The Ecological Risk Assessment of PPCPs Based on Different Endpoints in Urban Rivers from The Pearl River

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Abstract. With rapid development of the cities along the Pearl River, the ecological system of urban rivers is being threatened by pharmaceuticals and personal care products (PPCPs). In this study, the distribution of four common PPCPs triclocarban, diclofenac, ibuprofen and triclosan was summarized from literatures and the ecological risk of the PPCPs in surface water of urban rivers from the Pearl River was evaluated based on six different endpoints. Among these PPCPs, ibuprofen was the most predominant compound with the highest concentration of 1417 ng/L, and triclocarban had the lowest PNECs of 2.4 ng/L derived from reproduction toxic data. Additionally, PNECs of diclofenac and triclocarban derived from reproduction toxic data were lower than those derived from other effects, while the PNECs of ibuprofen and triclosan derived from biochemical toxic data (endocrine disruption effect) were lower than those derived from other effects. All the PPCPs exhibited high risk on certain effects, especially for triclocarban exhibited high ecological risk on cellular, growth, mortality and reproduction of aquatic life. The results demonstrated that triclocarban, diclofenac, ibuprofen and triclosan had adverse effects on aquatic life in the Pearl River and actions needed to be taken for PPCPs, especially for triclocarban.

Keywords. Urban river, Risk quotient, No observed effect concentration, Predicted no effect concentration, Toxic effect.

1. Introduction
The pharmaceuticals and personal care products (PPCPs), first proposed by Daughton and Ternes in 1999, were characterized as emerging pollutants which would pose potential threatens to environment (Daughton and Ternes 1999). They include prescription for the treatment or prevention of human and animal diseases, such as antibiotics, lipid regulators, and anti-inflammatory drugs etc. Most of the PPCPs in wastewater are from wastewater treatment plants, pharmaceutical manufactories, livestock farms and hospitals. Due to lack of specialized treatment for PPCPs in wastewater treatment plants, PPCPs have been frequently detected in various environment, such as surface water, groundwater, drinking water and sediment (Liu and Wong 2013). Although the concentrations of PPCPs in water are low, they are
easily transferred in the environment and through the food chain to humans and animals. Researches indicate that PPCPs may be harmful to the ecological system (Isidori et al. 2005; Schlesinger 2004).

The Pearl River Basin is the second largest river basin in China. It includes the rivers of Xijiang, Dongjiang, Beijiang and the Pearl River Delta. It is also one of the most developed regions in China, and has formed the Guangdong-Hong Kong-Macau Greater Bay Area. In 2018, the GDP of the nine cities from Guangdong province in the Pearl River Delta reached 8 trillion CNY (approx. 1.16 trillion USD). Rapid economic development and population growth posed severe challenges to water safety. Researches demonstrated that pharmaceuticals were widely detected in the Pearl River (Huang et al. 2011). Thus, it is urgent to understand to what extent the adverse effect imposed by PPCPs to the Pearl River.

Most of the studies used risk quotient (RQ) to evaluate the risk of pollutants in the water (Kim et al. 2007; Sanderson et al. 2003). Generally, RQ is calculated by dividing a point of exposure by a point estimate of effects (predicted no effect concentration, PNEC). The traditional PNEC was normally calculated based on all the endpoints, which may underestimate certain toxic endpoint, and thus was incapable of providing adequate protection for aquatic species (Zheng et al. 2017).

In this study, the concentrations of four common PPCPs triclocarban, diclofenac, ibuprofen and triclosan in surface water of urban rivers from the Pearl River were summarized from literatures. PNECs of four PPCPs were derived based on six endpoints of behaviour, biochemical, cellular, growth, mortality and reproduction. Then RQ was used for ecological risk assessment. The present study would provide a reference for decision makers to understand the risk of PPCPs in the Pearl River and set emission standards to the PPCPs.

2. Ecological risk assessment

The chronic toxic data of no observed effect concentrations (NOECs) were obtained from the ECOTOX EPA database (https://cfpub.epa.gov/ecotox/) and academic literatures. The geometric mean is selected when same species have multiple reliable toxicity data. All the data were considered appropriateness and reliability before application and used to gain predicted no effect concentration (PNEC) by the following formula.

\[
PNEC = \frac{NOEC}{AF}
\]  

(1)

Table 1 shows the assessment factors (AF) corresponding to different toxic data groups provided by the European Chemicals Agency.

| Toxic data group | AF |
|------------------|----|
| One group of chronic toxic data NOEC (fish or crustaceans) | 100 |
| Two groups of chronic toxic data NOEC (fish or crustaceans or algae) | 50 |
| Three groups of chronic toxic data NOEC (fish or crustaceans or algae) | 10 |

The ecological risk assessment in the surface water was performed by the following formula (Sun et al. 2013).

\[
RQ = \frac{C_w}{PNEC}
\]  

(2)

Where Cw is the measured concentration, PNEC is the predicted no effect concentration. The four risk levels were classified based on previous research (Yan et al. 2015).

- HQ < 0.1, there is no risk;
- 0.1 ≤ HQ < 1.0, the risk is low;
- 1.0 ≤ HQ < 10, the risk is moderate;
- HQ > 10, the risk is high.
3. Distribution of the ppcps
Table 2 shows the concentrations of PPCPs in the surface water of the Pearl River from different literatures. All the four PPCPs were commonly detected PPCPs for frequency and concentration. The highest concentration of PPCPs detected was 1417 ng/L of ibuprofen. Compared with other studies, ibuprofen was higher in the Pearl River than in the Yellow River (416 ng/L), Hai River (127 ng/L), Liao River (246 ng/L) and 139 American streams (1000 ng/L) (Kolpin et al. 2002; Wang et al. 2010). The differences in the concentration between regions and nations might be due to medication habits.

Table 3 shows the main physicochemical properties of the selected PPCPs. Among these parameters, octanol-water partition coefficient (Kow) is a key one to understand the fate and behaviour of PPCPs. The logkow of PPCPs was found to be dispersive (from 0.45 to 5.13), indicating that PPCPs have different water solubility.

4. Predicted no effect concentration
All the PNECs were calculated based on formula 1, i.e. the minimum NOEC of the toxic data group was divided by the corresponding AF. The derivation of PNECs based on six toxic effects is shown in table 4. The results showed PNECs ranged from several ng/L to μg/L concentration level. The lowest PNEC of the four PPCPs was 2.4 ng/L from triclocarban. It demonstrated that triclocarban is more toxic to aquatic life compared with other PPCPs. Our results were in good agreement with previous research. Zhao et al. (2010) demonstrated PNEC of triclocarban based on all the toxic effects was 58 ng/L, which was in the range of the PNECs based on six different endpoints in the present study. Besides, PNECs of diclofenac and triclocarban derived from reproduction toxic data were lower than those derived from other effects, while the PNECs of ibuprofen and triclosan derived from biochemical toxic data (endocrine disruption effect) were lower than those derived from other effects. It demonstrated that diclofenac and triclocarban was more toxic to reproduction system of aquatic life and ibuprofen and triclosan was more toxic to endocrine system.

5. Risk quotient
The RQs of PPCPs based on calculated PNECs are shown in Fig. 1. The results showed that diclofenac had the highest risk on reproduction system of aquatic life in the Pearl River. Besides, all the PPCPs exhibited high risk on certain effects, especially for triclocarban exhibited high risk on cellular, growth, mortality and reproduction effects. Previous research showed triclocarban had a propensity to be bioaccumulated and toxic to aquatic invertebrate and fish (Brausch and Rand 2011). It demonstrated that significant potential adverse effects of PPCPs could be observed in the Pearl River.

6. Conclusions
PPCPs have been hotspot of environmental research for twenty years. While the ecological risk assessment of PPCPs are still in hot debate due to uncertainties of risk process. To improve the accuracy of the risk assessment, we selected toxic data based on endpoints of behaviour, biochemical, cellular, growth, mortality and reproduction to derive PNECs. In the present study, the distribution of four typical PPCPs in urban rivers of the Pearl River was summarized and the ecological risk based on the six different toxic effects was evaluated. The results demonstrated that all the PPCPs selected had adverse effects on aquatic life. Moreover, triclocarban was the most toxic compounds than other PPCPs. Besides, PPCPs imposed adverse effects on aquatic life to different level in the form of different endpoints. The present study would provide a reference for decision makers to understand the risk of PPCPs in the Pearl River and set emission standards to the PPCPs. Future work need to focus on species sensitive distribution and the probabilistic risk assessment methods, which allows the variability of exposure concentrations and toxic effects in the ecological risk assessment process.
Table 2. Distribution of the PPCPs in surface water of the Pearl River.

| Location | PPCPs          | Concentration (ng/L) | Reference             |
|----------|----------------|----------------------|-----------------------|
| Main stream of the Pearl River, Shijing River, Sha River, Liede River, Chebei River, Liuxi River | Triclocarban | 2.37-210             | (Peng et al. 2017)    |
|          | Diclofenac     | ND-645               |                       |
|          | Ibuprofen      | ND-1417              | (Peng et al. 2008)    |
|          | Triclosan      | 35-1023              | (Zhang et al. 2013)   |

*ND: Not detected.

Table 3. Physicochemical properties of the PPCPs.

| Name      | CAS          | Use type       | Molecular formula | Formula weight | Logkow (pH 7.4) |
|-----------|--------------|----------------|-------------------|----------------|-----------------|
| Triclocarban | 101-20-2    | Disinfectant  | C_{13}H_{9}Cl_{3}N_{2}O | 315.6          | 2.41            |
| Triclosan   | 3380-34-5   | Disinfectant  | C_{12}H_{7}Cl_{3}O_{2} | 289.5          | 5.13            |
| Ibuprofen  | 15687-27-1 | Anti-inflammatory drug | C_{13}H_{18}O_{2} | 206.3          | 0.45            |
| Diclofenac | 15307-86-5 | Anti-inflammatory drug | C_{14}H_{11}Cl_{2}NO_{2} | 296.1 | 1.37 |

Table 4. The toxic parameters used for calculating the predicted no effect concentrations (PNEC) of PPCPs for ecological risk assessment.

| PPCPs | Toxic effects | Test species          | Assessment factor | PNEC (ng/L) |
|-------|---------------|-----------------------|-------------------|-------------|
|       | Behavior      | Crustaceans, Fish     | 50                | 200         |
|       | Behavioral    | Fish                  | 100               | 6305        |
|       | Cellular      | Fish                  | 100               | 65          |
| Diclofenac | Growth   | Fish                  | 100               | 200000      |
|       | Mortality     | Crustaceans, Fish     | 50                | 202         |
|       | Reproduction  | Crustaceans           | 100               | 3.6         |
|       | Behavior      | Crustaceans, Fish     | 50                | 200000      |
|       | Biochemical   | Fish, Algae           | 50                | 100         |
|       | Cellular      | Fish                  | 100               | 1067        |
|       | Mortality     | Crustaceans, Fish     | 50                | 502         |
|       | Reproduction  | Crustaceans, Fish     | 50                | 6325        |
|       | Behavior      | Crustaceans, Fish     | 50                | 520         |
|       | Biochemical   | Fish                  | 100               | 40          |
|       | Cellular      | Fish                  | 100               | 7.9         |
| Ibuprofen | Growth     | Crustaceans, Fish     | 50                | 4.2         |
|       | Mortality     | Crustaceans, Fish     | 50                | 7.9         |
|       | Reproduction  | Crustaceans, Fish, Algae | 100              | 2.4         |
|       | Behavior      | Crustaceans, Fish     | 50                | 3400        |
|       | Biochemical   | Algae, Crustaceans    | 10                | 45          |
|       | Cellular      | Fish                  | 100               | 51          |
| Triclocarban | Growth   | Crustaceans, Fish     | 50                | 4.2         |
|       | Mortality     | Crustaceans, Fish     | 50                | 7.9         |
|       | Reproduction  | Crustaceans, Fish, Algae | 100              | 2.4         |
|       | Behavior      | Crustaceans, Fish     | 50                | 3400        |
|       | Biochemical   | Algae, Crustaceans    | 10                | 45          |
|       | Cellular      | Fish                  | 100               | 51          |
| Triclosan | Growth     | Crustaceans, Fish     | 50                | 720         |
|       | Mortality     | Crustaceans, Fish     | 50                | 326         |
|       | Reproduction  | Algae, Crustaceans    | 10                | 3305        |
Figure 1. Ecological risk assessment of the PPCPs based on six toxic effects in surface water in the Pearl River.

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