A review of spatiotemporal patterns of neonicotinoid insecticides in water, sediment, and soil across China

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Abstract

Neonicotinoid insecticides (NNIs) have been widely used to control insect pests, while their environmental residues and associated hazardous impacts on human and ecosystem health have attracted increasing attention worldwide. In this study, we examined the current levels and associated spatial and temporal patterns of NNIs in multiple environmental media across China. Concentrations of NNIs in surface water, sediment, and soil were in the range of 9.94-755 ng·L^{-1}, 0.07-8.30 ng·g^{-1} DW, and 0.009-356 ng·g^{-1} DW, respectively. The high levels of NNIs in surface water, such as in Yangtze River (755 ng·L^{-1}), North River (539 ng·L^{-1}), Nandu River (519 ng·L^{-1}), and Minjiang River (514 ng·L^{-1}), were dominated by imidacloprid, thiamethoxam, and acetamiprid due to their extensive use. The levels of NNIs in sediments were relatively low and the highest concentration (8.30 ng·g^{-1} DW) was observed in Dongguan Ditch. Sediment-water exchange calculated from fugacity fraction indicated that NNIs in sediment can be released back into the water due to their high solubility and low K_{OW}. Soils from agricultural zones contained the largest residual NNIs, with imidacloprid concentrations in cultivated soil reaching 119 ng·g^{-1} DW. The calculated leaching potential showed that clothianidin has the highest migration potential to deep soil or groundwater. The monitored data of NNIs presented a decreasing trend from 2016 to 2018, which might be caused by the implementation of relevant control policies for NNIs applications. The high levels of NNIs mainly occurred in southern China due to frequent agricultural activities and warm and humid meteorological conditions. Results from this study improve our understanding of the pollution levels and environmental behavior of NNIs in different environmental media across China and provide new knowledge that is needed for making future control policies for NNIs production and application.

Keywords: neonicotinoid insecticides, spatiotemporal distributions, sediment-water exchange, leaching potential

Introduction

Neonicotinoid insecticides (NNIs) were developed in the 1980s, and the first commercially available NNI, imidacloprid (IMI), was launched in the early 1990s (Kollmeyer et al. 1999). Since then NNIs, including IMI, thiamethoxam (THM), acetamiprid (ACE), clothianidin (CLO), thiacloprid (THA), dinotefuran (DNT), nitenpyram (NTP), flonicamid (FLO), and imidaclothiz (IMIT), have been widely used in crop pest control worldwide (Morrissey et al. 2015; Li et al. 2018a). NNIs can be effectively applied to control aphids, whitefly, leafhoppers, and other coleoptera pests for numerous plant species (Bass et al. 2015; Pastor-Belda et al. 2016; Li et al. 2018b). They primarily bind powerfully to nicotinic acetylcholine receptors (nAChRs) and peripheral nerves in the postsynaptic membrane of the insect nervous system, thereby blocking the conduction of the central nervous system of insects, resulting in excitability, paralysis, and ultimately death (Goulson 2013; Bonmation et al. 2015; Wu et al. 2020).

In addition, due to their high water solubility, high efficiency, and broad spectrum, NNIs have become one of the most important chemical classes of insecticides globally (Zhang et al. 2018a). To date, NNIs have been licensed for use on more than 140 types of crops in 120 countries (Simon-Delso et al. 2014; Bass et al. 2015; Mahai et al. 2019). The consumption of NNIs accounted for more than 25% of the global total insecticide sales in 2014 (Bass et al. 2015). The three broadest-spectrum NNIs, including THM (37.6%), IMI (33.5%), and CLO (14.7%), accounted for more than 85% of the total market share of NNIs in 2012 (Bass et al. 2015).

NNIs have a variety of application methods, such as foliar spraying, seed coating, and soil treatment, and the different ways in which pesticides are used affect their residue and environmental behavior. According to the report by Jeschke et al. (2011), about 60% of NNIs worldwide are used for seed coating treatment. In addition, NNIs are also used in the spray for controlling plant diseases and pests during crop growth. However, in this scenario, honey bees and other beneficial insects can be exposed to residual pesticides by gathering pollen or nectar, causing “colony collapse disorder” (Cox-Foster et al. 2007; Zhang et al. 2020a) and resulting in bee damage or death. It is certainly alarming that the pollination pathways of crops will be affected by NNIs application, which may prevent crops from normal growing (Stanley et al. 2015). Given the potential health impacts and ecological risks from NNIs usage, the European Union (EU) has completely banned the outdoor usage of IMI, THM, and CLO since 2018 (EU 2018a, 2018b, 2018c).

In fact, large fractions of NNIs applied to crops would end up in other environmental media (Pietrzak et al. 2020). For example, only 1.6% to 28% of NNIs could be directly absorbed by plants after being applied through seed treatment, and the remaining NNIs will migrate into other environmental media (e.g., air, soil, and water) (Sur and Stork 2013). Meanwhile, NNIs can accumulate in the food chain and subsequently threaten human and ecosystem health (Pastor-Belda et al. 2016; Wu et al. 2020). For example, Marfo et al. (2015) found a correlation between urinary concentrations of N-desmethyl-acetamiprid and typical symptoms such as recent memory loss, finger tremors, generalized fatigue, abdominal pain, headache, and chest pain. Due to their high solubility and low volatility, NNIs that are not utilized by plants would end up more in soil and water than air. For instance, high levels of NNIs were observed in Australian rivers with the highest concentrations of IMI, THA, and CLO being 4560, 1370, and 420 ng·L^{-1}, respectively (Sánchez-Bayo and Hyne 2014). The geometric mean of the reported average surface water NNIs concentrations from 19 studies was at 130 ng·L^{-1}, and that of the reported peak surface water NNIs concentrations from 27 studies was at 630 ng·L^{-1} during 1998-2013 (Morrissey et al. 2015).

The migration pathways of NNIs in the environment mainly include surface runoff of farmland, vertical leaching of soil, field drainage, wet and dry deposition of atmospheric NNIs originated from spraying or spray drift, volatilization during the application, and infiltration of groundwater and surface water (Bonmatin et al. 2015; Pietrzak et al. 2020). Surface runoff is likely the main process by which NNIs enter into surface water from agricultural areas, especially during extreme rainfall events. To date, studies on the fates and behavior of NNIs in the environment have been conducted in several countries, such as Canada (Xue et al. 2015; Limay-Rios et al. 2016), the U.S. (Stewart et al. 2014; Sadaria et al. 2016; Craddock et al. 2019), and Spain (Campo et al. 2013; Masiá et al. 2013). China owes 7% of the world's arable land and is the largest consumer of pesticides worldwide (Zhang et al. 2019a, 2019b; Cui et al. 2021). Several studies have focused on NNIs in different environmental media in China, e.g., in surface water (Chen et al. 2019; Mahai et al. 2019; Xiong et al. 2019), sediments (Huang et al. 2020; Wang et al. 2020a), particulate matters (Zhou et al. 2020), drinking water (Mahai et al. 2021), and soil (Zhou et al. 2018; Zhang et al. 2020b). However, none of the existing studies has systematically compared the contamination and distribution of NNIs and their environmental behavior between different media. The present study aims to fill this knowledge gap through a thorough review of the reported NNIs data in China and then identify the spatiotemporal variations of NNIs in different environmental media across the country.

Data compilation

Published NNIs data in various environmental media in China, obtained from China National Knowledge Infrastructure (http://www.cnki.net/) and Web of Science (http://apps.webofknowledge.com/) up to January 2022, were compiled in this study to characterize their occurrence and spatiotemporal patterns and to explore their fate and environmental behavior among different media. Sampling sites with available data are shown in **Fig. 1** and related sampling information is presented in **Table S1**. It should be pointed out that the spatiotemporal patterns of NNIs presented in this study were based on available data from the literature, which may not have proper spatial and/or temporal coverage. Nevertheless, knowledge generated from this dataset is expected to be useful in improving our understating of the current status of NNIs across multiple environmental media on the national scale in China.

Data analyses were performed using the SPSS (version 26.0). The total and average values of NNI concentrations were generally quoted directly from the corresponding literature, or obtained by summing the concentrations of all the detected NNIs. A zero value was used for any NNIs reported as "not detected" or "below detection limit". Kruskal-Wallis test was used to analyze the homogeneity of variance at a significance level of $p < 0.05$.

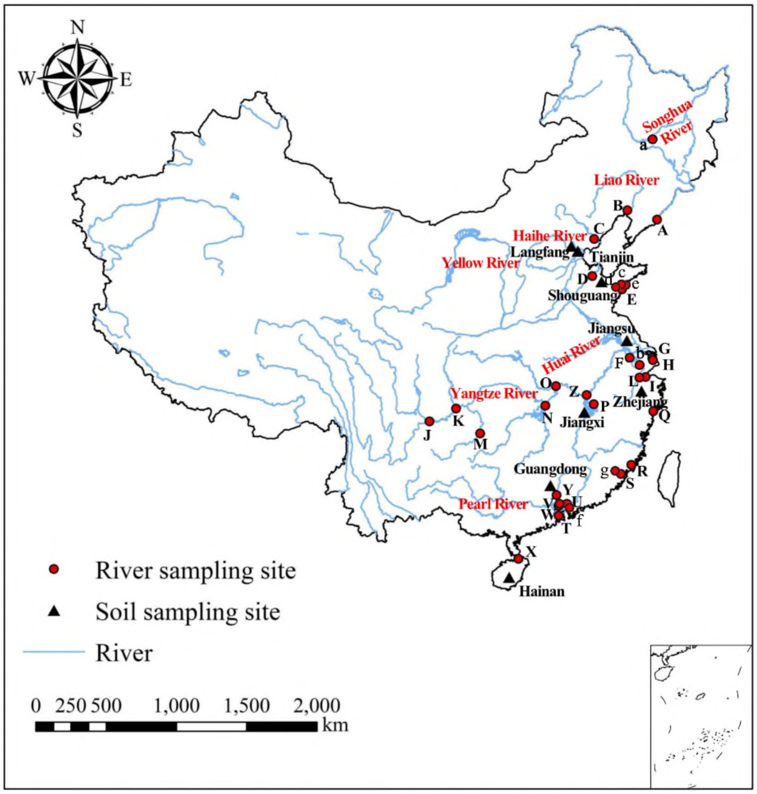

Fig. 1 Sampling sites of neonicotinoid insecticides in water, sediment, and soil in China. Labels inside the figure are sites names from available studies.

NNIs levels in the aquatic environment

Water

With the rapid development of industry and agriculture, a large number of organic pollutants enter the water environment through anthropogenic activities, causing serious water pollution problems (Ke et al. 2022; Wang et al. 2022). Generally, rivers are the most important sink areas for NNIs and other pesticides (Morrissey et al. 2015). Available measurements of NNIs concentrations in the water of China are shown in **Fig. 2**. To some extent, the results of the comparison indicate the pollution levels and the composition characteristics of NNIs, although the sampling season/duration and methods, the numbers of detected NNIs, and the analytical processes are different among these studies. Existing studies on the major rivers in China mainly focused on the rivers in South China, especially in Pearl River Basin and the Yangtze River Basin, and those on the other basins are highly scarce.

The residue of the total NNIs at all the sampling locations on water bodies ranged from 9.94 to 755 ng·L^{-1} (**Fig. 2**). A threshold value of 200 ng·L^{-1} was previously proposed for avoiding short-term acute (STA) or 35.0 ng·L^{-1} for avoiding long-term chronic (LTC) on sensitive aquatic invertebrates (Morrissey et al. 2015). NNIs concentrations in many rivers in China were close to or even higher than the STA threshold value of 200 ng·L^{-1}. For example, the highest reported concentrations in water were from Yangtze River (755 ng·L^{-1}), North River (539 ng·L^{-1}), Nandu River (519 ng·L^{-1}), Minjiang River (514 ng·L^{-1}), Liao River (283 ng·L^{-1}), Huangpu River (241 ng·L^{-1}), and West River (219 ng·L^{-1}). The average concentrations of NNIs in some other rivers were close to the STA threshold value, such as in Hanjiang River (170 ng·L^{-1}), Luan River (163 ng·L^{-1}), East River (158 ng·L^{-1}), Jiulong River (157 ng·L^{-1}), and Pearl River (148 ng·L^{-1}). Besides rivers, lakes and estuaries are also major sink areas for NNIs. Among the lakes, Dongting Lake (281

$ng\cdot L^{-1}$) is the most polluted (> 200 $ng\cdot L^{-1}$), followed by Poyang Lake (79.4 $ng\cdot L^{-1}$), and Taihu Lake (52.8 $ng\cdot L^{-1}$). Dongting Lake is a vital storage lake in the Yangtze River Basin with frequent water exchange all the time (Liu et al. 2018; Wei et al. 2019), and one of the birthplaces of conventional Chinese farming. On the whole, the total NNIs concentrations at all the sampling sites, except those in Jiaozhou Bay and the Yangtze Estuary, were higher than the LTC value of 35.0 $ng\cdot L^{-1}$, indicating potential long-term adverse impacts on non-target invertebrates in the majority of the aquatic environments in China. Overall, surface water samples are more polluted with NNIs in southern than in northern China, and thus, ecological risks from NNIs are expected to be higher in southern China.

Among the main NNIs, IMI and THM were detected at all the sampling sites in water bodies with their concentrations in the range of 0.23-216 $ng\cdot L^{-1}$ and 0.13-92.8 $ng\cdot L^{-1}$, respectively, while ACE was also observed at all sampling sites, except in Yalu River, with its concentration in the range of ND-100 $ng\cdot L^{-1}$. This is because these NNIs have long been used and they all have high water solubility (IMI: 610 $mg\cdot L^{-1}$; THM: 4100 $mg\cdot L^{-1}$; ACE: 2950 $mg\cdot L^{-1}$, **Table S2**). As reported by Tan et al. (2019), the NNIs with the most registered products in China are IMI, ACE, and THM, with the number of products being 1314, 700, and 391, respectively. The commodity, including IMI, ACE, and THM, is therefore likely to be used by planters, resulting in higher detection frequencies and residual levels at the sites studied. At several monitoring sites, however, relatively high residual concentrations were observed for NTP and DNT, with their average concentrations in the Yangtze River reaching 245 ng·L^{-1} and 408 ng·L^{-1}, respectively, indicating shifting applications from other NNIs species to NTP and DNT.

It was reported that less than 20% of NNIs applied in the agricultural sector can be absorbed by crops (Mahai et al. 2021), while the remaining portions would enter other environmental media. For example, runoff and direct drainflow transport a portion of NNIs from the soil into water systems (Zhang et al. 2021). Meanwhile, a portion of sprayed NNIs can be adsorbed onto atmospheric particulate matter (Zhou et al., 2020), some of which can then end up in surface water through atmospheric deposition (Cui et al. 2020b; Zhou et al. 2020). In addition, NNIs have also been used for urban ornamental plant pest control, which may cause NNIs to directly enter the receiving river or wastewater treatment plant along with the urban sewage pipe network. However, conventional sewage treatment was not efficient enough in removing all NNIs (Sadaria et al. 2016; Yi et al. 2019), causing the long-term presence of NNIs in water.

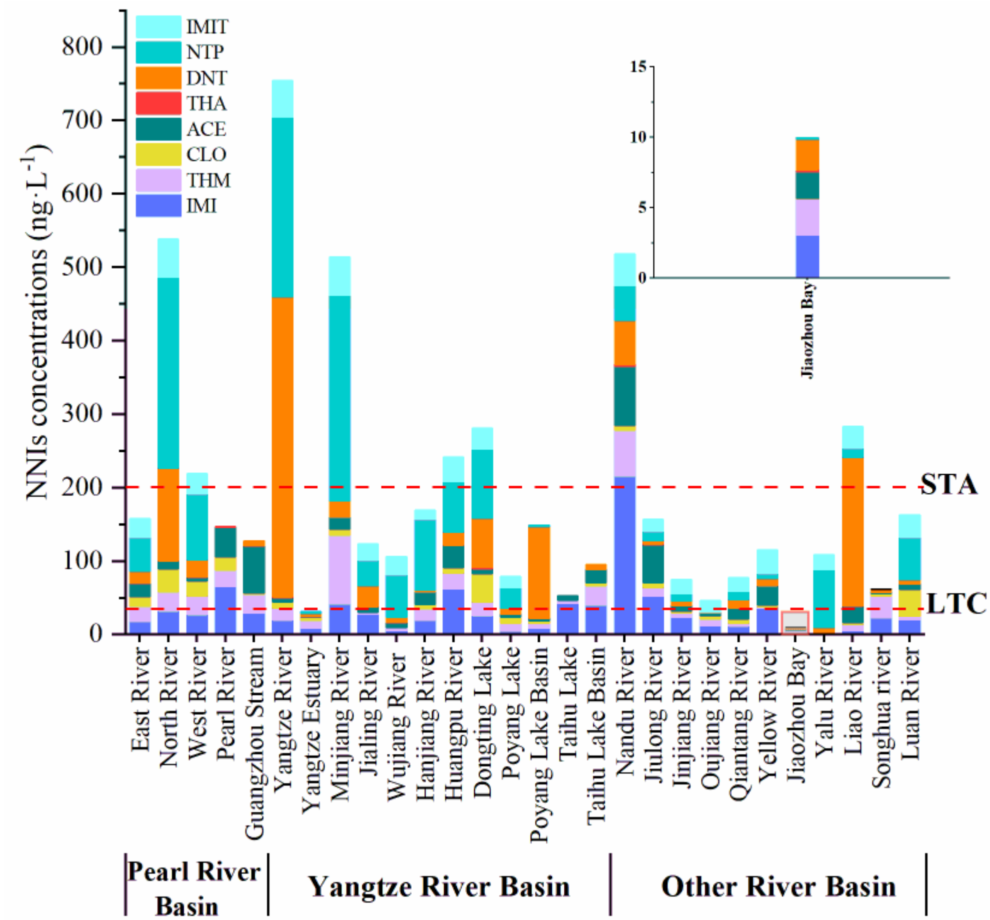

Fig. 2 Average NNIs concentrations in water in different rivers in China.

Sediments

Sediments are an important storage reservoir for many pollutants, which can also release pollutants back into other environmental media (water and air) (Garcia-Chevesich et al. 2014; Cui et al. 2016, 2020a). Knowledge of the residue and environmental behavior of NNIs in sediments is still limited. Concentrations of the six common NNIs in sediments reported in the literature are summarized in **Table 1**.

NNIs concentrations in sediments ranged from 0.07 to 8.30 ng·g^{-1} DW, with higher values being detected in sediments of ditches (Longyan 7.68 ng·g^{-1} DW, Dongguan 8.30 ng·g^{-1}

DW) than rivers. As ditches are normally situated around the planting field with low water flow, they are susceptible to pollution from the surrounding farmland through runoff. NNIs pollution is severer in sediments of several urban rivers, such as Guangzhou Urban Streams, East River, and North River (2.71 $ng \cdot g^{-1}$, 2.83 $ng \cdot g^{-1}$, 2.20 $ng \cdot g^{-1}$ DW, respectively), than other rivers. It is noted that large areas of urban villages are interspersed in the city due to the uneven development of urbanization in Guangzhou, where large quantities of pesticides have been widely used in cultivation (Xiong et al. 2019). In contrast, only two NNIs were found from all samples in Jiaozhou Bay and its inflow rivers, with a total concentration in the range of 0.07-0.24 $ng \cdot g^{-1}$ DW.

The majority of the studies showed much higher concentrations of IMI than the other NNIs ($p < 0.05$) (**Table 1**). To a certain extent, the high IMI residue in the sediments can reflect its historical use, amount, and physicochemical properties. Compared to the other NNIs, IMI has a relatively low water solubility and high log K_{OW} (**Table S2**), which restrict its release from sediment to water (Wu et al. 2020). Besides, the half-life time (DT_{50}) of IMI through chemical decomposition in water-sediment systems is 129 d, which is much longer than those of the other NNIs, such as THM (40 d), CLO (56.4 d), and THA (14.8 d) (**Table S2**). However, for different NNIs, the water solubility is mainly affected by the functional group [=X—Y] in the molecular structure pharmacophore [-N—(C(Z))=X—Y] and increases in the order [=N—NO_2] < [=N—CN] < [=CH—NO_2] (Jeschke et al. 2011). Lower concentrations of THM and THA than those of IMI were measured in the sediments ($p < 0.05$). The low concentrations of THM was due to its high hydrophilicity and low log K_{OW}, which makes it difficult to be adsorbed by sediments. The low concentrations of THA in both water and sediments was because of its short DT_{50} and late date entering the market, with only 37 registered products in China (Tan et al. 2019). CLO concentration in sediments ranged from ND-0.64 ng·g^{-1} DW, with residual levels similar to that of THM. Currently, CLO is only permitted for use in agriculture in China and the number of products is relatively small. In addition, it is worth noting that the possible source of CLO in the environment is derived from the metabolism of THM (Morrissey et al. 2015; Wu et al. 2020).

Table 1 The concentration of NNIs in sediments from various sampling sites in China (ng·g^{-1} DW).

Location	Neonicotinoid insecticides and concentrations							Reference
	IMI	THM	CLO	ACE	THA	DNT	ΣNNIs	
Pearl River	ND[a]	0.12	0.09	1.05	0.15		1.41	Yi et al. 2019
Urban Streams, Guangzhou	1.21	0.26	0.25	0.43	0.31	0.25	2.71	Huang et al. 2020
Longyan Streams	0.21	0.10	0.25	ND	0.01	0.03	0.60	Huang et al. 2020
Longyan Ditch	7.25	0.04	0.21	0.08	0.08	0.04	7.70	Huang et al. 2020
Dongguan Streams	0.86	0.43	0.25	0.75	0.25	0.36	2.90	Huang et al. 2020
Dongguan Ditch	2.23	0.57	0.64	4.06	0.25	0.55	8.30	Huang et al. 2020
East River	1.16	0.14	0.21	1.21	0.11		2.83	Zhang et al. 2019a
North River	1.33	0.19	0.31	0.29	0.08		2.20	Zhang et al. 2019a
West River	0.62	0.08	0.17	0.14	0.01		1.02	Zhang et al. 2019a
Jiulong River	0.18			0.22			0.40	Chen et al. 2015
Moshui River	ND	ND	ND	0.07	ND	ND	0.07	Wang et al. 2020a
Dagu River	ND	0.13	ND	0.11	ND	ND	0.24	Wang et al. 2020a
Licun River	ND	ND	ND	0.17	ND	ND	0.17	Wang et al. 2020a
Songhua River	2.25	0.51	0.12	0.75	ND	ND	3.63	Liu et al. 2021a

[a] ND: not detected.
IMI: imidacloprid; THM: thiamethoxam; CLO: clothianidin; ACE: acetamiprid; THA: thiacloprid; DNT: dinotefuran.

NNIs residues in sediments can reflect their historical applications in surrounding environments, whereas those in water bodies reflect their recent applications (Furihata et al. 2019). In particular, sampling sediments at different depth may better reveal the relationship between NNIs' concentrations and historical applications, studies of which are still lacking to date and should be addressed in the future. In addition, NNIs can be exchanged between water and underlying sediments through diffusion (Cui et al. 2020a). Sediment-water exchange of NNIs is an important process affecting water quality and the fate of NNIs (Cui et al. 2020a). A detailed calculation procedure for sediment-water exchange is presented in the supplementary information. In the present study, we focused on the coexistence of NNIs in paired water and sediment samples collected at the same sampling sites, including the Pearl River Basin (IMI, THM, CLO, ACE, and THA) and Songhua River (IMI, THM, and CLO) (**Table S3**). The calculation of individual NNI fugacity fraction (*ff*) values fluctuated in a small range (**Fig. S1**), with *ff* greater than 0.9 at all the sampling sites in the Pearl River basin and Songhua River. The very similar *ff* values shown in **Fig. S1** indicate the similar sediment-water exchange processes of the individual NNIs across the Pearl River basin and Songhua River, and NNIs mainly diffuse from the sediment to the water. These results also revealed that the sediment cannot obstruct the release of NNIs into the water bodies due to low affinities for sediments sorption and high dissolvability and mobility in water (Liu et al. 2021a). Therefore, once the hydrological conditions change, pollutants that exist in the sediment can be re-released into the water, resulting in secondary contamination of the water body (Cui et al. 2019; 2020c). The relative contributions between this and other known sources of NNIs to water pollution need to be quantified in future studies.

NNIs levels in soil

NNIs are commonly found in soil because they are widely used in seed coating treatments as well as in plant spray (Jeschke et al. 2011; Stewart et al. 2014; Limay-Rios et al. 2016). According to a report by Jeschke et al. (2011), lipophilic NNIs are better suited for seed treatment applications (e.g. THA) than hydrophilic components (e.g. NTP and DNT) because the former is more efficient for root absorption and translocation. In addition, K_{OW} is an essential parameter affecting the transfer and migration ability of chemicals (Liu et al. 2021b), and NNIs can be further transferred from soil to plants. Therefore, there is an urgent need for a systematic understanding of the residue status of NNIs in the soil. Reported soil NNIs concentrations in China are shown in **Table 2**. Among the NNIs, IMI was the most prevalent and has been detected in various soil types, likely because it was the first commercialized NNI and has been widely used worldwide in agricultural activities (Zhang et al. 2020c).

From the perspective of different land-use types, the cultivated soils, especially those for planting vegetables and rice, were the most polluted. For example, Zhang et al. (2020b) found that the highest soil concentrations of NNIs were observed in agricultural soils (mean of 1.69 $ng \cdot g^{-1}$ DW), followed by commercial areas (0.70 $ng \cdot g^{-1}$ DW) in Guangzhou.

In Shouguang, known as the “Hometown of vegetables”, soil NNIs concentrations with greenhouse tomato and cucumber were in the range of 0.73-11.4 $ng \cdot g^{-1}$ DW and 0.36-19.2 $ng \cdot g^{-1}$ DW, respectively. In addition, Zhou et al. (2021) reported that the total concentrations of NNIs can reach 356 $ng \cdot g^{-1}$ DW in the soil of greenhouses in Tianjin. The high temperature, high humidity, confined production environment, and long growing cycles in greenhouses are conducive for the incidence of pests and diseases, leading to pesticide overdoses, multiple applications, and the mixing of different pesticides. High soil NNIs concentrations were also observed in paddy fields, e.g., in Guangdong (19.3 $ng \cdot g^{-1}$ DW), Jiangxi (11.3 $ng \cdot g^{-1}$ DW), Zhejiang (15.6 $ng \cdot g^{-1}$ DW), and Jiangsu (13.8 $ng \cdot g^{-1}$ DW). The somewhat higher soil NNIs concentrations in Guangdong than those in the other places were likely because rice was usually planted two or three times a year in this hot area and pesticide was applied 4 to 6 times annually (Huang et al. 2020). Meanwhile, Southern China is located in a subtropical region where agriculture practices are often carried out under warm, heavy rainfall, and wet weather; these conditions also promote the breeding of pests (Li et al. 2014). Therefore, the application frequency of NNIs in Southern China is high, resulting in relatively high residue levels in the soil. It should be pointed out that, to meet the requirements of national safety standards for crop residues, NNIs with a short half-life were typically sprayed on vegetables while those with a longer lifespan were sprayed on rice and fruit for sustaining a longer insecticidal effect while minimizing the application frequency and cost of NNIs (Huang et al. 2020).

NNIs have also been used in horticulture, urban landscaping, household pest bait, and pet flea control (Miranda et al. 2011; Goulson 2013; Sadaria et al. 2016), resulting in NNIs residues in non-agricultural soils. For example, soils in the park and residential area in Tianjin were detected with NNIs concentrations in the range of ND-404 $ng \cdot g^{-1}$ DW and ND-952 $ng \cdot g^{-1}$ DW, respectively (Zhou et al. 2021). Also, to promote the reuse of wastewater, reclaimed water was often used for urban green irrigation (Dinh et al. 2017), which is considered as one of the potential sources of NNIs in urban soils.

Table 2 The concentration of NNIs in soil in China (ng·g^{-1} DW).

Land-use types	Regions	Soil environment	IMI	THM	CLO	ACE	THA	DNT	NTP	IMIT	FLO	Reference
Cultivated land	Shouguang	Tomato	(ND[a]-6.02)[c]	(ND-4.87)	(0.076-1.36)	(0.10-7.13)	ND	(ND-1.22)	(ND-0.58)	(0.066-0.27)		Wu et al. 2020
		Cucumber	(0.15-8.51)	(ND-7.47)	(ND-1.28)	(0.035-2.13)	ND	(ND-0.31)	ND	(0.045-0.50)		Wu et al. 2020
	Langfang	Radish	0.009				ND		ND			Tan et al. 2016
		Cauliflower	0.13				ND		ND			Tan et al. 2016
		Chinese cabbage	0.026				ND		ND			Tan et al. 2016
	Guangzhou[b]		0.58	0.02	0.04	0.06	0.004					Zhang et al. 2020b
	Guangzhou	Vegetables	31.0		8.30	2.30		0.37		1.80	0.26	Yu et al. 2021
		Rice	17.0		1.90	1.80		0.37		0.78	0.26	Yu et al. 2021
		Fruit	15.0		2.60	0.77		0.33		0.31	0.26	Yu et al. 2021
	Beijing	wheat	24.3			4.50						Tao et al. 2021
	Hainan	Vegetables and rice	119			7.45						Tan et al. 2020
	Zhejiang	Rice	2.61	5.03	6.84	ND	ND	0.33	0.34	0.22	0.21	Li 2017
	Jiangsu	Rice	9.33	1.79	0.71	0.22	0.21	1.4	0.16	ND	ND	Li 2017
	Guangdong	Rice	5.96	3.54	2.79	0.6	ND	5.07	1.2	ND	0.12	Li 2017
	Jiangxi	Rice	2.72	3.54	1.63	1.49	ND	1.34	0.25	ND	0.34	Li 2017
	Tianjin	Farm	32.2	4.34	0.81	17.5	ND	ND	ND		ND	Zhou et al. 2021
		Greenhouse	138	205	11.1	1.58	ND	ND	ND		ND	Zhou et al. 2021
		Orchard	59.5	19.9	2.05	1.47	0.03	ND	ND		ND	Zhou et al. 2021
Garden	Tianjin	Parks	49.2	5.82	0.98	6.14	0.86	1.35	ND	0.71		Zhou et al. 2018
		Parks	70.2	1.40	0.17	3.65	1.74	0.16	ND		ND	Zhou et al. 2021
	Guangzhou[b]	Parks	0.003	0.001	0.003	0.03	0.004					Zhang et al. 2020b
Urban soils	Tianjin	Residential areas	19.6	2.50	4.78	2.20	0.04	ND	ND	0.44		Zhou et al. 2018

	Residential areas	69.9	1.85	0.71	5.79	1.00	ND	ND		ND	Zhou et al. 2021
Guangzhou[b]	Residential zones	0.006	0.002	0.01	0.04	0.004					Zhang et al. 2020b
	Traffic zones	0.003	0.005	0.03	0.07	0.007					Zhang et al. 2020b
	Commercial zones	0.13	0.003	0.02	0.03	0.003					Zhang et al. 2020b
	Educational zones	0.003	0.001	0.004	0.02	0.09					Zhang et al. 2020b
	Industrial zones	0.005	0.005	0.003	0.05	0.009					Zhang et al. 2020b

[a] ND: not detected; [b] The data are presented as geometric mean; [c] means the concentration range.

IMI: imidacloprid; THM: thiamethoxam; CLO: clothianidin; ACE: acetamiprid; THA: thiacloprid; DNT: dinotefuran; IMIT: imidaclothiz; FLO: flonicamid.

Soil is an important storage reservoir and redistribution center for NNIs (Li et al. 2020). NNIs in soil are affected by a variety of biogeochemical processes, such as adsorption, degradation, and crop uptake, which may reduce their concentration and slow the rate of migration. Inside soil, NNIs can exist in pore water or dissolved organic matter. Meanwhile, the N, S, and Cl in the NNIs molecule can act as hydrogen bond acceptors and form hydrogen bonds with the hydrogen donating functional groups in the soil (Zhang et al. 2018b). Thus, NNIs can flow with the water. Besides, soil pores, especially the large ones, are the main channel for NNIs to migrate. Therefore, to further explore the leaching ability of NNIs, the soil leaching potential (L_P) was calculated, as shown in **Table S2**. The L_P values for individual NNIs are in the following decreasing order: CLO (98.7) > THM (11.1) > IMI (9.90) > NTP (8.94) >DNT (0.90)>THA (0.13)> ACE (0.09). Obviously, CLO had the highest percolation potential and was more likely to migrate to deeper soil layers even to groundwater. The partition coefficient values of CLO are in the range of 0.62-1.94 $dm^3 \cdot kg^{-1}$ (Henry's sorption isotherm) and 0.99-3.39 $dm^3 \cdot kg^{-1}$ (Freundlich's sorption isotherm) (Pietrzak et al. 2020), further confirming its lowest soil sorption capacity. Under the same environmental conditions, the solubility, vapor pressure, and organic-carbo sorption constant of an organic pollutant can influence its migration behavior between soil and water. Due to their high water solubility, low log K_{OW}, and low soil adsorbability, NNIs molecules adsorbed in the soil can be easily desorbed under changing environmental conditions, thereby entering soil water and groundwater, and then migrating and spreading into the aquatic ecosystem (Goulson 2013; Morrissey et al. 2015). Previous studies have found the NNIs existing in groundwater in China, and the highest concentration can reach several hundred ng·L^{-1} (Mahai et al. 2021).

Soil NNIs can also move laterally or leach out, and pollute nearby or even remote water bodies through surface runoff driven by rainfall (Wang et al. 2020b; Zhang et al. 2020b). For example, Radolinski et al. (2019) investigated a case of coated maize seeds by THM and detected THM in soil and drainage throughout the corn growing season. The key transport carrier was identified to be surface runoff generated by heavy rain, i.e. soil THM was transported by rainfall driven runoff. This finding is consistent with what Zhang et al. (2020b) found that the composition of soil NNIs residues was relatively consistent in the sediment, suggesting that soil directly migrated to the river through runoff erosion.

Temporal variations of NNIs contamination in China

Existing studies on NNIs contamination in China are still very limited, and most of the studies were conducted between 2015 and 2018 (**Fig. 3**). Available data suggest that NNIs concentrations decreased from 2016 to 2018 in most rivers of China, especially in the West River and the Yangtze River, except for the Pearl River, which actually showed a small increasing trend.

According to data from the National Bureau of Statistics (www.stats.gov.cn/), the consumption of pesticides in China was 1.78 million tons in 2015 and 1.50 million tons in 2018, a decrease of 15.7% during the three-year period. It is noteworthy that the consumption of NNIs in China has been rising from 2013 to 2018 (**Fig. S2**, internal data), despite the downward trend of the total pesticide usage in China during the same period. This is likely due to the withdrawal of highly toxic pesticides (e.g., organophosphates, carbamates) from the market, and gradually replaced with NNIs, mainly N-nitroguanidines, which became the most prominent insecticides. Therefore, the threat to the eco-environment posed by the increased NNIs application in China should be given further attention. Surprisingly, the concentration residues in water have an opposite trend to the amount of NNIs usage in China. The decreasing NNIs residue concentrations in water were likely caused by a combination of several actions adopted in China, such as the implementation of the "Action Plan for Water Pollution Prevention and Control" (The State Council of PRC, 2015), the use of large and medium-sized effective machinery, and the strengthening of ecological management.

Seasonal variations of NNIs concentrations in water showed higher values in summer than spring, such as in Yangtze River, East River, North River, and West River (Mahai et al. 2019; Zhang et al. 2019a), which were mainly caused by the more frequent NNIs spray applications in summer (Mahai et al. 2019). Meanwhile, surface runoff and sediment release of NNIs caused by rainfall (**Table S4** and **S5**) were the main mechanisms causing increased NNIs in water bodies (Armbrust and Peeler 2002; Chiovarou and Siewicki 2008; Morrissey et al. 2015; Mahai et al. 2019; Zhang et al. 2019a). However, some water bodies had higher concentrations in dry than wet seasons (Chen et al. 2019), which may be due to the dilution effect caused by frequent water exchange during the rainy season, especially stormy weather.

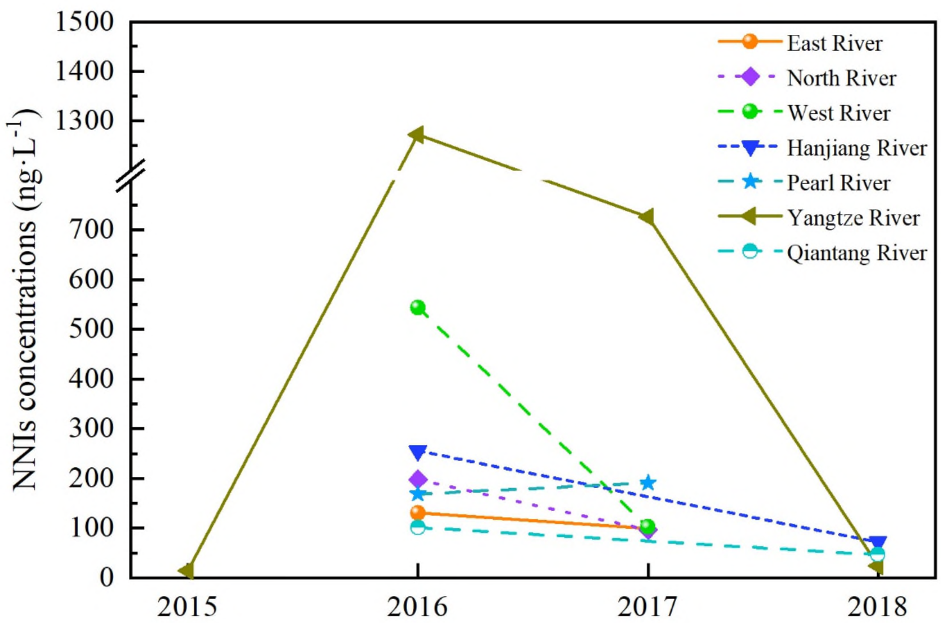

Fig. 3 Temporal trends of NNIs levels in water in some rivers of China.

Spatial variations of NNIs contamination in China

Through the investigation of spatial distribution characteristics of NNIs, we can systematically understand the impact of human activities on NNIs emissions in different regions across China and provide a scientific basis for controlling NNIs pollution. Available data (**Table S1**) suggest that NNIs pollution was more serious in southern China, especially in the Yangtze River Basin, than in northern China, and the heavy use of NNIs in agricultural practices is directly responsible. In the Yangtze River Basin, NNIs concentrations in the mainstream (755 ng·L^{-1}) were substantially higher than those in the tributaries (maximum concentration in Minjiang River: 514 ng·L^{-1}), due to the large catchment size and the wide range of pollutant sources of the Yangtze River mainstem. This also indicates the accumulated contributions from tributaries to the mainstream. For example, the NNIs in the mainstream of the Harbin section of the Songhua River mainly came from the inflow of high-polluted tributaries (Liu et al. 2021a).

In general, NNIs concentrations in various media (water, sediment, soil, air) tend to be high in land use dominated by agricultural activities (Cui et al. 2020a). Extreme NNIs pollution in China was indeed concentrated in areas with extensive agricultural activities. For example, the Yangtze River Basin owns approximately 20% of the country's total arable land, but produced about 40% of the country's total agricultural output (Sun et al. 2019). In China, all registered NNIs are available for rice cultivation (**Table S6**), and the distribution of NNIs coincides with the rice-growing areas (Li et al. 2019). Therefore, intensive rice cultivation is an important source of NNIs contamination. In addition, two or even three seasons of cropping every year are very common, especially in southern China with mild temperature, heavy rainfall, and humid weather (Yuan et al. 2017), providing rich opportunities for insect propagation. Hence, NNIs have been used more frequently in southern than northern China. Besides, southern China is also an important production base for fruits and vegetables, and thus high concentrations of NNIs occurred in surface water and groundwater due to the large amounts of NNIs application and the warm and humid climatic conditions (Li et al. 2014). He et al. (2021) found a similar spatial increasing trend from northern to southern China in NNIs residues in tap water, which was mainly attributed to the larger application of NNIs in southern China. The above results indicate that the influence of climatic conditions, cropping patterns, and crop types have caused the massive application of NNIs in southern China, which subsequently resulted in heavier pollution in southern than northern China.

Conclusions

Literature reported NNIs data across China were summarized in this study to explore their pollution characteristics in different environmental media including water, sediment, and soil. NNIs were commonly detected in different media due to its large usage, with their total concentrations being at the level of ng·L^{-1} in water and ng·g^{-1} DW in sediment and soil. IMI, THM, and ACE were the most frequently detected NNIs. NNIs residues were severer in some rivers and sediments in Southern China than in the other regions. NNIs in most monitored water bodies exceeded the threshold level set for chronic risk for sensitive non-target invertebrates. NNIs in water and sediments were mainly originated from surface runoff and domestic sewage. Soil contamination of NNIs was severer in arable land than other land use. The spatial distributions of NNIs showed gradual decreasing levels from south to north direction across China. NNIs levels have been decreasing in most regions of China during 2016-2018. Considering the very limited studies on the contamination characteristics of NNIs in China, a nationwide research is urgently needed, especially for inland areas of China. A study design covering multi-media environments and including major atmospheric and biogeochemical processes can best describe the sources, fates, and environmental behavior of NNIs as well as the interactions between different media.

Supplementary Information

The online version contains supplementary material available at

Authors Contributions

Song Cui and Zhikun Liu drafted the paper. Fuxiang Zhang and Yuxin Ke analyzed the data. Shuang Wang, Peng Hu and Lihui An created the figures and established methods. Zhikun Liu, Yunqing Zhao and Zulin Zhang designed the experiments and organized resources. Leiming Zhang, Yi-Fan Li, Rupert Hough and Song Cui finalized the paper. All authors approved the final manuscript.

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Data availability

All data used in this study are included in this published article and its supplementary information file.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication All authors agree to publish.

Conflict of interest The authors declare no conflict of interest

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