

Article

# Neonicotinoid detection in rainwater in Japan

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# ABSTRACT

Since 1993, neonicotinoid insecticides have been used extensively in Japan, primarily for rice cultivation and pine forest protection. The spread of neonicotinoids to the natural environment is largely through runoff from agricultural lands; however, precipitation could also become a potential medium even though neonicotinoids have low vapor pressures. While previous studies have reported the dry deposition and particulates of neonicotinoids in the air, this study investigated the wet deposition of these insecticides. Rainwater samples from Tsukuba and Kashiwa, Japan, were collected and analyzed by liquid chromatography–tandem mass spectrometry in April, June, and September 2023, as well as in January, April, June,



August, and September 2024. Results revealed that 91% of the samples contained neonicotinoids, with the highest total concentration of 1.72 ng/L detected in August 2024. Acetamiprid ranked first with a detection frequency of 82% and an average concentration of 0.36 ng/L, followed by thiacloprid (73%, 0.28 ng/L) and dinotefuran (45%, 0.52 ng/L). This research is the first report on neonicotinoid presence in precipitation, suggesting that neonicotinoids, as low volatile matter, can still be dispersed to the environment via precipitation.

Key words: neonicotinoid; pollution; precipitation; rainwater; Japan

# **INTRODUCTION**

Neonicotinoids are a class of systemic chemical insecticides that target the nervous system of insect pests by acting selectively on post-synaptic nicotinic acetylcholine receptors and interfering with synaptic transmission (Buszewski et al., 2019). These insecticides have been used widely around the globe (Morrissey et al., 2015), including in Japan. Neonicotinoids were first registered in Japan in November 1992 and have been extensively used since then. In recent times, they have ranked second among the top insecticides used in Japan with an average nationwide shipment value of 420.18 tons or kL in 2019–2021 (NIES, 2024). Currently, seven compounds are circulating within the community in the country, namely acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid, and thiamethoxam, notably for cultivating

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rice, which is the most important crop in Japan (MAFF, 2023). Furthermore, neonicotinoids in Japan are used to protect pine trees from pine wilt disease by spraying insecticides over large areas using a jet-spray machine or helicopter (Ikenaka et al., 2019).

Despite their function in combating pests, neonicotinoids are persistent in water owing to their low log Kow values, high water solubility, and high resistance to hydrolysis (Table 1), resulting in contamination in aquatic environments. In Japan, previous studies have confirmed the occurrence of neonicotinoids in various types of environmental waters, including estuarine waters (Hano et al., 2019), rivers (Sato et al., 2016; Nakayama and Nishima, 2019; Hayashi et al., 2021; Sugino et al., 2023), and lakes (Sugino et al., 2023). Several other studies have also investigated neonicotinoid pollution in environmental waters throughout the world, such as in China (Liu et al., 2021; Naumann et al., 2022; Luo et al., 2023), South Korea (Kim et al., 2023; Lee et al., 2024; Park et al., 2024), Canada (Lalonde and Garron, 2020; Schaafsma et al., 2019), Australia (Laicher et al., 2022; Warne et al., 2022), USA (Berens et al., 2021; Silvanima et al., 2022),



Compound	Lipophilicity (log Kow)	Water solubility at 20°C (mg/L)	Water hydrolysis (DT <sub>50</sub> in days) <sup>a)</sup>	Water photolysis (DT <sub>50</sub> in days)	$\begin{array}{c} \text{Soil} \\ \text{persistence} \\ (\text{DT}_{50} \text{ in days})^{\text{b})} \end{array}$	Soil affinity (log Koc)	Molecular mass (g/mol)	Vapor pressure at 25°C (Pa)
Acetamiprid	0.80	2950	Stable	34	2-20	2.3	222.7	$1 \times 10^{-6}$
Thiacloprid	1.26	184	Stable	10 - 63	9-27	3.67	252.7	$8 \times 10^{-10}$
Dinotefuran	- 0.55	39830	Stable	<2	50 - 100	1.41	202.2	$5 \times 10^{-5}$
Clothianidin	0.91	340	Stable	< 1	13-1386	2.08	249.7	$1.3 \times 10^{-10}$
Thiamethoxam	-0.13	4100	Stable	2.7 - 39.5	7-72	1.75	291.7	$6.6 \times 10^{-9}$
Imidacloprid	0.57	610	Stable	< 1	104 - 228	2.19 - 2.90	255.7	$9 \times 10^{-10}$
Nitenpyram	- 0.66	590000	Stable	< 1	1-15	1.78	270.7	$1.1 \times 10^{-9}$

Table 1 Neonicotinoid physicochemical properties (Morrissey et al., 2015; Ikenaka et al., 2019)

<sup>a)</sup> Under acidic or neutral pH conditions.

<sup>b)</sup> Under anaerobic conditions.

Portugal (Sousa et al., 2020), Vietnam (Wan et al., 2021), Indonesia (Putri et al., 2022; Putri et al., 2023), and the Philippines (Bonmatin et al., 2021). Neonicotinoid pollution in aquatic environments decreased the abundance and biomass of nontarget aquatic insects such as Coleoptera, Diptera, Ephemeroptera, Odonata, and Trichoptera (Barmentlo et al., 2021), and crustacea such as Copepoda (Schepker et al., 2020), causing a population decline of their predators (Yamamuro et al., 2019; Li et al., 2020; Duchet et al., 2023).

Neonicotinoids as pesticides enter environmental waters primarily through runoff and drainage from applied areas, such as agricultural fields (Bonmatin et al., 2015; Morrissey et al., 2015); however, precipitation could potentially become another dispersion medium. As a pesticide, neonicotinoids can move into the atmosphere through evaporation, spray drift, dust drift, and wind erosion of contaminated soils during and after application (USGS, 2014). Although these insecticides have low volatilities owing to low vapor pressures (Table 1), their application in granular form and wettable powders can lead to the development of dust containing neonicotinoids (Bonmatin et al., 2015; Zhou et al., 2020). Aerial spraying by unmanned aircraft can also result in the penetration of neonicotinoid into soils (Kobayashi et al., 2014) and recontamination of the atmosphere as soil dust. Atmospheric neonicotinoids and their dry deposition were studied in advance at several different times and distances from the applied areas, such as Canada (Forero et al., 2017), China (Zhou et al., 2020), Italy (Biocca et al., 2014), and Japan (Ichikawa et al., 2008; Takenouchi and Aoi, 2016; Ikenaka et al., 2019), showing that these insecticides could be carried by the wind to other areas and remained in the air for some time. As they are highly water-soluble, neonicotinoids may return to the Earth's surface with precipitation and, at the end, join the environmental water.

To date, the possible contribution of precipitation in dispersing neonicotinoids in the environment is unclear. No study has investigated neonicotinoid content in precipitation while it can be a medium for dispersing pollutants to the aquatic environment that threatens nontarget organisms. Therefore, this study was conducted with the aim of observing neonicotinoid presence in the rainwater in Japan. To the best of our knowledge, this study is the first to provide information on neonicotinoid occurrence in precipitation and enrich knowledge about its environmental fate.

## MATERIALS AND METHODS

#### **CHEMICALS**

Seven certified neonicotinoid standard solutions (acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid, and thiamethoxam; 20  $\mu$ g/mL) with a purity >99% were obtained from Fujifilm Wako Pure Chemical Corporation, Japan. The internal standard solution of the compounds (acetamiprid-d3, clothianidin-d3, target dinotefuran-d3, imidacloprid-d4, nitenpyram-d3, thiacloprid-d4, and thiamethoxam-d3; 10  $\mu$ g/mL) with a purity  $\ge$  98% was purchased from Hayashi Pure Chemicals Industries, Ltd., Japan. The LCMS grade methanol, 99% (v/v) formic acid solution, and 1 mol/L ammonium acetate solution were obtained from Fujifilm Wako Pure Chemical Corporation, Japan. Ultrapure water was prepared using a PURELAB flex3 machine from ELGA LabWater, UK.

The mixed working standard solution was prepared at  $200 \ \mu g/L$  for all compounds, and their mixed working internal standard solution was prepared at  $100 \ \mu g/L$  by mixing each with 20% (v/v) methanol. Subsequently, the diluted working neonicotinoid standard solution was used to make standard solutions for calibration with concentrations of 0.5, 1, 2, 5, 10, 30, and  $100 \ \mu g/L$  by mixing it with the diluted working internal standard solution and 20% (v/v) methanol. All standard and internal solutions were placed in amber glass vials and stored in a refrigerator at  $8^{\circ}$ C.

#### STUDY AREA AND SAMPLE COLLECTION

A total of 11 rainwater samples were collected from one location in Tsukuba (36°04'14.5884" N, 140°07'01.6392" E) on April 15, 2023, June 2, 2023, September 8, 2023, January 21, 2024, June 23, 2024, and August 22, 2024, and from one location in Kashiwa (35°54'1.296" N, 139°56'2.3064" E) on January 21, 2024, April 24, 2024, June 18, 2024, August 16, 2024, and September 1, 2024. Tsukuba is in the Ibaraki Prefecture, which is the 7<sup>th</sup> highest rice producer in Japan, with an annual rice production of 360,000 tons (MAFF, 2023). Kashiwa is a city in Chiba Prefecture, which is the 9<sup>th</sup> highest rice producer in function of 297,500 tons

	]	lbaraki p	refectur	е		Chiba pi	refecture	9
Compound	2019	2020	2021	Mean	2019	2020	2021	Mean
Acetamiprid	1.05	0.92	0.85	0.94	0.77	0.79	0.69	0.75
Thiacloprid	0.38	0.35	0.41	0.38	0.65	0.44	0.77	0.62
Dinotefuran	3.89	4.51	4.88	4.43	4.48	4.78	4.95	4.74
Clothianidin	4.77	5.14	5.57	5.16	2.20	2.36	2.29	2.28
Thiamethoxam	1.46	1.62	1.82	1.63	0.88	0.87	1.27	1.01
Imidacloprid	2.70	3.14	3.25	3.03	1.82	1.72	2.16	1.90
Nitenpyram	0.54	0.57	0.70	0.60	0.47	0.49	0.46	0.47
Total	14.76	16.25	17.48	16.16	11.27	11.45	12.59	11.77

Table 2 Average shipment value of neonicotinoids (tons or kL) in Ibaraki and Chiba prefectures in 2019–2021 (NIES, 2024)<sup>a)</sup>

<sup>a)</sup>Data were not available for recent years.

Table 3 Meteorological conditions during rainwater sampling and pH of the samples

	Meteorologio		
Sample	Precipitation (mm)	Air temperature (°C)	pH <sup>b)</sup>
Tsukuba samples			
April 15, 2023	27.5	13.8	6.2
June 2, 2023	174.5	20.9	6.2
September 8, 2023	91.0	22.5	6.1
January 21, 2024	33.0	9.1	5.8
June 23, 2024	29.5	22.0	6.0
August 22, 2024	1.5	26.4	5.6
Kashiwa samples			
January 21, 2024	37.5	7.3	5.9
April 24, 2024	12.5	14.7	6.1
June 18, 2024	74.5	18.7	6.2
August 16, 2024	29.5	26.5	6.3
September 1, 2024	6.5	26.5	5.7

<sup>a)</sup> Data were derived from the Japan Meteorological Agency website: the nearest station was in Tsukuba for the Tsukuba samples and in Abiko for the Kashiwa samples (JMA, 2024).

<sup>b)</sup> pH was measured using a pen-type pH meter PH-009 IA from Fuzhou Hedao Trade Co., Ltd., China, with an accuracy of ±0.1 pH.

(MAFF, 2023). Ibaraki and Chiba are also the  $4^{\text{th}}$  and  $13^{\text{th}}$  largest consumers of neonicotinoids among prefectures in Japan, with average shipment values of 16.16 tons/kL and 11.77 tons/kL, respectively, from 2019 to 2021 (Table 2). The meteorological conditions during the sample collection times and the pH of each sample are presented in Table 3.

Rainwater was sampled using a clean polypropylene 8.9L-sealed bucket that was rinsed with ultrapure water and dried at room temperature before use. The bucket was placed on the second floor of a building in Tsukuba and on the rooftop of a building in Kashiwa to prevent contamination from the soil at the ground. Approximately 400 mL of the rainwater sample was collected at each sampling time and placed in a black high-density polyethylene J bottle 1530-15 series (Nikko Hansen & Co., Ltd., Japan) to prevent the photolysis of neonicotinoids in the sample. Samples were filtered using Whatman glass microfiber filter paper (GF/F with a pore size of 0.7  $\mu$ m) after collection to remove the suspensions and prevent degradation. The filtered samples were then stored in a refrigerator (8°C) for further analysis in the laboratory.

#### **NEONICOTINOID EXTRACTION**

The neonicotinoid extraction method followed that of Yamamuro et al. (2024) with modifications. 40 µL of mixed working internal standard solution (100  $\mu$ g/L) was added to 200 mL of the filtered water sample. Solid phase extraction (SPE) cartridges (Inertsep® Pharma FF 60 mg/3 mL, used for Tsukuba rainwater collected in 2023 and January 2024 and for Kashiwa rainwater collected in January 2024; and Inertsep® Pharma FF 200 mg/6 mL, used for the rest of the samples) were conditioned by flowing 10 mL of methanol and 50 mL of ultrapure water, with a 10 mL/min flow rate using AQUALoader AL898U from GL Sciences, Japan. The filtered water sample was passed through the cartridge to capture neonicotinoids at a 5 mL/min flow rate. The cartridges were then washed with 50 mL of ultrapure water at the same flow rate as the water sample to remove the water sample remaining inside the tube. The remaining water in the cartridges was then blown out using a syringe, and the cartridges were dehydrated by placing them in a centrifuge for 10 min at a velocity of 4,000 rpm. The neonicotinoids and internal standards were then eluted from the cartridges using 6 mL of methanol with a flow rate of 1 drop / 3 s at a GL-SPE vacuum manifold (GL Sciences, Japan). The extracts were concentrated to dryness using nitrogen gas and a heater (40°C) and then reconstituted with 400  $\mu$ L of a 20% (v/v) methanol solution. The extract solutions were mixed using a vortex mixer and centrifuge (for 1 min at 4,000 rpm) and then transferred into vials for analysis.

## LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY (LC-MS/MS) ANALYSIS

Neonicotinoids were analyzed using a LC-MS/MS instrument by injecting 10  $\mu$ L of eluate containing neonicotinoids into a Nexera HPLC system coupled to an LCMS-8030 triple quadrupole mass spectrometer (Shimadzu Corporation, Japan). Each compound was separated by a Cadenza CX-C18 UP column (3  $\mu$ m, 2 mm × 150 mm) (Imtakt, Japan) at an oven temperature of 40°C. The mobile-phase solvents comprised ultrapure water (A) and methanol (B), both of which contained 0.1% (v/v) formic acid and 10 mM ammonium acetate. The chromatographic separation was performed at a 0.2 mL/min flow rate with gradient shifting as follows: t = 0 to 2 min, 10% solvent B; t = 6 min, 40% solvent B; t = 12 min, 65% solvent B; t = 14 to 17 min, 95% solvent B; and then equilibration for 2.9 min to return to the initial condition of 10%. All compounds and their internal standards were analyzed in a positive-ion polarity mode using multiple reaction monitoring (MRM) with one precursor ion and three product ions (Table 4). The product ion with the largest peak area was chosen for quantification, while the product ions with the second and third largest peak areas were used for confirmation.

# ANALYTICAL METHOD VALIDATION AND QUALITY CONTROL

The linearity of each target compound was evaluated using calibration curves that were constructed by plotting the compound peak area ratios against the concentration of the corresponding calibration standards at several different levels (0.5–100  $\mu$ g/L). Good linearity was obtained for the calibration curves of all the target compounds, with a coefficient of determination (R<sup>2</sup>) of 0.999 for all the compounds (Table 5). Method detection limits (MDL) and method quantitation limits (MQL) were determined by spiking ultrapure water with 1 ng/L of neonicotinoid standards with seven replications; the calculation followed the guidelines of the Ministry of Environment of Japan (MoE, 2004). MDL values ranged from 0.086 to 0.264 ng/L, while MQL values ranged from 0.239 to 1.091 ng/L (Table 5). The total recovery rate

Table 4 MRM of the target neonicotinoids and their internal standards

	Precursor ion $(m/z)$	Product ion for quantification $(m/z)$	Product ion for confirmation 1 $(m/z)$	Product ion for confirmation 2 $(m/z)$	Retention time (min)
Neonicotinoid					
Acetamiprid	223.00	126.00	56.10	99.00	10.050
Thiacloprid	252.90	126.00	99.00	90.10	11.260
Dinotefuran	203.00	129.10	73.10	114.15	6.012
Clothianidin	249.90	169.10	131.95	113.05	9.389
Thiamethoxam	291.90	211.05	181.05	132.00	7.867
Imidacloprid	256.00	209.00	175.10	128.00	9.220
Nitenpyram	271.00	225.10	56.10	126.00	6.403
Internal standard					
Acetamiprid-d3	226.00	126.00	59.10	99.00	10.014
Thiacloprid-d4	256.90	126.00	99.05	90.10	11.218
Dinotefuran-d3	206.00	132.10	76.10	116.15	5.988
Clothianidin-d3	253.00	172.05	131.95	113.05	9.354
Thiamethoxam-d3	295.00	214.10	184.10	132.00	7.841
Imidacloprid-d4	259.70	213.05	179.15	214.10	9.210
Nitenpyram-d3	273.90	228.10	126.00	257.05	6.393

Table 5 Linearity and detection limits of the analytical method used

SPE cartridge <sup>a)</sup>					Inertsep® FF 60 mg	Pharma g/3 mL	Inertsep® FF 200 m	Pharma g/6 mL
Compound	Calibration equation	$\mathbb{R}^2$	IDL (pg)	IQL (pg)	MDL (ng/L) <sup>b)</sup>	MQL (ng/L)	MDL (ng/L) <sup>b)</sup>	MQL (ng/L)
Acetamiprid	y = 0.89400x - 0.01134	0.999	0.685	1.762	0.143	0.369	0.086	0.239
Thiacloprid	y = 0.90405x - 0.02186	0.999	0.451	1.161	0.099	0.255	0.089	0.241
Dinotefuran	y = 1.38540x - 0.03589	0.999	0.439	1.130	0.140	0.361	0.131	0.371
Clothianidin	y = 0.89747x - 0.05050	0.999	0.522	1.344	0.230	0.591	0.158	0.551
Thiamethoxam	y = 0.84343x + 0.00299	0.999	0.294	0.758	0.109	0.280	0.159	0.810
Imidacloprid	y = 1.74590x - 0.08820	0.999	0.659	1.695	0.244	0.629	0.264	1.091
Nitenpyram	y = 0.84940x + 0.07450	0.999	0.471	1.211	0.156	0.402	0.093	0.328

<sup>a)</sup> Different types of SPE cartridges were used because of stock shortage.

<sup>b)</sup> MDL values were used as the detection limits for neonicotinoids in the rainwater samples.

		Recovery (%)		Intraday precision (%)		Recovery (%)		Intraday precision (%)
SPE cartridge <sup>a)</sup>	Inertsep® Pharma FF 60 mg/3 mL Inertsep® Pharma FF 2				FF 200 mg/6 r	nL		
Spike level	1ng/L	2 ng/L	$20 \text{ ng/L}^{\text{b}}$	1 ng/L	1ng/L	2 ng/L	$20 \text{ ng/L}^{\text{b}}$	1 ng/L
	Mean ± RSD	Mean ± RSD	Mean ± RSD	RSD	Mean ± RSD	Mean ± RSD	Mean ± RSD	RSD
Acetamiprid	64 ± 7.84	$96 \pm 0.37$	98 ± 4.70	3.34	99 ± 1.38	86 ± 5.36	$99 \pm 0.29$	2.53
Thiacloprid	$91 \pm 8.83$	$98 \pm 3.09$	$99 \pm 4.04$	2.40	$94 \pm 3.36$	$84~\pm~5.31$	$95 \pm 0.07$	2.63
Dinotefuran	$101~\pm~6.79$	$109~\pm~6.26$	$106 \pm 5.75$	3.09	$100~\pm~1.29$	$86~\pm~4.69$	$100~\pm~1.11$	3.87
Clothianidin	$105~\pm~6.82$	$110 \pm 2.14$	$102~\pm~5.86$	5.39	$114 \pm 3.28$	$101 \pm 2.90$	$100 \pm 2.29$	4.67
Thiamethoxam	$97~\pm~9.09$	$103~\pm~1.12$	$101 \pm 6.67$	2.79	$128~\pm~9.60$	$114~\pm~8.47$	$103 \pm 2.18$	4.69
Imidacloprid	$89 \pm 7.53$	$104~\pm~4.81$	$102~\pm~5.46$	5.70	$113 \pm 5.18$	$106~\pm~0.04$	$104~\pm~1.91$	7.76
Nitenpyram	$84 \pm 8.53$	$95 \pm 2.84$	$103~\pm~4.85$	3.69	$111~\pm~1.03$	$100~\pm~8.55$	$101~\pm~0.63$	2.74

Table 6 Recovery and precision of the analytical method used

<sup>a)</sup> Different types of SPE cartridges were used because of stock shortage.

<sup>b)</sup> Recovery analysis for the mentioned spike level used ultrapure water because of the rainwater shortage.

was examined to test the method's accuracy by spiking 200 mL of rainwater samples with 1 ng/L, 2 ng/L, and 20 ng/L of neonicotinoid standards following three replications each. The recovery rates of all target compounds were in the range of 64%–128% for 1 ng/L, 84%–114% for 2 ng/L, and 95%–106% for 20 ng/L (Table 6). Precision was tested through repeatability using ultrapure water spiked at 1 ng/L of neonicotinoid standards with seven replications, analyzed on the same day (intraday), and expressed in the form of a relative standard deviation (RSD). The precision values varied between 2.4% and 7.76% (Table 6).

Furthermore, all rainwater samples were processed in duplicate with an RSD of less than 10%. The analysis of a solvent blank consisting of methanol/ultrapure water (20:80, v/v) was also conducted directly after calibration standards and after every tenth sample to monitor any carryover of target compounds from one sample to the next during LC-MS/MS analysis. The procedural blank was prepared using ultrapure water, which then underwent the entire preparation and analytical procedure in the same manner as the rainwater sample to assess any contamination that occurred during any part of the analysis process. A blank spike was also made to ensure that the analytical procedure was performed correctly by spiking ultrapure water with 2, 10, and 20 ng/L of neonicotinoid standards, which was then prepared and analyzed through the same procedure as the rainwater sample. No target compounds were detected in the solvent and procedural blanks, and the blank spike contained target neonicotinoids at concentrations similar to the spike level.

### **RESULTS AND DISCUSSION**

The rainwater samples contained neonicotinoid compounds in a relatively small concentration, presumably owing to their low volatilities. Data showed a 91% detection rate of neonicotinoids in the rainwater samples, with an average total concentration of 0.90 ng/L (Table 7). Acetamiprid was the most frequently detected compound (a detection frequency of 82%), followed by thiacloprid (73%) and dinotefuran (45%) (Table 7). The highest average concentration was dinotefuran (0.52 ng/L), while the second-highest was clothianidin (0.39 ng/L); acetamiprid was placed third with 0.36 ng/L (Table 7). Thiamethoxam had the lowest detection frequency (27%) and average concentration (0.19 ng/L) (Table 7). In contrast, imidacloprid and nitenpyram were not detected in any of the samples. The Spearman correlation analysis revealed a moderate negative relationship between the total concentrations of neonicotinoids and the total precipitation (Spearman's  $\rho$  of – 0.410), meaning that higher precipitation could result in lower total concentrations of neonicotinoids as the insecticides would be highly diluted. However, the correlation was not significant ( $\rho$  = 0.21); thus, the presence of neonicotinoids in the rainwater samples might be more affected by other factors, such as their properties and usage.

Acetamiprid has the second-highest vapor pressure and smallest molecular mass (Table 1) compared to other compounds, which possibly allowed it to vaporize, even though its average shipment values in Ibaraki Prefecture and Chiba Prefecture ranked fifth and sixth, respectively (Table 2). This compound was also more water-soluble and resistant to hydrolysis and photolysis than most other compounds (Table 1), resulting in its higher detection and third-highest average concentration in rainwater. Meanwhile, dinotefuran had the highest average concentration and third-highest detection compared to other compounds, probably due to its highest vapor pressure, smallest molecular mass, and second-highest water solubility (Table 1). The high utilization rate in the regions (Table 2), especially for rice cultivation, also accounts for its high concentration in rainwater. Similarly, in the urban and rural areas of Zhengzhou, China, the PM<sub>2.5</sub> imidacloprid concentration was the highest owing to its extensive use in urban landscaping and agricultural activities (Zhou et al., 2020)

Clothianidin had the second-highest average concentration, presumably owing to its utilization ranking first and second in Ibaraki and Chiba Prefectures, respectively (Table 2). Thiacloprid had the second-highest detection even though the average shipment value of this compound was the lowest

Neonicotinoid	Detection frequency (%)	Detected month	Mean <sup>a)</sup> (range) (ng/L)	MDL (ng/L) <sup>b)</sup>	MDL (ng/L) <sup>c)</sup>
Acetamiprid	82	April, June, and September 2023; April, June, August, and September 2024	0.36 (nd-0.58)	0.143	0.086
Thiacloprid	73	April and June 2023; April, June, August, and September 2024	0.28 (nd-0.50)	0.099	0.089
Dinotefuran	45	June 2023; January, June, and August 2024	0.52 (nd-0.79)	0.140	0.131
Clothianidin	36	June, August, and September 2024	0.39 (nd-0.41)	0.230	0.158
Thiamethoxam	27	June, August, and September 2024	0.19 (nd-0.21)	0.109	0.159
Imidacloprid	-	_	-	0.244	0.264
Nitenpyram	-	_	-	0.156	0.093
Total concentration	91	April, June, and September 2023; January, April, June, August, and September 2024	0.90 (nd-1.72)		

Table 7 Detection frequency and concentration of neonicotinoids in rainwater samples (N =
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"nd" indicates that neonicotinoid was not detected (< MDL).

<sup>a)</sup> Mean concentration was calculated only for samples in which neonicotinoids were detected.

<sup>b)</sup> Using Inertsep® Pharma FF 60 mg/3 mL.

<sup>c)</sup> Using Inertsep<sup>®</sup> Pharma FF 200 mg/6 mL.

one (Table 2); its vapor pressure was the third-lowest (Table 1). The occurrence of this compound in rainwater was presumably because of its lowest water photolysis rate compared to other compounds (Table 1). Imidacloprid was not detected in the rainwater samples, mainly because of its lower vapor pressure (Table 1) despite its high utilization by farmers (Table 2). Likewise, Ikenaka et al. (2019) detected a very low concentration of atmospheric clothianidin during and after application in Nagano Prefecture in 2016, even though its average shipment value in this prefecture was the second-highest compared to other compounds (NIES, 2024). Furthermore, the desorption of imidacloprid from soil organic matter occurred at a low rate when the concentrations were low (Bonmatin et al., 2015), presumably resulting in its low release into the atmosphere. Nitenpyram was not detected either because it is highly unstable under solar exposure or is easily transformed into its metabolites (González-Mariño et al., 2018).

The neonicotinoids detected in the samples were mostly expected to arise from their application by aerial spraying, particularly dinotefuran, acetamiprid, and thiacloprid. The highest total concentration (Fig. 1) occurred in August in Tsukuba and Kashiwa, which is in line with the spraying schedule of rice fields in Japan (between May-September with highest application in July and August, mainly dinotefuran). Some previous studies have detected atmospheric neonicotinoids in the air during planting events, such as in Canada (Forero et al., 2017) and Italy (Biocca et al., 2014). Aerial spraying was also conducted on pine forests in Japan between May-July (highest application in June) (Environmental Agency Water Quality Conservation Bureau 1997) using highly concentrated neonicotinoid solutions (mainly acetamiprid and thiacloprid) to control pine wilt disease (Ichikawa et al., 2008; Takenouchi and Aoi, 2016; Ikenaka et al., 2019). This was reflected in the results of the June samples in both cities, which were dominated by these two compounds (Fig. 1), where acetamiprid was expected from the pine forest, as it is not intended for rice cultivation in Japan (Furihata et al.,

2019). Similarly, Ikenaka et al. (2019) also observed that acetamiprid and thiacloprid concentrations in the atmosphere were higher during spraying in the pine forest in Nagano. The use of neonicotinoids in rice nursery boxes might not substantially impact their atmospheric presence, as these insecticides are highly water-soluble and the rice paddies are submerged, likely limiting their release into the air.

In addition to direct contamination of the air during spraying, neonicotinoids sprayed could gradually penetrate soils, possibly remaining there for a long time (Kobayashi et al., 2014) and returning to the atmosphere at a later time together with soil particles (Boonupara et al., 2023). The high detection of acetamiprid and thiacloprid might also be attributed to their higher soil affinity compared to other compounds (Table 1), resulting in a stronger attraction to soil particles and longer existence in soils. This might explain the neonicotinoid occurrence in January and April when neonicotinoids were not used or were rarely used. Previously, Kobayashi et al. (2014) found thiacloprid and acetamiprid in soils for up to 5 and 3 months after spraying pine forests, respectively. Moreover, a simulation by the Research Institute of Pesticide Residues (2018) suggested more than a 28-day existence of sprayed dinotefuran for rice in the air. Neonicotinoid application for other purposes, including in other agricultural crops, might not significantly contribute to their existence in the atmosphere because they are used in smaller amounts and in closed areas, including in greenhouses.

Figure 1 illustrates that Tsukuba rainwater had a higher average concentration (1.10 ng/L) than Kashiwa rainwater (0.63 ng/L). Ibaraki Prefecture, where Tsukuba is located, has larger rice fields (about 67,800 ha) than Chiba Prefecture, where Kashiwa is located (about 55,400 ha) (MAFF, 2023). The results were also supported by the larger shipment values of neonicotinoids in Ibaraki than in Chiba (Table 2). In China, Zhou et al. (2020) showed that the average total neonicotinoid concentration in PM<sub>2.5</sub> was higher in rural areas surrounded by orchards and irrigated land than in urban areas with no large farmland nearby. Furthermore, the sam-



Fig. 1 Total neonicotinoid concentration in rainwater samples based on sampling time

pling location in Tsukuba was closer to the rice fields (about 700 m) compared to the one in Kashiwa (about 4,000 m); this was in line with Forero et al. (2017) in Canada, who reported that the farther the distance from the source, the smaller the atmospheric neonicotinoid concentration would be.

In terms of pine forests, Ibaraki has a slightly smaller pine forest area (613 ha, Ibaraki Prefectural Government 2018) than Chiba (700 ha, Chiba Prefectural Government 2024). However, the shorter distance from the pine forest to the sampling location in Tsukuba (about 43 km) than in Kashiwa (about 68 km) presumably influenced the higher concentration in Tsukuba. Previously, in pine wilt disease control areas of Nagano Prefecture, Japan, Takenouchi and Aoi (2016) in 2013 found the aerial thiacloprid beside sprayed spots of neonicotinoids with a maximum concentration of  $1.9 \text{ ng/m}^3$  on the second day after spraying. In a residential area a few kilometers from the pine wilt disease control locations in the same prefecture, thiacloprid in the dust was detected at a concentration of 0.045 ng/m<sup>3</sup> after spraying in 2016 (Ikenaka et al., 2019). Thus, the current study also suggested that neonicotinoid concentrations in rainwater might potentially be higher in a larger area of rice fields and pine forests where neonicotinoids might originate and with a shorter distance from the sampling location.

#### CONCLUSION

In this study, neonicotinoids were still detected in rainwater at small concentrations even during the off-season of their application, although they are considered as low volatile matter. Thus, precipitation may serve as a potential dispersion medium for these insecticides to a wider surface environment for a long time. It also became one of the pathways for neonicotinoids to pollute the wider aquatic environment because they are highly water-soluble. Furthermore, the neonicotinoids detected in the rainwater may have originated from their application by aerial spraying. Therefore, this type of application method is presumably not recommended because the solutions are more concentrated, permitting neonicotinoids to be deposited in soils and returned to the atmosphere at a later time. Direct contamination of the environment with neonicotinoids contained in precipitation and their harmful impacts may be unavoidable as the fall in precipitation is difficult to control.

The present study possessed limited samples; therefore, monitoring research in different areas is suggested to be conducted in the future by taking environmental and meteorological conditions into consideration. The original locations of neonicotinoids in precipitation were deemed crucial to be observed as well as to track their mobilization in the atmosphere. Future studies are expected to provide a better understanding of the role of precipitation in the environmental fate of neonicotinoids to prevent their harmful impact on the environment.

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