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Occurrence, distribution and risk assessment of pesticides in a river-reservoir system

Yihan Chen[a], Kaifeng Yu[a], Muhammad Hassan[a], Cong Xu[a], Bo Zhang[a], Karina Yew-Hoong Gin[b,c], Yiliang He[a,d,*]

[a] School of Environmental Science & Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
[b] Department of Civil and Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, E1A 07-03, Singapore 117576, Singapore
[c] NUS Environmental Research Institute, National University of Singapore, 5A Engineering Drive 1, #02-01, Singapore 117411, Singapore
[d] Shanghai Institute of Pollution Control and Ecological Security, 800 Dongchuan Road, Shanghai 200240, China

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ABSTRACT

The water environment from river to reservoir has been considered as a hybrid river-reservoir system due to pronounced environmental properties. This study investigated the distribution and potential environmental behavior of pesticides in river-reservoir system, examining 31 target pesticides in water phase from a key drinking water source (Dongjiang River). The concentrations of Σ_8OCPs, Σ_{16}OPPs and Σ_7SPs with the corresponding occurrence were in the range of 107.57–340.35 ng/L (moderate level), 232.65–1197.95 ng/L (moderate level) and 125.23–245.09 ng/L (low level), respectively. Ecological risk assessments indicated that most of the pesticides posed a high level of risk to the aquatic organisms. Moreover, seasonal agricultural application, rainfall and temperature could influence the levels and compositions of Σ_8OCPs, Σ_{16}OPPs and Σ_7SPs in the river system, while seasonal hydrological processes could only influence their compositions in the reservoir system. In the wet season, the levels of Σ_8OCPs and Σ_7SPs decreased from the river system to reservoir system probably via biogeochemical processes, while the level of Σ_{16}OPPs decreased along the environmental gradient probably via dilution process. Additionally, longer hydraulic retention time of the reservoir system could contribute to the biogeochemical processes for OPPs and SPs exported from the river system, but it might fail to facilitate this process for OCPs. Taken together, this study highlighted that the distributions and environmental behavior of pesticides in river-reservoir system varied seasonally from river system to reservoir system.

1. Introduction

Pesticides are considered as an essential component of modern farming, with an estimated 1–2.5 million tons of active pesticide ingredients used annually in the world and playing a vital role in maintaining highly efficient agricultural productivity (Fenner et al., 2013; McKnight et al., 2015; Jallow et al., 2017). Among these pesticides, organochlorine pesticides (OCPs) were initially restricted or banned worldwide due to the fact that they were identified as one of the most important groups of persistent organic pollutants in the 1980s (Grung et al., 2015; Singare, 2015). In contrast to the OCPs, some pesticides (organophosphates pesticides and synthetic pyrethroids) are often characterized as being relatively less persistent. Consequently, they have been widely applied into the pest control, and their usage is still growing (McKnight et al., 2015; Li et al., 2017). However, the widespread application of organophosphorus pesticides (OPPs) and synthetic pyrethroids (SPs) also presented very high acute and chronic toxicity to aquatic organisms, especially to invertebrates, mollusks and fish (Tsaboula et al., 2016; Zheng et al., 2016; Korkmaz et al., 2018). Given all these factors, pesticides are now considered among the most harmful types of compounds influencing surface water safety (McKnight et al., 2015).

Aquatic ecosystems were reported to be highly susceptible to pesticide contamination (Masia et al., 2015). In particular, rivers located in agricultural catchments are facing more serious challenges due to the rich drainage system and rapid growing increase in the applications of pesticides (Net et al., 2015). Furthermore, there are numerous reservoirs located in the upstream river to control and manage the water resources for agricultural irrigation, drinking water supplies, mitigating floods and producing hydropower (Maavara et al., 2017). The number of reservoirs has increased dramatically over past decades, reaching about 16 million dams and more than 50,000 large dams worldwide

* Corresponding author at: School of Environmental Science & Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China.
E-mail address: ylhe@sjtu.edu.cn (Y. He).

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(Lehner et al., 2011). As a result, river-reservoir system along the environmental gradient from river system to reservoir system is very important and universal; however, it is largely ignored in the freshwater ecosystem assessments. Recently, many monitoring programs and scientific studies have put more focus on the occurrence, distribution and fate of pesticides and their potential ecological effects in individual rivers, reservoirs and lakes (He et al., 2016; Zheng et al., 2016; Yang et al., 2017). Available literature has not comprehensively investigated the environmental behavior of pesticides in river-reservoir system, particularly in source water of river-reservoir system. Therefore, exploring variation trends in the occurrence, distribution and ecological effects of pesticides from river system to reservoir system will be of great significance for better understanding of the biogeochemical process of these hazardous materials in actual aquatic environment.

To achieve the above mentioned points, a field study was conducted in an idea river-reservoir system in the South China (Headwater Region of the Dongjiang River: HRDR), which also plays an important role in supplying drinking water for the cities of Guangzhou, Shenzhen and Hong Kong (Sun et al., 2016). This watershed comprises two rivers and one reservoir with a catchment area of 5150 km^2, which is affected by intensive agricultural activity (Chen et al., 2008). Here, we performed the first comprehensive and comparative research on distribution and transport of representative pesticides during different hydrological seasons in the river-reservoir system. The main goals of our comparative study were to illustrate the occurrence, distribution, ecological risk of the pesticides in the water phase of Headwater Region of the Dongjiang River, and to systematically investigate their distribution and composition along the environmental gradient from upstream river system to downstream reservoir system.

2. Materials and methods

2.1. Study sites and sampling

This study was carried out in the HRDR situated in south Jiangxi Province and north Guangdong Province, China (Fig. 1). The most important tributaries are the Beiling River (with 140 km length, 2363 km^2 of catchment area) and Xunwu River (with 138 km length, 2697 km^2 of catchment area), which flow downstream into the Fengshuba Reservoir. Periodically, this reservoir may effectively regulate the hydrological conditions of the aforementioned two tributaries in periodic manner. The basic hydrological information of the river-reservoir system can be found in Table 1. According to their catchment characteristics, land uses and degree of human activities, the catchment was classified into two areas, a river system located in agricultural area (S1–S8) and a reservoir system located in natural area (S9–S13) (Supplementary Fig. S1). In the agricultural area, pesticides were used intensively for navel orange orchard and crops production (Supplementary Text S1). However, apart from the pesticide inputs from the river system, we hypothesize that the reservoir in natural environment with no typical farmland was less directly contaminated with pesticides due to forestry projects and reservoir resettlement. Specifically, environmental gradient mainly consists of the variations in both the degree of anthropogenic contamination and hydrological gradient from the rivers and reservoir in this watershed.

Two sampling campaigns at the 13 sites were conducted in the summer (on 18–20th of July 2015, wet season) and autumn (on 25–27th of November 2015, dry season), which are representative months for agricultural management season and agricultural harvest season, respectively (Text S2, Fig. S2). Three surface water samples (3 L) from each site of the river system (S1–S8) were collected randomly and bulked together to form one composite sample. However, at each site in the reservoir system (S9–S13), three water samples (3 L) were collected separately from the surface water (0.5 m below surface), the middle water (half of the depth) and the bottom water (about 2–4 m above bottom), subsequently the three samples from different layers were combined to form a sample. The samples were transported to the laboratory immediately and kept at 4 °C for up to one week until further analysis.

2.2. Chemicals

All solvents used in mixture solution of all standards and solid phase extraction (SPE) process are all chromatographically pure grade

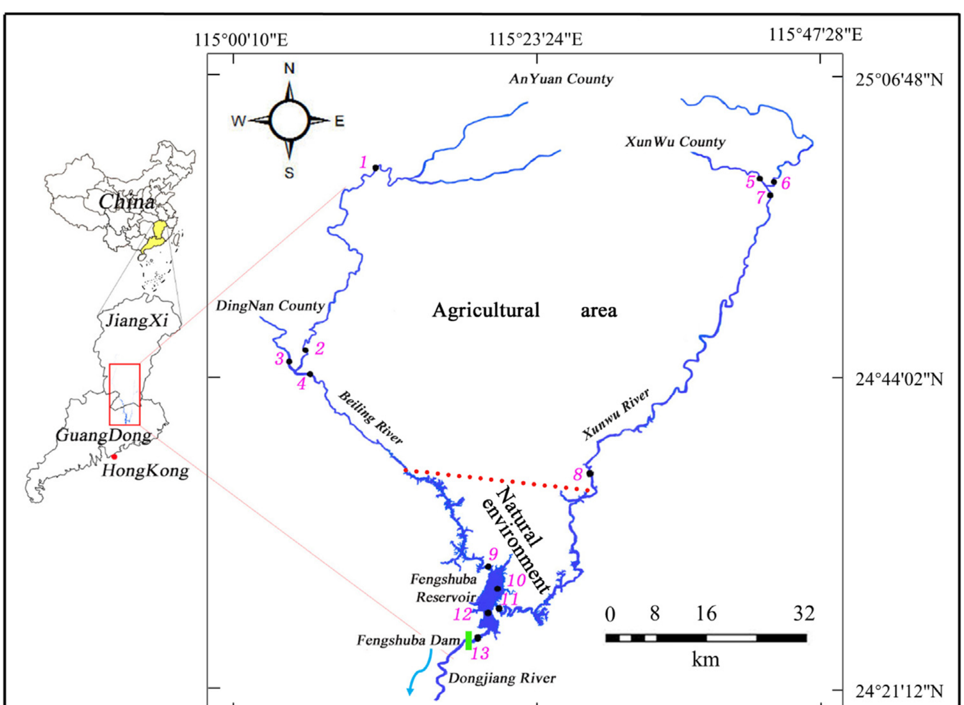

Fig. 1. Map showing the location of Headwater Region of the Dongjiang River (HRDR) and the 13 sampling stations.