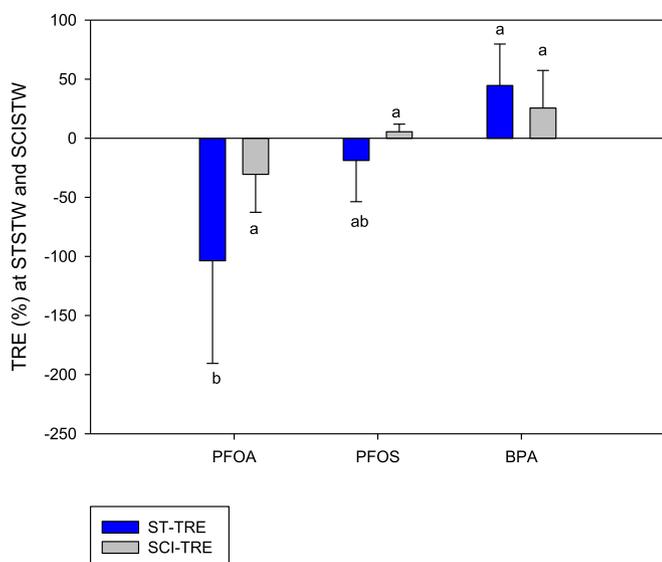


Fig. 1. The total removal efficiencies of PFOA, PFOS and BPA at STSTWs and SCISTWs. Remarks: ST-TRE: The total removal efficiencies at STSTW. SCI-TRE: The total removal efficiencies at SCISTW.

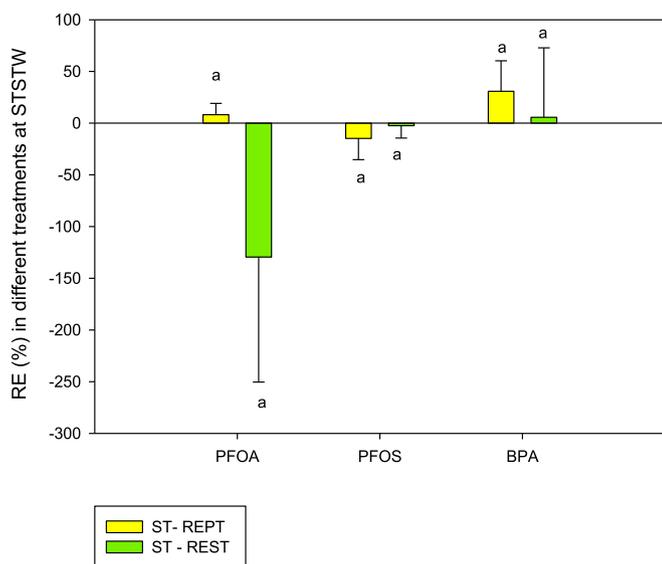


Fig. 2. The removal efficiencies of PFOA, PFOS and BPA in primary treatment and secondary treatment at STSTW. Remarks: ST-REPT: The removal efficiencies in primary treatment at STSTW. ST-REST: The removal efficiencies in secondary treatment at STSTW.

photodegradation effects (Staples et al., 1998; Guerra et al., 2015). However, the present results did not align with the hypothesis, which further confirmed the occurrence of precursors could be subsequently transformed to PFOA and PFOS (Ma and Shih, 2010; Pan et al., 2016). The PFOA and PFOS derived from precursors might have compensated the loss of molecules in biodegradation in activated sludge process. Consequently, negative and highly varied TREs of PFOS and PFOA were resulted (Fig. 2).

The concentrations of BPA (13.7 ± 18.3 ng/L) in sludge/cake were much lower than those observed in China (145 ng/g to 311 ng/g) and Greece (1600 ng/g). It might be due to the industrial production of BPA-related products such as CDs, eyeglasses, water bottles etc. in China and Greece (Fu and Kawamura, 2010; Huang et al., 2012). On the other hand, the concentrations of PFOA (0.453 ± 0.308 ng/L)

in sludge/cake were comparable to China Guangzhou STW (PFOA: 1.20 ± 0.560 ng/L), while the concentrations of PFOS (1.88 ± 0.0345 ng/g) in sludge/cake were much lower than those obtained in China Guangzhou STW (12.7 times), Shanghai (71.8 times) and Greece (3.88 times) (Table 1), where PFOS were used in electrochemical fluorination process (Martin et al., 2010).

3.2. Distributions of PFOA, PFOS and BPA in solid and liquid phases of sewage samples

The distribution coefficients of PFOA, PFOS and BPA in FE-T and sludge/cake are illustrated in Fig. 3. It was found that the effluent with particulate matter (FE-T) contained much more PFOA, PFOS and BPA (PFOA: $95.6 \pm 1.00\%$ and $94.5 \pm 3.13\%$; PFOS: $77.7 \pm 1.48\%$ and $72.6 \pm 6.07\%$; BPA: $99.2 \pm 0.950\%$ and $92.8 \pm 7.25\%$ in STSTW and SCISTW, respectively) than the sludge/cake did (PFOA: $4.45 \pm 1.00\%$ and $5.47 \pm 3.13\%$, PFOS: $22.3 \pm 1.48\%$ and $27.4 \pm 6.07\%$, BPA: $0.844 \pm 0.950\%$ and $7.20 \pm 7.25\%$, respectively) (Fig. 3). Comparing the distribution coefficients in FE-T of the three studied chemicals in STSTWs and SCISTWs, BPA, PFOA and PFOS were generally in an ascending order ($p < 0.05$) (Fig. 3).

The relatively lower partition percentage in FE-T of PFOS than PFOA and BPA might be related to the soil organic carbon-water partitioning coefficient (K_{oc}). The $\log K_{oc}$ of PFOS (2.57) was the highest among three studied chemicals (PFOS, PFOA and BPA), while PFOA and BPA are 2.06 and 2.061 (US EPA, 2014; US EPA, 2015b, 2016). The high $\log K_{oc}$ revealed that PFOS inclined to adsorb onto soil organic carbon instead of liquid. In contrast, the lower $\log K_{oc}$ values of PFOA and BPA demonstrated a higher solubility in liquid phase. In addition, the acid dissociation constant (pK_a) might also help to explain the results. There was an increasing trend of pK_a values from PFOS (0.140) to PFOA (3.80) to BPA (9.59–11.3), which suggested that the PFOS is a stronger acid than the other two chemicals (ATSDR, 2015; US EPA, 2015a). The cation of PFOS was more likely to adsorb onto the soil organic carbon due to the formation of stronger bonding through chemisorption mechanisms (Ware et al., 2006). Therefore, it showed a higher partition ratio in sludge/cake than in FE-T. Although the distribution coefficients of PFOA, PFOS and BPA seemed to be varied, there was no significant difference obtained between SCISTW and STSTW

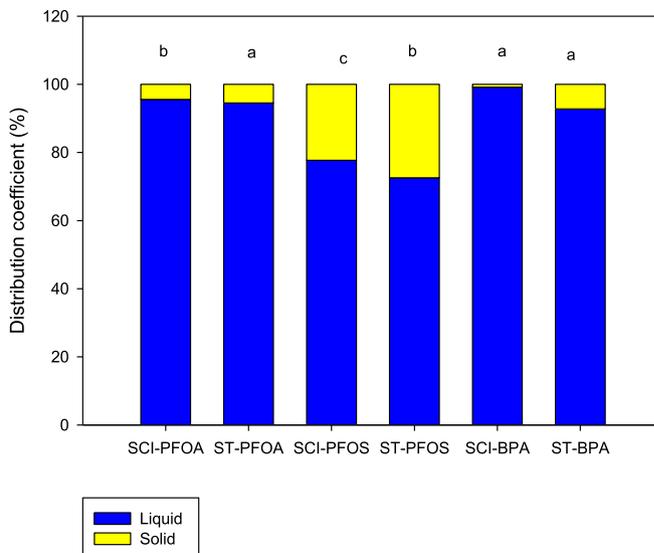


Fig. 3. Distribution coefficients of PFOA, PFOS and BPA in FE-T and cake from STSTW and SCISTW.

($p > 0.05$). This indicated that the two sewage treatment facilities adopted different treatment methods (i.e. chemical enhance primary treatment and secondary biological treatment) possess similar capabilities in partitioning PFOA, PFOS and BPA in different partitions of sewage discharge.

3.3. Mass loading of PFOA, PFOS and BPA in the two STWs

Domestic discharge is one of the major sources releasing PFOA and PFOS to STWs (Yu et al., 2009). The PFOA, PFOS, their precursors and BPA may enter to the wastewater through washing and cleaning the products containing these chemicals throughout the product life-cycle (Wang et al., 2015). There were still considerable levels of PFOA, PFOS and BPA released into natural water bodies via the discharge of effluent from STWs (Table 1). Therefore, the mass loadings of these contaminants in the STSTW and SCISTW were examined, and the total amounts of PFOA, PFOS and BPA discharged into the ocean were estimated.

The average masses of PFOA, PFOS and BPA in influent of SCISTW (PFOA: 2.33 ± 0.909 kg/year; PFOS: 2.24 ± 0.324 kg/year; BPA: 1140 ± 1420 kg/year) were much higher than those in STSTW (PFOA: 0.327 ± 0.108 kg/year; PFOS: 0.344 ± 0.005 kg/year; BPA: 24.9 ± 14.0 kg/year). It is because SCISTW had higher PFOA, PFOS and BPA concentrations (4.62 ± 1.80 ng/L, 4.51 ± 0.652 ng/L, 2280 ± 2870 ng/L) with a relatively higher average influent flow rate ($1\,400\,000$ m³/day). The average flow rate was nearly 6 times lower in STSTW ($250\,000$ m³/day) and the PFOA, PFOS and BPA concentrations were comparable to SCISTW (4.11 ± 1.32 ng/L, 4.32 ± 0.120 ng/L, 309 ± 169 ng/L) (DSD, 2009a,b).

Mass loss of PFOA, PFOS and BPA was expected after the sewage treatment. Nevertheless, there was no significant difference between the masses of PFOA, PFOS and BPA in the influent and the total final effluent and sludge/cake of both STWs ($p > 0.05$), which might be caused by the large variation of total mass weights among samples (Fig. 4a and b). After the sewage purification process, the final effluent of STSTW contained much higher PFOA, PFOS and BPA (PFOA: 0.638 ± 0.227 kg/year; PFOS: 0.409 ± 0.126 kg/year; BPA: 10.4 ± 3.83 kg/year) and SCISTW (PFOA: 3.08 ± 1.42 kg/year; PFOS: 2.13 ± 0.452 kg/year; BPA: 714 ± 768 kg/year) than those in the sludge/cake from STSTW (PFOA: 0.0360 ± 0.0250 kg/year; PFOS: 0.149 ± 0.00100 kg/year; BPA: 1.09 ± 1.47 kg/year) and SCISTW (PFOA: 0.139 ± 0.067 kg/year; PFOS: 0.606 ± 0.078 kg/year; BPA: 3.05 ± 3.95 kg/year) (Fig. 4a and b). This revealed that most of the PFOA, PFOS and BPA was stored in the effluent instead of sludge/cake in discharge.

The sewage treatment methods employed in STSTW and SCISTW did not significantly change the overall mass of PFOA and PFOS in the system. Secondary biological treatment was specifically designed for removing the organic matter from wastewater in STSTW (DSD, 2009a). However, PFOS and PFOA could not be biodegraded in activated sludge process due to the strong thermal and chemical stability (strong C–F bonding) (Yu et al., 2014; Inyang and Dickenson, 2017), which have already been mentioned in Section 3.1. Precursors such as perfluoroalkyl phosphates, fluorotelomer alcohols and fluorotelomer sulfonates may be degraded to PFOS and PFOA through biotransformation during the biological treatment process and increase the mass of PFOS and PFOA in the sewage (Yu et al., 2009). Therefore, some PFOS and PFOA may be formed from the small amount of the precursors present in the crude sewage and resulted in negative removal efficiencies of PFOA (SCISTW: $-36.5 \pm 32.9\%$; STSTW: $-114 \pm 84.7\%$) and PFOS (SCISTW: $-21.6 \pm 6.04\%$; STSTW: $-62.2 \pm 34.4\%$) (Table S3, Supplementary information). Yu et al. (2009) also suggested that the mass loadings of PFOA and PFOS increased by 17.6–144% and 69.8–143% respectively and Guerra et al. (2014) reported that there

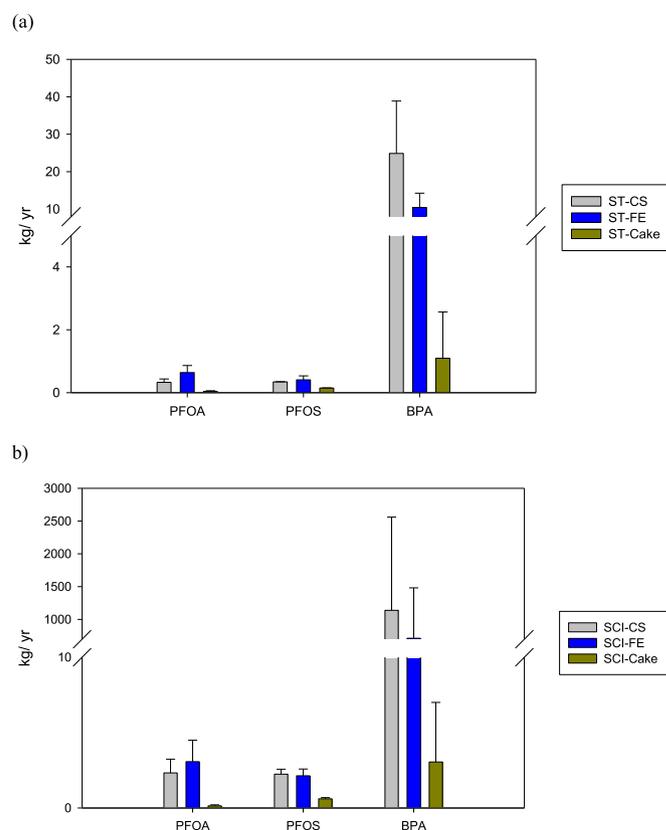


Fig. 4. a) Releases of PFOA, PFOS and BPA from STSTW through the discharge of final effluent and cake and b) Releases of PFOA, PFOS and BPA from SCISTW through the discharge of final effluent and cake.

were formations of PFOA and PFOS during the biological treatment process, leading to an increment of 56.0% and 92.0% respectively, compared with the raw sewage. Dauchy et al., 2017 provided further evidence and proved that the mass flow of PFOA was apparently raised after the degradation of precursors in the secondary treatment. The PFOA was then slightly reduced by the adsorption process by the sludge (Arvaniti and Stasinakis, 2015; Dauchy et al., 2017). Our results align with the findings obtained by Dauchy et al. (2017) that the majority of PFOA and PFOS presented in the effluent rather than in the activated sludge due to their oleophobic characteristics (Zhou et al., 2010). Hence, most of the PFOA and PFOS would be present in the effluent and discharged to the environment.

On the other hand, BPA could be removed by photo-degradation and biodegradation (Staples et al., 1998; Sun et al., 2017). BPA would be photo-degraded in the sedimentation tank by UV light during the sedimentation process and secondary biological treatment (Staples et al., 1998; Sun et al., 2017). Therefore, STSTW (58.2%), which employed this extra biological treatment step, removed 1.6 times more of BPA in the mass than SCISTW (37.4%). The BPA could also be adsorbed onto the suspended solid and sludge from the sewage during the treatment process (Staples et al., 1998; Stasinakis et al., 2008; Guerra et al., 2015). Sun et al. (2017) found that 80.7% of the total mass of BPA was removed through biodegradation from 7 secondary wastewater treatment plants in Xiamen City, China. Stasinakis et al. (2008) summarized the data collected from 6 secondary wastewater treatment plants located in Greece, and obtained similar observation that 72.0% and 15.0% of the total BPA in mass was biodegraded and adsorbed onto the sludge, respectively. Nevertheless, SCISTW and STSTW only removed

24.7 ± 33.0% and 40.5 ± 34.8% of the total mass of BPA, respectively in the present study. Furthermore, there was also no significant difference in the mass removal of BPA between SCISTW and STSTW, which elucidated that the secondary treatment did not remove more BPA than the CEPT did in SCISTW. This could be due to the different operational conditions of the STWs. For example, the nitrification efficiency of the wastewater would potentially affect the degradation of BPA in sewage (Guerra et al., 2015).

4. Conclusions

Results from the present study deviated from the hypothesis regarding the removal rates of PFOA, PFOS and BPA in different sewage treatment systems. Although SCISTW was receiving sewage influent with higher concentrations of PFOA, PFOS and BPA than STSTW, there was no significant difference between their capabilities in removing these emerging contaminants ($p > 0.05$). This elucidated that the chemically enhanced primary treatment (CEPT) accomplished similar removal efficiencies as the secondary treatment did in conventional municipal sewage treatment works. In addition, there was no significant difference ($p > 0.05$) in removal rates of BPA, PFOS and PFOA between primary and secondary treatments of STSTW. This is provided further evidence that the biological process did not surpass primary treatment in removal of PFOA, PFOS and BPA. Majority of PFOA, PFOS and BPA presented in the effluent rather than in the activated sludge due to the oleophobic characteristics of PFOA and PFOS, and moderate hydrophobicity of BPA ($K_{ow} = 3.32$), though adsorption was believed as the major pathway for removing these chemicals from the sewage. In consideration of the substantial amount of PFOA, PFOS and BPA potentially discharged into the Victoria Harbor, Hong Kong from SCISTW (719 kg/year) and STSTW (11.5 kg/year) every year, there is a need to explore a more advanced sewage treatment system and more stringent discharge regulation. More importantly, the general public could help in source reduction and avoid domestic use of the products contained or treated with these chemicals as much as possible.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2017.10.001>.

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