Occurrence and risks of triclosan and triclocarban in the Pearl River system, South China: From source to the receiving environment

Jian-Liang Zhao, Guang-Guo Ying*, You-Sheng Liu, Feng Chen, Ji-Feng Yang, Li Wang

State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China

ARTICLE INFO

ABSTRACT

We investigated two commonly used antimicrobial agents triclosan (TCS) and triclocarban (TCC) in the Pearl River system in China (i.e., Liuxi, Zhujiang and Shijing Rivers) and four sewage effluents during dry and wet seasons. The median values for TCS and TCC were the highest in the surface water and sediments of the Shijing River, followed by the Zhujiang River and Liuxi River. Screening level risk assessment using the risk quotient (RQ) method showed that TCS and TCC in surface water posed median risks in the Zhujiang and Liuxi Rivers (RQs: 0.28–0.62 for TCS, and 0.15–0.80 for TCC) and high risks in the Shijing River (RQs: 5.15–9.55 for TCS, and 3.32–5.83 for TCC). Higher risks (RQs: 3.63–28.47 for TCS, and 3.13–24.54 for TCC) were found in the sediments than in surface water of the Pearl River system. The four sewage effluents and Shijing River as well as other urban streams in Guangzhou metropolitan area were identified as the sources of the two compounds in the main river Zhujiang River. The mass inventories of TCS and TCC in the Pearl River system indicate that the sediments are not only an important sink but also a potential source for the two compounds in surface water.

1. Introduction

Triclosan (TCS; 5-chloro-2-(2,4-dichloro-phenoxy)-phenol) and triclocarban (TCC; *N*-(4-chlorophenyl)-*N*-(3,4-dichlorophenyl) urea) are two antimicrobial agents commonly used in many personal care products, including hand disinfecting soaps, kitchen detergents, body washes, toothpastes and medical disinfectants [1,2]. These products normally contain 0.1–2% of TCS or TCC by weight in their formula [3,4]. After discharge of these personal care products into domestic sewage, TCS or TCC may reach the environment due to their incomplete removal in wastewater treatment plants or direct discharge of wastewater without treatment [5].

These two compounds (TCS and TCC) have been reported in wastewaters and surface waters ranging from 9 ng/L to 6.7 μg/L [5–11]. Owing to their hydrophobic nature, TCS and TCC were found at 0.09–51 mg/kg levels in sludges [8,12]. So far there have still been few studies on the fate of these two compounds in the receiving aquatic environment, especially their levels in aquatic sediments and potential ecotoxicological risks.

Fate modeling and laboratory experiments showed that TCS and TCC are persistent in the environment under both aerobic and anaerobic conditions [13]. Limited toxicity data are available in the literature: green algae [14], crustacean [15] and fish [4,16], suggesting potential risks to aquatic organisms at environmental concentrations. TCS has been labeled as RED pesticide on the Reregistration Eligibility Decision by USEPA [17], while TCC is listed as a High-Production-Volume (HPV) chemical and ranked to have high risks to aqueous organisms [16].

Guangzhou region has a population of more than 10 million people, which generate nearly 2000 mega liters of domestic sewage per day from the four wastewater treatment plants (WWTPs). Direct discharge of untreated wastewater to the Pearl Rivers still occurs in some parts of the city and surrounding towns. To the best of our knowledge there has so far been no report on TCS and TCC in the aquatic environment of China. The aim of this study is to investigate the occurrence of TCS and TCC in surface water and sediment of the Pearl River system (Zhujiang River, Liuxi River and Shijing River) and in effluents of four WWTPs in Guangzhou, China. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) was developed to determine the levels of these two compounds in the environmental samples. Potential risks of the two compounds to aquatic organisms were also assessed by using calculating risk quotients (RQs) based on the measured environment concentrations (MECs) and predicted no effect concentrations (PNECs) which derived from toxicity data available in the literature.

* Corresponding author. Tel.: +86 020 85290200; fax: +86 020 85290200.
E-mail addresses: guangguo.ying@gmail.com, guang-guo.ying@csiro.au
(G.-G. Ying).

Table 1
Physical–chemical properties of triclosan and triclocarban.

Property	Triclosan	Triclocarban
CAS number	3380-34-5	101-20-2
Molecular formula	$C_{12}H_7Cl_3O_2$	$C_{13}H_9Cl_3N_2O$
Molecular weight	289.5	315.6
Melting point	56.5 °C	255.3 °C
Boiling point	434.57	373.62
Vapor pressure (mm Hg at 25 °C)	5.2×10^{-6}	3.45×10^{-13}
Water solubility (mg/L at 20 °C)	12	11
Henry's law constant (atm-m^3/mole)	1.5×10^{-7}	$<1 \times 10^{-8}$
Dissociation constant (pK_a) (20 °C)	8.14[a]	N/A[b]
log K_{ow} (at 25 °C and pH 7)[b]	4.7	4.9
Sorption coefficient (K_{oc})	18408[c]	50118[d]
Bioconcentration factor (BCF)	2.7–90[e]	137[f]
Photodegradation (half-life in aqueous solution)	41 min[a]	0.5 days[d]
Biodegradation (half-life in aerobic soil)[c]	18 days	108 days
Biodegradation (anaerobic condition)	No degradation within 70 days[c]	No biodegradation in 3 months[d]

[a] Ref. [17].
[b] Not available.
[c] Ref. [13].
[d] Ref. [16].
[e] To aquatic organisms [17].
[f] Measured in catfish [16].

2. Materials and methods

2.1. Materials

Triclosan (TCS) and triclocarban (TCC) were both purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Their physiochemical properties are given in Table 1. The internal standards $^{13}C_{12}$-TCS for TCS and TCC-d7 for TCC were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, U.S.). The stock solutions for TCS and TCC as well as their corresponding internal standards were prepared in methanol at the concentration of 100 mg/L, and stored at −18 °C for later use. All solvents used were HPLC grade and purchased from Merck Corporation (Shanghai, China). Neutral silica gel (100–200 mesh, Qingdao, China) was Soxhlet extracted with methanol and dichloromethane for 48 h prior to use. Anhydrous sodium sulfate was baked at 400 °C and stored in a sealed desiccator. All glassware was hand-washed with detergent and tap water, rinsed with Milli-Q water, and baked at 400 °C for at least 4 h prior to use.

2.2. Sample collection

Surface water samples and sediments were collected from the Liuxi River, Shijing River and Zhujiang River of the Pearl River system (Fig. 1). Liuxi Reservoir (S0) with little human activity was used as the control site located upstream of Liuxi River. Another three sites (S1–S3) were located downstream in the Liuxi River. Seven sites (S4–S10) were located in the Zhujiang River and four sites (S11–S14) were selected in the Shijing River. Effluent samples were collected from four wastewater treatment plants (W1–W4) during the dry and wet seasons. All samples were collected on December 17–18, 2007 in the dry season and on September 10–12, 2008 in the wet season.

Surface water samples in 1 L amber glass bottles were taken from 2 to 3 positions across the river section at each sampling site with the samples being collected from 0.5 m below the water surface. Two composite 1 L surface water samples were collected at each site, and 50 mL of methanol and 400 µL of 4 M H_2SO_4 were added immediately into each 1 L bottle after sample collection to adjust pH to 3.0 and suppress microbial activity. Surface sediment (0–10 cm) was collected using a stainless steel grab sampler from two positions of the section which were 10–20 m away from river bank. One gram of sodium azide was added for each liter of sedi-

ment immediately. The collected water and sediment samples were transported in coolers to the laboratory and stored in a cold room at 4 °C. The collected water samples were processed within 48 h using solid phase extraction (SPE), while the sediment samples were freeze-dried and stored at 4 °C for later analysis.

2.3. Sample extraction and purification

Water extraction was performed using solid phase extraction (SPE) method. Before SPE extraction, water samples (1 L each) were spiked with the internal standards (100 µL of 1 mg/L of $^{13}C_{12}$-TCS and TCC-d7) and then extracted using Waters Oasis HLB cartridges (6 cm^3, 500 mg sorbents) which had been conditioned with methanol and water. The cartridges were eluted with 7 mL of methanol and 5 mL of dichloromethane in sequence. The eluates were combined and dried under a gentle nitrogen stream, and then the extracts were immediately reconstituted in 1 mL of methanol.

Sediment extraction was performed using an ultrasonic extraction method. Briefly, 5 g of less polluted dry sediment samples (S0–S10) or 2 g of heavily polluted dry sediment samples (S11–S14) was weighted into a 30-mL centrifuge tube. Two replicate sediments were spiked with 100 ng of each internal standard. The sediments were then manually mixed and stored at 4 °C overnight. The samples were then extracted using 10 mL of ethyl acetate by vortex mixing thoroughly for 2 min, and ultrasonicating for 15 min. The tubes were centrifuged at 1370 × g for 10 min, and each supernatant was transferred into another test tube using a glass pipette. The extraction step was repeated twice. The supernatants from the same sample were combined and dried under a gentle nitrogen stream, and the extracts were redissolved in 1 mL of methanol.

The extracts of surface water and sediment samples were purified by passing through a silica gel column (1 g), and eluted with 6 mL of n-hexane, 6 mL of ethyl acetate, and 6 mL of methanol in sequence. The target compounds TCS and TCC as well as their internal standards ($^{13}C_{12}$-TCS and TCC-d7) were in the ethyl acetate phase. The final extracts were then dried under a nitrogen stream, reconstituted in 1 mL of methanol, and kept in −18 °C prior to instrumental analysis.

2.4. Instrumental analysis

The target compounds were analyzed using rapid resolution liquid chromatography-tandem mass spectrometry (RRLC-MS/MS)
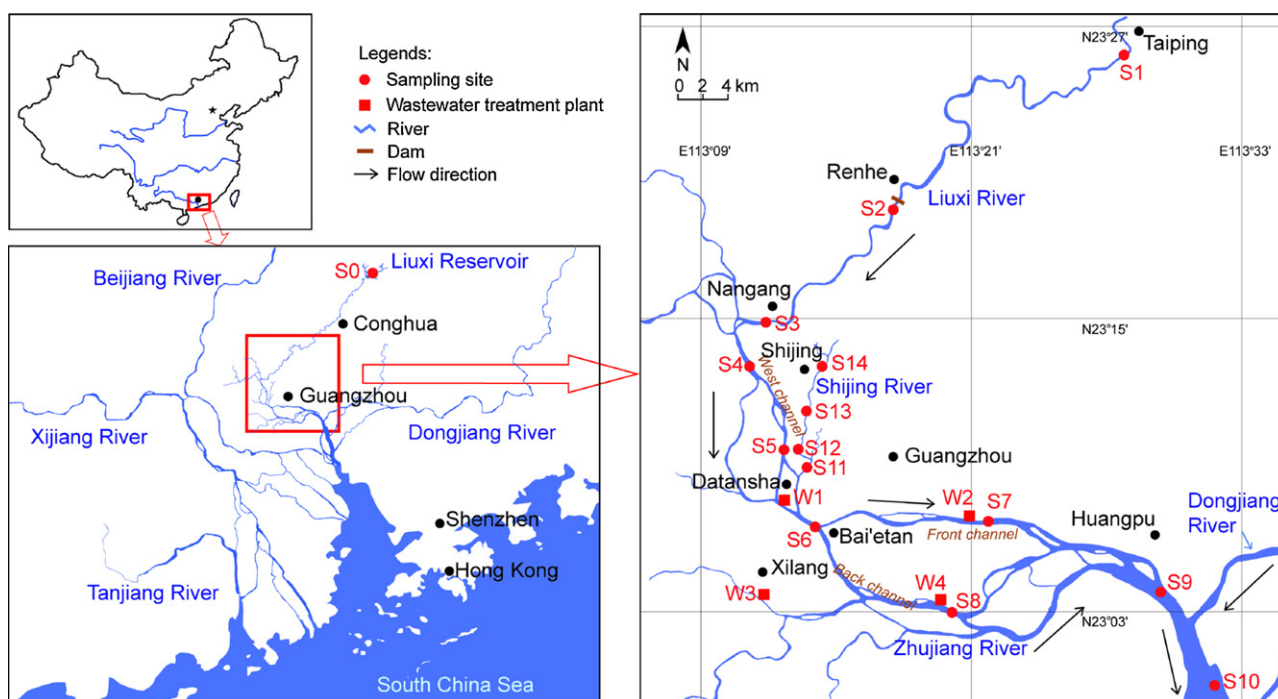
Fig. 1. Map of sampling sites in the Pearl River system, South China. Sites S0–S3 are in the Liuxi River, sites S4–S10 are in the Zhujiang River, and sites S11–S14 are in the Shijing River. W1–W4 are sewage treatment plants.

with electrospray ionization (ESI) in the negative mode. The instrument used in the analysis was an Agilent 1200 HPLC coupled to an Agilent 6460 Triple quadruple mass spectrometry, which was equipped with an ESI source using Agilent Jet Stream Technology (Agilent Corporation, U.S.). The data collection and processing were performed by using Agilent MassHunter software (v 1.0). The analytes were separated on a SB C18 column (100 mm × 3.0 mm i.d., 1.8 μm particle size), which was kindly provided by Agilent Technologies (Shanghai, China). Before analysis, samples was redissolved in methanol:Milli-Q water (1:1, v/v), and a sample volume of 10 μL was injected. A binary mixture of water (A) and acetonitrile (B) was used as the mobile phase, with the following gradient: 20% B at the beginning, increasing to 60% B at 15 min, then to 90% B at 20 min, and held for 5 min. The ionization source conditions used were as follows: the nebulizer gas 8 L/min, and sheath gas 12 L/min at a temperature of 350 °C; the nebulizer pressure 50 psi and the capillary voltage 3500 V. The mass spectrometric operating parameters were optimized using Agilent Optimizer Software (V 1.0) for the target compounds (Table 2).

Quantification was performed using internal standard method ($^{13}C_{12}$-TCS for TCS and TCC-d7 for TCC). Recoveries for TCS and TCC in surface water and sediments were obtained by spiking 5 ng/L, 100 ng/L and 200 ng/L in Liuxi Reservoir water and 2 ng/g, 20 ng/g and 100 ng/g in dried Liuxi Reservoir sediments, respectively. The recoveries obtained for all spiked concentrations were 106 ± 6% for TCS and 94 ± 10% for TCC in surface water, and 110 ± 9% for TCS and 106 ± 5% for TCC in sediment, respectively. The limit of detection (LOD) and limit of quantitation (LOQ) of the target analytes were calculated based on the standard deviations (SD) of seven replicates of the spiked samples at the concentration of 5 ng/L for water and 2 ng/g for sediment. LOD is defined as 3 times of the SD, and LOQ is 10 times of the SD [18]. The LODs and LOQs of TCS are 1.2 ng/L and 4.1 ng/L in surface water, and 0.6 ng/g and 1.9 ng/g in sediment. And the LODs and LOQs of TCC are 1.2 ng/L and 3.9 ng/L in surface water, and 0.6 ng/g and 1.9 ng/g in sediments.

2.5. Risk assessment

Aquatic chronic NOEC (no observed effect concentration) literature values of TCS and TCC were used to calculate PNECs according to European Commission Technical Guidance Document [19]. The PNEC was calculated by dividing the lowest chronic NOEC value from the most sensitive specie by an assessment factor. According to the TGD, when NOEC values from long-term exposure for one, two, or three trophic levels were available, an assessment factor of 100, 50 or 10 was used correspondingly for PNEC calculations [19]. For TCS, assessment factor 10 was used based on the three trophic level chronic NOEC values available in the literature [5,12]. For TCC, NOEC value was 2.9 μg/L for water flea (*Daphnia magana*) after 21 days of exposure, and the NOEC value was 5 μg/L for fathead min-

Table 2

Instrumental operating conditions for the target compounds.

Compound[a]	Retention time (min)	Precursor ion (*m/z*)	Product ions (*m/z*)	MS/MS parameters	
				Fragmentor (volts)	Collision energy (volts)
$^{13}C_{12}$-TCS	19.95	299	35.1	65	1
TCS	19.97	287	35.1	65	1
TCC-d7	19.68	320	163.1	107	5
TCC	19.77	313	160.1	86	5
		313	126.1	86	13

[a] $^{13}C_{12}$-TCS: $^{13}C_{12}$-triclosan; TCS: triclosan; TCC-d7: triclocarban-d7; and TCC: triclocarban.

Table 3
Flow rates of effluents and different river reaches in the Pearl River system, river reaches information and dilution factors of effluents, the Liuxi River and Shijing River relative to the Zhujiang River.

Site	Inhabitants serviced	Location	River reach length (km)	Width average (m)	Flow (m³/s)		Dilution factor[a]	
					Dry season	Wet season	Dry season	Wet season
WWTP								
Datansha (W1)	1,500,000	West channel	–	–	6.4[b]	6.4	27.5	154
Liede (W2)	2,150,000	Front channel	–	–	7.4	7.4	23.6	132
Xilang (W3)	600,000	Back channel	–	–	4.6	4.6	17.3	86.4
Lijiao (W4)	1,350,000	Back channel	–	–	2.3	2.3	43.5	244
River								
Liuxi River (S1)	–	–	11.27	285	17.3[c]	156[c]	16.2	5.8
Shijing River (S14)	–	–	19.35	34	3.5[d]	5.7[d]	80.0	158
Zhujiang River (West channel, S4, S5)	–	–	18	336	280[c]	900[c]	–	–
Zhujiang River (Front channel, S7)	–	–	28	432	175[c]	980[c]	–	–
Zhujiang River (Back channel, S8)	–	–	32	525	200[c]	1120[c]	–	–

[a] Dilution factor is defined as the ratio of the flow of effluent or river versus the flow of Zhujiang River.
[b] All of the STP effluent flow data were obtained from Guangzhou Sewage Treatment Co., Ltd.
[c] Data were provided by Guangdong Hydrology Bureau.
[d] [22].

nows (*Pimephales promelas*) after 35 days of exposure [16]. Hence, the assessment factor 50 was used based on the two trophic levels of chronic NOEC values available.

Risk assessment for the two compounds in surface water was conducted by calculating risk quotient (RQ) of each chemical at each river based on its maximum MEC and PNEC. Commonly used risk ranking criteria were applied in the present study: RQ < 0.1 means minimal risk, $0.1 \leq RQ < 1$ means median risk, and $RQ \geq 1$ means high risk [20]. The risk assessment for sediment was also performed by converting the concentrations of the two compounds into their corresponding pore water concentrations using the following equation:

$$C_{\text{pore water}} (\text{ng/L}) = \frac{1000 \cdot C_{s,i}}{K_{\text{oc}}} (\text{ng/g}) \cdot \% \text{ total organic carbon},$$

where K_{oc} value is the organic carbon partitioning coefficient and $C_{s,i}$ is the concentration in sediment. The risks for TCS and TCC in pore water were then assessed using the same method applied for surface water [21].

2.6. Calculation of dilution factor

The dilution factor used here is defined as dilution ratio when certain water (or effluent) is discharged into the Zhujiang River. For WWTP effluents and tributary rivers, the dilution factors are calculated as the ratio of the flows of the Zhujiang River versus the effluents or tributary rivers. The flow data from the local government and literature [22] and the calculated dilution factors are given in Table 3. In order to determine the contribution of the WWTP effluents and tributary rivers discharged into the main river Zhujiang River for each antimicrobial agent, the following equation is used:

$$\% \text{ contribution} = \frac{C/\text{dilution factor}}{C_{\text{Zhujiang River}}} \times 100,$$

where C is the concentration measured in a certain effluent, Shijing River (S14) or Liuxi River (S1), $C_{\text{Zhujiang River}}$ is the average concentration in receiving water (S4–S9 in the Zhujiang River). The percentage contributed by effluents is the sum of the four effluents (i.e. W1–W4). This calculation assumes that no degradation took place during the transport of the chemicals in the rivers.

To further assess the distribution of TCS and TCC in the Pearl River system, the mass inventory of TCS and TCC in the sediments of the Zhujiang River, Shijing River and Liuxi River were calculated. The mass inventory (I_s, in kilogram) was calculated by the following equations:

$$I_s = \sum k C_{s,i} A_i d \rho,$$

where $C_{s,i}$ is the average sediment concentration (ng/g) at area i, A_i is the area of the reaches (km²) calculated from the average width and length of corresponding reaches (Table 3), and d is the thickness of sediment sampled (cm), ρ is the average density of the dry sediment particles (g/cm³), and k is a conversion factor of 1×10^{-2}. The assumed sediment density of 1.5 g/cm³ and a sediment thickness of 5 cm are used [23].

3. Results and discussion

3.1. Levels of antimicrobial agents in surface water, effluents and sediments

The two antimicrobial agents TCS and TCC were detected in most of samples from the Liuxi River, Zhujiang River and Shijing River as well as the effluents from the four WWTPs (Table 4). The concentrations of TCS and TCC in the Liuxi Reservoir

Table 4
Concentration ranges, mean and median values, and detection frequency of triclosan and triclocarban measured in the Pearl River system and the effluents of the four sewage treatment plants.

Site	Triclosan				Triclocarban			
	Liuxi River	Zhujiang River	Shijing River	Effluents	Liuxi River	Zhujiang River	Shijing River	Effluents
Water								
Concentration range (ng/L)	<LOQ–26.2[a]	6.5–31.1	90.2–478	10.9–241	<LOQ–13.9	4.5–46.2	68.8–338	23.9–342
Mean (ng/L)[b]	13.7	16.8	242	71.0	7.4	19.9	158	104
Median (ng/L)[b]	11.9	16.2	238	41.2	6.0	17.1	145	47.8
Frequency (%)[b]	75	100	100	100	83	100	100	100
Sediments								
Concentration range (ng/g)	<LOQ–116	12.2–196	345–1329	ND[c]	<LOQ–426	58.0–904	748–2633	ND
Mean (ng/g)[b]	56.5	72.6	739	ND	173	327	1305	ND
Median (ng/g)[b]	50.5	58.8	693	ND	134	264	1039	ND
Frequency (%)[b]	67	100	100	ND	75	100	100	ND

[a] <LOQ, below limit of quantification.

[b] Mean value, median value and frequency are calculated based on those with concentrations higher than the limit of quantification.

[c] ND, not determined, below the limit of detection.

were below the detection limits (LOD: 1.2 ng/L for both compounds).

The highest concentrations for TCS and TCC in surface water were 478 ng/L and 338 ng/L, which were both found in Shijing River. This is consistent with water quality data reported for the three rivers [22,24]. Median values of TCS and TCC in the Liuxi River, Zhujiang River were both lower than 20 ng/L, while detected median values of TCS and TCC in the Shijing River were 238 ng/L and 145 ng/L, respectively. The concentrations of these two compounds (TCS and TCC) in the Shijing River are nearly 15 and 9 times those in Zhujiang River, respectively.

As found in surface water, TCS and TCC were found at the highest concentrations of 1329 ng/g and 2633 ng/g in the sediment from site 14 of Shijing River, respectively. The median values of TCS and TCC found in the Shijing River were approximately 10 and 4 times higher than those in the Zhujiang River. The monitoring data for TCS and TCC in surface water and sediment indicated that the Shijing River was heavily polluted by the two antimicrobial agents and other emerging contaminants (4-nonylphenol, bisphenol A and estrogens) which has been reported in our previous study [11].

TCS and TCC were also detected in all effluents from the four WWTPs in Guangzhou urban area. The mean concentrations for TCS and TCC in the effluent samples were 71 ng/L and 104 ng/L, respectively (Table 4), which were lower than those in the Shijing River, but higher than that in Zhujiang River. The highest concentrations for TCS and TCC were both found in the effluents from W2, which is the largest sewage treatment plant in the city of Guangzhou with daily treatment volume of 640 mega liters. The concentration ranges of TCS (10.9–241 ng/L) and TCC (23.9–342 ng/L) in the effluents measured in the present study are similar to those reported in U.S., Australia, Japan and Switzerland [1,5,7,8,10,12], but higher than those in Spain [25].

The concentrations of TCS in surface water of Liuxi and Zhujiang Rivers fall within the ranges reported in Switzerland, Hong Kong and Japan [1,9,10,26]. However, higher concentrations of TCS were often detected in U.S. streams with the median and maximum concentrations of 140 ng/L and 2300 ng/L [6]. The concentrations of TCS in the Shijing River fall in this concentration range (Table 4). In contrast to TCS, few studies reported the occurrence of TCC in surface water. The reported TCC concentrations range from <LOD in Ebro River of Spain [25] to 5600 ng/L in Greater Baltimore area, U.S. [7,27].

There have been few reports on the concentrations of TCS and TCC in sediments [28–30]. TCS was found at a mean concentration of 37 ng/g in Hudson River Estuary [30], while TCC was reported at a mean concentration of 12 ng/g in the downstream of sewage treatment plants [28]. However, higher concentrations

of TCC (700–1600 ng/g) were found in the Back River of the Chesapeake Bay watershed close to a sewage effluent discharge point [29]. Miller et al. [29] also found that TCC was about 14 times higher than that of TCS (<LOQ–80 ng/g). The concentrations of TCC were also 2–5 times higher than those of TCS in the present study. The difference in concentrations between the two antimicrobial agents is believed to be related to their different consumption and environmental behavior. This present study and previous studies showed that sediment is the major sink for the two compounds in the aquatic environment due to their hydrophobic nature.

3.2. Temporal and spatial distribution

In order to explore the influence of temporal change on the occurrence of TCS and TCC in surface water and sediment in the three rivers, the data from the two sampling events (dry season and wet season) were compared. Figs. 2 and 3 display the temporal and spatial distributions of TCS and TCC in surface water and sediments, respectively. The statistical method of one-way analysis of variance (ANOVA) was used to assess the differences. Significant seasonal differences of TCS ($F = 1.23$, $p = 0.049$) and TCC ($F = 5.16$, $p = 0.039$) were observed in Shijing River in surface water. The mean values of TCS and TCC in dry season were 1.60 and 1.62 times, respectively, those in wet season in surface water. The temporal discrepancy of TCS and TCC in the Shijing River were mainly attributed to the different flow rates in dry and wet seasons (Table 3), since contaminant stream could be easily diluted by rain water in wet season. Compared with the Shijing River, no significant temporal derivations were observed in the Zhujiang River and Liuxi River for both of TCS and TCC in surface water ($p > 0.05$), despite quite large difference of flow rates between dry and wet seasons of the two rivers. The reason may be due to the discharge of more untreated sewage wastewater from urban streams into the river in wet season. There are more than 200 small streams in Guangzhou metropolitan area, which are discharged straight into to Zhujiang River during rain events, but they are dammed and pumped to WWTPs during dry season. Statistical analysis also showed no significant seasonal variations for TCS and TCC in the three rivers in sediments ($p > 0.05$), indicating long-term accumulation and relative stability of TCS and TCC in the sediments.

Spatial differences of TCS and TCC were obvious when we compared the concentrations in the three rivers. The mean values and median values for TCS and TCC in surface water and sediment showed order-of-magnitude differences among the three rivers (Table 4). Subtle variations were also obvious within each river. Due to little human activity, Liuxi Reservoir was found to have TCS and TCC below the limit of quantification both in surface water and sed-
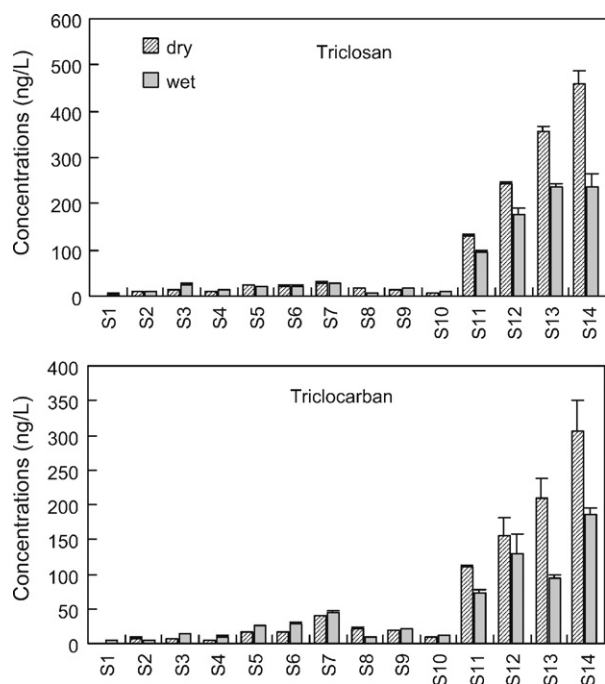
Fig. 2. Seasonal variation and spatial distribution of the two antimicrobial agents in surface water of the Pearl River system. TCS, triclosan; TCC, triclocarban. Sampling was conducted in dry season and wet season (i.e. December 17–18, 2007 and September 10–12, 2008, respectively). Sites S1–S3 are in the Liuxi River, sites S4–S10 are in the Zhujiang River, and sites S11–S14 are in the Shijing River. The error bars indicate the standard deviations of the measured concentrations (n = 4).

iment. Towards the downstream of the Liuxi River near Guangzhou city, TCS and TCC were detected at increasing concentrations. In the Zhujiang River, the two compounds were determined at slightly higher concentrations from the metropolitan sites (S5–S7) than
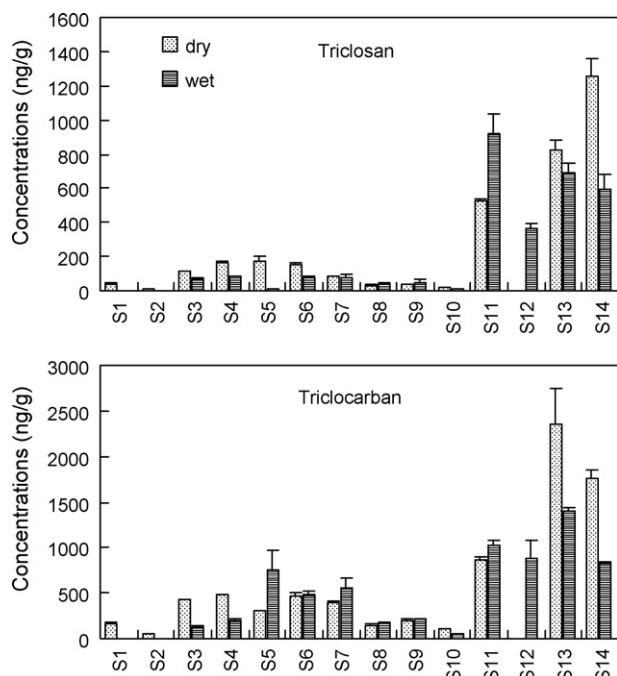

Fig. 3. Seasonal variation and spatial distribution of the two antimicrobial agents in sediments (0–10 cm) of the Pearl River system. TCS, triclosan; TCC, triclocarban. Sampling was conducted in dry season and wet season (i.e. December 17–18, 2007 and September 10–12, 2008, respectively). Sites S1–S3 are in the Liuxi River, sites S4–S10 are in the Zhujiang River, and sites S11–S14 are in the Shijing River. The error bars indicate the standard deviations of the measured concentrations (n = 4).

those sites (S9, S10) far away from metropolitan area (Figs. 2 and 3). In the Shijing River, higher concentrations for both compounds were detected in the upstream where domestic wastewater was directly discharged without treatment. Therefore we can conclude that municipal sewages from Guangzhou were the original sources of TCS and TCC in the Pearl River.

3.3. Screening level risk assessment

To demonstrate their potential impact, we conduct a screening level risk assessment of TCS and TCC to aquatic organisms in the Pearl River system. The PNECs for TCS and TCC were 50 ng/L and 58 ng/L based on the calculation using assessment factors of 10 and 50, respectively [19]. Measured environmental concentrations (MECs) were used in the screening level risk assessment. Table 5 presents the "worst case scenario" by using maximum MECs in the calculation of RQs for the two antimicrobial agents. The RQ values for TCS and TCC in surface water of the Shijing River were both higher than 1, while the RQs for both of them in surface water of the Zhujiang and Liuxi Rivers were between 0.1 and 1. When using the RQ classification scheme used in Hernando et al. [20], TCS and TCC pose a median risk in surface water of the Zhujiang and Liuxi Rivers and a high risk in surface water of the Shijing River.

Sediment risks were assessed by using calculated pore water concentrations for the two compounds. Compared with the risks in surface water, pore water derived from the sediments in the three rivers showed obviously higher RQs (Table 5). The RQs for TCS and TCC were higher than 1 in pore water of the three rivers (the maximum RQ up to 24.54), indicating a high risk to organisms in these rivers.

Risks caused by TCS in receiving surface water were also assessed in other regions. Reiss et al. [31] reported some algal species would be affected by TCS immediately downstream of WWTP discharges in U.S. by comparing the estimated concentrations with toxicity endpoint concentrations for the most sensitive species. In Australia, TCS also showed a high risk (RQ = 9.76) to aquatic organisms in receiving water from wastewater discharge sites based on the "worst case scenario" [5]. However, risk assessment of TCC in surface water has seldom been reported, neither has it been done for TCS and TCC in river sediments. Therefore, the risk assessment conducted for TCS and TCC in the present study provides an insight into their potential impact in the Pearl River system. Moreover, the higher risks from the two compounds in the sediments suggest that more attention should be paid to the fate of these two compounds in sediment.

3.4. Contribution and mass inventory in the Pearl River system

Further investigation into the contribution percentages by the four WWTP effluents, Shijing River and Liuxi River to the main river Zhujiang River and the mass inventories in the sediments would

Table 5
Risk quotients (RQs) of each antimicrobial agent in the Pearl River system based on the "worst case scenario".

Site	Triclosan		Triclocarban	
	Dry season	Wet season	Dry season	Wet season
Water				
Liuxi River	0.28	0.52	0.15	0.24
Zhujiang River	0.62	0.59	0.68	0.80
Shijing River	9.55	5.15	5.83	3.32
Sediments				
Liuxi River	5.11	3.63	4.41	3.13
Zhujiang River	6.53	4.04	5.63	3.48
Shijing River	19.38	28.47	16.70	24.54

Table 6
The contributions expressed as percentages (%) of effluents from the sewage treatment plants, the Shijing and Liuxi Rivers for each antimicrobial agent to the concentrations in the main river Zhujiang River.

Item	Triclosan	Triclocarban
Dry season		
Effluents	28.9	33.4
Shijing River	34.6	21.5
Liuxi River	1.0	1.2
Wet season		
Effluents	20.3	23.8
Shijing River	8.9	5.4
Liuxi River	4.4	3.3

facilitate better understanding of the distribution of TCS and TCC in the Pearl River system (Table 6). For the two antimicrobial agents, the four effluents and Shijing River contributed 28.9–33.4% and 21.6–34.6% to the Zhujiang River in dry season, respectively. While in the wet season, the four effluents and Shijing River only contributed 20.3–23.8% and 5.4–8.9%, respectively. This suggested that the effluents and Shijing River were the major contributing sources for the two compounds in the Zhujiang River in dry season, which contributed totally more than 50% in the Zhujiang River. However, during the wet season the contribution percentages decreased to 30% from the two sources, suggesting potential inputs from other sources especially those small tributary streams in the urban area. There are more than 200 urban streams along the Zhujiang River. Most of the urban streams are dammed in the dry season, but some of them flow to the Zhujiang River directly during the heavy rain events in the wet season; hence any contaminants in the urban streams could directly enter the Zhujiang River.

TCS and TCC have the tendency to adsorb onto particulate matter and then accumulate in sediments by deposition and partitioning processes since the two antimicrobial agents have high log K_{ow} values of 4.7 and 4.9, respectively [13,29,32]. The mass inventories (I_s) of TCS and TCC were then estimated for the three rivers. The I_s of TCS in the sediments of the Zhujiang River, Shijing River and Liuxi River were 204 kg, 36.5 kg and 18.4 kg, respectively; and the I_s of TCC in the sediments of the three rivers were 925 kg, 64.4 kg and 62.1 kg, respectively. Owing to their persistence [13], these massive amounts of TCS and TCC in the sediments could be potential pollution sources through desorption process [32]. Therefore, sediment is not only a sink of the two compounds, but also a potential pollution source for surface water in the Pearl River system.

4. Conclusions

TCS and TCC were found to be almost ubiquitous in surface water and sediments of the Pearl River system (Zhujiang River, Liuxi River and Shijing River). The highest concentrations of these two compounds were found in the Shijing River, and relatively lower concentrations were detected in the Zhujiang River and Liuxi River. Significant temporal differences of TCS and TCC concentrations were observed only in surface water of the Shijing River. Municipal sewages were the original sources for TCS and TCC in the Pearl River system. The TCS and TCC in surface water of the Liuxi River and Zhujiang River could pose median risks to aquatic organisms while those in the Shijing River could pose high risks. The two compounds in the sediments of the three rivers exhibited higher risks than in surface water. The four effluents, Shijing River and some urban streams were identified as the major sources for the two compounds in the Zhujiang River. Due to the accumulation of these two compounds in the sediments of the three rivers, sediments could be a sink for the two compounds, but also a source for release back into the surface water.

References

[1] H. Singer, S. Muller, C. Tixier, L. Pillonel, Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments, Environ. Sci. Technol. 36 (2002) 4998–5004.
[2] S.W. Tsai, M.W. Shih, Y.P. Pan, Determinations and residual characteristics of triclosan in household food detergents of Taiwan, Chemosphere 72 (2008) 1250–1255.
[3] C. Liu, Determination of chloroxylenol, triclocarban and triclosan in cosmetics and detergents using reversed-phase high performance liquid chromatography, Chin. J. Chromatogr. 22 (2004) 659–660 (in Chinese).
[4] T.E.A. Chalew, R.U. Halden, Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban, J. Am. Water Res. Assoc. 45 (2009) 4–13.
[5] G.G. Ying, R.S. Kookana, D.W. Kolpin, Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies, J. Environ. Monit. 11 (2009) 1498–1505.
[6] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance, Environ. Sci. Technol. 36 (2002) 1202–1211.
[7] R.U. Halden, D.H. Paull, Co-occurrence of triclocarban and triclosan in US water resources, Environ. Sci. Technol. 39 (2005) 1420–1426.
[8] G.G. Ying, R.S. Kookana, Triclosan in wastewaters and biosolids from Australian wastewater treatment plants, Environ. Int. 33 (2007) 199–205.
[9] S.Y. Zhang, Q.A. Zhang, S. Darisaw, O. Ehie, G.D. Wang, Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA, Chemosphere 66 (2007) 1057–1069.
[10] I. Nishi, T. Kawakami, S. Onodera, Monitoring of triclosan in the surface water of the Tone Canal, Japan, Bull. Environ. Contam. Toxicol. 80 (2008) 163–166.
[11] J.L. Zhao, G.G. Ying, L. Wang, J.F. Yang, X.B. Yang, L.H. Yang, X. Li, Determination of phenolic endocrine disrupting chemicals and acidic pharmaceuticals in surface water of the Pearl Rivers in South China by gas chromatography – negative chemical ionization – mass spectrometry, Sci. Total Environ. 407 (2009) 962–974.
[12] J. Heidler, A. Sapkota, R.U. Halden, Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment, Environ. Sci. Technol. 40 (2006) 3634–3639.
[13] G.G. Ying, X.Y. Yu, R.S. Kookana, Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modeling, Environ. Pollut. 150 (2007) 300–305.
[14] L.H. Yang, G.G. Ying, H.C. Su, J.L. Stauber, M.S. Adams, M.T. Binet, Growth-inhibiting effects of 12 antimicrobial agents and their mixtures on the freshwater microalga Pseudokirchneriella subcapitata, Environ. Toxicol. Chem. 27 (2008) 1201–1208.
[15] D.R. Orvos, D.J. Versteeg, J. Inauen, M. Capdevielle, A. Rothenstein, V. Cunningham, Aquatic toxicity of triclosan, Environ. Toxicol. Chem. 21 (2002) 1338–1349.
[16] USEPA, Risk-Based Prioritization Document: Initial Risk-Based Prioritization of High Production Volume (HPV) Chemicals: Triclocarban, United States Environmental Protection Agency, Washington, DC, 2009.
[17] USEPA, Reregistration Eligibility Decision for Triclosan, List B, Case No. 2340, United States Environmental Protection Agency, Washington, DC, 2008.
[18] P.M. Berthouex, L.C. Brown, Statistics for Environmental Engineers, second ed., Lewis Publishers, Washington, 2002.
[19] European Chemicals Bureau, European Commission Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No. 1488/94 on Risk Assessment for Existing Substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Official Journal of the European Commission, EUR 20418 EN/1, 2003.
[20] M.D. Hernando, M. Mezcua, A.R. Fernandez-Alba, D. Barcelo, Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments, Talanta 69 (2006) 334–342.
[21] L. Viganò, E. Benfenati, A.v. Cauwenberge, J.K. Eidem, C. Erratico, A. Goksøyr, W. Kloas, S. Maggioni, A. Mandich, R. Urbatzk, Estrogenicity profile and estrogenic compounds determined in river sediments by chemical analysis, ELISA and yeast assays, Chemosphere 73 (2008) 1078–1089.
[22] Q. Li, X.P. Sun, X.H. Chen, J. Liu, H.X. Yu, Z. Tao, Pilot-scale study on restoring polluted river water in the Shijing River, Guangzhou City, Acta Sci. Nat. Univ. Sunyatseni 47 (2008) 131–135 (in Chinese).

[23] S.J. Chen, X.J. Luo, B.X. Mai, G.Y. Sheng, J.M. Fu, E.Y. Zeng, Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the northern South China Sea, Environ. Sci. Technol. 40 (2006) 709–714.

[24] J.H. Luo, On water pollution of Shijing River in Guangzhou and its influence on the drinking water source (in Chinese), Chongqing Environ. Sci. 24 (5) (2002) 70–72.

[25] M. Pedrouzo, F. Borrull, R.M. Marce, E. Pocurull, Ultra-high-performance liquid chromatography-tandem mass spectrometry for determining the presence of eleven personal care products in surface and wastewaters, J. Chromatogr. A 1216 (2009) 6994–7000.

[26] J.L. Wu, N.P. Lam, D. Martens, A. Kettrup, Z.W. Cai, Triclosan determination in water related to wastewater treatment, Talanta 72 (2007) 1650–1654.

[27] R.U. Halden, D.H. Paull, Analysis of triclocarban in aquatic samples by liquid chromatography electrospray ionization mass spectrometry, Environ. Sci. Technol. 38 (2004) 4849–4855.

[28] A. Sapkota, J. Heldler, R.U. Halden, Detection of triclocarban and two co-contaminating chlorocarbanilides in US aquatic environments using isotope dilution liquid chromatography tandem mass spectrometry, Environ. Res. 103 (2007) 21–29.

[29] T.R. Miller, J. Heidler, S.N. Chillrud, A. Delaquil, J.C. Ritchie, J.N. Mihalic, R. Bopp, R.U. Halden, Fate of triclosan and evidence for reductive dechlorination of triclocarban in estuarine sediments, Environ. Sci. Technol. 42 (2008) 4570–4576.

[30] B. Wilson, J. Zhu, M. Cantwell, C.R. Olsen, Short-term dynamics and retention of triclosan in the lower Hudson River Estuary, Mar. Pollut. Bull. 56 (2008) 1230–1233.

[31] R. Reiss, N. Mackay, C. Habig, J. Griffin, An ecological risk assessment for triclosan in lotic systems following discharge from wastewater treatment plants in the United States, Environ. Toxicol. Chem. 21 (2002) 2483–2492.

[32] B. Wilson, R.F. Chen, M. Cantwell, A. Gontz, J. Zhu, C.R. Olsen, The partitioning of triclosan between aqueous and particulate bound phases in the Hudson River Estuary, Mar. Pollut. Bull. 59 (2009) 207–212.