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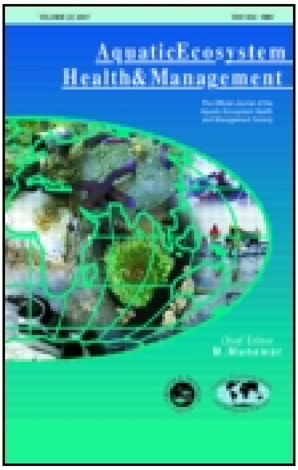

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Levels, spatial distribution and sources of selected antibiotics in the East River (Dongjiang), South China

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Levels, spatial distribution and sources of selected antibiotics in the East River (Dongjiang), South China

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Eleven selected antibiotics in the East River, South China, were measured using high performance liquid chromatography-electrospray ionization tandem mass spectrometry (HPLC-EI-MS-MS). Erythromycin, roxitromycin, azithromycin, clarithromycin, sulfadimidine, sulfamethoxazole, sulfadiazine and trimethoprim were detected with frequencies of more than 75%, and average concentrations ranging from 0.9 to 67.4 ng l^{-1}. The other three compounds' (sulfathiazole, sulfacetamide and spiramycin) concentrations were below detection limits. In general, the concentrations of sulfonamides and trimethoprim were higher than those of macrolides. The concentrations of macrolides showed a spatial distribution pattern of delta > lower reach > middle reach (or urban area > agriculture area), while sulfonamides and trimethoprim did not have a significant spatial pattern. Principal component analysis and comparison with wastewater were further used to explore source information of the antibiotics. The results suggested that macrolides in the East River were mainly associated with domestic sewage, while sulfonamides and trimethoprim may be more related to agriculture wastewater, especially livestock industrial wastewater. It is suggested that to ensure/improve the drinking water quality in the region, a better pollution control of livestock industry in the lower and middle reaches is of critical importance.

Keywords: pharmaceuticals, macrolides, sulfonamides, trimethoprim, Pearl River Delta

Introduction

Antibiotics have been used for several decades in both human and veterinary medicine for their antibacterial properties, as well as for animal growth promoters. Their consumption is gradually increasing in most countries. However, many of these antibiotics cannot be thoroughly metabolized, absorbed or eliminated in a biotic body and thus a high percentage of them will be excreted into the ecosystem via urine and feces (Hirsch et al., 1999; Li et al., 2009). Therefore, the occurrence, fate and potential toxic effects of antibiotics have become a focus of research in environmental science because of their potential influence on the spread and maintenance of

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resistance in bacterial pathogens and post-therapeutic effects.

In China, it has been estimated that the annual usage of antibiotics is about 180,000 tons (including health and agricultural use) (Tian, 2010). This means that each person consumes 138 grams of antibiotics every year, which is ten times the amount used in America (Tian, 2010). Considering the large consumption and the lack of effective management of antibiotics in China, especially in metropolitan areas, the occurrence and potential negative effects of antibiotics and personal care products on aquatic ecosystems and human health deserve detailed monitoring and investigation (Xu et al., 2009). However, to date, few data on the residues of antibiotics in aquatic environment are available from China (Minh et al., 2009; Peng et al., 2008; Xu et al., 2007, 2009). In these recent investigations, some antibiotics were detected in the aquatic environment in the Pearl River Delta with maximum concentration close to several μg l^{-1} level (Peng et al., 2008; Xu et al., 2007), and in the Yellow River and its tributaries with maximum concentration up to hundreds of ng l^{-1} (Xu et al., 2009). According to these studies, it is obvious that the aquatic environment in China is more heavily polluted by antibiotics compared with that of Europe and other developed countries.

The East River (Dongjiang) is one of the major tributaries of the Pearl River, which is the third largest river in China in the context of water flow. It is 435 km long, with a catchment area of 31,840 km^2. Along the river are important cities including Heyuan, Huizhou, Dongguan, Shenzhen and part of Guangzhou which together form the eastern part of the Pearl River Delta (PRD), one of the most important economic engines in China and the largest industrial manufacture base in the world. The East River is also the most important source water of the eastern part of the PRD, as well as Hong Kong. Rapid industrialization and urbanization during the last three decades in the catchment has led to a deterioration of water quality, in particular in the delta of the East River. In view of the importance of the East River as source water, both mainland China and Hong Kong governments have paid great attention to its water quality. It has been selected as a nationwide demonstration field venue for catchment-scale water quality protection/management by various funding bodies including the central government. Besides conventional water pollutants (e.g. N and P), micro-pollutants such as persistent organic pollutants (POPs) and pharmaceuticals and personal care products (PPCPs) were included as target chemical pollutants in the studies. The water quality and river sediments of the East River have been investigated for heavy metals and some POPs (Ho and Hui, 2001; Luo et al., 2008a,b; Ren et al., 2009). There has been no research yet on the occurrence of antibiotics in the East River.

The objectives of the study were to assess the levels, distribution and sources of common antibiotics in the East River. Eleven target compounds from the groups of macrolides (MLs), sulfonamides (SAs) and diaminopyrimidines (DMs) were selected owing to their wide use and occurrence in the environment (Tamtam et al., 2008; Xu et al., 2007). Statistics tools such as principal component analysis (PCA) were used to explore the source information of antibiotics.

Materials and methods

Sampling

A total of 63 river water samples were collected from the middle and lower reaches (14 samples) of the river, as well as twelve waterways of the river delta (49 samples) during July 15–26, 2009, when it was high water level season (Figure 1). Meanwhile, two wastewater samples from two outfalls to the river were collected for comparison purposes. One wastewater was discharged from a chemical factory and the other from domestic sewage.

The river water samples were collected (about 50 cm below the surface) using a stainless steel bucket in a fishing vessel at the centre of flow. Wastewater samples were obtained from the outfalls at the river bank. Water samples were immediately transferred to a 5-litre pre-cleaned amber glass bottle and each bottle was rinsed with sample water three times prior to sampling. The samples were kept at 4°C in a cold storage room before further treatment and analysis in laboratory.

Chemicals and standards

Sulfadiazine (SDZ), sulfamethoxazole (SMX), sulfadimidine (SDM), sulfathiazole (STZ), sulfacetamide (SAAM), erythromycin (ETM), spiramycin (SRM), azithromycin (AZM), clarithromycin (CTM), roxitromycin (RTM) and trimethoprim (TMP) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). $^{13}C_3$-caffeine

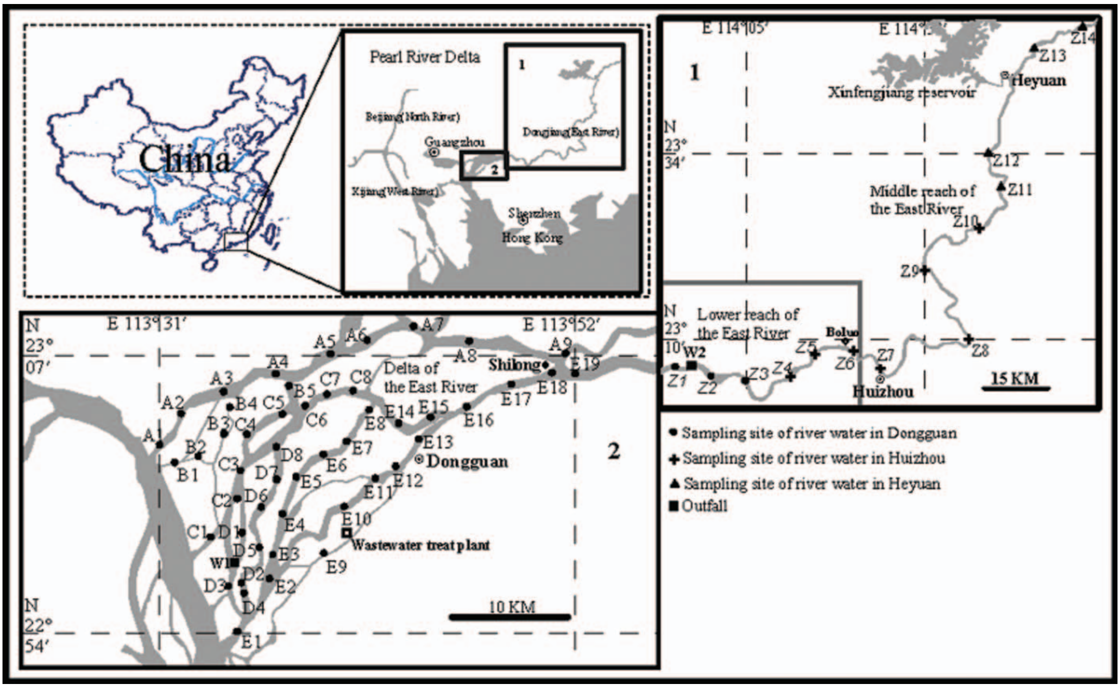

Figure 1. Sampling sites in the East River (Dongjiang). (Color figure available online.)

solution was obtained from Cambridge Isotope Labs (1 mg ml^{-1} in methanol, USA) and used as a surrogate standard. All antibiotic compounds were dissolved in methanol and stored in a freezer. Erythromycin-H_2O (ETM-H_2O), the major degradation product of erythromycin, was obtained by acidification using the method described in McArdell et al. (2003). Methanol (HPLC grade) was obtained from Merck (Darmstadt, Germany). Formic acid and ammonium acetate were purchased from CNW (Germany). Disodium edetate dihydrate (Na_2EDTA) was analytical grade and obtained from Tianjin Chemical (Tianjin, China). Ultra-pure water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Unless otherwise indicated, chemicals used in the analysis were analytical grade or above.

Sample extraction and analysis

Antibiotics in water were concentrated through a solid-phase extraction (SPE) by an Oasis HLB cartridge using the method described in Xu et al., 2007. In summary, water samples (2 l river water or 500 ml wastewater) were filtered through 0.45 μm glass fiber filters and then was acidified to pH = 3.0. The HLB column was then rinsed with 10 ml of ultra-water (pH 3.0), and dried under nitrogen gas for 1 h. After drying, the cartridge was eluted with methanol.

The extracted antibiotics were analyzed using high performance liquid chromatography–electrospray ionization tandem mass spectrometry (HPLC-ESI-MS-MS) with multiple reaction monitoring (MRM). The conditions of liquid chromatography and mass spectrometric were described in previous studies (Tang, 2009; Tang et al., 2009; Xu et al., 2007).

For the recovery experiments, 2 l of filtered river water fortified with 100 ng of target analytes were treated in the same procedure as the field samples.

Identification and quantification

Quantitative analysis of each compound was performed using HPLC-ESI-MS-MS with MRM mode using two of the highest characteristic precursor ion/product ion transitions. Together with retention times, the characteristic ions were used to ensure correct peak assignment and peak purity. The $^{13}C_3$-caffeine was added as a surrogate standard to all samples prior to enrichment and the

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control to compensate possible losses during the analytical procedure.

The limits of quantification (LOQ) for each compound in river water, obtained using the method described in the reference (Tang, 2009; Xu et al., 2007), was from 0.2 to 1 ng l^{-1}. And the recovery rates of these spiked antibiotics in river water were from 68% to 82%.

Results and discussion

Occurrence of the selected antibiotics in the East River water

The analytical results are presented in Table 1. The concentrations of antibiotics detected in the East River water ranged from nd (not detected or less than LOQ) to 475.8 ng l^{-1} with high detection frequencies of more than 75%. ETM-H_2O, SMX and SDM were detected in all of the samples. TMP, AZM and RTM also exhibited high detection frequencies of more than 90%, followed by CTM (85.7%) and SDZ (77.8%). SAAM, STZ and SRM were below detection limits in the samples. It should be noted that erythromycin was detected as its dehydration product erythromycin-H_2O (ETM-H_2O). It was reported that ETM-H_2O was the predominant form of ETM in aquatic environment (McArdell et al., 2003).

In general, the MLs antibiotics concentrations were lower than SAs and TMP. The concentrations of ETM-H_2O in river water ranged from 2.5 to 37.3 ng l^{-1} with a mean value of 16.8 ng l^{-1}, which was the highest among four targeted MLs compounds. The maximum concentration of ETM-H_2O in this study was comparable to the levels in Ebro River in Spain (nd–30 ng l^{-1}) (Gros et al., 2006) and Elbe River in German (30–40 ng l^{-1}) (Wiegel et al., 2004). It was less than the reported levels in Pearl River in China (13–636 ng l^{-1}) (Xu et al., 2007), Yellow River in China (nd–102 ng l^{-1}) (Xu et al., 2009), streams in the United States (max: 1700 ng l^{-1}) (Kolpin et al., 2002), Tyne River in England (4–70 ng l^{-1}) (Roberts and Thomas, 2006) and Youngsan River in South Korea (0–450 ng l^{-1}) (Kim and Carlson, 2007), but was higher than those measured in Victoria Harbour in Hong Kong, China (Xu et al., 2007).

The average concentrations of RTM, AZM and CTM were 2.1, 1.8 and 0.9 ng l^{-1}, respectively, obviously lower than that of ETM-H_2O. This agreed well with a previous study showing the highest concentration and detection frequency of ETM-H_2O followed by RTM and CTM in Chinese rivers (Peng et al., 2008; Tang, 2009; Xu et al., 2007). The concentration level of RTM in this river studied was less than that in Pearl River in South China (mean: 20 ng l^{-1}) (Xu et al., 2007), Yellow River in North China (nd–95 ng l^{-1}) (Xu et al., 2009) and Elbe River in German (<30–40 ng l^{-1}) (Wiegel et al., 2004). The level of CTM in Arc River, Southern French (Feitosa-Felizzola and Chiron, 2009) and in Po River, northern Italy (Calamari et al., 2003) was generally found to be in the several μg l^{-1} levels, which was noticeably higher than that we observed in the East River.

SDM, SMX and TMP were measured at nearly 100% detected frequency. The concentration of SDM ranged from 17.4 ng l^{-1} to 475.8 ng l^{-1}, with a mean value of 67.4 ng l^{-1}. It is the most abundant species among all the analytes. Compared with

Table 1. Summary results for the selected antibiotics in the East River water and sewage water.

		Macrolides				Sulfonamides			
(ng l^{-1})		ETM-H_2O	CTM	AZM	RTM	SDZ	SMX	SDM	TMP
River water	DF[a] (%)	100	85.7	96.8	93.7	77.8	100	100	98.4
	Mean[b]	16.8	0.9	1.8	2.1	1.0	14.9	67.4	5.6
	STD	7.6	0.6	1.1	1.4	1.2	4.9	68.4	2.5
	Range	2.5–37.3	nd[c]–2.7	nd–4.7	nd–8.4	nd–8.2	7.9–30.4	17.4–475.8	nd–15.5
Sewage water	W1	5.6	nd	0.6	nd	nd	1.0	5.4	nd
	W2	145.7	6.2	15.2	6.2	33.8	2.6	14.5	16.0
W2/River water[d]		8.7	7.3	8.4	3.0	2.3	2.5	0.2	2.9

[a]Detection frequencies. [b]Mean values were calculated using the measured values if above reporting limits, or the reporting limit value if below; [c]nd presents no detected or below LOQ; [d]ratios of selected antibiotics concentrations in W2 to those in the river water.

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reference data, the level was higher than those in the Pearl River in China (4–179 ng l^{-1}) (Xu et al., 2007), Yellow river in China (nd) (Xu et al., 2009), Victoria Harbour in Hong Kong (nd) (Xu et al., 2007), Seine River in France (<10 ng l^{-1}) (Tamtam et al., 2008), Elbe River in German (<30 ng l^{-1}) (Wiegel et al., 2004) and Youngsan River in South Korea (10–20 ng l^{-1}) (Kim and Carlson, 2007) . As SDM was exclusively used in veterinary medicine (Tamtam et al., 2008), the occurrence of SDM with a high level in the East River may indicate a significant contribution from livestock industry by the river. The concentration of SMX (range: 7.9–30.4 ng l^{-1}; mean: 14.9 ng l^{-1}) was lower than SDM concentration. Its level was lower than those in many other rivers, such as Pearl River in China (2–165 ng l^{-1}), Seine River in France (40–140 ng l^{-1}), Elbe River in German (30–70 ng l^{-1}) and Youngsan River in South Korea (0–110 ng l^{-1}), but comparable to those measured in Yellow River in China (nd–56 ng l^{-1}), and higher than those detected in Victoria Harbour in Hong Kong (nd), Ebro River in Spain (nd), Arc River in South France and Ebro River in Spain (nd).

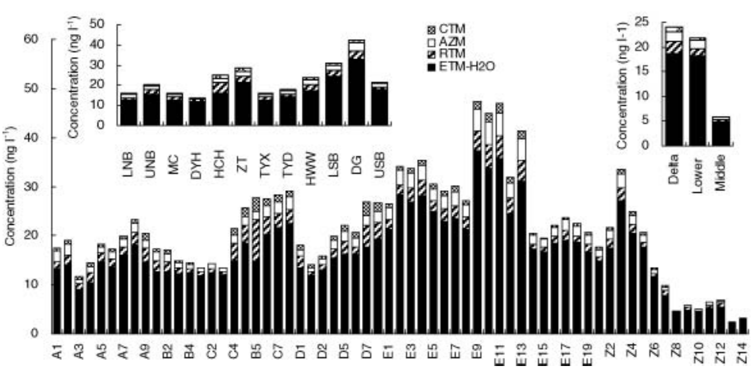
The synergist TMP is often prescribed in combination with SAs, notably SMX (fixed ratio of 1/5), has similar properties to SAs. TMP occurred at a mean concentration 5.5 ng l^{-1}, with a TMP/SMX ratio higher than 1/3. This may suggest that either they are subjected to different metabolism pathways and environmental fates, or SMX was used with other SAs compounds. The extensive coexistence of SDM, SMX and TMP further demonstrates that these chemicals in the water were from common sources, for example, livestock industrial wastewater. There is a great concern for these molecules as they are mobile in soil and therefore may contaminate the groundwater (Batt et al., 2006). In addition, their relatively weak sorption ability into particulate phase leading to a low removal rate in wastewater treatment plant (WWTP) treatments (Gobel et al., 2007; Lindberg et al., 2005; Tamtam et al., 2008). The extensive applications and high potential to resist degradation have led to a wide occurrence of these antibiotics in environment.

In summary, the concentrations of most antibiotics except SDM in the East River were somewhat lower than values in other areas in China and other countries. This may be due to the fact that both the mainland China and Hong Kong governments have paid great attention to its water quality in view of the importance of the East River as source water. However, this river was polluted by many antibiotics extensively to a certain degree and these pollutants may cause potential risk to environment and human health.

Spatial distribution of the selected antibiotics in the East River water

The MLs compounds showed a similar spatial distribution feature (Figure 2). In particular, there were significant correlation between ETM-H_2O and ATM ($r = 0.956$, $p < 0.01$) and between RTM and CTM ($r = 0.933$, $p < 0.01$). The average concentrations of each MLs compounds in the delta, lower and middle reaches of the river showed the same order: the delta > lower reach > middle reach.

The spatial distribution of MLs was likely related to the surrounding population and domestic sewage discharge. The following facts may explain



Note
Waterways in the delta of the East River:
Lower segment of the north branch of the East River (LNB): A1-A5
Up segment of the north branch of the East River (UNB): A6-A9
Machong Waterway (MC): B1-B4
Daoyunhai Waterway (DYH): C1-C3
Hengchongha i(HCH): C4,C5,B5
Zhongtang Waterway (ZT): C6-C8
Taiyangzhouxihai (TYX): D1,D3
Taiyangzhoudonghai (TYD): D2,D4
Hongwuwo Waterway (HWW): D5-D8
Lower segment of the south branch of the East River (LSB): E1-E8
Dongguan Waterway (DG): E9-E13
Up segment of the south branch of the East River (USB): E14-E19

Figure 2. Macrolides antibiotics concentrations in the East River water.

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the feature. Firstly, as an indicator substance, CTM is only registered for human therapy and consequently, domestic sewage would be the sole source of this substance in rivers. It is ingested and excreted by human body and would show positive correlation with population (Feitosa-Felizzola and Chiron, 2009). Moreover, MLs are the second most important antibacterial agents used for human therapy after the β-lactam family (Feitosa-Felizzola et al., 2009). Therefore, domestic sewage maybe the priority source of MLs in the environment. Last but not least, the population and domestic sewage discharge spatial distribution in this study shows similar feature with MLs antibiotics spatial distribution. As shown in Figure 1, the river delta is mainly located in Dongguan. By the end of 2009, it is estimated that there were more than 7 million residents in Dongguan and the population density of this city reached nearly 3000 people per square kilometre. The wastewater discharged into river by Dongguang in 2008 was 930 million tons (Water Reasearch Department of Guangdong Provience [WRDoGD], 2009). The lower reach is partly (Z1–Z3) in Dongguan and the other part (Z4–Z6) is in Huizhou. Huizhou has approximately 4 million people and the population density is less than 400 people per square kilometre. In 2008, Huizhou discharged 474 million tons of wastewater into river (WRDoGD, 2009). The middle reach is partly (Z7–Z10) in Huizhou and the other part (Z11–Z14) is in Heyuan. Heyuan has amount of mountains and is with about 200 people in one square kilometre. Nearly 362 million tons wastewater were discharged into river in 2008 in Heyuan (WRDoGD, 2009). It should be noted that the upper stream of the East River flows mainly through mountain/agriculture area with much fewer residents and industrial factories. Therefore, the MLs concentrations in the upper reaches (agricultural area) were all much lower than those in the lower reaches (urban area). The MLs antibiotics distribution presented similar character in the delta. For ETM-H_2O and AZM, their concentrations in Dongguan waterway (DG, E9–E13) were the highest in the delta. This is due to the fact that the DG waterway received the highest amount of domestic sewage discharge among all the waterways because it is located in the downtown area of Dongguan and the city's chief WWTP is located around this waterway.

The spatial distribution of SAs and TMP shows a different feature from that of MLs (Figure 3). In general, SDM, TMP and SDZ concentration in the delta was significantly higher than that in the

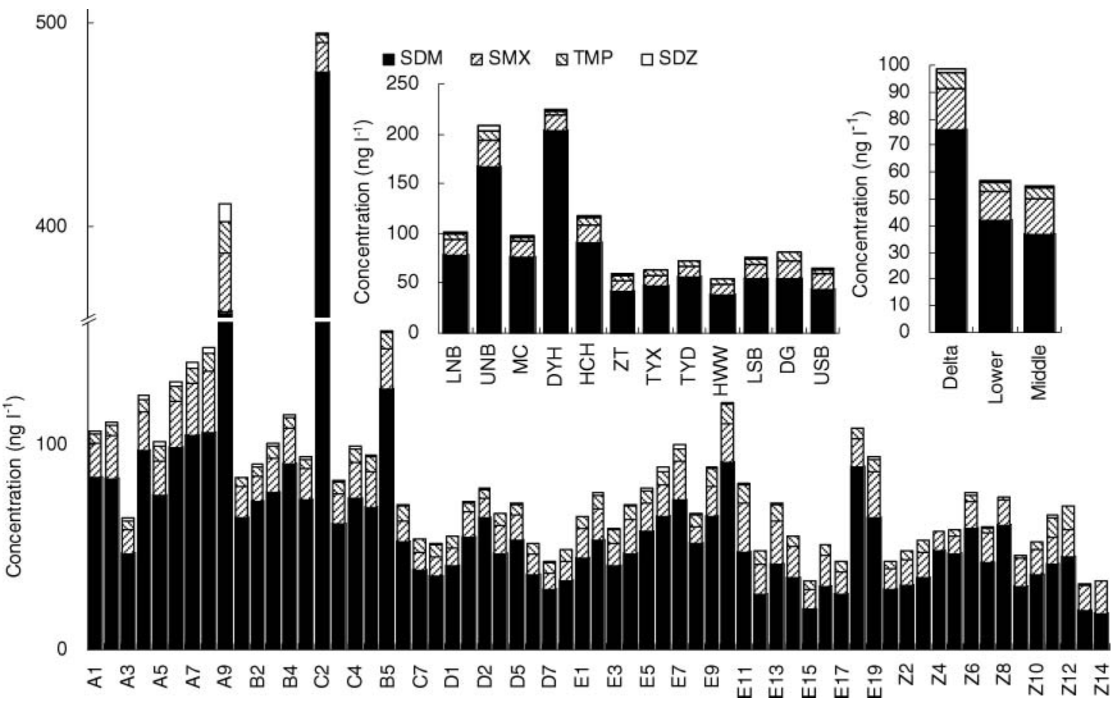

Figure 3. Sulfonamides antibiotics and trimethoprim concentrations in the East River water.

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lower and middle reach. However, the difference in SMX concentration was insignificant among the delta, lower and middle reach of the East River. Excluding the two special sites of A9 and C2, a similar concentration level of SAs and TMP was observed in the 12 waterways in the river delta. In general, the distribution character did not closely relate to surrounding population and domestic sewage discharge. In Dongguan, 707 million m^3 water was for domestic use, 1,003 million m^3 for industry and 141 million m^3 for agriculture in 2008, while the corresponding value is 251 million, 537 million and 1,274 million in Huizhou and 195 million, 484 million and 1098 million in Heyuan, respectively (WRDoGD, 2009). Therefore, we suggest that domestic sewage may contribute the major part of SAs and TMP residues in Dongguan, while agricultural wastewater may contribute mostly in Huizhou and Heyuan.

More closely, the highest concentration (476 ng l^{-1}) for SDM was measured at site C2, which was much higher than its average concentration (67 ng l^{-1}) in this study. It may be caused by point pollution, such as livestock industrial wastewater, hospital wastewater or certain factory wastewater. And the second highest concentration (358 ng l^{-1}) for SDM was observed at site A9. Meanwhile, concentrations of SDZ and TMP at site A9 were higher than the other sites. Concentration of SMX at site A9 was also higher than the other sites (except A8). It indicates that river water at A9, where Sha River pours into the East River, was seriously polluted by SAs and TMP. This contamination might be related to the inflow of water from Sha River, which was polluted by livestock industrial wastewater.

Principal components analysis

A principal component analysis (PCA) was employed to further explore the source information of antibiotics in the East River. PCA provides a means of reducing the complexity of the total antibiotics data set. Principal component (PC) loading values provide information about the relationship among the variables. The PC loading of antibiotics in the East River water were shown in Figure 4. The result shows that all SAs and TMP were grouped together nicely as well as all the MLs. The first two components (43% and 31%) account for 74% of the variance in the data. The first principal component was largely contributed from all MLs antibiotics. The second component was mainly related to SAs and

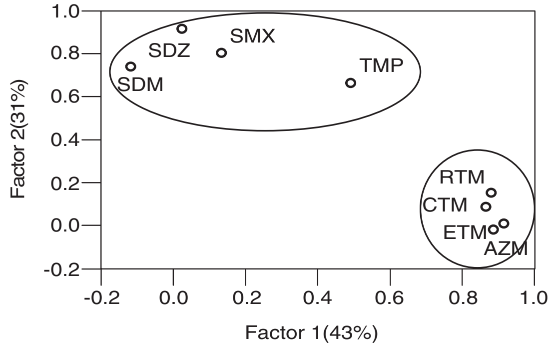

Figure 4. Principal component analysis (PCA): loading for antibiotics in the East River.

TMP. This may indicate different sources and/or different environmental fate of MLs and SAs/TMP. It is likely that PC1 is essentially the domestic sewage factor and PC2 represents the livestock industrial wastewater.

Occurrence of selected antibiotics in wastewater and source information

W1 and W2 were chemical factory wastewater and domestic sewage sample, respectively. Only four compounds were detected in W1. They were ETM-H_2O, AZM, SDM and SDZ with concentrations of 5.6, 0.6, 5.42 and 1.04 ng l^{-1}, respectively (Table 1). Their concentrations were lower than the corresponding average concentrations in the East River water.

All of the eight antibiotics detected in the river water were detected in the domestic sewage as well with concentrations range from 2.6 to 145.7 ng l^{-1}. Their concentrations were higher than corresponding concentrations in the river water except for SDM.

The correlate relationship of some compounds' concentrations in the river water or sewage may possibly be used to estimate their source. Ratios of some compounds concentrations in the possible source to the river water may serve as an index to estimate antibiotics' source of the river water. The ratios of selected antibiotics in the domestic sewage and river were shown in Table 1. As CTM is used as a tracer from human source (Feitosa-Felizzola and Chiron, 2009), the dilution ratio of CTM in domestic sewage to river water may serve as a index to estimate antibiotics' source. The concentration ratios of ETM-H_2O and AZM in the domestic sewage and in the East River are similar to that of CTM in the two

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environments. Therefore, ETM-H_2O, AZM and CTM may come from same source: domestic sewage. Other compounds, such as RTM, SDM, SMX, SDZ and TMP, presenting lower ratios, might be subject to pollution sources other than domestic sewage in this area. Of course, the discussion above was based on the hypothesis that these antibiotics presented similar environmental fate in river water and sewage. Therefore, detailed study like modelling is needed for a better understanding of their sources and fate in the East River.

Implication to drinking water quality in the PRD

The East River is the most important source water in the PRD and adjacent regions. Apart from Heyuan, Huizhou, Dongguan and Shenzhen, the river also supplies water to Guangzhou (partly) and Hong Kong. This may cover a population of >20 million. The feeding points for the regional water supply system are mostly located at the river segments upper than Shilong (Figure 1) to avoid tidal affection, corresponding to the lower reach of the river as termed in the above description. As discussed above, our results found that the river segments serving as the source water receives more pollution from agriculture wastewater in particular livestock industrial wastewater in the context of antibiotics, characteristics of high concentrations of SAs and TMP. Therefore, our results suggested that pollution control in agriculture wastewater, especially livestock industrial wastewater, is of critical importance to ensure/improve the drinking water quality in the PRD.

Conclusions

This study aimed to investigate the levels, spatial distribution and sources of common antibiotics in the East River. Eleven antibiotics from the groups of MLs, SAs and DMs were measured in water samples from the delta, lower and middle reaches of the river. Two wastewater samples were also analyzed for comparison. PCA was employed to explore potential source information of the antibiotics. The result showed that 8 selected antibiotics (ETM-H_2O, RTM, AZM, CTM, SDM, SMX, SDZ and TMP) widely occurred in the East River with detection frequencies of more than 75%; while the concentration levels may reach hundreds of ng l^{-1} in the aqueous phase. Concentrations of SAs and TMP were generally higher than MLs. Spatially, the average concentrations of each MLs decreased in the order of: river delta > lower reach > middle reach (or urban area > agriculture area). However, 9 the spatial variations of SAs and TMP concentration were insignificant. It may be concluded from these results that MLs in the East River were associated mainly with domestic sewages, while SAs and TMP were more related to agricultural wastewater, e.g. livestock industrial wastewater. Our findings suggested that attention must be paid to better pollution control of livestock industry in the lower and middle reaches of the East River, where the regional drinking water sources are located.

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