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Chemical composition of fog water at Mt. Tateyama near the coast of the Japan Sea in Central Japan

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Abstract

Measurements of the chemical composition of fog water at Murododaira (altitude, 2,450 m), on the western slope of Mt. Tateyama near the coast of the Japan Sea, were performed during the summers of 2004 and 2008. Strong acidic fogs (pH < 4) containing high concentrations of $nssSO_4^{2-}$ were observed in 2008, when the air mass at Mt. Tateyama originated mainly from the polluted regions of Asia. The mean ionic concentrations in the summer of 2008 were higher than those in the autumn from 2004 to 2007. The ratio of $NO_3^-/nssSO_4^{2-}$ in fog water was relatively high in 2004, when the air mass originated from central and western Japan. Transport processes of air pollution may significantly influence the chemical characteristics of fog water at Mt. Tateyama.

1. Introduction

Acid fogs are thought to contribute to the decline of forests at high elevation locations, where mountain slopes are frequently immersed in fog or cloud water (e.g., Blank 1985). Chemical measurements of fog water have been performed at high elevation sites, especially in the United States and Europe (e.g., Mohnen and Kadlecek 1989; Collett et al. 1990). The chemical composition of cloud or fog water has also been measured in East Asian countries, such as China (Lu and Niu 2009), South Kores (Kim et al. 2006) and Japan (Igawa et al. 1998; Watanabe et al. 1999, 2001, 2006; Tago et al. 2006). However, there is a shortage of fog water chemistry data from high elevation sites in Japan, where the decline of forests has become a serious environmental problem.

Recently, large amounts of acidic species have been deposited in the Hokuriku District, along the Japan Sea coast in central Japan (Honoki et al. 2007). Mt. Tateyama, a part of the mountain range in the Hokuriku District, is near the Japan Sea coast, where a large amount of air pollution may be transported from Asia as well as from industrial regions in Japan. In previous studies of Mt. Tateyama, high concentrations of pollutants derived from the continent, such as O_3, SO_2, and aerosols, were observed (Kido et al., 2001; Osada et al. 2009). Preliminary measurements of the chemical constituents of several fog water samples were also made at Mt. Tateyama in 2003 (Watanabe et al. 2005). A strong acidic fog, probably affected by trans-boundary air pollution, was detected. Furthermore, a serious decline of the forest in the vicinity of Mt. Tateyama has been observed (Kume et al. 2009). Air pollution may contribute to the damage to vegetation.

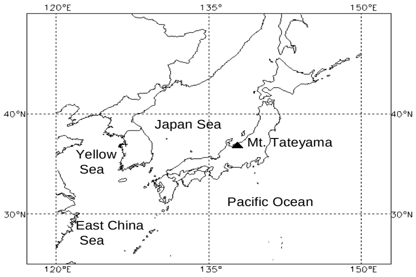

Fig. 1. Map of Japan showing the location of Mt. Tateyama.

From 2004, we systematically performed fog chemistry observations at Mt. Tateyama, and the chemical composition of fog water in the autumn (September and October) was described (Watanabe et al. 2010). The chemical characteristics of cloud or fog showed year-to-year variation. According to Osada et al. (2009), the volume concentration of submicrometer aerosols near the summit of Mt. Tateyama was significantly higher in the summer than in the autumn. To evaluate vegetation damage by acid fogs, it is important to understand the fog water chemistry during the summer. In this paper, the chemical characteristics of the fog water sampled at Murododaira near the summit of Mt. Tateyama in the summer are discussed.

Table 1. Summary of the chemistry of fog water at Murododaira (altitude, 2,450 m) during the summer. The units of the ionic concentrations are micro-equivalents per liter. N denotes the number of samples.

Year	N	pH	Cl^-	NO_3^-	SO_4^{2-}	$nssSO_4^{2-}$	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	$nssCa^{2+}$
2004	7	4.4-5.1	8-16	15-83	38-69	35-65	12-30	15-82	1-5	3-14	11-59	10-57
2008	4	3.7-4.2	23-35	63-146	146-296	138-293	27-31	77-181	0-4	8-14	26-58	25-56

2. Methods

Fog water collection was performed at Murododaira (altitude, 2,450 m), which is located on the western slope of Mt. Tateyama near the Japan Sea coast and far from the heavy industrial areas of Japan, from late July (21 July 2004 and 24 July 2008) to the end of August of 2004 and 2008. A map of Japan with the location of Mt. Tateyama is shown in Fig. 1. Due to severe conditions, such as heavy snow cover from winter to early summer, observation can be usually carried out only in the summer and autumn. Unfortunately, fog water sampling was not made during the summer from 2005 through 2007. Fog events are usually observed by extended clouds (not local upslope fogs) at Murododaira because local upslope fogs are mainly observed at altitudes below 2,000 m (lower than the altitude of Murododaira) at Mt. Tateyama.

Floud water was collected using a passive thin-string sampler (Model FWP-500) from Usui Kogyo Kenkyusho, Inc., as described in detail by Watanabe et al. (2005). The passive sampler, which does not require electricity, is advantageous for use at high elevations and has been used at Mt. Fuji (Dokiya et al. 2001; Watanabe et al. 2006). A hood with a diameter of 1 m for keeping out rain droplets was also mounted. However, perfect sampling of fog water without contamination of rain or drizzle may be impossible. Dry deposition of particles onto thin-strings during clear days may also affect the chemical composition of samples. In this study, water collected using the passive sampler is regarded as a fog water sample. The fog water collected with the sampler was stored in a tank with a volume of 5 liters and recovered every 3-14 days. The weight (volume) of the cloud water samples was measured *in situ*. The samples were carried back to Toyama Prefectural University and stored in a refrigerator. The fog water sampler as well as the tank was washed using pure water every 3-14 days after recovery of the fog water samples. The collection efficiency of the passive sampler is affected by the wind speed. In particular, the volume of fog water samples is small when wind velocity is low. Wind speed is usually relatively high during fog occurrence at the sampling site, therefore, cloud water could be collected effectively even with the passive sampler. In this study, the mean chemical concentrations in fog water were calculated by the concentrations and the weight (volume) of the samples.

The pH of the fog water was measured with an electrode using a pH meter. The analysis of the dissolved ionic species was performed using an ion chromatograph.

3. Results and Discussion

Table 1 shows the range of the concentrations of major ions and pH in fog water at Murododaira during the summers of 2004 and 2008. The pH of fog water ranged from 3.7 to 5.1. The acidity of fog water in the summer was comparable with that in the autumn. The pH of fog water at Murododaira ranged from about 3.5 to 6.3 in September and October from 2004 through 2007 (Watanabe et al. 2010).The chemical characteristics of fog water at Murododaira was dramatically different during those two years. Highly acidic fogs were frequently observed in 2008, on the other hand, the pH of fog water was relatively high in 2004. The concentrations of $nssSO_4^{2-}$ were high during the summer of 2008.

The volume-weighted mean concentrations of major ions in fog water during the summers of 2004 and 2008 are shown in Fig. 2. The mean pH of cloud water in 2004 and 2008 was 4.5 and 4.0 (3.95), respectively. The concentrations of chemical constituents in 2008 were much higher than those in 2004. The mean ionic concentrations in the summer of 2008 were also higher than those in the autumn from 2004 to 2007 (Watanabe et al., 2010). First of all, the chemical concentrations in fog water are highly dependent on the liquid water content (LWC) or fog duration. Unfortunately, the LWC was not directly measured with a LWC analyzer in this study. The total weight of all samples which correlates with the LWC and fog duration was about 1.5 times higher in 2004 than in 2008 (about 6,000 g/month in 2004 and about 4,000 g/month in 2008). The concentrations of total ions in 2008 were 3 times

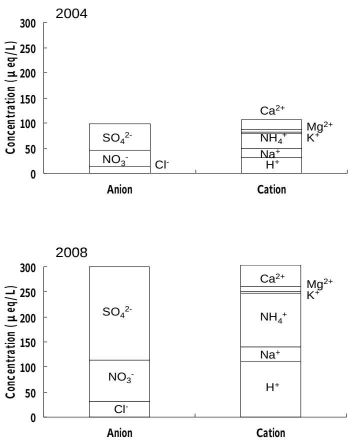

Fig. 2. Weighted mean concentrations of major ions in fog water at Murododaira in the summers of 2004 (upper panel) and 2008 (lower panel).

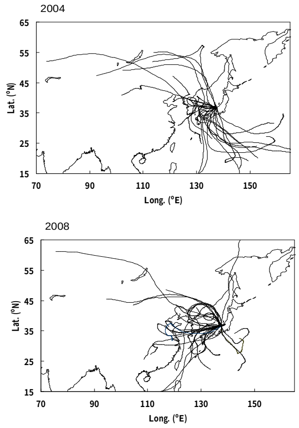

Fig. 3. Results of the 5-day backward trajectory analysis at altitudes of 2,500 m in the summer of 2004 (upper panel) and 2008 (lower panel). The trajectories are plotted once daily, and the starting time is 9:00 JST (0:00 UTC).

higher than those in 2004 (Fig. 2). The chemical characteristics in the two years cannot be explained by the amount of samples alone. Osada et al. (2009) showed submicrometer aerosols in the summer (August) at Murododaira were much higher in 2008 than in 2004. Air pollution might have been easily transported in the summer of 2008.

The $nssSO_4^{2-}$ concentration was usually higher than the NO_3^- concentration at Murododaira, and the equivalent ratio of $NO_3^-/nssSO_4^{2-}$ in fog water was quite different from the ratio in fog water at the mountainous sites near the industrial regions of Japan. The NO_3^- concentration is usually higher than the $nssSO_4^{2-}$ concentration (the $NO_3^-/nssSO_4^{2-}$ ratio is higher than 1) in fog or cloud water highly affected by polluted air from urban areas in Japan (Igawa et al. 1998; Tago et al. 2006). The $NO_3^-/nssSO_4^{2-}$ ratio at Murododaira seems to show year-to-year variation. While the concentration of NO_3^- was lower than that of $nssSO_4^{2-}$, the ratio of $NO_3^-/nssSO_4^{2-}$ was relatively high in 2004. Some samples showed that the concentrations of NO_3^- were higher than those of $nssSO_4^{2-}$ in 2004 (Table 1). The $NO_3^-/nssSO_4^{2-}$ ratio in the summer of 2004 was also higher than that in the autumn (Watanabe et al. 2010). The most predominant cation other than H^+ was NH_4^+ (Fig. 2).

The chemical characteristics in the two years might have been due to the difference in the transport processes of air pollution. The results of a 5-day backward trajectory analysis arriving at altitudes of 2,500 m during the sampling periods of 2004 and 2008 are shown in Fig. 3. The trajectories are plotted once daily. Fig. 3 presents predominant transport processes of air mass during both years. The analysis was based on the HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model, 1997 (Web address: National Centers for Atmospheric Research (NCEP-NCAR)

The air mass usually came from central and western Japan in the summer of 2004, whereas that at Murododaira in 2008 was mainly derived from Asia, especially from the coasts of the Yellow Sea and East China Sea, where SO_2 (and NH_3) emission is large (Ohara et al. 2007). In the summer, central Japan is usually under the influence of a maritime air mass, however, the continental air mass seemed to be predominant in 2008. Predominant air mass must significantly influence the chemical compositions of fog water at Murododaira, Mt. Tateyama. Watanabe et al. (2010) examined the relationship between the chemistry of fog water collected intensively (every 2-4 hours of sampling) at Murododaira in the autumn and transport processes of the air mass. High concentrations of $nssSO_4^{2-}$ and low pH were observed under the influence of the air mass transported from the polluted regions in Asia (Watanabe et al. 2010). Large amounts of air pollutants, such as sulfate aerosols (e.g., $(NH_4)_2SO_4$), might have been easily transported from the Asian continent to Mt. Tateyama in the summer of 2008.

The acidification of fog water must be accelerated by the trans-boundary pollution. According to the results of the backward trajectory analysis in 2008, the cloud water chemistry might also have been affected by the air pollution from western Japan. Therefore, the ionic concentrations might have been high in the summer of 2008. On the other hand, chemical constituents in cloud water in 2004 might have been mainly affected by the air pollution from the industrial regions of Japan, where SO_2 emission is restricted. As a result, a relatively high $NO_3^-/nssSO_4^{2-}$ ratio was observed in 2004.

4. Summary and Conclusions

Strong acidic fogs that contained high concentrations of $nssSO_4^{2-}$ were observed at Murododaira, Mt. Tateyama in the summer of 2008. The mean ionic concentrations in the summer of 2008 were also higher than those in the autumn from 2004 to 2007. According to the results of the backward trajectory analysis, the air mass at Mt. Tateyama was derived primarily from the polluted regions of Asia in 2008, and the trans-boundary air pollution might have contributed to cloud water acidification at Murododaira. In the summer, central Japan is usually under the influence of a maritime air mass, however, the continental air mass seemed to be predominant in 2008. On the other hand, acidic clouds might have been produced by pollutants from central and western Japan in 2004, and the ratio of $NO_3^-/nssSO_4^{2-}$ in fog water was relatively high.

Acknowledgements

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