

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

Masaki Takeuchi • Yuki Miyazaki • Hideji Tanaka • Takaharu Isobe • Hiroshi Okochi • Hiroko Ogata

M. Takeuchi • H. Tanaka

Institute of Biomedical Sciences, Tokushima University Graduate School, 1-78-1 Shomachi, Tokushima 770-8505, Japan

Y. Miyazaki

Graduate School of Pharmaceutical Sciences, Tokushima University, 1-78-1 Shomachi, Tokushima 770-8505, Japan

T. Isobe • H. Okochi • H. Ogata

Graduate School of Creative Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

Corresponding author: M. Takeuchi

Email: [masaki.takeuchi@tokushima-u.ac.jp](mailto:masaki.takeuchi@tokushima-u.ac.jp)

Telephone: +81-88-633-7286

Fax: +81-88-633-9507

**Abstract** This is the first paper that describes the atmospheric sulfur dioxide (SO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) 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 SO<sub>2</sub> while the nitrate from gas-phase HNO<sub>3</sub> was detectable in 97.8% of air samples at the southeastern foot and 88.4% at the summit. The average concentrations of SO<sub>2</sub> and HNO<sub>3</sub> were, respectively,  $0.061 \pm 0.071$  and  $0.031 \pm 0.020$  ppbv at the summit ( $n = 672$ ), and  $0.347 \pm 0.425$  and  $0.146 \pm 0.070$  ppbv at the southeastern foot ( $n = 1344$ ) of Mt. Fuji. Both the acidic gases at the southeastern foot and the HNO<sub>3</sub> at the summit showed a diurnal pattern with daytime maxima and nighttime minima. Meanwhile, the SO<sub>2</sub> at the summit did not show a distinct shift, which indicates the SO<sub>2</sub> 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 ( $\text{SO}_2$ ), 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  $\text{SO}_2$  (Diehl et al. 2012; Jurkat et al. 2010; Mori et al. 1993). In contrast, nitric acid ( $\text{HNO}_3$ ) is a by-product of the oxidation of nitrogen compounds, *e.g.* nitric oxide ( $\text{NO}$ ) and nitrogen dioxide ( $\text{NO}_2$ ) 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  $\text{HNO}_3$  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  $\text{SO}_2$  and  $\text{HNO}_3$  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  $\text{SO}_2$  and  $\text{HNO}_3$  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  $\text{SO}_2$  and  $\text{HNO}_3$  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  $\text{SO}_2$  and  $\text{HNO}_3$  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 SO<sub>2</sub> and HNO<sub>3</sub> 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<sup>-1</sup>. The denuder liquid (0.5 mM hydrogen peroxide) was delivered to flow down both the plates at 0.5 mL min<sup>-1</sup> plate<sup>-1</sup>. 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<sup>-1</sup>. 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<sup>-1</sup>. Note that the sampling volume of ambient air per sample at the summit (125 L, 25 min at 5 L min<sup>-1</sup>) was 1.7 times larger than that at the southeastern foot (75 L, 15 min at 5 L min<sup>-1</sup>). 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  $\sigma$  and  $S$  are the residual standard deviation and slope of the regression line) for SO<sub>2</sub> and HNO<sub>3</sub> 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 SO<sub>4</sub><sup>2-</sup> from gas-phase SO<sub>2</sub> while the NO<sub>3</sub><sup>-</sup> from gas-phase HNO<sub>3</sub> was detectable in 97.8% of air samples at the southeastern foot and 88.4% at the summit. The HNO<sub>3</sub> concentrations less than the LODs were treated as zero when calculating the average concentration of HNO<sub>3</sub>.

### 3.2 Acidic gases concentrations on the summit and southeastern foot

Figure 1 shows the temporal variations of atmospheric SO<sub>2</sub> and HNO<sub>3</sub> concentrations at both the sampling sites along with the meteorological data. The average and median concentrations of SO<sub>2</sub> at the summit were  $0.061 \pm 0.071$  ppbv ( $n = 672$ ) and 0.051 ppbv, respectively. The episodic elevation of SO<sub>2</sub> 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 SO<sub>2</sub> concentration event crossed over the southern edge of Korean Peninsula before flowing into the summit. With the exception of the high SO<sub>2</sub> event, the SO<sub>2</sub> levels observed at the summit are comparable to the background pollution of SO<sub>2</sub> reported previously. Dokiya et al. (1995) measured acidic gases at the summit of Mt. Fuji using a filter based offline approach, which provided the SO<sub>2</sub> concentration every 4 h with the LOD of 0.01 ppbv. They found that the SO<sub>2</sub> 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 SO<sub>2</sub> concentration at the summit of Mt. Fuji using a commercially available pulse UV fluorescence instrument, and reported that the average concentration of SO<sub>2</sub> was  $0.05 \pm 0.26$  ppbv in July, 1994. Kato et al. (2016) also monitored the SO<sub>2</sub> concentration with a commercial SO<sub>2</sub> analyzer at the summit of Mt. Fuji during July 18 – August 22 in 2013, but described that the SO<sub>2</sub> concentrations were mostly below the LOD (hourly average of 0.06 ppbv).

The average and median concentrations of HNO<sub>3</sub> at the summit of Mt. Fuji observed in the present study were  $0.031 \pm 0.020$  ppbv ( $n = 672$ ) and 0.031 ppbv, respectively. These concentrations were almost half as high as those of SO<sub>2</sub> observed simultaneously at the summit. There have been no reports available on the HNO<sub>3</sub> concentration at the summit of Mt. Fuji. Throughout the world, only a few studies have so far reported on the HNO<sub>3</sub> 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 HNO<sub>3</sub> 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 HNO<sub>3</sub> in September 2004. Our observed value of HNO<sub>3</sub> at the summit is several times lower than those at the European sampling sites mentioned above. The HNO<sub>3</sub> concentration observed on the summit of Mt. Fuji is likely to represent the background pollution of HNO<sub>3</sub> over Japan.

The average (median) concentrations of SO<sub>2</sub> and HNO<sub>3</sub> at the southeastern foot of Mt. Fuji were  $0.347 \pm 0.425$  (0.201) ppbv ( $n = 1344$ ) and  $0.146 \pm 0.070$  (0.130) ppbv ( $n = 1344$ ), respectively. The SO<sub>2</sub> and HNO<sub>3</sub> 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 SO<sub>2</sub> and HNO<sub>3</sub> 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 SO<sub>2</sub> and HNO<sub>3</sub> concentrations, air temperature, and relative humidity at the summit and southeastern foot of Mt. Fuji. The SO<sub>2</sub> concentration at the southeastern foot showed a diurnal pattern with daytime maxima and nighttime minima. The primary source of atmospheric SO<sub>2</sub> is fuel combustion (Streets and Waldhoff 2000), thereby the ground-level SO<sub>2</sub> 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 SO<sub>2</sub> concentration appeared to be partly influenced by local emission from anthropogenic sources. The removal rate of SO<sub>2</sub> 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 SO<sub>2</sub> removal rate between the daytime and nighttime may also contribute to the SO<sub>2</sub> diurnal change at the southeastern foot.

In contrast to the diurnal behavior of SO<sub>2</sub> at the southeastern foot, the SO<sub>2</sub> 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 SO<sub>2</sub> 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 (CO<sub>2</sub>) on the summit of Mt. Fuji in July to October 1981, and revealed that the CO<sub>2</sub> 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 (O<sub>3</sub>), NO, NO<sub>2</sub>, and SO<sub>2</sub> 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 O<sub>3</sub> concentrations at 20 points from base to summit of Mt. Fuji in July 2005, and found that the O<sub>3</sub> concentration changed considerably on the border of around 1,500 m a.s.l. The circadian variations of SO<sub>2</sub> 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 HNO<sub>3</sub> concentration at both the sampling sites showed an obvious diurnal pattern with daytime maxima and nighttime minima. The HNO<sub>3</sub> 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 HNO<sub>3</sub> formation at both the sampling sites. Indeed, strong correlations were obtained between the concentrations of HNO<sub>3</sub> 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 (NH<sub>4</sub>NO<sub>3</sub>) also could be the

possible source for HNO<sub>3</sub> during the daytime because high temperature accelerates the dissociation of NH<sub>4</sub>NO<sub>3</sub> (Harrison and Allen 1990; Kitto and Harrison 1992). The HNO<sub>3</sub> concentrations at both the sampling sites would be primarily controlled by the homogeneous reaction and equilibration with NH<sub>4</sub>NO<sub>3</sub>. Consequently, the HNO<sub>3</sub> concentrations at both the sampling sites showed the analogous diurnal cycle.

#### **4 Conclusions**

In summary, the concentrations of atmospheric SO<sub>2</sub> and HNO<sub>3</sub> 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 SO<sub>2</sub> and HNO<sub>3</sub> at the high-altitude mountain site are tracked with the time resolution of 30 min. The average concentrations of SO<sub>2</sub> and HNO<sub>3</sub> at the summit were, respectively,  $0.061 \pm 0.071$  and  $0.031 \pm 0.020$  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 HNO<sub>3</sub> showed the diurnal pattern with daytime maxima and nighttime minima due to the enhanced HNO<sub>3</sub> formation during the daytime, meanwhile the SO<sub>2</sub> 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 SO<sub>2</sub> concentrations. The particles corresponding to SO<sub>2</sub> and HNO<sub>3</sub>: particulate sulfate (SO<sub>4</sub><sup>2-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>), exist in the free troposphere, and the existence phase of these reactive substances varies rapidly with meteorological conditions. Simultaneous measurement of SO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> 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 SO<sub>2</sub> 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

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Fig. 1

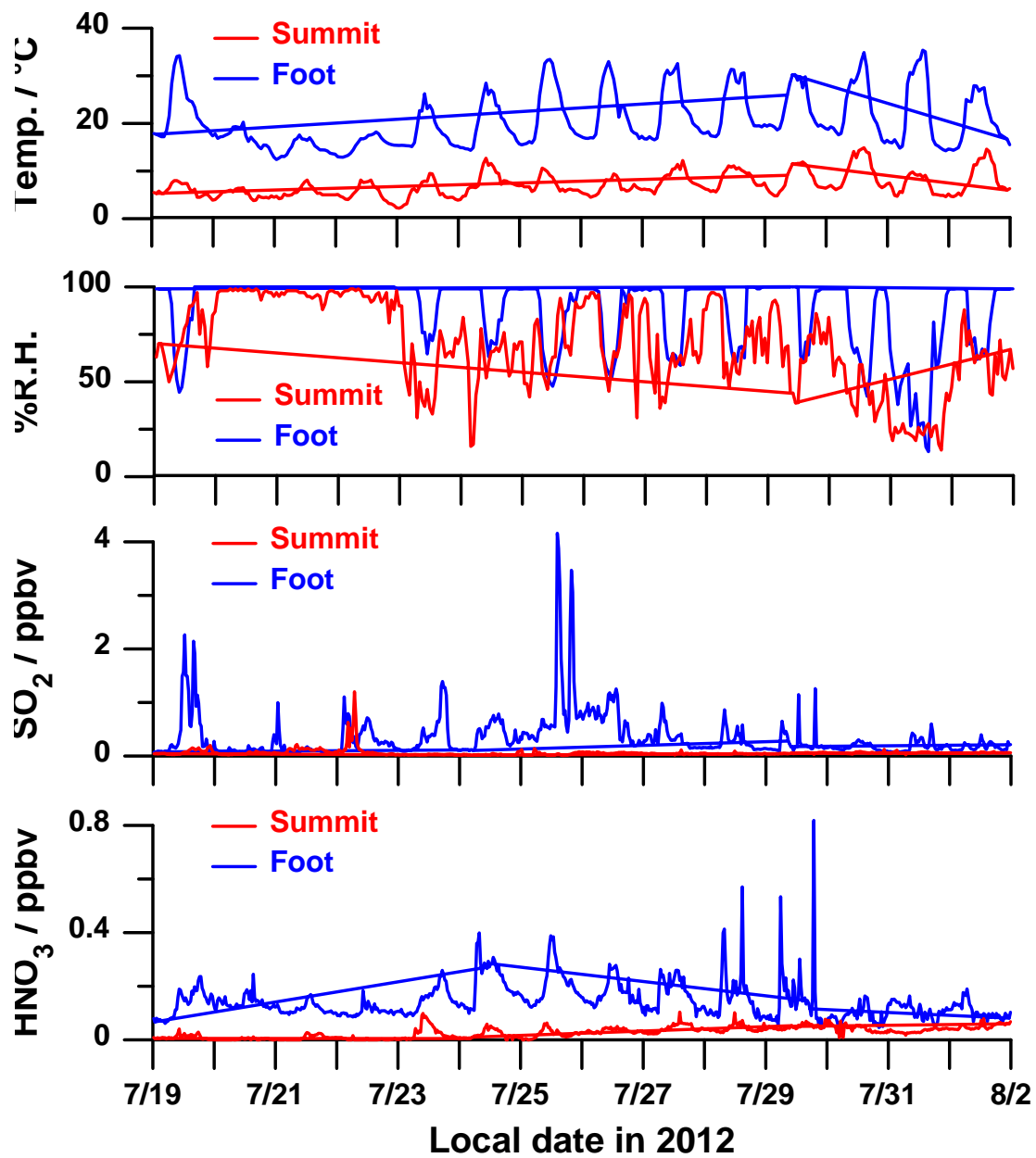


Fig. 2

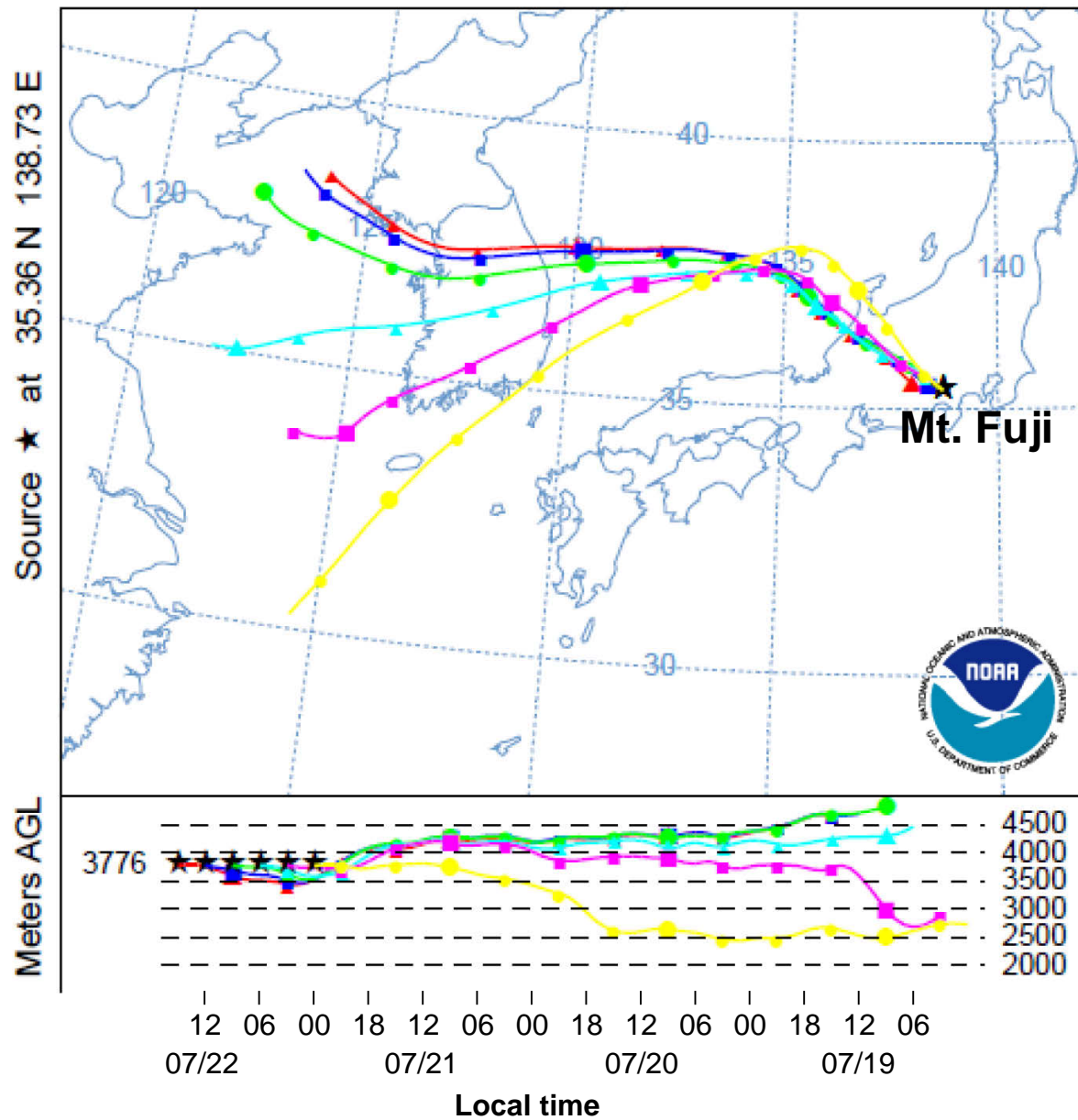


Fig. 3

