二零一一年五月十二日　　　　　　　　　　　　　文件HE 19/2011
討論文件

沙田區議會
衞生及環境委員會

環境保護及優化城門河工作小組
"沙田城門河水質檢測" 報告書 (初稿)

請委員考慮通過夾附由環境保護及優化城門河工作小組提交的"沙田城門河水質檢測"報告書(初稿)。香港浸會大學嘉漢林業珠三角環境應用研究中心代表將於會上介紹報告書的內容和解答委員的詢問。

沙田區議會秘書處
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初稿

Water quality monitoring program in Shing Mun River
(沙田城門河水質改善研究)

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Water quality monitoring program in Shing Mun River

Introduction

The water quality of the Shing Mun River has been significantly improved from 1990s through the legal measures. The water quality of the Shing Mun River main channel improved from “Very Bad” in 1986 to “Excellent” in 2008 according to EPD’s statistics. However, at times, odour problems, fluctuating water quality and presence of infectious pollutants concern the recreational user. Abnormal results with high pollutant levels and E. Coli concentrations have been obtained occasionally in the EPD’s regular water sample analysis. According to water samples collected from 2007 to 2009, the E. coli level of one third of these samples were still exceeding 1000 colony forming unit (CFU)/ 100 ml of water. Though there is no specific guideline on E. coli standard in local river water, the geometric mean of E. coli in marine bathing water (for recreational use) is set at the limit of 180 CFU/100 ml (Lui et al. 2007) according to a literature studying the case of Hong Kong.

It is suspected that some illegal sewage discharges or non-point sources pollution from some unsewered rural areas and expedient connections to the storm drainage may still exist. Although Shing Mun River is primarily designed for the drainage of storm water from Shatin with a catchment area of 37 km^2, it is also a popular place for recreational uses such as boating, canoeing and fishing. The Shing Mun River main channel has also been chosen as the site for the rowing event of the 2009 East Asian Games. Occasionally high level of pollutants and *E. Coli* concentrations in the river water post a serious threat to the health of the users and the public. The accidental swallowing of contaminated water may cause the general gastrointestinal disease, and *E. coli* can cause endophthalmitis of the eye which is a rare complication of *E. coli* septicemia.

Therefore to increase our understating on the pollutants present in Shing Mun River, this study had the following objectives:

i. To monitor the levels of water pollutants (mainly organic) in newly selected sampling points along Shing Mun River; and

ii. To evaluate possible implications of the river contamination in health perspectives for the members of Hong Kong's society;

Additionally, occurrence of selected antibiotics was also considered as they are being reported in many river systems around the world.

Methodology

Sampling and sampling points

Water samples from three locations were collected during 31.12.2009 and 7.7.2010 to represent the dry and wet seasons, respectively. The sampling points are indicated in Figure 1. The sampling point of SMR-upper (Tai Wai) is close to the HK EPD's sampling point of TR19 that enables to compare the water quality data. Water samples, three replicates from each sampling point were collected in clean methanol and Milli-Q washed polypropylene containers; immediately transported to the lab for the analyses.

Chemical analyses

The samples were analyzed for pH, electrical conductivity (EC) and salinity onsite; while, total suspended solids (TSS), total nitrogen (TN), ammonium-nitrogen (NH4-N), total phosphorus (TP), Escherichia coli and biochemical oxygen demand (BOD5) were analyzed in the lab following standard methods (APHA, 2005). The total organic carbon (TOC) contents of the samples were analyzed using a Shimadzu TOC analyzer.

Figure 1. Water sampling points in the Shing Mun River

Antibiotic extraction and analysis

The extraction and analyses of antibiotics from the river water samples were performed as described by Chen *et al*. (under revision). Briefly, after adding 0.5 g Na_2EDTA and adjusting the pH to 4.0, the antibiotics were concentrated using HLB columns (Waters) eluted with 0.1% formic acid in methanol/ acetonitrile (1:1), concentrated under N_2 stream and reconstituted in acetonitrile/water (1:9) Antibiotics were analyzed using a Agilent 1200 HPLC tandem Applied Biosystems 3200 Q Trap MS/MS. The samples were separated using RP C18 column with a flow rate of 0.3 ml/min. The mobile phases were (A): 0.3% formic acid and 0.1% ammonium formate and (B) acetonitrile:methanol, 1:1 with the gradient of 5% B for 2 minutes, increased to 88% B in 12.5 min, increased to 100% B in 13 min and maintained up to 16 min. The precursor $[M+H]^+$ of the antibiotics and their product ions monitored in MRM mode; and the recovery obtained are summarized in Table 1. Recoveries for most analytes were higher than 75%; exception was sulfadiazine (64.9%). However, the recovery was consistent throughout the study.

Results and Discussion

Water quality parameters

Results of water quality parameters are presented in Tables 1-2 and Figure 2. One of the sampling points of this study, upper was close to the EPD's sampling point of TR19 that enables a comparison with the EPD data on the water quality. In contrast, SMR-middle and SMR-lower was not considered by EPD. Although EPD's sampling point TR19I is close to the SMR-middle point of this study, samples from this site were not analyzed by the EPD; therefore, SMR-middle and SMR-lower points of this study would reveal more information to supplement the water quality data of HKEPD. Especially, SMR-lower has the influence of Shatin STP and the back flow due to tidal movement from the Tolo harbor would also affect the river quality of the Shing Mun River.

Salinity values were higher during the wet (summer) season than the dry (winter) seasons indicating more influence or higher tidal back flow into the rivers during this season. This also influenced the conductivity values which were 2-3 folds higher in the wet season than the dry season. There were not much difference among the pH values between different seasons; however a marginal increase was observed during the dry seasons. Biochemical oxygen demand, *E. coli* population, TSS and total phosphorus values were also higher during the wet season than the dry seasons; whereas, nitrogen contents (ammonium-N and total Kjeldahl nitrogen) were higher during the dry season than the wet season. Ammonium-N contents were almost similar in both in dry and wet seasons. Among these, *E. coli* population was quite high in the wet season and a gradient was evident indicating that the source of the *E. coli* located near the upper sampling location. If the source is of livestock-origin, then the continuously higher levels could be expected. Occasional very high concentrations could be linked with some illegal sewage discharges or accidental release of pollutants at certain point. Further EPD data suggest that the *E. coli* population could reach even up to 90,000 CFU/100 ml that needs specific attention to control the pollution.

Among the different sampling points, electrical conductivity, BOD, *E. coli* population and total organic carbon were higher in the upstream and gradually decrease towards the downstream points indicating potential non-point source pollution near the upstream point. Particularly, the *E. coli* populations ware almost 3-4 folds higher in the upstream than the middle and down streams and the values were quite high in the upstream reaching 18400 CFU/100 ml during the wet season; in contrast during the dry season the population fluctuated and exhibited higher population at the middle stream. Surprisingly, total suspended solids were almost similar among the different sampling points.

When comparing the SMR-upper data with the EPD's sampling point TR19 data (Table 3), most of the values were almost similar, except conductivity, total suspended solids and total organic carbon. These differences could be due to the differences in the exact sampling points. Besides, for these parameters the standards variations were up to 30% indicating the high variations among the replicate samples. Further, the EPD analyses included only one sample per sampling point. Therefore it is essential to take at least three replicates to have a uniform data. Particularly, the electrical conductivity values may not change significantly between the sampling points that may vary a few yards, indicating the possibility of changes between the sampling time between the EPD and our study.

Table 1. Water quality of the Shing Mun River in the wet season

Parameter	Tai Wai (SMR-Upper) - Wet		Shatin (SMR-Middle) - Wet		STSTP (SMR-Lower) - Wet	
	Range	**Mean ± SD**	**Range**	**Mean ± SD**	**Range**	**Mean ± SD**
Water temperature (°C)	25.6-26.5	26.0 ± 0.5	23.2-24.2	23.8 ± 0.5	22.1-23.5	22.9 ± 0.7
Salinity (%)	18.1-19.3	18.7 ± 0.6	31.0-32.4	31.6 ± 0.7	31.4-31.8	31.6 ± 0.2
pH	7.51-8.25	7.77 ± 0.42	7.55-7.93	7.77 ± 0.20	7.83-7.87	7.85 ± 0.02
EC (mS/cm)	47.9-48.3	48.1 ± 0.2	46.5-49.4	47.7 ± 1.5	29.2-30.2	29.8 ± 0.5
Dissolved oxygen (mg/L)	7.4-8.4	8.0 ± 0.6	6.5-9.5	7.5 ± 1.7	10.8-12.3	11.6 ± 0.7
BOD (mg/L)	23.7-24.7	24.3 ± 0.6	21.3-25.3	23.3 ± 2.0	15.7-18.0	17.0 ± 1.2
E. coli (CFU/100 ml)	11300-18400	14867 ± 3550	3700-6100	4667 ± 1266	3100-4000	3500 ± 458
TSS (mg/L)	31.0-47.6	37.0 ± 9.2	29.2-35.6	32.2 ± 3.2	35.4-40.0	37.9 ± 2.3
TOC (mg/L)	4.7-6.6	5.7 ± 0.9	3.9-7.4	5.6 ± 1.8	3.4-4.3	3.9 ± 0.5
NH_4-N (mg/L)	0.04-0.05	0.04 ± 0.00	0.07-0.09	0.09 ± 0.01	0.08-0.10	0.09 ± 0.01
Total N (mg/L)	0.34-0.48	0.43 ± 0.08	0.43-0.49	0.46 ± 0.03	0.44-0.45	0.45 ± 0.00
Total P (mg/L)	0.80-0.94	0.86 ± 0.07	0.83-1.06	0.96 ± 0.12	0.88-0.96	0.92 ± 0.04

Table 2. Water quality of the Shing Mun River in the dry season

Parameter	Tai Wai (SMR-Upper) -Dry		Shatin (SMR-Middle) -Dry		STSTP (SMR-Lower) -Dry	
	Range	**Mean ± SD**	**Range**	**Mean ± SD**	**Range**	**Mean ± SD**
Water temperature (°C)	17.9 - 18.0	18.0 ± 0.1	18.0 – 18.0	18.0 ± 0.0	16.1 - 16.1	16.1 ± 0.0
Salinity (%)	1.0 - 1.6	1.3 ± 0.3	2.5 - 2.6	2.6 ± 0.0	3.1 - 3.1	3.1 ± 0.0
pH	7.66 - 7.75	7.72 ± 0.05	7.95 - 7.99	7.96 ± 0.02	8.17 - 8.22	8.20 ± 0.03
EC (mS/cm)	15.0 - 21.1	18.3 ± 3.1	17.9 - 24.6	20.7 ± 3.5	23.5 - 23.9	23.7 ± 0.2
Dissolved oxygen (mg/L)	7.3 - 7.8	7.5 ± 0.3	7.4 - 9.1	8.4 ± 0.9	10.8 - 11.0	10.9 ± 0.1
BOD (mg/L)	3.1 - 3.7	3.3 ± 0.3	3.1 - 3.8	3.4 ± 0.3	0.9 - 1.4	1.1 ± 0.3
E. coli (CFU/100 ml)	310 - 1080	710 ± 386	890 - 1150	1063 ± 150	20 - 70	47 ± 25
TSS (mg/L)	16.0 - 21.2	18.3 ± 2.7	19.4 - 22.4	20.9 ± 1.5	19.6 - 22.6	21.3 ± 1.6
TOC (mg/L)	3.1 - 5.9	4.3 ± 1.5	3.4 - 5.2	4.2 ± 0.9	3.4 - 4.8	4.2 ± 0.8
NH_4-N (mg/L)	0.11 - 0.14	0.13 ± 0.02	0.16 - 0.19	0.17 ± 0.02	0.23 - 0.25	0.24 ± 0.01
Total N (mg/L)	0.52 - 0.53	0.52 ± 0.01	0.50 - 0.60	0.54 ± 0.06	0.41 - 0.47	0.45 ± 0.03
Total P (mg/L)	0.68 - 0.99	0.89 ± 0.18	0.34 - 0.51	0.41 ± 0.09	0.29 - 0.32	0.31 ± 0.01

Table 3. Comparison of upper (Tai Wai) sampling point of this study with sampling point TR19 of HKEPD. Since data for 2010 are not available from the EPD, data of 2009 July was compared with the wet season.

Parameter	2009	Wet season		Dry season	
	EPD data –Range of Values	**This study (7-7-2010)**	**EPD data (16-7-2009)**	**This study (3-12-2009)**	**EPD data (14-12-2009)**
Water temperature (°C)	18.7-30.6	26.0 ± 0.5	29.6	18.0 ± 0.1	22.0
Salinity (%)	0.1-2.1	18.7 ± 0.6	0.6	1.3 ± 0.3	0.9
pH	7.3-8.8	7.77 ± 0.42	7.9	7.72 ± 0.05	8.2
Electrical conductivity (mS/cm)	1.9-4.2	48.1 ± 0.2	1226	18.3 ± 3.1	1.6
Dissolved oxygen (mg/L)	8.1-12.6	8.0 ± 0.6	8.4	7.5 ± 0.3	9.4
BOD (mg/L)	0.3-15	24.3 ± 0.6	1.6	3.3 ± 0.3	4.2
E. coli (CFU/100 ml)	1200-91000	14867 ± 3550	12000	710 ± 386	1300
TSS (mg/L)	4.1-55	37.0 ± 9.2	4.2	18.3 ± 2.7	8.9
TOC	<1 - 2	5.7 ± 0.9	1	4.3 ± 1.5	<1
NH_4-N	0.21-0.33	0.04 ± 0.00	0.041	0.13 ± 0.02	0.056
Total N	0.15-1	0.43 ± 0.08	0.33	0.52 ± 0.01	1
Total P	0.03-0.27	0.86 ± 0.07	0.09	0.89 ± 0.18	0.05

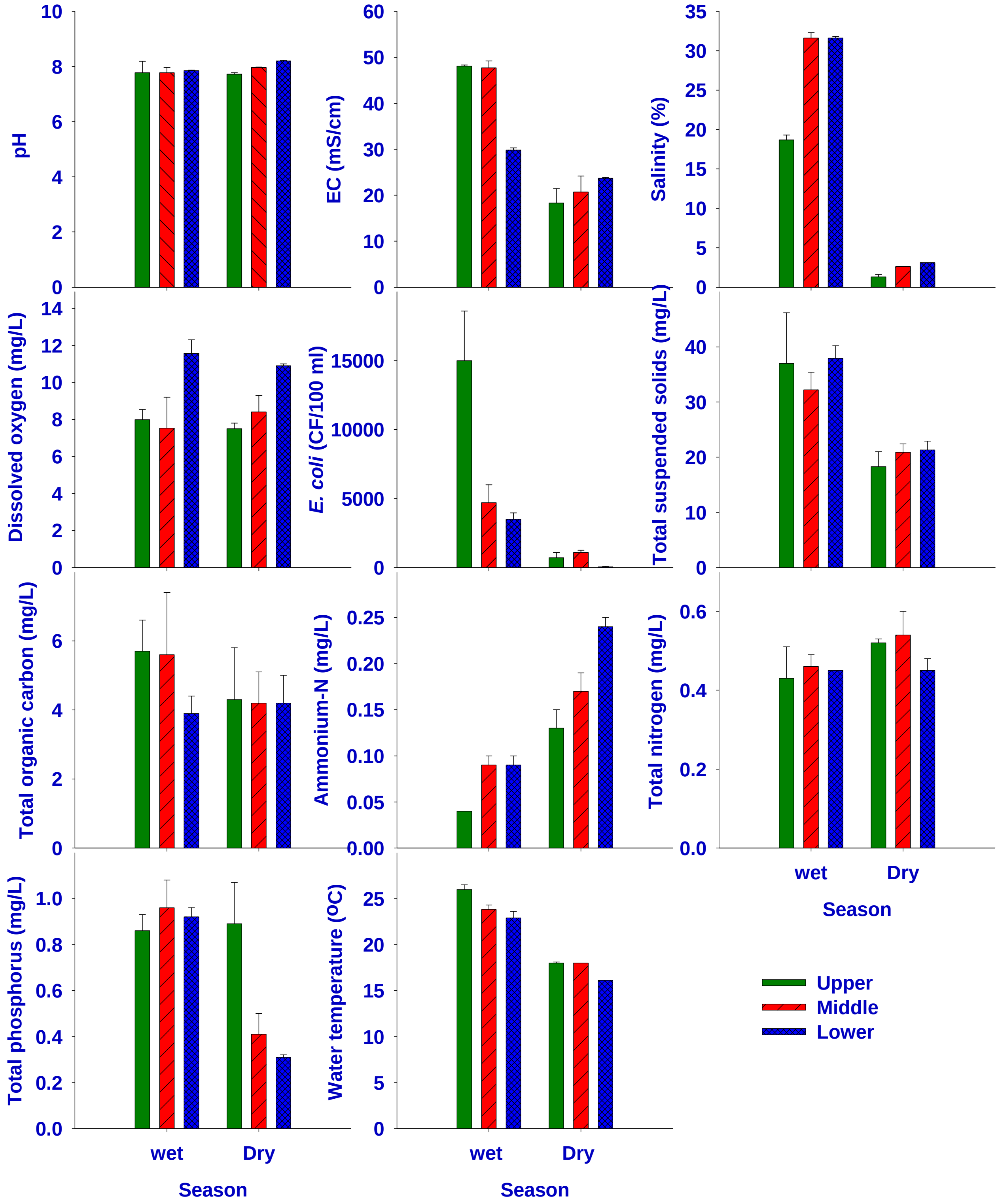

Figure 2. Water quality of the Shing Mun River waters during dry and wet seasons.

Antibiotics

Generally, antibiotic concentrations in the Shing Mun River did not exhibit a gradient indicating either the possibilities of non-point source pollutions near all the sampling points or back flow from the Tolo harbor due to the tidal movement. During the dry season tetracycline, sulfadiazine, sulfamethoxazole, ofloxacin and erythromycin were detected; sulfamethoxazole and erythromycin were not detected during the wet season. Besides, during the dry season, the concentrations were higher than the wet season, especially tetracyclines were 4-fold higher.

Oxytetracycline and chlortetracycline were not detected; whereas significant quantities of TET were observed; however, the variations among the replicates were very high during the dry season. Similarly, SDZ concentrations were also higher in upstream in dry season and gradually declined to downstream with very high variations. Concentrations of sulfamethoxazole (2-3 ng/L), ofloxacin (6-8 ng/L) and erythromycin (1-4 ng/L) were very low; while ciprofloxacin, norfloxacin and roxithromycin were not detected. Tetracyclines (TCs) and sulfonamides (SAs) are an important group of pharmaceuticals in today's human and veterinary medicine practice. Influence of livestock activities could also be linked with the presence of tetracyclines and sulfonamides, because if the antibiotics present are mainly due to the human origin then the fluoroquinolones (ciprofloxacin, norfloxacin and ofloxacin) and macrolides (erythromycin and roxithromycin) should also be present in significant quantities. Further, Gulkowska et al. (2008) reported 600, 370 and 100 ng/L concentrations of ERY-H_2O, TET and NOR in the effluent of STP in Shatin that has an influence on the downstream of SMR (SMR down-STSTP). In SMR only TET was detected at 112, 115 and 78 ng/L in up, middle and down streams, respectively; whereas ERY and NOR was not at all detected, making the case suspect towards the other sources such as livestock or sewage discharge contamination in the upstream. Besides, the absence of oxytetracycline and chlortetracycline, most likely originated from the livestock industries, were absent making the suspect towards the influence of sewage intrusion.

When comparing the antibiotics levels of Shing Mun River with the Yuen Long and Kam Tin rivers, the antibiotic levels were 4-5 folds lower and can be termed relatively clean. Besides, other river waters also shown to have similar levels of antibiotics from the published reported around the world. Presence of antibiotics often linked with the development of antibiotic resistant bacteria. Although the consequences were not completely understood there is a risk if the resistance transferred to a human pathogen and especially if the recreation involves bathing. More studies such as the levels of antibiotic resistant bacteria and resistance against antibiotic of human importance and the population of human pathogens are required to completely understand the situation.

Table 4. Antibiotic concentrations in the Shing Mun River.

Antibiotics (ng/L)	Tai Wai (SMR-Upper)		Shatin (SMR-Middle)		STSTP (SMR-Lower)	
	Wet	Dry	Wet	Dry	Wet	Dry
Chlortetracycline	-	-	-	-	-	-
Oxytetracycline	-	-	-	-	-	
Tetracycline	18.9±4.3	112.3±85.0	17.4±1.5	115.4±97.2	23.2±1.6	78.3±10.6
Sulfadiazine	1.9±0.1	29.5±26.7	-	15.5±16.4	1.4±0.2	8.2±7.6
Sulfamethoxazole	-	2.8±0.4	-	2.8±0.3	-	2.7±0.1
Ciprofloxacin	4.0 ± 0.4	-	1.9±1.0	-	2.1±0.9	
Ofloxacin	2.9±0.4	7.3±0.8	-	7.1±0.1	-	6.1±0.1
Norfloxacin	-	-	-	-	-	
Erythromycin	-	3.0±1.4	-	1.5±0.3	-	-
Roxithromycin	-	-	-	-	-	

Chloramphenicol	-	-	-	-	-	-

- Below detection limit.

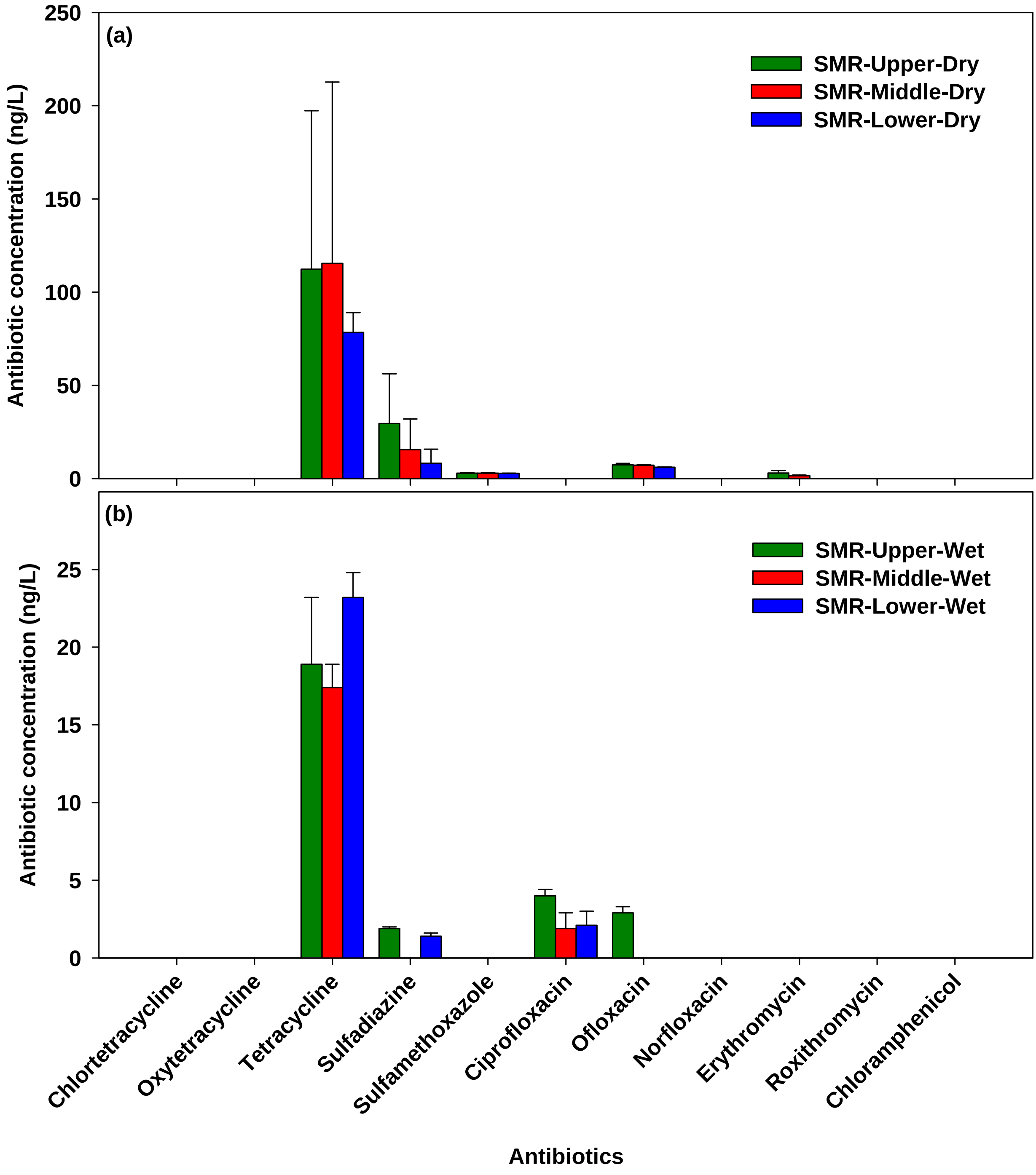

Figure 3. Antibiotic concentrations in the Shing Mun River waters during (a) dry and (b) wet seasons.

Conclusion

The water quality data obtained in our study were almost similar with data reported by the EPD, except a few parameters that requires the increase of replicates in each site. As we observed early, the *E. coli* population of the Shing Mun River was quite high often exceeding 15,000 CFU/100 ml that requires special attention to trace the source of pollution, especially in the upstream location. Antibiotics such as tetracycline, sulfadiazine, sulfamethoxazole, ofloxacin and erythromycin were detected. Of these only tetracycline concentrations were higher than other antibiotics. Although, development of antibiotic resistant in human pathogens could be expected due to the antibiotic occurrence in the river systems, more complete study required. The antibiotic concentrations were higher during the dry season. The high concentrations in the upstream in the dry season could be linked with non-point source pollution near the upstream that may contribute to the *E. coli* population in the river.

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