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Contribution of Water-Insoluble Organic Nitrogen to Nitrogen Deposition on a Forest: a Case Study in a Red Pine Forest on the Northern Foot of Mt. Fuji, Japan

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Abstract The observations of rainfall, throughfall, stemflow, and aerosols were conducted at a forested site on the northern foot of Mt. Fuji in Japan. The aims of this study were to understand the deposition fluxes and processes of the water-insoluble organic nitrogen (WION) from the atmosphere to the forest canopy and floor. The deposition flux of the total nitrogen (TN) that includes all nitrogen species to the forest floor was 1.944 mgN m^{-2} day^{-1} on average. The contribution of the WION to the TN deposition flux was about 29%, which suggests the importance of the WION for discussing the nitrogen deposition from the atmosphere to forests and the nitrogen cycle in the forest ecosystem. The estimation by a canopy budget model indicated that the dry deposition of aerosols on the canopy was the most important process for the WION deposition.

Keywords Nitrogen deposition · WION · WSON · Canopy budget model · Throughfall · Rainfall

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1 Introduction

Atmospheric deposition of bioavailable nitrogen through the wet and dry processes is an important external nitrogen supply to the forest ecosystem. The increase in the atmospheric bioavailable nitrogen due to anthropogenic activities, such as fossil fuel burning and fertilization, certainly causes an increase in the external nitrogen supply to the forest, which can lead to "nitrogen saturation." Under the condition of nitrogen saturation, the nitrogen supply is in excess of biological demand and all incoming nitrogen cannot be retained in the forest ecosystem (Aber et al., 1989; Wright et al., 1995).

Water-soluble inorganic nitrogen species, that is, NO_3^--N, NO_2^--N, and NH_4^+-N, have been focused on in many previous studies about bioavailable nitrogen in the atmospheric deposition, and some studies have also reported that the water-soluble organic nitrogen (WSON) occupies a significant portion of the bioavailable nitrogen (Cao et al., 2019; Cornell, 2011; Cornell et al., 2003; Matsumoto et al., 2020; and references therein). Recently, our study reported that a significant amount of nitrogen was detected in the

water-insoluble fraction of the atmospheric deposition (Matsumoto et al., 2019), which can be expected to be composed of the water-insoluble organic nitrogen (WION). Despite of the significant abundance of the WION in the atmospheric nitrogen deposition, the measurement of the WION in the atmospheric deposition has not been sufficiently conducted compared to water-soluble nitrogen species. To the best of our knowledge, the only one reported was by Matsumoto et al. (2019).

The measurement of the throughfall and stemflow has been considered to be able to quantify the deposition flux of the atmospheric substances to the forest canopy because the throughfall and stemflow waters include both wet and dry deposition substances on the canopy, although the stemflow has the small or negligible contribution compared to the throughfall (Ahmadi et al., 2009; Ikawa, 2007; Matsumoto et al., 2020; Toba & Ohta, 2005). A canopy exchange process, which includes the adsorption of deposition substances by the canopy and stem and leaching of chemical substances from the canopy and stem, can change the chemical concentrations and composition of the deposition substances. This process leads to a discrepancy in the chemical composition and concentrations of the throughfall and stemflow waters from those of the atmospheric deposition on the canopy. Although the measurements of the throughfall and stemflow cannot directly indicate the chemical composition and concentrations of the atmospheric deposition, they can indicate the net supply of deposition substances into the forest floor.

To quantify the contributions of the atmospheric deposition and canopy exchange processes to the deposition fluxes of the chemical substances to the forest floor, the canopy budget model has been used in many previous studies (Staelens et al., 2008, and references therein). In this model, the deposition fluxes by the throughfall and stemflow can be considered to result from the wet and dry deposition and canopy exchange processes as follows:

$$\mathrm{TD} + \mathrm{SD} = \mathrm{WD} + \mathrm{DD} + \mathrm{CE}, \quad (1)$$

where the *TD*, *SD*, and *WD* denote the deposition flux by the throughfall, stemflow, and rainfall, respectively, and the *DD* and *CE* denote the dry deposition flux to the canopy and the canopy exchange amount, respectively. Using the measurements of the *TD*, *SD*, and *WD*, the sum of the *DD* and *CE* can be estimated. Because the direct measurement of the *DD* and/or *CE* is generally difficult, many previous studies have estimated the *DD* by using the chemical composition of the wet deposition or aerosols (Matsumoto et al., 2020; Staelens et al., 2008), and then calculated the *CE*. It can be considered that the chemical substance leached from the canopy when the *CE* is estimated to be positive, whereas the substance was taken into the canopy when the *CE* is negative.

In the present study, samples of the rainfall, throughfall, and stemflow waters, and aerosols were collected at a forested site on the northern foot of Mt. Fuji in Japan to evaluate the importance of the WION on the nitrogen deposition from the atmosphere to the forest and to determine which deposition process is important for the WION deposition on the forest using the canopy budget model.

2 Experiment

2.1 Sample Collection

Sample collections were conducted at the experimental forest (red pine), with tree heights of 10–15 m, of the Mt. Fuji Research Institute, Yamanashi Prefectural Government, located on the northern foot of Mt. Fuji. The average temperature and annual rainfall amount for 2020 were 11.7 °C and 1651 mm, respectively. The forest floor has numerous exposures of lava, and the soil is immature. The location of the sample collection site is shown in Fig. 1. Simultaneous collections of the rainfall, throughfall, and aerosol samples were intermittently conducted during 2020 (8 January to 13 April, 21 May to 18 June, and 30 July to 24 December). The collection time of each sample was about 14 days.

The collections of the rainfall and aerosol samples were conducted at an open space in the experimental forest. The distance from the rainfall and aerosol samplers to the nearest trees was about 10 m. A polysulfone cylindrical funnel with an inner diameter of 70 mm was set about 2 m above the ground surface, and connected to a filter holder with a quartz fiber filter (QR100; Toyo Roshi Kaisha, Ltd.), then to a lightproof polypropylene bottle. Before each sample collection, the filter was heated at 850 °C for 4 h, and 0.01 g of $CuSO_4$ was added

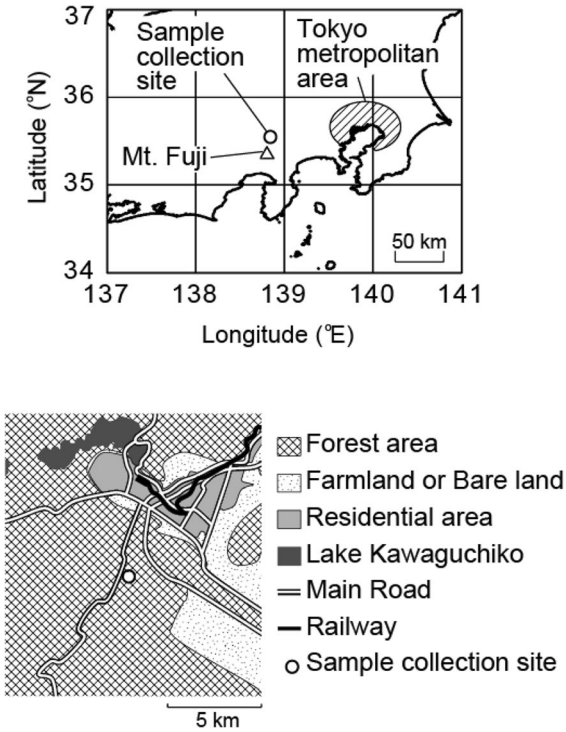

Fig. 1 The location of the sample collection site

to the bottle as a biocide. The rainfall water was collected by the funnel, then drained into the bottle through the filter. Coarse-mode ($d = 2.0$–10 μm) and fine-mode ($d < 2.0$ μm) aerosols were collected on quartz fiber filters (QR100; Toyo Roshi Kaisha, Ltd.) that were preheated at 850 °C for 4 h using a filter holder with two-stage impactors (NL Series; Tokyo Dylec Corp.) at the flow rate of 20.0 L min^{-1}. As with the rainfall collectors, the filter holder was installed about 2 m above the ground surface.

The collections of the throughfall samples were conducted using three trees (red pine) of which the tree height, chest-height diameter, and canopy diameter were about 15 m, 37 cm, and 5.5 m on average, respectively, in the experimental forest. Two throughfall samples were collected under each of the three trees, and six throughfall samples were collected during each sampling period. These three trees were located within the distance of about 10 m from each other, and about 70 m from the nearest forest edge and about 80 m from the collection site of the rainfall and aerosol samples. The throughfall samples were collected by the same collector and procedure as for the rainfall samples, but the funnel was set about 1.5 m above the ground surface.

After the sample collection, the six throughfall sample waters were mixed together. The volumes of the mixed throughfall sample water and the rainfall sample water were measured by a measuring cylinder. These sample waters were poured into glass vials and stored below − 20 °C. The filters that were used for the collection of the rainfall, throughfall, and aerosol samples were also stored below − 20 °C. In this study, a total of 17 sample sets with complete rainfall, throughfall, and aerosol samples were obtained and used in the following analyses and discussion.

The stemflow samples were collected three times during the period from 12 October to 27 November 2020, simultaneously with the collection of the rainfall, throughfall, and aerosol samples. The collections of the stemflow samples were conducted using the three trees that were used to collect the throughfall samples. One stemflow sample was collected from each of the three trees, and three stemflow samples were collected during each sampling period. The stemflow samples were collected by a pre-rinsed gauze that encircled the stem twice with an inclined angle at chest-height (Sassa et al., 1990; Shigihara et al., 2008). Both edges of the gauze were connected to a filter holder containing a quartz fiber filter (QR100; Toyo Roshi Kaisha, Ltd.) that was connected to a light-proof polypropylene bottle, and the stemflow waters were dripped into the bottle. The filter was preheated at 850 °C for 4 h, and 0.1 g of $CuSO_4$ was added to the bottle before each sample collection as a biocide. After the sample collection, the three stemflow sample waters were mixed together, and the volume of the mixed stemflow sample water was measured by a measuring cylinder. The sample water was poured into a glass vial and stored below − 20 °C. The filters that were used for the collection of the stemflow samples were also stored below − 20 °C.

During the sample collections, operational blank tests for the rainfall, throughfall, stemflow, and aerosol sample collections were performed at given intervals. Because the rainfall, throughfall, and stemflow samples were not stored under refrigeration at the sample collection site, it should be noted that some volatile components such as ammonia may be volatilized and underestimated during the warm season.

2.2 Sample Analysis

The dissolved total nitrogen (DTN) in the filtrate of the rainfall, throughfall, and stemflow samples

was measured by a total organic carbon (TOC)/total nitrogen (TN) analyzer (Model TOC-Vcsh/TNM-1, Shimadzu). The ion species (Cl-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in the filtrate were measured by ion chromatographs (DX-120; Dionex Corp. and ICS-1100; Thermo Fisher Scientific, Inc.). The DTN can be considered to be the water-soluble total nitrogen (WSTN) in the sample water. The concentration of the total inorganic nitrogen (IN) was calculated from the sum of the concentrations of NO_2^--N, NO_3^--N, and NH_4^+-N, and the difference between the DTN and IN concentrations can be considered to be the WSON concentration. The TN in the filter residue of the rainfall, throughfall, and stemflow samples was measured using a CHN elemental analyzer (MT-6; Yanaco Analytical Industry Co., Ltd.). The TN in the filter residue can be considered to be the WION.

The ultrasonic extraction of the aerosol sample collected on the filter was conducted using ultrapure water in a glass vial. After the filtration of the extract by a PTFE membrane filter (13HP045AN; Toyo Roshi Kaisha, Ltd.), the DTN and ion species in the extract were measured using the TOC/TN analyzer and ion chromatographs, respectively. The TN on the filter that collected the aerosol sample was measured by the CHN elemental analyzer. The difference in the TN and DTN is defined as the WION in the aerosols.

The averaged blank measurements of the DTN, ion species, and TN were subtracted from the measurements of the collected samples. The detection limits (DL) of each component were described in detail in our previous paper (Matsumoto et al., 2019).

3 Results and Discussion

3.1 Nitrogen Deposition Flux by Rainfall and Throughfall

The deposition flux (D; mgN m^{-2} day^{-1}) of a chemical substance by the rainfall and throughfall was calculated by the following equation:

$$D = C \times V / A_f / T, \quad (2)$$

where C is the concentration of the chemical substance in the sample water (mgN l^{-1}), V is the volume of the sample water (l), and T is the duration time for each sample collection (day). For the rainfall sample, A_f is the cross-section area of the top of one funnel for the sample collection (m^2), whereas A_f of the throughfall sample is the sum of those of the six funnels for the sample collection (m^2).

Figure 2 shows the averaged deposition fluxes of the nitrogen species and contributions of each nitrogen species to the deposition flux of the TN that includes all the nitrogen species. The deposition fluxes of the TN were 1.204 and 1.944 mgN m^{-2} day^{-1} on average by the rainfall and throughfall, respectively. Our previous study found that the influence of the dry deposition on the rainfall sample obtained by the collector used in this study cannot be negligible; about 20% of the WSTN and IN were estimated to be derived from the dry deposition (Matsumoto et al., 2018). Therefore, both the deposition fluxes by rainfall and throughfall were likely overestimated by about 20% of that by

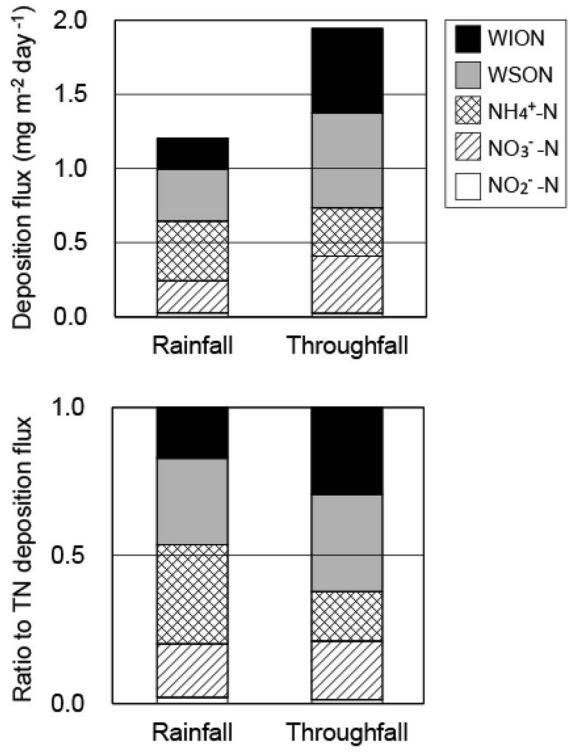

Fig. 2 Averaged deposition fluxes of nitrogen species (upper panel) and contributions of each nitrogen species to the TN (bottom panel) in the deposition by rainfall and throughfall

rainfall. The difference in both deposition fluxes can be attributed to the dry deposition on the canopy and the canopy exchange processes. The contributions of the WION to the TN in the deposition by the rainfall and throughfall were about 17% and 29%, respectively, suggesting that the WION is an important fraction of the nitrogen deposition from the atmosphere to the forest canopy and floor. There are few studies about the wet deposition of the WION. Neff et al. (2002) suggested the existence of the WION in the wet deposition based on the comparisons of the organic nitrogen in the unfiltered samples with those in the filtered samples. Our recent study measured the WION in the wet deposition collected at the urban site and showed that the WION contributed about 5% of the wet deposition flux of the TN by rainfall (Matsumoto et al., 2019). On the other hand, the measurement of the WION in the throughfall water has never been reported.

The organic nitrogen (ON) that is the sum of the WION and WSON occupied about 46% and 62% of the TN in the deposition by rainfall and throughfall, respectively, suggesting a great contribution of the ON to the atmospheric nitrogen deposition. About half or more of the nitrogen deposition can be explained by the organic forms. The contribution of the WION to the ON in the deposition by rainfall and throughfall was about 37% and 47%, respectively. The present study demonstrated the importance of the water-insoluble fraction of organic nitrogen for discussing the nitrogen deposition from the atmosphere to forests and the nitrogen cycle in the forest ecosystem.

3.2 Contribution of Stemflow to Nitrogen Deposition Flux

As already mentioned, small or negligible contributions of the stemflow to the transport of the deposition substances from the canopy to the forest floor have been found in the past studies (Ahmadi et al., 2009; Ikawa, 2007; Toba & Ohta, 2005). Our previous study at the same site as the present study also indicated that the contribution of the stemflow to the nitrogen deposition on the forest floor was quite small (about 1%) for the water-soluble inorganic and organic nitrogen species (Matsumoto et al., 2020).

In the present study, stemflow samples were collected simultaneously along with the throughfall samples during the three sample collection periods to check the contribution of the stemflow to the WION deposition on the forest. Table 1 summarizes the averages of the deposition fluxes of the nitrogen species by the throughfall and stemflow and the ratios of the deposition flux by the stemflow to that by the throughfall for the three sample collection periods. The deposition flux of the chemical substance by stemflow was calculated by the following equation:

$$D = C \times V/A_c/T, \quad (3)$$

where A_c is the sum of the canopy projection areas of the three trees for the sample collection (m^2).

As shown in Table 1, the present study also demonstrated that the contribution of the stemflow to the deposition fluxes of the WION and other water-soluble nitrogen species was negligible compared to the throughfall. This indicated that the nitrogen supply to the forest floor can be estimated only by the measurement of the throughfall at least at the present observation site. The deposition fluxes of the nitrogen species by the throughfall shown in Fig. 2, therefore, can be considered to be the nitrogen deposition fluxes to the forest floor at the site.

3.3 Nitrogen Deposition Processes on the Forest Canopy and Floor

When the contribution of the stemflow to the deposition flux of the chemical substance to the forest floor

Table 1 Average deposition fluxes of nitrogen species by throughfall and stemflow (unit: mg m^{-2} day^{-1}) and the ratios of those by stemflow to by throughfall

	WION	WSON	NO_2^--N	NO_3^--N	NH_4^+-N	*n*
Throughfall	4.71×10^{-1}	3.98×10^{-1}	1.40×10^{-2}	1.77×10^{-1}	1.18×10^{-1}	3
Stemflow	4.50×10^{-11}	9.51×10^{-4}	b.d.*	1.11×10^{-5}	1.45×10^{-4}	3
Stemflow/throughfall	9.56×10^{-11}	2.38×10^{-3}	0.00	6.26×10^{-5}	1.22×10^{-3}	3

*b.d., below the detection limit

can be negligible, Eq. (1) can be written as the following Eq. (4):

$$TD = WD + DD + CE. \quad (4)$$

Many previous studies have estimated the *DD* by using Na^+ as a tracer substance that can be considered to be derived only from the atmospheric deposition and not affected by the canopy exchange process (Staelens et al., 2008). In the estimation the *DD* of the chemical substance *X* (DD_X), the ratios of the *DD* to the concentration in the coarse-mode aerosol can be assumed to be the same between the *X* and Na^+ when the existence of the *X* in the gas phase can be negligible (Matsumoto et al., 2020), which is expressed by the following equation:

$$DD_X/C_X = DD_{Na}/C_{Na}, \quad (5)$$

where the C_X and C_{Na} denote the concentration of the *X* and Na^+, respectively, in the coarse-mode aerosol, and DD_{Na} denotes the *DD* of Na^+. Here, deposition velocities for the *X* and Na^+ in the coarse-mode aerosols were assumed to be similar. In addition, the fine-mode aerosols were ignored because their deposition velocities are quite low compared to those of the coarse-mode aerosols (Seinfeld & Pandis, 1998). The WION can be considered to exist only in the aerosols and not in the gas phase, so the WION in the dry deposition can be considered to be derived only from the aerosols. Therefore, the *DD* of the WION (DD_{WION}) can be estimated by Eq. (5) as follows:

$$DD_{WION} = (TD_{Na} - WD_{Na}) \times (C_{WION}/C_{Na}), \quad (6)$$

where the TD_{Na} and WD_{Na} denote the *TD* and *WD*, respectively, of Na^+. Note that the Na^+ has been originally used as a tracer substance of the atmospheric deposition for ion species in the canopy budget model, and this study is the first attempt to use it for the WION. The CE_{WION} can be estimated using the measurements of the *TD* and *WD* of the WION (TD_{WION} and WD_{WION}, respectively) and the estimated DD_{WION} as follows:

$$CE_{WION} = TD_{WION} - WD_{WION} - DD_{WION}. \quad (7)$$

Figure 3 shows the averages of the measurements of the WD_{WION} and TD_{WION} and the estimations of the DD_{WION} and CE_{WION}. The dry deposition of aerosols on the canopy was the most important process for the WION deposition on the forest floor. About 58% of the WION deposition can be explained by the dry deposition process. The second most important process for the WION deposition was the wet deposition process (about 36%). On the other hand, the contribution of the canopy leaching process to the WION deposition was estimated to be small (about 5%). It should be noted that this result may slightly overestimate the WD due to the influence of the dry deposition on the rainfall and throughfall collectors as discussed above.

4 Summary

The present study evaluated the atmospheric deposition of the WION on the forest for the first time, although there were some uncertainties, such as the overestimation of the wet deposition due to the dry deposition on its collector and the assumption of similar dry deposition velocities for the WION and Na^+ in the coarse-mode aerosols. The contribution of the WION to the deposition flux of the TN to the forest floor was about 29%, indicating the importance of the water-insoluble fraction of the organic nitrogen for discussing the nitrogen deposition from the atmosphere to forests and the nitrogen cycle in the forest ecosystem. The dry deposition of aerosols on the canopy was estimated to be the most important process for the WION deposition on the forest floor. Significant deposition fluxes of the WION found in this study suggest the necessity for the study on its atmospheric behaviors, sources, and roles in the forest ecosystem.

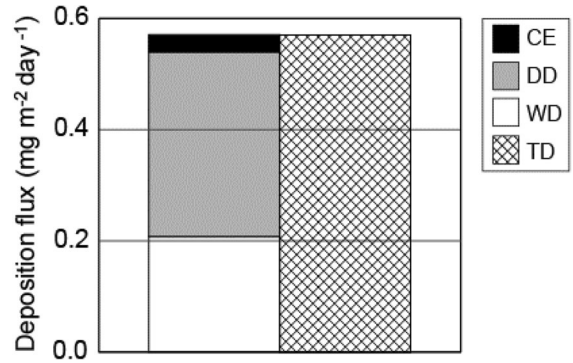

Fig. 3 Averages of the measurements of the WD and TD, and the estimations of the DD and CE for the WION

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of Interest The authors declare no competing interests.

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