

Synthesized measurements of reactive nitrogen fluxes onto a forest using gradient and relaxed eddy accumulation method

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Abstract

Synthesized measurements of vertical profiles and exchange fluxes of reactive nitrogen and relevant species, which are fine (PM_{2.5}) and coarse aerosol components (NO₃⁻, NH₄⁺ SO₄²⁻) and gas components (HNO₃, NH₃, SO₂), were carried out in a deciduous forest, suburban Tokyo. Average vertical profiles in daytime and nighttime during the experiment showed the down ward fluxes (depositions). Differences of decreasing rates among the components were approximately in accordance with theoretical deposition velocities, except NO₃⁻ in PM_{2.5}. Decreasing ratio of NO₃⁻ in PM_{2.5} from upper to lower canopy was significantly larger than that of SO₄²⁻ in PM_{2.5} or NO₃⁻ in coarse aerosols. From the measurements by relaxed eddy accumulation, deposition velocities of NO₃⁻ in PM_{2.5} were larger than those of SO₄²⁻ in PM_{2.5}. The large deposition velocity was possibly caused by an effect of shifts in equilibrium between aerosol phase (NH₄NO₃) and gas phase (HNO₃, NH₃) near surfaces. It was indicated that NH₄NO₃ could be quickly removed as well as HNO₃ in some conditions.

Key Words

Aerosols, ammonium nitrate, HNO₃, vertical profile, deposition velocity

Introduction

In order to assess effects of reactive nitrogen on ecosystems, it is very important to estimate the rates of atmospheric deposition accurately. According to a review of Fowler et al. (2009), chemical transport models are able to estimate the depositions with uncertainties of the order of 30% in wet deposition and 50% in dry deposition for the main chemical species such as sulfur and nitrogen compounds. Moreover from an intercomparison among inferential models to estimate dry depositions of reactive nitrogen, differences between the models reach a factor 2–3 and are often greater than differences between monitoring sites (Flechard et al., 2011). Therefore estimations of reactive nitrogen dry deposition by the models still have large uncertainties. To improve the models, further understanding of dry deposition mechanisms by measurement-based studies is required.

In this study, we carried out a synthesized measurements of the fluxes of reactive nitrogen and relevant species in aerosol and gas phase onto a forest. The fluxes and deposition velocities were measured by relaxed eddy accumulation (REA) method. The vertical profiles from top of the canopy to the forest floor were also measured at the same time.

Methods

We established a synthesized measurement system of reactive nitrogen fluxes at a 30-m-high walk-up tower in a forest of the Field Museum Tamakyuryo (FM Tama) of the Tokyo University of Agriculture and Technology, which is located in a western suburb of Tokyo (35°38'N, 139°23'E). Deciduous trees (*Quercus*) were dominant around the tower, and Japanese cedar (*Cryptomeria*) was lightly distributed. The system consists of vertical profile, aerosol flux (REA-aerosol) and gas flux (REA-gas) sampling parts (Fig. 1).

Vertical profile measurements

To measure concentrations of fine and coarse aerosol components, HNO₃, NH₃ and SO₂, a filter pack with an impactor (flow rate 20 L/min) was used. The filter pack was composed of coarse aerosol, fine aerosol (PM_{2.5}), alkali impregnated (HNO₃, SO₂) and acid impregnated (NH₃) filter stages. Four filter packs were placed on the tower at heights of 1, 8, 23 and 30 m (2 heights above canopy, 2 heights below canopy) to obtain the vertical profiles (Fig. 1).

Flux measurements

In both REA-aerosol and REA-gas sampling parts, samples of updraft and downdraft were collected onto separate filters with a flow rate of 5 L/min. The updraft or downdraft was determined by the sonic anemometer. The fluxes (F) were determined as

$$F = \beta \sigma_w (C_u - C_d),$$

where β is an empirical coefficient, σ_w is the standard deviation of the vertical wind speed, and C_u and C_d are the average concentrations in the updraft and downdraft sample filters, respectively (Matsuda et al., 2015).

Deposition velocities (V_d) were determined as

$$V_d = -F / C,$$

where C is the average concentration during sampling period.

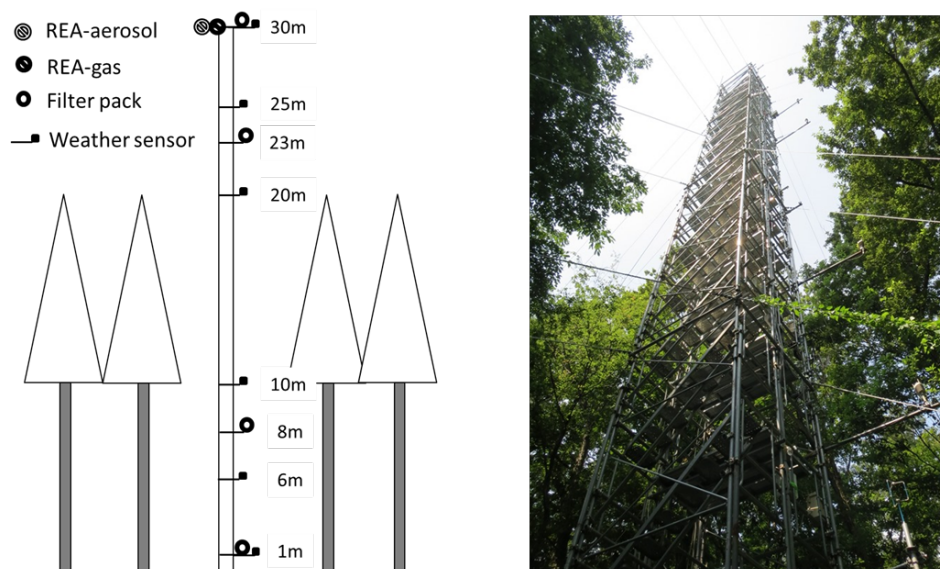


Fig. 1 Illustration of synthesized measurement system of reactive nitrogen fluxes installed at the tower.

The REA-aerosol part measures fluxes of $PM_{2.5}$ components, mainly NO_3^- and SO_4^{2-} . Specifications of the REA-aerosol part are the same as Matsuda et al. (2015) (Fig. 2 (a)). Because HNO_3 is easy to be removed by sampling line such as cyclone and impactor, we separated the REA-gas part and the REA-aerosol part. The REA-gas part measures fluxes of HNO_3 , NH_3 and SO_2 . We used the 4-stage filter pack method adopted by Acid Deposition Monitoring Network in East Asia (EANET, 2013) to measure their C_u and C_d (Fig. 2 (b)). The 4-stage filter pack was composed of PTFE (total aerosols), Nylon (HNO_3), alkali impregnated (SO_2) and acid impregnated (NH_3) filter stages.

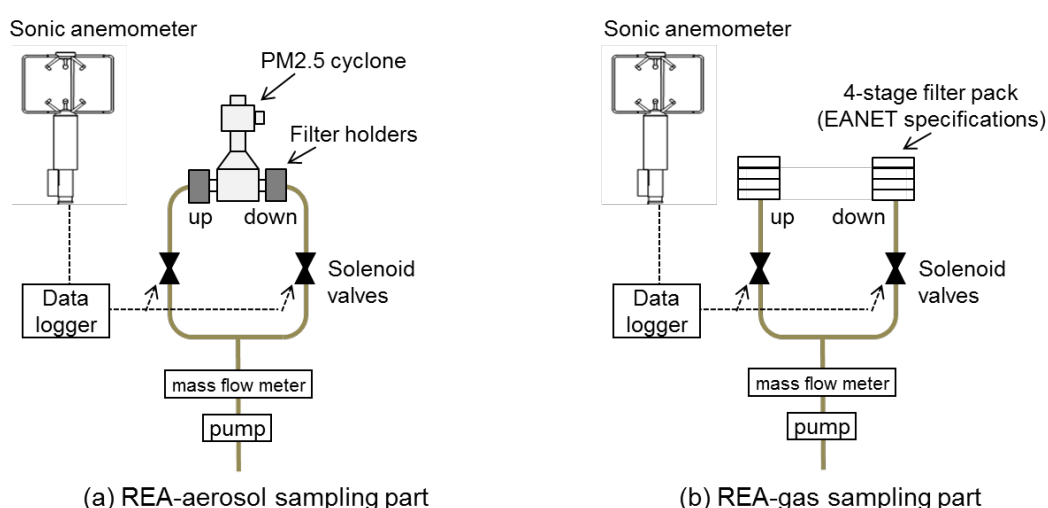


Fig. 2 Illustration of REA sampling methods for aerosols (a) and gases (b).

We carried out an experiment from 21 to 31 in July 2015. During the period, the forest canopy was leafy and the leaf area index was estimated about 4–5. The samplings were continuously performed in the daytime (6:00–18:00) and in the nighttime (18:00–6:00) during the experiment, except rainy days. After each sample

was taken, inorganic ions were extracted from the samples by ultrasonic extraction into deionized water, and then they were analyzed by an ion chromatography.

Results and discussion

Vertical profiles

Vertical profiles of aerosol and gas components indicate their properties of deposition or emission. Decreases and increases of components from upper to lower canopy generally mean the downward fluxes (depositions) and the upward fluxes (emission), respectively. Moreover the large decreasing rates indicate the large deposition velocities due to fast removal. The average profiles in daytime and nighttime during the experiment showed the downward fluxes (depositions) (Fig. 3). The differences of decreasing rates were approximately in accordance with theoretical deposition velocities, except NO_3^- in $\text{PM}_{2.5}$. Deposition velocities of aerosols largely depend on the size in general. However the decreasing ratio of NO_3^- was significantly larger than that of SO_4^{2-} (Fig. 3), although both of them existed in submicron size as $\text{PM}_{2.5}$. Moreover larger decreasing ratio of NO_3^- in $\text{PM}_{2.5}$ than in coarse aerosols also indicated the discrepancy to the size dependence (Fig. 3). Decreases of NO_3^- in $\text{PM}_{2.5}$ from upper to lower canopy were also clearly found in each sampling period, compared with SO_4^{2-} in $\text{PM}_{2.5}$ (Fig. 4).

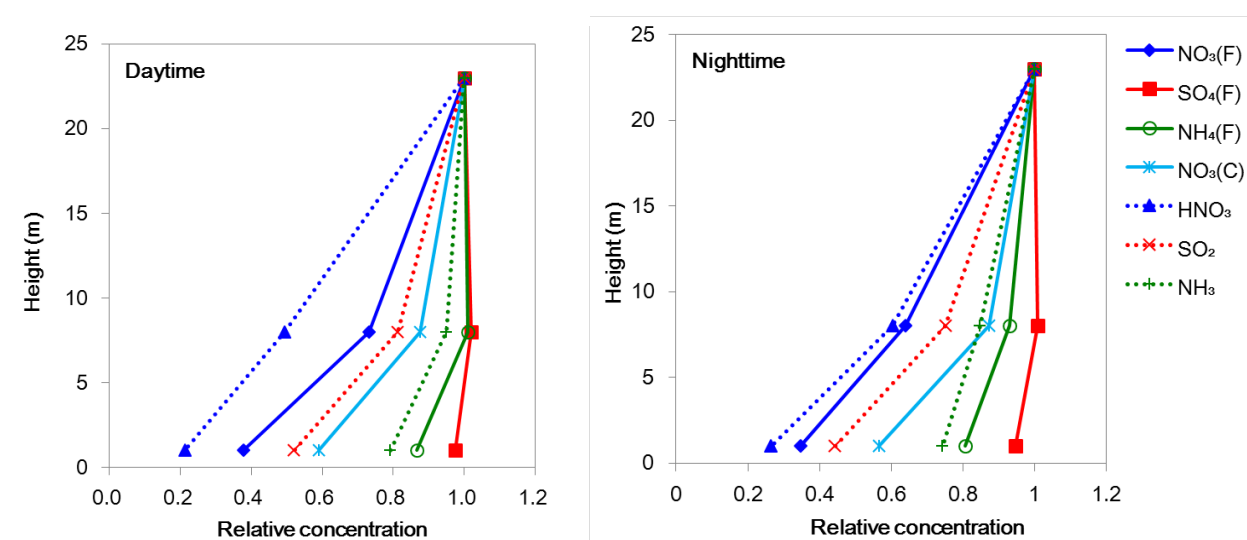


Fig. 3 Vertical profiles of relative concentrations of $\text{PM}_{2.5}$ components (NO_3^- : $\text{NO}_3(\text{F})$, SO_4^{2-} : $\text{SO}_4(\text{F})$, NH_4^+ : $\text{NH}_4(\text{F})$), NO_3^- in coarse aerosols ($\text{NO}_3(\text{C})$), HNO_3 , SO_2 and NH_3 .

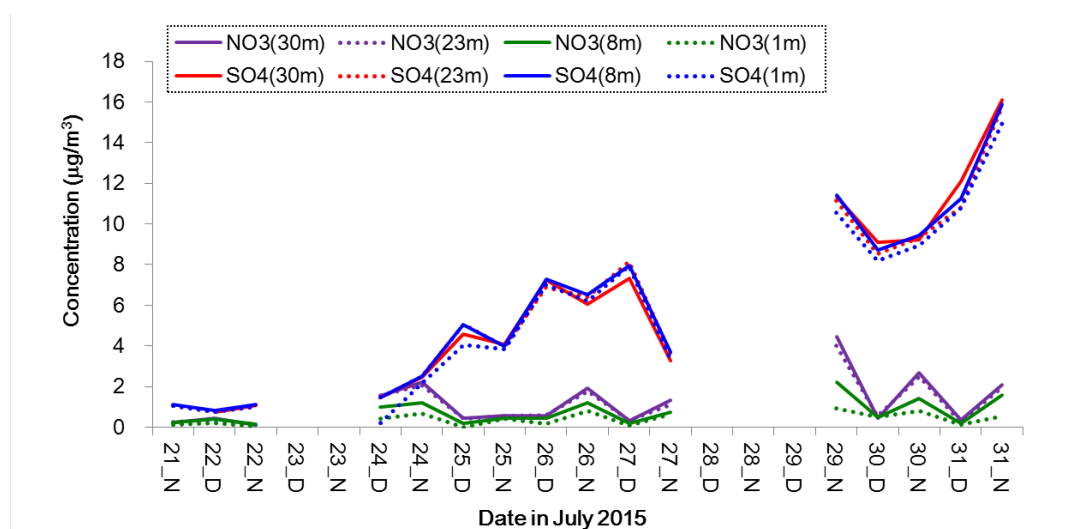


Fig. 4 Variations of concentrations of NO_3^- (NO_3) and SO_4^{2-} (SO_4) in $\text{PM}_{2.5}$ at 30m, 23m, 8m and 1m. “D” and “N” mean daytime sample (6:00-18:00) and nighttime sample (18:00-6:00), respectively.

From the analysis of ion balance in PM_{2.5} inorganic components, most of NO₃⁻ and SO₄²⁻ existed as NH₄NO₃ and (NH₄)₂SO₄, respectively. The discrepancy is probably due to the differences of chemical properties between NH₄NO₃ and (NH₄)₂SO₄. Wyers and Duyzer (1997) also found large deposition velocities of NH₄NO₃ over a forest by gradient measurements, and indicate there is an effect of shifts in equilibrium between aerosol phase (NH₄NO₃) and gas phase (HNO₃, NH₃) near surfaces.

Deposition velocities

Under the effect of equilibrium shifts, large decreasing rates do not mean large deposition rates. Therefore to investigate the influence of the effect on deposition process, direct measurements of deposition velocities by REA method are effective. As results of measurements by REA-aerosol, average V_d of NO₃⁻ and SO₄²⁻ in PM_{2.5} were 2.8 and 0.04 cm/s, respectively. Those averages were calculated from the integrated flux divided by the average concentration during the experimental period.

Individual V_d of NO₃⁻ were distributed in a wider range than V_d of SO₄²⁻, especially in daytime, probably because of uncertainties under the low concentrations of NO₃⁻ in daytime (Fig. 4) and higher blank values of NO₃⁻ than those of SO₄²⁻. Artifacts associated with volatilization of NH₄NO₃ on a sample filter also possibly increased the uncertainties in daytime. Therefore we selected the samples in the nighttime of 29 (29_N) and 30 (30_N) July as low-uncertainty samples because of relatively higher concentrations of both components in nighttime (Fig. 4). The V_d of NO₃⁻ and SO₄²⁻ were 1.4 and 0.01 cm/s on 29_N; 1.6 and -0.4 cm/s on 30_N, respectively. In both sampling periods, the V_d of NO₃⁻ were clearly higher than those of SO₄²⁻ as well as the average V_d during the experimental period. These differences of V_d between NO₃⁻ and SO₄²⁻ indicate that the effect of shifts in equilibrium between aerosol phase (NH₄NO₃) and gas phase (HNO₃, NH₃) near surfaces possibly enhances dry deposition of ammonium nitrate. Since the V_d of HNO₃ measured by REA-gas were 1.3 cm/s on 29_N and 2.8 cm/s on 30_N, it is possible that NH₄NO₃ was quickly removed by the forest as well as HNO₃.

Conclusion

Synthesized measurements of the fluxes of reactive nitrogen and relevant species in aerosol and gas phase using gradient and REA method were effective to better understand their deposition mechanisms. The decreasing ratio of NO₃⁻ in PM_{2.5} from upper to lower canopy was significantly larger than that of SO₄²⁻ in PM_{2.5} or NO₃⁻ in coarse aerosols in both of daytime and nighttime. Measured V_d of NO₃⁻ in PM_{2.5}, mainly as NH₄NO₃, were larger than V_d of SO₄²⁻ in PM_{2.5}, mainly as (NH₄)₂SO₄. Large decreasing ratios and V_d of HNO₃ were also found. Therefore NH₄NO₃ could be quickly removed as well as HNO₃ in some conditions. The effect of shifts in equilibrium between aerosol phase (NH₄NO₃) and gas phase (HNO₃, NH₃) near surfaces possibly enhances dry deposition of NH₄NO₃.

Matsuda et al. (2015) reported that dry deposition ratios of SO₄²⁻ in PM_{2.5} estimated by an inferential model was in good agreement with that measured by the REA-aerosol at the same site. Therefore current dry deposition ratios of NO₃⁻ in PM_{2.5} is possibly underestimated, because the effect of shifts in equilibrium is usually not included in inferential methods.

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