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PAPER

Occurrence of selected antibiotics in Jiulongjiang River in various seasons, South China

Dandan Zhang,[ab] Lifeng Lin,[a] Zhuanxi Luo,[a] Changzhou Yan[a] and Xian Zhang*[a]

The concentrations of six sulfonamides (SAs) and three tetracyclines (TCs) were investigated in Jiulongjiang River during the low water season and the high water season. They were monitored in both surface water and sediment. Total concentrations of all these antibiotics varied from 31 to 25 771 ng g^{-1} in sediment samples. In water they ranged from 60 to 2607 ng L^{-1} during the low water season and from ND (not detected) to 134 ng L^{-1} during the high water season. At the sites nearby breeding farms, chlorotetracycline was found to have the highest concentration of 1036 ng L^{-1} in water and 14 666 ng g^{-1} in sediments. According to the published data, the concentrations of sulfamethazine, sulfameter and TCs at these sites were higher than that in most rivers. The concentrations during the low water season were tens to hundreds of times higher than that in the high water season. The lower concentrations of TCs in the high water season might result from both dilution and photo-degradation, while dilution and bio-degradation might lead to the lower concentrations of SAs. However, further study is needed to clarify the specific reasons. Concerning the relationship between sediment and water samples, the pseudo-partitioning values of TCs were much higher than SAs. It indicates that the TCs are prone to accumulate in the sediment.

1. Introduction

Antibiotics are probably the most common drugs used for preventing and treating diseases of human and animals. They are also used as growth promoters in the animal industry. Most of the antibiotics are poorly absorbed by humans and animals after intake, and a high percentage is excreted into the natural ecosystem *via* urine and feces.[1] Antibiotic residues in the aquatic environment may kill aquatic species and breed antibiotic resistant microbes. Furthermore, in terrestrial environments it may inhibit the growth of plants.[2–4] Antibiotic resistant bacteria have become an important environmental issue because they pose

a potential threat to human health.[5–7] In particular, the occurrence of the superbug antibiotic resistant gene NDM-1 in South Asia and in Britain caused a big panic in 2010. It was said that there were almost no drugs to treat this superbug and it could spread around the world.[8] Because of antibiotic resistant bacteria and genes, the occurrence of antibiotics in environment is receiving increased attention.

There have been some studies on the occurrence of antibiotics in surface water,[4] wastewater,[9] groundwater,[10] drinking water,[11,12] as well as soil[13] and sediments[14] in many countries. Jiulongjiang River is the second longest river in Fujian Province, South China. It is composed of two major tributaries (Xixi River and Beixi River) and many small tributaries with 285 km of river length and 14 000 square kilometres of watershed. It is the most important source of drinking water, industrial and agricultural activities in Southern Fujian Province. Livestock breeding is one of the main economic activities along Jiulongjiang River. But

[a]Key Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, PR China. E-mail: xzhang@iue.ac.cn; Fax: +86 592 6190518; Tel: +86 592 6190519
[b]Graduate University of Chinese Academy of Sciences, Beijing, 100049, China

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Environmental impact

Antibiotic residues in the environment are receiving significant attention because of their potential adverse effects on ecosystems and human health. Available information on the occurrence of antibiotics in the aquatic environment is limited. The objectives of this study were to determine the occurrence of nine kinds of antibiotics and the seasonal variability of these contaminants, and to understand the dynamics of antibiotics between sediment and surface water phases. The study develops an occurrence database of the antibiotics in spatial and temporal scale in Jiulongjiang River, South China.

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most farms do not have facilities to treat and dispose of mature and wastewater, which leads to potential antibiotics input from livestock waste to the river.

Sulfonamides (SAs) and tetracyclines (TCs) are two classes of the antibiotics commonly used in livestock therapy to promoting growth. Both of them exhibit a broad-spectrum antimicrobial activity against a variety of disease-producing bacteria. In this study, six kinds of sulfonamides (sulfadiazine, sulfamerazine, sulfamethazine, sulfameter, sulfadimethoxine, sulfamethoxazole) and three kinds of tetracycline (tetracycline, oxytetracycline, chlorotetracycline) were selected as target antibiotics. They were analyzed by liquid chromatography in combination with tandem mass spectrometry (LC–MS/MS) in surface water and sediment samples collected from the Jiulongjiang River. The aims of this study were: (1) to determine the antibiotics levels in the water and sediment of Jiulongjiang River in the high and low water seasons for an understanding of the occurrence of common antibiotics in this region; and (2) to understand the dynamics of antibiotics between sediment and surface water phases.

2.   Materials and methods

2.1.   Chemicals and materials

Sulfadiazine (SD), sulfamerazine (SM1), sulfamethazine (SM2), sulfameter (SMT), sulfadimethoxine (SDM), sulfamethoxazole (SMZ), tetracycline (TC), oxytetracycline (OTC) and chlorotetracycline (CTC) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Oasis HLB solid phase extraction (SPE) cartridges (200 mg, 6 mL for water sample extraction and 500 mg, 6 mL for the sediment extraction) were obtained from Waters Corporation (Milford, MA, USA). HPLC-grade methanol, acetone and acetonitrile were purchased from TEDIA Company (Fairfield, OH, USA). Milli-Q water was used throughout the study. Unless indicated, chemicals used in the analysis were analytical grade.

Nine kinds of antibiotic standard solutions (100 mg L^{-1}) were prepared by dissolving 5 mg standard antibiotic in 50 mL 10% methanol solution, individually. They were kept in brown glass vials in the refrigerator (4 °C). Phosphate buffer (0.2 mol L^{-1}, pH = 3) was prepared by dissolving 31.2 g sodium dihydrogen phosphate (NaH_2PO_4) in Milli-Q water and diluted to 1.0 L, pH = 3.0 was obtained by adding 6 mol L^{-1} HCl.

2.2.   Sampling

2.2.1.   Sample location.
Samples were collected from nineteen sites along the Jiulongjiang River, Fujian Province in South China. In this study, Jiulongjiang River is divided into three regions: Beixi River (B), Xixi River (X) and estuary (E) (Fig. 1). There were eleven sites located in region B, three in region X and five in region E. Sites B1 and B2 are located in the downtown area of Longyan City. It should be noted that many swine farms were found near to Longyan City. B3 is sited downstream of the sewage treatment plant of Longyan City. B4 is located in Yanshi Town which has a developed swine breeding industry. B5 is at the confluence of the Wanan Stream and the Yanshi Stream. The samples of B6 and B7 were collected from upstream and downstream of Zhangping City, respectively. B8 and B9 are sited upstream and downstream of Hua'an County. X1, X2 and X3
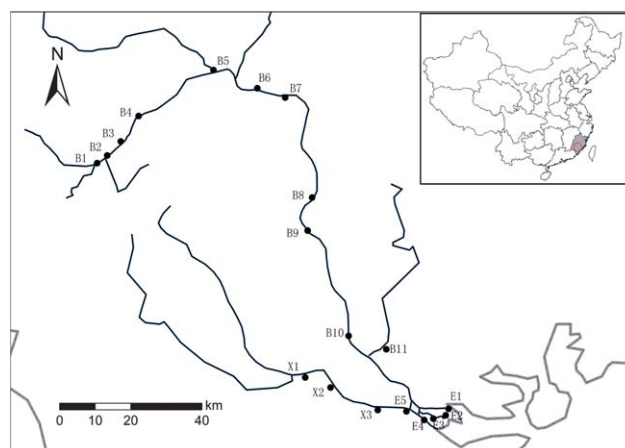

Fig. 1 Sampling sites along the Jiulongjiang River.

were collected from Xixi Stream, B10 is situated at a sand quarrying site on Beixi River. B11 was collected from Longjinxi Stream. E1 to E5 are located in the estuary of Jiulongjiang River. Throughout the survey, a global positioning system (GPS) was used to locate the sampling locations.

2.2.2.   Sample collection.
According to the record of runoff information, the water flow of Jiulongjiang River was the lowest in January which accounted for only 2.6% of the annual runoff. From June to August, the water flow was at a high level which accounted for 45% of the annual runoff. The low water season therefore occurs in January, and the high water season begins in June, running on to August. Surface water samples were collected in low water season (January 2010) and high water season (August 2010), respectively. All water samples were stored in pre-cleaned brown glass bottles and stored in 4 °C.

Duplicate samples of sediment were collected by a grab sampler from each site in January 2010 (low water season). Each sample collected was more than 500 g. Collected samples were stored in clean aluminium containers and kept at −18 °C before extraction and analysis.

2.3.   Sample pre-treatment

2.3.1.   Water sample extraction.
The water samples were filtered through 0.45 μm fiber filters within 24 h of sample collection. One litre of water sample was acidified to pH = 3.0 by adding 6 mol L^{-1} HCl, followed by addition of 0.2 g Na$_2$EDTA. The samples were extracted using Oasis HLB (200 mg, 6 mL) extraction cartridges. Each cartridge was sequentially pre-conditioned with 6.0 mL of acetone, 6.0 mL of methanol and 6.0 mL of 5 mmol L^{-1} ammonium acetate dissolved in 0.1% formic acid solution (v/v). The water samples were then passed through the pre-conditioned cartridges at a flow rate of approximately 10 mL min^{-1}. After that, the cartridge was rinsed with 6 mL of 5 mmol L^{-1} ammonium acetate dissolved in 0.1% formic acid solution (v/v) and dried under nitrogen gas for 20 min. After drying, the cartridge was eluted with 6.0 mL methanol. Finally, the target fraction was collected in a 10 mL test tube, the volume reduced to almost dryness under a gentle nitrogen stream, and

then re-dissolved in 10% methanol solution to a final volume of 1.0 mL. Final extracts were transferred to 2 mL amber vials for LC–MS/MS analysis.

2.3.2. Sediment sample extraction. The sediment samples were all freeze-dried and grounded into 80 mesh. 1.00 g of each sample was weighed into centrifuge tubes. 0.1 g of Na_2EDTA and 10 mL of the mixed solution containing phosphate buffer (pH = 3.0) and acetonitrile (1 : 1, v/v) were added into each centrifuge tube. Tubes were shaken in a shaker with a speed of 250 rpm for 20 min, sonicated for 10 min, and then centrifuged at $7000 \times g$ for 10 min. The supernatant was transferred to a beaker. The extraction process was performed 3 times in each sample. The obtained supernatants were combined and then diluted to 500 mL with Milli-Q water before SPE purification. The following SPE process was performed according to the exaction method of water samples.

2.4. Analysis of antibiotic compounds

The target antibiotic compounds were analyzed by LC–MS/MS system (ABI 3200 Q TRAP). Separation of the target antibiotics was done on an Inertsil® ODS-SP column (4.6 mm × 150 mm, 5 μm, GL Science Inc. Japan). The chromatographic mobile phase was consisted of pure methanol (A) and 5 mmol L^{-1} ammonium acetate dissolved in 0.1% formic acid solution (HCOOH : H_2O = 0.1 : 99.9, v/v) (B). The mobile phase gradient was ramped at a flow rate of 1.0 mL min^{-1} from 20% (A) to 30% in 2 min, 30% to 75% in 6 min, and 75% to 90% in 1 min, kept for 6 min, then ramped to 20% in 1 min and kept for 4 min. The column temperature was set to 40 °C.

The antibiotic compounds were detected by electrospray tandem mass spectrometry in positive-ion mode. Data acquisition was performed in the multiple reaction monitoring (MRM), by recording two MRM per compound. The optimal conditions for analytes monitoring are summarized in Table 1.

2.5. Calibration, recoveries and limits of quantification (LOQ)

Quantification of target analytes was based on external calibration curves, which were constructed from a plot of the peak area ratio of the analyte signal for the product ion of highest intensity. Six multi-component standards (from 10 μg L^{-1} to 500 μg L^{-1}) were direct injected to form the calibration. Each standard contained every analyte at the same concentration. The correlation coefficients (r^2) of the calibration curves were exceeded

0.996 for all of the analytes. Recoveries of the antibiotics in surface water were determined at two different concentration levels (50 and 100 ng L^{-1}) in triplicate, and calculated as the percentages of the measured concentrations relative to the spiked concentrations. 100 ng spiking standards were added into 1.00 g sediment sample and mixed well to determine the recovery, each sample was done in triplicate. Limits of quantification (LOQ) of the antibiotics were calculated with signal/noise ratios (S/N) of 10 (Table 2).

2.6. Detection of total organic carbon (TOC)

The sediment samples were ground into 200 mesh after freeze-drying in order to determine the total organic carbon (TOC). Total carbon (TC) and inorganic carbon (IC) were determined by a TOC-VCPH SSM 5000A elemental analyzer (Shimadzu, Japan). TOC is calculated by subtraction of the IC value from the TC the sample. Each sample was done in triplicate.

3. Results and discussion

3.1. Results of water samples

3.1.1. Occurrence of antibiotics in low water season. The results of the surface water samples in the low water season are presented in Table 3. All the selected antibiotics were detected in most of the sampling sites except SM1. The concentrations of SAs ranged from ND to 775 ng L^{-1} for SM2, from ND to 316.2 ng L^{-1} for SD, from ND to 86.8 ng L^{-1} for SMT, from 2.6 to 58.3 ng L^{-1} for SMZ and from 0.6 to 1.9 ng L^{-1} for SDM in the low water season. SM2, which is only used in veterinary medicine, showed the highest concentration among the sulfonamides at most of the sampling locations. The maximum concentration of SM2 was as high as the influent of the sewage treatment plants in the Pearl River Delta.[15] The very high concentrations suggested that there must be a large amount of breeding wastewater discharged to Jiulongjiang River. SM1 was not detected in the Jiulongjiang River which was found with concentrations of 160 ng L^{-1} in Höje River[16] and 694 ng L^{-1} in Choptank River.[16,17] The amount of SMZ in the Pearl River,[4] ground water of USA,[10] Seine River,[18] Rio[9] and Queensland[19] were much higher than that in Jiulongjiang River. The concentration of CTC was the highest among the tetracycline classes in Jiulongjiang River, which was up to 1036 ng L^{-1} (at B1). According to the published data, it was the highest concentration of CTC in a river. TC was found from ND to 190 ng L^{-1} in the Jiulongjiang River, which had been

Table 1 The optimum LC–MS/MS parameters including precursor and product ions and collision energy (CE), declustering potential (DP), entrance potential (EP), collision cell entrance potential (CEP), collision cell exit potential (CXP)

Compound	Abbreviation	Precursor ion	Product ion	CE (eV)	DP (eV)	EP (eV)	CEP (eV)	CXP (eV)
sulfadiazine	SD	251	91.9	35	46	5.5	19	2
sulfadimethoxine	SDM	310.9	155.9	27	46	8.5	20	2
sulfamerazine	SM1	265	107.8	35	41	6	22	2
sulfameter	SMT	281	91.9	41	41	5.5	16	2
sulfamethazine	SM2	279	186.1	23	46	6	18	2
sulfamethoxazole	SMZ	253.9	92.1	37	41	5.5	14	2
tetracycline	TC	445.1	410.1	25	45	8	37	13
oxytetracycline	OTC	479	444	25	45	8	18	17
chlorotetracycline	CTC	461	426	26	51	9	18	20

Table 2 Retention time, correlation coefficient, recovery and LOD of the samples

Compound	Retention time (min)	r^2	Water sample recovery (%)	Sediment sample recovery (%)	Water sample LOD (ng L^{-1})	Sediment sample LOD (ng g^{-1})
SD	5.03	0.9984	45.4 ± 2.8	35.5 ± 1.3	0.26	0.45
SM1	6.56	0.9994	46.6 ± 3.0	39.6 ± 1.0	0.22	0.57
SM2	7.63	0.9996	73.0 ± 4.5	45.3 ± 2.2	0.28	0.55
SMT	7.47	0.9977	43.8 ± 3.5	48.7 ± 1.2	0.41	0.73
SDM	10.03	0.9999	40.6 ± 3.6	49.0 ± 2.8	0.09	0.24
SMZ	8.35	0.9997	40.8 ± 2.3	53.9 ± 1.4	0.35	0.53
TC	7.43	0.9991	105.6 ± 15.6	47.3 ± 4.4	14.7	15.2
OTC	7.53	0.9995	118.2 ± 12.5	42.4 ± 1.6	2.94	5.28
CTC	9.28	0.9964	227.5 ± 17.0	54.9 ± 11.7	20.0	23.6

reported with a concentration of 1340 ng L^{-1} in surface water.[20] Kolplin *et al.* found CTC, OTC and TC in the USA were at concentrations of 690, 340, and 110 ng L^{-1}, respectively.[21] These indicated that a large amount of TCs were used in many areas.

The data of antibiotic concentrations during the low water season showed large differences between the sampling locations. The highest concentrations of these antibiotics were observed in B1, which were always slightly higher than those detected at B3. Both sites were much more seriously contaminated by antibiotics than other sites. B1 and B2 are situated in the urban area of Longyan City, where municipal wastewater without disposal was discharged. In addition, there were lots of swine farms upstream from the city. Most of the swine farms did not have facilities for the treatment and the disposal both of manure and wastewater, which were discharged into the Jiulongjiang River directly. We have analyzed the wastewater from one of these swine farms. SD, SMZ, TC, CTC and OTC were detected in the wastewater with concentrations of 74.66 μg L^{-1}, 86.73 μg L^{-1}, 43.12 μg L^{-1}, 87.65 μg L^{-1} and 38.55 μg L^{-1}, respectively. Due to the wastewater, high concentrations of antibiotics would be found both in B1 and B2. But actually, the concentrations in B2 were much lower than

that in B1. This is probably because they were diluted by the water from a tributary called Xiaoxi Stream. B3 is sited downstream of the sewage treatment plant of Longyan City. The effluents of the sewage treatment plant were discharged into the River resulting in high concentration of antibiotics at this site. B4 is located at an area with a developed swine breeding industry where a large amount of swine breeding wastewater without treatment was discharged into Jiulongjiang River. Therefore, the concentration of TCs in this site was higher than all the other sites except B1 and B3. The concentrations of SAs at X2 and X3 were at a comparatively high level. This is probably because they were near to the city of Zhangzhou where small amounts of municipal wastewater without treatment are discharged into Jiulongjiang River. The concentrations of TCs in the Xixi Stream and estuary were below 25 ng L^{-1}, which were much lower than that in Beixi River. Sun *et al.* found the TCs were not detected in the estuary of Jiulongjiang River (E region) and Xiamen Bay.[22] It could be inferred that the usage of TCs in the estuary area was not large. For that reason the concentrations of antibiotics were much higher in the swine breeding region (B1–B4) than that in other regions, TC sand SAs in Jiulongjiang River were

Table 3 Occurrence of antibiotics detected at 19 locations in low water season[a]

Locations	Concentrations of antibiotics (ng L^{-1})								
	SD	SDM	SM1	SMT	SM2	SMZ	OTC	TC	CTC
B1	238.0 ± 0.4	1.9 ± 0.8	ND	86.8 ± 34.0	775.5 ± 33.5	58.3 ± 16.3	221.0 ± 56.0	189.5 ± 75.5	1036.5 ± 328.2
B2	32.7 ± 0.0	0.9 ± 0.0	ND	24.3 ± 0.0	605.3 ± 0.0	35.0 ± 0.0	23.7 ± 0.0	24.0 ± 0.0	58.8 ± 0.0
B3	316.2 ± 7.8	1.5 ± 0.4	ND	41.3 ± 15.1	742.4 ± 11.0	52.4 ± 5.2	204.5 ± 27.6	173.5 ± 16.3	906.0 ± 38.2
B4	164.1 ± 13.8	1.3 ± 0.2	ND	16.0 ± 10.0	361.1 ± 99.0	27.5 ± 7.4	42.6 ± 0.0	28.7 ± 0.0	124.0 ± 0.0
B5	26.0 ± 10.2	0.7 ± 0.0	ND	12.2 ± 1.7	256.6 ± 13.9	16.3 ± 8.7	14.7 ± 0.6	UC	25.5 ± 0.1
B6	19.0 ± 4.6	0.7 ± 0.1	ND	4.4 ± 6.0	161.7 ± 58.2	14.4 ± 2.6	13.7 ± 2.0	UC	23.0 ± 4.9
B7	15.0 ± 3.8	0.7 ± 0.0	ND	3.1 ± 1.2	158.8 ± 1.5	18 ± 3.9	19.5 ± 0.0	16.7 ± 0.0	31.7 ± 0.0
B8	ND	0.6 ± 0.0	ND	ND	ND	2.6 ± 0.0	15.1 ± 0.0	16.8 ± 0.0	24.6 ± 0.0
B9	1.5 ± 0.0	0.6 ± 0.0	ND	ND	ND	3.2 ± 0.0	17.8 ± 0.0	14.9 ± 0.0	23.9 ± 0.0
B10	24.2 ± 4.1	0.7 ± 0.1	ND	5.5 ± 1.4	93.9 ± 28.2	13.2 ± 4.1	12.1 ± 0.2	UC	UC
B11	51.9 ± 4.6	0.9 ± 0.1	ND	14.6 ± 2.6	373.3 ± 72.8	14.9 ± 6.0	12.3 ± 0.7	UC	UC
X1	50.4 ± 7.3	0.7 ± 0.1	ND	8.4 ± 4.2	178.5 ± 6.6	30.9 ± 0.0	14.3 ± 0.8	UC	24.9 ± 1.3
X2	122.8 ± 2.7	0.9 ± 0.0	ND	32.8 ± 1.6	543.2 ± 14.6	47.2 ± 2.7	12.2 ± 0.0	UC	UC
X3	115.0 ± 3.5	0.8 ± 0.2	ND	21.6 ± 10.6	566.5 ± 47.6	48.5 ± 1.6	12.8 ± 0.4	UC	UC
E1	7.0 ± 1.5	0.6 ± 0.1	ND	ND	ND	13.7 ± 0.5	13.0 ± 2.1	15.7 ± 2.0	22.1 ± 6.9
E2	34.1 ± 4.4	0.7 ± 0.1	ND	7.9 ± 1.2	131.4 ± 35.1	26.7 ± 4.9	12.3 ± 0.3	UC	UC
E3	51.0 ± 0.0	0.8 ± 0.0	ND	ND	213.1 ± 0.0	32.1 ± 0.0	13.1 ± 0.0	UC	UC
E4	55.3 ± 22.8	0.8 ± 0.1	ND	14.9 ± 8.2	281.4 ± 67.5	28.2 ± 10.9	15.0 ± 4.3	15.3 ± 2.3	23.7 ± 10.3
E5	29.9 ± 0.0	0.7 ± 0.0	ND	8.8 ± 0.0	182.1 ± 0.0	12.3 ± 0.0	11.2 ± 0.0	UC	UC

[a] ND—not detected, UC—unquantified concentration.

Table 4 Correlations of SAs and TCs in low water season

	SD	SDM	SMT	SM2	SMZ	OTC	TC	CTC
SD	1.000							
SDM	0.912[a]	1.000						
SMT	0.828[a]	0.845[a]	1.000					
SM2	0.861[a]	0.932[a]	0.910[a]	1.000				
SMZ	0.837[a]	0.805[a]	0.745[a]	0.833[a]	1.000			
OTC	0.169	0.315	0.225	0.295	0.331	1.000		
TC	0.158	0.317	0.271	0.244	0.233	0.851[a]	1.000	
CTC	0.146	0.284	0.308	0.294	0.288	0.940[a]	0.811[a]	1.000

[a] Correlation is significant at the 0.01 level.

considered to originate mainly from the discharge of swine breeding wastewaters.

Data was analyzed by SPSS 16.0 software to determine the Spearman's coefficient among these compounds. The Spearman's coefficient may reveal some clear relationship between the occurrence of the compounds, which may result from a similar source or similar physicochemical properties. The results showed that Spearman's coefficients were higher than 0.745 among the analyzed SAs and higher than 0.811 among the TCs (Table 4). While the coefficients between SAs and TCs were lower than 0.331. Significant correlation was only found between the compounds of the same class which indicated that the correlations may be attributed to the similar physicochemical properties.

3.1.2. Occurrence of antibiotics in high water season. The results from the surface water samples in the high water season are presented in Table 5. SM2 still showed the highest concentration among the SAs at most of sampling locations (up to 55.6 ng L^{-1}). SMT was detectable in B2–B4, B10 and X2–X3, with concentrations ranging from 0.8 to 5.4 ng L^{-1}. At the same time, levels of SMZ in water during the high water season varied from 0.5 to 15.5 ng L^{-1}, except that no detectable levels were measured at B1. SD was detected at B2–B4, B5–B8 and E1–E3, and the highest concentration of SD was 50.7 ng L^{-1} (at B11). SM1 and SDM could not be detected and concentrations of CTC were lower than the LOQ. The concentrations varied from ND to 49.6 ng L^{-1} for TC and from ND to 33.6 ng L^{-1} for OTC. The concentrations of the SAs in the high water season were lower than that detected in the Pearl River,[4] but higher than in Three Gorge Reservoir.[23] Additionally, the contamination of SAs in Jiulongjiang River was more serious than those in Arno River and Po River in Italy and Llobregat River in Spain. The maximum concentrations of SAs in these rivers were only 11.4 ng L^{-1}, 2.39 ng L^{-1}[24] and 11.9 ng L^{-1},[25] respectively.

3.1.3. Seasonal variations of antibiotic in the Jiulongjiang River water. Significant differences were observed between the two sampling times. Considerably higher concentrations were found in the low water season. A higher frequency of antibiotics detection was also found in the low water season. In particular, SDM and CTC were not detected in any sample during the high water season. However, they were found in the low water season with the frequency of 100% and 63%, respectively. The average concentrations of other target antibiotics in the low water season were tens to hundreds of times higher than those in the high water season. Kolpin *et al.* found that the concentrations of SMZ and TC in the low water season were 70 and 300 ng L^{-1}, respectively.[26] The concentrations in early spring were about 2–15 times higher than in summer in the Pearl River.[4] One reason for the differences in concentrations is that the storm water and flood in high water season dilute the concentrations of pollutants in river. The precipitation in the high water season is about 2.5 times higher than that in the low water season in Fujian Province. For Jiulongjiang River, the water flow in January accounted for only 2.6% of the annual runoff, but approximately 20% in August. There were also other reasons for the seasonal

Table 5 Occurrence of antibiotics detected at 19 locations in high water season[a]

Locations	Concentrations of antibiotics (ng L^{-1})								
	SD	SDM	SM1	SMT	SM2	SMZ	OTC	TC	CTC
B1	ND	ND	ND	ND	ND	ND	UC	UC	UC
B2	2.7 ± 2.1	ND	ND	1.2 ± 0.1	24.9 ± 10.9	2.7 ± 0.7	33.4 ± 4.4	41.5 ± 4.5	UC
B3	15.3 ± 11.0	ND	ND	2.7 ± 0.0	55.6 ± 44.9	15.5 ± 10.5	30.3 ± 5.8	11.1 ± 3.6	UC
B4	10.4 ± 1.7	ND	ND	5.4 ± 0.0	39.5 ± 30.3	9.3 ± 6.9	27.6 ± 10.0	32.2 ± 8.4	UC
B5	ND	ND	ND	ND	2.7 ± 0.1	2.1 ± 0.6	7.2 ± 1.4	19.7 ± 3.9	UC
B6	ND	ND	ND	ND	7.9 ± 1.2	4.0 ± 0.3	14.4 ± 8.8	28.2 ± 12.0	UC
B7	ND	ND	ND	ND	13.7 ± 1.0	4.5 ± 0.2	8.0 ± 0.5	49.6 ± 1.2	UC
B8	ND	ND	ND	ND	10.6 ± 2.7	5.2 ± 1.2	8.6 ± 2.8	36.8 ± 1.5	UC
B9	0.6 ± 0.0	ND	ND	ND	16.8 ± 2.4	10.0 ± 1.1	8.9 ± 0.5	29.4 ± 6.4	UC
B10	5.7 ± 0.7	ND	ND	0.4 ± 0.2	23.2 ± 1.0	10.8 ± 0.6	8.7 ± 4.9	UC	UC
B11	50.7 ± 21.4	ND	ND	ND	22.1 ± 13.0	4.8 ± 2.9	7.8 ± 3.9	UC	UC
X1	5.6 ± 0.1	ND	ND	ND	15.8 ± 2.1	6.5 ± 3.2	10.3 ± 0.5	21.0 ± 6.6	UC
X2	9.6 ± 2.4	ND	ND	0.8 ± 0.7	36.1 ± 7.1	9.0 ± 1.8	4.6 ± 0.4	UC	UC
X3	17.0 ± 9.0	ND	ND	1.0 ± 0.4	39.3 ± 20.3	10.6 ± 3.2	5.8 ± 3.8	UC	UC
E1	ND	ND	ND	ND	8.7 ± 1.2	3.3 ± 2.3	6.3 ± 3.4	16.2 ± 18.2	UC
E2	ND	ND	ND	ND	0.3 ± 0.2	0.5 ± 0.2	7.8 ± 2.9	UC	UC
E3	ND	ND	ND	ND	2.0 ± 1.4	1.7 ± 0.5	7.6 ± 2.3	16.1 ± 5.6	UC
E4	10.5 ± 2.2	ND	ND	ND	16.2 ± 1.6	5.6 ± 1.3	8.9 ± 5.8	16.1 ± 3.5	UC
E5	7.7 ± 5.2	ND	ND	ND	19.3 ± 7.0	5.5 ± 2.3	7.8 ± 2.2	16.1 ± 1.2	UC

[a] ND—not detected, UC—unquantified concentration.

variations. According to the literature, another reason is that the degradation of antibiotics is faster in high water season. Photo-degradation by sun irradiation plays an important role in the process of natural elimination of antibiotics. The TCs were prone to be photo-degraded by solar radiation. Lunestad et al. found that the OTC in the surface sea water was completely eliminated by solar radiation in 21 days.[27] Solar irradiation is more effective in the high water season in this region. Consequently, the concentrations of TCs would be lower in this season. Bio-degradation adds another important part in the natural elimination of antibiotics. Temperature plays a catalytic role on the bio-degradation process.[27,28] According to the literature, SAs are prone to be biodegraded. Castiglioni et al. found the removal rates of SMZ in the summer and winter were 71% and 17%, respectively.[29] The high temperature in summer accelerated the biological degradation of SAs. In the study region, the average temperature is 27 °C in the high water season which is 17 °C higher than that in the low water season. Therefore, the degradation of SAs during the high water season was much faster so that the concentrations were much lower. Therefore, the lower concentrations of TCs in the high water season resulted from both dilution and photo-degradation. Both dilution and bio-degradation led to the lower concentrations of SAs. It remains unclear which reason was dominant, or whether another reason existed. Further investigations are needed in the future.

3.2. Occurrence of antibiotics in sediments samples

The levels of SAs in the sediments are shown in Table 6. Five (SD, SM1, SM2, SMT and SMZ) out of the six target SAs were detected. The concentrations ranged from ND to 13.4 ng g^{-1} for SM2, from ND to 5.6 ng g^{-1} for SD, from ND to 1.8 ng g^{-1} for SMT, from 1.2 to 3.4 ng g^{-1} for SMZ and from ND to 5.5 ng g^{-1} for SM1. However, SDM was found below the limit of

quantification. The concentrations of the SAs were different in sampling locations, but the variation was quite small.

TC, OTC and CTC were found in the sediment samples and reached concentrations of 713 ng g^{-1}, 10 363 ng g^{-1} and 14 666 ng g^{-1}, respectively. TC and OTC were found by Yang et al. in Pearl River sediments with concentrations of 81 ng g^{-1} and 232 ng g^{-1}, respectively.[14] Liu et al. found that the highest concentrations of TC and OTC were 312 ng g^{-1} and 335 ng g^{-1} in the sediments of Nanming River (Guiyang, China).[30] In the sediments of Cache La Poudre River (Northern Colorado, USA), the highest concentrations of TC and OTC were 102 ng g^{-1} and 56 ng g^{-1}, respectively.[31] The concentrations of TCs in the sediments listed above were much lower than that in Jiulongjiang.

The Spearman's coefficients of the TCs, SAs and TOC of the sediments are present in Table 7. TC showed significant correlations with OTC and CTC at the 0.01 level. It indicated that the TCs have similar properties of distribution in the sediments. The concentrations of TCs were significantly correlated with TOCs which indicated that the distributions of TCs were related to the TOCs in sediments. It was difficult to find significant correlations in SAs and correlations between the TOCs and the concentrations of SAs are hard to find.

3.3. The relationship between water and sediment

Pseudo-partitioning values should be introduced here to get a better understanding of the dynamics of antibiotics between sediment and surface water phases.[31] The pseudo-partitioning values were calculated from the antibiotic concentrations in sediments divided by their corresponding concentrations in surface water.[14] Since the dynamic sorption and desorption between sediments and water of a river system are not at equilibrium, this value cannot be regarded as a real partitioning coefficient. However, calculated pseudo-partitioning values can be a valuable indicator of the sorption characteristics of

Table 6 Concentrations of the antibiotics in sediment samples[a]

Locations	Concentrations of antibiotics (ng g^{-1})								
	SD	SDM	SM1	SMT	SM2	SMZ	OTC	TC	CTC
B1	5.6	ND	5.5	1.8	13.4	1.3	10363.6	713.7	14666.7
B2	3.9	ND	ND	ND	9.4	1.2	148.2	27.6	481.1
B3	4.4	ND	5.4	1.5	12.0	1.2	2672.7	264.7	5977.8
B4	5.3	ND	5.5	1.7	15.8	1.4	9818.2	756.9	13888.9
B5	4.3	ND	5.5	1.7	11.0	1.3	1333.3	115.3	4611.1
B6	3.9	ND	ND	1.4	8.5	1.2	71.5	12.6	197.8
B7	3.8	ND	ND	ND	7.3	1.2	286.1	22.0	1755.6
B8	ND	ND	ND	1.6	8.8	1.2	228.5	27.9	2055.6
B9	3.9	ND	5.3	1.4	5.9	1.2	56.1	6.9	ND
B10	3.9	ND	ND	ND	ND	1.5	34.7	8.3	ND
B11	3.9	ND	5.4	ND	6.8	1.2	52.4	9.3	ND
X1	4.5	ND	ND	1.5	7.5	3.4	75.2	13.4	241.1
X2	4.1	ND	ND	ND	7.8	1.5	63.9	7.9	163.3
X3	ND	ND	ND	ND	7.6	2.2	17.8	8.4	ND
E1	ND	ND	ND	1.4	6.4	1.5	10.2	6.9	ND
E2	3.9	ND	5.3	1.4	7.3	1.2	79.1	9.3	ND
E3	3.9	ND	5.4	1.5	7.3	1.4	1563.6	13.1	83.2
E4	4.6	ND	ND	ND	7.9	2.7	267.0	12.2	87.9
E5	3.9	ND	ND	1.5	7.6	2.0	31.2	7.8	ND

[a] ND—not detected.

Table 7 Correlations of TOC, the concentrations of SAs and TCs

	SD	SM1	SMT	SM2	SMZ	OTC	TC	CTC	TOC
SD	1.000								
SM1	0.512[a]	1.000							
SMT	0.394	0.590[b]	1.000						
SM2	0.540[a]	0.336	0.523	1.000					
SMZ	0.215	−0.309	−0.046	−0.094	1.000				
OTC	0.598[b]	0.608[b]	0.544[a]	0.671[b]	−0.288	1.000			
TC	0.480[a]	0.499[a]	0.552[a]	0.783[b]	−0.293	0.881[b]	1.000		
CTC	0.530[a]	0.380	0.559[a]	0.835[b]	−0.235	0.842[b]	0.917[b]	1.000	
TOC	0.311	0.257	0.437	0.676[b]	−0.066	0.547[a]	0.654[b]	0.740[b]	1.000

[a] Correlation is significant at the 0.05 level. [b] Correlation is significant at the 0.01 level.

Table 8 The average pseudo-partitioning values (L kg^{-1})

SD	SDM	SMT	SM2	SMZ	OTC	TC	CTC
220	2480	650	30	110	31 170	2750	26 290

Table 9 Correlations of the antibiotics concentrations of sediment and surface water samples

SD	SDM	SMT	SM2	SMZ	OTC	CTC	TC
0.003	0.005	−0.088	−0.132	−0.152	0.654[a]	0.691[a]	0.640[a]

[a] Correlation is significant at the 0.01 level.

individual compounds. Since microbial antibiotic resistance most likely originates in the benthic sediments, it is important to be able to characterize the sorption characteristics in an actual aquatic system.[32] Previous research has determined that the pseudo-partitioning values of SAs ranged from 10^0 to 10^1 L kg^{-1} whereas those of TCs ranged from 10^2 to 10^6 L kg^{-1}.[33–36] Our results showed that the average pseudo-partitioning values in Jiulongjiang River ranged from 0 to 650 L kg^{-1} for SAs and from 2750 L kg^{-1} to 31 170 L kg^{-1} for TCs (Table 8). All the reports indicated that the pseudo-partitioning values of TCs were much higher than the SAs. This suggests that TCs accumulate more easily in the sediments and soils. The distribution variety of SAs and TCs was due to their different chemical structures and different physicochemical properties. SAs are hydrophilic enough to transport into the aquatic environment while TCs tend to accumulate in sediments.[37]

The correlations of TCs in sediment with those in water were determined, all were found to be significant at 0.01 levels. But no relations were found between SAs in water and those in sediment (Table 9). The reason could be that TCs are easier to accumulate in sediments than SAs.

4. Conclusion

The Jiulongjiang River water was more seriously contaminated in low water season by SM2, SMT and TCs than most other studied rivers. TCs and SAs in Jiulongjiang River were attributed mainly to the discharge of swine breeding wastewaters. The concentrations during the low water season were tens to hundreds of times higher than those in the high water season. The lower concentrations of TCs in the high water season might result from both dilution and photo-degradation, while both dilution and bio-degradation might lead to the lower concentrations of SAs. Further study is needed to clarify the specific reasons. Concerning the relationship between sediment and water samples, the pseudo-partitioning values of TCs were much higher than SAs. It indicates that the TCs were prone to accumulate in the sediment.

Acknowledgements

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