Neonicotinoid insecticides in paddy field: Dissipation dynamics, migration, and dietary risk

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4 FIGURES

1 TABLE

Abstract

Neonicotinoid insecticides (NNIs) have caused widespread contamination of multiple environmental media and posed a serious threat to ecosystem health by accidentally injuring non-target species. This study collected samples of water, soil, and rice plant tissues in a water-soil-plant system of paddy fields after spaying imidacloprid (IMI), thiamethoxam (THM), and clothianidin (CLO) to analyze their distribution characteristics and migration procedures and to assess related dietary risks of rice consumption. In the paddy water, the concentrations of NNIs showed a dynamic change of increasing and then decreasing during about a month period, and the initial deposition of NNIs showed a trend of CLO (3.08 μg/L) > THM (2.74 μg/L) > IMI (0.97 μg/L). In paddy soil, the concentrations of the three NNIs ranged from 0.57 to 68.3 ng/g, with the highest residual concentration at 2 h after application, and the concentration trend was opposite to that in paddy water. The initial deposition amounts of IMI, THM, and CLO in the root system were 5.19, 3.02, and 5.24 μg/g, respectively, showing a gradual decrease over time. In the plant, the initial deposition amounts were 19.3, 9.36, and 52.6 μg/g for IMI, THM, and CLO, respectively, exhibiting concentration trends similar to those in the roots. Except for IMI in soil, the dissipation of the NNIs conformed to the first-order kinetic equation in paddy water, soil, and plant. The results of bioconcentration factors (BCFs) and translocation factor (TF) indicated that NNIs can be bi-directionally transported in plants through leaf absorption and root uptake. The risk of NNIs intake through rice consumption was low for all age groups, with a slightly higher risk of exposure in males than in females.

Keywords: neonicotinoid insecticides; dissipation dynamics; bioconcentration factors; translocation factor; dietary risk

1. Introduction

Rice is the third largest food crop in the world after maize and wheat, and more than half of the world's population depends on rice as a staple food (Rajamoorthy et al., 2015; Wang et al., 2022). Nutrient elements (carbohydrate, protein, and cellulose) contained in rice are essential to support human life activities and maintain normal metabolic function. Therefore, the yield and quality of rice are crucial to feeding people and ensuring food security. However, throughout its growth cycle, rice is extremely vulnerable to various pests such as rice planthopper (Fu et al., 2022). Paddy pests are often large in scale and high in frequency, posing a major threat to rice production and quality. Chemical pesticides are thus frequently applied in paddy fields to protect rice from pests and diseases. Of the pesticides applied in agricultural history, neonicotinoid insecticides (NNIs) have become one of the successful types due to their high water solubility, high efficiency, and broad spectrum. NNIs selectively act on nicotinic acetylcholine receptors in the central nervous system of insects, causing death by blocking transmission in the insect's nervous system (Bass et al., 2015; Morrissey et al., 2015). Unlike contact pesticides that remain on the surface of leaves, NNIs can be absorbed by plants and transported to all of plant tissues (roots, stems, leaves, flowers, and fruits, etc.) (Goulson, 2013). Extensive application of NNIs have caused water contamination, which declined aquatic insects (Kuechle et al., 2022) and insectivorous bird populations (Li et al., 2020).

China is the world’s largest producer of rice, with a sowing area of 29.45 million hectares and an annual production of 208.49 million tons in 2022 (National Bureau of Statistics, 2023). Currently, more than 3000 commodities of NNIs are registered in China, all of which can be used for paddy pest control. The use of these commodities has been rising from 2013 to 2018, exceeding 30,000 tons per year since 2016 (Liu et al., 2022). Existing research on NNIs in China predominantly focused on detecting their pollution levels in different environmental media (Chen et al., 2019; Zhou et al., 2021; Liu et al., 2022; Niu et al., 2022). For example, the residual concentrations of NNIs are as high as several thousand ng/L in water bodies and several hundred ng/g in river sediments and agricultural soil (Liu et al., 2022; Niu et al., 2022). The concentration of NNIs in the Yangtze River are higher during the dry season compared to the wet season, with localized concentrations reaching a peak of 3240 ng/L (Chen et al., 2019). The highest residual concentrations of NNIs in soil are observed in greenhouse environments, followed by orchards, parks, residential areas, and farms, with the concentration of imidacloprid (IMI) in peach greenhouse soil reaching up to 1056 ng/g (Zhou et al., 2021). In particular, NNIs in soils can accumulate continuously over years of use, e.g., higher residues were observed in soils cultivated after 14-17 years than 8-9 years (Wu et al., 2020). Furthermore, most studies related to NNIs in plants were conducted in laboratory environments, with very limited studies in open field experiments (Liu et al., 2023a). A comprehensive systematic study on the uptake, migration, and fate of NNIs in real-world environmental condition is urgently needed, which motivated the present study.

Our previous study identified IMI, thiamethoxam (THM), and clothianidin (CLO) as the primary contaminants in multi-media environments in Heilongjiang Province, northeast China (Liu et al., 2021; 2023b). The present study also focused on these three NNIs, but aimed to obtain a systematic investigation covering multiple environmental media such as plants, soil, and water bodies in an area highly affected by NNIs. The specific goals include (1) characterizing the distribution, dissipation, and residue accumulation of NNIs in a water-soil-plant system of rice fields; (2) clarifying the dynamic migration process of NNIs in rice fields; and (3) assessing the risks of chronic dietary exposure of different age populations through rice consumption based on the final residue concentrations of NNIs in rice. Results from this study fill the current knowledge gaps of NNIs distribution and migration patterns within water-soil-plant systems, which are needed for guiding safe production of rice.

2. Materials and methods

2.1 Chemicals and agents

Standards of IMI (chemical purity 99.8%), THM (99.2%), and CLO (99.8%) were purchased from Alta Scientific Co., Ltd. (Tianjin, China). IMI 10% wettable powder (WP), THM 20% water dispersible granule (WDG), and CLO 20% suspension concentrate (SC) were purchased from Jiangsu Kesheng Group Co., Ltd. (Yancheng, China), Xianzhengda Nantong Crop Protection Co., Ltd. (Nantong, China), and Hebei Veyong Bio-Chemical Co., Ltd. (Shijiazhuang, China), respectively. HPLC-MS grade acetonitrile and methanol were obtained from Fisher Chemical, Inc. (Waltham, MA, USA). Primary secondary amine (PSA) and graphitized carbon black (GCB) were purchased from Agela Technologies (Tianjin, China) and Wogao Laboratory Instruments Ltd. (Jinan, China), respectively. Anhydrous magnesium sulphate ($MgSO_4$) and sodium chloride (NaCl) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Field experiments

Field experiments were carried out in Fujin City (131.97° E, 47.02° N), Heilongjiang Province in northeast China from June to October 2020. This region has a temperate continental monsoon climate. Black soil is one of the main soils in Fujin City. It mainly distributes in the plains and rolling hill areas, covers an area of 9714 thousand hectares, contains 4-5% organic matter, and has a depth of 20-30 cm. The experiments were designed following NY/T 788-2004 (MARA, 2004) promulgated by the Ministry of Agriculture and Rural Affairs of the People's Republic of China. There were four treatments, including three formulation treatments and a control treatment, in the field experiments. Each experimental plot was 100 m^2 and aisles were provided between the different experimental plots.

To examine the dissipation of the three NNIs in rice plant, paddy water, and soil, the recommended high dosage of active ingredient per hectare (a.i. ha^{-1}) for 150 g IMI 10% WP, 36 g THM 20% WDG, and 150 g CLO 20% SC were dissolved in water and applied through foliar spray at a tillering stage of rice for only once. Samples (paddy water, soil, and rice plant) were collected at 2 h and 1, 3, 5, 11, 15, 25, 36, 51, and 86 days after application. 30 rice plant samples, with each sample having a volume of at least 1 kg, were collected randomly using the diagonal method, chopped and thoroughly mixed, split into quarters (each is about 250 g), placed in a clean sealed plastic bag, and stored at -20°C. 24 paddy water samples, with each sample having a volume of at least 1 L, were randomly collected in every experimental plot from a minimum of 10 sampling points; after mixing, about 1 L of which was sealed in a clean plastic bottle. 30 paddy soil samples were collected concurrently from 10 to 12 random sampling points at 0-10 cm depth to a size of 1 to 2 kg, and an auger boring was used to remove debris, weeds, and other debris from the soil.

2.3 Sample processing

The paddy water samples were extracted, purified, and analyzed according to the method established by our previous study (Liu et al., 2021). The same treatment procedure as for the sediment samples was also applied to all the soil samples. Details of the pretreatment methods for water and soil samples are given in the Supporting Information (SI) (**Text S1**). The rice plants, rice roots, rice husk, and rice grain were freeze-dried and crushed using a grinder. Briefly, rice plant (2 g), roots (1 g), rice husk (5 g), and rice grain (5 g) were accurately weighed into a 50 mL PTFE centrifuge tube containing 5 mL of ultrapure water and 15 mL acetonitrile, shaken for 1 min, and left for 1 h. The samples were sonicated for 30 min before the addition of 3 g $MgSO_4$ and 1 g NaCl to the PTFE tubes. The tubes were capped tightly and shaken vigorously manually for 1 min. Samples were then centrifuged at 5000 rpm for 5 min. For rice plant samples, 6 mL of the supernatant was added to a centrifuge tube containing 900 mg of $MgSO_4$, 300 mg of PSA, and 100 mg of GCB, and then shaken vigorously for 1 min. For rice roots, rice husk, and brown rice samples, 6 mL of the supernatant was added to a centrifuge tube containing 900 mg of $MgSO_4$, 300 mg of PSA, and 100 mg of C_{18}, and then shaken vigorously for 1 min. The extract was centrifuged at 5000 rpm for 5 min again. An aliquot (5 mL) of the upper organic solution was evaporated to near dryness by a gentle nitrogen stream and reconstituted in 1 mL of 25% acetonitrile in water. The extract was filtrated through a 0.22 mm PTFE membrane for HPLC-MS/MS analysis.

2.4 Chemical analysis

Chemical analysis was carried out on AB SCIEX Triple Quad 5500 HPLC-MS/MS (Framingham, MA, USA). The separation of IMI, THM, and CLO was achieved on a Phenomenex Kinetex® C18 column (100 mm × 2.1 mm, 1.7 μm) maintained at 25℃. The mobile phase for HPLC analyses was 0.1% formic acid-water solution (A) and acetonitrile (B) flowing at 0.3 mL/min. To improve sample separation accuracy, a gradient program of the mobile phase was performed as follows: 0.1% formic acid-water solution (A) was linearly decreased from 95% to 65% in 3 min, then decreased to 45% in 6 min, and finally reverted to 95% in 9 min before ending the program in 12 min. The injection volume was 2 μL. The MS detection conditions were as follows: a drying gas temperature of 550℃, curtain gas (N_2) pressure of 35 psi, collision gas of 7 psi, and ion spray voltage of 5500 V. In addition, collision cell exit and entrance potential were 16.0 and 10.0 V, respectively. The MS/MS acquisition parameters (MRM mode) used for the quantification of the target compounds are provided in **Table S1**. The retention times of IMI, THM, and CLO were 3.61, 3.08, and 3.45 min, respectively.

2.5 Quality assurance and quality control

Before sample analysis, procedural blank, laboratory blank, and matrix spiked samples were carried out. The recoveries of the eight target compounds ranged from 86.3 to 92.1% for water, from 79.8 to 96.2% for soil, and from 84.5% to 93.6% for plant samples. The method detection limit (MDL) of target analytes in the sample was calculated from the S/N ratio of 10 (**Table S1**). If the detected concentration in the sample is lower than the MDL, the value is set to zero. All results for soil and plant samples were reported on a dry weight (dw) basis.

2.6 Dissipation dynamics and translocation analysis

The dissipation of the three NNIs was calculated according to the first-order kinetic equation as follows:

$$C_t = C_0 e^{-kt} \tag{1}$$

$$T_{1/2} = \frac{\ln 2}{k} \tag{2}$$

where C_0 and C_t are concentrations of the individual NNIs initially and at time t, respectively; $T_{1/2}$ is the half-life period of individual NNIs (in the unit of day (d)); and k is the first-order rate constant.

The concentrations of pesticides uptaken and accumulated by roots, plants, and subcellular constituents were expressed as bioconcentration factors (BCFs), including the root concentration factor (RCF), plant concentration factor (PCF), and translocation factor (TF). These parameters were used to calculate the transfer ability of pesticides from roots to plants as follows:

$$RCF = C_{\text{root}} / C_{\text{water}} \tag{3}$$

$$PCF = C_{\text{plant}} / C_{\text{water}} \tag{4}$$

$$TF_{\text{root/plant}} = C_{\text{root}} / C_{\text{plant}} \tag{5}$$

where C_{root}, C_{water}, and C_{plant} are the concentrations of an individual pesticide in root, paddy water, and plant, respectively.

2.7 Dietary-risk assessment

Rice serves as a primary source of carbohydrates in daily diets, and the residue levels of pesticides in rice have become a focal point of concern for dietary risks to human health. Based on the residue concentrations of NNIs in brown rice and utilizing dietary structure data from the 'Status of nutrition and health among Chinese Residents' (Jin, 2008), daily rice intake and average body weight for different age groups in China were calculated. The long-term dietary risks associated with rice consumption were then assessed for various population groups as follows:

$$NEDI=(C_i \times F_i)/bw \tag{6}$$

$$TMDI=(MRL \times F_i)/bw \tag{7}$$

$$RQ_N = NEDI / ADI \tag{8}$$

$$RQ_T = TMDI / ADI \tag{9}$$

where *NEDI* is the estimated national daily intake (in the unit of mg/kg/d); C_i is the pesticide residue concentration detected in the brown rice (mg/kg); TMDI is the theoretical maximum daily intake (mg/kg/d); *MRL* is the maximum residue level in the rice (mg/kg); F_i is the daily consumption of a particular food item by the general population (kg/d); *bw* is the average body weight of the general population (kg); RQ_N and RQ_T values are risk quotients corresponding to NEDI and TMDI, respectively; and ADI is the acceptable daily intake (mg/kg/d).

3. Results and discussion

3.1 Dynamics of neonicotinoid insecticides in paddy water

The initial deposition of NNIs in paddy water was measured 2 h after application, which showed the highest value for CLO (3.08 μg/L), followed by THM (2.74 μg/L) and IMI (0.97 μg/L). Because of the application method of spraying, a portion of NNIs was intercepted by the rice plants, a very small portion evaporated into the air, and the remaining portion entered into the paddy water, leading to high initial deposition in the paddy water and correspondingly high potential of water pollution. As shown in **Fig. 1**, the three NNIs gradually migrated to the water in the paddy field after application, with their concentrations gradually increasing during the first several days before starting decreasing in later days. For example, in the collected paddy water samples, the peak concentrations of IMI (8.09 μg/L) and THM (5.00 μg/L) appeared on the third day after application, while that of CLO (19.5 μg/L) appeared on the fifth day.

The concentrations of the three NNIs in paddy water decreased rapidly afterwards due to various factors such as rainfall, light intensity, and temperature. Specifically, rainfall can scour the plant, causing the NNIs concentration to increase in the paddy water, while heavy rainfall can dilute the NNIs concentration in the paddy water and can also cause runoff loss. NNIs inside the water bodies can undergo photodegradation, a process that is controlled by light intensity and temperature (Xie et al., 2009; Lu et al., 2015). For example, Lu et al. (2015) found that the half-life time of the degradation of

THM was only 0.2 days in summer, but as long as 1.49 days in winter due to different seasonal temperatures.

In addition, the "shallow, wet, and dry" irrigation mode is adopted during the tillering stage of rice growth. The method of sunbathing at the end of effective tillering by receding water from the farmland, a process that prevents water and fertilizer supply, can stop the growth of high-position young tiller buds and reduce their nutrient consumption, so that the main stem and large tillers can get more nutrient supply. The mass of NNIs that migrated through the drainage can be estimated from their concentrations in the paddy water at the 5th day and the typical depth of paddy water of about 10-15 cm, resulting in migration mass in the ranges of 6.69-10.0, 4.44-6.66, and 19.5-29.3 g a.i. ha^{-1} for IMI, THM, and CLO were, respectively, accounting for 4.46-6.69%, 12.3-18.5%, and 13.0-19.5% of their respective application volume. Thus, drainage is one of the major processes causing NNIs pollution in the aquatic environment. After the sunbathing treatment, the paddy field was replenished with water, which led to a sharp decrease in the concentration of NNIs at the 11^{th} day. Meanwhile, the uptake of water and nutrients increases with vigorous rice growth, resulting in continuous absorption of NNIs by the plant through the root system, thus accelerating the dissipation of NNIs in paddy water.

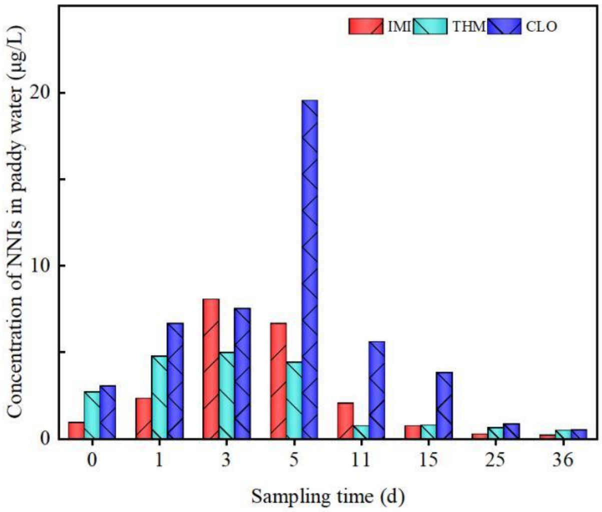

Fig. 1 Time evolution of NNIs concentrations in paddy water.

The dissipation dynamics of IMI, THM, and CLO in paddy water was in accordance with the first-kinetic model (**Table S2**). The dissipation rate was much faster for CLO (with a $T_{1/2}$ of about 6.00 d) and IMI (~6.11 d) than THM (~10.5 d). The dissipation rates of IMI, THM, and CLO all reached the highest value (97.0%, 89.7%, and 97.3%, respectively) on the 36th day after their application. With the growth of rice, the degradation of NNIs will be accelerated with increasing ambient temperature, light intensity, and light duration (Chen et al., 2017). The similar dissipation trends between IMI and CLO and different ones between these two species and THM should be caused by their similar and different physicochemical properties. In addition, the natural water body is a complex system with many different metal ions and dissolved organic matter, which also affected the dissipation of NNIs after their entrance into the water (Todey et al., 2018).

3.2 Dynamics of neonicotinoid insecticides in soil

Residues of NNIs in soil accumulate through multiple pathways such as application, adsorption, and diffusion. At the initial stage of spray, NNIs can be enriched in the soil through deposition. However, NNIs are highly water-soluble and with high mobility, they are easily desorbed from the soil and enter the water body, which reduces the concentration of NNIs in soil (Pietrzak et al., 2020; Niu et al., 2022). As the water demand decreases in the later stages of rice plant growth, paddy water gradually disappears due to evaporation and seepage, causing NNIs to reaccumulate in the soil. Therefore, the concentrations of NNIs in the soil decreased first and then increased throughout the rice growth cycle. Soil residual concentrations of NNIs were on the order of ng/g dw (IMI: 2.41-68.3 ng/g dw; THM: 0.57-6.81 ng/g dw; CLO: 0.76-27.1 ng/g dw) (**Fig. 2(a)**), similar to those reported for the Qixing River basin (Liu et al., 2023b). The residual concentrations of NNIs in soil were the highest at 2 h after application, with IMI, THM, and CLO at 68.3, 6.80, and 27.1 ng/g, respectively. At harvest, the concentrations of IMI, THM, and CLO in the soil were 15.7, 0.59, and 11.9 ng/g, accounting for 22.9%, 0.87%, and 43.9% of the initial deposition, respectively. By fitting the first-order reaction kinetic equation to NNIs in soil (**Table S3**) resulted in $T_{1/2}$ of THM and CLO being about 6.06 d and 5.43 d, respectively. However, the IMI dissipation process in soil did not follow the first-order kinetic equation, likely due to its different physicochemical properties.

To investigate the distribution characteristics of the three NNIs in soil-water systems, K_d (C_{soil}/C_{water}) values during exposure were calculated, as shown in **Fig. 2(b)**. The K_d values of IMI decreased from days 0-5, then increased from days 5-36, and finally decreased again afterwards; the K_d values of THM decreased from days 0-5, followed by an increase, reaching the maximum at 11th day, and then decreased afterwards; and the K_d values of CLO decreased from days 0-11 and then increased afterwards. K_d values of IMI and CLO were the highest at 2 h, which were 0.07 and 0.0088, respectively. The maximum K_d value of THM appeared at 11th day, which was 0.0030, slightly higher than 0.0025 at 2 h. The decrease in K_d values of NNIs were likely because of their high water solubility, for example, a previous study on sediment-water exchange showed that the three NNIs in sediment can diffuse into water as a secondary release source (Liu et al., 2021). The activities of microorganisms in the soil can also decrease NNIs concentrations continuously, resulting in a downward trend in their K_d value. In addition, the changing water demand during rice growth period is one of the influencing factors leading to changes in K_d values.

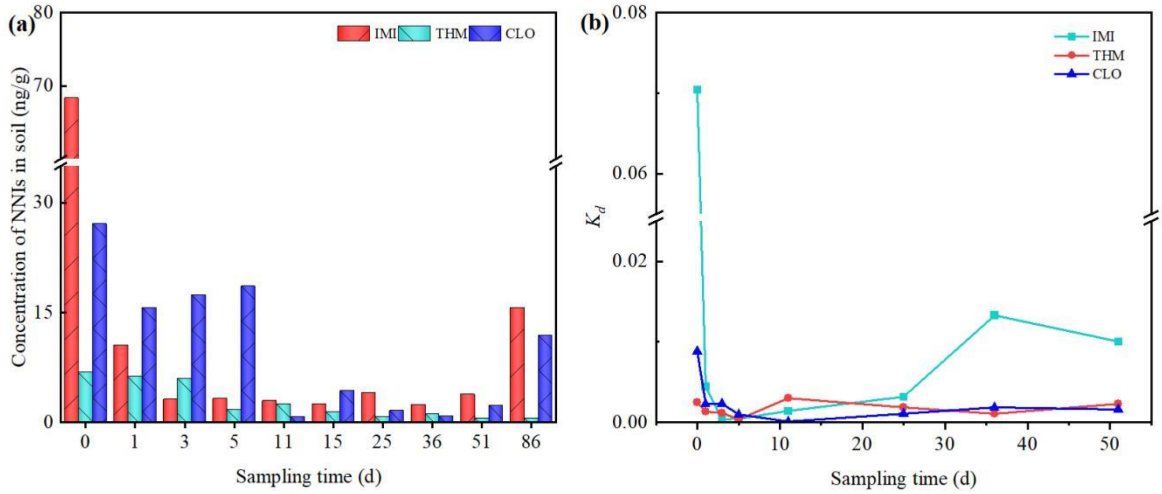

Fig. 2 Concentrations of NNIs in soil (a) and K_d values of NNIs in the soil-water system (b).

3.3 Dynamics of neonicotinoid insecticides in rice plants

The concentrations and dynamic procedures of NNIs in rice roots are shown in **Fig. 3(a)**. The three NNIs showed the same time trends in the rice roots, in which the highest concentrations of NNIs were found at the beginning of the application period. The maximum root concentrations of IMI (5.19 μg/g), THM (3.02 μg/g), and CLO (5.24 μg/g) all appeared at 2 h after their application. However, the concentration of NNIs in the roots decreased continuously in the following days due to the growth and metabolism of rice, and the trend observed in the present study is similar to that previously reported by Liu et al (2023a). Their dissipation dynamics were consistent with the first-order reaction kinetic equation (**Table S4**). NNIs can be quickly absorbed systemically after application and then transmit to various parts of the plant, thus effectively controls pests reproduction. Meanwhile, the high water solubility of NNIs results in high concentrations in soil pore water, which in turn causes high residual concentrations in the rice root after application, noting that it is the NNIS amount dissolved in soil pore water that determines the amount that can be taken up by plants (Li et al., 2022).

Stem and leaf were investigated together at the early stages of rice plant growth due to their indistinct differentiation in this period and were only separately investigated at later growth stages. From **Fig. 3(b)** it can be seen that the residual concentrations of NNIs in the plants had a similar trend to that in the root system, with the highest initial deposition observed for CLO (52.6 μg/g), followed by IMI (19.3 μg/g) and THM (9.36 μg/g). This may be mainly caused by the different amounts of NNIs used per unit area and the chemical composition of pesticides. From the 25th day to the harvest stage, the NNIs concentrations in both stems and leaves showed a decreasing trend **(Fig. 3(c)** and **3(d)**, respectively. Other factors such as weather, environmental conditions, physicochemical properties of the compounds, and the dilution effect of the rapid growth of rice were also the reasons for the decreases of the NNIs concentrations.

The dissipation dynamics of the three NNIs in both roots and plants followed the first-kinetic model (**Table S4**). The $T_{1/2}$ of IMI, THM, and CLO in the root were about 1.07, 0.51, and 3.52 d, respectively, and in the plant were about 1.32, 0.99, and 1.96 d, respectively. The $T_{1/2}$ of these NNIs were all less than 30 days, indicating that they are easily digestible pesticides. The longer $T_{1/2}$ of CLO than IMI and THM indicated CLO has a longer duration of efficacy and a higher residue risk than the latter two species. Thus, it is necessary to consider the application period when using CLO to ensure its residues to be at safe levels.

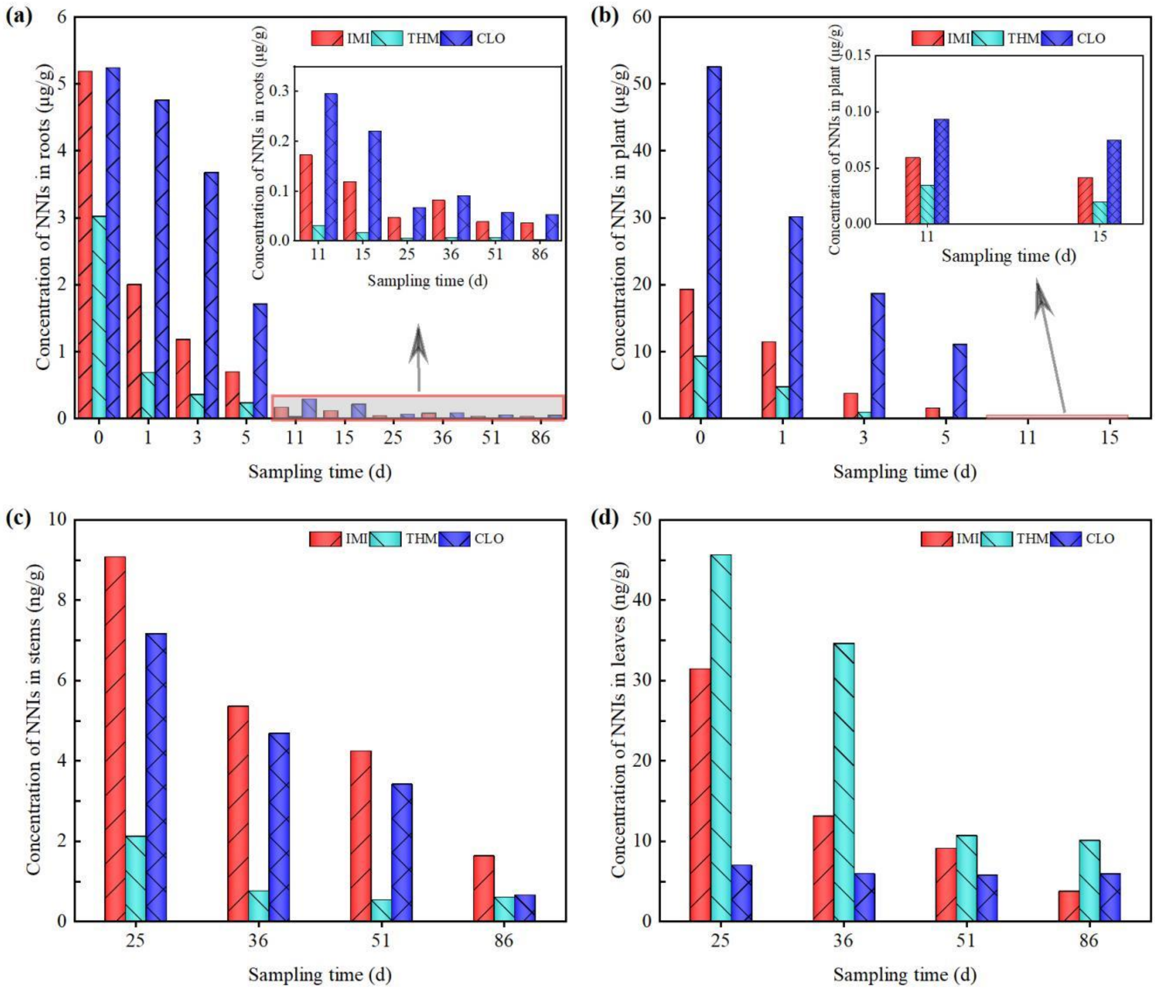

Fig. 3 Concentrations of NNIs in roots (a), plant (b), stems (c), and leaves (d).

3.4 Migration of neonicotinoid insecticides in paddy fields

From discussions above we know that residues of NNIs in rice plants are mainly caused by direct spraying, with the highest residual concentrations appeared at the early stage of application. The residual concentrations in rice plants gradually decrease due to the combined effects of rice metabolism and various environmental factors (rainfall, temperature, etc.). For example, the 56.5 mm rainfall accumulated between July 6-12 (6-12 days after spraying) lowered substantially the residual concentrations of NNIs in water, soil, and plants in the paddy field through surface runoff, which also leads to NNIs pollution in other environmental media. Meanwhile, irrigation and drainage behavior during different growth periods of rice also cause outward migration of NNIs. In recent years, the prolonged and frequent applications of NNIs have rendered wetland and river environments most vulnerable due to the impact of agricultural drainage processes and the high solubilities of NNIs. It is thus imperative to decrease the dosage and frequency of NNIs application in order to safeguard water environments.

Fig. 4(a) and **(b)** illustrate the BCFs of the three NNIs in rice roots and plant tissues. IMI exhibits the highest BCFs, followed by CLO and THM, indicating that IMI has the strongest ability to accumulate within rice plants. Particularly in roots, RCF of both IMI and CLO decreased initially and then increased slightly with time, suggesting the potential upward migration of NNIs from rice roots. For example, a study by Liu et al. (2023a) found that NNIs primarily accumulate in rice leaves, indicating their strong upward translocation ability from the root system.

From **Fig. 4(c)** it can be observed that both IMI and CLO have $TF_{root/plant}$ values less than 1 during 0-5 days after application, but greater than 1 during 11-25 days after application. However, THM only shows a $TF_{root/plant}$ value greater than 1 on the 5th day after application, indicating its ability to migrate downward. The translocation ability depends on the insecticide type (its physicochemical properties) and growth stage of the crop. Li et al. (2018) investigated the uptake and translocation differences of five NNIs in komatsuna by examining RCF and TF, and found that THM had a weaker ability to translocate to the leaves and tended to accumulate in the roots, while acetamiprid exhibited the opposite trend. When log K_{ow} of a pesticide is higher, it tends to accumulate in the plant roots and has a weaker translocation ability towards the upper leaves; otherwise, it can be absorbed by the plant roots and has the ability to migrate towards the upper leaves (Qiu et al., 2016; Gong et al., 2020). Additionally, in most cases, log K_{ow} of a pesticide positively correlates with RCF and negatively correlates with TF (Namiki et al., 2018).

Therefore, NNIs can be absorbed by plants through foliar application as well as root absorption from paddy field water, achieving bidirectional translocation within the plant tissues. In general, pesticides transported through the phloem can be translocated both upward and downward within the plant, while those transported through the xylem predominantly move from the roots toward the upper parts of the plant (Zhang et al., 2022).

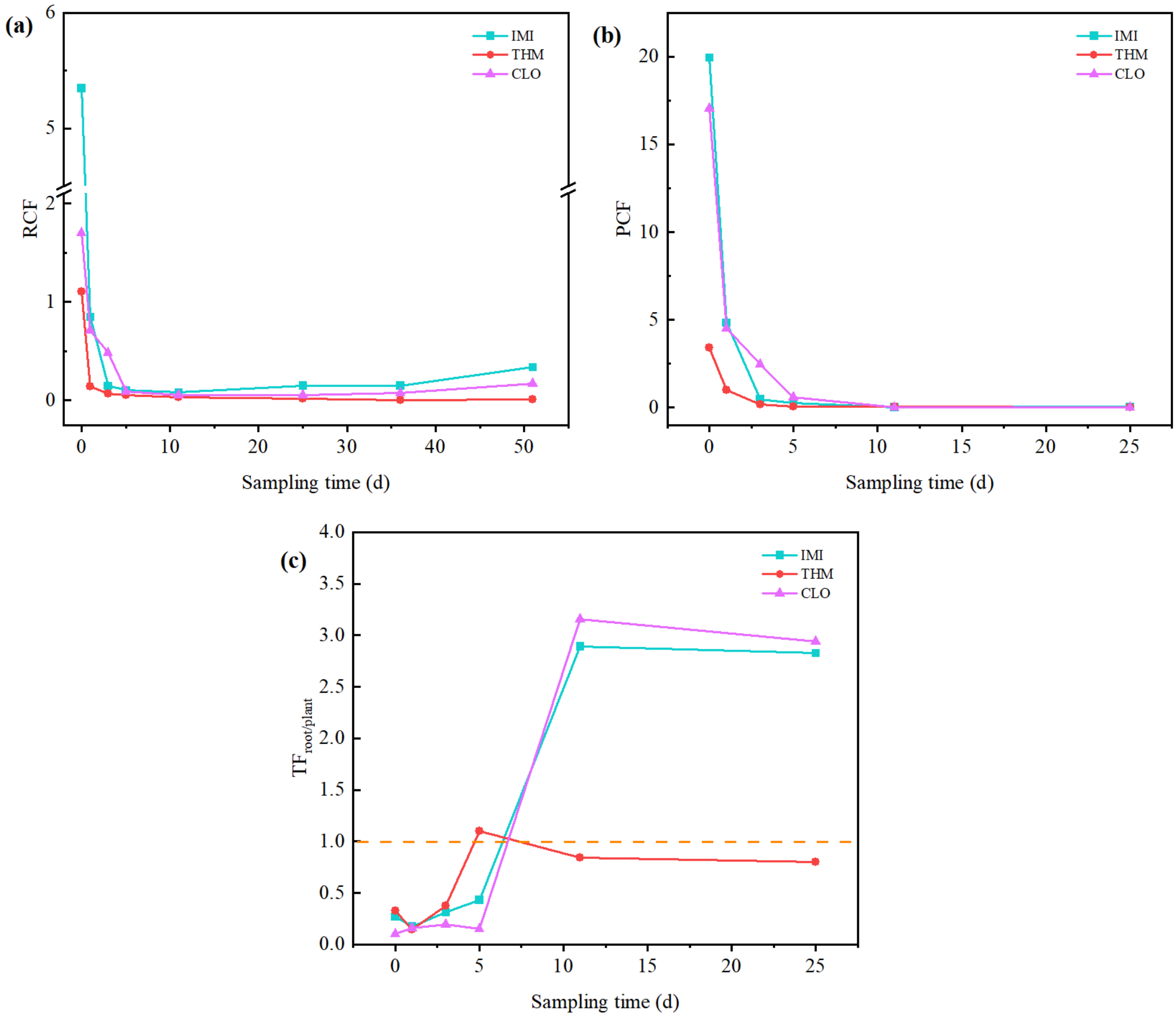

Fig. 4 Bioconcentration factors of NNIs in rice roots (a) and plant tissues (b) and translocation factor of NNIs in rice (c).

3.5 Dietary risk assessment for neonicotinoid insecticides in brown rice

The residual concentrations of IMI, THM, and CLO in brown rice at the harvest are 0.82, 0.07, and 0.11 ng/g, respectively, which are much lower than the maximum pesticide residue levels specified for rice (0.05, 0.1, and 0.2 mg/kg) (GB 2763-2021) (NHC et al., 2021). The long-term chronic risk values were determined by the ratio of

NEDI or TMDI to ADI and were subsequently used for dietary risk assessments for different age groups, as shown in **Tables S5** to **S7**. Overall, dietary exposure risk is slightly higher for male than female, and long-term dietary exposure risk decreases with increasing age. Among the different age groups, the 2-3- and 4-6-year-old populations exhibit the highest long-term chronic dietary risks due to their lower body weight and relatively higher rice intake. Therefore, special attention is needed for young children and toddlers. The risk values for the three NNIs, RQ_N and RQ_T, are all less than 1 (**Table 1**). Consequently, the dietary risks associated with the intake of NNIs through rice consumption are generally low for all age groups although such risks differ for different age and gender groups.

Table 1 Risk quotients of NNIs in brown rice for the Chinese population.

Age (years)	IMI				THM				CLO			
	Male		Female		Male		Female		Male		Female	
	RQ_N	RQ_T	RQ_N	RQ_T	RQ_N	RQ_T	RQ_N	RQ_T	RQ_N	RQ_T	RQ_N	RQ_T
2-3	1.13×10^{-4}	6.90×10^{-3}	1.18×10^{-4}	7.17×10^{-3}	7.25×10^{-6}	1.04×10^{-2}	7.53×10^{-6}	1.08×10^{-2}	9.11×10^{-6}	1.66×10^{-2}	9.46×10^{-6}	1.72×10^{-2}
4-6	1.13×10^{-4}	6.90×10^{-3}	1.05×10^{-4}	6.40×10^{-3}	7.25×10^{-6}	1.04×10^{-2}	6.72×10^{-6}	9.60×10^{-3}	9.11×10^{-6}	1.66×10^{-2}	8.45×10^{-6}	1.54×10^{-2}
7-10	1.02×10^{-4}	6.21×10^{-3}	9.72×10^{-5}	5.93×10^{-3}	6.52×10^{-6}	9.32×10^{-3}	6.22×10^{-6}	8.89×10^{-3}	8.20×10^{-6}	1.49×10^{-2}	7.82×10^{-6}	1.42×10^{-2}
11-13	8.28×10^{-5}	5.05×10^{-3}	7.39×10^{-5}	4.51×10^{-3}	5.30×10^{-6}	7.57×10^{-3}	4.73×10^{-6}	6.76×10^{-3}	6.66×10^{-6}	1.21×10^{-2}	5.95×10^{-6}	1.08×10^{-2}
14-17	6.95×10^{-5}	4.24×10^{-3}	5.81×10^{-5}	3.54×10^{-3}	4.45×10^{-6}	6.36×10^{-3}	3.72×10^{-6}	5.32×10^{-3}	5.60×10^{-6}	1.02×10^{-2}	4.68×10^{-6}	8.50×10^{-3}
18-29	6.03×10^{-5}	3.68×10^{-3}	5.84×10^{-5}	3.56×10^{-3}	3.86×10^{-6}	5.51×10^{-3}	3.74×10^{-6}	5.34×10^{-3}	4.85×10^{-6}	8.82×10^{-3}	4.70×10^{-6}	8.55×10^{-3}
30-44	5.78×10^{-5}	3.52×10^{-3}	5.80×10^{-5}	3.54×10^{-3}	3.70×10^{-6}	5.28×10^{-3}	3.71×10^{-6}	5.30×10^{-3}	4.65×10^{-6}	8.45×10^{-3}	4.67×10^{-6}	8.49×10^{-3}
45-59	5.88×10^{-5}	3.59×10^{-3}	5.64×10^{-5}	3.44×10^{-3}	3.76×10^{-6}	5.38×10^{-3}	3.61×10^{-6}	5.16×10^{-3}	4.73×10^{-6}	8.61×10^{-3}	4.54×10^{-6}	8.25×10^{-3}
60-69	5.27×10^{-5}	3.21×10^{-3}	5.27×10^{-5}	3.21×10^{-3}	3.37×10^{-6}	4.82×10^{-3}	3.37×10^{-6}	4.82×10^{-3}	4.24×10^{-6}	7.71×10^{-3}	4.24×10^{-6}	7.71×10^{-3}
> 70	5.20×10^{-5}	3.17×10^{-3}	5.16×10^{-5}	3.15×10^{-3}	3.33×10^{-6}	4.76×10^{-3}	3.31×10^{-6}	4.72×10^{-3}	4.19×10^{-6}	7.61×10^{-3}	4.16×10^{-6}	7.56×10^{-3}

4. Conclusions

NNIs have become one of the main types of insecticides used in rice fields, which have led to reduced efficacy and increased dosage due to years of continuous use and multiple use in one single season. Results of our study showed that the dissipation of the three NNIs in the water-soil-plant system of paddy field mostly followed the first-order kinetic equations, demonstrating that they belong to the easily digestible class of pesticides. The high water solubility of NNIs results in their high susceptibility to desorption from soil into paddy water, indicating that aquatic ecosystems affected by farmland drainage are vulnerable. NNIs can be absorbed by rice plants through foliar spray as well as through root absorption once the active ingredients dissolve into paddy water, realizing bidirectional conduction in plants. The final residual concentrations of NNIs in rice would be at a safe level if only spray once at the tillering stage. Knowledge gained from this study improved our understanding of the uptake, migration, and distribution mechanisms of the three NNIs in the water-soil-plant system of paddy fields, and provided a scientific basis for managing NNIs usage and safeguarding food security. To protect the water environment and reduce pest resistance and the toxicity of non-target organisms, it is necessary to reduce the dosage and frequency of NNIs applications. Monitoring NNIs residues in groundwater and surface water in rice cultivation area is strongly recommended, especially during the NNIs application periods.

Conflict of interest

The authors declare no conflict of interest.

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