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Insecticides in sediment cores from a rural and a suburban area in South China: A reflection of shift in application patterns

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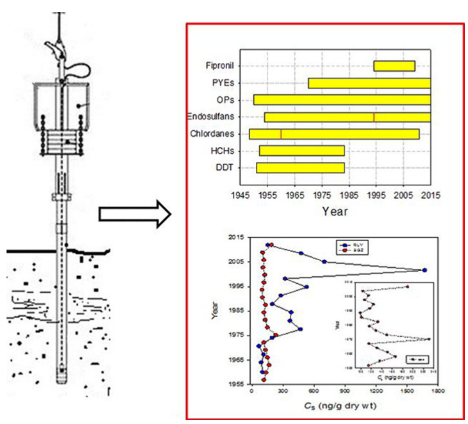
HIGHLIGHTS

- Various pesticides were detected in dated sediment cores from rural and urban rivers.
- A shift in pesticide application pattern to CUPs was recorded by sediment cores.
- Pesticide concentrations and composition showed spatial difference between cores.
- Temporal profiles of insecticides reflected local economic conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

A shift in pesticide application pattern has occurred in recent decades, yet little information is available in the consequence of this shift. To better understand how the shift is reflected in aquatic environment, two sediment cores were collected from a rural (RLY) and a suburban (SGZ) river in South China. A variety of legacy organochlorine pesticides (OCPs) and current-use pesticides (CUPs), including organophosphate, pyrethroid and phenylpyrazole insecticides were quantified at distinct increments of the sediment cores. Total insecticide concentrations were in the ranges of 67.6–1671 and 99.2–231 ng/g dry weight in RLY and SGZ with pyrethroids and organochlorines being the dominant components, respectively. In general, the shifting profile of sediment-bound insecticides from legacy OCPs to CUPs over time followed their historical application pattern, but significant differences were noted between the temporal profiles of the rural and suburban cores in regards to concentrations and composition of insecticides. The observed difference between the suburban and rural cores was synchronous with land use pattern and local economic changes. A steep increased occurrence of CUPs in the 1990s was observed in the RLY core, which is consistent with the onset of economic growth in this area. In contrast, the suburban SGZ area has been historically contaminated by legacy OCPs, with fresh input of OCPs in SGZ believed to be caused by soil erosion, caused by land reclamation activities associated with urban expansion. The

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current study shows the shift in insecticide application pattern from legacy OCPs to CUPs leading to an elevated CUP occurrence in the environment. It also suggests a stronger need for understanding not only environmental fate and risk, but also how their use pattern and land use changes impact the occurrence of pesticides.

1. Introduction

The global use of pesticides continues to rise, as well as their ecological risks (Köhler and Triebskorn, 2013; Li et al., 2014a, 2014b). Pesticides may reach surface water through various pathways, such as atmospheric deposition, surface runoff, and sewage drainage (Lin et al., 2008; Jiang and Gan, 2012). As a consequence, pesticide pollution in aquatic ecosystems has gained worldwide awareness because of their ubiquity in the environment and potential risk to aquatic organisms and human health (Beketov et al., 2013; Malaj et al., 2014).

Hydrophobic pesticides are most likely to adhere to particulate matter and eventually be deposited in bed sediment (Li et al., 2014a). Sediment deposition continues over time, making sediment core a geochronometer to record historical variations in contaminant occurrence and to reflect anthropogenic activity in watersheds (Eisenreich et al., 1989). Since the beginning of large-scale use of synthetic pesticides in the 1950s, several generations of insecticides have been developed with the ban or phase out of older generations (Denholm et al., 2002). Organochlorine pesticides (OCPs), e.g., dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs) were the first-generation synthetic insecticides, being historically used in large quantities globally. After OCPs, pesticide use transitioned to the less-persistent organophosphate insecticides (OPs), and then gradually to pesticides that showed less mammalian toxicity, such as pyrethroids (PYEs) and phenylpyrazoles (e.g., fipronil). Nevertheless, even with new generations of insecticides, ecological risks to nontarget aquatic organisms may also be still apparent (Weston et al., 2004; Delgado-Moreno et al., 2011; Mehler et al., 2011; Stehle and Schulz, 2015).

Although shifts in insecticide application have been well documented, their impact on the occurrence and risk of insecticide residues in aquatic environment are poorly understood. Sediment cores may provide a useful tool for reconstructing a historical record of pesticide input into freshwater ecosystems and help to elucidate the temporal impacts of human activities on pesticide pollution (Eisenreich et al., 1989; Sabatier et al., 2014). Previous studies using cores have generally focused on OCPs (mainly DDTs and HCHs) and have noted a generally decreasing trend over time except for fresh input of DDTs in some areas such as Quanzhou Bay in South China and Gwangyang bay in South Korea (Gong et al., 2007; Kim et al., 2008; Wang et al., 2013; Cheng et al., 2014). In comparison to OCPs, very little information is available on the distribution and composition of current use pesticides (CUPs) in sediment cores worldwide (Daniels et al., 2000; Sabatier et al., 2014; Wu et al., 2015). Although CUPs were designed to be less-persistent than OCPs, their degradation rates are greatly reduced when found in sediment compared to water (Gan et al., 2005). Recently, Sabatier et al. (2014) analyzed DDTs and CUPs in sediment cores from a lake receiving runoff from a vineyard watershed and found pesticide concentrations in the cores corresponded with their historical applications. Interestingly, the use of an herbicide glyphosate increased soil erosion (as it killed plants and changed the stability of the associated land) and subsequently resulted in the remobilization of soil-stored DDTs into the lake, suggesting the emerging need to study legacy and current-use pesticides simultaneously.

The main objective of the current study was to evaluate temporal profiles of both legacy (OCPs) and CUPs (OPs, PYEs, fipronil) insecticides in sediment cores in relation to their application patterns and historical land-use activities in a rural and a suburban area of South China. Understanding the usage of pesticides in the past in relationship to changes in land-use and economic status of an area would provide information for better understanding the occurrence and risk of pesticides in areas which are under development.

2. Materials and methods

2.1. Sediment core collection and dating

Two sediment core samples were collected from South China in July 2012 (Supplementary material, Fig. S1, "S" represents figures and tables in the Supplementary material thereafter). One core was sampled from a rural river in Longyan, Fujian (RLY, 24°56′49″N, 116°26′38″E). This river is surrounded by rice fields and has seen heavy use of pesticides for pest control (Li et al., 2014b). The other core was sampled from a suburban river near Guangzhou, Guangdong (SGZ, 23°03′33″N, 113°20′23″E). After several decades of urbanization, the SGZ catchment has changed from small suburban villages to one of the largest ecological parks in Guangzhou (Sun et al., 2015). Sampling occurred in both rivers at depths of approximately 1.5 m. Sediment cores were collected using standard stainless steel static gravity coring equipment with an eight cm internal diameter. The length of cores RLY and SGZ was 32 and 38 cm, respectively. The cores were sliced into two cm slices on site, packed in aluminum foils, transported back to the laboratory and stored at −20 °C in the darkness until analysis.

Assuming a constant deposition rate after 1963, sediment core dating was accomplished by measuring ^{137}Cs activity with gamma spectrometry at 662 keV on a Caberra S-100 multi-channel spectrometer coupled with a GCW3022 H-P Ge coaxial detector (Caberra, Meriden, USA). ^{137}Cs is an artificial radionuclide and a by-product produced from nuclear weapon testing or nuclear reactor accidents. This gamma technique was used to identify the 1963 nuclear weapon peak and the 1986 nuclear accident of the Chernobyl Nuclear Power Plant (Zhang, 2005; Liu et al., 2012).

2.2. Chemicals and reagents

Sediment cores were analyzed for 14 OCPs, 10 OPs, nine PYEs, and fipronil and its two metabolites, fipronil sulfide and fipronil sulfone (FIPs) (Tables S1 (RLY core) and S2 (SGZ core) and the sum concentrations of individual classes of insecticides were defined as ΣOCP, ΣOP, ΣPYE and ΣFIP, respectively. Neat compounds of OCPs and FIPs were bought from AccuStandard (New Haven, CT, USA), and OPs and pyrethroid standards were purchased from ChemService (West Chester, PA, USA) with an exception for tefluthrin and chlorpyrifos which were from Sigma-Aldrich (St. Louis, MO, USA) and Ultra (Kingstown, RI, USA), respectively. The purities of all neat compounds were greater than 97% as labeled by the manufacturers. Three surrogates, including 4,4′-dibromooctafluorobiphenyl (DBOFB), polychlorinated biphenyl (PCB)-67 and PCB-209 were obtained from Supelco (Bellefonte, PA, USA). Additionally, PCB-24, PCB-82, PCB-189 (Supelco), parathion-d10, and cypermethrin-d6 (Cambridge, Andover, MA, USA) were used as internal standards for quantifying target insecticides on gas chromatography/mass spectrometry (GC/MS).

Dichloromethane and acetone (analytical grade) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China) and redistilled before use, and HPLC grade hexane was gained from Burdick and Jackson (Ulsan, Korea). Copper powder was activated using diluted HCl, and then washed with distilled water and acetone sequentially. Solid phase extraction (SPE) cartridges packed with granular carbon black and primary/secondary amine were purchased from Sigma-Aldrich.