Atmospheric Environment 191 (2018) 267–272

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Water-soluble organic nitrogen in the aerosols and rainwater at an urban site in Japan: Implications for the nitrogen composition in the atmospheric deposition

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ARTICLE INFO

Keywords:
Water-soluble organic nitrogen
Nitrogen deposition
Dry deposition
Wet deposition
Aerosols

ABSTRACT

Simultaneous measurements of the water-soluble organic nitrogen (WSON) in the aerosols and rainwater were conducted to clarify the deposition pathway of the atmospheric WSON. In the aerosols, about 10% of the water-soluble total nitrogen (WSTN) was in an organic form, and a large portion (about 81% on average) of the WSON was distributed in the fine-mode range. Concentrations of the fine-mode WSON were associated with the acidity of the fine particles, suggesting the secondary production of the WSON in the acid fine particles. On the other hand, it was suggested that the coarse-mode WSON was derived from bio-particles, such as plant debris, although its concentrations were low and widely scattered. Dry deposition amounts of the WSON estimated from the concentrations and dry deposition velocities of the particulate WSON suggested that almost all of the dry deposition of the particulate WSON was derived from the coarse-mode particles. The contribution of the fine-mode particles to the dry deposition was negligible. About 10% of the WSTN in the bulk precipitation was in an organic form. The bulk deposition amounts of the WSON were largely dependent on the rainfall amounts and coarse-mode WSON concentrations. Although about 30% of the WSON in the bulk deposition was from the dry deposition, the wet deposition significantly contributed to the WSON deposition, especially in the rainy season. Wet deposition is the major removal process of WSON from spring to autumn; however, in winter, dry and wet deposition are comparable.

1. Introduction

Atmospheric bioavailable nitrogen compounds enter nitrogen pool in aquatic and terrestrial ecosystems both through wet and dry deposition processes (Aber et al., 1989; Duce et al., 1991; Jassby et al., 1994; Cornell et al., 1995). Inorganic nitrogen compounds (NO_3^-, NO_2^-, and NH_4^+) have been reported to account for a major part of the bioavailable nitrogen in the atmospheric deposition. Water-soluble organic nitrogen (WSON) has also been paid attention in recent studies for the atmospheric input of the bioavailable nitrogen to the ecosystems. The bioavailability of the organic nitrogen species in the atmospheric deposition has been determined in past studies (Peierls and Paerl, 1997; Seitzinger and Sanders, 1999).

Many pioneering studies for the atmospheric deposition of the WSON have focused on rainwater samples of wet and/or bulk (wet + dry) deposition, and reported that the WSON contributes about 10–50% of the water-soluble total nitrogen (WSTN) in the deposition (Cornell et al., 2003, and references therein). In contrast to the measurements of the wet and bulk precipitations, the dry deposition amounts of the WSON have been rarely reported. González Benítez et al. (2009) and Violaki et al. (2010) directly measured the dry deposition that included both the particulate and gaseous WSON by using a surrogate; a polypropylene funnel and glass beads bed, respectively. These studies reported that the WSON contributes 30–40% of the WSTN in the dry deposition, and the dry process largely contributed to the atmospheric deposition of the WSON rather than the wet process. On the other hand, the dry deposition of the WSON only from the aerosols has been estimated from the measurement of the aerosols and subsequent calculation by a micrometeorological model. Qi et al. (2013) reported that the WSON contributes 24.3% of the WSTN in the dry deposition from the aerosols. They also found that the amounts of the WSON in the dry deposition from the aerosols can be estimated to be comparable to those in the wet deposition. Matsumoto et al. (2014) also demonstrated that 26% of the WSTN in the dry deposition from the

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https://doi.org/10.1016/j.atmosenv.2018.07.056
Received 20 February 2018; Received in revised form 24 July 2018; Accepted 30 July 2018
Available online 31 July 2018
1352-2310/

aerosols can be accounted for by organic forms. Both studies also found that coarse particles largely contributed to the dry deposition of the WSON from the aerosols.

Deposition processes of water-soluble organic nitrogen species should be understood to discuss the spatial and temporal variabilities in the atmospheric deposition of the bioavailable nitrogen and to forecast its future changes. In order to do that, the present study simultaneously measured the WSON in the aerosols and precipitation, and discussed the deposition processes of the WSON.

2. Experiment

2.1. Sample collection

Sample collections were conducted at an urban site in Kofu, Japan. Kofu is the capital city of Yamanashi Prefecture located in the Kofu basin, about 100 km from the center of the Tokyo Metropolis, with a population of about 200,000. The sampling site in Kofu is located on the building roof of the University of Yamanashi (about 18 m above the ground) surrounded by residential areas at a distance of about 2 km from the city center. Details of the sampling site were previously described (Matsumoto et al., 2014).

Two size-fractionated aerosol samples with diameters of 2.0–10 μm (coarse-mode) and < 2.0 μm (fine-mode) were collected on quartz fiber filters (QR100; Toyo Roshi Kaisha, Ltd.) using an NILU filter holder with a two-stage aluminum alloy impactor (NL Series; Tokyo Dylec Corp.). Before the sample collections, the quartz fiber filters had been heated at 850 °C for 4 h. Sample collections were conducted at the flow rate of 20.0 L min^{-1}.

Precipitation samples were collected by a polysulfone cylindrical funnel with a caliber of 70 mm connected to a filter holder that installed a glass fiber filter (GF/F; Whatman) pre-heated at 450 °C for 4 h, and then drained into a 1 L polypropylene bottle in a refrigerator. A 0.01 g of $CuSO_4$ was added to the bottle before each sample collection as a biocide.

The samples of two size-fractionated aerosols and the precipitation were collected from 12 February 2013 to 22 January 2014. Collections for these samples were synchronized with each other with the sampling time of about 14 days.

In addition to these sample collections, 9-size fractionated aerosol samples, with diameters of < 0.43 μm, 0.43–0.65 μm, 0.65–1.1 μm, 1.1–2.1 μm, 2.1–3.3 μm, 3.3–4.7 μm, 4.7–7.0 μm, 7.0–11 μm, and > 11 μm, were collected using an Andersen low volume air sampler (AN-200; Tokyo Dylec Corp.) in order to obtain high-resolution size distributions of the particulate nitrogen compounds. Quartz fiber filters (QR100; Toyo Roshi Kaisha, Ltd.) that had been heated at 850 °C for 4 h before the sample collections were used for the aerosol collection. Monthly samples were obtained from 7 February 2014 to 2 February 2015 at the flow rate of 28.3 L min^{-1}.

After the sample collections, the funnel of the precipitation sampler was rinsed with 50 ml of ultrapure water to collect the dry deposition on the funnel. The rinse solution was drained into the sampling bottle through the glass fiber filter, and mixed with the rainwater sample, which is a bulk precipitation sample including both the dry and wet depositions. The precipitation sample was poured into a glass vial after measurement of its volume. All of the filter and precipitation samples were stored below −20 °C until chemically analyzed.

2.2. Blank measurements

During the sample collections, field operational blank tests were performed at given intervals. Sixteen blank filter samples were obtained for the 2-size fractionated aerosol samples, 12 for the 9-size fractionated aerosol samples, and 9 for the bulk precipitation samples. All the blank samples were stored in the same manner as already described.

2.3. Evaluation of the effect of dry deposition on the bulk precipitation sample

As already mentioned, the bulk precipitation samples collected in this study included not only wet deposition but also dry deposition. Although the comparisons of bulk deposition with the wet-only or dry-only deposition have been investigated in past studies (Zhang et al., 2008; González Benítez et al., 2009), the effect of the dry deposition on a bulk sampler would be largely dependent on the configuration of the sampler, meteorological factors, and atmospheric concentrations of the particulate and gaseous species. In order to investigate the effect of the dry deposition on our bulk precipitation samples, simultaneous collections of the bulk precipitation sample and dry-only deposition sample were conducted from 16 May to 13 October 2016 with a sampling time of 14 days. Two bulk precipitation samplers were placed at the sampling site, and one sampler was automatically closed with a cover during rain events that were detected by a rain sensor (NS-100; Ogasawara Keiki Co., Ltd.). After the sample collections, the samples were treated in the same manner as already described.

2.4. Sample analysis

One-fourth of the filter collected aerosol sample from the 2-size fractionated aerosol sampler and half of the filter from the 9-size fractionated aerosol sampler were ultrasonically extracted with 20 ml of ultrapure water (specific resistivity > 18 MΩ cm) in a glass vial. The water extracts were filtered using a PTFE membrane filter (13HP045AN; Toyo Roshi Kaisha, Ltd.). The dissolved total nitrogen (DTN) in the extracts were measured using a total organic carbon (TOC)/total nitrogen (TN) analyzer (Model TOC-Vcsh/TNM-1, Shimadzu) that can detect the DTN by an ozone chemiluminescence detection after a thermo-catalytic oxidation process. The DTN is considered to be the WSTN in this study. The ion species (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in the extracts were measured using ion chromatographs (DX-120; Dionex Corp. and ICS-1100; Thermo Fisher Scientific, Inc.). The concentrations of the total inorganic nitrogen (IN) were calculated from the sum of the NO_2^--N, NO_3^--N and NH_4^+-N concentrations, and the difference between the concentrations of the DTN and IN is considered to be the WSON.

The bulk precipitation sample was also analyzed for the DTN and ion species, and the difference between the concentrations of the DTN and IN is considered to be the WSON.

2.5. Quality assurance and quality control

Only for the aerosol samples, the ion balance that is the equivalent ratio of the anion species (Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}) to the cation species (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) was calculated, and all the samples showed an ion balance within 0.68–1.25.

The averaged blank values of the DTN and ion species were subtracted from the measurements of the collected samples. The definitions of the detection limit (DL) of the measured species and WSON were explained in our previous paper (Matsumoto et al., 2017).

2.6. Meteorological data

Hourly meteorological data obtained at the Kofu Local Meteorological Observatory (KLMO) were used for the data analyses in this study. The KLMO is located about 2 km from the sampling site.

2.7. Estimation of dry deposition amount

The dry deposition flux (F) of the atmospheric particulate species can be estimated by

$$F = V_d C,$$