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Spatial and seasonal variations of organic corrosion inhibitors in the Pearl River, South China: Contributions of sewage discharge and urban rainfall runoff

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ABSTRACT

While organic corrosion inhibitors are ubiquitous in aquatic environments, knowledge on their occurrence, sources and transport in urban surface water is still scarce. In this study, the spatial and seasonal variations of organic corrosion inhibitors and their potential sources were investigated in the Pearl River Delta (PRD), one of the most highly urbanized watersheds in China. A total of 8 compounds belonging to benzothiazole (BTH) and benzotriazole (BTR) groups respectively, were identified in the Pearl River. In addition, there were clear spatial and temporal differentiations in the concentration profiles. The dry season provided higher concentrations of BTH (213-1082 ng L^{-1})

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and BTR (112-1279 ng L^{-1}) compared to the wet season (30-574 ng L^{-1} for BTH and 23-482 ng L^{-1} for BTR), indicating a dominant process of dilution. Remarkably higher concentrations and similar composition features of targets were observed in the effluent samples from two sewage treatment plants (STPs). Our study indicated that rainfall runoff from urban traffic roads during wet season may also be an important contributor to the Pearl River water environment. The annual total mass loading of corrosion inhibitors from the main channel of the Pearl River is 53.2 tons and exhibited strong seasonal variation.

Effluents discharge from STPs and urban rainfall runoff from traffic roads are main sources of corrosion inhibitors to the Pearl River

Keywords: Organic corrosion inhibitors; Benzotriazole; Benzothiazole; Pearl River; Rainfall runoff

1. Introduction

Organic corrosion inhibitors are extensively utilized in broad industrial and household applications including rubber manufacturing, corrosion inhibitors and fungicides (van Leerdam et al., 2009). Among the organic corrosion inhibitors, benzothiazole (BTH) and benzotriazole (BTR), as well as their derivatives, are the most common classes (Fig. S1); they are used in a variety of consumer products and industrial applications (Kloepfer et al., 2005). For BTR and its derivatives (BTRs), they can retard the corrosion of metal surfaces by forming metal-BTR complexes (Wang et al., 2013), and often used in dishwashing agents, de-icing and anti-icing agents, and pigments (Cornell et al., 2000; la Farre et al., 2008). BTH and its derivatives (BTHs) are widely used in aircraft de-icing/anti-icing fluids (ADAF) as corrosion inhibitors and in rubber production as vulcanization accelerators (van Leerdam et al., 2009).

Due to their wide application, both families of BTRs and BTHs have been detected in different water environments (Karthikraj and Kannan, 2017; Liu et al., 2016). Remarkably high BTRs and BTHs, up to μg L^{-1}, were reported in wastewater due to their incomplete removal in sewage treatment plants (STPs) (Asimakopoulos et al., 2013a; Karthikraj and Kannan, 2017; Kloepfer et al., 2005; Zhao et al., 2017). Since BTRs and BTHs generally have a relatively high hydrophilicity and low octanol/water partitioning coefficients, they are highly mobile in aquatic systems and have a high potential to be introduced into aquatic environments. Recent studies indicate that BTRs and BTHs compounds are hard to be biologically and photochemically degraded in the aquatic environment, which has led to their accumulation in various water environments (Hart et al., 2004; Liao et al., 2018a; Shi et al., 2019). During the past 30 years, the presence of BTRs and BTHs was reported in different rivers and lakes from global areas, and even in tap water and groundwater (Birkholz et al., 2014; Giger et al., 2006; Howard and Haynes, 1993; Kiss and Fries, 2009; Ni et al., 2008). For example, up to 200 mg L^{-1} of BTRs were detected in groundwater of a well close to an airport in North America (Cancilla et al., 1998). Recent studies have demonstrated that these compounds exposed in tap water samples from European cities, and even in human urine (van Leerdam et al., 2009; Wang et al., 2016). However, the exposure pathways remain unknown.

BTHs and BTRs have attracted the attention of the scientific community as well as the public due to their potentially adverse effects on aquatic organisms, microbial communities and mammals, as well as their long-term effects on aquatic environments (Birkholz et al., 2014; Sorahan, 2008). They have been classified as emergent pollutants, even though the acute toxicity of BTHs and BTRs for mammals is relatively low. However, a number of studies suggested that BTHs and BTRs show acute aquatic toxicity in various test systems at relatively high concentrations (Liao et al., 2018b; Reemtsma et al., 1995). BTH and 5-methyl-1H-benzotriazole (5-Me-BTR) are toxic to luminescent bacteria, plants, and aquatic animals (Cancilla et al., 1998). Previous studies also indicated that BTHs and BTRs could produce estrogenic effects in animals (He et al., 2012; Schlumpf et al., 2001). However, the chronic toxic effects induced by both BTRs and BTHs to higher trophic level organisms still remain poorly characterized (Liao et al., 2018a; Parajulee et al., 2017). The presence of BTRs in human urine from several countries was recently reported (Asimakopoulos et al., 2013b). In addition, their bioaccumulation in human adipose tissue has also been observed (Wang et al., 2016).

The Pearl River, the third longest river in China, has the most complex water system in South China (Fig.1). The Pearl River Delta (PRD) is one of the fastest developing and most urbanized regions in China and as well as in the world. This region has become one of the largest BTRs and BTHs consumption and manufacturing regions in China (Ni et al., 2008). Remarkably high concentrations of BTRs and BTHs were detected in the surface water of the Pearl River systems in the PRD region (Ni et al., 2008; Xu et al., 2015), which is a cause of great concern. However, there have been limited studies on the environmental behaviors of BTRs and BTHs in this region. Therefore, in this study, we conducted a broad survey of BTRs and BTHs in the Pearl River to: (i) investigate their occurrence and distribution with respect to their spatial and seasonal variations, and (ii) identify and assess the contributions of sewage discharge and urban rainfall runoff to their exposures in the Pearl River water environments, and (iii) investigate annual mass flux of BTHs and BTRs from the PRD to the Pearl River Estuary (PRE) and coastal environments.

2. Materials and methods

2.1 Sample collection and preparation

The sampling campaigns in the Pearl River were conducted during August 2017 and January 2018; these were representative months for the wet season and dry season, respectively. A total of 30 sampling sites that were widely distributed in the Pearl River were selected during the two sampling campaigns (Fig. 1). At each sampling location, three duplicated water samples were collected as 1-h composite samples using a peristaltic pump (BT50b, Prefluid). Later, the three duplicated water samples were combined into one composite sample. Effluent samples were collected from two municipal sewage treatment plants (STPs), which are located in the city center of Guangzhou (Fig.1). The STPs (STP1 and STP2) generally utilize a mechanical treatment for the separation of solids followed by an activated sludge treatment. The effluent samples were collected as 24-h composite samples (from 7 am on the first day to 7 am on the next day; five duplicate samples were analyzed). Rainfall runoff samples were collected during two different rainfall events on April 16 and June 8, 2018, in the outlet of a collection pipe from Guangzhou Bridge. Three sequential runoff samples were collected as 30-min composite (started after 20 min of rainfall) samples using a peristaltic pump. During the water sample collection, the sampling bottles were rinsed three times with the samples before a final sample was collected. All the water samples were kept at 5°C in a cold storage room until analysis.

2.2 Samples treatment and analysis

The treatment method was reported in our previous study (Xu et al., 2015), and only a brief description is given here. The targets from water samples were enriched by solid phase extraction (SPE) method and analyzed by GC-MS equipped with DB-5MS fused-silica capillary column in electron impact (EI) mode. Detailed information is present in the Supplementary material (the section of Instrumental analysis).

2.3 Quality assurance and quality control

The retention times and two qualifier ions were used to identify each compound, and internal standard method based on 9-point calibration curve was used to quantify the targets. Procedural blanks and duplicate samples were inserted to the each set of sample sequence. Two surrogates (BTR-d_4 and BTH-d_4) were added to all water samples before treatment procedure. The limits of quantification (LOQ) in the river water and effluent samples were 0.10-1.8 ng L^{-1} and 0.10-4.0 ng L^{-1}, respectively (Table S1). The mean recoveries of the target analytes at different aquatic matrices ranged from 51% to 129%, with relative standard deviations (RSDs) below 11%.

3. Results and discussion

3.1 Environmental exposure and spatial variation of corrosion inhibitors in the Pearl River

Table 1 summarizes the concentration profiles of BTHs and BTRs in the Pearl River during the dry and wet seasons. Generally, four BTHs (BTH, 24MoBT, MTBT, and 2-OH-BTH) and four BTRs (BTR, 4-Me-BTR, 5-Me-BTR, and 5-Cl-BTR) were detected in all samples at a different frequency. The mean concentrations during the dry season ranged from 12 to 1082 ng L^{-1} with BTH as the most prominent compound (mean of 545 ng L^{-1}) among the BTHs followed by MTBT (mean of 138 ng L^{-1}), 24MoBT (mean of 109 ng L^{-1}) and 2-OH-BTH (mean of 55 ng L^{-1}). For the wet season, the similar trend of occurrence was found but with an evidently lower mean concentration. Other compounds were below the detection limits or slightly higher than the detection limits in a few water samples; they are not listed in Table 1. Similar to BTH, BTR is the predominant compound (range: 112-1279 ng L^{-1}; mean: 480 ng L^{-1} during the dry season) among the BTRs. BTR and BTH were detected in all water samples, suggesting their ubiquitous distribution in water environments in the PRD region. The high levels of BTH and BTR is mainly due to a combination of their high production volumes and the transformations from their derivatives via hydrolyzation or biodegradation after entering the aquatic environments. In a number of previous studies, 4-Me-BTR and 5-Me-BTR were reported as a mixture of both isomers denoted as TTR because they are hard to separate using chromatographic methods (Wang et al., 2016; Wolschke et al., 2011). In this study, 5-Me-BTR was remarkably higher than 4-Me-BTR, which was consistent with most previous studies of urban water environments (Wolschke et al., 2011). However, 4-Me-BTR has been proven to be more resistant to biodegradation in environments compared to 5-Me-BTR, causing the higher consumption of 5-Me-BTR in the study area (van Leerdam et al., 2009). In addition, apparent positive correlations are observed between BTR and TTR (Fig. S2) during the dry season, which indicated that they could come from the same or similar pollution sources (Wolschke et al., 2011). However, the correlation was relatively weaker during the wet season, suggesting complicated sources during that time. A comparison of BTH and BTR concentrations in the environmental matrices from different countries is shown in Table S2. In general, BTR and 5-Me-BTR were detected with remarkably higher frequencies in global surface water, indicating their worldwide use. The BTHs and BTRs concentrations detected in this study during the dry season were comparable with those in rivers in China and India (Dsikowitzky et al., 2014), but higher than in most rivers in Europe, such as the Elbe and Danube (Giger et al., 2006).

Fig. 2 exhibited the spatial and seasonal variations of corrosion inhibitors in the Pearl River. All water sample locations were divided into four areas: city center, mixed agricultural-suburban area, industrial area, and mixed region (main channel). The samples from the city center have remarkably higher concentrations than those in suburban regions and other areas, which predominantly results from the high density of the population and large number of traffic roads. Relatively higher 5-Me-BTR and BTR were detected at W19 in a suburban area, which were likely due to the wastewater discharged from a point source (in this case, a tire factory) (Kumata et al., 2002). Most compounds in the main channel (W25-W30) generally showed a decreasing trend toward the estuary, which was mainly due to the effect of dilution.

3.2 Seasonal variation of corrosion inhibitors

Significant variations were observed for all compounds between the two sampling seasons. In comparison to the wet season, considerably higher concentrations were found in the dry season, suggesting a dominant process of dilution during the wet season by heavy rainfall and strong surface runoff (Xu et al., 2007a). Due to the concurrence of continuous rainfall and strong tides, the water level of the Pearl River in the wet season is 3-4 times higher than that in the dry season. In addition, biodegradation and photo-degradation might be stronger in the summer due to the higher activity of microorganisms and increased sunlight.

It is interesting to note that the maximum concentrations of several compounds during the wet season were similar to, or even slightly higher than, those of the dry season. Considering the dilution effect, the results strongly suggest extra targets may be discharged into the Pearl River from point sources, such as untreated wastewater and urban rainfall runoff. It is reasonable because the storm water and flooding during the wet season may not only dilute the concentrations in the river water, but may also input additional BTHs and BTRs from fields wash off during wet season. It could be further confirmed by the concentration fluctuation at sampling stations in the same sampling area during the wet season. In addition, the composition variations of the BTR isomers between different seasons could act as an indication for the unequal emission sources in aquatic environments. Previous studies demonstrated that the ratio of BTR/TTR could be a suggestion of emission source apportionment (Wolschke et al., 2011). In this study, a higher BTR/TTR ratio in the dry season was observed, which indicated the enhanced application of BTR in colder months due to the use of weather conditioned intended purpose.

3.3 Discharge of corrosion inhibitors from effluents of STPs

Fig.3 exhibits the concentration profiles of organic corrosion inhibitors in the effluents from the two STPs from Guangzhou. It shows that the composition features of both BTHs and BTRs were highly similar to those in the Pearl River water. Considering that the Pearl River is the sole receiving body for the STPs, this result strongly indicated that sewage water discharge is the predominant source of corrosion inhibitors in the Pearl River. In general, most compounds in STP 1 are slightly higher than those in STP2. It is reasonable because STP1 is located in the highest population density district (Zhujiang New Town) of Guangzhou and serves more than 2 million inhabitants. Unlike the remarkable change of BTHs and BTRs between seasons in the Pearl River, most BTHs and BTRs in the effluent samples from the two STPs at the dry season are similar to those at the wet season. It confirmed that the main reason for the seasonal variation in the receiving river water was the dilution effect. Table S2 shows that BTHs and BTRs in STPs' effluent samples from Guangzhou are generally consistent with those detected from other countries. It is also worthy to note that particularly high concentrations of BTH and BTR were observed in the effluent STP samples from India and Switzerland, respectively, suggesting their massive use in those countries (Karthikraj and Kannan, 2017; Voutsa et al., 2006).

Many previous studies documented that effluent discharge is the primary source of most contaminants in the receiving surface water (Wang et al., 2018). In this study, a dilution factor of 1:10 (recommended by the U.S. Federal Drug Administration) was used to estimate the maximum expected concentrations in the receiving water from the STPs' effluent data (FDA, 1998). The maximum expected concentrations of the most frequently detected BTHs and BTRs for the Pearl River are shown in Table 2. The measured concentrations were remarkably higher (4-10 times) than the calculated concentrations. It indicated that untreated wastewater was likely discharged into the Pearl River due to the fact that the treatment ratio for domestic sewage In Guangzhou was only higher than 60% (Xu et al., 2007b). In addition, the highest differences for 5-Me-BTR and MTBT, up to almost 10 times between the calculated and detected concentrations, were observed during the wet season. This result strongly indicated that except for the untreated wastewater discharge, other contaminant sources, such as urban rainfall runoff during the wet season, may exist.

3.4 Urban rainfall runoff of corrosion inhibitors

Urban rainfall runoff is one of the major sources of a variety of pollutants from road traffic emissions into urban surface water environments (Asheim et al., 2019; Parajulee et al., 2017). Fig. 4 shows the concentration profiles of BTH and BTR compounds at two different rainfall events. Three BTHs (BTH, 24MoBT, and MTBT) and three BTRs

(BTR, 4-Me-BTR, and 5-Me-BTR) were quantified in the rainwater runoff samples with mean concentrations ranging from 125-303 ng L^{-1} and 122-316 ng L^{-1}, respectively. Guangzhou Bridge is a heavily trafficked road in Guangzhou with a daily vehicle flowrate of more than 140,000 per day. The BTH compounds detected in the samples were likely derived from the emissions of the tire tread debris, motor oil, and brake linings of the vehicles. It is interesting to note that the 24MoBT concentrations in the rainfall runoff samples were equal to or slightly higher than those in the sewage effluent, which indicated that the urban 24MoBT from road runoff had become one of the most significant sources in the Pearl River water environment. 24MoBT, an impurity of the vulcanization accelerator OBS, was evaluated as a possible molecular marker for rubber tire debris and road dust transported in urban road runoff water (Kumata et al., 1996; Kumata et al., 2002; Pan et al., 2012). For instance, the relatively high levels of the 24MoBT may indicate that the traditional accelerator OBS is still used in rubber tires in the PRD region (Ni et al., 2009).

Consistent with the observations of the Pearl River water, BTR and 5-Me-BTR were the predominant compounds among the BTRs observed in the rainwater runoff water samples. BTRs are generally used as corrosion inhibitors in anti-freezing agents and technical fluids for cars and anti-icing/de-icing formulations for roads (Giger et al., 2006; Weiss et al., 2006). In this study, both the BTHs and BTRs detected in the rainfall runoff samples were remarkably lower than those observed in Europe and North America (Parajulee et al., 2017). This difference can be partly attributed to the usage of road salt in certain European and North American locations (Parajulee et al., 2017).

Since the average temperature in Guangzhou is usually higher than 20°C (with the minimum higher than 5°C), road salt is not needed. The long-term usage of road salts commonly resulted in buildup of salts in the subsurface, which could change the elevated stream baseflow conductivities (Howard and Haynes, 1993). A strong correlation between BTR concentration and electrical conductivity was found in Parajulee's study, and it also indicated that BTR source and transport were related to the road salts (Parajulee et al., 2017). The extremely high level of 4-Me-BTR (1670 μg L^{-1}) and 5-Me-BTR (2160 μg L^{-1}) have been observed in the surface runoff of an airport due to the heavy use of aircraft de-icing and anti-icing fluids (ADAF)(Corsi et al., 2006). By contrast, Fig. 4 shows that the target compound concentrations in rainwater Event 1 are evidently higher than those from Event 2. It is known that an antecedent dry period to the rainwater runoff sampling affects the level of contaminant accumulated on the road. August is the rainiest month, with a high frequency of rainfall in Guangzhou. The interval between rainfall Event 2 and the first rainfall was relatively short, which may have reduced the amount of road particles entering the rain drains (Zeng et al., 2004). Moreover, higher temperatures in August could have accelerated the degradation of the target compounds.

3.5 Mass loading of corrosion inhibitors from the main channel of the Pearl River

The annual total mass loading of corrosion inhibitors from the main channel of the Pearl River is 53.2 tons (Fig.5). And most of them will finally enter the South China Sea (SCS) via the Pearl River estuary. It should be noted that the mass data was a rough estimate because it was calculated based on limited concentrations data during two seasons. In addition, it was likely to be underestimated due to the fact that the compounds in particulate phase were not included in the calculation. The annual inputs of BTH, BTR and 5-Me-BTR, the three dominant compounds, were 18.3, 8.0 and 11.3 tons per year, respectively, which were comparable to those in the other outlets of the Pearl River (Ni et al., 2008). Fig.3S exhibited that the total mass flux during the wet season was two times higher than that during dry seasons. This strongly seasonal variation can be largely attributed to the remarkably higher water flow during the wet season, even though relatively lower concentrations were detected during this period. However, in view of the exposure of corrosion inhibitors in rainfall runoff and the high frequency of rainfall during the wet season in the PRD region, it strongly suggested that the discharge of rainwater runoff from land surfaces (such as the traffic roads and airport) may also be a significant source to the Pearl River during wet season. Therefore, further studies on the transfer process of corrosion inhibitors via rainwater runoffs are needed in order to clarify the effects of rainwater runoffs to surface water environments.

4. Conclusions

High levels of BTHs and BTRs were detected in Pearl River water samples during both wet and dry seasons, suggesting their high production/utility in the PRD region. The concentrations of most contaminants observed during the dry season were evidently higher than those during the wet season, indicating a process of river water dilution. In the PRD region, the major sources of BTHs and BTRs in the Pearl River are likely STP effluents. In addition, the strongly seasonal variation of annual total mass loading of corrosion inhibitors of the Pearl River strongly suggested that the discharge of rainwater runoff from land surfaces may also be an important contributor to the Pearl River water environments.

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Table 1 Concentration profiles of BTHs and BTRs in the Pearl River during different seasons (ng L^{-1})

Compounds	Dry season		Wet season	
	Range	Mean±SD	Range	Mean±SD
BTH	213-1082	545±222	30-574	268±142
24MoBT	36-204	109±42	42-252	97±78
MTBT	35-314	138±76	30-270	100±83
2-OH-BTH	12-128	55±47	10-75	19±23
BTR	112-1279	480±313	23-482	186±141
4-Me-BTR	4-117	46±32	20-150	42±41
5-Me-BTR	40-531	228±133	64-678	211±93
5-Cl-BTR	12-136	72±35	14-135	46±37

Table 2

Calculated and detected concentrations of corrosion inhibitors in the Pearl River during different seasons (ng L^{-1})

Compounds	Dry season		Wet season	
	Calculated[a]	Detected[b]	Calculated[c]	Detected
BTH	202	1082	96	505
MTBT	61	314	33	270
BTR	213	1256	101	456
5Me-BTR	72	443	35	304

Notes: [a] Calculated from the effluent of STP 1 at dry season using a dilution factor of 1:10; [b] Data from W4 sampling site; [c] A dilution factor of 1:20 is used based on the fact that the water level of the Pearl River during wet season is generally 2-3 times higher than at dry season

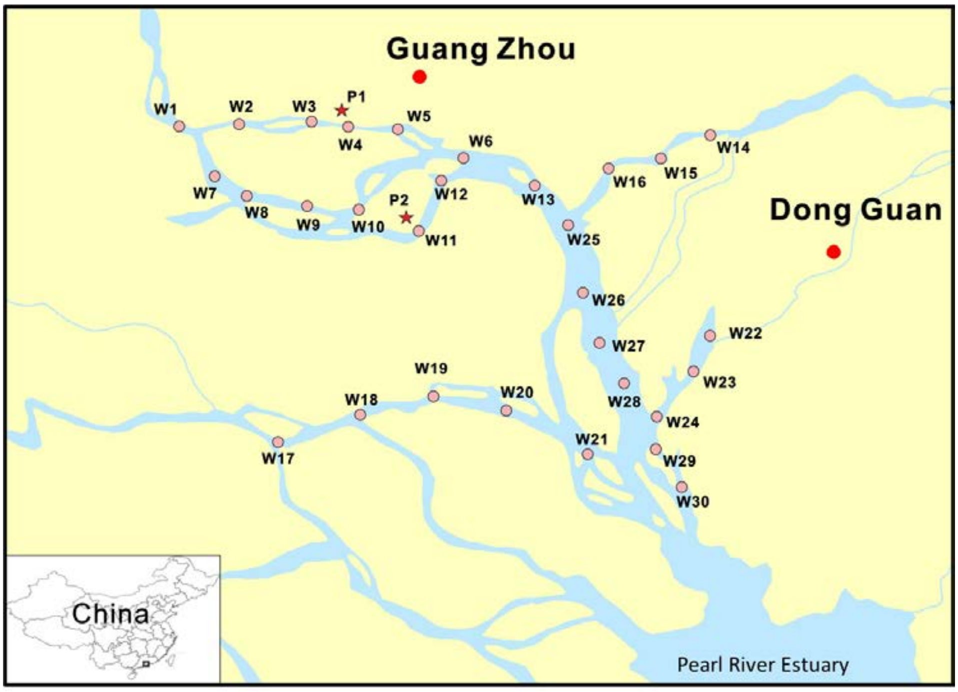

Fig.1 Sampling locations in the Pearl River watershed

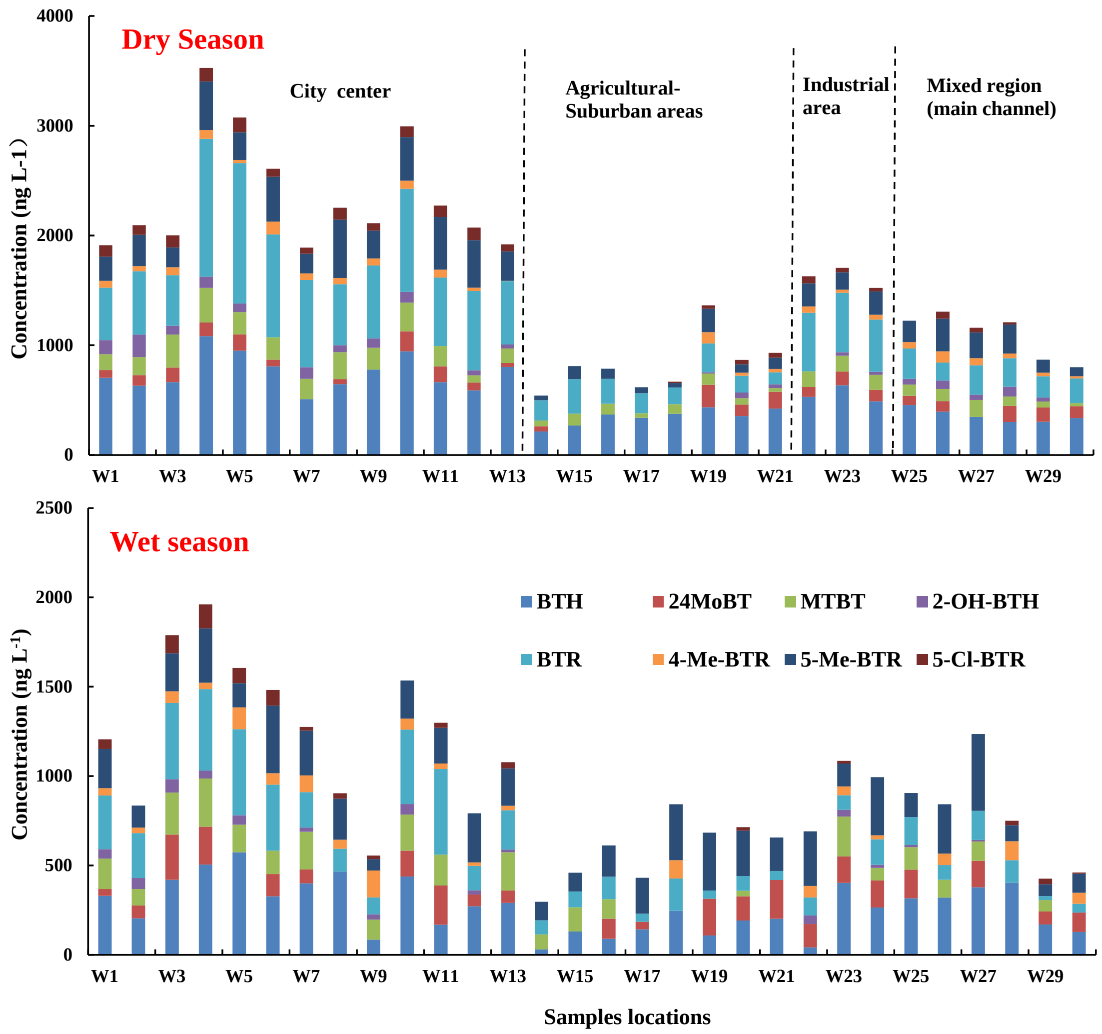

Fig.2 Distributions of BTHs and BTRs in the Pearl River during dry and wet seasons

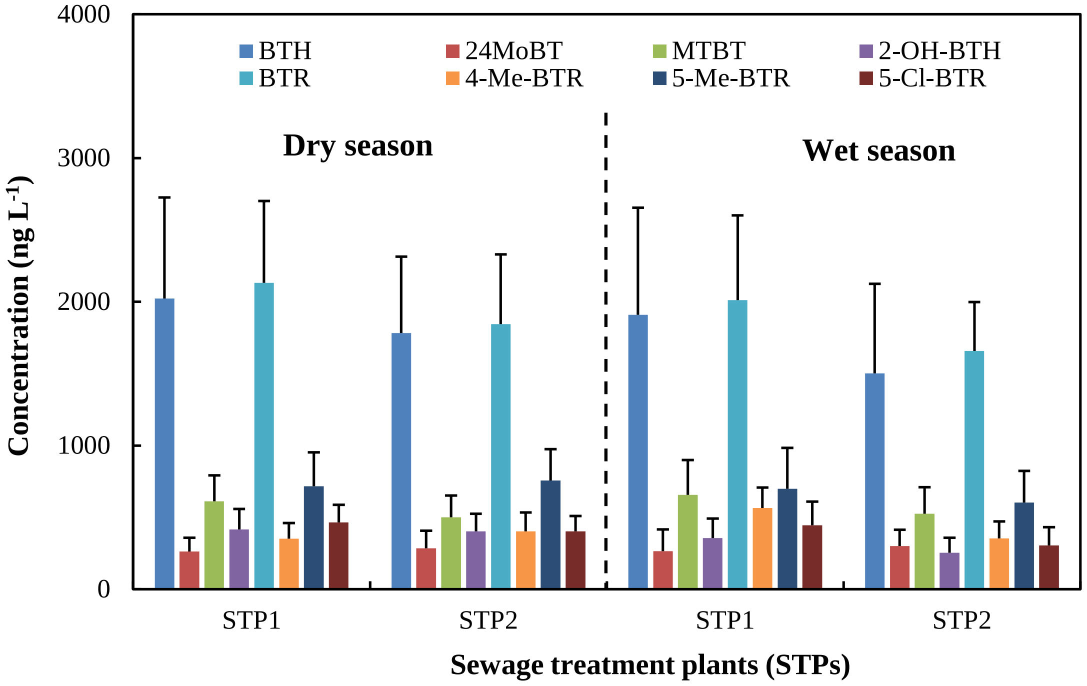

Fig. 3 BTHs and BTRs concentrations (mean) in effluent samples from the STPs

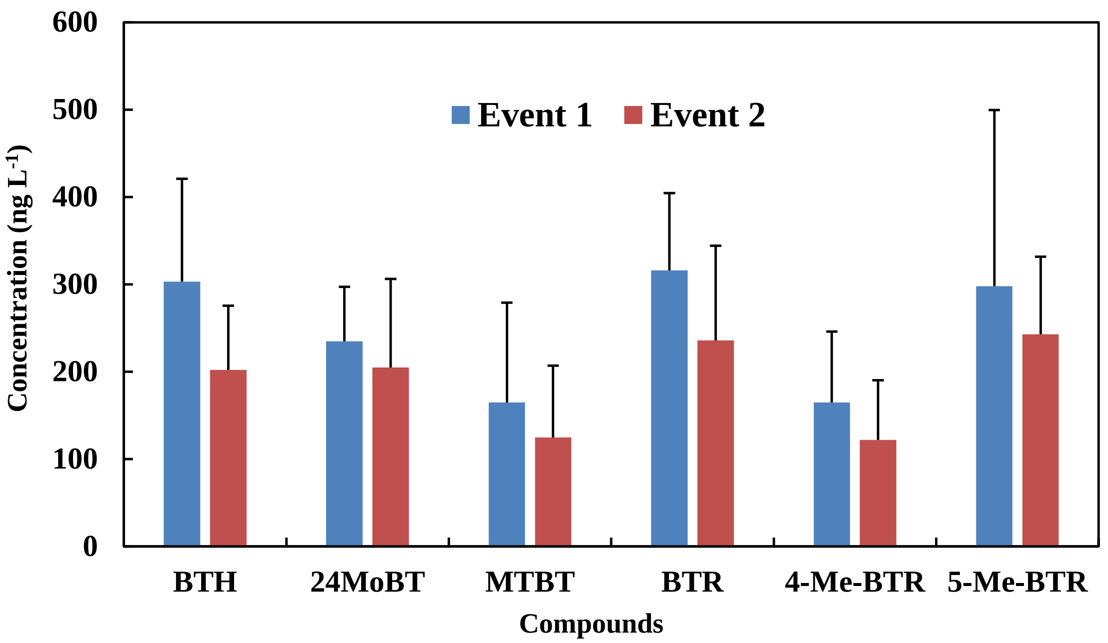

Fig. 4 BTHs and BTRs concentrations in rainwater runoff samples at two rain events

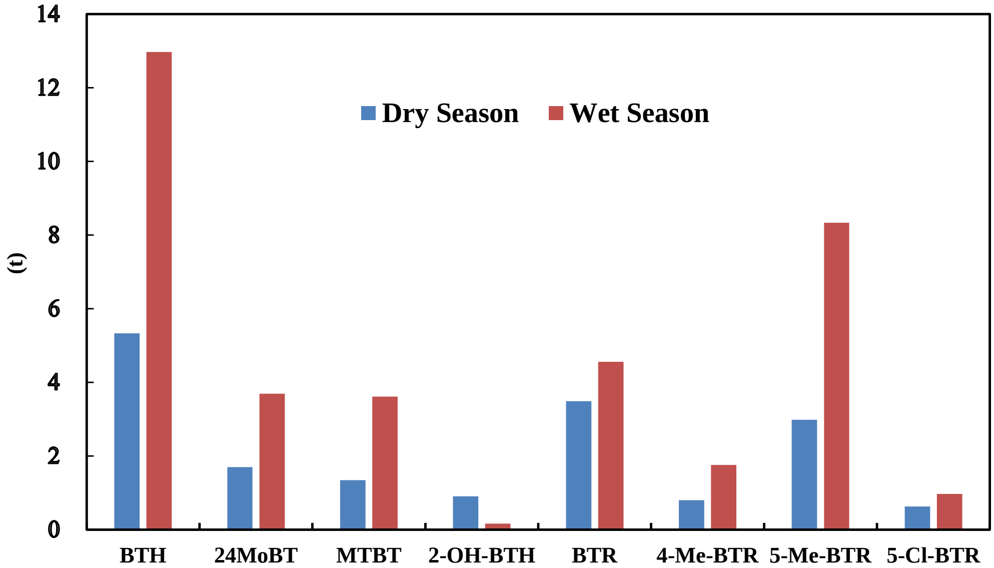

Fig. 5 Annual input of corrosion inhibitors from main channel of the Pearl River