

MEASUREMENT OF NITROGEN AND SULFUR DEPOSITION TO LAKE PALDANG IN KOREA

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ABSTRACT

Nitrogen and sulfur deposition was measured on Lake Paldang from March 2002 to October 2003. Wet and dry depositions were separately measured using wet- and dry-only samplers, respectively. In order to measure the dry deposition to the water body, a dry deposition sampler composed of three pans filled with pure water, called the deposition water, was used. Since ammonium was generally in excess in ambient air, more than half of ammonium was present in the gaseous form. Ammonium concentration was also generally higher than the sum of major anion concentrations in the deposition water because gaseous species were much easily deposited than the species in fine particles. Nevertheless, the contribution of gaseous ammonia to the deposition of ammonium was not high as well as that of particulate ammonium while the contribution of gaseous nitric acid was much higher than that of particulate nitrate. Annual wet deposition fluxes of nitrogen and sulfur were five and six times higher than their dry deposition fluxes, respectively. Except for ammonium, the dry deposition flux estimated in the present work was a half of the previous results. This was mainly caused by much smaller dry deposition velocities over the water than over the ground.

INTRODUCTION

Lake Paldang, formed by a dam located on the Han River, is a main resource of drinking water in the greater Seoul area (Figure 1). The lake is surrounded by forests and farmland, but on the downwind side of prevailing westerlies from Seoul. It is susceptible that the lake would be affected by various pollutants from Seoul [1].

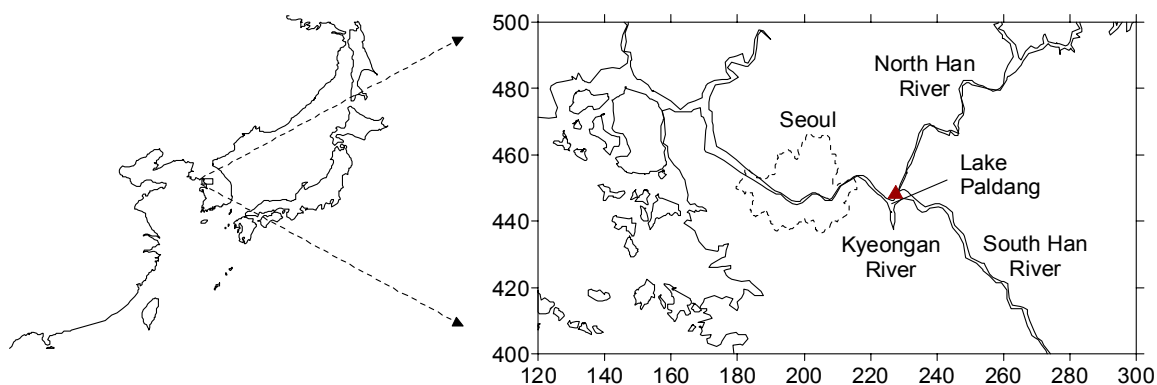


Figure 1. Location of Lake Paldang. Numbers on the axes on the right panel indicate the distance in km in the Transverse Mercator coordinate. Filled triangle denotes the measurement site.

In fact, any pollutants in the air can fall and degrade the water quality. Among them, oxidized nitrogen and sulfur are representative acidic compounds that can acidify lakes and streams. Despite considerable amounts of acidic deposition, the pH of major lakes and streams in Korea is well between 6.5 and 8.5. On the other hand, the nutrient level of major lakes that are the resource of drinking water is either over-enriched or enriched [2]. Although phosphorus is limiting, it shows a decreasing trend while nitrogen concentration has increased or at least not decreased in major lakes during the past ten years [3].

In the present work, deposition of nitrogen and sulfur compounds has been measured on the spot of Lake Paldang for two years since May 2002. Nitrogen was measured because it is a key factor of eutrophication; sulfur was measured as an indicator of anthropogenic influence that cannot be taken into account with nitrogen alone.

METHODS

Wet and dry depositions were separately measured by wet-only and dry-only samplers, respectively. The dry deposition sampler was composed of three pans filled with pure water. An average concentration increase during the measurement period, after removing an abnormal value if existed, was considered as the input by deposition. The amount of dry deposition was measured for 24 hours along with total suspended particulates (TSP) and acidic and ammonia gases in ambient air. It was measured every day during the intensive measurement period lasting around one or two weeks in spring and fall each year (Figure 2). In other period it was measured at intervals of around 15 days. The amount of wet deposition was measured either daily or event base.

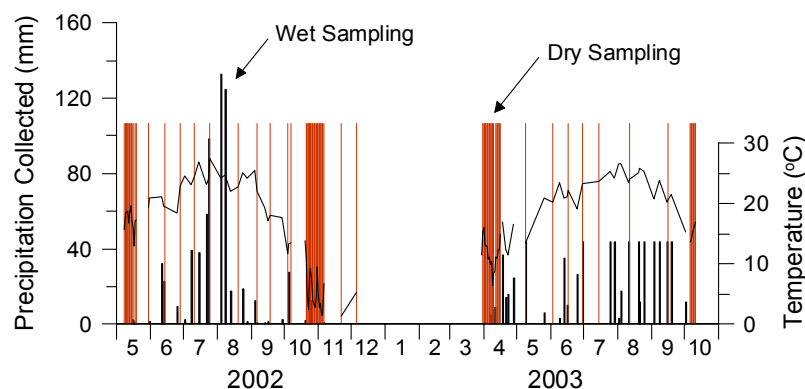


Figure 2. Sampling schedule for measuring wet and dry depositions. Only sampling date is indicated for the dry deposition, but the amount of precipitation collected is also indicated for the wet deposition. Air temperature is shown for the reference.

Both TSP and gases were sampled using a low volume sampler at the flow rate of 16.7 L/min with a three-stage filter holder for 47 mm filters (Savillex #0-47). A Teflon filter (Gelman Zeflur) was used at the first stage to collect TSP. Nylon membrane filter (Gelman Nylasorb) and citric acid impregnated quartz fiber filter (Whatman QM-A) were used at the second and third stages to collect nitric acid and ammonia, respectively. Anions such as Cl^- , NO_3^- , and SO_4^{2-} were analyzed by ion chromatography (Dionex-120). Cations such as Ca^{2+} , K^+ , Mg^{2+} , and Na^+ were analyzed by atomic absorption spectrometer (Perkin Elmer AAnalyst 300). NH_4^+ was determined with a spectrophotometer (Spectronic Genesys 2) after developing color by the indophenol blue method.

RESULTS AND DISCUSSION

Figure 3 shows the variations in nitrogen and sulfur compounds and TSP in ambient air. In this work, gaseous nitric acid and ammonia were separately measured after the TSP filter. However, since they were semi-volatile they could evaporate from and sorb to particles according to the surrounding conditions, e.g., temperature and relative humidity. Therefore, the total concentration summing gas and particulate concentrations was given on the top panel along with the gas fraction on the next.

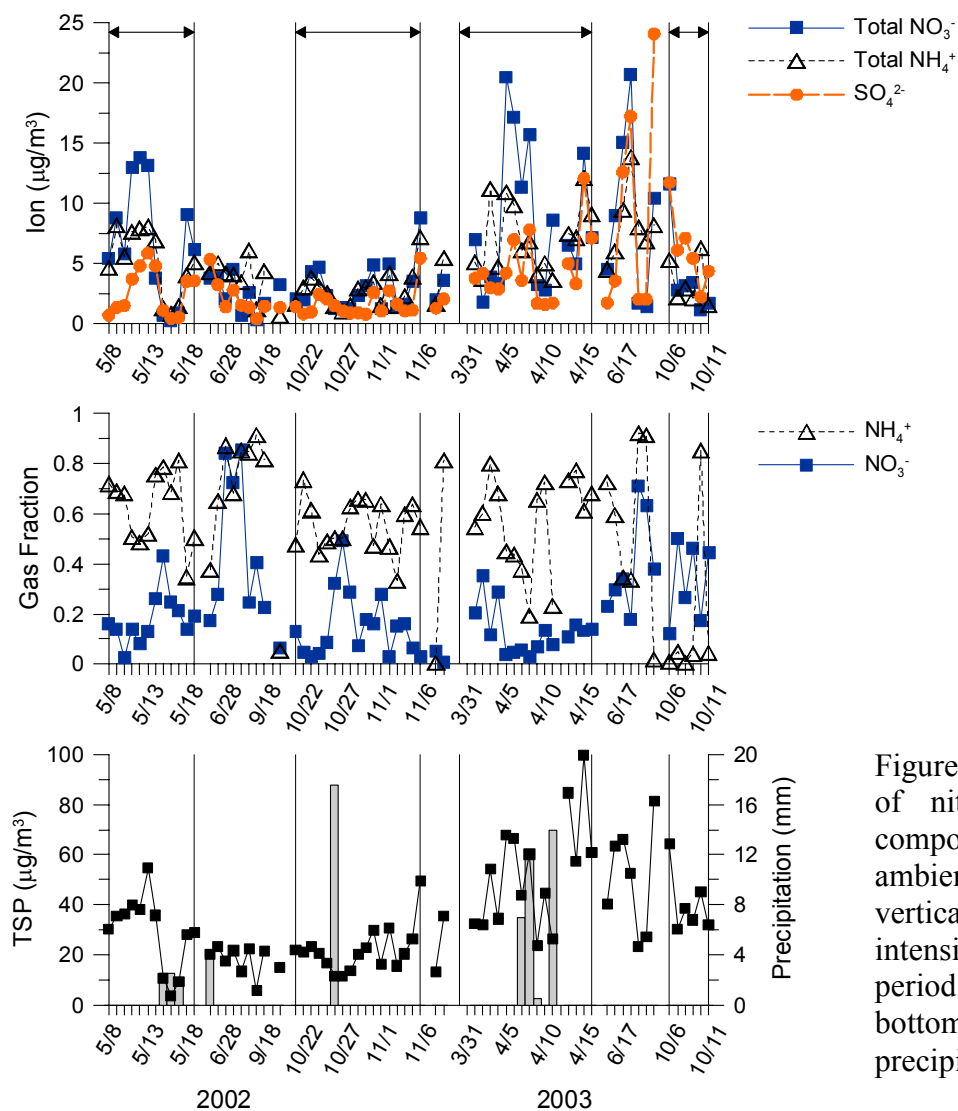


Figure 3. Concentrations of nitrogen and sulfur compounds and TSP in ambient air. Arrows and vertical lines indicate the intensive measurement period. Bar graph on the bottom panel shows precipitation.

Ion concentrations as well as TSP were higher in 2003 than in 2002. Meteorological variables such as wind speed, temperature, and precipitation were compared between 2002 and 2003, but any plausible explanation was not found. High concentration of TSP in spite of precipitation was also unusual except for May 2002.

The gas fraction of ammonium was generally more than 50% while that of nitrate was high only in summer with high temperatures. This was caused by substantially large amount of

ammonia over the Lake Paldang area compared with sulfate and nitrate. Sulfate is mostly present in the particulate phase, and is usually neutralized by ammonium in a polluted environment. Remaining ammonia will combine with nitrate to form ammonium nitrate, but it is semi-volatile and can be in both gas and particulate phases as mentioned.

Average equivalent ratio of ammonia to sulfate was 1.9 in Figure 3. Average equivalent ratio of ammonia to sulfate and nitrate was 0.83 in the particulate phase. Although the value less than 1.0 looks like an indication of shortage of ammonia, total ammonia summing gas and particulate ammonium was sufficiently large to neutralize all nitrate. In fact, equivalent ratio of total ammonia to sulfate and total nitrate was 2.2 well above 1.0. As a result, some amount of nitrate was in the gas phase, but much more amount of ammonia was in the gas phase as shown on the middle panel of Figure 3.

Because of such high concentration of ammonia in the gas phase and also because of higher deposition velocity of gaseous species than that of fine particles, ammonium concentration was generally higher than the sum of major anion concentrations in the deposition water. Nevertheless, ammonium concentration in the deposition water was not so high compared with large amount of ammonia in the gas phase and so was the deposition flux, which will be explained as follows.

Table 1 shows the correlation between dry deposition flux and atmospheric concentrations. High correlation coefficient and contribution of gaseous nitric acid indicate that the deposition of nitrate was led by gaseous species. On the other hand, both correlation coefficient and contribution of gaseous ammonia were not high as well as those of particulate ammonium. This means that the deposition of gaseous ammonia was suppressed for some reason. Although saturation of the deposition water by ammonia could be inferred [4], ammonium concentration in the deposition water was only in $\mu\text{eq/L}$ that should be far below the saturation point.

Table 1. Dry deposition flux and atmospheric concentrations.

Dry deposition flux	Correlation coefficient (r^2)		Relative contribution ^a	
	Particulate species	Gaseous species	Particulate species	Gaseous species
NO_3^-	0.24 (NO_3^-) ^b	0.81 (HNO_3)	0.04 (NO_3^-)	0.83 (HNO_3)
NH_4^+	0.10 (NH_4^+)	0.15 (NH_3)	0.14 (NH_4^+)	0.15 (NH_3)
SO_4^{2-}	0.10 (SO_4^{2-})	-	0.07 (SO_4^{2-})	

^aCoefficients of the multiple linear regression on nitrogen and sulfur bases, respectively.

^bCorresponding atmospheric species.

Figure 4 shows precipitation concentrations and wet depositions of major ions. Since ion concentration in the precipitation was inversely proportional to the precipitation amount, it was generally high in spring and fall with less precipitation and low in summer with much precipitation. Wet deposition flux is expressed as concentration in the precipitation multiplied by the precipitation intensity. As a result, wet deposition flux cannot be large only with high ion concentration caused by little precipitation and with much precipitation accompanying almost zero ion concentration. In fact, the highest four fluxes in Figure 4 were resulted from neither very high concentration nor very much precipitation,

As mentioned earlier, dry deposition was measured on a daily basis while wet deposition was measured mainly on an event basis. Annual amount of dry deposition was estimated with the daily mean amount of dry deposition and the number of days on which dry deposition was dominated over wet deposition. The effective number of days for dry deposition was obtained by excluding the number of days on which the amount of precipitation was more than 10 mm. Annual amount of wet deposition was estimated with the mean amount of wet deposition per mm of precipitation and annual total of precipitation in mm.

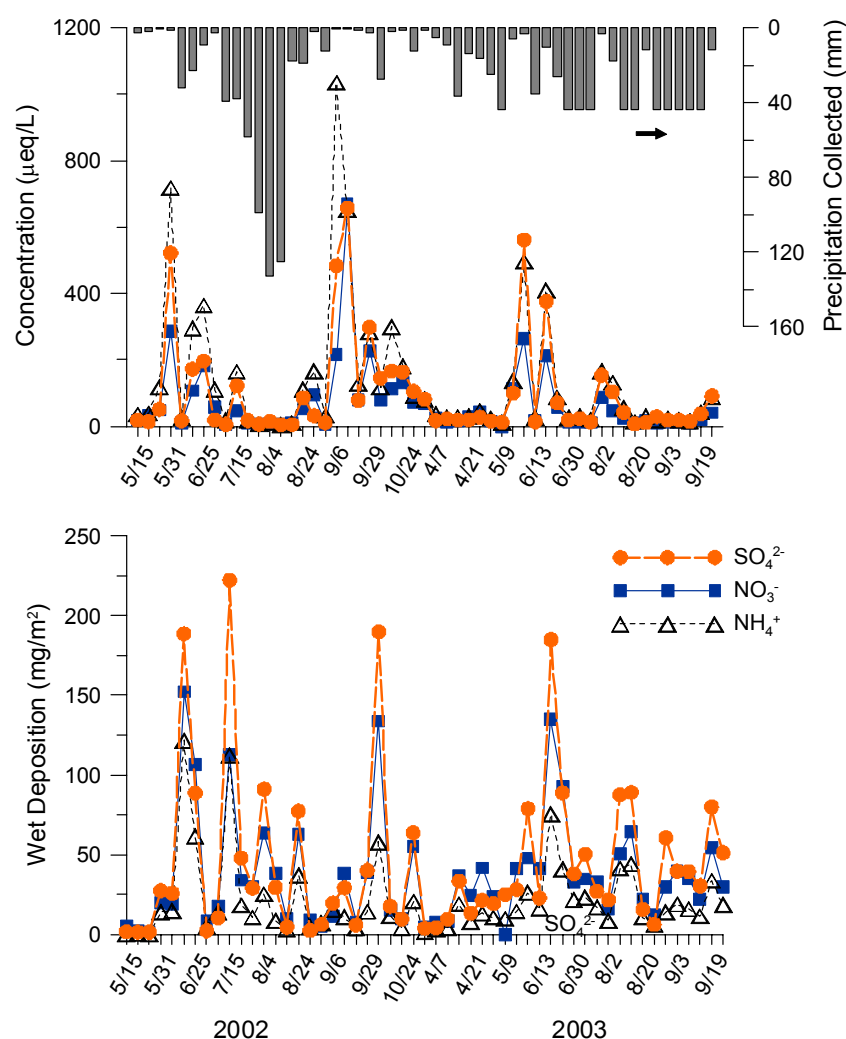


Figure 4. Precipitation concentrations and wet depositions of NO_3^- , NH_4^+ and SO_4^{2-} .

Table 2. Annual wet and dry deposition fluxes of nitrogen and sulfur ($\text{mg/m}^2 \cdot \text{year}$)

Deposition	N		Total	S
	NO_3^-	NH_4^+		SO_4^{2-}
Wet	623	1,211	1,834	1,110
Dry	85	288	373	182
Wet/dry ratio	7.3	4.2	4.9	6.1

During the past ten years several teams have tried to estimate dry and wet depositions both near Lake Paldang and nationwide. In general, wet deposition has been estimated by

measuring precipitation while dry deposition has been estimated by using deposition velocity. Table 2 shows annual deposition fluxes estimated in the present work. The amount of wet deposition in Table 2 was not much different from those in the previous works. The amount of dry deposition of ammonium was also similar to the previous result. But the dry depositions of nitrate and sulfate were one fifth and one tenth of the previous results, respectively.

Apparently, difference between the present and the previous works came in part from the emission change. For example, wet deposition of nitrogen in Table 2 was two times higher than that measured in the mid 1990s while that of sulfur was similar. However, large differences in dry depositions of sulfate and nitrate were mainly because the dry depositions in Table 2 were obtained from the measurements of the deposition water over the lake. It is known that deposition velocity over the water is three to six times lower than that over the ground [5].

Although variations due to the emission change and the difference of the deposition velocity between over the water and over the ground were taken into account, dry depositions of nitrate and sulfate in Table 2 were still a half of the previous results. This could be attributable to the fact that the dry deposition in the present work was obtained from the measurement while those in the previous works were obtained by estimating deposition velocities. Nevertheless, dry deposition of ammonium in Table 2 was larger than the previous results owing to large amount of ammonia although its deposition seemed limited to some extent compared with its high concentration in the air.

ACKNOWLEDGMENTS

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