Water-soluble organic nitrogen in the gas phase measured by the denuder–filter pack method

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ABSTRACT

The WSON in the gas phase and aerosols were simultaneously measured by the denuder–filter pack method. Approximately 33 ± 18% of the WSON in the atmosphere existed in the gas phase. A large portion (approximately 76 ± 33%) of the gaseous WSON collected in the present sampling method was occupied by basic species. The gaseous basic and acid WSON showed about one-sixth of the nitrogen concentrations of the gaseous NH₃ and HNO₃, respectively. These results indicate that the gaseous WSON is also an important fixed nitrogen species in the atmosphere.

Keywords: Water-soluble organic nitrogen, gas phase, aerosol, denuder–filter pack, fixed nitrogen species

1. Introduction

Water-soluble organic nitrogen (WSON) has been considered to account for a significant fraction of the fixed nitrogen deposition from the atmosphere. About 10–50% of the water-soluble total nitrogen (WSTN) in the wet or bulk (wet + dry) deposition has been attributed to the WSON in previous reports (Cornell et al., 2003 and references therein). On the other hand, the dry deposition of the WSON has been measured only by a few researchers (González Benítez et al., 2009; Violaki et al., 2010). The particulate WSON has been investigated in many previous studies, and its dry deposition has also been estimated in some previous studies (Qi et al., 2013; Matsumoto et al., 2014). However, very few researches were conducted for the gaseous WSON, and its effects on the dry deposition have not yet been discussed.

The total amount of the WSON in the gas phase has rarely been determined in previous investigations although the measurements of the individual gaseous organic nitrogen species, such as alkylamines and alkylnitrates, have been conducted, which is opposite to that of the case of the WSON in the particulate phase. Only a few studies reported the measurements of the WSON in the gas phase (González Benítez et al., 2010; Zamora et al., 2011), but their results would overestimate the gaseous WSON due to volatilization loss of the particulate WSON on the aerosol-cut filter. Matsumoto and Yamato (2016) demonstrated that some parts of the particulate WSON would volatilize from the aerosol collection filter during filter sampling, whereas the denuder-filter pack sampling can separately measure the gaseous and particulate WSON with less sampling artifacts. In the present study, the gaseous and particulate WSON were simultaneously measured by the denuder-filter pack method to clarify the concentration level of the gaseous WSON and to discuss the gas/particle distribution of the WSON in the atmosphere.

2. Experiment

2.1. Sample collection

The sample collections were conducted once each month from January to December, 2015, with a sampling time of two weeks at an urban site in Kofu, Japan. Kofu is located in the Kofu basin, about 100 km from the center of the Tokyo Metropolis, with a population of about 200,000. The samplers were installed on the building roof of the University of Yamanashi (about 18 m above the ground), which is surrounded by a residential area at a distance of about 2 km from the city center.

Both the particulate and gaseous WSON were measured by the denuder-filter pack method (Matsumoto and Yamato, 2016). An air sample was introduced into a cyclone (URG-2000 series; URG Corp.) for removing the particles with diameters larger than 2.5 μm, then passed through two annular denuders (URG-2000 series; URG Corp.) and a filter holder connected in this order. The upstream denuder was coated with 2% H₃PO₄/1% glycerol and the downstream denuder was coated with 2% Na₂CO₃/1% glycerol. The filter holder consisted
of a quartz fiber filter (47 mm φ, QR100; Toyo Roshi Kaisha, Ltd.) preheated at 850 °C for 4 h, a 2% Na₂CO₃/1% glycerol impregnated-cellulose filter (47 mm φ, 5A; Toyo Roshi Kaisha, Ltd.), and a 2% H₃PO₄/1% glycerol impregnated-cellulose filter in this order. The denuders can collect gaseous basic and acid species and the quartz fiber filter behind the denuders collects the particulate matters with diameters smaller than 2.5 μm (PM₂.₅). Some parts of the particulate species in the PM₂.₅ collected on the filter might volatilize during the sampling due to the change in their equilibrium state, but they can be collected by the basic or acid reagent-impregnated filter (Harrison and Kitto, 1990; Matsumoto and Okita, 1998). Therefore, the results from the acid and basic reagent-coated denuders are considered to be the measurements of the basic and acid gaseous species, respectively, and the sum of the results from the three filters in the filter holder are considered to be the measurements of the particulate species. The flow rate of the sample air was 10 L min⁻¹.

Simultaneously with the denuder-filter pack sampling, two size-fractionated aerosol samples with diameters of 2.0–10 μm (coarse particles) and smaller than 2.0 μm (PM₁₀) were collected by a two-stage impactor with a backup filter (NL Series; Tokyo Dylec Corp.). The quartz fiber filter (47 mm φ, QR100; Toyo Roshi Kaisha, Ltd.) that was preheated at 850 °C for 4 h was used for the aerosol collections. The flow rate of the sample air was 20 L min⁻¹.

After the sample collections, the gas samples collected by the denuder were immediately recovered by rinsing the inside wall of the denuder with 5 ml of ultrapure water. The rinse solution samples and filter samples were stored below −20 °C until chemically analysed. Operational blank tests were performed 5 times at arbitrary intervals. All the blank samples were stored in the same manner as already described.

### 2.2. Sample analysis

Details of the sample analysis were described in our previous paper (Matsumoto and Yamato, 2016). Brief explanations are provided in the following sections.

The filter sample was ultrasonically extracted with ultrapure water. The water extract was filtered using a polytetrafluoroethylene membrane filter (pore size; 0.45 μm, 13HP045AN; Toyo Roshi Kaisha, Ltd.) that was preheated at 850 °C for 4 h was used for the aerosol collections. The flow rate of the sample air was 20 L min⁻¹. The rinse solution sample of the denuder was also analysed using a polytetrafluoroethylene membrane filter (pore size; 0.45 μm, 13HP045AN; Toyo Roshi Kaisha, Ltd.). The dissolved total nitrogen (DTN) in the extract solution was measured using a total organic carbon/to-total nitrogen analyzer (Model TOC-Vcsh/TNM-1; Shimadzu, Corp.). The DTN is considered to be the WSTN in the present study. The definitions of the DL were described in our previous paper (Matsumoto and Okita, 1998).

### 3. Results and discussion

Measurements of the gaseous and particulate WSON obtained in the present study are summarized in Table 1. The gaseous WSON concentration was estimated from the sum of the measurements from the two denuders. The average blank values of the ion species and DTN were subtracted from their respective measurements of the collected samples. Random errors in the analyses of each nitrogen species (NO₃⁻, NO₂⁻, NH₄⁺, and TN) in the collected and blank samples and systematic errors between ion chromatography and TN analyzer would contribute to the uncertainty of the WSON measurement and determine its detection limit (DL). The definitions of the DL were described in our previous paper (Matsumoto and Yamato, 2016). The WSON measurements below the DL were set to zero in this paper.

|          | Gas phase | PM₁₀ | PM₁₀ | Coarse-mode |
|----------|-----------|------|------|-------------|
| Mean     | 0.107     | 0.177| 0.131| 0.017       |
| S. D.    | 0.105     | 0.090| 0.064| 0.017       |
| Median   | 0.075     | 0.187| 0.127| 0.013       |
| I. R.    | 0.075     | 0.119| 0.079| 0.017       |
| Maximum  | 0.397     | 0.336| 0.225| 0.056       |
| Minimum  | 0.000     | 0.009| 0.000| 0.000       |
| n        | 12        | 12   | 12   | 12          |

Table 1. Measurements of the WSON in the gas phase and fine-mode particles (PM₁₀) from the denuder-filter pack system, and in the fine-mode particles (PM₁₀) and coarse-mode particles (d > 2 μm) from the impactor with a backup filter. ‘S. D.’ and ‘I. R.’ denote the standard deviation and interquartile range, respectively. Unit is μg m⁻³ except for ‘n’.
due to not only the size difference between the PM_{2.5} and PM_{2}, but also to other factors, such as the difference in the aerosol deposition amount on the inside wall between the denuder and impactor and the systematic error of the flow meters between the two sampling systems, which was not thoroughly investigated in this study. The average concentration of the WSON in the PM_{2.5} from the denuder-filter pack system was 0.177 μg m⁻³, whereas that in the PM_{2} from the backup filter of the impactor was 0.131 μg m⁻³. The WSON concentration in the PM_{2} was obviously lower than that in the PM_{2.5}, although the difference in the SO₄²⁻ concentrations between the PM_{2} and PM_{2.5} was negligible, which can be attributed to the volatilization loss of the particulate WSON from the backup filter.

Although the direct comparison of the results from the PM_{2.5} with those from the coarse particles (d > 2 μm) would be controversial due to the overlap fraction between both particle size ranges, the WSON in the atmosphere is considered to exist in the gas phase, fine particles (PM_{2.5}) and coarse particles with the concentration ratio of approximately 33:58:9 on average. The influence of the overlapped fraction on this estimate would be low because the difference in the SO₄²⁻ concentrations between the PM_{2} and PM_{2.5} was low as already described. González Benítez et al. (2010) and Zamora et al. (2011) reported that 55–67% of the WSON in the atmosphere was detected in the gas phase although these would overestimate the gaseous WSON concentration due to the loss of the WSON from the aerosol collection filter (Matsumoto and Yamato, 2016). The present result showed that approximately 33 ± 18% (mean ± standard deviation) of the WSON in the atmosphere existed in the gas phase. Size-fractionated aerosol samplings in many previous studies have demonstrated the dominance of the particulate WSON in the fine-mode range (e.g. Nakamura et al., 2006; Lesworth et al., 2010; Violaki and Mihalopoulos, 2010; Matsumoto et al., 2014). The present result also showed that only about one-eighth of the particulate WSON was detected in the coarse-mode range.

The concentrations of the basic and acid fractions of the gaseous WSON that were obtained by the acid and basic reagent-coated denuders, respectively, are summarized in Table 2. A large portion (approximately 76 ± 33%) of the gaseous WSON collected in the present sampling method was due to the basic species. Table 2 also listed the concentrations of the NH₃, HNO₃ and HNO₂ gases. The gaseous basic and acid WSON showed about one-sixth the nitrogen concentrations of the gaseous NH₃ and HNO₃, respectively. These results indicated that the WSON is an important fixed nitrogen species also in the gas phase.

Chemical compounds that consist of the gaseous WSON have not yet been sufficiently clarified, but aliphatic amines, such as methylamine, dimethylamine, trimethylamine, diethylamine and triethylamine, have been often detected in the gas phase (Schade and Crutzen, 1995; Gibb et al., 1999; Ge et al., 2011; VandenBoer et al., 2011; You et al., 2014). The concentrations of these aliphatic amines are largely dependent on local sources, but the nitrogen concentration ratios of these aliphatic amines with NH₃ have been estimated to be within about 0.001–0.16 in the ambient gas phase (Schade and Crutzen, 1995; Gibb et al., 1999; VandenBoer et al., 2011; You et al., 2014). In the present study, the ratio of the average nitrogen concentration of the basic WSON with that of NH₃ was 0.173, suggesting the possibility that chemical compounds other than these aliphatic amines contribute to the basic fraction of the gaseous WSON. Moreover, the chemical compounds of the acid WSON in the gas phase have not been identified in past studies.

The dry deposition amount of the atmospheric species can be estimated from the product of its atmospheric concentration and dry deposition velocity. The dry deposition velocity of the gaseous species is largely dependent on its chemical properties, so that the dry deposition amount of the gaseous WSON cannot be estimated at the present stage due to less understanding of the chemical composition of the gaseous WSON. As shown in Table 2, the present study demonstrated that the gaseous basic and acid WSON showed about one-sixth of the nitrogen concentrations of the gaseous NH₃ and HNO₃, respectively. This means that the dry deposition amount of the gaseous WSON was also about one-sixth the amount of the nitrogen dry deposition from both the gaseous NH₃ and HNO₃, if the dry deposition velocities of the gaseous basic and acid WSON are comparable to those of the gaseous NH₃ and HNO₃, respectively. Zhang et al. (2012) estimated that the contributions of the gaseous HNO₃ and NH₃ to the dry deposition amounts of the nitrogen species to the United States are about 55% and 29%, respectively. Russell et al. (2003) reported that the contributions of the gaseous HNO₃ and NH₃ to the dry deposition amounts of the WSTN to the mid-Atlantic coastal region in the United States are about 26% and 61%, respectively. The present study suggests a significant contribution of the gaseous WSON to the fixed nitrogen deposition through the dry process.

The present sampling system could not collect the gaseous neutral WSON, which would cause underestimation of the gaseous WSON, although the present system has the advantage of direct measurements of the gaseous and particulate WSON with less sampling artifacts compared to the other collection methods for the
The gaseous WSON (Matsumoto and Yamato, 2016). The influence of the neutral WSON on our experimental results should be verified in a future study, but the gaseous or semi-volatile neutral WSON species have been scarcely detected in the atmosphere compared to the basic WSON species (Cape et al., 2011 and references therein).

4. Summary

The gaseous and particulate WSON were simultaneously measured by the denuder-filter pack method to clarify the concentration level of the gaseous WSON and to discuss the gas/particle distribution of the WSON in the atmosphere. Although monthly results and seasonal trends were not discussed in this paper because only one sample was obtained each month and one sample covered only half of each month, the yearly averaged gas/particle partitioning of the WSON was clarified as below.

The present study showed that the WSON in the atmosphere is considered to exist in the gas phase, fine particles (PM_{2.5}) and coarse particles with the concentration ratio of approximately 33:58:9. Approximately 33 ± 18% of the WSON in the atmosphere existed in the gas phase. A large portion (approximately 76 ± 33%) of the gaseous WSON collected in the present sampling method was occupied by basic species. The gaseous basic and acid WSON showed about one-sixth the nitrogen concentrations of the gaseous NH\textsubscript{3} and HNO\textsubscript{3}, respectively. These results indicated that the WSON is an important fixed nitrogen species also in the gas phase.

Assuming the dry deposition velocities of the gaseous basic and acid WSON are comparable to those of the gaseous NH\textsubscript{3} and HNO\textsubscript{3}, respectively, the dry deposition of the gaseous WSON is also important for the nitrogen deposition to the earth’s surface. In order to more precisely estimate the dry deposition amount of the gaseous WSON, characterization of the chemical compounds in the gaseous WSON fraction is necessary. The nitrogen concentration ratios of the basic WSON with NH\textsubscript{3} in the present study suggests the possibility that chemical compounds other than the aliphatic amines reported in previous studies contribute to the basic fraction of the gaseous WSON. Characterization of the chemical compounds in the gaseous WSON fraction should be targeted in a future study.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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