Occurence and fate of typical PPCPs in the aquatic environment of the Pearl River Delta, China

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Abstract

A scoping profile was presented about the residues of typical pharmaceuticals and personal care products (PPCPs), including antibacterials, natural and synthetic steroid estrogens, endocrine-disrupting phenols, and acid pharmaceuticals in wastewater, urban river water, and estuarine sediment of the Pearl River Delta, South China. Antimicrobials have been detected at low μg L^{-1} in the raw wastewater. The concentrations of antimicrobials did not show substantial changes after primary mechanical sedimentation but some of them were obviously removed after biological treatment. Estrone was detected in >60% water samples with a maximum concentration of 65 ng L^{-1}. Endocrine-disrupting phenols were found to be widely present at rather high concentrations in the urban riverine water. Salicylic acid, clofibric acid and ibuprofen were detected in most water samples with maximum concentrations of up to low μg L^{-1}. Both the detection frequencies and median concentrations of the PPCPs appeared higher during the low-flow season than during the high-flow season, which might probably be attributed to the dilution effect caused by the rainfall. PPCPs in the urban riverine water of Guangzhou originated mainly from random discharge and/or leakage of municipal wastewater. Temporal distribution of nonylphenol (NP) and bisphenol A (BPA) in sedimentary cores in recent decades in the Pearl River Estuary showed coincidence with the rapid economic growth in China. Downward penetration and persistence of NP in the estuarine sediment were revealed. The environmental loadings of NP and BPA in the PRE sediments were roughly estimated to be 124 t and 1.7 t respectively over the past 30 years.

Introduction

The occurrence, fate, and potential for ecological effects of residues of pharmaceuticals and personal care products (PPCPs) in water bodies have caused increasing environmental concern. PPCPs and their metabolites continuously enter the aquatic environment through treated and untreated wastewater and may be of ecological potential[1]. For instance, steroid estrogens and phenolic chemicals are well known endocrine disrupting contaminants that interfere mainly with the sexual functions in animals, causing feminization, imposex, decreased fecundity, and developmental abnormalities[2-4]. Residues of antibacterials in the environment may promote antibiotic resistance in bacteria. Pharmaceuticals are designed to treat diseases for humans and animals. They can also cause unwanted effects due to their bioactivity[5]. For example, the wide-spread veterinary use of diclofenac has indirectly caused the near extinction of vultures in South Asia[6]. Furthermore, these chemicals may act together to play mixture affects even when each compound is present below the threshold of detectable effects[3].

PPCPs have been widely detected in the waters of North America[7-13], Europe[14-18] et al., 2004), and Japan[19].

Their harmful effects and potential risks to aquatic organisms at environmental levels have also been documented[2]. In contrast, reports of PPCPs contamination in the environment in China are still limited. This work provided a screening profile of the occurrence and fate of typical PPCPs in the aquatic environment of the Pearl River Delta (PRD) in the subtropical South China. Seasonal variations of the selected PPCPs were primarily investigated. The environmental persistence of PPCPs was also discussed.

Materials and Methods

PPCP compounds were mainly purchased from Sigma-Aldrich Chemicals (Oakville, ON, Canada). Isotopic labelled standards were obtained from Cambridge Isotope Laboratories (Andover, MA, USA) Sigma-Aldrich Chemicals. Sodium azide was washed with methanol prior to use.

The Pearl River Delta (PRD) is one of the most developed and densely populated areas in China. About 40-70% of municipal wastewater in the PRD is treated in sewage treatment plants (STPs). The treated and remaining untreated municipal wastewaters are all discharged into the Pearl River. Industrial wastewaters are basically treated in the plants prior to discharge. The annual discharge of raw wastewater and STP effluents to the PRE through the Pearl River and its tributaries totalized to > 2.0 billion tons in recent years. Therefore, wastewater has become an important contributor to the environmental deterioration in the PRD and the Pearl River Estuary (PRE).

Wastewater samples were grab collected from two sewage treatment plants (STPs) in Guangzhou[20]. River water samples were collected from the urban section of the Pearl River at Guangzhou. Samplings were conducted seasonally during both the low-flow and the high-flow seasons[21]. Water samples were collected in amber glass bottle without headspace. Appropriate amount of sodium azide were added immediately after sampling to suppress potential biodegradation. Samples were transported in boxes packed with ice and were stored at 4 ^{o}C upon arrival at the laboratory until they were treated within 48 hours.

Three sedimentary cores were collected at the PRE and the adjacent South China Sea (SCS)[22]. The cores were sectioned at 2-cm and 1-cm intervals, respectively onboard immediately after collection. The sectioned sediment samples were wrapped with aluminum foil (baked at 450 ^{o}C) prior to being packed into polyethylene bags and stored at -20 ^{o}C before treatment.

Water samples were passed through pre-baked GF/F glass microfibre filters (Whatman, Maidstone, England). An aliquot of the filtrate (500-1000 mL) was added with surrogate standards prior to enrichment by solid phase extraction (SPE). The steroid estrogens and phenolic compounds were extracted at pH 7.0 with C18 SPE (Supelco, Bellefonte, PA, USA) cartridges, while the antibacterials and acid pharmaceuticals were extracted at pH 4.0 with HLB cartridges (Waters, USA). Estrogens, phenols, and acid pharmaceuticals were derivatized with MSTFA and BSTFA respectively prior to GC-MS analysis in the selected ion monitoring mode (SIM). Antibacterials were determined by HPLC-UV/FLD and LC-MS. Quantification of the analytes was achieved using internal standard methods. The method detection limits (MDLs) were 0.1-5 ng L^{-1} for estrogens, phenols, and acid pharmaceuticals, and 50-150 ng L^{-1} for the antibacterial.

Sediment was freeze-dried, homogenized, and treated by ultrasonication with 5 ml of mixture of acetone and dichloromethane (1:1, v/v). The extract was evaporated to about 1 ml and then fractionated on a silica gel column. The polar fraction that contained NP and BPA was blown down to just dryness and then derivatized with

PFPA. The PFPA derivative was finally analyzed by GC-MS in SIM mode.

Results and Discussion

The distributions and seasonal variations of typical PPCPs in urban river water of Guangzhou are shown in Fig 1. Estrone was the most frequently detected steroid estrogen with a maximun concentration of 65 ng L^{-1}. The concentrations of E1 in the urban riverine water of Guangzhou were comparable to those reported in streams of the North America, the Tama River of Japan, and rivers of European. Estradiol (E2) and 17α-estrodial (αE2) were detected at trace level (≤2 ng L^{-1}), which were similar to those reported in the rivers Germany[14] and in the Mississippi River[13], but slightly lower than that of the Tama River in Japan[19]. Typically, αE2 is assumed to originate from animal excretion and it was reported to be at trace levels (< 2 ng L^{-1}) in Europeans rivers [14]. However, E1, E2 and αE2 have been reported to be able to transform each other[23]. The source of αE2 and the fate of the steroid estrogens in the riverine water of Guangzhou await further study. Other estrogens were only sporadically or not detected.

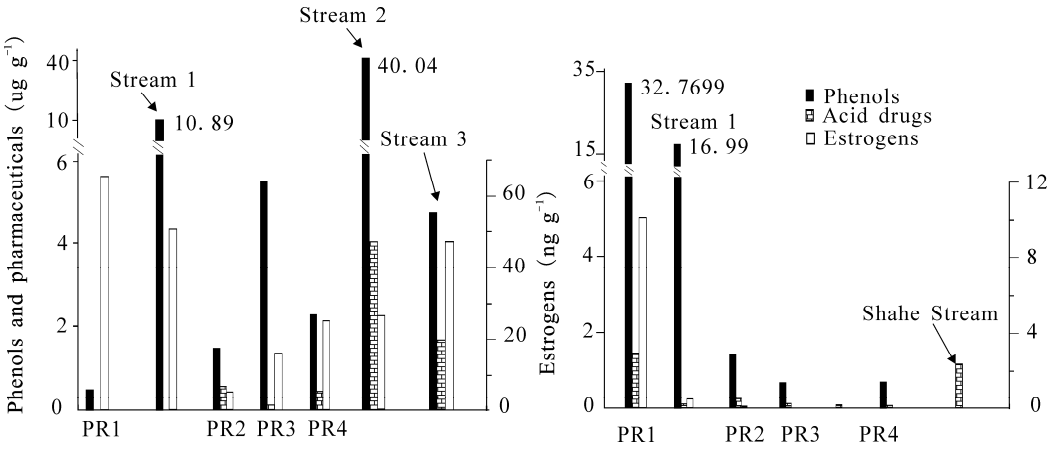

Fig. 1. Distribution and seasonal variations of the PPCPs in surface water of Guangzhou.

Nonylphenol (NP), bisphenol A (BPA), and triclosan (TCS) were widely detected in urban river water at Guangzhou, ranged from 36 to 33231 ng L^{-1}. Both levels and detection frequencies of NP, BPA and TCS in this work appeared higher than those reported in other regions[9,14,19], which may indicate the great amount of usage of these chemicals due to the large population in Guangzhou. Parabens are widely used preservative / antioxidant in cosmetics and other personal care products, and are also referred as endocrine-disrupting chemicals[10]. Like triclosan, 2-phenylphenol (PHP) is also commonly used as a surface disinfectant in lotions and other personal care products. There were few reports of parabens and PHP in natural waters[12]. The concentrations of PHP, methylparaben and propylparaben were comparable to those of the wastewaters in Canada[10].

Salicylic acid (SCA) was the most frequently detected acid drug in the riverine water of Guangzhou, since it is also widely used additive in cosmetics and foodstuff and occurs naturally in the environment[24]. Ibuprofen (IPF) occurred in most water samples, whereas naproxen (NPX) was less frequently detected, with maximum concentrations of sub-to low μg L^{-1}, respectively. IPF is listed as one of the four most often - used anti-inflammatory pharmaceuticals in China (>1000 tons/y), while NPX is relatively less produced. The relatively low abundances IPF and NPX may also be associated with the degradation in the warm weather and

strong sunshine of Guangzhou because they are vulnerable to biodegadation and photodegradation in the environment[16,18]. Clofibric acid was detected in most samples, slightly higher than those in North America and Europe. Gemfibrozil was not detected although it has been reported as ubiquitous in Canadian STP effluents and the recipient stream waters. The difference in the occurrence of the acid pharmaceutical residues in this work from reports in literature may mirror the different usage patterns of these drugs in China from Europe and North America.

The detection frequencies and median concentrations of the PPCPs were generally higher during the low-flow season than those during the high-flow season. Assuming that the discharges of wastewater containing the investigated PPCPs were relatively constant through the year, the dilution factor by rainfall seem to be an important cause of the occurrence variations of the PPCPs in waters of the urban streams and the Major Pearl River at Guangzhou. The dilution effect of water flow on the occurrence of PPCP contaminants was also reported for the stream waters, drinking water and reclaimed wastewater in the USA[12].

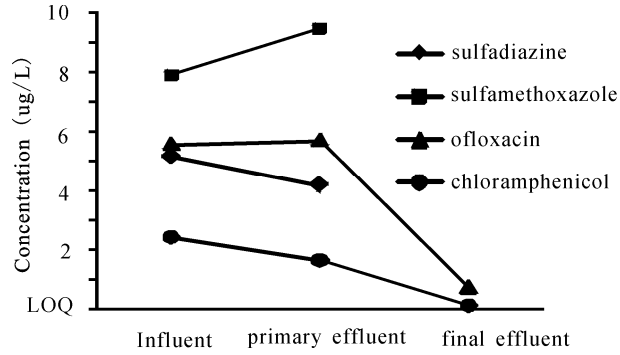

Fig. 2 Concentrations of antibacterials in wastewater of Guangzhou, China

Antimicrobials have been detected in raw sewages in Guangzhou at low μg L^{-1} (Fig.2), relatively higher than those reported in Europe[25]. Primary mechanical sedimentation led to no obvious reduction in antibacterial concentrations. However, some antibacterials were unquantifiable after the activated sludge treatment. This work is only a preliminary study by grab samples. More work is needed to be done in detail in order to better illustrate the occurrence and fate of antibiotics in wastewaters and during sewage treatment in China.

The downcore variations of the fluxes of NP and BPA in the PRE and the near-shore SCS are illustrated in Fig.3. In the PRE, the flux of NP and BPA remained constant prior to the early 1980s. The peak flux occurred in the mid-1980s, basically coincident with the rapid economic growth in the PRD. The NP flux declined at the end of 1980s but began increasing slightly since the mid-1990s, which might be attributed to the implementation of wastewater treatment in major cities in the PRD from the late 1980s but inefficiency of treatment facilities. The NP fluxes in the SCS peaked from the early to the mid-1970s, declined from 1980s, but showed increasing trends since 1990s, which were consistent with the PRE. Upcore decreasing trends of NP were reported for sediment in the Tokyo Bay, Japan[26] and in Shiwa Lake, Korea[27] due to possible decrease of input resulted from implementation of some legal regulations on industrial wastes and sewage treatment. The reason for the increasing fluxes of the two phenolic EDCs in PRE and the adjacent SCS is more likely that the wastewater is not efficiently treated prior to discharge due to the lack of adequate wastewater treatment facilities in this region. The coincidence of the increasing fluxes between the sedimentary cores after 1990s further confirm the seaward

transport of the two anthropogenic phenolic EDCs from the PRE to the SCS.

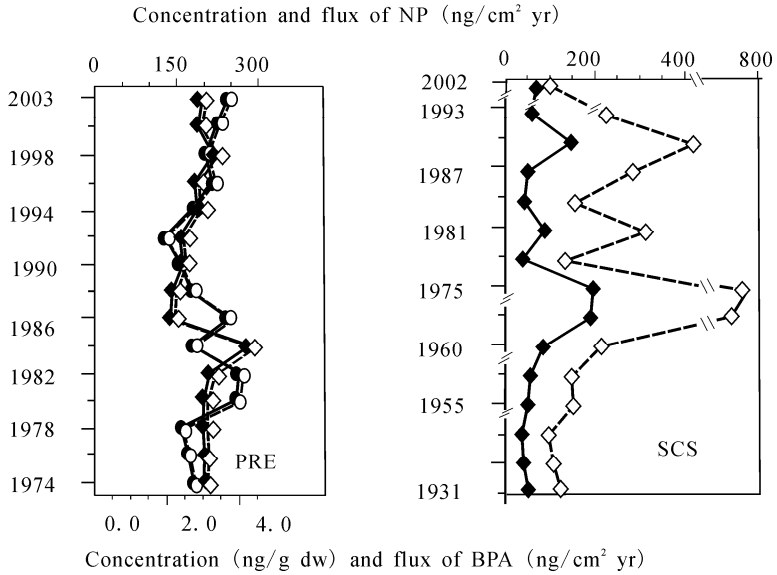

Fig.3. Temporal variation of the concentration and flux of NP and BPA in the PRE and SCS

The peak pattern of NP was fairly uniform throughout the sediment cores and was quite similar to that of the technical mixture standard, suggesting that isomer-selective degradation of NP after deposition did not occur significantly, and that NP composition in technical mixture is relatively constant during the past decades. NP fluxes in PRE and SCS were slightly lower than those in the Tokyo Bay[28]. The inventory of NP in the PRE was 4 μg cm^{-2} in the past 30 years

Acknowledgements

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References

1. Daughton C.G. *Environ Impact Assess Rev* 2004; 24: 711.
2. Madsen S.S., Skovbølling S., Nielsen C., Korsgaard B. *Aqua Toxicol* 2004; 68: 109.
3. Brian J.V., Harris C.A., Scholze M., Kortenkamp A., Booy P., Lamoree M., Pojana G., Jonkers N., Marcomini A., Sumpter J.P. *Environ Sci Technol* 2007; 41: 337.
4. Kang J., Kondo F., Katayama Y. *Toxicology* 2006; 226: 79.
5. Van der Ven K., Keil D., Moens L.N., Van Hummelen P., Van Remortel P., Maras M., De Coen W. *Chemosphere* 2006; 65: 1836.
6. Oaks J.L., Gilbert M., Virani M.Z., Watson R.T., Meteyer C.U., Rideout B.A., Shivaprasad H.L., Ahmed S., Chaudhry M.J., Arshad M., Mahmood S., Ali A., Khan A.A. *Nature* 2004; 427: 630.
7. Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.T. *Environ Sci Technol* 2002; 36: 1202.
8. Metcalfe C.D., Miao X.S., Koenig B.G., Struger J. *Environ Toxicol Chem* 2003; 22: 2881.
9. Boyd G.R., Palmeri J.M., Zhang S., Grimm D.A. *Sci Total Environ* 2004; 333: 137.

10. Lee H.B., Peart T.E., Svoboda M.L. *J Chromatogr A* 2005; 1094: 122.
11. Brun G.L., Brenier M., Loise R., Doe K., Jackman P., Lee H.B. *Environ Toxicol Chem* 2006; 25: 2163.
12. Lorain G.A., Pettigrove M.E. *Environ Sci Technol* 2006; 40: 687.
13. Zhang S., Zhang Q., Darisaw S., Ehie O., Wang G. *Chemosphere* 2007; 66: 1057.
14. Kuch H.M., Ballschmitter K. *Environ Sci Technol* 2001; 35: 3201.
15. Stachel B., Ehrhorn U., Heemken O.P., Lepom P., Reincke H., Sawal G., Theobald N. *Environ Pollut* 2003; 124: 497.
16. Tixier C., Singer H.P., Oellers S., Muller S.R. *Environ Sci Technol* 2003; 37: 1061.
17. Ashton D., Hilton M., Thomas K.V. *Sci Total environ* 2004; 333: 167.
18. Vieno N.M., Tuhkanen T., Kronberg L. *Environ Sci Technol* 2005; 39: 8220.
19. Furuichi T., Kannan K., Giesy J.P., Masunaga S. *Water Res* 2004; 38: 4491.
20. Peng X., Wang Z., Kuang W., Tan J., Li K. *Sci. Total Environ* 2006;371: 314.
21. Peng X., Yu Y., Tang C., Tan J., Huang Q., Wang Z. *Sci Total Environ* 2008, 397: 158.
22. Peng X., Wang Z., Mai B., Chen F., Yang C. *Sci Total Environ* 2007; 384: 393.
23. Czajka C.P., Londry K.L. *Sci Total Environ* 2006; 367: 932.
24. Verenitch S.S., Lowe C.J., Mazumder A. *J Chromatogr A* 2006; 1116: 193.
25. Gobel A., McArdell C. S., Suter M. J., Giger W. *Anal. Chem*. 2004; 76: 4756.
256. Isobe T., Nishiyama H., Nakashima A., Takada H. *Environ Sci Technol* 2001; 35: 1041.
27. Li Z., Li D., Oh J.R., Je J.G. *Chemosphere* 2004; 56: 611.
28. Kawahata H., Ohta H., Inoue M., Suzuki A. *Chemosphere* 2004; 55: 1519.