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Ecological risks caused by neonicotinoid pesticides in sediments: A case study of freshwater basins in China

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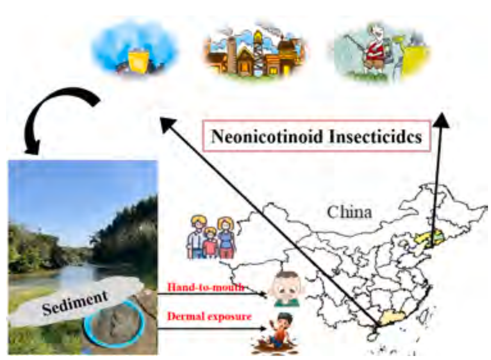
HIGHLIGHTS

- NNIs were higher in sediment from southern China than from northern.
- Different agricultural production may result in different NNIs content.
- The risks of NNIs in sediments are higher in the South than in the North.
- The risks of NNIs must be further closely monitored.

GRAPHICAL ABSTRACT



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ABSTRACT

Neonicotinoid insecticides (NNIs) are extensively used in agricultural production in China due to their selective neurotoxicity towards target insects. In recent years, the rapid development of agriculture has increased the use and residue of NNIs. Consequently, the sediment environment, serving as the ultimate sink, is significantly impacted by NNIs. Upon release into the environment, NNIs can enter the human body through the food chain, posing potential ecological and human health risks. This study analyzed 79 sediment samples from two major river basins in North and South China, the Liaohe River basin in Liaoning Province and the Jianjiang River basin in Guangdong Province. The content, composition, distribution, and source of eight NNIs were analyzed, and assess the ecological and human health risks of the target compounds in these regions. The results indicated that the average concentration of NNIs in the sediments of the Jianjiang River basin (2.34 μg/kg) is slightly higher than that of the Liaohe River basin (2.32 μg/kg), and the sources of NNIs in the two areas were different, with differences in the sources of NNIs likely attributable to varying types of agricultural production. The risk assessment revealed that the ecotoxicological and public health risks were more pronounced in the Jianjiang

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River basin compared to the Liaohe River basin, underscoring the critical need for surveillance and management of hazardous substances like NNIs. The insights findings from this study can provide scientific guidance for the risk evaluation and environmental management of NNIs.

1. Introduction

Neonicotinoid insecticides (NNIs) were developed based on the structure of nicotine and boast high efficacy, a broad spectrum, and favorable environmental compatibility (Pang et al., 2023; Tu et al., 2023), which significantly improve agricultural production. Since their invention and launch in the 1980s (Tison et al., 2023; Tooker and Pearsons, 2021), NNIs have become the most utilized class of pesticides globally, comprising over 25 % of total pesticide market sales (Lucas et al., 2023; Wang et al., 2023b). Due to their considerable mobility within environmental matrices, only 5 % of the active ingredient applied in the form of NNIs is taken up by crops, with 90 % infiltrating the soil and the remainder dispersing into water bodies and the atmosphere (Xu et al., 2021; Zhang et al., 2023a). Additionally, NNIs inevitably accumulate in the water environment through atmospheric transport and precipitation and thus into the sediment environment, posing a potential risk to the ecological integrity of the affected areas (Li and Kannan, 2020; Zhang et al., 2023a).

There has been significant progress in global research on the monitoring, toxicology, and fate of NNIs. In 2019, Furihata et al. detected NNIs at concentrations ranging from 7×10^{-3} to 2.53 μg/kg in sediments around rice fields across Japan (Furihata et al., 2019). In 2019, Bonmatin et al. detected NNIs in lake waters in the Central American country of Belize at levels of 1×10^{-3}-14×10^{-3} μg/L and 1.4×10^{-2}-3.48×10^{-1} μg/kg in sediment, with the main source of contamination coming from the application of NNIs in agricultural land surrounding the lake (Bonmatin et al., 2019). In China, Xiong detected NNIs in the urban sewers of the Pearl River in Guangzhou at an average level of $>10.9\times10^{-3}$ μg/L (Xiong et al., 2021). However, the study of NNIs residues in Chinese sediments is not comprehensive.

NNIs remainin crops, such as fruits and vegetables, at high concentrations and enter the biological systems through the food chain, leading to adverse effects (Zhang et al., 2022; Zhang et al., 2023b). Previous studies have found that imidacloprid is linked to cognitive impairment in invertebrate insects and colony collapse disorder, as well as physiological effects in non-target organisms such as rats and birds (Ma et al., 2023; Yuan et al., 2019). In humans, exposure to NNIs causes symptoms such as dizziness, headache, muscle weakness, and vomiting (Kathage et al., 2018; Tian et al., 2022). Hence, the global community should pay considerable attention to the risks posed by NNIs. In response to these concerns, in 2013, the European Union and some neighboring countries implemented restrictions on specific NNIs. This underscores the critical necessity for in-depth research into the environmental persistence of NNIs, their ecological risks, and the potential health hazards they present to humans.

Therefore, based on extensive field investigations, sample collections, and laboratory analyses, this study focuses on eight NNIs: imidacloprid (IMI), acetamiprid (ACE), nitenpyram (NIT), imidaclothiz (IMIZ), thiacloprid (THA), thiamethoxam (THM), clothianidin (CLO), and dinotefuran (DIN). The Liaohe and Jianjiang River basins serve as the primary study locales. Employing the Relative Potency Factor (RPF) method, the USEPA's soil ingestion risk assessment model and the 2013 edition of the Chinese Ministry of Environmental Protection (MEP) *Chinese Population Exposure Parameter Manual Adult Volume* as the basis of the risk assessment model, to analysis the residual characteristics and associated risk of NNIs in sediments samples from both northern and southern China.

2. Materials and methods

2.1. Chemicals

Eight targeted individual neonicotinoid insecticides, including IMI, ACE, NIT, IMIZ, THA, THM, CLO, and DIN (purity: 98.0 % - 99.9 %), as well as two isotope-labeled standards (IMI-d_4 and CLO-d_3, purity: 98.0 % - 99.9 %) were all purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile (HPLC-MS grade), QuEChERS purification tubes, and its purification filler PSA, C_{18}, and $MgSO_4$ were all obtained from ANPEL Laboratory Technologies (Shanghai) Inc. (Shanghai, China).

2.2. Study area and sampling collection

With a total watershed area of 69200 km^2, the Liaohe River basin is located in the north temperate zone of Liaoning province, including the Daliaohe River (DLH), Hunhe River (HH), Shehe River (SH), Suzihe River (SZH), Taizihe River (TZH) and Dahuofang Reservoir (DHF), which accounts for 46.76 % percent of the total area of Liaoning province. It is not only a significant source of agricultural imports for agricultural products in northern China, but also an important source of imports for agricultural products from South Korea, Japan and the European Union. With a watershed area of 9464 km^2, the Jianjiang River basin is located in the subtropical agricultural powerhouse Maoming City, Guangdong Province, and consists of 10 watersheds, including the Gaozhou Reservoir (GZ), Huanghuajiang River (HHJ), Jianjiang River (JJ), Luodingjiang River (LDJ), Meihuajiang River (MHJ), Mingzhou Reservoir (MZ), Xiaodongjiang River (XDJ), Yangmeihe River (YMH), Zaitouhe River (ZTH) and Luojiang River (LJ). As an important food and vegetable supply base in the Guangdong-Hong Kong-Macao Greater Bay Area (GBA), the Jianjiang River basin has favorable conditions for agricultural production. Therefore, researching NNIs in these relevant areas is of great practical significance.

In November 2021, sediment samples were collected from the Liaohe River basin (39 samples) and the Jianjiang River basin (40 samples) (Fig. 1). The sampling sites avoided pollution sources such as villages, garbage dumps, and factories. The surface sediment (10 cm) was cleared of leaves and stones and then collected in polypropylene (PP) tubes. All samples were chilled during transportation and then stored at −40 °C in the laboratory until analysis.

2.3. Sample extraction and instrumental analysis

The sediment samples were lyophilized and milled to pass through a 100-mesh screen before extraction using the QuEChERS pesticide residue extraction method. After adding 10 g of freeze-dried sediment sample, the surrogate standards (clothianidin-d_3), 25 mL acetonitrile, and 5 mL Milli-Q water were added into a 50 mL PP centrifuge tube. The sediment slurry was vortexed for 10 min (2200 rpm), sonicated for 15 min (30 °C), centrifuged for 8 min (4000 rpm), and then decanted the supernatant. The extraction process were done twice and the extract were mixed. Subsequently, 2 g NaCl was added to the mixed liquid, vortex for 1 min (2200 rpm), and stand for 15 min. Take out the vector supernatant and add it to the prepared QuEChERS purification tube. The ratio of primary secondary amine (PSA) adsorbent and C_{18} is 3:1, vortex for 5 min (2200 rpm), centrifuge for 5 min (4000 rpm). The supernatant was transferred to a new 15 mL polypropylene centrifuge tube, dried under nitrogen blow, and resuspended in 1 mL acetonitrile. The extracts were filtered through a 0.2 μm nylon filter to the LC vial and brought to an Agilent 1260 LC/AB Sciex 4000 Qtrap MS (LC-MS/MS, Agilent

Technologies, Santa Clara, CA, USA) analysis. 10 μL of a 5 μg/mL solution of internal standard (IMI-d_4) was added to the LC vial before instrumental analysis. Instrumental analysis was performed by LC-MS/MS in an electrospray ionization source. A CORTECSTM C_{18} column (4.6 × 100 mm; 2.7 μm, Waters, USA) was used for the separation of NNIs at 40 °C. Mobile phases A and B were acetonitrile and 1 % formic acid aqueous solution with a flow rate was 0.4 mL/min. The gradient elution scheme of the instrument and the mass spectrum parameters of NNIs are listed in Tables S1-S2.

2.4. Quality assurance and quality control

The quality control system, including procedural blank, laboratory blank, matrix blank, and matrix spiked samples, was used to validate the precision and accuracy of the experimental method before chemical analyses. The instrument was calibrated using external standards before analysis to ensure the stability of performance (within 20 % variation for the individual compounds). The blank samples for all target neonicotinoids were below the method detection limit (MDL). The recovery for the target insecticides ranged from 78.38 % to 122.67 % in the matrix spiked samples. The recoveries of the internal standards were ranged from 81.49 % to 121.71 %. Quantification was based on an internal calibration standard with an 8-points curve ($R^2 > 0.999$, range between 1 and 200 μg/L) (Tables S3-S4).

2.5. Statistical analysis

A comprehensive risk assessment model was used in this study. It employ the Relative Potency Factor (RPF) method to calculate the ecotoxicological risk of the target compounds, and the Human Health Risk Assessment Model of the US EPA combined with the actual health exposure of the Chinese population to derive the risk of the target compounds to population health, to comprehensively assess the risk of the target compounds. The software for statistics and analysis of experimental results is SPSS 25.0 (IMB, USA), Origin 2018 (OriginLab, Northampton, MA), Microsoft Excel 2019, and Minitab19. All sampling point information maps are drawn with ArcGIS 12.

2.5.1. Relative Potency Factor (RPF) method

The Relative Potency Factor (RPF) method (Liu et al., 2021; Oya et al., 2021) is a model that identifies an indicator chemical within a group of chemicals with a common mechanism of action and then calibrates the exposure to each chemical using the ratio of the efficacy of each chemical to the efficacy of the indicator chemical as a correction factor to assess the total exposure to the concentration of that class of compounds.

In this survey, the RPF approach was used to assess the combined exposure concentrations (IMI_{RPF}) of the 8 NNIs in the samples, and the total risk entropy $\boldsymbol{\alpha}$ of the NNIs was calculated from the exposure concentrations. When the overall risk entropy obtained was >1, it was determined that there was a greater ecotoxicological risk in the area (Li and Kannan, 2020; Zhang et al., 2023a). As IMI is frequently detected in all types of environmental media, more established toxicological data are available (Nakamura et al., 2019; Peterson et al., 2021). Therefore, based on the Reference Daily Dose (cRfDs) data provided by the US EPA, we selected DIN, ACE, NIT, THA, IMI (pesticide banned), CLO, THM, and IMIZ to calculate combined exposure concentrations IMI_{RPF}, and IMI as a standard control neonicotinoid insecticide.

First, by using the Reference Daily Dose (RfD) of each NNIs to account for the concentration of imidacloprid, the Chronic Reference Dose cRfD and Average Daily Intake (ADI) of the 8 NNIs are shown in Table S5. As the cRfD values for NIT and IMIZ were not available, we set the RPF of IMIZ to be the same as that for IMI as 1, based on the similar structure of IMIZ and IMI. Set the RPF of NIT to 3.62 (Mahai et al., 2019). calculated as Eqs. (1)–(3):

Toxicity factors

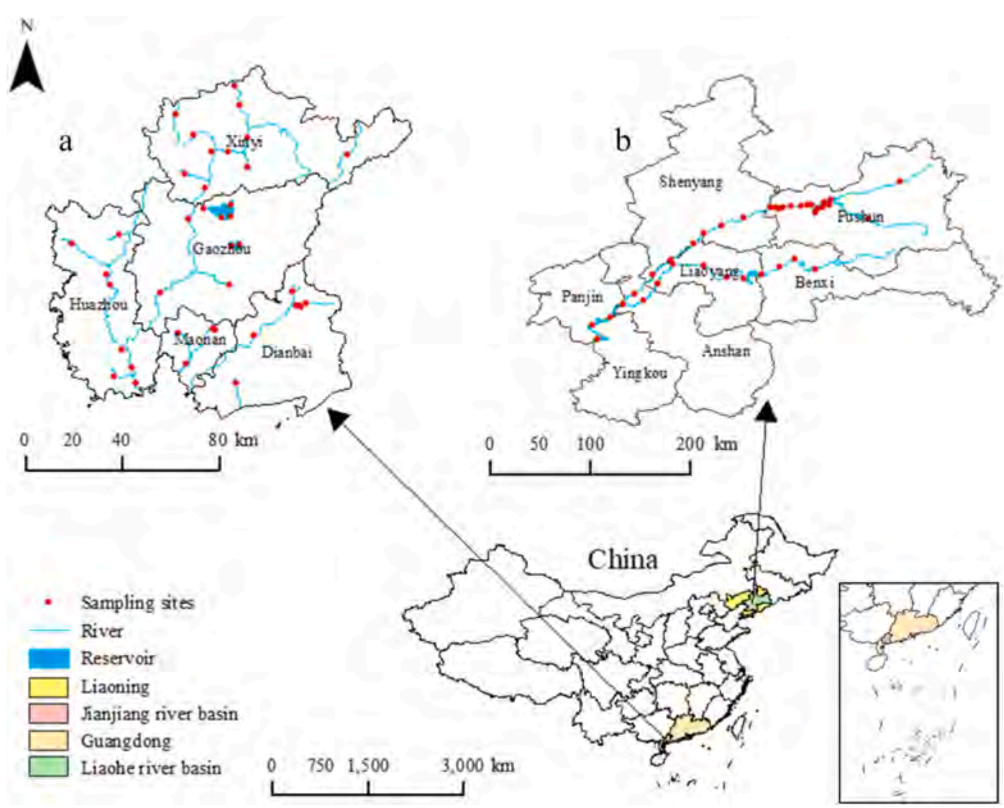

Fig. 1. Map of the sediment sampling sites in the Liaohe and Jianjiang River basin. Study area a is located in Guangdong Province, and study area b is located in Liaoning Province.

$$RPF_i = RfD_{IMI}/RfD_i \tag{1}$$

Total exposure concentration

$$\begin{aligned} IMI_{RPF} = & \sum_i^n (\text{NNIs}^{\times} RPF_i) \\ & = \text{DIN} \times 2.85 + \text{ACE} \times 0.803 + \text{NIT} \times 3.62 \\ & + \text{THA} \times 14.25 + \text{IMI} + \text{CLO} \times 5.816 \\ & + \text{THM} \times 9.5 + \text{IMIZ} \end{aligned} \tag{2}$$

Entropy of risk

$$\alpha = \sum_i^n (NNIs \times RPF_i/ADI) \tag{3}$$

In the formula, IMI_{RPF} is the combined exposure concentration of the same mechanism compound neonicotinoid pesticides. RfD_i is the exposure concentration of compound *i*. RfD_{IMI} is the efficacy factor of the benchmark indicator compound imidacloprid. *ADI* is the safety guideline value of the indicator compound. In this study, α is the sum of 8 NNIs risk quotients. If α is bigger than 1 indicating that there is a greater ecotoxicological risk in the region, the relevant parameters are shown in Table S5.

2.5.2. Human health risk (HHR) assessment model

The HHR model is used to quantify the risks to human health (non-carcinogenic and carcinogenic risks) of contaminants exposure from various sources. This study evaluates the health risks associated with NNIs in the study area based on the HHR model proposed and the actual human health situation in China. Due to the lack of criteria for carcinogenic factors for NNIs, we did not calculate the carcinogenic risk, only the non-carcinogenic risk. Owing to the nature of NNIs and the composition of the samples, we calculated the health risk from NNIs by the two major routes of hand-to-mouth ingestion and skin exposure (Guo et al., 2023; Wang et al., 2022), but not by the route of inhalation. The average daily exposure measures for the target compounds via the two exposure routes were calculated as Eqs. (4)–(5):

Hand-to-mouth ingestion

$$ADD_i = \frac{C_i \times R_{ing} \times EF \times ED}{BW \times AT} \times CF \tag{4}$$

Skin exposure

$$ADD_{i_{dermal}} = \frac{C_i \times TSA \times SER \times SL \times ABF \times EF \times ED}{BW \times AT} \times CF \tag{5}$$

In the formula, C_i is NNIs' content (μg/kg); R_{ing} is Hand-to-mouth intake rate (mg/day); *EF* is outdoors annual exposure frequency (days/year); *ED* is exposure years (year); *TSA* is total skin area (cm^2); *SER* is skin exposure ratio; *SL* is skin adhesion factor (mg/cm^2/day); *ABF* is Skin absorptive factor; *BW* is average body weight (kg); *AT* is average exposure time (year); CF is the conversion factor (10^{-6}). The various parameters in the formula represent the meaning and specific parameter values are shown in Table S6.

The Hazard Index (HI) is used to assess the non-carcinogenic risk of a target compound to humans and is calculated as the sum of the Hazard Quotient (HQ) from different exposure routes (Chen et al., 2021; Huang et al., 2022; Wang et al., 2023a). The hazard index (HI) is calculated as Eqs. (6)–(7):

$$HQ_i = \frac{ADD_i}{RfD_i} \tag{6}$$

$$HI_i = \sum\nolimits_i^n HQ_i \tag{7}$$

When HI < 1, it indicates a low or no non-carcinogenic risk; HI > 1, it indicates a non-carcinogenic risk. Where the reference dose RfD is taken as shown in Table S5.

3. Results and discussion

3.1. Occurrence and distribution of neonicotinoids in sediment

The detection frequencies and concentration data of the eight NNIs in sediments from the Liaohe River basin and the Jianjiang River basin are presented in Table 1. Except for the Liaohe River basin, where the detection frequencies for ACE, THA, and THM were 92 %, 85 %, and 95 %, respectively, all NNIs were detected with a frequency of 100 %. The coefficients of variation for the eight compounds exceeded 41 % in both catchments, indicating substantial spatial variability likely influenced by exogenous factors (Leimberger et al., 2022). The highest average concentrations of NNIs in the sediments of the Liaohe and Jianjiang River basins were observed for IMIZ at 4.8×10^{-1} μg/kg and NIT at 6.1×10^{-1} μg/kg, respectively. These findings suggest relatively high application rates of these compounds in these regions. IMIZ, effective in controlling aphids, thrips, lice, and other pests, addresses the limitation of pyridine pesticides being less effective at lower temperatures. Despite the global distribution of aphids, they are predominantly found in temperate regions, partly explaining the presence of IMIZ residues in the Liaohe River basin. NIT is primarily used for pest control in rice, fruit, tea, and vegetable crops, elucidating the elevated levels of NIT in the Jianjiang River basin, a significant food and vegetable supply base for the Greater Bay Area.

The NNIs with the lowest average sediment levels in both catchments were consistently THA, measuring 4×10^{-2} μg/kg and 1.2×10^{-1} μg/kg, respectively, likely due to their short half-life and rapid decomposition in soil and water bodies (Leimberger et al., 2022). The levels of NNIs also exhibit notable variability in the sediments of different rivers within the Liaohe and Jianjiang River basins. In the Liaohe River basin, ACE and NIT were predominant in HH and TZH, respectively, while DIN was highest in DLH and SH, and CLO and IMIZ in DHF and SZH, respectively. This suggests that the content of target compounds in sediments may be affected by different exogenous substances and human activities (Pan et al., 2021). Notably, all eight target compounds were present at higher levels in HH sediments compared to other catchments, suggesting that this is an important source of pollution (Hudson et al., 2023; Stara et al., 2021). According to Table S7, the variations in the levels of NNIs in the sediments of different river types within the Jianjiang River basin. NIT is the predominant regional pollutant, with higher mean values across various water bodies compared to the other seven NNIs. In general, the levels of 7 NNIs in JJ sediments were higher than that in other rivers, but the levels of IMIZ in JJ (2.74 μg/kg) was lower than that in GZ (3.06 μg/kg). Such differences may be attributed to regional sources of exogenous pollution. However, the total content of 8 NNIs in JJ was still higher than that of GZ, which ranked second. This indicates that JJ contributed more to the levels of target compounds in regional river sediments. The relatively flat topography of the JJ and GZ areas, coupled with developed agriculture and higher pesticide consumption, likely explains the elevated pesticide levels in these areas.

In order to understand the degree of pollution in this study, NNIs in different regions at native and foreign were compared. According to Table 1, in this study, the concentration of NNIs in Liaohe River basin was 4×10^{-2}-4.8×10^{-1} μg/kg and in Jianjiang River basin was 1.2×10^{-1}-6.1×10^{-1} μg/kg. The concentration of NNIs detected in sediments in Belize is 1.4×10^{-2}-3.48×10^{-1} μg/kg (Bonmatin et al., 2019), which is at a low level of pollution compared to this study. The NNIs (7×10^{-3}-2.53 μg/kg) in the rice paddy sediments of Japan (Furihata et al., 2019), the NNIs (1.12 μg/kg) in the Pearl River sediments of China (Yi et al., 2019), and the NNIs (4.1×10^{-1}-3.87 μg/kg) in the sediments of Jiangsu (Huang et al., 2022) are all higher than the pollution levels in this study. However, the amount of NNIs residues detected in the soil of Belize reached 17.1 μg/kg (Bonmatin et al., 2019), which was relatively consistent with the level of NNIs pollution in GZ in this study (Table S7).

Table 1
Detection frequency (DF) and concentrations of NNIs in sediment samples in Liaohe and Jianjiang River basins.

	Compounds	DF (%)	Coefficient of variation (%)	Concentration (μg/kg dry weight)			
				Mean	Standard deviation	Maximum	Minimum
Liaohe River basin	DIN	100	42.86	0.42	0.18	1.15	0.18
	ACE	92	119.35	0.31	0.37	1.45	<RL[a]
	NIT	100	60.47	0.43	0.26	1.43	0.17
	THA	85	225.00	0.04	0.09	0.55	<RL[a]
	IMI	100	63.16	0.19	0.12	0.70	0.04
	CLO	100	62.96	0.27	0.17	0.70	0.05
	THM	95	141.18	0.17	0.24	1.11	<RL[a]
	IMIZ	100	110.42	0.48	0.53	3.21	0.16
	∑NNIs[b]	100	49.00	2.32	1.14	6.04	1.10
Jianjiang River basin	IMI	100	82.50	0.40	0.33	1.53	0.13
	ACE	100	78.57	0.14	0.11	0.51	0.05
	NIT	100	83.61	0.61	0.51	2.45	0.11
	IMIZ	100	41.67	0.12	0.05	0.27	0.06
	THA	100	59.09	0.22	0.13	0.48	0.06
	THM	100	52.00	0.25	0.13	0.78	0.09
	CLO	100	62.50	0.32	0.20	1.23	0.15
	DIN	100	79.31	0.29	0.23	0.94	0.07
	∑NNIs[b]	100	46.00	2.34	1.08	5.28	0.86

[a] Less than the reporting limit (RL).
[b] The sum of the concentrations of IMI, ACE, NIT, IMIZ, THA, THM, CLO, and DIN in sediment.

3.2. Percentage of 8 neonicotinoids in sediments

According to the analysis the content of eight NNIs as a percentage of the total content in sediment samples from the two study areas (Fig. 2), it was found that sediments from the Liaohe River basin are dominated by IMIZ, NIT, and DIN, accounting for 21 %, 19 %, and 18 %, respectively, with THA contributing the smallest proportion at 2 %. The percentage composition of NNIs in sediments across different river environments in the Liaohe River basin is generally consistent with the overall distribution, but there are differences in the main pollutants in each river. In SH, IMIZ is the predominant compound, constituting 53 %, possibly indicating an exogenous contamination source. In DLH and SZH, DIN (29 %) and CLO (25 %) are the dominant compounds, respectively. In HH and TZH, ACE and NIT are predominant, accounting for 24 % and 28 %, respectively. The level of NNI contamination in sediments varies from sampling area to sampling area and may be related to farmer use patterns (Huang et al., 2022).

In the Jianjiang River basin, NIT and DIN dominate the NNIs in sediment samples, accounting for 26 % and 17 %, respectively, with THA at the lowest proportion of 5 %. NIT levels in the HHJ, JJ, and MHJ basins account for >30 %. THA percentages in the LDJ, YMH, ZTH, and XDJ watersheds are all above 10 %, which was higher than the regional average, indicating a substantial contribution to THA in the regional. The percentages of target compounds in GZ and MH sediments are consistent with regional mean values.

3.3. Spatial distribution characteristics of neonicotinoids

The spatial distribution of NNIs in the sediments of the Liaohe River basin is relatively consistent, with high-value areas located in Liaoyang City in central Liaoning Province and Fushun City in the east. This distribution is likely related to the region's high level of agricultural intensification and continuous farmland (Fig. 3). The DIN content in the central area of Liaoyang City was higher than 1.15 μg/kg. ACE was mainly concentrated in the central part of Shenyang and the eastern part of Fushun, and was about 1.02 μg/kg, were primarily in central Shenyang City and eastern Fushun City. NIT concentrations, exceeding 1.54 μg/kg, were mainly in the border areas of Liaoyang, Shenyang, and

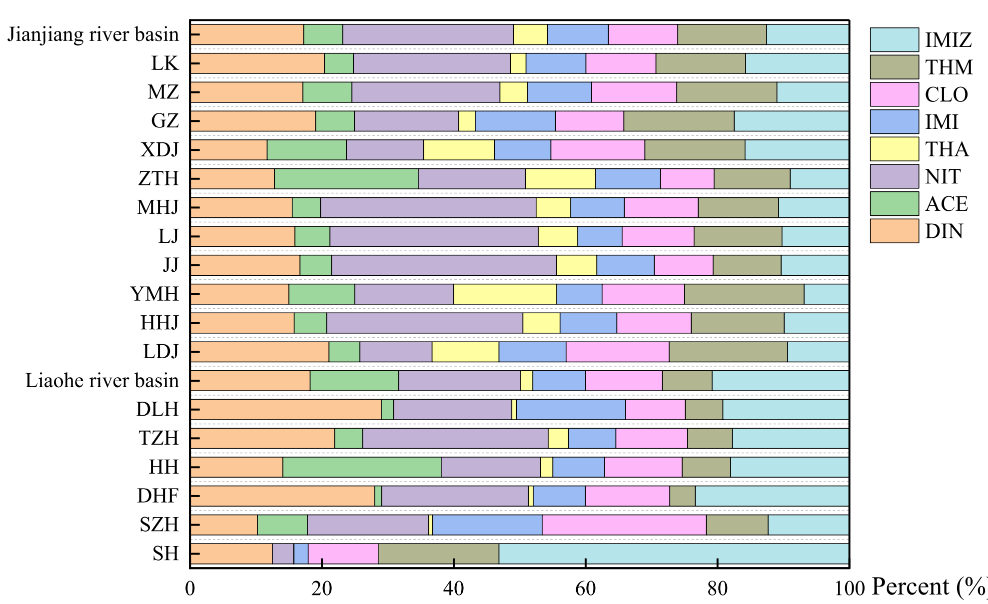

Fig. 2. The percentage of 8 NNIs in total NNIs in Jianjiang and Liaohe river basins.

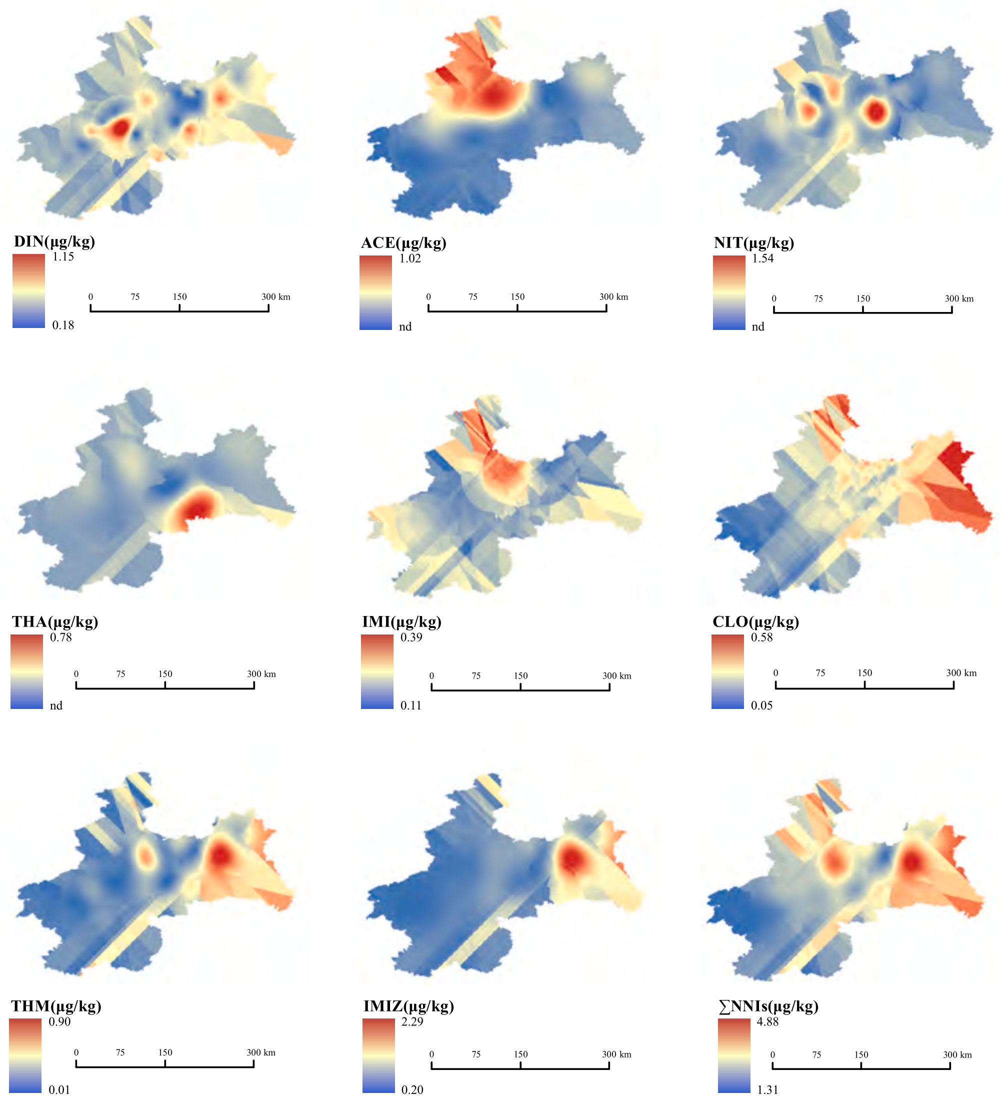

Fig. 3. Spatial distribution of NNIs in sediments from the Liaohe River basin.

Benxi City. THA, with values of 0.78 μg/kg, was concentrated in eastern Benxi City, while IMI values, around 0.39 μg/kg, were in Shenyang City. The content of CLO was higher in the eastern part of Fushun City (0.58 μg/kg), and THM was concentrated in Fushun City and Benxi City (0.90 μg/kg). IMIZ had high values exceeding 2.29 μg/kg. The maximum total content of the eight NNIs in the Liaohe River basin was 4.88 μg/kg, located in Fushun, in the eastern basin.

In the Jianjiang River basin, the content of the eight NNIs showed spatial distribution differences, with high-value areas mainly in central and eastern Gaozhou City and eastern Dianbai District, likely due to regional topography and agricultural practices (Fig. 4). DIN values, around 1.06 μg/kg, were mainly in the eastern basin. ACE, with values of 0.20 μg/kg, was found in the southern basin. NIT, around 1.98 μg/kg, was concentrated in the northern and central basin. THA, with values of 0.22 μg/kg, was in the central and northern part of the southern basin. IMI values, 0.40 μg/kg, were in the central area. CLO, with high values of 0.34 μg/kg, was found in eastern Gaozhou District and Dianbai District. THM, with values of 0.49 μg/kg, showed spatial continuity in the eastern basin. IMIZ, with high values of 0.74 μg/kg, was concentrated in central Gaozhou District and eastern Dianbai District. The maximum value of the eight NNIs in the Jianjiang River basin was 3.28 μg/kg, located in Gaozhou City and Dianbai City. Overall, the maximum values of the eight NNIs in sediments were lower in the Jianjiang River basin than in the Liaohe River basin.

3.4. Explanation of the spatial origin of NNIs

In the Jianjiang River basin, PCA analysis (Fig. 5a) extracted two main factors from the eight NNIs, with a cumulative variance of 86.61 %. PC1 accounted for 65.79 %, primarily explaining IMI, THM, IMIZ, CLO, and DIN, likely from spray residues of fruits and vegetables such as lychee and choy sum, and horticultural agriculture spray residues. PC2 accounted for 20.83 %, mainly explaining THA and ACE, likely from food crops such as rice. The PCA analysis of NNI sources in sediment samples from the Liaohe River basin (Fig. 5b) identified two main influencing factors, accounting for a cumulative variance of 65.25 %. PC1 explained 46.93 % of the variance, primarily associated with CLO, IMIZ, DIN, and THM, likely from spray residues of sugar beet, beans, and

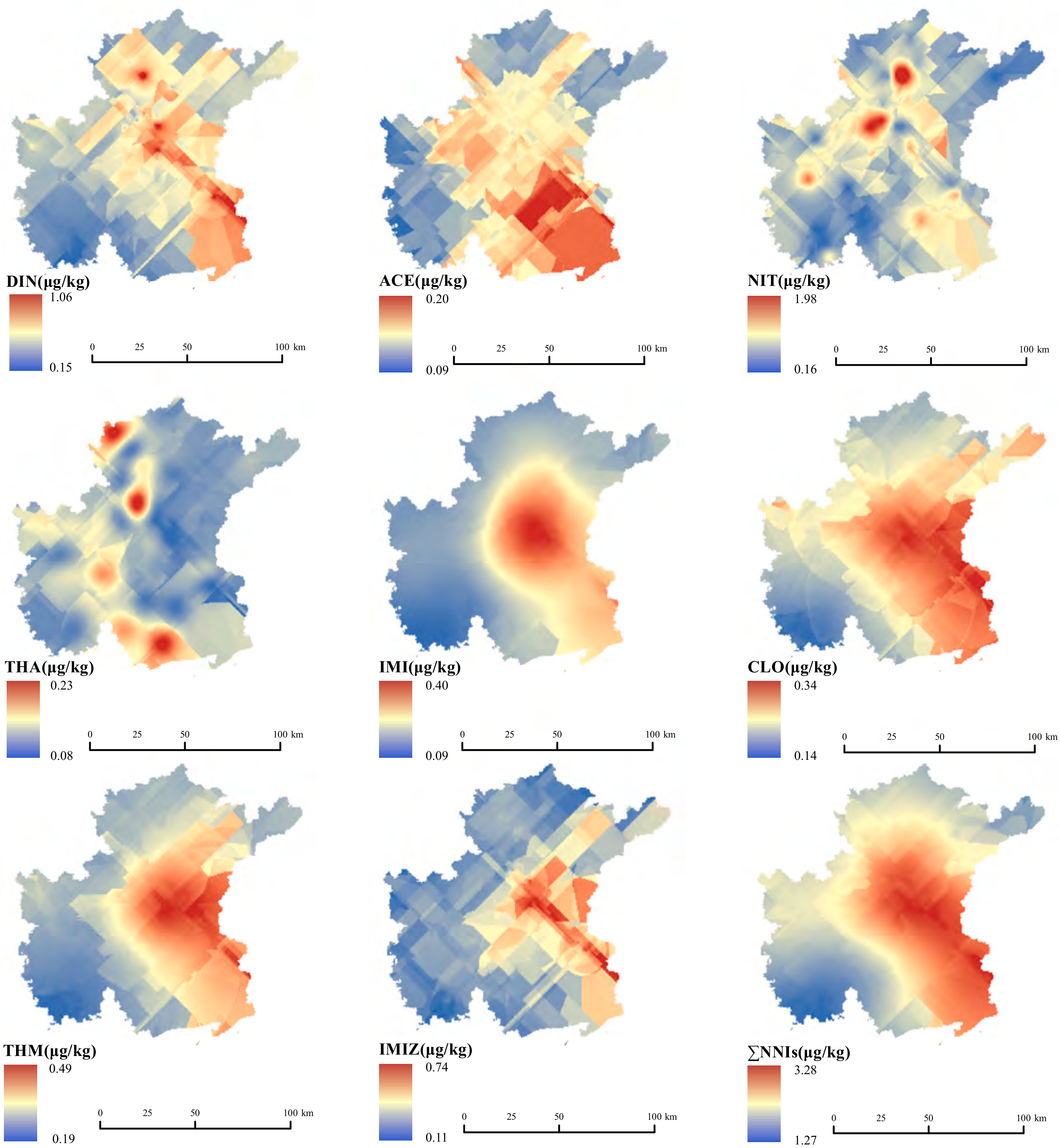

Fig. 4. Spatial distribution of NNIs in sediments from the Jianjiang River basin.

other cash crops (Dai et al., 2023). PC2 explained 18.32 % of the variance, mainly related to ACE and IMI, likely from spray residues of grain crops such as wheat and corn (Lalchawimawia et al., 2023).

The samples in different basins are similar and their sources are similar. The Liaohe River basin is a major grain production area with a one-year cropping system, while the Jianjiang River basin is a key vegetable supply area with a multi-year cropping system. Thus, PCA showed that NNI residues are more associated with crop type and agricultural production methods in both catchments.

3.5. *Risk assessment of NNIs*

3.5.1. *Results of the ecotoxicity risk assessment*

The combined exposure concentration (IMI_{RPF}) and total risk entropy

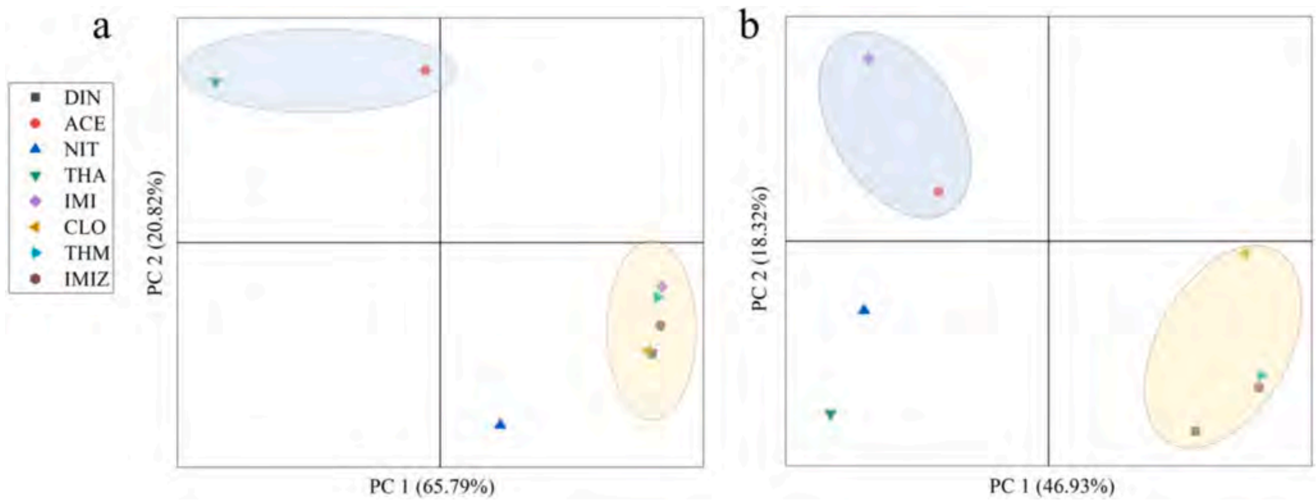

Fig. 5. PCA analysis of NNIs' sources in sediment samples from Jianjiang (a) and Liaohe (b) River basins.

(α) of NNIs in sediments from the Liaohe and Jianjiang River basins were determined through an ecotoxicological risk assessment using the RPF method (Table 2). The mean IMI_{RPF} and α for target compounds in Liaohe River sediments were 7.50 and 0.32, respectively. In contrast, sediments from the Jianjiang River basin showed higher mean values, with an IMI_{RPF} of 10.12 and an α of 0.59.

Relative efficiency factors of NNIs in various samples were calculated, and radar charts illustrating joint exposure concentrations and risk entropy of NNIs in sediments from different regions of both river basins were constructed. Analysis of Fig. 6 revealed significant differences in joint exposure concentrations of the eight NNIs across different water bodies in the Liaohe River basin, with SH exhibiting the highest concentration. Similarly, substantial variations were observed in the GZ and LK reservoirs with the highest joint exposure concentration. The risk entropy α in each basin correlated with the joint exposure concentration IMI_{RPF}, and the α value of some sampling points was >1, indicating ecological risk.

3.5.2. Population health risk assessment results

In this assessment, the exposures and health risks associated with eight NNIs in sediments from the Liaohe River basin and the Jianjiang River basin were evaluated using a health risk model (Table 3). Results indicated that IMIZ exhibited the highest exposure levels, while THA

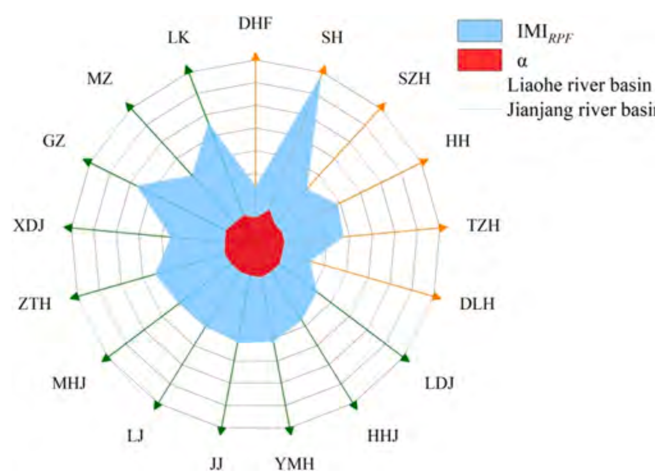

Fig. 6. Joint exposure concentration and risk entropy radar maps of NNIs in sediment samples from Liaohe and Jianjiang River basins.

Table 2
Total combined exposure concentration IMI_{RPF} and total risk entropy α of NNIs in sediments of Liaohe and Jianjiang River basins.

	Waters	IMI_{RPF}				α			
		Mean	Median	Minimum	Maximum	Mean	Median	Minimum	Maximum
Liaohe River basin	DHF	4.26	4.09	3.17	6.15	0.11	0.08	0.04	0.25
	HH	8.61	7.82	3.94	19.32	0.38	0.24	0.04	1.27
	SH	20.46	20.46	20.46	20.46	1.50	1.50	1.50	1.50
	SZH	6.57	6.57	6.57	6.57	0.26	0.26	0.26	0.26
	TZH	8.19	6.85	4.32	20.26	0.33	0.16	0.07	1.52
	DLH	4.00	3.97	3.48	4.59	0.13	0.15	0.10	0.15
	∑Liaohe river	7.50	6.57	3.17	20.46	0.32	0.20	0.04	1.52
Jianjiang River basin	GZ	14.06	11.40	9.50	24.31	0.89	0.71	0.48	1.74
	HHJ	8.09	8.09	6.67	9.34	0.47	0.45	0.42	0.56
	JJ	9.52	7.86	4.52	18.23	0.50	0.50	0.32	0.82
	LDJ	6.67	6.67	6.67	6.67	0.47	0.47	0.47	0.47
	MHJ	9.22	9.22	8.45	10.00	0.49	0.49	0.42	0.56
	MZ	8.98	11.15	4.35	11.46	0.53	0.59	0.29	0.72
	XDJ	7.73	7.73	6.82	8.64	0.56	0.56	0.50	0.62
	YMH	9.43	9.43	9.43	9.43	0.73	0.73	0.73	0.73
	ZTH	10.34	10.34	10.34	10.34	0.72	0.72	0.72	0.72
	LK	13.79	13.23	9.84	18.87	0.74	0.70	0.41	1.16
	LJ	9.11	8.28	5.24	13.37	0.52	0.55	0.36	0.68
	∑Jianjiang river	10.12	9.38	4.35	24.31	0.59	0.55	0.29	1.74

Table 3
Exposure and health risks of NNIs in sediment samples of Liaohe and Jianjiang River basins.

Areas	Types	DIN	ACE	NIT	THA	IMI	CLO	THM	IMIZ
Liaohe River basin	Children								
	$ADD_{H\text{-}M}$	1.28×10^{-6}	9.83×10^{-7}	1.30×10^{-6}	1.30×10^{-7}	5.77×10^{-7}	8.33×10^{-7}	5.53×10^{-7}	1.46×10^{-6}
	ADD_{SKIN}	3.26×10^{-9}	2.50×10^{-9}	3.32×10^{-9}	3.32×10^{-10}	1.47×10^{-9}	2.12×10^{-9}	1.41×10^{-9}	3.71×10^{-9}
	$NCR_{H\text{-}M}$	6.40×10^{-8}	1.38×10^{-8}	8.29×10^{-8}	3.26×10^{-8}	1.01×10^{-8}	8.50×10^{-8}	9.22×10^{-8}	2.56×10^{-8}
	NCR_{SKIN}	1.63×10^{-10}	3.53×10^{-11}	2.11×10^{-10}	8.30×10^{-11}	2.58×10^{-11}	2.17×10^{-10}	2.35×10^{-10}	6.52×10^{-11}
	$HI_{Liaohe\text{-}children}$	6.42×10^{-8}	1.39×10^{-8}	8.31×10^{-8}	3.27×10^{-8}	1.01×10^{-8}	8.53×10^{-8}	9.24×10^{-8}	2.56×10^{-8}
	Adult								
	$ADD_{H\text{-}M}$	7.17×10^{-7}	5.50×10^{-7}	7.30×10^{-7}	7.29×10^{-8}	3.23×10^{-7}	4.67×10^{-7}	3.10×10^{-7}	8.16×10^{-7}
	ADD_{SKIN}	2.57×10^{-9}	1.97×10^{-9}	2.62×10^{-9}	2.61×10^{-10}	1.16×10^{-9}	1.67×10^{-9}	1.11×10^{-9}	2.93×10^{-9}
	$NCR_{H\text{-}M}$	3.58×10^{-8}	7.75×10^{-9}	4.64×10^{-8}	1.82×10^{-8}	5.67×10^{-9}	4.76×10^{-8}	5.16×10^{-8}	1.43×10^{-8}
	NCR_{SKIN}	1.28×10^{-10}	2.78×10^{-11}	1.66×10^{-10}	6.54×10^{-11}	2.03×10^{-11}	1.71×10^{-10}	1.85×10^{-10}	5.13×10^{-11}
	$HI_{Liaohe\text{-}adult}$	3.60×10^{-8}	7.78×10^{-9}	4.66×10^{-8}	1.83×10^{-8}	5.69×10^{-9}	4.78×10^{-8}	5.18×10^{-8}	1.44×10^{-8}
Jianjiang River basin	Children								
	$ADD_{H\text{-}M}$	1.22×10^{-6}	4.18×10^{-7}	1.83×10^{-6}	3.65×10^{-7}	6.52×10^{-7}	7.44×10^{-7}	9.50×10^{-7}	8.88×10^{-7}
	ADD_{SKIN}	3.11×10^{-9}	1.07×10^{-9}	4.66×10^{-9}	9.28×10^{-10}	1.66×10^{-9}	1.89×10^{-9}	2.42×10^{-9}	2.26×10^{-9}
	$NCR_{H\text{-}M}$	6.10×10^{-8}	5.89×10^{-9}	1.16×10^{-7}	9.11×10^{-8}	1.14×10^{-8}	7.59×10^{-8}	1.58×10^{-7}	1.56×10^{-8}
	NCR_{SKIN}	1.55×10^{-10}	1.50×10^{-11}	2.96×10^{-10}	2.32×10^{-10}	2.91×10^{-11}	1.93×10^{-10}	4.03×10^{-10}	3.97×10^{-11}
	$HI_{Jianjiang\text{-}children}$	6.12×10^{-8}	5.91×10^{-9}	1.16×10^{-7}	9.14×10^{-8}	1.15×10^{-8}	7.61×10^{-8}	1.59×10^{-7}	1.56×10^{-8}
	Adult								
	$ADD_{H\text{-}M}$	6.83×10^{-7}	2.34×10^{-7}	1.02×10^{-6}	2.04×10^{-7}	3.65×10^{-7}	4.16×10^{-7}	5.32×10^{-7}	4.97×10^{-7}
	ADD_{SKIN}	2.45×10^{-9}	8.39×10^{-10}	3.67×10^{-9}	7.31×10^{-10}	1.31×10^{-9}	1.49×10^{-9}	1.91×10^{-9}	1.78×10^{-9}
	$NCR_{H\text{-}M}$	3.42×10^{-8}	3.30×10^{-9}	6.50×10^{-8}	5.10×10^{-8}	6.40×10^{-9}	4.25×10^{-8}	8.87×10^{-8}	8.72×10^{-9}
	NCR_{SKIN}	1.22×10^{-10}	1.18×10^{-11}	2.33×10^{-10}	1.83×10^{-10}	2.30×10^{-11}	1.52×10^{-10}	3.18×10^{-10}	3.13×10^{-11}
	$HI_{Jianjiang\text{-}adult}$	3.43×10^{-8}	3.31×10^{-9}	6.53×10^{-8}	5.12×10^{-8}	6.43×10^{-9}	4.26×10^{-8}	8.90×10^{-8}	8.75×10^{-9}

showed the lowest, across both exposure pathways in the Liaohe River basin. Among the eight NNIs, THM presented the highest non-carcinogenic risk, whereas IMI posed the lowest. Specifically, the non-carcinogenic risk of THM via hand-to-mouth exposure was 9.22×10^{-8} for children and 5.16×10^{-8} for adults. For dermal exposure, the risks were 2.35×10^{-10} for children and 1.85×10^{-10} for adults. Combining the risks from both exposure routes, THM had the highest total risk value (Children and adults, 9.24×10^{-8} and 5.18×10^{-8}) and IMI the lowest (Children and adults, 1.01×10^{-8} and 5.69×10^{-9}).

In the Jianjiang River basin, NIT had the highest exposure and THA the lowest across both pathways. THM again posed the greatest non-carcinogenic risk, while ACE posed the least. The non-carcinogenic risk of THM via hand-to-mouth exposure was 1.58×10^{-7} for children and 8.87×10^{-8} for adults, and via dermal exposure, 4.03×10^{-10} for children and 3.18×10^{-10} for adults. The combined total risk values for the eight NNIs showed THM with the highest risk (Children and adults, 1.59×10^{-7} and 8.90×10^{-8}) and ACE with the lowest (Children and adults, 5.91×10^{-9} and 3.31×10^{-9}). By analyzing the two different exposure pathways, health risk trends were similar for the 8 NNIs, with a higher non-carcinogenic risk for children in both watersheds from hand-to-mouth ingestion. This approach significantly increases overall population health risks.

4. Conclusion

This study measured the residual concentrations of eight NNIs in sediments from the Liaohe and Jianjiang River basins. The results indicate that NNIs were widespread in both regions, and high concentrations of NNIs were mainly distributed in the north-central part of the Liaohe River Basin and the east-central part of the Jianjiang River Basin, and that the residue levels were influenced by crop types and agricultural practices. Human health risk assessment shows that hand-oral ingestion is the main exposure route. Therefore, due to the inherent hazards of NNIs and its environmental persistence, it is necessary to monitor and pay attention to different areas of the country in the future to explain its migration and transformation in the environment.

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CRediT authorship contribution statement

Xiaoxia Chen: Writing – review & editing, Writing – original draft. **Pengchong Wen:** Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Yanan Sun:** Methodology, Investigation. **Ping Ding:** Validation. **Haibo Chen:** Writing – review & editing. **Hui Li:** Investigation. **Xin Li:** Investigation. **Limei Cai:** Supervision, Software. **Yunjiang Yu:** Visualization, Validation. **Guocheng Hu:** Project administration, Funding acquisition.

Declaration of competing 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177547.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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