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Legacy and Current-Use Insecticides in Agricultural Sediments from South China: Impact of Application Pattern on Occurrence and Risk

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Supporting Information

ABSTRACT: Legacy and current-use insecticides were analyzed in sediments collected from a typical rice-planting region in South China. Total concentrations of insecticides varied from 1.63 to 775 ng g^{-1} with mean and median values of 67.0 and 11.5 ng g^{-1}, respectively. Pyrethroids predominated pesticide composition (31.7%), followed by organophosphates (23.0%) and fiproles (20.8%). Sediment risk analysis showed that pyrethroids, fiproles, and abamectin posed significant risk to benthic invertebrates in one-third of sediments. Different distributions of pyrethroids and organophosphates in urban and agricultural areas were consistent with their application patterns, whereas legacy organochlorine pesticides showed no region-specific distribution because of rapid transition of land use pattern from agricultural to urban areas. Likely illegal use of pyrethroids and fipronil caused serious ecological risks in agricultural waterways. Pyrethroids and fipronil were restricted to use in paddy fields, but their occurrence and risk in agricultural waterways were high, calling for better measures to regulate the illegal use of insecticides.

KEYWORDS: *agricultural waterways, sediment, legacy and current-use insecticides, risk, application pattern*

INTRODUCTION

Pesticides are released into the environment in large quantities due to their intensive use in both agricultural and urban areas. Owing to their high biological activity, insecticides are regarded as one of the key stressors jeopardizing freshwater biodiversity and ecosystem functioning on a global scale.[1,2] Pesticide pollution is a global issue, yet studies on the occurrence and risk of insecticide residues in aquatic ecosystems are largely limited in developed countries.[3,4] Little information is available in developing countries, but insecticide-induced risk to aquatic ecosystems in these regions should not be ignored, particularly in countries with intense agricultural activities and urbanization.[5,6] As the world's most populous nation, China has been facing tremendous challenges to balance the benefit and risk of agricultural use of pesticides. Overuse and abuse of pesticides make the case even worse.[7,8]

With continuously increasing demand for pesticides worldwide, the application pattern of insecticides has shifted over time.[9,10] New generations of insecticides, such as organophosphate insecticides (OPs, e.g. chlorpyrifos), pyrethroids (e.g., cypermethrin), phenylpyrazoles (e.g., fipronil), and biopesticides (e.g., abamectin) have been developed to replace legacy insecticides (e.g., organochlorine pesticides (OCPs)). Legacy OCPs, such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyl trichloroethane (DDT), are highly persistent, resulting in their co-occurrence with current-use pesticides (CUPs) in the environment, although they have been banned for use decades ago.[11]

Many insecticides are hydrophobic and tend to accumulate in sediment, posing a threat to benthic organisms. Therefore, it is imperative to monitoring sediment-associated insecticides. Previous studies on pesticide residues in aquatic environment in China mostly focused on OCPs, especially HCHs and DDTs.[6,11] Recently, researchers started to pay attention to the ecological risk of sediment-associated CUPs in China, yet most studies were conducted in urban settings.[5,12,13] Information on CUP residues in agricultural waterway sediments in China was less known.[9] In China the most use of pesticides in agriculture was for grain production, accounting for 68% of the total agricultural demand for pesticides, which was significantly higher than those for commercial crops (15%), vegetables (11%), and tea and fruits (5.3%).[14] Wang et al.[15] analyzed CUPs in sediment in a Chinese lake receiving water from both agricultural and urban areas and found OPs in lake sediments were mainly originated from agricultural use, whereas pyrethroids were from urban runoff. Sun et al.[9] found the historical profiles of insecticide composition in sediment cores from agricultural and suburban areas were significantly different. These studies suggested that distinct application patterns of insecticides in agricultural and urban areas may result in different insecticide risks in aquatic ecosystems.

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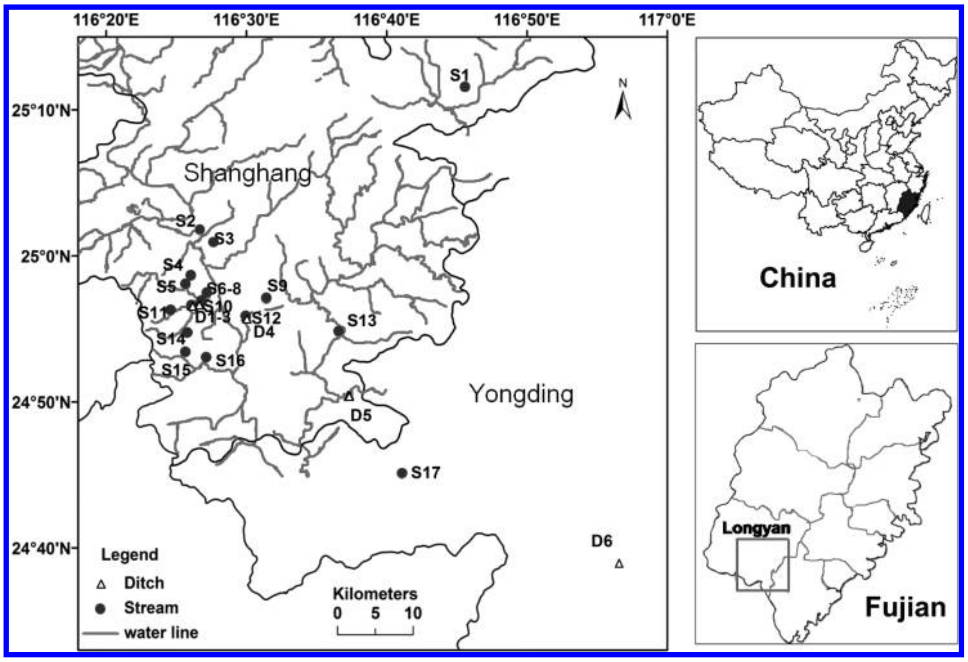

Figure 1. Map of sediment sampling sites in rice-planting waterways in Shanghang and it adjacent area, Fujian, South China. Circles show sampling sites in streams and triangles those in ditches.

The objectives of the present study are to evaluate the occurrence and composition of a battery of legacy and current-use insecticides in agricultural waterways in South China and better understand the impact of application pattern on ecological risk of insecticide residues in sediment. To achieve the goals, several classes of insecticides were analyzed in sediments collected from a watershed mainly serving rice-planting practice. The composition, distribution, and risk of sediment-bound insecticides were assessed. Finally, data from the present study and the literature were compared by classifying the sampling sites into three categories, namely, agricultural, mix-land (agricultural mixed with urban), and urban areas.

■ MATERIALS AND METHODS

Study Area and Sediment Collection. Rice planting is the main agricultural practice in South China where pesticide application rate ranks highest in China.[6] A sampling campaign was conducted in September 2014, and 23 surface sediment samples (0−5 cm) were collected from agricultural waterways (ditches and streams) that received water from rice-planting fields in Shanghang and it adjacent area, Fujian, South China (Figure 1). The coordinates and description for sampling sites are presented in Table S1 ("S" represents figures and tables in the Supporting Information hereafter).

On the basis of the distance from sampling sites to the nearest rice field, the sampling waterways were defined as ditches (distance < 5 m, D1−D6) and streams (distance > 5 m, S1−S17). Sediment samples were collected using a shovel by wading into the water in the depositional zones, sieved with a 425 μm sieve for removing large debris, stored in ice, transported to the laboratory, and kept at −20 °C in darkness. After removal of the inorganic carbonates using 1 mol L^{-1} HCl, the contents of total organic carbon (TOC) of sediment samples were analyzed using a Vario EL III Elemental Analyzer (Hanau, Germany).

Chemical Analysis. A total of 40 insecticides were analyzed in sediment samples (Table S2). After addition of the surrogate standards (4,4′-dibromooctafluorobiphenyl (DBOFB), ^{13}C-polychlorinated biphenyl (PCB)-141, and PCB-209) to sediment samples, OCPs, OPs, pyrethroids, and fiproles (fipronil and its degradation products, fipronil sulfide, and fipronil sulfone) were extracted from sediments using ultrasound-assisted microwave extraction, and the extracts were cleaned with solid phase extraction cartridges. The target analytes were analyzed on an Agilent 7890-5975 and a Shimadzu QP-2010 plus GC-MS upon the addition of the internal standards (PCB-24, PCB-82, PCB-189, parathion-d_{10}, and *trans*-cypermethrin-d_6). Meanwhile, abamectin and emamectin benzoate (ABAs) in sediment were extracted with ultrasound extraction and analyzed on a Shimadzu DGU-30A and AB SCIEX triple-quad 5500 HPLC-MS/MS, and clothianidin-d_3 and imidacloprid-d_4 were used as the surrogate and internal standard for ABAs, respectively. Detailed procedures for sample preparation and chemical analysis are provided in the Supporting Information, and HPLC-MS/MS conditions including precursor ions, product ions, collision energy, and retention time of ABAs are shown in Table S3.

Quality Assurance and Quality Control. The instrument was checked with a calibration standard every 10 injections, and the variation of each analyte was within 20%. Two sets of quality assurance and quality control samples were analyzed along with the 23 samples, including a procedural blank, a matrix blank, and three matrix-spiked samples. The performances of analytical procedures were checked with quality control samples. The concentrations of individual insecticides in blank sample were all less than the lowest concentration of the calibration standards. The recoveries (mean ± standard deviation) for OCPs, OPs, pyrethroids, fiproles, and ABAs in the spiked samples were 95 ± 28, 84 ± 36, 86 ± 25, 79 ± 16, and 80 ± 37%, respectively. The recoveries of the surrogates in all samples were 62 ± 14, 81 ± 12, 93 ± 17, and 99 ± 11% for DBOFB, ^{13}C-PCB-141, PCB-209, and clothianidin-d_3, respectively.

Data Analysis. The sum concentrations of 15 OCPs, 9 OPs, 11 pyrethroids, 3 fiproles, and 2 ABAs were defined as Σ_{15}OCP, Σ_9OP, Σ_{11}PYE, Σ_3FIP, and Σ_2ABA, respectively. The concentrations of insecticides in sediment are presented on a dry weight basis hereafter unless it is pointed out to be TOC-based. The reporting limits (RLs) were defined as the lowest concentration of standards used in the calibration curves multiplied by the final volume of the extract and then divided by the dry weight of extracted sediment (5 g). The lowest concentrations of the calibration standards and final volumes of the extract were 10, 5, and 5 ng mL^{-1} and 100, 500, and 100 μL for individual OCPs, ABAs, and other insecticides, respectively. Accordingly, the RLs were calculated as 0.2, 0.5, and 0.1 ng g^{-1} dry weight for individual OCPs, ABAs, and other insecticides, respectively.

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Half of the RL was used for calculating the sum concentrations and composition of individual class of insecticides when an insecticide was found in sediment at a concentration less than the RL.

Significance in pesticide concentrations among sampling sites was determined using one-way analysis of variance. Welch's t test was used for the comparison between two sets of samples with unequal variances in the present and previous studies. The criterion of significance was defined as $p < 0.05$ in all statistical analyses.

A pesticide toxicity index for sediment (sediment-PTI) has been proposed as a quantitative indicator to evaluate the risk of sediments contaminated by multiple pesticides, and it is calculated using eq 1.[16]

$$\text{sediment-PTI} = (\text{sum-LEBQ or sum-TEBQ}) = \sum_{p=1}^{n} \left(\frac{C_p}{\text{LEB or TEB}} \right) \quad (1)$$

where C_p is the TOC-normalized concentration of a pesticide p (μg g^{-1} OC) and n is the number of detected pesticides in a sediment sample. The likely effect benchmark (LEB, μg g^{-1} OC) defines the concentration of a pesticide in sediment above which there is a high probability of adverse effects to benthic invertebrates, and the threshold effect benchmark (TEB, μg g^{-1} OC) is the concentration below which adverse effects of a pesticide are unlikely to happen. The Q in LEBQ and TEBQ stands for quotients. Thus, a LEBQ of individual or sum pesticides higher than 1 indicates the likely occurrence of adverse effects, and a TBEQ value lower than 1 indicates no adverse effect to benthic organisms.

RESULTS

A variety of insecticides were detectable in waterway sediments from the rice-planting area, and the concentrations of individual OCPs, OPs, pyrethroids, fiproles, and ABAs are shown in Tables S4–S7, respectively. As summarized in Table 1, the total insecticide concentrations varied site by site from 1.63 to 775 ng g^{-1} with mean and median values of 67.0 and 11.5 ng g^{-1}, respectively. In general, insecticide concentrations were higher in the ditches than the streams and the highest concentration of insecticides was detected in sediment D6 followed by D5 and D4 (Figure 2a).

Table 1. Detection Frequency (DF) and Concentrations (Range, Mean ± Standard Deviation (SD), Median) of Different Classes of Insecticides in Sediments Collected in Agricultural Waterways near Rice-Planting Areas in Shanghang and It Adjacent Area in South China

		sediment concentration (ng g^{-1} dry weight)		
insecticide class	DF (%)	range	mean ± SD	median
$\sum_{15}$OCP[a]	91	nd[g]–476	23.5 ± 98.8	0.40
$\sum_{9}$OP[b]	100	0.30–204	15.3 ± 42.7	2.09
$\sum_{11}$PYE[c]	100	0.47–79.1	12.4 ± 21.3	3.46
$\sum_{3}$FIP[d]	100	<RL[h]–147	11.7 ± 31.8	1.94
$\sum_{2}$ABA[e]	100	<RL–25.7	3.97 ± 7.00	0.86
$\sum_{40}$insecticide[f]	100	1.63–775	67.0 ± 165	11.5

[a]Individual concentrations of organochlorine pesticides (OCPs) are shown in Table S4. [b]Individual concentrations of organophosphate insecticides (OPs) are shown in Table S5. [c]Individual concentrations of pyrethroid insecticides are shown in Table S6. [d]Individual concentrations of fipronil and its metabolites (fiproles) are shown in Table S7. [e]Individual concentrations of abamectin and emamectin benzoate (ABAs) are shown in Table S7. [f]The sum concentrations OCPs, OPs, pyrethroids, fiproles, and ABAs. [g]Not detected. [h]Less than the reporting limit.

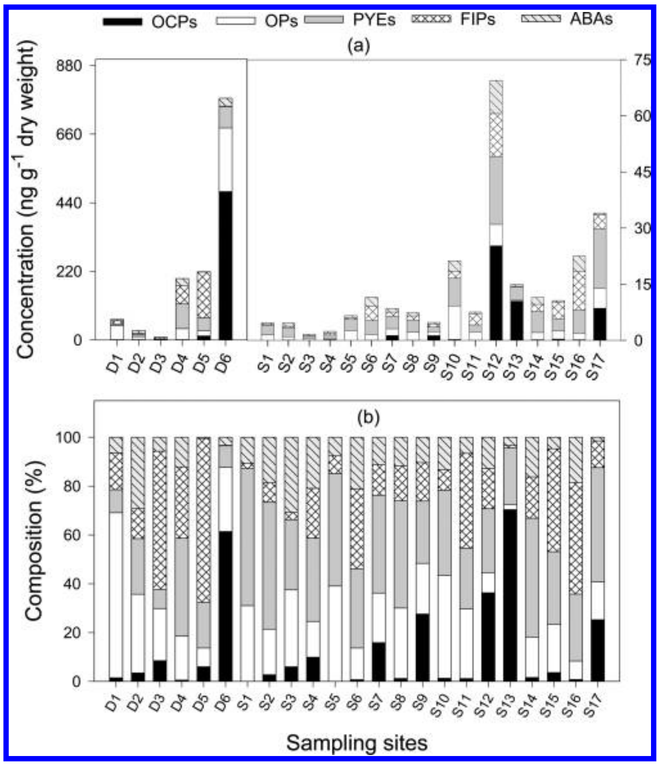

Figure 2. Concentrations (a) and compositions (%, b) of individual classes of insecticides in sediment samples collected from rice-planting areas in Shanghang and it adjacent area in South China. OCPs, OPs, PYEs, FIPs, and ABAs are acronyms of organochlorine pesticides, organophosphate pesticides, pyrethroids, fiproles, and abamectin and emamectin benzoate, respectively.

The composition of individual classes of insecticides varied significantly among sites (Figure 2b). Pyrethroids were the most dominant insecticides in 39% of the sediment samples and accounted for 31.7% of the total insecticide abundance on average, followed by OPs (23.0%), which were the most abundant insecticides in four sediments (D1, D2, S3, and S10). Occasionally, OCPs and fiproles had sediment concentrations greater than pyrethroids and OPs in some sites, contributing 12.5 and 20.8% to the sum insecticide concentrations, respectively. The average contribution of ABAs to the sum insecticide abundance (12.0%) was similar to OCPs, but they never dominated insecticide composition in any sediment. Individual insecticides within the same class also showed distinct composition pattern among sediments, and the occurrence and composition of individual classes of insecticides are discussed below by chemical class.

OCPs. As shown in Table S4, sediment concentrations of Σ_{15}OCP were from not detected (nd) to 476 ng g^{-1}, with the highest one at site D6. Fewer than three OCPs were detected in a single sediment except for S13, which contained six OCPs. The majority of OCPs were detected in fewer than 4 of the 23 sediments, whereas α-chlordane and p,p'-DDE were detectable in 10 and 18 sediments, respectively. Sediment concentrations of α-chlordane were all less than the RL, and p,p'-DDE was quantified in 14 sediments at concentrations greater than the RL (0.13–3.19 ng g^{-1}, Table S4).

As the most abundant OCP, p,p'-DDE contributed to approximately half of Σ_{15}OCP. Comparatively, its parent insecticide p,p'-DDT was not often detected. Interestingly, as long as p,p'-DDT was found in sediment, its concentrations

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(23.7, 2.06, 3.71, and 421 ng g^{-1} in S12, S13, S17, and D6, respectively) were much higher than those of its degradation products *p,p*′-DDD (nd, 0.40, nd, and 51.5 ng g^{-1}, respectively) and *p,p*′-DDE (1.63, 0.31, 0.43, and 3.19 ng g^{-1}) (Table S4). Endosulfan and its degradation product (endosulfan sulfate) were found in only a few sediments (S13, D1, and D2) with concentrations being from less than the RL to 7.07 ng g^{-1}.

OPs. Sediment concentrations of Σ_9OP ranged from 0.30 to 204 ng g^{-1} (mean = 15.3 ng g^{-1}, median = 2.09 ng g^{-1}) (Table 1). Compared with OCPs, more OPs were detected in sediments. The target OPs were all found in at least one sediment, although the concentrations of ethion, parathion-methyl, parathion, and tebupirimfos were less than the RLs in all samples. Chlorpyrifos was the most frequently detected OP and contributed 89.4% of the abundance of Σ_9OP (Figure S1). As one of the most heavily used pesticides, chlorpyrifos was detected in all sediment samples and ranged from less than the RL to 203 ng g^{-1} with mean and median values of 15.0 and 1.95 ng g^{-1}, respectively (Table S5). The detection frequencies of other OPs were lower than that of chlorpyrifos, and only three, one, three, and four sediment samples contained diazinon (0.15−0.48 ng g^{-1}), malathion (0.68 ng g^{-1}), profenofos (0.12−3.19 ng g^{-1}), and terbufos (0.10−0.30 ng g^{-1}) at concentrations higher than the RLs.

Pyrethroids. The detection frequency of pyrethroids was high, and the concentrations of individual pyrethroids in sediment are presented in Table S6. At least four pyrethroids were found in each sediment. All 11 pyrethroids were detectable in sediment S5, with individual pyrethroids accounting for 1.65−21.1% of Σ_{11}PYE. λ-Cyhalothrin and cypermethrin were detected in all sediment samples with concentrations of 0.13−28.1 ng g^{-1} and less than the RL to 42.3 ng g^{-1}, respectively. Bifenthrin, dimefluthrin, esfenvalerate, fenpropathrin, and tetramethrin were detected in most of the samples (65.2−95.7%) with concentration ranges of nd−55.5, nd−0.10, nd−8.81, nd−1.64, and nd−0.35 ng g^{-1}, respectively. The remaining pyrethroids (allethrin, cyfluthrin, deltamethrin, and permethrin) were less often found (<35% of the samples), and their highest concentrations were 0.40, 0.38, 0.12, and 0.93 ng g^{-1}, respectively.

As shown in Figure S2, λ-cyhalothrin was detected at the highest concentration in the sediments, contributing to one-third of Σ_{11}PYE. Cypermethrin and esfenvalerate were also detected at high concentrations, accounting for 28.6 and 20.7% of Σ_{11}PYE, respectively. Overall, the three pyrethroids contributed to over three-fourths of pyrethroid abundance in >80% of samples (Figure S2). Bifenthrin contributed 6.3% to the concentrations of Σ_{11}PYE and was the most prevailing pyrethroid in sediment D6, accounting for >80% of Σ_{11}PYE at this site. The remaining pyrethroids, although detectable, were at relatively low concentrations with mean contribution to pyrethroid abundance being <6%.

Fiproles. Fipronil and its degradation products were detectable in all samples with Σ_3FIP greater than the RLs in 21 sediments (range, <RL−147 ng g^{-1}; mean, 11.7 ng g^{-1}; median, 1.94 ng g^{-1}) (Table 1). The degradation products dominated the composition of Σ_3FIP, with fipronil sulfide (<RL−23.0 ng g^{-1}) and fipronil sulfone (nd−43.6 ng g^{-1}) being detected at 100 and 91% of sediment samples, respectively. Fipronil sulfone was the most prevalent fiprole from agricultural waterways in Shanghang and it adjacent area, accounting for 57.0% of Σ_3FIP concentrations, and the contribution of fipronil sulfide was 38.6% (Figure S3). Although fipronil was rarely detected in sediments, it was found at an exceptionally high concentration in sediment D5 (121 ng g^{-1}) (Table S7).

ABAs. Abamectin and emamectin benzoate were found in all samples, with their concentrations higher than the RLs in 12 and 4 sediment samples, respectively (Table S7). The highest concentrations for both compounds were detected in sediment D6. Sediment concentrations of abamectin were generally higher than those of emamectin benzoate, ranging from <RL to 19.7 ng g^{-1} and from <RL to 12.7 ng g^{-1}, respectively.

■ DISCUSSION

Occurrence and Composition of Insecticides in Sediment. Legacy and current-use insecticides co-occurred in sediments collected from rice-planting areas in Shanghang and it adjacent area (Figure 2 and Tables S4−S7). Comparatively, sediment concentrations of legacy OCPs were lower than CUPs, and *p,p*′-DDE predominated OCP composition. This is reasonable because most OCPs were banned for use in China decades ago, and sediment residues of *p,p*′-DDE were mainly due to historical use of *p,p*′-DDT.[17] Surprisingly, high concentrations of *p,p*′-DDT were detected in several sediments (S12, S13, S17, and D5) with the ratios of (*p,p*′-DDD + *p,p*′-DDE)/*p,p*′-DDT being <1 (0.07−0.34), which indicated possible fresh input of DDT near these sites.[18] The use of dicofol may be one of the reasons for the release of DDT into the environment as a byproduct.[19] Although endosulfan is still in use in China, it was seldom detected in the present study. Restriction on the use of endosulfan has been initiated in 2011 and is proposed to be forbidden in 2019,[20] which probably explains the low detection frequency and residues of endosulfan and its degradation product in the studied area. The significant decrease of endosulfan and its degradation products in a sediment core since 2012[9] supported the conclusion.

Current-use insecticides, for example, OPs, pyrethroids, fiproles, and ABAs, gradually replaced legacy OCPs for agricultural use, as demonstrated by temporal profiles of insecticides in sediment core samples.[9] This explained the finding of high levels of CUPs in agricultural waterways. Chlorpyrifos was the most abundant OP in sediments, in accordance with previous studies in the Pearl River Delta,[12,13] Chao Lake,[15] and Tai Lake in China[21,22] and the Sarno River in Italy.[23] High levels of chlorpyrifos residues in sediment were reasonable for its intensive use for rice-planting practice[24] and relatively higher hydrophobicity (log K_{ow} = 5.11) than other OPs, such as parathion (log K_{ow} = 2.15) and malathion (log K_{ow} = 2.89).[25]

Although the use of pyrethroids for rice production was restricted in 2001 in China, they were detected in all sediment samples. Sun et al.[9] analyzed a sediment core sample collected from the study area and found that pyrethroid concentrations increased over time since the 1970s until reaching a peak concentration of 1631 ng g^{-1} in 2002. The total concentration of pyrethroids in surface sediment collected in 2012 was 98 ng g^{-1},[9] and it was similar to the highest concentration of Σ_{11}PYE in the present study (79.1 ng g^{-1}).

As shown in Figure S2, λ-cyhalothrin was the most frequently detected pyrethroid with the greatest concentration among pyrethroids, similar to the finding by Sun et al.[9] In addition, cypermethrin and esfenvalerate were also frequently detected. This was consistent with the fact that λ-cyhalothrin was one of the most commonly used pesticides for rice-planting practice in

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China,[24] and cypermethrin and esfenvalerate were widely used in agriculture as well.[5,26] Comparatively, the composition pattern of individual pyrethroids in sediments from the agricultural area was different from that in urban areas of the Pearl River Delta[12] and Guangzhou, South China,[13] in which cypermethrin prevailed. In addition, pyrethroid composition in agricultural areas was more diverse than that in urban areas; for example, sediment S5 contained all target pyrethroids analyzed in the current study (Figure S2). Although pyrethroids were restricted to use in rice-planting practice, the illegal sale of pyrethroids in local retail stores was noted in the study area. In addition, application of various pyrethroids in cycle for mosquito control has been recommended to reduce pesticide resistance.[27−29] Frequent detections of multiple pyrethroids in sediments from agricultural areas may be the result of using different pyrethroids. The increasing use of insecticide mixtures in recent years was also reported by Sun et al.[9]

Agricultural use of fipronil was prohibited in China in 2009, but fiproles were detectable in all sediments (Table S7). The mean concentration of fipronil (0.04 ng g^{-1}) was much lower than those of fipronil sulfide (1.52 ng g^{-1}) and fipronil sulfone (4.00 ng g^{-1}) in all sediments with the exception of D5, suggesting significant degradation of fipronil in sediment. Fipronil sulfone was the main degradation product. This was similar to previous studies in urban streams, in which fiproles were mainly in the forms of the degradation products.[13,30,31] The reported half-lives of fipronil varied across matrices, for example, water (13.2 and 87.9 days at pH 10 and 7, respectively),[32] soil (1.5−342 days),[33−35] and sediment (anaerobic, 4.6−18.5 days; facultative, 25−91 days).[36] The pH values in paddy fields were from weakly acidic (pH 6.5)[37] to alkaline (pH 9.11),[38] and alkaline conditions may accelerate the degradation of fipronil.

Exceptionally, 121 ng g^{-1} of fipronil was detected at site D5, accounting for 82.1% of Σ_3FIP abundance. This implied the possible presence of fresh input of fipronil, which was supposed to have been banned for years. Notably, packing bags for fipronil were found near this site, which confirmed the assumption of illegal use of fipronil in agricultural areas. The continuously upward trend of Σ_3FIP concentrations in sediment core samples was another piece of evidence for the likely illegal use of fipronil in agricultural areas in China after 2009.[9]

Little information is available for the environmental occurrence of ABAs, although they have been extensively used in rice production in China.[24] The concentration of abamectin in the present study was significantly higher than those in the agricultural region of California's Central Valley in the United States (nd−0.5 ng g^{-1}),[39] but lower than those in urban waterways of Guangzhou, China (nd−45.5 ng g^{-1}).[13] Higher sediment concentrations of abamectin in China were possibly related to its greater consumption in China than in the United States. Worldwide, abamectin was mainly produced in China, and most abamectin was for domestic usage; for example, approximately 3500 tons of technical ingredients was produced in China in 2014, and only 538 tons were for exportation.[40]

As one of the most commonly used pesticides in China,[8] emamectin benzoate was detected in sediments at concentrations from less than the RL to 12.7 ng g^{-1}. To our knowledge, no other data of sediment-bound emamectin benzoate in agricultural areas are available. Emamectin benzoate was used not only in agricultural practice[24] but also in fin fish aquaculture to control parasitic sea lice[41] and was highly toxic to crustaceans.[42] Lalonde et al.[43] found elevated concentrations of emamectin benzoate in sediments from aquaculture facilities in Atlantic Canada (<10−2500 ng g^{-1}), suggesting that this insecticide could deposit to sediment and post a threat to sediment-dwelling crustaceans.

Overall, legacy and current-use insecticides were ubiquitous in sediment samples from rice-planting areas in Shanghang and it adjacent area (Tables 1 and S4−S7). Pyrethroids dominated insecticide composition, accounting for 32% of the total insecticide concentrations, followed by OPs (23%), fiproles (21%), ABAs (12%), and OCPs (12%). The frequent detections of pyrethroids and fiproles, which were restricted for use in rice-planting practice, revealed that illegal use of these insecticides in agricultural areas in China was possibly common, calling for better measures of pesticide control.

Ecological Risk of Insecticides in Sediment. To date, little information is available on the ecological risk of sediment-bound insecticides in agricultural areas in China, particularly the risk of agricultural CUPs.[11] To assess the risk of insecticide residues to nontarget benthic organisms, sediment-PTI was calculated following a method reported by Nowell et al.,[16] and the values for individual insecticides that had LEBQ and TEBQ values >0.01 in at least one sample are provided in Tables S8 and S9, respectively. The sum-LEBQ of all insecticides was >1.0 for 16 of the 23 sediments (69.6%) (Table S8), and the sum-TEBQ was >1.0 for all sediment samples (Table S9). The results demonstrated that sediment-bound insecticides due to rice-planting practice posed a significant risk to benthic invertebrates in adjacent waterways. This provided an additional piece of evidence from Asian developing countries to validate the statement by Stehle and Schulz[2] that insecticides for agricultural use have threatened the freshwater ecosystem at a global scale in a review on pesticide residues in aquatic environment, mainly in Europe and North American.

The contribution of individual insecticides to sediment risk varied greatly. The sum-LEBQ and sum-TEBQ of Σ_{15}OCP were all <1.0 except for sum-TEBQ in sediment S13 (7.02), which contained a high level of α-endosulfan. This showed that the toxicity contribution from OCPs to benthic invertebrates was low at most sites. However, their ecological effects should not be overlooked because most OCPs are bioaccumulative and possibly cause endocrine disruption effects and reproductive dysfunction.[44]

The ecological risk from OPs to benthic invertebrates was mainly focused on the ditches, which were close to rice fields (Tables S8 and S9). The sum-LEBQ of Σ_9OP was 2.83 in site D6, with chlorpyrifos concentration exceeding its LEB value. When TEB was used as threshold, five of the six ditch sites had sum-TEBQ > 1.0 for Σ_9OP, with the maximum value of 28.5 at D6. Chlorpyrifos, again, was the only OP exceeding the TEB value. In stream sediments, sum-TEBQ values for Σ_9OP ranged from 0.02 to 0.93. This suggested that the application of OPs in rice fields posed considerable risk to benthic organisms in nearby water bodies, but the adverse effects attenuated in the streams far from the field.

Comparatively, sediment risk was high from pyrethroids and fiproles, which were supposed to have been banned for use of rice production but ubiquitous in sediments from rice-planting areas. The sum-LEBQ of Σ_{11}PYE was >1.0 in 8 of 23 samples (34.8%), and 21 sediments had a sum-TEBQ > 1.0, with the concentrations of bifenthrin, λ-cyhalothrin, cypermethrin, and esfenvalerate exceeding their respective LEB and TEB values in

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some sites. The risk from pyrethroids in this area was greater than the observation by Nowell et al.,[16] who found the sum-LEBQ and sum-TEBQ were >1.0 in only 1.5% of samples in the U.S. Midwest, with bifenthrin and cypermethrin exceeding their respective LEB and TEB values. The sum-LEBQ and sum-TEBQ of fiproles were >1.0 in 5 and 19 sediment samples, with maximum values of 134 and 1360 at site D5, respectively, indicating significant risk (Tables S8 and S9). Because the degradation products of fipronil had toxicities similar to that of the parent compound,[16] degradation of this insecticide in sediment showed no help in reducing its ecological risk. Moreover, abamectin concentrations also exceeded LEB and TEB values in 6 and 17 sediment samples, respectively.

Pyrethroids contributed the most to sediment-PTI, accounting for 41 and 40% of LEBQ and TEBQ, respectively, followed by the fiproles (29 and 30%, respectively) and abamectin (23 and 24%, respectively), yet OCPs and OPs played little role in sediment-PTI (<5%) (Figure 3). According to the LEBQ and

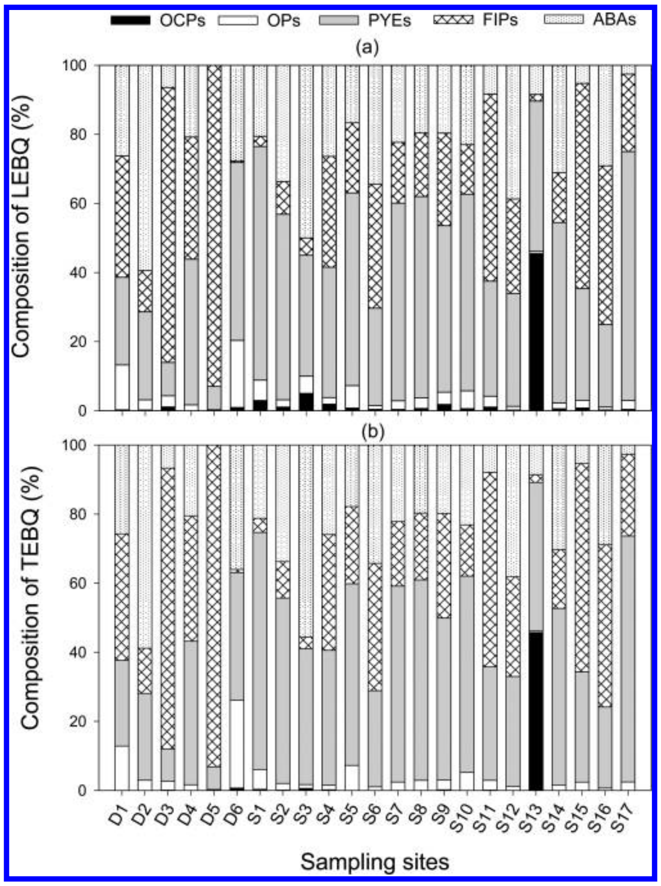

Figure 3. Composition (%) of the quotients of likely effect benchmark (LEBQ) (a) and the quotients of threshold effect benchmark (TEBQ) (b) of individual classes of insecticides in sediment samples from rice-planting areas in Shanghang and it adjacent area in South China. OCPs, OPs, PYEs, FIPs, and ABAs are acronyms of organochlorine pesticides, organophosphate pesticides, pyrethroids, fiproles, and abamectin and emamectin benzoate, respectively.

TEBQ values, pesticide risk could be classified as a likelihood of high, intermediate, or low.[16] In the study area, pyrethroids, fiproles, and abamectin posed intermediate risk to benthic species in most of the sites and high risk in one-third of the samples. Conversely, OCPs had an unlikely effect except for endosulfan in one sediment, and OPs were intermediately risky in the ditches but not in the streams (Tables S8 and S9). Similarly, pyrethroids and fiproles were identified as key sediment-associated toxicants in urban waterways in China[13,45] and the United States,[46,47] as well as agricultural watersheds in the United States[46,48−50] and Argentina.[51,52] The present study revealed that pyrethroids and fipronil were likely illegally used in rice-planting areas in China and caused severe ecological risks in agricultural waterways. The use of pyrethroids and fipronil in paddy field was restricted years ago, but the occurrence and risk of pyrethroids and fiproles in agricultural waterways were still high. To reduce insecticide application, it is vital to enforce the law and train farmers.[6]

Regional Difference of Insecticides in Sediment. To better understand the impact of application patterns of insecticides on the distribution of sediment-bound insecticides in agricultural and urban regions, insecticide occurrence in the present study was compared with previous studies in China that were published from 2007 to 2016 and had detailed pesticide concentrations. Most of the studies were about OCPs (28 publications, Table S10), followed by pyrethroids (10, Table S11), OPs (8, Table S12), and fiproles (3, Table S13). Sediment concentrations of abamectin were reported only for an urban creek in Guangzhou;[13] thus, they were not included in the comparison. According to their locations, the sampling sites were classified into three categories, namely, agricultural, mix-land, and urban regions (Tables S10−S13).

The concentrations of individual class of insecticides (OCPs, OPs, pyrethroids, and fiproles) in agricultural, mix-land, and urban regions in China are summarized in Figure 4. The

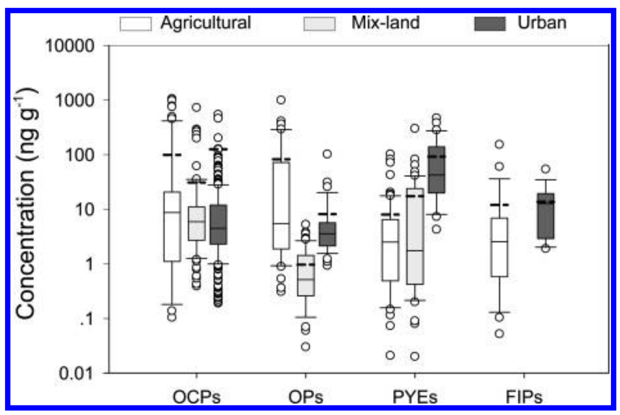

Figure 4. Concentrations of individual classes of pesticides (ng g^{-1} dry weight) in sediment samples collected from agricultural, mix-land, and urban regions in China. OCPs, OPs, PYEs, and FIPs are acronyms of organochlorine pesticides, organophosphate pesticides, pyrethroids, and fiproles, respectively. Error bars adjacent to the bottom and upper parts of each box stand for the 10th and 90th percentiles, respectively, and horizontal lines from the bottom to the top of each box stand for the 25th, 50th, and 75th percentiles. The dotted lines represent mean concentrations. Data used in the statistical analysis are from the current study and previous studies, and detailed information on the data is presented in Tables S10−S13.

concentrations of OCPs showed no difference among regions (p > 0.05). This would be explained by the rapid transition from agricultural to urban land in China over the past three decades. Liu et al.[53] pointed out that increasing construction land was the major reason for decreasing agricultural areas, and conversion to construction land accounted for 46 and 55% of reduction of agricultural land in 1990−2000 and 2000−2010, respectively. Therefore, there was no clear relationship between

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land-use type and the occurrence of legacy OCPs, which were historically used before the transition of the land-use pattern.[12]

The land-use pattern affected the distribution of CUPs in sediment. Sediment concentrations of OPs in agricultural areas were significantly higher than those in mix-land and urban regions ($p < 0.05$). Several OPs with high mammalian toxicity were phased out in 2007,[9] but OPs still dominated the insecticide market in China and accounted for 64.8% of total insecticide demand in 2015.[24] Specifically, chlorpyrifos, phoxim, and diazinon were on the list of the 10 most commonly used insecticides for crop planting in China (phoxim, chlorpyrifos, abamectin, emamectin benzoate, λ-cyhalothrin, imidacloprid, isoprocarb, cypermethrin, diazinon, and *Bacillus thuringiensis*).[24] Accordingly, agricultural use of OPs in large quantities resulted in their higher residues in agricultural areas than in urban areas.

On the contrary, significantly higher concentrations of pyrethroids were present in urban regions, followed by mix-land and agricultural regions ($p < 0.05$). A similar trend was noted globally for pyrethroids, which have been intensively used for urban landscape maintenance and sanitary purposes.[5] The concentrations of fiproles in urban areas were slightly higher than those in the agricultural region, but their mean concentrations were comparable ($p > 0.05$). As discussed above, agricultural use of fipronil has been restricted in China since 2009, and its use is only in urban areas for sanitary purposes.[9] The similar concentrations of fiproles in agricultural and urban areas in China supported the finding of illegal use of fipronil in agriculture.

Overall, legacy and current-use insecticides were ubiquitous in agricultural waterways in the vicinity of a typical rice-planting region in South China, with pyrethroids as the most dominant insecticides in sediment, followed by OPs, fiproles, ABAs, and OCPs. Sediment-PTI values showed that pyrethroids, fiproles, and abamectin in sediment posed significant risk to benthic invertebrates in one-third of the samples in the study area. Discrepant distribution patterns of OPs and pyrethroids in sediment in urban and agricultural areas were in accordance with their application preferences, whereas the rapid transition of land-use pattern over the past three decades explained that there was no distribution difference of legacy OCPs among sites. In addition, likely illegal use of fipronil in agriculture caused its concentrations in agricultural areas to be higher than expected.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.7b00620.

> Details of chemicals and reagents and procedures of chemical analysis; tables listing sediment concentrations of individual insecticides in the present study and previous studies; figures showing compositions of individual OPs, pyrethroids, and fiproles (PDF)

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Notes

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