

High Time-Resolution Monitoring of Free-Tropospheric Sulfur Dioxide and Nitric Acid at the Summit of Mt. Fuji, Japan

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Abstract This is the first paper that describes the atmospheric sulfur dioxide (SO₂) and nitric acid (HNO₃) monitored with a good time-resolution at the summit (3,776 m a.s.l.), which is located in the free troposphere, and southeastern foot (1,284 m a.s.l.) of Mt. Fuji, Japan. During the summer of 2012, two analytical systems consisting mainly of a parallel-plate wet denuder and ion chromatograph operated simultaneously at both the sampling sites. All the samples collected at both the sampling sites contained detectable levels of sulfate from gas-phase SO₂ while the nitrate from gas-phase HNO₃ was detectable in 97.8% of air samples at the southeastern foot and 88.4% at the summit. The average concentrations of SO₂ and HNO₃ were, respectively, 0.061 ± 0.071 and 0.031 ± 0.020 ppbv at the summit (*n* = 672), and 0.347 ± 0.425 and 0.146 ± 0.070 ppbv at the southeastern foot (*n* = 1344) of Mt. Fuji. Both the acidic gases at the southeastern foot and the HNO₃ at the summit showed a diurnal pattern with daytime maxima and nighttime minima. Meanwhile, the SO₂ at the summit did not show a distinct shift, which indicates the SO₂ concentrations at the summit would be principally controlled by the advection of air parcel in the free troposphere.

Keywords Sulfur dioxide • Nitric acid • Mt. Fuji • Denuder • Ion chromatograph • On-site analysis • Free troposphere

1 Introduction

Mt. Fuji, the highest mountain in Japan, is an isolated peak, the summit of which is located in the free troposphere. Once the air pollutants that were emitted from the Asian Continent rise to the free troposphere, they are transported to over Japan by the westerlies (Igarashi et al. 2010). The summit is therefore a suitable platform to observe the long-range transportation of the air pollutants from East Asia to Japan in free troposphere. Moreover, the observation on the summit provides a useful piece of information about the level of air pollutants not directly affected by anthropogenic pollution sources (background pollution) over Japan.

Sulfur dioxide (SO_2), the predominant anthropogenic sulfur-containing air pollutant, is directly emitted from power plants and industrial plants on factories (Garg et al. 2001; Streets and Waldhoff 2000). Volcanic activity and biomass burning also emit a significant amount of SO_2 (Diehl et al. 2012; Jurkat et al. 2010; Mori et al. 1993). In contrast, nitric acid (HNO_3) is a by-product of the oxidation of nitrogen compounds, *e.g.* nitric oxide (NO) and nitrogen dioxide (NO_2) in vehicular exhaust, soil release, and biomass burning (Kitto and Harrison 1992; Sadanaga et al. 2006; Seinfeld and Pandis 1998). Hydrolysis of dinitrogen pentoxide is also a dominant route to HNO_3 during the nighttime (Kitto and Harrison 1992). These pollutants cause the acidification of rain-, fog-, and dew water (Igawa et al. 1998; Takeuchi et al. 2000). In addition, both the acidic gases have a key role as precursors of $\text{PM}_{2.5}$ (particulate matter with an aerodynamic diameter of less than $2.5 \mu\text{m}$), which causes diseases related to respiratory and circulatory systems (Wang et al. 2015; Xing et al. 2016).

Atmospheric SO_2 and HNO_3 have been conventionally monitored by offline collection via impregnated filters or coating denuders, followed by sample extraction, and analysis by ion chromatography (IC). Several research groups (Dokiya et al. 1995; Kasper and Puxbaum 1998; Preunkert et al. 2007) applied the filter/denuder based offline approaches for the determination of acidic gases at high-altitude mountain sites in the free troposphere. These offline approaches are simple but leads to both positive and negative artifacts during air sampling, and more importantly, cannot provide good time-resolution (Benner et al. 1991; Zhang and McMurry 1991, 1992). In contrast, wet denuder technique coupled with IC avoids the artifacts and enables near-real-time monitoring with the time resolution being limited by the chromatographic time cycle (Keuken et al. 1988; Takeuchi et al. 2004; Ullah et al. 2006). The high-time resolution data help us a lot to investigate the origins of air masses and formation mechanisms of the acidic gases. The automated online measurement is more attractive than the filter/denuder based offline approaches. There are many high time-resolution data on the atmospheric concentrations of SO_2 and HNO_3 at ground level (Boring et al. 2002; Takeuchi et al. 2004, 2013; Ullah et al. 2006). However, as far as we know, no one has successfully detected the free-tropospheric SO_2 and HNO_3 with a high time-resolution because of the difficulties in logistics, maintenance, and detection performance among other things.

In the summer of 2012, we tackled the continuous determination of free-tropospheric SO_2 and HNO_3 at

the summit of Mt. Fuji, using a parallel-plate wet denuder coupled IC (PPWD-IC) which allows for highly sensitive and high time-resolution monitoring of acidic gases (Boring et al. 2002; Takeuchi et al. 2011, 2013). We report here the first time in the world, the concentration level and diurnal behavior of SO₂ and HNO₃ in the free troposphere with the time resolution of 30 min.

2 Materials and Methods

2.1 Sampling sites

The ambient air was collected at two sampling sites of Mt. Fuji. One site is the Tarobo shelter located on the southeastern foot of Mt. Fuji (35.33°N, 138.81°E, 1,284 m a.s.l.). This sampling site is located in forests, and abutted on a lightly-trafficked road that leads to a starting point of the mountain trail. The other sampling site is the Mount Fuji Research Station (MFRS, formerly known as Mt. Fuji Weather Station) located at the summit of Mt. Fuji (35.36°N, 138.73°E, 3,776 m a.s.l.). The summit is beyond a tree line, and considered to be the free troposphere through a whole year from the standpoint of the trace gases observation (Igarashi 2009).

2.2 Gas monitoring systems

The PPWD-IC was set up in the Tarobo shelter at the southeastern foot of Mt. Fuji, and operated during July 16 – August 2 in 2012. Details of the PPWD have been described previously (Boring et al. 2002; Takeuchi et al. 2011). In short, the PPWD is composed of two textured Plexiglas plates and a Teflon spacer (each with a 6 × 42 cm active area, separated by 0.3 cm). The ambient air was aspirated from the bottom of the PPWD through a 2 m of PFA Teflon tube (3.96 mm i.d., 6.35 mm o.d.), and passed between the inner plates at 5 L min⁻¹. The denuder liquid (0.5 mM hydrogen peroxide) was delivered to flow down both the plates at 0.5 mL min⁻¹ plate⁻¹. The entire PPWD effluent containing the dissolved gases was sent to one of two anion concentrator columns (IonPac TAC-2, Dionex Corp.) that were connected to a 10-port injection valve (Cheminert C2, Valco Instruments). After 15 min sample loading, the analyte was determined by means of an IC (Dionex ICS 1500 ion chromatograph with an IonPac AG20 2-mm guard column, an IonPac AS20 2-mm separation column, an ASRS300 2-mm electrochemical suppressor, and a CRD 2-mm carbon dioxide removal device). A 9 mM potassium hydroxide eluent was used isocratically at a flow rate of 0.25 mL min⁻¹. The guard/separation columns and conductivity cell were maintained at 30°C.

During July 19 – August 2 in 2012, a second PPWD-IC was continuously operated at the summit of Mt. Fuji. The PPWD-IC was set up on the second floor of the main building at the MFRS. A 2 m of PFA Teflon tube (3.96 mm i.d., 6.35 mm o.d.) was used for the inlet of ambient air. The second IC portion differs from the one used at the southeastern foot of Mt. Fuji as follows. The second IC (Dionex ICS 2100 ion

chromatograph) contains an IonPac TAC-2 anion concentration column that is connected to a 6-port injection valve, an IonPac AG18 2-mm guard column, an IonPac AS18 2-mm separation column, an ASRS300 2-mm electrochemical suppressor, and a CRD 2-mm carbon dioxide removal device. At the end of 25 min sample loading, the injection valve was switched to an injection mode for 5 min. An eluent of 26 mM potassium hydroxide was provided isocratically with an electrochemical potassium hydroxide generator (Dionex Corp.) at a flow rate of 0.25 mL min⁻¹. Note that the sampling volume of ambient air per sample at the summit (125 L, 25 min at 5 L min⁻¹) was 1.7 times larger than that at the southeastern foot (75 L, 15 min at 5 L min⁻¹). In each PPWD-IC, both acquisition of the detector signals and system control were carried out under a software control (Chromleon ver. 6.7, Dionex Corp.). Calibrations were performed offline by injecting mixed standard solutions of sulfate and nitrate at the beginning and end of the campaign.

2.3 Meteorological conditions

The data of air temperature and relative humidity at the summit were provided by the Japan Meteorological Agency, while those at the southeastern foot were recorded by a temperature and humidity logger (Ondotori TR-72U, T&D Corp.). The data of sunrise and sunset at both the sampling sites were provided by the National Astronomical Observatory of Japan. Three-day backward trajectories of air mass reaching the summit (35.36°N, 138.73°E) were calculated using the NOAA HYSPLIT 4 model. A meteorological data set was used for GDAS along with model vertical velocity data for vertical motion. The initial elevation reading by the trajectory analysis was 3,776 m.

3 Results and Discussion

3.1 Performance of instruments

The PPWD-ICs located at both the sampling sites have successfully operated without any maintenance for the duration of continuous measurement except for the replacements of IC eluent and denuder liquid. The limits of detection (LODs, calculated by $3\sigma/S$, where σ and S are the residual standard deviation and slope of the regression line) for SO₂ and HNO₃ were, respectively, 0.017 parts per billion by volume (ppbv) and 0.034 ppbv at the southeastern foot, and 0.011 ppbv and 0.010 ppbv at the summit. These LODs would be acceptable, even for relatively unpolluted air. Indeed, all the samples collected at both the sampling sites contained detectable levels of SO₄²⁻ from gas-phase SO₂ while the NO₃⁻ from gas-phase HNO₃ was detectable in 97.8% of air samples at the southeastern foot and 88.4% at the summit. The HNO₃ concentrations less than the LODs were treated as zero when calculating the average concentration of HNO₃.

3.2 Acidic gases concentrations on the summit and southeastern foot

Figure 1 shows the temporal variations of atmospheric SO₂ and HNO₃ concentrations at both the sampling sites along with the meteorological data. The average and median concentrations of SO₂ at the summit were 0.061 ± 0.071 ppbv ($n = 672$) and 0.051 ppbv, respectively. The episodic elevation of SO₂ concentration at the summit (max. 1.20 ppbv) was recorded in the early morning of July 22. As shown in Figure 2, the backward trajectory analysis revealed that the air parcel during this high SO₂ concentration event crossed over the southern edge of Korean Peninsula before flowing into the summit. With the exception of the high SO₂ event, the SO₂ levels observed at the summit are comparable to the background pollution of SO₂ reported previously. Dokiya et al. (1995) measured acidic gases at the summit of Mt. Fuji using a filter based offline approach, which provided the SO₂ concentration every 4 h with the LOD of 0.01 ppbv. They found that the SO₂ concentration ranged from <LOD to 0.11 ppbv during July 26 – August 3 in 1993, and from <LOD to 0.10 ppbv during July 26 – 30 in 1994. Igarashi et al. (2004) determined the SO₂ concentration at the summit of Mt. Fuji using a commercially available pulse UV fluorescence instrument, and reported that the average concentration of SO₂ was 0.05 ± 0.26 ppbv in July, 1994. Kato et al. (2016) also monitored the SO₂ concentration with a commercial SO₂ analyzer at the summit of Mt. Fuji during July 18 – August 22 in 2013, but described that the SO₂ concentrations were mostly below the LOD (hourly average of 0.06 ppbv).

The average and median concentrations of HNO₃ at the summit of Mt. Fuji observed in the present study were 0.031 ± 0.020 ppbv ($n = 672$) and 0.031 ppbv, respectively. These concentrations were almost half as high as those of SO₂ observed simultaneously at the summit. There have been no reports available on the HNO₃ concentration at the summit of Mt. Fuji. Throughout the world, only a few studies have so far reported on the HNO₃ concentration at high-altitude mountain site. Kasper and Puxbaum (1998) collected water-soluble gases at the summit of Mt. Sonnblic, Austria (3,106 m a.s.l.) using a filter packs method, and reported that monthly average concentrations of HNO₃ were 0.17 ppbv for July 1992 and 0.10 ppbv for July 1993. Preunkert et al. (2007) sampled acidic gases at the summit range of the Mont Blanc massif in the French Alps (4,360 m a.s.l.) using a coating denuder technique, and determined 0.17 ppbv of HNO₃ in September 2004. Our observed value of HNO₃ at the summit is several times lower than those at the European sampling sites mentioned above. The HNO₃ concentration observed on the summit of Mt. Fuji is likely to represent the background pollution of HNO₃ over Japan.

The average (median) concentrations of SO₂ and HNO₃ at the southeastern foot of Mt. Fuji were 0.347 ± 0.425 (0.201) ppbv ($n = 1344$) and 0.146 ± 0.070 (0.130) ppbv ($n = 1344$), respectively. The SO₂ and HNO₃ concentrations were higher at the southeastern foot than the summit, the southeastern foot/summit concentration ratio being 5.7 and 4.7, respectively. Some episodic peaks of SO₂ and HNO₃ were irregularly observed at the southeastern foot, which indicate that the air flowing into the southeastern foot is influenced by local pollutants.

3.3 Circadian variations of acidic gases on the summit and southeastern foot

Our gas monitoring technique, PPWD-IC provides the sufficient time-resolution needed to investigate the circadian variation of acidic gases. Figure 3 shows the circadian variations of SO₂ and HNO₃ concentrations, air temperature, and relative humidity at the summit and southeastern foot of Mt. Fuji. The SO₂ concentration at the southeastern foot showed a diurnal pattern with daytime maxima and nighttime minima. The primary source of atmospheric SO₂ is fuel combustion (Streets and Waldhoff 2000), thereby the ground-level SO₂ concentration tends to rise in the morning with human activities and reach the maxima during the daytime (Takeuchi et al. 2013; Tanaka and Hashimoto 1977). Our sampling site at the southeastern foot is located at comparatively high above sea level (1,284 m) but the SO₂ concentration appeared to be partly influenced by local emission from anthropogenic sources. The removal rate of SO₂ by oxidation to sulfate is positively correlated with the relative humidity (Khoder 2002; Kadowaki 1986). As shown in Figure 3, the southeastern foot was highly humid from sunset (19:00) to sunrise (04:41). Hence, the difference in SO₂ removal rate between the daytime and nighttime may also contribute to the SO₂ diurnal change at the southeastern foot.

In contrast to the diurnal behavior of SO₂ at the southeastern foot, the SO₂ concentration at the summit did not show a distinct shift. This result suggests the possibility that the summit is free from the vertical mixing by mountain and valley winds. Therefore, the SO₂ concentrations at the summit would be principally controlled by the advection of air parcel in the free troposphere. Several studies have so far been reported to clarify the effects of local wind circulation on the concentrations of gaseous substances at the summit of Mt. Fuji. Nakazawa et al. (1984) measured carbon dioxide (CO₂) on the summit of Mt. Fuji in July to October 1981, and revealed that the CO₂ concentrations showed little diurnal variation, and were close agreement with the concentrations expected from the vertical profiles obtained by aircraft measurements. Yokota et al. (2009) measured the vertical distributions of ozone (O₃), NO, NO₂, and SO₂ concentrations at Mt. Fuji in July to November 2007, and concluded that the atmospheric boundary layer existed near 2,000 m a.s.l. Murosaki et al. (2006) also monitored O₃ concentrations at 20 points from base to summit of Mt. Fuji in July 2005, and found that the O₃ concentration changed considerably on the border of around 1,500 m a.s.l. The circadian variations of SO₂ observed in the present study will be a useful piece of data in evaluating the quality of air at the summit of Mt. Fuji.

The HNO₃ concentration at both the sampling sites showed an obvious diurnal pattern with daytime maxima and nighttime minima. The HNO₃ is formed by the homogeneous reaction of nitrogen dioxide with hydroxyl radical (Kitto and Harrison 1992; Sadanaga et al. 2006). The hydroxyl radicals produced by higher solar radiation intensity during the daytime may have accelerated HNO₃ formation at both the sampling sites. Indeed, strong correlations were obtained between the concentrations of HNO₃ and the air temperatures, which used as indicators of solar radiation intensity, at both the sampling sites ($r = 0.926$ for summit and $r = 0.866$ for southeastern foot). Particulate ammonium nitrate (NH₄NO₃) also could be the

possible source for HNO₃ during the daytime because high temperature accelerates the dissociation of NH₄NO₃ (Harrison and Allen 1990; Kitto and Harrison 1992). The HNO₃ concentrations at both the sampling sites would be primarily controlled by the homogeneous reaction and equilibration with NH₄NO₃. Consequently, the HNO₃ concentrations at both the sampling sites showed the analogous diurnal cycle.

4 Conclusions

In summary, the concentrations of atmospheric SO₂ and HNO₃ at the summit and southeastern foot of Mt. Fuji, Japan have been successfully measured with the PPWD-ICs that provided the data in only a fraction of the time. This is the first report in the world that the SO₂ and HNO₃ at the high-altitude mountain site are tracked with the time resolution of 30 min. The average concentrations of SO₂ and HNO₃ at the summit were, respectively, 0.061 ± 0.071 and 0.031 ± 0.020 ppbv during July 19 – August 2 in 2012 ($n = 672$). These high time-resolution data revealed the diurnal behaviors of acidic acids in the free troposphere: the HNO₃ showed the diurnal pattern with daytime maxima and nighttime minima due to the enhanced HNO₃ formation during the daytime, meanwhile the SO₂ did not show the distinct shift because not only gas phase reactions at the sampling site but the advection of air parcel in the free troposphere controls the SO₂ concentrations. The particles corresponding to SO₂ and HNO₃: particulate sulfate (SO₄²⁻) and nitrate (NO₃⁻), exist in the free troposphere, and the existence phase of these reactive substances varies rapidly with meteorological conditions. Simultaneous measurement of SO₂, HNO₃, SO₄²⁻, and NO₃⁻ with high time-resolution is, therefore, desired so as to clarify the behavior of air pollutants in the free troposphere.

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Figure captions

Fig. 1 Temporal variations of acidic gas concentrations and meteorological data during summer on the summit and southeastern foot of Mt. Fuji, Japan. The tick mark of x-axis indicates midnight of the date

Fig. 2 Backward trajectories during the high SO₂ concentration event on the summit of Mt. Fuji, Japan. The starting times of trajectory were at 00:00, 03:00, 06:00, 09:00, 12:00, and 15:00 on July 22, 2012.

Fig. 3 Circadian variations of average acidic gas concentrations and meteorological data during summer on the summit and southeastern foot of Mt. Fuji, Japan. Each plot shows the average level of two weeks data (July 19 – August 1 in 2012). The positive error bars represent the one standard deviation. The average times of sunrise and sunset were, respectively, 04:37 and 19:05 on the summit, and 04:41 and 19:00 on the southeastern foot

References

- Benner, C. L., Eatough, D. J., Eatough, N. L., Bhardwaja, P. (1991). Comparison of annular denuder and filter pack collection of $\text{HNO}_3(\text{g})$, $\text{HNO}_2(\text{g})$, $\text{SO}_2(\text{g})$, and particulate-phase nitrate nitrite, and sulfate in the south-west desert. *Atmospheric Environment*, 25A, 1537-1545.
- Boring, C. B., Al-Horr, R., Genfa, Z., Dasgupta, P. K., Martin, M. W., Smith, W. F. (2002). Field measurement of acid gases and soluble anions in atmospheric particulate matter using a parallel plate wet denuder and an alternating filter-based automated analysis system. *Analytical Chemistry*, 74, 1256-1268.
- Diehl, T., Heil, A., Chin, M., Pan, X., Streets, D., Schultz, M., Kinne, S. (2012). Anthropogenic, biomass burning, and volcanic emissions of black carbon, organic carbon, and SO_2 from 1980 to 2010 for hindcast model experiments. *Atmospheric Chemistry and Physics Discussions*, 12, 24895-24954.
- Dokiya, Y., Tsuboi, K., Sekino, H., Hosomi, T., Igarashi, Y., Tanaka, S. (1995). Acid deposition at the summit of Mt. Fuji: Observations of gases, aerosols and precipitation in summer, 1993 and 1994. *Water, Air, & Soil Pollution*, 85, 1967-1972.
- Garg, A., Shukla, P. R., Bhattacharya, S., Dadhwal, V. K. (2001). Sub-region (district) and sector level SO_2 and NO_x emissions for India: Assessment of inventories and mitigation flexibility. *Atmospheric Environment*, 35, 703-713.
- Harrison, R. M., Allen, A. G. (1990). Measurements of atmospheric HNO_3 , HCl and associated species on a small network in eastern England. *Atmospheric Environment* 24A, 369-376.
- Igarashi, Y. (2009). Aerosol research using Mt. Fuji and its challenges. *Erozoru Kenkyu*, 24, 90-96 (in Japanese).
- Igarashi, Y., Naoe, H., Takahashi, H., Inomata, Y. (2010). Observation of atmospheric chemistry by using mountains, research trends and its challenges-a mini review. *Low Temperature Science*, 68, 69-78 (in Japanese).
- Igarashi, Y., Sawa, Y., Yoshioka, K., Matsueda, H., Fujii, K., Dokiya, Y. (2004). Monitoring the SO_2 concentration at the summit of Mt. Fuji and a comparison with other trace gases during winter. *Journal of Geophysical Research*, 109, D17304.

Igawa, M., Tsutsumi, Y., Mori, T., Okochi, H. (1998). Fogwater chemistry at a mountainside forest and the estimation of the air pollutant deposition via fog droplets based on the atmospheric quality at the mountain base. *Environmental Science and Technology*, 32, 1566-1572.

Jurkat, T., Voigt, C., Arnold, F., Schlager, H., Aufmhoff, H., Schmale, J., Schneider, J., Lichtenstern, M., Dörnbrack, A. (2010). Airborne stratospheric ITCIMS measurements of SO₂, HCl, and HNO₃ in the aged plume of volcano Kasatochi. *Journal of Geophysical Research*, 115, D00L17.

Kasper, A., Puxbaum, H. (1998). Seasonal variation of SO₂, HNO₃, NH₃ and selected aerosol components at Sonnblick (3106 m a.s.l.). *Atmospheric Environment*, 32, 3925-3939.

Kato, S., Shiobara, Y., Uchiyama, K., Miura, K., Okochi, H., Kobayashi, H., Hatekeyama, S. (2016). Atmospheric CO, O₃, and SO₂ measurements at the summit of Mt. Fuji during the summer of 2013. *Aerosol and Air Quality Research*, 16, 2368-2377.

Keuken, M. P., Schoonebeek, C. A. M., Wensveen-Louter, A., Slanina, J. (1988). Simultaneous sampling of NH₃, HNO₃, HCl, SO₂ and H₂O₂ in ambient air by a wet annular denuder system. *Atmospheric Environment*, 22, 2541-2548.

Khoder, M. I. (2002). Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area. *Chemosphere*, 49, 675-684.

Kitto, A.-M. N., Harrison, R. M. (1992). Nitrous and nitric acid measurements at sites in south-east England. *Atmospheric Environment*, 26A, 235-241.

Kadowaki, S. (1986). On the nature of atmospheric oxidation processes of sulfur dioxide to sulfate and of nitrogen dioxide to nitrate on the basis of diurnal variations of sulfate, nitrate, and other pollutants in an urban area. *Environmental Science and Technology*, 20, 1249-1253.

Mori, T., Notsu, K., Tohjima, Y., Wakita, H. (1993). Remote detection of HCl and SO₂ in volcanic gas from Unzen Volcano, Japan. *Geophysical Research Letters*, 20, 1355-1358.

Murosaki, M., Fujita, S.-I., Takahashi, A., Hayami, H., Miura, K. (2006). Measurements of ozone vertical distribution at Mt. Fuji using a passive sampler. *Journal of Japan Society for Atmospheric Environment*, 41, 347-354 (in Japanese).

Nakazawa, T., Aoki, S., Fukabori, M., Tanaka, M. (1984). The concentration of atmospheric carbon dioxide on the summit of Mt. Fuji (3776 m), *Japan. Journal of the Meteorological Society of Japan*, 62, 688-695.

Preunkert, S., Legrand, M., Jourdain, B., Dombrowski-Etchevers, I. (2007). Acidic gases (HCOOH, CH₃COOH, HNO₃, HCl, and SO₂) and related aerosol species at a high mountain Alpine site (4360 m elevation) in Europe. *Journal of Geophysical Research*, 112, D23S12.

Sadanaga, Y., Kondo, S., Hashimoto, K., Kajii, Y. (2006). Measurement of the rate coefficient for the OH + NO₂ reaction under the atmospheric pressure: Its humidity dependence. *Chemical Physics Letters*, 419, 474-478.

Seinfeld, J. H., Pandis, S. N. (1998). *Atmospheric Chemistry and Physics: From air pollution to climate change*. New York: Wiley-Interscience Publication.

Streets, D. G., Waldhoff, S. T. (2000). Present and future emissions of air pollutants in China: SO₂, NO_x, and CO. *Atmospheric Environment*, 34, 363-374.

Takeuchi, M., Li, J., Morris, K. J., Dasgupta, P. K. (2004). Membrane-based parallel plate denuder for the collection and removal of soluble atmospheric gases. *Analytical Chemistry*, 76, 1204-1210.

Takeuchi, M., Miyazaki, Y., Tsunoda, H., Tanaka, H. (2013). Atmospheric acid gases in Tokushima, Japan, monitored with parallel plate wet denuder coupled ion chromatograph. *Analytical Sciences*, 29, 165-168.

Takeuchi, M., Okochi, H., Igawa, M. (2000). A study on chemical components and acidification mechanism of dew-water. *Journal of Japan Society for Atmospheric Environment*, 35, 158-169 (in Japanese).

Takeuchi, M., Tsunoda, H., Tanaka, H., Shiramizu, Y. (2011). Parallel-plate wet denuder coupled ion chromatograph for near-real-time detection of trace acidic gases in clean room air. *Analytical Sciences*, 27, 805-810.

Tanaka, S., Hashimoto, Y. (1977). Studies on behaviors of sulfur compounds (SO₂, SO₃, and H₂S) in the atmospheric air. *Nippon Kagaku Kaishi*, 5, 712-715 (in Japanese).

Ullah, S. M. R., Takeuchi, M., Dasgupta, P. K. (2006). Versatile gas/particle ion chromatograph. *Environmental Science Technology*, 40, 962-968.

Yokota, K., Nagahuchi, O., Yamane, S., Honda, A., Isezaki, U. (2009). Vertical distribution of gaseous in environmental atmosphere at Mt. Fuji using passive sampler. *Journal of Ecotechnology Research*, 15, 31-36.

Wang, C., Tu, Y., Yu, Z., Lu, R. (2015). PM_{2.5} and cardiovascular diseases in the elderly: An overview. *International Journal of Environmental Research and Public Health*, 12, 8187-8197.

Xing, Y., Xu, Y., Shi, M., Lian, Y. (2016). The impact of PM_{2.5} on the human respiratory system. *Journal of Thoracic Disease*, 8, E69-E74.

Zhang, X., McMurry, P. H. (1991). Theoretical analysis of evaporative losses of adsorbed or absorbed species during atmospheric aerosol sampling. *Environmental Science and Technology*, 25, 456-459.

Zhang, X., McMurry, P. H. (1992). Evaporative losses of fine particulate nitrates during sampling. *Atmospheric Environment*, 26A, 3305-3312.

Fig. 1

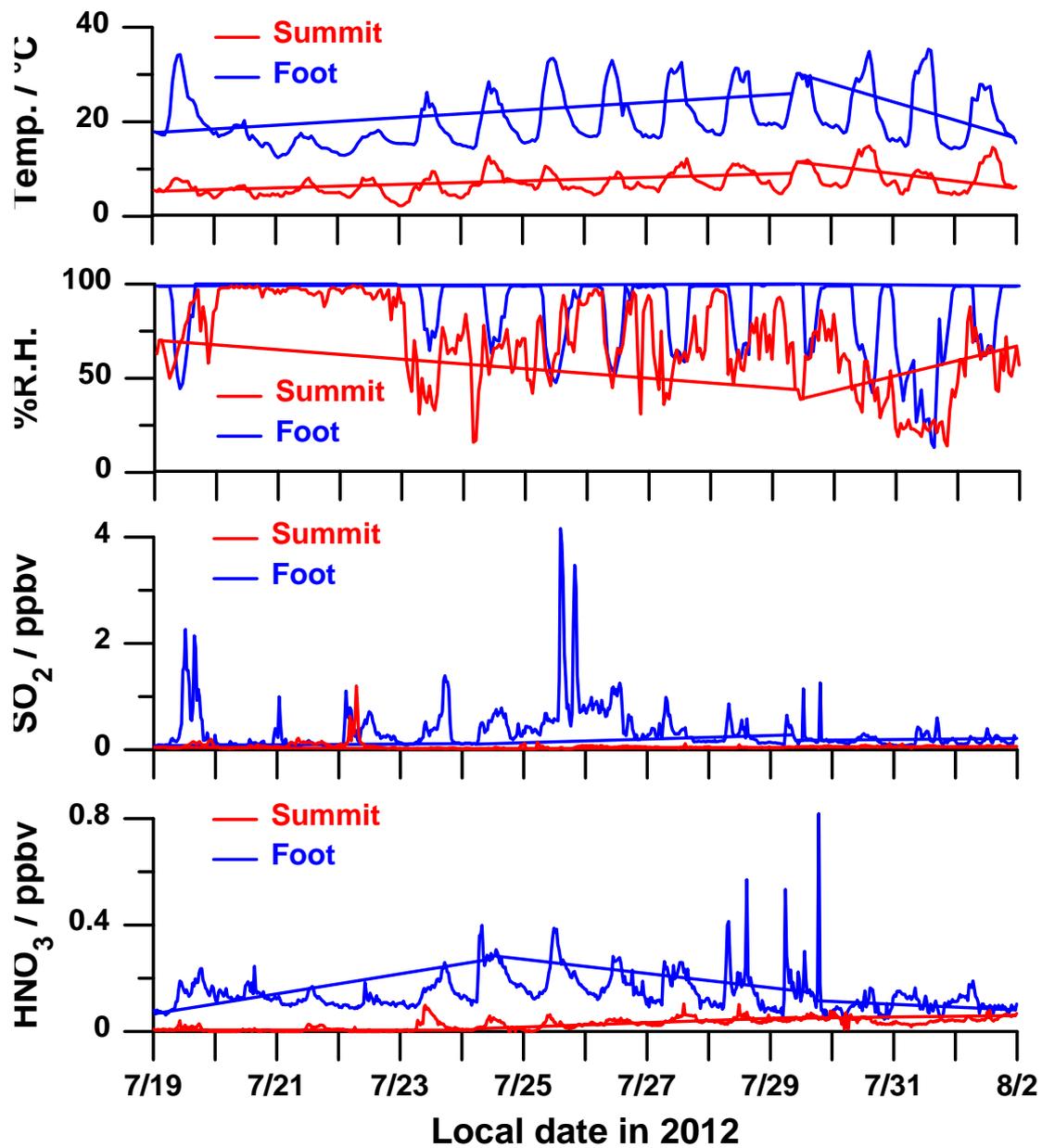


Fig. 2

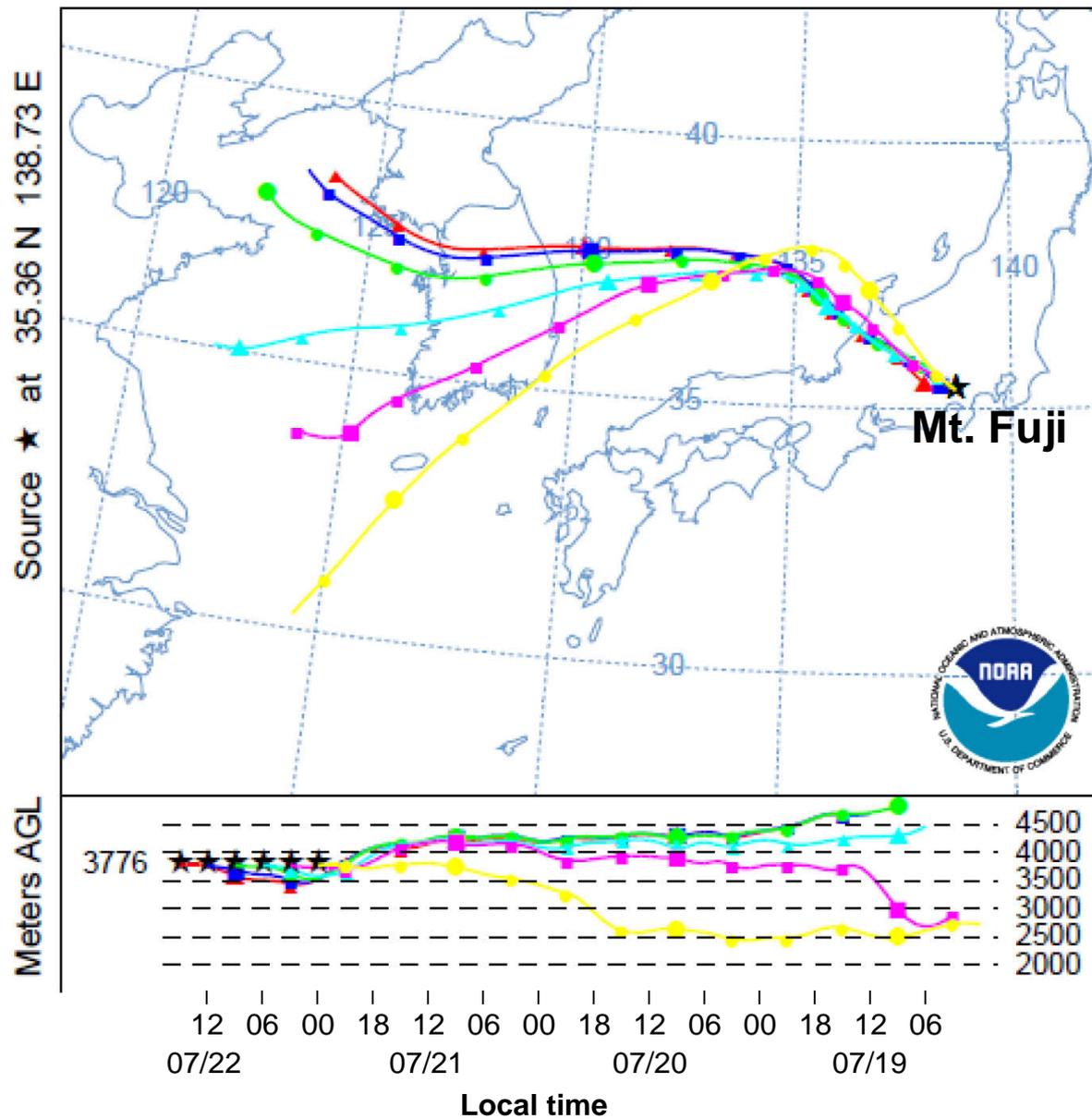


Fig. 3

