



Uncertainties in the measurements of water-soluble organic nitrogen in the aerosol



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HIGHLIGHTS

- Traditional filter sampling underestimates the WSON concentration in the aerosols.
- Approximately 32.5% of the WSON in the PM_{2.5} was lost during the filter sampling.
- Gaseous WSON showed approximately quarter concentrations of the WSON in the PM_{2.5}.

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ABSTRACT

In order to evaluate the positive and negative artifacts in the measurements of the water-soluble organic nitrogen (WSON) in the aerosols by filter sampling, comparative experiments between the filter sampling and denuder-filter sampling were conducted during both the warm and cold seasons. The results suggest that the traditional filter sampling underestimates the concentrations of the particulate WSON due to its volatilization loss, but this effect on the ratio of the WSON to the water-soluble total nitrogen (WSTN) was small probably because inorganic nitrogen species were also lost during the filter sampling. Approximately 32.5% of the WSON in the PM_{2.5} was estimated to be lost during the filter sampling. The denuder-filter sampling also demonstrated the existence of the WSON in the gas phase with approximately quarter concentrations of the WSON in the PM_{2.5}. On the other hand, the filter sampling would overestimate the gaseous WSON concentration due to the loss of the WSON from the aerosol collection filter.

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1. Introduction

Water-soluble organic nitrogen (WSON) has been paid considerable attention in recent aerosol studies because it has been recognized that the WSON could account for a significant fraction of particulate nitrogen (e.g., Cornell et al., 2001; Zhang et al., 2002; Mace et al., 2003a, 2003b; 2003c; Nakamura et al., 2006; González Benítez et al., 2010; Violaki and Mihalopoulos, 2010; Miyazaki et al., 2011; Matsumoto et al., 2014). In these studies, aerosol samples are usually collected by filter sampling using a quartz fiber filter that had been often pre-heated to remove the organic blank. In the measurements of the particulate inorganic nitrogen compounds, such as NO₃⁻ and NH₄⁺, by the filter sampling, volatilization loss of particulate species collected on the filter

(negative artifact) and adsorption of gaseous species on the filter materials or particulate substances already collected on the filter (positive artifact) have been pointed out in many previous studies (Stelson et al., 1979; Appel et al., 1980, 1984; Appel and Tokiwa, 1981; Andersen and Hovmand, 1994). To avoid these artifacts, the collection of gas samples by a denuder before the aerosol collection has been recommended in previous studies, which can separately quantify these inorganic nitrogen compounds in the particulate and gas phases with less uncertainty (Shaw et al., 1982; Harrison and Kitto, 1990; Andersen and Hovmand, 1994; Matsumoto and Okita, 1998).

In contrast to these inorganic nitrogen compounds, the possibility of these artifacts in the measurements of the particulate WSON by filter sampling has not been examined. Both positive and negative artifacts have also been reported in the measurements of particulate organic carbonaceous compounds by filter sampling (Eatough et al., 1989; Novakov et al., 1997; Huebert and Charlson,

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2000). González Benítez et al. (2010) and Zamora et al. (2011) detected the WSON in the gas phase samples with concentrations comparable to that in the aerosols, and concluded that significant amounts of the WSON also exist as gaseous or semi-volatile forms in the atmosphere. These studies imply the possibility that the measurements of the WSON in the aerosols by the filter sampling are also affected by the positive and negative artifacts.

In the present study, comparative experiments between the filter sampling and denuder-filter sampling were conducted to evaluate the positive and negative artifacts in the measurements of the particulate WSON by the filter sampling. Underestimation of the particulate WSON by the filter sampling was found in this study, which will be discussed in this paper together with the gas/particle distribution of the WSON in the atmosphere.

2. Experiment

2.1. Sample collection

The sampling systems are shown in Fig. 1. Air sample was introduced into a cyclone (URG-2000 series; URG Corp.) for removing the particles with diameters larger than $2.5\ \mu\text{m}$, and then passed through three annular denuders (URG-2000 series; URG Corp.) and a filter holder. In the filter holder, a quartz fiber filter ($47\ \text{mm}\ \phi$, QR100; Toyo Roshi Kaisha, Ltd.) preheated at $850\ ^\circ\text{C}$ for 4 h (F_1), a 2% $\text{Na}_2\text{CO}_3/1\%$ glycerol-impregnated cellulose filter ($47\ \text{mm}\ \phi$, 5A; Toyo Roshi Kaisha, Ltd.) (F_2), and a 2% $\text{H}_3\text{PO}_4/1\%$ glycerol-impregnated cellulose filter (F_3) were installed in this order. In the system a-1, two denuders (D_{a1} and D_{a2}) were coated with 2% $\text{H}_3\text{PO}_4/1\%$ glycerol and one denuder (D_{b1}) was coated with 2% $\text{Na}_2\text{CO}_3/1\%$ glycerol. In the system a-2, one denuder (D_{a1}) was coated with 2% $\text{H}_3\text{PO}_4/1\%$ glycerol and two denuders (D_{b1} and D_{b2}) were coated with 2% $\text{Na}_2\text{CO}_3/1\%$ glycerol. Air sampling by using only the filter holder with the three filters (F_4 , F_5 , and F_6) was also conducted both in the systems a-1 and a-2.

The systems a-1 and a-2 were operated 4 times each during the warm season from July to September 2014 and 4 times each during the cold season from December 2014 to March 2015 with a sampling time of 7 days. The flow rate of the sample air in the denuders was set at $10\ \text{L}\ \text{min}^{-1}$. The D_{a1} and D_{b1} denuders can collect gaseous basic and acid species, respectively, and the F_1 filter collects the particulate matters with diameters smaller than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$). Some parts of the particulate species in the $\text{PM}_{2.5}$ collected on the F_1 filter might volatilize during the sampling due to the change of their equilibrium state, but they can be collected by the F_2 or F_3 filter (Harrison and Kitto, 1990; Matsumoto and Okita, 1998). Therefore, the results from the D_{a1} , D_{b1} , and $F_1+F_2+F_3$ are considered to be the measurements of the gaseous basic, gaseous acid, and particulate species, respectively, without the influence of the artifacts. The results from the F_4 , F_5 , and F_6 filters, on the other hand, are considered to be the measurements of the particulate, gaseous acid, and gaseous basic species, respectively, which would be affected by the artifacts. The D_{a2} or D_{b2} denuder was installed to evaluate the collection efficiencies of the gaseous nitrogen species by the denuder.

As will be discussed later, the present sampling system could not collect the gaseous neutral WSON, which would cause uncertainties in the estimation of the sampling artifact and gas/particle distribution of the WSON. However, the present system has the advantage of direct measurements of the gaseous and particulate WSON together with inorganic nitrogen compounds, which cannot be achieved by the activated carbon denuder system that has been often used for the collection of gaseous organic species (Eatough et al., 1989, 1996; Matsumoto et al., 2003). The influence

of the neutral WSON on our experimental results should be verified in a future study, although 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 the references therein).

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 (specific resistivity $>18\ \text{M}\Omega\ \text{cm}$). The rinse solution samples and filter samples were stored below $-20\ ^\circ\text{C}$ until chemically analyzed. Operational blank tests were performed 5 times at arbitrary intervals. All the blank samples were stored in the same manner as described above.

In the present experiments, both sampling lines with and without denuders were simultaneously operated and the measurements from both lines were compared to each other. In order to check the systematic error between the two lines, air sampling only with a quartz fiber filter preheated at $850\ ^\circ\text{C}$ for 4 h (F_7 and F_8) was conducted simultaneously in both sampling lines (system b in Fig. 1) with a sampling times of 7 days. Five duplicate aerosol samples were obtained from September to December 2015. The difference between the measurements from the F_7 and F_8 filters can be attributed to the systematic error between the two sampling lines. The filter samples were also stored in the same manner as described above.

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 is located on the building roof of the University of Yamanashi (about 18 m above the ground) surrounded by residential areas with a distance of about 2 km from the city center. Details of the sampling site were described in our previous report (Matsumoto et al., 2014).

2.2. Sample analysis

One-fourth of the filter collected aerosol sample (F_1 , F_4 , F_7 , and F_8) was ultrasonically extracted with 20 ml of ultrapure water in a glass vial. The water extract was filtered using a polytetrafluoroethylene (PTFE) membrane filter (pore size; $0.45\ \mu\text{m}$, 13HP045AN; Toyo Roshi Kaisha, Ltd.). The dissolved total nitrogen (DTN) in the extract was measured using a total organic carbon (TOC)/total nitrogen (TN) analyzer (Model TOC-Vcsh/TNM-1; Shimadzu, Corp.) that can detect the DTN by ozone chemiluminescence detection after a thermo-catalytic oxidation process. The DTN is considered to be water-soluble total nitrogen (WSTN) in this study. Ion species (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) in the extract were measured using ion chromatographs (DX-120; Dionex Corp. and ICS-1100; Thermo Fisher Scientific Inc.). The concentration of the total inorganic nitrogen (IN) was 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 entire amount of the filter collected acid or basic gases (F_2 , F_3 , F_5 , and F_6) was ultrasonically extracted in 40 ml of ultrapure water in a glass vial, and the extract was filtered using a PTFE membrane filter. NO_2^- , NO_3^- , and NH_4^+ in the extract were measured using the ion chromatographs to determine the concentrations of the gaseous HNO_2 , HNO_3 , and NH_3 , respectively. The DTN in the extract was measured using the TOC/TN analyzer. The rinse solution sample of the denuder was also analyzed for NO_2^- , NO_3^- , NH_4^+ , and DTN in the same manner as the extract of the filter sample. The difference between the concentrations of the DTN and IN is considered to be the gaseous WSON.

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