Cite this: *Environ. Sci.: Processes Impacts*, 2014, **16**, 1076

Occurrence and removal of benzotriazole ultraviolet stabilizers in a wastewater treatment plant in China.†

Shanjun Song, Ting Ruan, Thanh Wang, Runzeng Liu and Guibin Jiang*

Benzotriazole ultraviolet stabilizers (BZT-UVs) have previously been found in sludge from wastewater treatment plants (WWTPs), which might be potential sources of BZT-UVs to the surrounding environment. In this work, the occurrence and fate of seven emerging 2-hydroxyphenyl substituted BZT-UVs were investigated in a Chinese WWTP. This group of hydrophobic BZT-UVs possess log K_{ow} values ranging from 4.31 to 7.67 which could be associated with their fate in WWTPs. Field samples including 24 h flow composites of influent, effluent and grab sludge samples from different treatment processes were collected and analyzed. Concentrations of BZT-UVs dissolved in aqueous-phases were in the range of 4.88 ± 1.35 (UV-234) to 34.5 ± 12.4 ng L⁻¹ (UV-P) in the primary influent, while only UV-P and UV-328 were detected in the final effluent at concentrations of 10.5 ± 6.59 and 2.74 ± 1.73 ng L⁻¹, respectively. Considering the amount of target BZT-UVs adsorbed to total suspended solids (TSS), the daily mass flux in the primary influent of the WWTP ranged from 22.3 g day⁻¹ (UV-P, 7.99%) to 74.0 g day⁻¹ (UV-234, 26.5%). Total removal efficiency of the integrated treatment process ranged from 89.7% for UV-P to 99.7% for UV-234 suggesting nearly complete removal. Organic solid sedimentation in primary and secondary clarifiers was the dominant elimination route for BZT-UV analogues, which constituted 96.3% of the total removal efficiency. Advanced treatment (using ultraviolet disinfection) in this plant might further contribute to the high removal efficiencies (ranging from 19.6% to 77.3%).

Received 17th September 2013
Accepted 15th January 2014

DOI: 10.1039/c3em00483j

rsc.li/process-impacts

Environmental impact

Benzotriazole UV stabilizers (BZT-UVs) have received increasing attention due to their potential environmental persistence and bioaccumulation properties. They are high production chemicals that are found in various consumer products. Research into the occurrence and behavior of various BZT-UVs in wastewater treatment plants is still scarce in China, especially for newly identified analogues such as UV-329 and UV-234. In this paper, a detailed investigation into the occurrence and removal of seven widely used BZT-UVs was performed to provide information on the quantity and routes of how BZT-UVs might enter the environment from wastewater treatment plants. Mass balance calculations are applied to both aqueous and solid phases to estimate the removal efficiency of each treatment process, and the possible mechanisms of removal are further discussed.

Introduction

Benzotriazoles (BZTs) are a series of chemicals that have been widely used in the chemical industry. Due to the absorption

ability in the full spectrum of UV-A (320–400 nm) and UV-B (280–320 nm) light, benzotriazole ultraviolet stabilizers (BZT-UVs) are applied to protect from ultraviolet radiation damage in a variety of daily-use and industrial products such as car accessories, film, shoes, building materials, photography antifogging agents and aeroplane defogging fluids.^{1–3} As a result of the extensive number of applications and very high production volume,⁴ BZT-UVs have received increasing attention in past decades, focusing on their environmental distribution and potential toxicological risks. The presence of certain BZT-UVs has already been proven in various environmental matrices.^{5–8} Previous research has indicated that a few BZT-UVs, such as 2-(3,5-di-*tert*-amyl-2-hydroxyphenyl) benzotriazole (UV-328), 2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole (UV-326), 2-(3,5-di-*tert*-butyl-2-hydroxyphenyl) benzotriazole (UV-320) and 5-chloro-2-(3,5-di-*tert*-butyl-2-hydroxyphenyl) benzotriazole (UV-327), were

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
E-mail: ghjiang@rcees.ac.cn; Fax: +86-10-62849334; Tel: +86-10-62849334

† Electronic supplementary information (ESI) available: Information of sampling WWTP (Table S1), optimized parameters for BZT-UVs analytes (Table S2), mass flux of dissolved and adsorbed BZT-UVs in water samples from each sampling sites (Table S3), concentrations of target BZT-UVs in primary and secondary sludge (Table S4). Physical-chemical properties of BZT-UVs calculated by EPI suite 4.1 and comparison between model calculation results and data from field samples (Tables S5 and S7). Removal percentages (%) of each treatment unit of five detected UV stabilizer congeners (Table S6). Chemical name, acronym, structure and LC-MS/MS chromatograms of BZT-UV analogues (Fig. S1 and S2). See DOI: 10.1039/c3em00483j

present in sediments from the marine environment and urban estuaries,^{9–11} while UV-328 and UV-327 have also been detected in blubber samples, suggesting that some BZT-UVs are bio-accumulative in the aquatic food chain.¹² The occurrence of BZT-UVs in indoor dust and sewage sludge further implies their ubiquity and persistence in the environment.^{11,13–15}

Information concerning the toxicity of BZTs is available from different animal experiments. Adverse reproductive effects were observed in the marine medaka (*Oryzias melastigma*), where the expression of vitellogenin and cytochrome oxidase (CYP1A1 and CYP19a) levels could be altered even at low exposure concentrations (0.01 mg L⁻¹) of benzotriazole corrosion inhibitors.¹⁶ UV-327, with a median lethal dose (LD₅₀) >2000 mg kg⁻¹ in rats and >25 mg L⁻¹ in fish,^{17,18} could cause hypertrophy of hepatocytes in young rats which was found to be gender-related.¹⁹ Similar gender-related hematological and histopathological changes were also observed for UV-320 in rats.²⁰

Generally, full scale WWTPs comprise physical and biochemical treatment systems. In the physical treatment process, sludge adsorption is usually the major removal mechanism, while the effectiveness of some organic chemical elimination is related to the biodegradation processes in the secondary treatment unit.²¹ For instance, estrogens could be efficiently removed from the dissolved phase in wastewater during biological treatment in WWTPs.²² However, contradictory conclusions were found for other chemicals such as triclosan, polybrominated diphenyl ethers (PBDEs) and tributyltin which were primarily adsorbed to sludge and removed in the physical treatment sections, while aerobic and anaerobic degradation removal was insignificant.^{23–25} Meanwhile, specific treatment processes have been investigated for their removal performance for hydrophilic BZT corrosion inhibitors. Activated sludge treatment in a bioreactor was found to be the major removal process accounting for 60% of benzotriazoles (1*H*-benzotriazole, tolyltriazole, xylotriazole and 1-hydroxybenzotriazole) and 30–75% of benzothiazoles (benzothiazole, 2-aminobenzothiazole, 2-hydroxybenzothiazole and 2-(methylthio)benzothiazole) removal.²⁶ Matamoros *et al.*²⁷ also reported high removal efficiencies for four benzotriazoles (ranging from 65–70%) and three benzothiazoles (0–80%) by activated sludge treatment while constructed wetlands exhibited better performances (89–93% and 83–90%). Beside conventional primary and secondary treatments, advanced oxidation processes (*e.g.* post-ozonation followed by sand filtration) were considered to be effective (>50% removal efficiency) for benzothiazole and 5-methylbenzotriazole degradation.²⁸ De la Cruz *et al.*^{29,30} pointed out that degradation efficiencies of UV, UV/H₂O₂ and neutral photo-Fenton at pilot scale for emergent hydrophilic BZT corrosion inhibitors were greater than 90% after various activated sludge treatments under aerobic conditions.

For many organic micropollutants, adsorption to suspended solids could be a key removal pathway during WWTP treatment which further leads to elevated residue levels in sewage sludge.³¹ WWTP effluents and sludge have therefore also been found to be potential sources of certain organic contaminants such as natural estrogens 17 α -estradiol (E2) and estrone (E1), PBDEs, parabens, polycyclic musks and certain UV filters (*i.e.*

4-methylbenzylidenecamphor, ethylhexyl-methoxy cinnamate and octocrylene).^{31–35} It is believed that the release of WWTP effluent and sludge could also be an important source of BZTs reaching the environment.³⁶

In this study, we focused our attention on the occurrence and removal efficiency of seven hydrophobic BZT-UVs: UV-P (2-(2-hydroxy-5-methylphenyl) benzotriazole), UV-234 ([3,5-bis(1-methyl-1-phenylethyl)-2-hydroxyphenyl] benzotriazole), UV-320, UV-326, UV-327, UV-328 and UV-329 (Fig. S1†) in a full scale WWTP in Shandong Province, China. This group of (2-hydroxyphenyl) benzotriazole derivatives are frequently used and are thought to cause widespread contamination in various parts of China, among which UV-234, UV-329, and UV-350 were newly identified in sewage sludge in China.¹⁵ Besides, the log *K*_{ow} values of these BZT-UVs differed widely from the hydrophilic BZT corrosion inhibitors which may be associated with various behaviors during WWTP treatments. To the best of our knowledge, specific research into the behavior of various BZT-UV homologues in WWTPs is still scarce. Thus, a mass balance investigation was initially performed on the fate, partitioning and mass loading of emerging BZT-UVs to provide valuable information on the quantity and route of how this group of chemicals might enter the environment from a full scale WWTP in China. Possible removal mechanisms in the different treatment processes are also discussed separately.

Materials and methods

Chemicals

Chemical names, acronyms and other relevant information about the BZT-UVs described in this article are shown in Fig. S1.† UV-P, UV-326, UV-327, UV-328 and UV-329 were purchased from TCI (Tokyo, Japan). UV-234 and internal standard (IS, Allyl-BZT) were obtained from Sigma-Aldrich (St. Louis, MO). UV-320 was purchased from Dr Ehrenstorfer (Augsburg, Germany). All chemicals have a purity of 98% or greater. HPLC-grade organic solvents were supplied by J. T. Baker (Phillipsburg, NJ). Ultrapure water (18.3 M Ω) was generated by a Milli-Q system (Millipore, Billerica, MA). Solid phase extraction columns used were HLB cartridges (500 mg, 6 cm³) from Waters Corporation (Milford, MA).

Sample collection

The selected municipal WWTP receiving domestic wastewater is located in Jinan city, Shandong Province in China, and serves 2 million local inhabitants with a loading capacity of 300 000 tonnes per day. The main treatment processes in this plant consist of a primary and a secondary treatment process followed by additional filtration and ultraviolet disinfection. The secondary treatment was mainly a biological AAO process while anoxic–oxic (AO) processes were integrated into one tank, in which the anoxic tank was combined with the oxic tank. Detailed information for the WWTP is summarized in Table S1 in the ESI.† All water samples were collected during the period June 25 to July 4 in 2012 under fine weather condition, covering the whole retention time period of the solids, in order to explore

the entire treatment removal efficiency. As shown in Fig. 1, influents and effluents of primary, secondary and advanced treatments were collected using flow proportional samplers (Global Water Inc., TX) as 24 h composite samples. As anoxic and oxic processes were combined in a unified tank, only the effluent of the anaerobic treatment process was collected. Sludge of primary and secondary clarifiers was collected during the middle of the sampling period. The channel for return sludge was airtight and thus sample collection was not possible. Solid samples were packed in aluminum foil and frozen at -20°C within 2 h and water samples were stored in pre-cleaned glass bottles, filtered and extracted within 12 h after collection.

Sample preparation and instrumental analysis

Water samples were filtered through a $0.7\ \mu\text{m}$ pore size GF/C glass fiber pad (Whatman, Maidstone, UK). After filtration, a 200 mL water sample was loaded onto a HLB SPE (solid phase extraction) cartridge (500 mg, $6\ \text{cm}^3$) which was preconditioned with 6 mL dichloromethane, 6 mL methanol and 6 mL purified water in sequence at a flow rate of $5\text{--}10\ \text{mL min}^{-1}$. After sample loading, the cartridge was washed with 6 mL purified water and eluted by 6 mL mixed solvent of dichloromethane and methanol (7 : 3, v/v). The collected eluate was dried under a gentle nitrogen stream and reconstituted with 1 mL methanol and spiked with a 50 ng internal standard before instrumental analysis.

The pretreatment procedure for sludge samples and total suspended solids (TSS) from water samples was similar to those previously reported, with minor modifications.¹⁵ Briefly, sludge samples were freeze dried, homogenized and sieved through a stainless steel 100-mesh sieve. Approximately 1 g sludge sample or 0.2–0.5 g TSS was extracted using accelerated solvent extraction (ASE 350, Dionex Inc., Sunnyvale, CA) at 90°C and 1500 psi in three static extraction cycles of 10 min with 15 g anhydrous sodium sulfate added as the dispersing agent. Hexane–dichloromethane (7 : 3, v/v) were utilized as the extraction solvent. The extract was concentrated to about 2 mL

by rotary evaporation followed by clean-up through a Biobeads S-X3 (Bio-Rad Laboratories, Hercules, CA) gel permeation chromatography column (GPC, $400 \times 30\ \text{mm}$, inner diameter). After the extract was loaded onto the column, the first 110 mL of eluate using a hexane–dichloromethane mixture (1 : 1, v/v) was discarded and the subsequent fraction of 120 mL was collected. For further purification, the collected eluate was rotary evaporated to about 1 mL and passed through a column filled with 8 g Florisil (60–100 mesh, Sigma-Aldrich, St. Louis, MO) which was pre-activated at 140°C for 7 h and 5% water-deactivated. The column was pre-conditioned with 30 mL hexane, and 50 mL hexane–dichloromethane mixture (1 : 1, v/v) was used for elution and collected after sample loading. Finally, the elution was concentrated to 2 mL and substituted with 1 mL methanol. The IS (100 ng) was spiked prior to instrumental analysis.

A HPLC-MS/MS system (Waters Inc., Milford, MA) consisting of an Alliance 2695 high-performance liquid chromatograph equipped with a Quattro Premier XE triple-quadrupole mass spectrometer was used for quantitative analysis.¹⁵ A Symmetry Shield RP18 analytical column ($4.6 \times 150\ \text{mm}$, $5\ \mu\text{m}$, Waters) was used for analyte separation with an injection volume of 20 μL . The mobile phase consists of methanol (solvent A) and deionized water (solvent B) and the elution gradient started from a composition of 8 : 2 (A : B, v/v) to 100% A in 20 min with a flow rate of $1\ \text{mL min}^{-1}$. Mass spectrometric analysis was operated in atmospheric pressure chemical ionization (APCI) positive mode with resolution tuned to 0.7 amu full-width half-maximum. The mass spectrometer parameters were set as follows: corona current was set as 3.0 μA , source temperature was 110°C , APCI probe temperature was optimized at 550°C , desolvation gas flow was $150\ \text{L h}^{-1}$ and argon pressure for ion collision was kept at $3.8 \times 10^{-3}\ \text{mbar}$. Detailed monitoring parameters for each of the compounds are given in Table S2 in the ESI.[†]

Quality assurance and quality control

Target BZT-UVs were positively identified and quantified by the following confirmation criteria according to Ruan *et al.*³⁷ The

Fig. 1 Mass flux of BZT-UVs (PI: primary influent, PE: primary effluent, AE: anaerobic effluent, A/AE: anoxic/aerobic effluent, SE: secondary effluent, FE: final effluent). Half of the MDL (method limits of detection) was employed for the calculation for the concentration of target BZT-UVs which were below the limit of detection.

retention time of field samples and the calibration standards should be within a tolerance level of 1.0%. The IS was spiked to real samples (100 ng in 1 g sludge and 100 ng in 200 mL water) which resulted in a recovery of $94.3 \pm 9.1\%$ indicating that the IS used was absent in the field samples and suitable as an internal standard in this study. The signal to noise ratio (S/N) was required to be greater than 10 : 1 for positive quantitation and the ratio of selected confirmation ions in field samples and reference standards should be within 20%. The recoveries of matrix spiked water samples (100 ng mL^{-1} for all target analytes) ranged from $53.4 \pm 4.1\%$ (UV-234, mean $\pm$ standard deviation) to $99.1 \pm 3.2\%$ (UV-326) with a mean value 82.3%, while solid samples ranged from $85.3 \pm 10.1\%$ (UV-350) to $98.5 \pm 11.3\%$ (UV-328) with a mean value 91.2% (100 ng g^{-1} for all analytes). One procedural blank was analyzed for each batch of seven samples and the results showed no contamination for almost all analytes except UV-326 in solid samples which contributed to less than 10% of average concentrations in each batch. Therefore, concentrations of UV-326 in blanks were subtracted during quantification. The method limits of detection (MDL) for all analytes were from 1.51 ng L^{-1} (UV-234) to 8.52 ng L^{-1} (UV-320) in water samples and from 0.19 ng g^{-1} to 0.91 ng g^{-1} in sludge (dry weight, d.w.). Calibration curves for all analytes were obtained within the range 0.1 to 500 ng mL^{-1} .

Results and discussion

Occurrence and concentrations of BZT-UV analogues during wastewater treatment

Detailed concentrations for all target BZT-UVs are summarized in Table 1. Among the seven BZT-UVs, five analogues (UV-P, UV-326, UV-329, UV-234 and UV-328) were positively detected both in water and sludge samples which suggested wide usage of these chemicals in this area. Total aqueous-phase concentration of the five BZT-UVs ($\sum \text{BZT-UVs}$) was $69.5 \pm 17.0 \text{ ng L}^{-1}$ in the influent of the primary clarifier. However, Fig. 2 shows a subsequent declining trend along the whole treatment process. Among the detected analogues, UV-P was the dominant compound in the aqueous-phase with concentrations ranging from 13.2 to 50.3 ng L^{-1} while the concentrations for UV-329, UV-234, UV-326 and UV-328 were $9.61 \pm 6.43 \text{ ng L}^{-1}$, $4.92 \pm 1.43 \text{ ng L}^{-1}$, $10.6 \pm 5.71 \text{ ng L}^{-1}$ and $9.90 \pm 9.41 \text{ ng L}^{-1}$, respectively. The contamination by several BZT-UVs in different

Fig. 2 Removal trends of target BZT-UVs in aqueous-phase (PI: primary influent, PE: primary effluent, AE: anaerobic effluent, BE: biotreatment effluent, SE: secondary effluent, FE: final effluent. Error bars indicate standard deviations of the concentrations ($n = 10$)).

regions has been reported with varied concentration levels and profiles. UV-326 and UV-329 were detected at $15 \pm 10 \text{ ng L}^{-1}$ and $227 \pm 13 \text{ ng L}^{-1}$ in the influent of a WWTP in Australia,³⁶ while in Spain, research showed UV-P, UV-326 and UV-328 existed in raw wastewater from an urban WWTP at concentrations up to 57 ng L^{-1} with no detectable UV-327.³⁸ UV-P, UV-326, UV-328 and UV-329 were considered as major BZT contaminants in different regions,^{2,13} which is similar to our data of field samples. Furthermore, UV-234 was detected in wastewater suggesting its usage and subsequent contamination potential, which is in accordance with previous reports.^{15,39} At the end of the whole treatment process including advanced treatment (ultraviolet disinfection), the BZT-UV analogues were barely detected in the final effluent except for UV-P and UV-328, which were determined at concentrations of 10.5 ± 6.61 and $2.74 \pm 1.73 \text{ ng L}^{-1}$ with a detection frequency of 100% and 57.1%, respectively.

Specifically, UV-326 and UV-329 could be removed in the aqueous-phase after the secondary clarifier while UV-234 was completely removed after advanced treatment. Conversely, the

Table 1 Sample concentrations, mass flux of target BZT-UVs and other relevant information in the treatment processes investigated

	Water flow ($\text{m}^3 \text{ day}^{-1}$)	TSS (g m^{-3})	Mass flux of TSS/sludge (kg day^{-1})	Concentrations of dissolved BZT-UVs (ng L^{-1})	Concentration of adsorbed BZT-UVs on TSS/sludge ($\text{ng g}^{-1} \text{ d.w.}$)	Dissolved mass flux (g day^{-1})	Adsorbed mass flux (g day^{-1})	Total BZT-UVs mass flux (g day^{-1})
Primary influent	3.00×10^5	550	1.65×10^5	69.5	1.69×10^3	20.9	279	300
Primary effluent	3.00×10^5	265	7.95×10^4	50.9	1.44×10^3	15.3	114	130
Anaerobic effluent	3.00×10^5	345	1.04×10^5	38.3	1.26×10^3	11.5	130	142
Anoxic-oxic effluent	3.00×10^5	355	1.07×10^5	37.9	1.14×10^3	11.4	121	133
Secondary effluent	3.00×10^5	7	2100	23.8	805	7.14	1.69	8.83
Primary sludge	3.00×10^5	—	8.50×10^7	—	1.92×10^3	—	—	163
Secondary sludge	3.00×10^5	—	9.0×10^7	—	1.34×10^3	—	—	120
Final effluent	3.00×10^5	5	1500	18.9	143	5.67	2.15×10^{-1}	5.88

detection of UV-P and UV-328 in the final effluent of the WWTP suggested that the conventional treatment process in this WWTP could not entirely eliminate these two chemicals in the aqueous-phase to levels below the MDL. This removal pattern shown in Fig. 2 might indicate that no specific treatment process was capable of completely eliminating these BZT-UVs in the aqueous-phase of the wastewater. For TSS in the primary influent, the composition pattern of the five detected BZT-UVs was in the following sequence (Table S3†): UV-234 (26.5%), UV-329 (23.5%), UV-326 (22.2%), UV-328 (19.8%) and UV-P (7.99%). As shown in Fig. 3, the mass flux of Σ BZT-UVs on the TSS was more than seven times higher than the aqueous-phase at each sampling station, implying the high adsorption capability of BZT-UVs onto organic solids.

The mass flux of Σ BZT-UVs significantly declined at the primary clarifier and secondary clarifier (170 g day^{-1} and 124 g day^{-1}) compared with the Σ BZT-UVs mass loading in the primary influent (299 g day^{-1} , Table 1). The results shown in Table S3† also revealed that the advanced treatment process was fairly effective for Σ BZT-UVs mass flux reduction on TSS (from 1.69 g day^{-1} to 0.247 g day^{-1}). Concentrations of BZT-UVs in sludge samples are presented in Table S4† and all results were reported using a dry weight (d.w.) basis. As primary sludge and secondary sludge were separately collected from this plant, the difference of the BZT-UVs composition profile could better distinguish the behaviour of BZT-UV during the secondary treatment process. As shown in Table S4,† UV-234 (mean concentration: $649 \text{ ng g}^{-1} \text{ d.w.}$) constituted 33.9% of total BZT-UVs in primary sludge, which was successively followed by UV-326 (mean concentration: $391 \text{ ng g}^{-1} \text{ d.w.}$, 20.4%), UV-329 ($388 \text{ ng g}^{-1} \text{ d.w.}$, 20.2%), UV-328 ($286 \text{ ng g}^{-1} \text{ d.w.}$, 14.9%) and UV-P ($203 \text{ ng g}^{-1} \text{ d.w.}$, 10.6%). In the secondary sludge, the composition slightly changed to UV-234 (24.3%), UV-326 (23.3%), UV-328 (21.8%), UV-329 (19.3%) and UV-P (11.3%). This rather similar profile could reflect the adsorption ability which is mainly affected by their log K_{ow} values (4.31 for UV-P to 7.67 for UV-234, Table S5†).⁴⁰

Mass balance calculation

The mass balance calculation is essential for understanding the fate of contaminants in each unit within a full scale WWTP. To

further estimate the contribution of each removal mechanism, the distribution of target chemicals between the aqueous and the solid phases was further investigated. The mass flux calculation of target BZT-UVs was performed on the basis of both aqueous-phase concentrations and solid adsorbed concentrations according to eqn (1).⁴¹

$$M = Q(C + S \times C_{TSS}) \quad (1)$$

$$\text{Removal efficiency (\%)} = M_{\text{lost}}/M_{\text{in}}; M_{\text{lost}} = M_{\text{in}} - M_{\text{out}} \quad (2)$$

M is the mass load of BZT-UVs (g day^{-1}), Q is the flow ($\text{m}^3 \text{ day}^{-1}$), C and C_{TSS} are the concentration log ratios of BZT-UVs dissolved in water (ng L^{-1}) and in the solid phase ($\text{ng g}^{-1} \text{ TSS}$), S is the suspended solids concentration (kg m^{-3}). Removal efficiency of each unit is calculated as the ratio of M_{lost} in each unit and M_{in} transferred in each unit (eqn (2)).⁴² M_{lost} is the difference between the mass flux entering the unit (M_{in}) and leaving the unit (M_{out}) in the treatment line. For the primary and secondary clarifiers, the BZT-UVs adsorbed onto the sludge were included in the M_{lost} .

As return sludge was inaccessible, the BZT-UV mass flux in this section was estimated as the difference between M_{lost} and mass flux adsorbed on secondary sludge. All results were calculated by the mean value from the field samples and shown in Fig. 1. In the primary influent of the plant, the combined mass flux of BZT-UVs (aqueous + solid phases) was about 300 g day^{-1} , consisting of 279 g day^{-1} in the fraction adsorbed to TSS and 20.9 g day^{-1} dissolved in the aqueous-phase. The ratio between the mass of BZT-UVs in the TSS and aqueous-phase in the primary influent was about 13 : 1 which showed that most BZT-UVs in raw wastewater were adsorbed onto the suspended solids. This distribution pattern indicates that the primary clarifier could eliminate approximately 56.7% Σ BZT-UVs due to the settling capacity of about 48.2% TSS in the primary influent which is calculated by the field sample results (Table 1). In the primary effluent, the mass flux of BZT-UVs declined to 43.3% of the primary influent while the primary sludge contained 54.3% of Σ BZT-UVs which was fairly consistent with the M_{lost} value (56.7%). In the anaerobic tank, the total BZT-UV mass flux slightly increased to 142 g day^{-1} which might be due to the input from return sludge and an increase of TSS content in the aqueous-phase by aeration (Table 1). Meanwhile, only a small decrease of total BZT-UV mass flux was observed with a mean value of 133 g day^{-1} in the anoxic and aerobic tank. However, a large mass flux decline occurred for the BZT-UVs after the secondary clarifier, resulting in detection of only 8.83 g day^{-1} BZT-UVs in the secondary effluent, among which UV-P contributed to 47.2% of total mass flux while the other four analogues accounted for 10.6% to 15.1%.

Removal efficiency and potential mechanisms

The removal percentages of the five target BZT-UVs were calculated assuming the mass flux in primary influent was 100% and total removal efficiency for BZT-UVs of the whole treatment process was 98.0% (Fig. 1). Removal efficiency for Σ BZT-UVs in the aqueous-phase was calculated to be more than

Fig. 3 Mass flux of target BZT-UVs in the aqueous-phase and TSS during the treatment processes.

72% and the final effluent of this WWTP might release only a minor amount of BZT-UVs to the local receiving waters. It is noteworthy that UV-P removal efficiency was only 89.7% while the other four analogues were all above 98.0% which might be related to the higher water solubility of UV-P among the five BZT-UVs (Table S5,† EPI suite v4.1).⁴⁰

Specific to each treatment unit, the removal efficiency was calculated by eqn (2) (Table S6†) and the results are presented in Fig. 4. The removal efficiency of the primary clarifier was 57.0% for Σ BZT-UVs and ranged from 42.6% (for UV-328) to 78.1% (for UV-234) for each individual component, which could be interpreted by the sedimentation of TSS in the raw wastewater. This assumption can also be concluded from the consistency in removal efficiency between the total amount of BZT-UVs and BZT-UVs in the TSS (Table 1). After the subsequent anaerobic tank digestion, 47.0% of BZT-UVs remained in the flow line, suggesting that the degradation efficiency in this treatment unit only contributed to a small proportion of the total BZT-UVs removed (UV-328 with removal efficiency of 14.4% while the mass flux of the other four BZT-UVs increased in the range 6.64% to 11.4%). In the anoxic-oxic tank, 8.21% of UV-329 and 7.50% of UV-328 were removed while UV-326, UV-P and UV-234 increased by 8.15%, 13.3% and 12.9%, respectively. All five target BZT-UVs showed substantial removal after the secondary clarifier, resulting in only 2.98% of the initial BZT-UVs remaining in the secondary effluent. The amount of residual BZT-UVs declined to about 2% after the advanced treatments. Compared to the primary (57.0%) and secondary clarifiers (93.3%), the removal efficiency of the secondary treatment (AAO units, -2.17%) was considered to be negligible for the target BZT-UVs. There are also reports concerning specific treatment processes that could have varied removal mechanisms of different BZT homologues. Previous research indicated that 1*H*-benzotriazole could not be efficiently removed by an 8 g h⁻¹ ozonation unit and a 1.4 m² slow sand filter which suggested its potential persistence in certain water treatment processes.⁴³ A similar phenomenon was found, in that generally aerobic

biodegradation was not efficient in eliminating 1*H*-benzotriazole and its methylated analogues (tolyltriazole) in WWTPs.^{44,45} Liu *et al.*³⁶ concluded that sorption onto organic solids eliminated the majority of UV-326 while biodegradation was more effective in the removal of 1*H*-benzotriazole and tolyltriazole. Despite these conclusions about the elimination of BZTs in various treatment steps, in this present study, sedimentation of solids with adsorbed BZT-UVs is still considered the major removal mechanism in WWTPs. To further elucidate this deduction, a model calculation (EPI suite v4.1) was performed. It was found that the BZT-UVs have higher log *K*_{ow} values (4.31 for UV-P to 7.67 for UV-234, Table S5†) compared with BZT corrosion inhibitors such as 1*H*-benzotriazole, tolyltriazole, 5,6-dimethylbenzotriazole and 5-chlorobenzotriazole (1.17 for 1*H*-benzotriazole to 2.17 for 5,6-dimethylbenzotriazole), which exhibited stronger adsorption tendencies. Removal efficiencies of WWTPs calculated from STPWIN32 (using the default setting for chemical half-lives of 10 000 h, summarised in Table S7†) were quite consistent with the calculation for the field samples, where the large proportion of adsorption (99.1–99.3% from calculations, 81.7–117% from field samples) contributed to the total removal mechanisms. From Fig. 4, it is interesting to note that the advanced treatment (ultraviolet disinfection) might also be an effective elimination step for BZT-UVs, and related to their physical-chemical properties, while advanced treatments (*e.g.* ozonation, UV, and UV/H₂O₂) were also reported to be effective in the removal of BZT corrosion inhibitors.^{28–30} Even so, the removal efficiency of the advanced treatment unit calculated by eqn (2) might not be properly evaluated, as the mass loading (8.83 g day⁻¹) into the advanced treatment unit obtained from field samples was extremely small.

Conclusions

In this work, the occurrence and fate of selected BZT homologues was investigated in a Chinese municipal WWTP. BZT-UVs were removed at varying elimination efficiencies during the different treatment processes. More than 89% Σ BZT-UVs were eliminated in the final effluent suggesting that WWTP treatment processes could be effective for BZT-UV elimination. High aqueous-phase removal (>72.0%) was observed for Σ BZT-UVs, in which the lowest removal efficiency was found, UV-P (69.7%) and highest UV-234 (85.7%). Elimination of BZT-UV analogues mainly occurred by the sedimentation process in the primary and secondary clarifiers, while the effects of biodegradation in the secondary treatment processes seemed to be insignificant (-2.17%). A large proportion of Σ BZT-UVs present in the secondary sludge also indicated that waste sludge could be a potential source of BZT-UVs reaching the environment. The fate of target BZT-UVs obtained in this work could help optimize operating parameters to improve the levels of removal efficiency of BZT-UVs in WWTPs. Due to limitations in the sampling number, WWTP scale and technical difficulties, further research is still needed to better understand the behaviour of BZT-UVs in different media during WWTP treatments, such as in the gaseous-phase and for removal efficiency by the different advanced treatments.

Fig. 4 Removal efficiencies (%) of target BZT-UVs in each treatment unit during the integrated processes in the WWTP.

Acknowledgements

This work was jointly supported by the National Natural Science Foundation (21207140, 20921063, and 21207148) and the National Basic Research Program of China (2009CB421605).

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