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Occurrence and risk assessment of current-use pesticides in a tropical drinking water source reservoir in Hainan Province, China†

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The agricultural sector plays a pivotal role in Hainan Province, China; therefore, the utilization of pesticides is indispensable. The current ban on traditional pesticides and ongoing replacement of current-use pesticides (CUPs) have not been accompanied by extensive research on the presence of CUPs in reservoirs, which are vital centralized sources of drinking water. In this study, 26 CUPs was investigated in a drinking water source reservoir, the surrounding watershed, and the surrounding agricultural and domestic discharge water in Hainan Province. The predominant detected CUPs in the study area were clothianidin (CLO), thiamethoxam (THM), acetamiprid (ACE), imidacloprid (IMI), and dichlorvos (DCH). Neonicotinoids (NNIs) were the primary type of pesticide contamination in the study area, with a concentration ranging from not detected (n.d.) to 755 ng L^{-1} (median of 71.0 ng L^{-1}). The upstream watersheds of the reservoir were primarily contaminated due to agricultural activities, and the highest concentration of individual CUPs, ranging from 102 to 821 ng L^{-1} (median of 468 ng L^{-1}), was found in agricultural source water. Source identification analysis revealed that the presence of CUPs in the reservoir primarily stemmed from three types of activities: the cultivation of fruit trees around the reservoir, the daily activities of residents, and the agricultural practices in the upstream watershed basin. Risk assessment indicated that DCH, IMI, and THM posed moderate or high risks to aquatic organisms, with an emphasis on the effects of NNIs. The chronic cumulative risk assessment of NNIs was conducted by the relative potency factor approach, and it indicated that infants and young children were the most vulnerable groups and exhibited heightened susceptibility. The potential exposure to NNIs through drinking water was below the recommended relative chronic reference dose, thereby posing no discernible health risks. The results of this study will support the regulation of CUPs in drinking water sources.

Environmental significance

A comprehensive investigation was conducted to assess the occurrence of 26 current-use pesticides (CUPs) in a drinking water source reservoir, its surrounding watershed, as well as the discharged agricultural and domestic wastewater within Hainan Province. Results revealed that contamination primarily originated from agricultural activities within upstream watersheds, with significantly higher concentrations of individual CUPs detected in agricultural source water. The entry pathways for these CUPs into the reservoir were identified as fruit tree cultivation near the reservoir area, daily human activities, and agriculture practices within the upstream watershed basin. These findings offer valuable insights for formulating effective regulatory measures aimed at managing CUP contamination risks associated with drinking water sources.

1. Introduction

Hainan Province, located in the tropics of China, has abundant agricultural resources that constitute a vital sector of its economy. Moreover, the prevalence of pests, diseases, and weeds in tropical regions necessitates the high usage of pesticides in this province.[1] However, the majority of the used pesticides do not target crops, instead, they persist in various environmental media and are commonly detectable in soil[2–4] and surface waters.[5–7] Pesticide residues can be introduced into rivers and reservoirs *via* the upstream precipitation and

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agricultural practices.[8,9] Therefore, pesticide residues in drinking water sources can pose a significant threat to the ecosystem, necessitating urgent attention and action.

Based on their properties, pesticides can be classified into several major groups, including organochlorine pesticides (OCPs), organophosphorus pesticides (OPPs), and the recently prominent neonicotinoid pesticides (NNIs).[10] Most OCPs are categorized as persistent organic pollutants (POPs) and are prohibited globally because of their high toxicity.[11] However, certain OCPs, such as aldrin, are still used in China.[12] Subsequent studies have demonstrated the detrimental impacts of OPPs on both human and animal health, leading to the prohibition of certain OPPs in agricultural practices.[12,13] Therefore, in recent years, the traditional pesticides characterized by high toxicity and persistence have been widely replaced by low-toxicity alternatives such as neonicotinoids.[14] Currently, NNIs occupy nearly a quarter of the insecticide market and have experienced continuous sales growth in recent years.[15] Research has shown that NNI exposure poses a threat to aquatic biodiversity,[16] and the potential human health risks associated with NNI contamination have recently garnered remarkable attention.

Drinking water sources play a vital role in the regional water environment, as they serve as the crucial resources for urban water supply.[17] The formation of reservoirs through surface runoff can lead to the pollutant accumulation, transforming drinking water sources into the potential pesticide repositories[18] and thereby causing harm to plants, animals, and humans. The studies of pesticides in large-scale drinking water sources, have primarily focused on the impacts of traditional pesticide pollutants.[9,19] However, few studies have examined the effects of multiple conventional and alternative pesticides on drinking water sources.[20]

A previous study indicated that the contamination of the Tighra reservoir in India was dominantly attributed to the utilization of pesticides in nearby agricultural fields.[21] Human activities have significantly influenced the environment, as evidenced by the elevated levels of OCPs observed in the upstream area of the Miyun Reservoir, which is predominantly characterized by cornfields and orchards.[3] Furthermore, herbicides have been found to pose a serve threat to the aquatic organisms in the tributaries and the reservoir itself.[22] Additionally, NNIs are extensively used pesticides, and their presence in the rivers and lakes in recent years has been the focus of various studies.[23,24] However, research on their presence in drinking water sources are limited.[25–27]

The upstream or vicinity of the drinking water source reservoir in Hainan Province is commonly characterized by frequent agricultural production activities. Furthermore, given the previous studies of the pesticide contamination in the drinking water sources primarily focused on individual traditional pesticides,[19] necessitate imminent investigation into multiple pesticides. High annual precipitation in the region facilitates the migration of pesticides from the terrestrial environment to the aquatic ecosystems, and their accumulation in the reservoirs. Therefore, it is imperative to deepen the understanding of the pollution characteristics and the potential risks associated with multiple pesticides in the drinking water sources.[28]

The aim of this study was to investigate the abundance, composition, and spatial distribution of multiple current-use pesticides (CUPs) in a drinking water source reservoir and its surrounding agricultural sources, domestic sources, and watersheds in Hainan Province. Furthermore, the sources of CUPs in the water environment were identified, and the potential risks to aquatic ecosystems and humans from pesticide contamination were assessed in the drinking water sources. The findings of this study will contribute to a comprehensive understanding of the occurrence and fate of CUPs in drinking water sources and their surrounding aquatic environments, thereby providing a theoretical foundation for evaluating levels of CUP contamination in reservoirs.

2. Materials and methods

2.1 Study area and sample collection

The study area serves as a crucial centralized urban drinking water source reservoir in Hainan Province, China (Fig. 1), which provides a daily supply of approximately 220 000 t of water. Surface water samples were collected from the reservoirs (n = 10), the upstream rivers (n = 4), the surrounding agricultural sources (n = 6), and the domestic sources (n = 9). Surface water samples were collected in May 2023. Agricultural sources refer to the surface water in cultivation area catchments with mangoes, longans, betel nuts, and other commercial crops located in the upstream of the reservoirs, whereas domestic sources refer to the effluent from the domestic wastewater treatment plants in the residential areas around the reservoirs. In each site, 1 L of surface water was collected and stored in a brown glass bottle. Afterward, 50 mL of methanol (MeOH) was added to each sample to inhibit microbial growth. All water samples were placed in the refrigerator (4 °C) for chilling within 48 h after the collection.

2.2 Chemicals and reagents

The target CUPs include 9 NNIs, 7 OPPs, and 10 other pesticides (OthPs; herbicides, fungicides, *etc.*). Dinotefuran (DNT), acetamiprid (ACE), nitenpyram (NTP), clothianidin (CLO), thiacloprid (THA), thiamethoxam (THM), imidacloprid (IMI), imidaclothiz (IMT), flonicamid (FLO), phoxim (PXM), dichlorvos (DCH), malathion (MLT), dimethoate (DMT), trichlorfon (TCF), phorate (PHT), chlorpyrifos (CPF), atrazine (ATR), butachlor (BTC), acetochlor (ATC), metalaxyl (MLX), carbendazim (CBZ), thiophanate-methyl (TPH), pyraclostrobin (PCT), spirodiclofen (SPD), indoxacarb (IDC), and emamectin benzoate (EMB) were purchased from First Standard (China). Four isotope-labeled internal standards (ISs), namely carbendazim-d$_3$ (CBZ-d$_3$), acetamiprid-d$_3$ (ACE-d$_3$), clothianidin-d$_3$ (CLO-d$_3$), and imidacloprid-d$_3$ (IMD-d$_3$), were also purchased from First Standard (China).

All other chemicals were of HPLC grade. Detailed information is provided in the ESI† (Text S1 and Table S1).

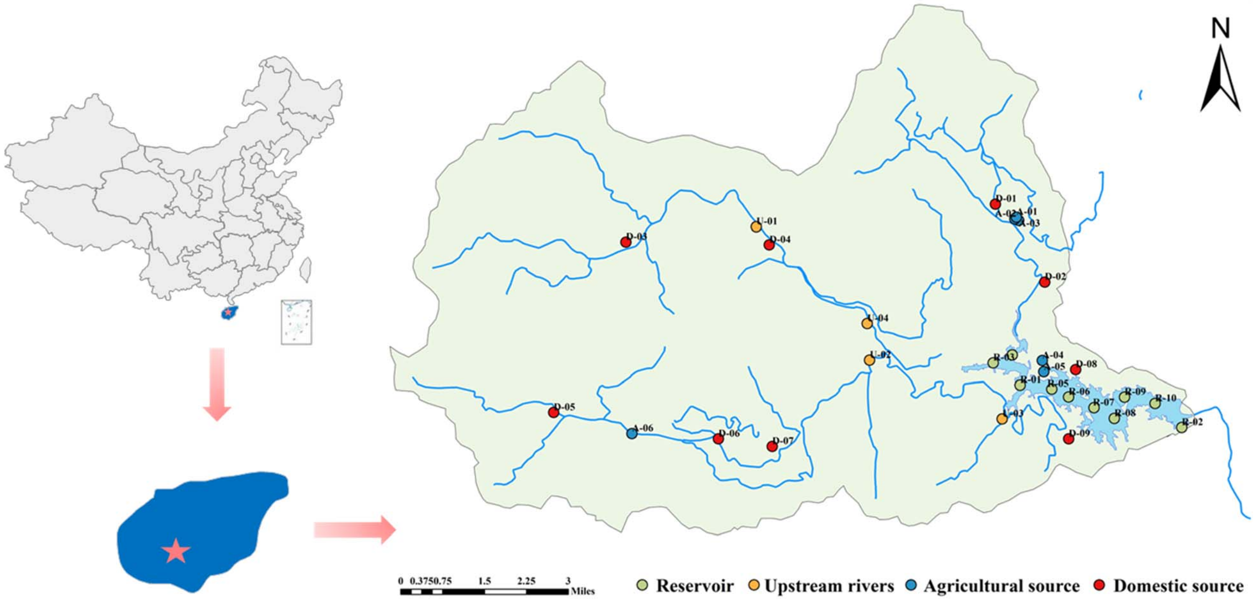

Fig. 1 Sampling sites in the study area (reservoirs, upstream watersheds, agricultural sources, and domestic sources).

2.3 Sample pre-treatment and instrumental analysis

One liter of water sample was spiked with ISs (CBZ-d_3, ACE-d_3, CLO-d_3, and IMD-d_3; 50 ng) and passed through an Oasis HLB SPE cartridge (Waters; 6 mL/500 mg). The SPE cartridge was sequentially pre-conditioned with 10 mL of MeOH, 10 mL of dichloromethane (DCM), and 10 mL of Milli-Q water. After loading the water sample, the cartridge was washed with 100 mL of 5% MeOH in Milli-Q water (v/v%). The cartridge was then subjected to vacuum drying for 1 h, followed by sequential elution of the target chemicals using 5 mL of MeOH, 4 mL of ethyl acetate (EtAC), and 3 mL of DCM. The eluates were subsequently evaporated to dryness under gentle nitrogen flow, reconstituted in 0.5 mL of MeOH, and filtered through a 0.22 μm nylon syringe filter into a glass vial.

Target chemicals were analyzed using a high-performance liquid chromatography-triple quadrupole mass spectrometer (UPLC-MS/MS; Waters, TQ-S Micro). The chromatographic and MS parameters are described in detail in the ESI† (Text S2).

2.4 Quality control and assurance

One program blank sample (replaced with Milli-Q water) was analyzed every 10 samples to assess the potential contamination, and the average levels of individual target chemicals detected in the program blanks ($n = 5$) were subtracted from the water samples. Additionally, 3 spiked blank samples were pretreated and analyzed using the same procedures as the water samples. The accuracy was calculated as the recoveries of analytes in the natural spiked samples, *i.e.*, 53.0–111.0%.

The method quantification limit (MQL) was defined as the mean value in the program blank multiplied by 3 times the standard deviation of each analyte in the program blank sample. For the analytes of not detected (n.d.) concentrations, in the program blank sample, the MQL was defined as the concentration of each analyte at a signal-to-noise ratio (S/N) of 10. The MQLs were 0.06–1.67 ng L^{-1} for target chemicals in the water samples. Details are provided in the ESI† (Table S3).

2.5 Risk assessment

The aquatic risk assessment for all detected CUPs was conducted using a risk quotient (RQ) approach, which involved comparing the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC) (eqn (1)).[29]

$$\mathrm{RQ} = \mathrm{MEC}/\mathrm{PNEC} \tag{1}$$

The no-observed-effect concentration (NOEC) values (or in their absence, EC_{50} values) were used to calculate the PNEC values. To mitigate the uncertainties associated with assessment, including accuracy, inherent variability, model errors, and insufficient toxicity data, the PNEC values were estimated by dividing the lowest NOEC or EC_{50} value of the most sensitive species by an appropriate safety factor (AF) for each trophic level—fish, algae, and aquatic invertebrates.[10] Hazard quotient data for risk assessment of the same pollutant may vary across different toxicological parameters. To avoid underestimating the existing ecological risks, we selected the lowest PNEC from the NORMAN Ecotoxicology Database as the input value, which are presented in Table S4† within this study.[30] The restrictive RQ ranking is determined as follows: a value of $0 \leq \mathrm{RQ} < 0.1$ indicates a low risk level; a value of $0.1 \leq \mathrm{RQ} < 1$ indicates a medium risk level; and an RQ value ≥ 1 indicates a high risk level.[31]

2.6 Health risks

The chronic reference dose (cRfD) of each NNI and the corresponding relative potency factor (RPF) were normalized to the

IMI,[32] as shown in Table S5.† We utilized the RPF method to assess the chronic cumulative risk of four NNIs (ACE, CLO, THM, and IMI) in the reservoir water samples.

$\mathrm{IMI}_{\mathrm{eq.}}$ was calculated as follows:

$$\begin{aligned}\mathrm{IMI}_{\mathrm{eq.}} &= \sum_i \mathrm{NNI}_i \times \mathrm{RPF}_i \\ &= \mathrm{IMI} \times 1 + \mathrm{THM} \times 9.5 + \mathrm{ACE} \times 0.803 \\ &\quad + \mathrm{CLO} \times 5.816 + \mathrm{DNT} \times 2.85 \end{aligned} \tag{2}$$

where $\mathrm{IMI}_{\mathrm{eq.}}$ is the total IMI-equivalent NEO concentration. The pesticide residues in the study area, which serves as a crucial drinking water source for the city, pose a potential threat to human health. However, the effectiveness of conventional drinking water treatment processes is limited in terms of pesticide removal efficiency.[33] We estimated the daily intake (EDI; ng kg^{-1} bw per d) of NNI in the reservoir, as follows:

$$\mathrm{EDI} = \mathrm{IMI}_{\mathrm{eq.}} \times \mathrm{DIR} \times \mathrm{AR} \tag{3}$$

where DIR represents the daily water ingestion rate (L per kg bw per day) (Table S6†), while AR denotes the absorption rate of a human, which remains constant at 100%.[34]

2.7 Statistical analysis

The statistical analysis was conducted utilizing the SPSS software (version 22.0; SPSS Inc., Chicago, IL, USA) for the analytes with a detection frequency (DF) > 50%. The normality of all data was assessed prior to the statistical analysis; non-parametric tests were employed for data that did not exhibit a normal distribution, and to examine the correlation between the concentrations of different compounds, a significance criterion of $P < 0.05$ was applied. For the statistical analysis, the chemical concentrations below the MQL were replaced with 1/2 MQL. Principal component analysis (PCA) was performed to evaluate the potential sources of CUPs in water.

3. Results and discussion

3.1 Levels of CUPs in surface water

The DFs and concentrations of CUPs are listed in Table S7.† Among the 26 targeted chemicals, 9 NNI, 4 OPPs, and 10 OthPs were present in water samples, with concentrations of n.d.–755 ng L^{-1} (median of 71.0 ng L^{-1}), n.d.–297 ng L^{-1} (median of 3.91 ng L^{-1}), and n.d.–439 ng L^{-1} (median of 28.3 ng L^{-1}), respectively (Fig. S1†). NNIs were the primary CUPs in the study area, and their relative contribution (62.7%) was significantly higher than OthPs (27.3%) and OPPs (9.98%) (Fig. S2†).

The main NNIs in surface water samples were CLO, THM, ACE, and IMI, with DFs of 89.7%, 75.9%, 72.4%, and 65.5%, respectively (Table S7 and Fig. S3†). CLO, THM, and IMI have also been detected predominantly in groundwater in Iowa, USA[35] and the Yangtze River, China 14. In this study, DNT was detected at only one sampling site in the agricultural source (A-

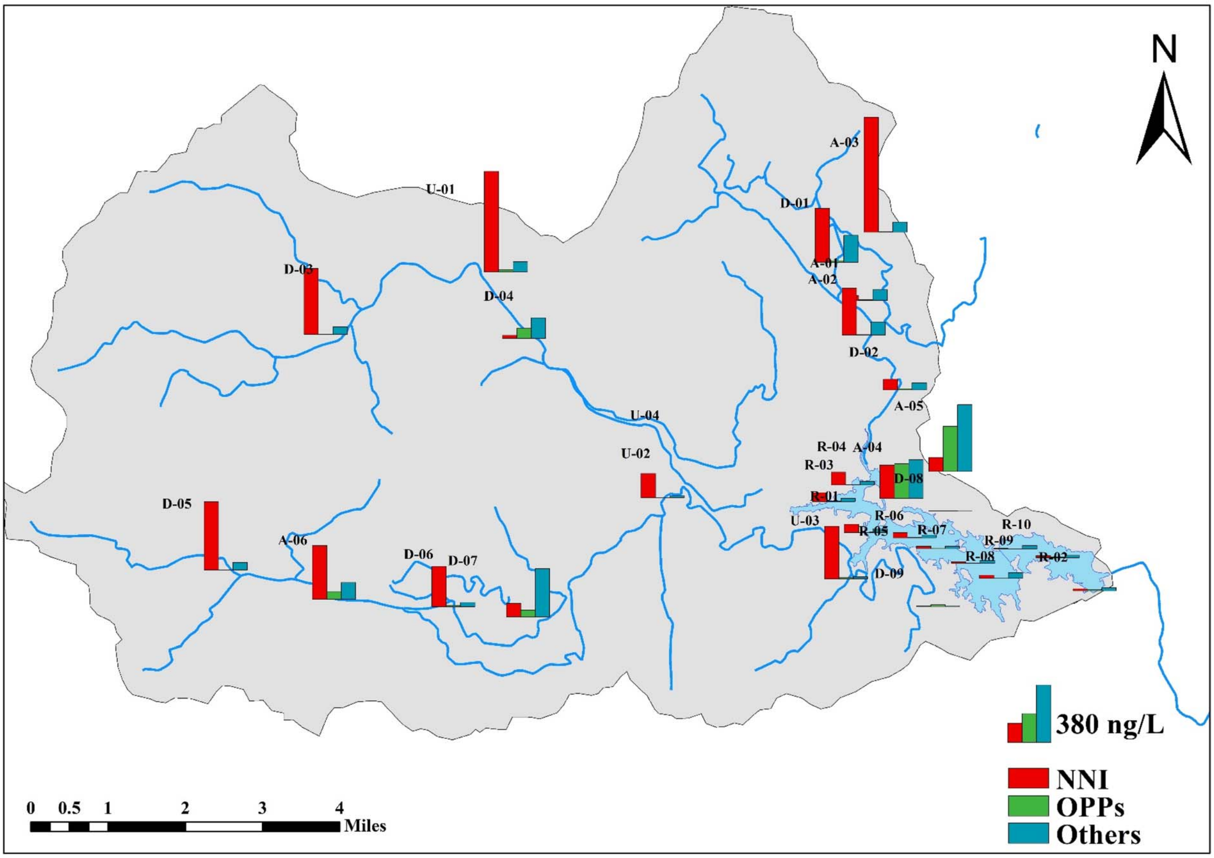

Fig. 2 Histogram of the spatial distribution of NNI, OPPs, and OthPs in the study area.

Table 1 Concentrations (ng L^{-1}) of pesticides in surface water in the reservoirs ($n = 10$), upstream watersheds ($n = 4$), agricultural sources ($n = 6$), and domestic sources ($n = 9$)

	Reservoirs				Upstream watersheds				Agricultural sources				Domestic sources			
Compounds	Range[a]	Median	Average	DF[b] (%)	Range	Median	Average	DF (%)	Range	Median	Average	DF (%)	Range	Median	Average	DF (%)
DNT	n.d.[c]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.–2.07	n.d.	0.35	0	n.d.	n.d.	n.d.	0
ACE	n.d.–0.56	0.37	0.28	60	n.d.–13.7	5.18	6.01	75	n.d.–95	9.63	22	66.7	n.d.–21.9	2.46	4.62	77.8
NTP	n.d.–n.d.	n.d.	n.d.	n.d.	n.d.–0.49	n.d.	0.12	25	n.d.–0.49	n.d.	0.08	16.7	n.d.	n.d.	n.d.	n.d.
CLO	2.7–16.2	6.93	8.12	100	n.d.–102	82.4	66.7	75	n.d.–210	69.1	80	66.7	n.d.–91.2	11.9	25.5	88.9
THA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.	n.d.–0.39	n.d.	0.043	11.1
THM	n.d.–60.3	10.8	20.3	90	n.d.–465	132	182	75	n.d.–539	15.2	144	66.7	n.d.–333	45.1	132	66.7
IMI	n.d.–6.94	n.d.	1.92	30	n.d.–96	26.1	37.1	75	n.d.–210	12.4	46.6	66.7	n.d.–92.9	17.8	25.9	88.9
IMIT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.–1.4	n.d.	0.156	11.1
FLO	n.d.–0.70	n.d.	0.193	30	n.d.–0.93	0.26	0.37	50	n.d.–2.04	n.d.	0.53	16.7	n.d.–0.54	n.d.	0.0596	11.1
$\sum_9$NNI	**3.38–84**	**17.7**	**30.8**	**100**	**n.d.–662**	**254**	**292**	**75**	**31.6–755**	**264**	**293**	**83.3**	**3.83–448**	**89.2**	**188**	**100**
PXM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
DCH	n.d.–6.05	2.41	2.42	70	n.d.–6.05	3.27	3.15	75	n.d.–286	4.17	84.1	66.7	n.d.–48.1	4.08	9.09	77.8
MLT	n.d.	n.d.	n.d.	n.d.	n.d.–0.55	n.d.	0.14	25	n.d.–16.3	0.28	4.2	66.7	n.d.–8.64	0.155	1.39	55.6
DMT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.
TCF	n.d.	n.d.	n.d.	n.d.	n.d.–4.15	1.62	1.85	50	n.d.–46.9	0.78	8.5	33.3	n.d.–6.48	n.d.	0.72	11.1
PHT	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
CPF	n.d.	n.d.	n.d.	n.d.	n.d.–3.61	0.88	1.34	50	n.d.–1.96	n.d.	0.63	33.3	n.d.–32	n.d.	5.46	33.3
$\sum_7$OPPs	**n.d.–6.05**	**2.41**	**2.42**	**70**	**n.d.–14.4**	**5.77**	**6.48**	**75**	**2.1–297**	**27.9**	**97.4**	**83.3**	**n.d.–65.4**	**7.47**	**16.7**	**77.8**
ATR	n.d.–1.39	n.d.	0.23	30	n.d.	n.d.	n.d.	0	n.d.–1.3	n.d.	0.22	16.7	n.d.–0.61	n.d.	0.068	11.1
BTC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0
ATC	n.d.	n.d.	n.d.	n.d.	n.d.–11.8	n.d.	2.94	25	n.d.–55.4	n.d.	9.23	16.7	n.d.–27.5	n.d.	3.06	11.1
MLX	10.2–21.1	12.9	13.8	100	n.d.–42.5	4.34	12.8	75	3.1–69.9	22.5	29.6	83.3	n.d.–36.8	6.99	12.5	88.9
CBZ	3.53–12.6	5.62	6.24	100	n.d.–6.79	5.2	4.3	75	n.d.–322	17.1	66.6	66.7	n.d.–139	8.93	32.2	77.8
TPH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.–6.14	n.d.	1.62	33.3
PCT	n.d.	n.d.	n.d.	n.d.	n.d.–7.65	1.39	2.61	75	0.177–63.7	1.78	13.5	83.3	n.d.–4.23	1.6	1.5	66.7
SPD	n.d.–2.9	1.09	1.28	50	n.d.–2.8	1.14	1.27	50	n.d.–245	12.4	51.9	66.7	n.d.–202	n.d.	37.9	33.3
IDC	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.–6.84	n.d.	0.76	11.1
EMB	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	0	n.d.–5.88	n.d.	0.653	11.1
$\sum_{10}$OthPs	**14.9–36.7**	**20.4**	**21.5**	**100**	**n.d.–68.7**	**13.5**	**23.9**	**75**	**66.4–439**	**98.1**	**171**	**83.3**	**n.d.–317**	**50.4**	**90.3**	**88.9**
$\sum_{26}$CUPs	**25.7–108**	**43.6**	**52.4**	**100**	**n.d.–730**	**267**	**316**	**75**	**102–821**	**468**	**464**	**83.3**	**3.83–533**	**293**	**278**	**100**

[a] Range: minimum–maximum. [b] DF: detection frequency. [c] n.d.: not detected.

06), which could be related to the fact that DNT is mainly applied in rice cultivation.[36] In contrast, the study area does not engage in rice cultivation.

DCH was the predominant OPP in this study, with a DF of 75.9%, whereas MLT, TCF, and CPF had DFs <50% (Table S7†). The concentrations of OPPs ranged from n.d. to 297 ng L^{-1} (median of 3.91 ng L^{-1}), with the highest value was observed at the agricultural source sites, likely due to the severe contamination of utilizing DCH (Fig. S4†).

OthPs were mainly represented by the fungicides, MLX and CBZ, with DFs of 93.1% and 86.2%, respectively. MLX and CBZ concentrations were n.d.–69.9 ng L^{-1} (median of 11.4 ng L^{-1}) and n.d.–322 ng L^{-1} (median of 5.71 ng L^{-1}), respectively (Table S7 and Fig. S3†). MLX has been widely detected in previous studies[37,38] because of its stable structure and long half-life (115 d at pH 9).[39] CBZ is a common fungicide, and the high concentration of CBZ in this study may be related to its high consumption and wide range of uses. However, the concentrations of CBZ in our study area were lower than the Huangpu River, China (41.9–607.0 ng L^{-1}),[40] and higher than the Vistonis Lake, Greece (<25 ng L^{-1}).[41]

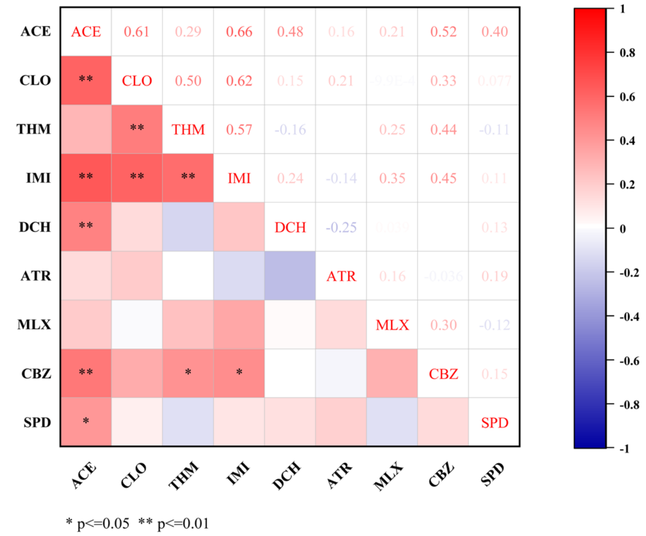

Fig. 3 Correlation between the nine predominant pesticides detected in water (** Correlation (Corr.) is significant at the 0.01 level (2-tailed). * Corr. is significant at the 0.05 level).

3.2 Spatial distribution and source identification

3.2.1 Spatial distribution. As shown in Fig. 2, all types of sampling sites in the upstream of the reservoir were generally contaminated with CUPs. Pesticide levels were usually low at the sampling sites in the reservoir, with $\sum$CUPs of 25.7–108.0 ng L^{-1} (median of 43.6 ng L^{-1}) (Table 1 and Fig. 2). $\sum$CUPs showed the highest concentrations (102–821 ng L^{-1}; median of 468 ng L^{-1}) in the surface runoff of the agricultural source sites (Table 1). The detection of numerous compounds from diverse categories primarily occurred at the agricultural source sites in relation to the pesticide contamination—especially at sites A-04 (mango cultivation) and A-05 (longan cultivation). This phenomenon can be attributed to the cultivation practices of fruit crops, and the specific pesticides employed during different periods,[42] and the persistent historical use of pesticides at this particular site. Previous studies have demonstrated that the primary pathway for the non-point emissions from pesticide land use is the surface runoff into streams.[15,43] Therefore, it is crucial to prioritize regulating pesticide use in the agricultural developments near the watersheds.

NNIs were widely detected in the agricultural sources. The highest value, 755 ng L^{-1}, was found at the agricultural source at site A-03 (Table 1). This site is part of the rice–vegetable crop rotation, where NNIs are commonly utilized, and THM and CLO are the dominant chemicals. Additionally, A-02 is mainly planted with betel nuts, and the NNI concentration there was 310 ng L^{-1}. This suggested that these neonicotinoids from the agricultural sources in the study area may have contaminated the surface water through the surface runoff (Fig. 1).

Among the upstream section sites, NNIs were absent only at site U-04, which is located downstream of site U-01. It is likely that the degradation of NNIs occurred during the discharge process downstream,[44] resulting in the absence of NNI at this particular site. However, in the other three upstream sampling sites (U-01, U-02, and U-03), $\sum$NNIs were in the range of 160–662 ng L^{-1}, with IMI, THM, and CLO being the predominantly chemicals (Fig. 3). Similarly, these CUPs were also the main NNIs in the domestic and the agricultural sources (Table 1). It has been shown that the activities in agricultural and urban areas are the primary sources of NNIs in the water environment.[45] The NNI pollution in the watersheds in this study should also be closely related to human activities.

OPPs were mainly found at the sampling sites A-04 (mango cultivation) and A-05 (longan cultivation), with DCH being the predominant chemical (Fig. 4). According to the latest report from the China Pesticide Information Network, despite being classified as a group 2B carcinogen by the World Health Organization in 2017 (**http://www.chinapesticide.org.cn**), DCH continues to be utilized in China because of its effective insecticidal properties, prompt decomposition rate, and relatively brief residual duration. Of the 7 OPPs, only DCH was detected in the reservoirs, albeit at a low concentration (n.d.–6.05 ng L^{-1}; mean of 2.42 ng L^{-1})—lower than the average level (17.8 ng L^{-1}) in surface water of China in a previous study.[46]

The most prominent sites for OthP concentrations, namely sites A-04 (254 ng L^{-1}), A-05 (439 ng L^{-1}), and site D-07 (317 ng L^{-1}) for the domestic sources, were included in the dataset (Fig. 2). This could be attributed to the transition of agricultural cultivation within the residential areas of this locality, as indicated by the increase of vegetable acreage in recent years (Fig. 2). The OthPs at site D-07 were mainly SPD and MLX.

The limited presence of CUPs in the reservoir sites may be attributed to the transfer or the degradation of CUPs from upstream watersheds before reaching the reservoirs coupled with their dilution through the continuous confluence of the tributary streams.[47]

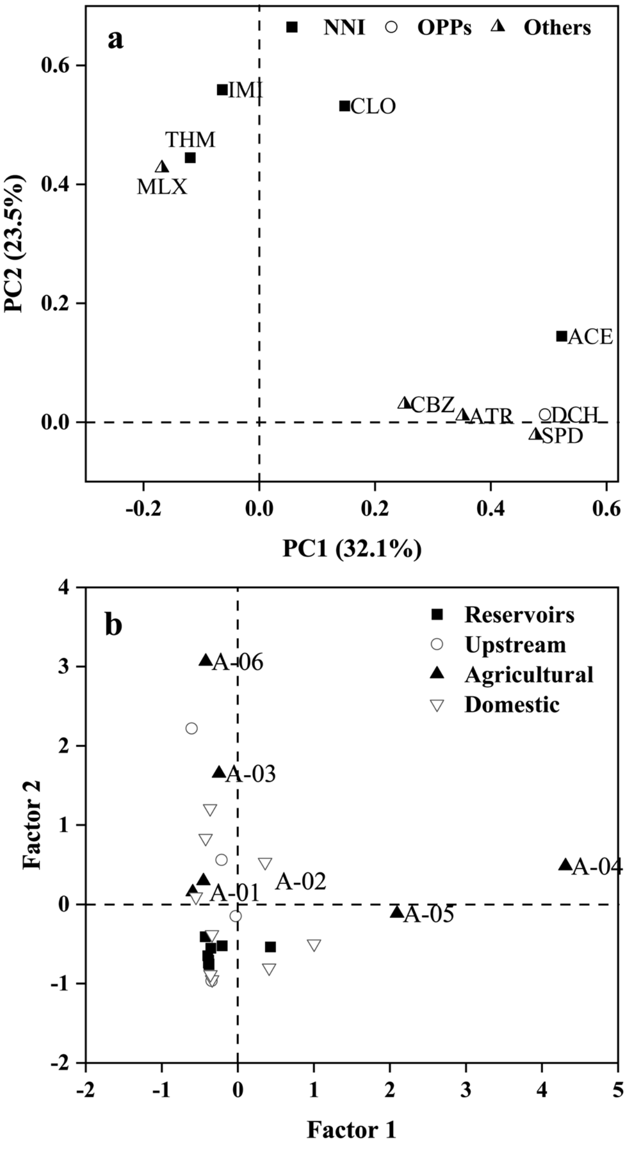

Fig. 4 Principal component analysis results based on the concentrations of NNI, OPPs, and Others (PC1, 32.1% variance; PC2, 23.5% variance). The figure legends represent the factor loadings (a) and factor scores (b).

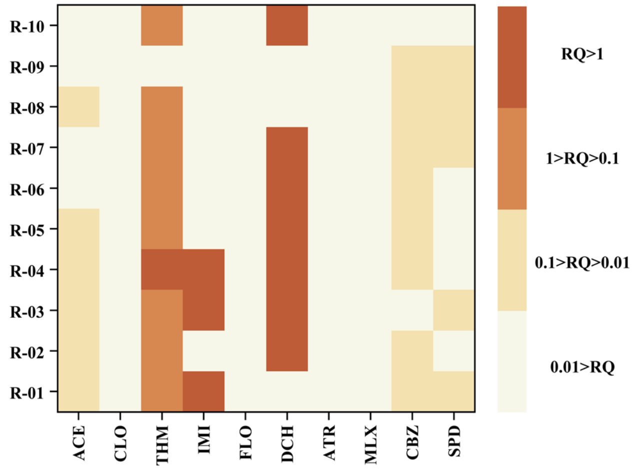

Fig. 5 Ecological risk map of pesticides detected in reservoirs, based on the calculation of RQ values in different ranges drawn, the darker the color, the greater the range in which the risk value is located, divided into four ranges corresponding to the color brother color segments, from dark to light, respectively, RQ > 1, 1>RQ > 0.1, 0.1>RQ > 0.01, 0.01>RQ.

3.2.2 PCA. The major compounds were subjected to correlation analysis and PCA to explore potential relationships between the CUPs and investigate the pollution patterns that impact different areas in this study (Fig. 4a and b).

The heatmap (Fig. 4a) demonstrated the significant positive correlations between IMI and ACE, CLO, and THM ($P < 0.01$), suggesting the potential synergistic utilization of IMI and the other three NNIs in the study area. The PCA plot showed that the first two principal components accounted for 32.1% and 23.5% of the total variance, respectively. CBZ, ATR, SPD, DCH, and ACE in the water were the main contributors to PC1, whereas IMI, THM, CLO, and MLX were the main contributors to PC2 (Fig. 5). A disparity in the origin of the two factors may exist: Factor 1 primarily comprises widely employed fungicides, herbicides, insecticides, acaricides and the only one neonicotinoid (ACE). Factor 2 comprises the common NNIs (IMI, THM, and CLO) and the MLX fungicide. The molecular structures of the compounds are closely related to K_{ow}, and the figure lists the nine molecular formulas mentioned above (Fig. S6 and S7†). Additionally, based on the scatter plot depicting the relationship between K_{ow} and MWs, the 3 NNIs in Factor 2 exhibit the lower K_{ow} values, indicating a comparatively higher solubility of these compounds in water (Fig. S7†), suggesting that these compounds may be more likely to transport from the upstream to the downstream reservoirs.

The factor score plot (Fig. 4b) indicated that the agricultural sources are distributed across both Factors 1 and 2. In contrast, Factor 1 is primarily associated with the agricultural source sites A-04 and A-05, which are near the reservoir perimeter and encompass extensive areas of fruit tree cultivation (mango and longan). Conversely, Factor 2 was closely linked to various agricultural and domestic sources, including the betel nut planting, the rubber planting, and the rice–vegetable crop rotation. Furthermore, the domestic source sites contributed to the watershed through the discharge of treated domestic wastewater. These findings demonstrated that the pesticide sources in Factor 1 were predominantly influenced by fruit tree planting around the reservoir, whereas pesticides from domestic and agricultural sources dominated Factor 2. These findings suggest that multiple factors drive pesticide pollution in the reservoir. The primary pesticide sources in drinking water reservoirs are associated with the following three types of pesticide usage: (i) the cultivation of fruit trees planted near the reservoir, (ii) the application by residents in residential areas, and (iii) the agricultural practices in the upstream watersheds. This comprehensive analysis underscores the critical need for developing targeted management strategies to address agricultural and domestic sources in order to mitigate pesticide pollution around water reservoirs.

3.3 Ecological risk assessment

The highest ecological risk posed by each pesticide was estimated based on the concentrations of individual pesticides in drinking water sources (Fig. 5). The presence of DCH in the reservoir at low concentrations posed a significant risk to aquatic organisms, as evidenced by the high-risk classification of all sites with DCH detection (RQ > 1; Fig. 5). This association was attributed to the low PNEC value of DCH ($0.0006\ \mu g\ L^{-1}$). A previous study[48] suggested that DCH in the surface waters in China posed a greater ecological risk to the aquatic organisms and may jeopardize the human health. Additionally, 30% of the sampling sites in the reservoir exhibited a high risk of IMI, and 3 of these sites were in the upstream river cross sections that had recently converged into the reservoir, highlighting the need for attention regarding pesticide convergence in the watershed areas and the effect on the aquatic organisms in drinking water sources. Similar to a previous study,[49] IMI and THM exhibited a high risk in the watershed waters in this study (Fig. 5). Certain pesticides have the potential to impact other species within the aquatic food chain by influencing plankton populations. Furthermore, these chemicals can disrupt water purification processes and diminish the self-purification capacity of water bodies through alterations in aquatic plant and microbial communities.[50] The potential impacts of NNIs on ecosystems have garnered global attention, leading to an increasing number of countries and regions implementing the restrictions on their use. Although China acknowledges the possible risks associated with NNIs, it has yet to enact specific policies banning their use. The low risk posed by CBZ and SPD at reservoir sites should also be carefully considered.

3.4 Human health exposure risk assessment

The IMI-equivalent estimated daily exposure (IMIeq EDI) of infants, toddlers, children, adolescents, and adults to NNIs from the reservoir water was calculated based on the U. S. Exposure Factors Handbook (Table S8†). The results indicated that THM has a relatively high IMIeq EDI compared to the other NNIs because of its higher concentration in water and low cRFD (0.006 mg kg^{-1} bw per d), emphasizing the need for carefully considering THM as a concerning compound. Infants consistently exhibited the highest exposure to NNIs through the drinking water across all age groups, followed by young children, which may be attributed to their higher water intake rates. Notably, all IMIeq EDIs for the exposure to drinking water were lower than the USEPA-published IMI cRFD (0.057 mg kg^{-1} bw per d), indicating no significant health risk associated with the presence of NNI in reservoirs. Nevertheless, future revisions may lead to downward adjustments in cRFDs for IMI, as studies have suggested the potential adverse effects on animals when recommended values are exceeded. The ingestion of low doses of IMI has adverse effects on the sperm and testes of rats,[51] and an *in vitro* study has shown that NNI has endocrine-disrupting effects.[52,53] Therefore, although the IMIeq EDI indicated no health risks, it is crucial to carefully consider potential risks in vulnerable populations, such as infants and young children. Infants and young children are at a higher risk of accumulating pesticide residues following exposure, owing to their underdeveloped organs and less efficient metabolism of toxic substances. Furthermore, research has demonstrated that certain pesticides may lead to developmental delays, behavioral abnormalities, or impaired cognitive function by disrupting the endocrine system or interfering with neurodevelopment.[54–56] Given the potential toxicity of these pesticides, it is imperative to establish effective management strategies within water reservoirs. This should encompass stringent regulations on pesticide usage as well as the establishment of riparian buffer zones to mitigate their adverse effects.

4. Conclusion

In summary, CUPs were frequently detected in water samples from the reservoir, upstream watersheds, and domestic and agricultural sources in Hainan, China. Notably, NNIs were the predominant CUPs, while OPPs and OthPs were present at relatively low concentrations. The upstream watersheds exhibited significant contamination by CUPs, particularly at sites with intensive agricultural activities. CUPs in the drinking water source reservoir primarily originated from pesticides used in fruit tree cultivation around the reservoir and human activities upstream. DCH, IMI, and THM posed substantial risks to the watershed ecosystem, reflecting the extensive use of NNIs in agriculture and their potential long-term impacts on water safety and ecosystems. Although the IMIeq EDI does not pose immediate health risks, its relative prominence warrants further attention to ensure public health in the region.

Data availability

Data for this article, including levels and calculations for risk assessment of CUPs, are available at figshare at **https://10.6084/m9.figshare.27614100**.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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