



## Practical usefulness of observing the free tropospheric acidic gases with a parallel plate wet denuder coupled ion chromatograph

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### ABSTRACT

Mountain observatories at high altitudes, far from local anthropogenic emission sources, are considered ideal for monitoring temporal variations of tropospheric air pollutants. During August 17–21 in 2013, we measured sulfur dioxide and nitric acid concentrations in the free troposphere at the top (3776 m a.s.l.) of Mt. Fuji, Japan. A parallel plate wet denuder-ion chromatographic system was used for the online measurement with 15 min temporal resolution. The continuous observations were successfully achieved without any problems. Of the samples collected, 97.8% of sulfur dioxide and 75.7% of nitric acid were above the limits of quantification. The average gas concentrations  $\pm$  standard deviation ( $n = 408$ ) were  $0.106 \pm 0.377$  ppbv for sulfur dioxide and  $0.015 \pm 0.014$  ppbv for nitric acid, respectively. Episodic elevations of sulfur dioxide concentration were recorded from August 20 to 21. Backward trajectory analyses indicated that the high-temporal resolution monitor detected the volcanic sulfur dioxide from Mt. Sakurajima, located 857 km from the sampling point. High-time-resolved observations in the free troposphere proved useful for source identification of air pollutants.

### 1. Introduction

The long-range transportation of atmospheric chemicals (Qu et al., 2016) occurs in the free troposphere. In that sense, the free troposphere's chemistry represents the quality of the Earth's atmosphere better than the atmospheric boundary layer below it. Mt. Fuji, Japan, is a free-standing mountain, and its top (3776 m a.s.l.) is located in the free troposphere, enabling continuous monitoring of the atmospheric gases and particles over Japan. In addition, Mt. Fuji is located at the eastern edge of the Asian Continent, downwind of the prevailing westerly winds. It is, therefore, suitable for observing long-distance transboundary air pollution from the Asian Continent to North America via the Pacific Ocean. However, there have been limited reports on atmospheric chemicals at the top of Mt. Fuji due to logistical difficulties.

Sulfur dioxide (SO<sub>2</sub>) is the primary anthropogenic chemical and not only adversely affects plants (Cotrozzi, 2020) but increases the risk of heart disease (Ma et al., 2021). The long-range transportation of SO<sub>2</sub> in East Asia is of increasing scientific interest (Qu et al., 2016). The average lifetime of SO<sub>2</sub> is longer in the free troposphere than in the atmospheric

boundary layer, ca. 2 weeks (Kajino and Tanaka, 2016). We have measured the free-tropospheric SO<sub>2</sub> and nitric acid (HNO<sub>3</sub>) at the top of Mt. Fuji (Takeuchi et al., 2017, 2022), applying a parallel plate wet denuder coupled ion chromatographic system (PPWD-IC) (Takeuchi et al., 2011). Similar to the diffusion scrubber- (Toda, 2004) and membrane denuder-based online techniques (Takeuchi et al., 2004a), the PPWD-IC has an advantage over conventional filter-based offline methods (Takeuchi et al., 2004b) in temporal resolution essential for the source identification of air pollutants. Following the ever-changing trajectory of air masses with 12- or 24-h offline measurements is challenging. Furthermore, the filter-based offline measurements are concerned not only with contamination from offline extraction to analysis but with positive or negative artifacts caused by gas-particle and particle-particle interactions on the sampling filters (Hitzenberger et al., 2004; Solomon et al., 2003). The PPWD-IC avoids these problems and enables near-real-time measurement of trace acidic gases.

During the 2013 summer campaign, we continuously observed free-tropospheric SO<sub>2</sub> and HNO<sub>3</sub> with 15 min temporal resolutions at the top of Mt. Fuji. The PPWD-IC has successfully revealed the variations in

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acidic gas concentrations at sub-ppb levels and responded fast enough to the elevation of volcanic sulfur dioxide concentration. In this paper, we update the acidic gas levels in the free troposphere and report the practical usefulness of observing the air pollutants with the PPWD-IC.

## 2. Material and methods

### 2.1. Acidic gas monitor

The PPWD-IC was used to continuously measure SO<sub>2</sub> and HNO<sub>3</sub> with 15 min temporal resolution. The details on the PPWD can be found in a previous paper (Takeuchi et al., 2011). Briefly, the PPWD permits the quantitative collection of common water-soluble acidic gases at least up to sampling flow rates of 8 L min<sup>-1</sup> (Takeuchi et al., 2011). Because of the direct contact between the air sample and the denuder liquid, the PPWD has a higher collection efficiency than the diffusion scrubber technique, which collects gas molecules through a porous membrane. In comparative measurements in a cleanroom, the PPWD-IC and an impinger-based offline method provided comparable levels of acidic gas concentration (Takeuchi et al., 2011). In addition, the PPWD's rapid response times to the analyte gas (10 → 90% rise and 90 → 10% fall times of ca. 3 min) enables near-real-time monitoring (Takeuchi et al., 2011). In the present study, the air sample was drawn from the bottom of the PPWD at 3.0 SLPM (standard liters per minute). The denuder liquid of 0.50 mmol L<sup>-1</sup> hydrogen peroxide flowed down the inner walls at 0.50 mL min<sup>-1</sup> plate<sup>-1</sup>. The sample from the PPWD was delivered to an anion concentrator (IonPac TAC-2, Dionex Corp.) connected to a 10-port switching valve (Cheminert C2, Valco Instruments). The sample loading/injection mode was switched every 15 min. The analytes were then measured employing Dionex ICS 2100 ion chromatograph with IonPac AG20/AS20 guard/separation columns, ASRS300 suppressor, and CRD carbon dioxide removal device. The eluent of 9.0 mmol L<sup>-1</sup> potassium hydroxide was used at 0.25 mL min<sup>-1</sup>. The columns and conductivity detector cell were maintained at 30 °C. The detector signals and system control were acquired under software control (Chromleon ver. 6.7, Dionex Corp). Calibration was conducted using standards of sulfate and nitrate. The linearity of the calibration curves, at least up to several ppbv levels, was good ( $r^2 > 0.998$ ). The limits of detection (LODs), calculated by  $3\sigma/S$ , where  $\sigma$  and  $S$  are the standard deviation of the blank and slope of the regression line, and the limits of quantification (LOQs,  $10\sigma/S$ ) were, respectively, calculated to be 1.5 pptv for SO<sub>2</sub>, 0.048 pptv for HNO<sub>3</sub> and 4.9 pptv for SO<sub>2</sub>, 0.16 pptv for HNO<sub>3</sub>.

### 2.2. Meteorological conditions and trajectory analysis

The temperature, relative humidity, and sunshine data at the sampling site were provided by the Japan Meteorological Agency. Four-day single backward air mass trajectories reaching the sampling point (35.36°N, 138.73°E, 3776 m a.s.l.) were calculated at 6 h using the NOAA HYSPLIT 4 model [19,20]. The initial elevation reading by the trajectory analysis was 3776 m, 3976 m, and 4176 m a.s.l.

## 3. Results and discussion

### 3.1. Acidic gas concentrations on the top of Mt. Fuji

During August 17–21 in 2013, the ambient air was sampled and analyzed at the Mt. Fuji Automated Weather Station located on the top of Mt. Fuji, Japan (35.36°N, 138.73°E, 3776 m a.s.l.). The PPWD-IC operated successfully without any troubles for the summer campaign. Of the samples collected ( $n = 408$ ), 97.8% for SO<sub>2</sub> and 75.7% for HNO<sub>3</sub> were above the LOQs. Although the number of samples below the LOQ for HNO<sub>3</sub> was somewhat high, increasing the sampling flow rate with the PPWD would increase the number of quantifiable samples. The acidic gas concentrations below the LOQs were treated as zero values. The average gas concentrations  $\pm$  standard deviation were 0.106  $\pm$

0.377 ppbv for SO<sub>2</sub> and 0.015  $\pm$  0.014 ppbv for HNO<sub>3</sub>, respectively. Fig. 1 shows the change in acidic gas concentrations during the campaign. Episodic elevations of SO<sub>2</sub> concentration were recorded from August 20 to the early hours of August 21. This high SO<sub>2</sub> concentration event will be discussed in the following section. Except for the high SO<sub>2</sub> period (20:45 on August 20 to 03:00 on August 21, SO<sub>2</sub> concentration >0.10 ppbv), the average SO<sub>2</sub> and HNO<sub>3</sub> concentrations ( $n = 383$ ) were, respectively, 0.035  $\pm$  0.013 ppbv and 0.016  $\pm$  0.013 ppbv, the concentration ratio of HNO<sub>3</sub> to SO<sub>2</sub> (N/S) being 0.46. These concentration levels and N/S are comparable to those measured during the 2012 summer campaign at the top of Mt. Fuji ( $n = 672$ , 0.061  $\pm$  0.071 ppbv for SO<sub>2</sub>, 0.031  $\pm$  0.020 ppbv for HNO<sub>3</sub>, N/S = 0.51) (Takeuchi et al., 2017).

The temporal changes in average SO<sub>2</sub> and HNO<sub>3</sub> concentrations and meteorological data during the summer campaign are shown in Fig. 2. Note that the high SO<sub>2</sub> concentration period data are excluded in Fig. 2. The average HNO<sub>3</sub> concentration (0.020 ppbv) during the daytime (05:00–19:00) was nearly twice higher than that during the nighttime (19:00–05:00), indicating that the photochemical production of HNO<sub>3</sub> and the vaporization of particulate nitrate to HNO<sub>3</sub> (Kitto and Harrison, 1992) accelerated during the daytime. The source of HNO<sub>3</sub> could be discussed in detail by simultaneous measurement of HNO<sub>3</sub>, nitrogen oxides, and particulate nitrate with high temporal resolution. Unlike the behavior of HNO<sub>3</sub>, there was no distinct shift in SO<sub>2</sub> concentration, and its concentration ratio between daytime and nighttime was 1.1. In atmospheric measurement at the ground level, the SO<sub>2</sub> concentration tends to be higher during the day (Takeuchi et al., 2017) when fossil fuel combustion and several industrial processes, e.g. copper smelting, are more active. Since no such tendency was observed in this summer campaign, the acidic gas data obtained are not significantly influenced by the anthropogenic sources' local emissions; in other words, the high temporal resolution monitor successfully determined the background pollution over Japan.

### 3.2. High SO<sub>2</sub> concentration event

As shown in Fig. 1, the SO<sub>2</sub> concentration remained in the low range for the first few days and increased rapidly from the night of August 20,

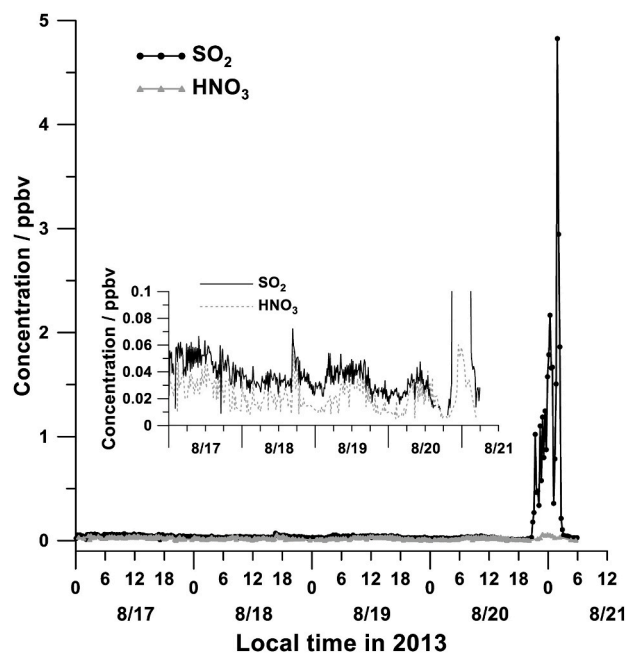


Fig. 1. Time variations of SO<sub>2</sub> and HNO<sub>3</sub> levels during the summer of 2013 on the top of Mt. Fuji, Japan. The inset shows a magnified view at the low-concentration range.

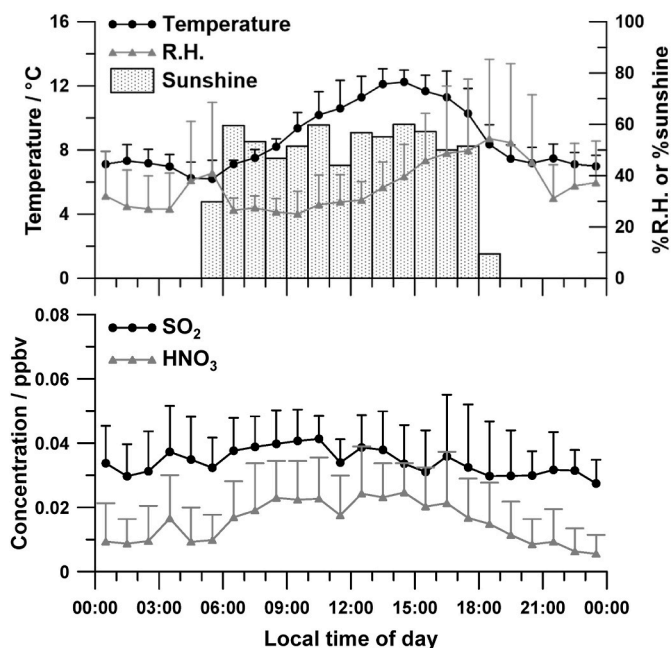


Fig. 2. Temporal changes of average acidic gas concentrations, temperature, relative humidity, and sunshine data during the summer campaign on the top of Mt. Fuji, Japan

The high  $\text{SO}_2$  concentration period data in Fig. 1 are excluded. The positive error bars indicate the one standard deviation. Sunshine shows the percentage of sunshine per hour.

2013. The high temporal resolution (15 min) data provided insights not available from 12- or 24-h offline measurement. The average and maximum levels of  $\text{SO}_2$  during the high  $\text{SO}_2$  concentration period were  $1.2 \pm 1.0$  ppbv ( $n = 25$ ) and 4.8 ppbv, respectively. During the same period, high  $\text{SO}_2$  spikes of up to about 5 ppbv were detected using a different analytical technique than the present study, pulsed UV fluorescence monitoring (temporal resolution: 1 min, detection limit: 0.06 ppbv) (Kato et al., 2016). As mentioned in the previous section, the  $\text{SO}_2$  observed in this summer campaign was almost entirely unaffected by the anthropogenic sources' local emissions.

The backward trajectory analysis shown in Fig. 3 indicates that the air masses during the high  $\text{SO}_2$  period passed over the Pacific, the Kyushu Island, and the Chugoku region in Honshu Island before reaching the sampling point. Mt. Sakurajima, located in the southern part of Kyusyu Island, is one of Japan's most active volcanoes. Volcanic eruptions release large amounts of rock debris and particles into the atmosphere and several gases, e.g., water vapor, carbon dioxide, and  $\text{SO}_2$  (Shinohara, 2013). Depending on the kind of volcano and the strength of the volcanic eruption, the fine particles and gases rise high up to the free troposphere and are transported over long distances (Hatakeyama et al., 2002). Mori et al. (1999) monitored the  $\text{SO}_2$  concentration at Mt. Unzen Nodake (1142 m a.s.l.), Japan from August to November 1989. They revealed that high concentrations of  $\text{SO}_2$  originated from the Sakurajima volcano using the upper meteorological observation data and trajectory analysis.

During the summer campaign, an explosive eruption occurred on the Sakurajima volcano at 16:31 on August 18, 2013. In conjunction with the eruption, a large plume rose to 5000 m above the Showa crater, and a large mass of  $\text{SO}_2$  ( $1400 \text{ tons day}^{-1}$ ) was released northwesterly in a short time (Japan Meteorological Agency, 2013). The backward trajectory analysis in Fig. 3 shows that the air masses that arrived over Mt. Fuji at 21:00 on August 21, when high  $\text{SO}_2$  concentrations began to be observed at the sampling point, passed over Sakurajima volcano at roughly 10:00 on August 18. There is a roughly 6-h gap between the arrival time of air masses during the Sakurajima eruption to Mt. Fuji and

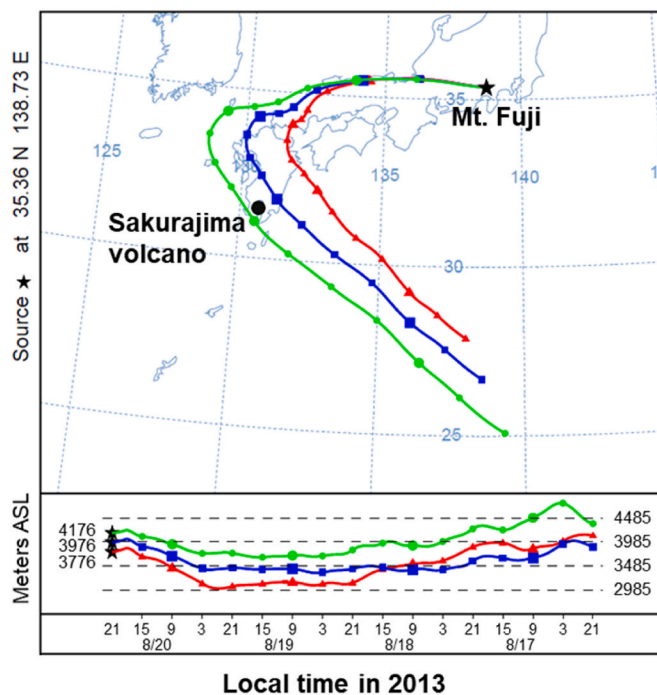


Fig. 3. Four-day backward trajectories during the high  $\text{SO}_2$  concentration event at the top of Mt. Fuji, Japan.

the observation period of elevated  $\text{SO}_2$  at the sampling site. However, the time gap is within the total error (15–30% of the travel distance) estimated in the trajectory analysis (NOAA Air Resources Laboratory). Thus, it can be concluded that the high  $\text{SO}_2$  levels observed at the top of Mt. Fuji were transported from Sakurajima volcano, located 857 km away from the sampling point.

#### 4. Conclusions

We have presented the usefulness of observing atmospheric acidic gases with a high temporal resolution at the top of Mt. Fuji. Our monitoring system revealed the background pollution levels and controlling factors of  $\text{SO}_2$  and  $\text{HNO}_3$  over Japan, which are in the range of concentrations undetectable by commercially available monitors. Besides, the PPWD-IC successfully detected the volcanic  $\text{SO}_2$  transported from 857 km away from the sampling point. High temporal resolution observations in the free troposphere have made it possible to estimate the sources of air pollutants transported over long distances, revealing that volcanic eruptions also impact the free tropospheric atmosphere. Thus, the PPWD-IC can significantly contribute to the  $\text{SO}_2$  and  $\text{HNO}_3$  monitoring in the global air on high-altitude mountain sites. It is desirable to clarify transboundary air pollution by applying the system to year-round monitoring, including the winter and spring seasons.

#### CRedit authorship contribution statement

**Masaki Takeuchi:** Conceptualization, Data curation, Funding acquisition, Methodology, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Shinya Nakagawa:** Formal analysis, Investigation. **Hiroki Watanabe:** Formal analysis, Investigation. **Hideji Tanaka:** Writing – review & editing. **Takaharu Isobe:** Investigation. **Hiroko Ogata:** Investigation. **Hiroshi Okochi:** Methodology, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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