3-25-2010

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Recommended Citation

Morris, Gary A., Walter D. Komhyr, Jun Hirokawa, James Flynn, Barry Lefer, Nicholay Krotkov, Fong Ngan, 2010: A balloon sounding technique for measuring so₂ plumes. *J. Atmos. Oceanic Technol.*, 27, 1318–1330. doi: 10.1175/2010JTECHA1436.1

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A Balloon Sounding Technique for Measuring SO₂ Plumes

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(Manuscript received 22 December 2009, in final form 25 March 2010)

ABSTRACT

This paper reports on the development of a new technique for inexpensive measurements of SO₂ profiles using a modified dual-ozonesonde instrument payload. The presence of SO₂ interferes with the standard electrochemical cell (ECC) ozonesonde measurement, resulting in -1 molecule of O₃ reported for each molecule of SO₂ present (provided [O₃] > [SO₂]). In laboratory tests, an SO₂ filter made with CrO₃ placed on the inlet side of the sonde removes nearly 100% of the SO₂ present for concentrations up to 60 ppbv and remained effective after exposure to 2.8×10^{16} molecules of SO₂ [equivalent to a column ~ 150 DU (1 DU = 2.69×10^{20} molecules m⁻²)]. Flying two ECC instruments on the same payload with one filtered and the other unfiltered yields SO₂ profiles, inferred by subtraction. Laboratory tests and field experience suggest an SO₂ detection limit of ~ 3 ppb with profiles valid from the surface to the ozonopause [i.e., $\sim (8\text{--}10$ km)]. Two example profiles demonstrate the success of this technique for both volcanic and industrial plumes.

1. Introduction

SO₂ is a trace atmospheric constituent with a lifetime of 1–2 days in the lower troposphere (Krueger et al. 2000; Benkovitz et al. 2004) and is emitted both naturally by volcanoes and anthropogenically by certain power plant and industrial facilities. The earth's radiative budget is impacted when SO₂ is converted to sulfate aerosols via reactions with H₂O₂ in clouds or OH (Seinfeld and Pandis 1998; Chin et al. 2000), although the extent of the influence of SO₂ on climate and atmospheric chemistry remains uncertain. The Intergovernmental Panel on Climate Change (Soloman et al. 2007) reports sulfate aerosol direct radiative forcing of -0.4 ± 0.2 W m⁻². Future implementation of pollution reduction policies, however, could lead to positive net forcings relative to today (Kloster et al. 2008).

Retrieval techniques for the measurement of SO₂ from satellite instruments were suggested by Krueger (1983) and refined by Krueger et al. (1995) and Krotkov et al. (1997). Because of its available wavelengths and spatial resolution (~ 50 km at nadir and ~ 100 km average), the Total Ozone Mapping Spectrometer (TOMS) SO₂ retrievals were limited to large amounts in volcanic eruptions (Krueger et al. 1995, 2000; Carn et al. 2003) and exceptional pollution events (Carn et al. 2004). Greatly improved sensitivity was demonstrated through the detection of volcanic and anthropogenic SO₂ in full-spectrum ultraviolet (UV) data provided by the Global Ozone Monitoring Experiment (GOME) (Eisinger and Burrows 1998; Burrows et al. 1999; Thomas et al. 2005; Khokhar et al. 2005) and the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) (Bovensmann et al. 1999; Bramstedt et al. 2004; Richter et al. 2006; Lee et al. 2008). However, GOME needs 3 days and SCIAMACHY 6 days to acquire a contiguous global map and hence could miss short-lived pollution events. Recently, Kearney et al. (2008) have developed an SO₂ retrieval for Moderate Resolution Imaging Spectroradiometer (MODIS) data.

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The Ozone Monitoring Instrument (OMI) (Levelt et al. 2006a,b) launched on the National Aeronautics and Space Administration (NASA) *Aura* satellite (Schoeberl et al. 2006) in July 2004 offers better spatial resolution ($13 \text{ km} \times 24 \text{ km}$ at nadir) and contiguous global daily coverage, permitting high-resolution, daily space-based UV measurements of SO_2 (Krotkov et al. 2006, 2007; Yang et al. 2007, 2009a,b; Lee et al. 2009). Validation of these satellite observations has been limited to aircraft in situ measurements over the eastern United States (Taubman et al. 2006) and eastern China (Dickerson et al. 2007; Krotkov et al. 2008), ground-based remote sensing [e.g., the Brewer UV spectrometer network described in Fioletov et al. (1998) and Krueger et al. (1995)], and, most recently, with miniature differential optical absorption spectroscopy (mini-DOAS) instruments (Galle et al. 2010). However, these ground-based techniques provide little information on the vertical profile of SO_2 , an important factor in satellite column SO_2 retrieval algorithms. To date, no inexpensive, regular in situ sampling program has been available to further these validation studies. The satellite community would find very valuable a sounding technique for in situ measurement of SO_2 of similar cost to the standard ozonesonde.

To review, the standard ozonesonde, originally presented in Komhyr (1969), uses an iodine–iodide redox electrochemical cell (ECC) made of two platinum electrodes immersed in potassium iodide (KI) solutions in separate cathode (0.5%–2% solution) and anode (saturated solution) polytetrafluoroethylene (Teflon) chambers (see Fig. 1). The chambers are linked by an ion bridge that allows for the exchange of charge but prevents mixing of the cathode and anode solutions. After charging the cells with the solutions, a transient potential difference results that is dissipated through the redistribution of charge across the ion bridge, such that the following equilibria are established:

When O_3 bubbles through the cathode solution, a chemical reaction imbalances the cathode solution in favor of I_2 :

To rebalance the cell, electrons must flow from the anode across the ion bridge to the cathode so that

FIG. 1. A schematic of the ECC sonde cathode and anode chambers, connected by an ion bridge and an external ammeter to measure the current between the cells, which is proportional to the O_3 concentration in the ambient air around the sonde.

If SO_2 is present, however, the cathode chamber chemistry is altered:

In the presence of both O_3 and SO_2 , therefore, reaction (1.6), rather than the anode solution reaction (1.4), supplies the electrons needed to rebalance the ECC after reaction (1.3). The result is that in the presence of both species with $[\text{SO}_2] < [\text{O}_3]$, the standard ozonesonde actually reports $[\text{O}_3] - [\text{SO}_2]$.

One approach to measure SO_2 directly, therefore, is to filter the incoming air to remove O_3 and electrically bias the cathode cell. When SO_2 enters, reaction (1.6) results in a flow of electrons from the cathode cell across the ion bridge to the anode. Figure 2 shows data previously unpublished from a flight in Pittsburgh, Pennsylvania, on 24 February 1983 that used this approach. The figure shows a low-altitude peak of ~ 35 ppbv of SO_2 just above the mixed layer, with a broader SO_2 peak of ~ 65 – 72 ppbv trapped between two temperature inversions at ~ 0.7 and 1.7 km. Such high levels of SO_2 are not observed in modern data, as U.S. emissions decreased by $\sim 37\%$ from the 1970 to 1996 (EPA 2000).

A second approach is to fly two instruments side-by-side, one with a filter to remove SO_2 and the other without, as shown in Fig. 3. Since the filtered sonde will measure $[\text{O}_3]$ and the unfiltered sonde will measure $[\text{O}_3] - [\text{SO}_2]$, the concentration of $[\text{SO}_2]$ can be derived by subtraction. The technique relies upon finding a filter that effectively removes SO_2 without impacting the O_3 concentrations.

In this paper we describe the development of such a technique using a modified dual-ozonesonde payload.

FIG. 2. The first sounding of SO_2 with temperature and relative humidity profiles made by W. Komhyr in Pittsburg, PA, on 24 Feb 1983.

Laboratory tests demonstrate the effectiveness of the technique for measuring tropospheric SO_2 profiles for $\sim 3 \text{ ppbv} < [\text{SO}_2] < [\text{O}_3]$. Two examples from field deployments demonstrate the effectiveness and utility of the technique: 1) volcanic emissions observed over Sapporo, Japan; and 2) industrial emissions observed over Houston, Texas. Since the filtered sonde and unfiltered sonde share the same balloon, parachute, payout-reel, and GPS and radiosonde units, the cost of a balloon flight with the dual payload is only about 40% higher than the cost of a standard ozonesonde.

2. Laboratory tests

We conducted a number of controlled laboratory tests during the development of our SO_2 sounding technique. The appendix describes tests performed on the various components used in the construction of the SO_2 filter, as well as the results of possible alternate SO_2 filter solutions. For all tests and flights, we use 0.5% buffered KI solutions in the cathode cell and saturated KI solutions in the anode cell (solutions prepared by B. Johnson, NOAA/Climate Monitoring and Diagnostics Laboratory, 2008–2009, personal communication), as recommended by the Jülich Ozone Sonde Intercomparison Experiment (JOSIE) (Smit et al. 2007).

The EnSci SO_2 filter consists of a Teflon cell ($\sim 5 \text{ cc}$) containing treated filter paper cut into $\sim 3 \text{ mm} \times \sim 12 \text{ mm}$ strips. The original filters used glass filter paper (2008 data; see the appendix), while the new filters use Teflon paper (2009 data, below). A 15-ml aqueous solution with 2.5 g of CrO_3 and 0.7 ml concentrated H_2SO_4 is used to

FIG. 3. The dual O_3 – SO_2 sonde payload. From left to right are the Väisälä RS80–15N radiosonde, the unfiltered ECC ozonesonde, and the SO_2 filtered ECC ozonesonde using the EnSci CrO_3 filter.

treat $\sim 400 \text{ cm}^2$ of filter paper. The paper is then dried in an oven at $80^\circ\text{--}90^\circ\text{C}$ for 1 h. Each strip is folded in half and inserted into the Teflon cell. Before use, it is recommended that the filter be exposed to high ozone in dry air for several hours. If the filter paper becomes damp, drying in an 80°C oven followed by high-ozone conditioning is recommended. The original suggestion for use of such a CrO_3 filter to remove SO_2 from sample air can be found in Saltzman and Wartburg (1965), while use of such a filter in surface SO_2 measurements is described in Warmbt and Herrmann (1977).

Laboratory tests on this filter demonstrated its effectiveness. The University of Houston (UH) test consisted of a Thermo Electron Corporation (TECO) 49C-PS ozone calibrator, a TECO 146C multigas calibrator (used to control the SO_2 concentrations), a manifold for mixing and distributing the gasses, a TECO Model 49C ozone analyzer using the U.S. Environmental Protection Agency standard measurement technique (EQOA-0880-047), a modified TECO 43S SO_2 analyzer (Luke 1997), an unfiltered ozonesonde, and a filtered ozonesonde. The experimental setup is shown in Fig. 4.

Tests were performed with O_3 concentrations of approximately 120, 80, and 40 ppbv (in that order) and SO_2 concentrations ranging from $\sim (2.5\text{--}65) \text{ ppbv}$. The data are shown in Tables 1–3. Each paired combination of O_3 and SO_2 was maintained for 3–5 min. An overall background level was established through data taken at $[\text{O}_3] = 0$ and $[\text{SO}_2] = 0$, and at each O_3 level, additional backgrounds are established with $[\text{SO}_2] = 0$. None of the data in Tables 1–3, however, have been adjusted for the background levels.

Within the 120- and 80-ppbv levels, the performance of the filter as a function of the integrated exposure to

FIG. 4. A schematic of the instruments used in the laboratory test of the EnSci CrO₃ version of the SO₂ filter conducted at the University of Houston in July 2009.

SO₂ changes very little. A linear regression analysis of the difference between the dual-sonde-derived and TECO-measured SO₂ concentrations as a function of integrated SO₂ exposure shows slopes of 0.005 ± 0.011 ppbv per Dobson unit (DU; $1 \text{ DU} = 2.69 \times 10^{20} \text{ molecules m}^{-2}$) and -0.0078 ± 0.0081 ppbv DU⁻¹, respectively. Between the two tests, an offset of ~ 1 ppbv of SO₂ is observed, as seen in the data in Tables 1 and 2.

Integrating the SO₂ concentrations passed through the filter as a function of time through the first two of the three O₃ levels in our test, we find a cumulative exposure of $\sim 2.8 \times 10^{16}$ molecules of SO₂. We can compute an equivalent column of SO₂ in flight from the equation

$$\text{Column SO}_2(\text{DU}) = \frac{N\dot{z}}{\dot{V}},$$

where N is the total number of molecules passed through the filter in the test, $\dot{z}$ is the rise rate of the balloon in flight (5 m s^{-1}), and $\dot{V}$ is the pump volume flow rate

TABLE 2. Individual readings for the ~ 80 ppbv ozone test. The mean ozone difference (sonde – TECO) = 1.2 ± 8.0 ppbv, while the mean SO₂ difference (sonde – TECO) = -1.2 ± 1.9 ppbv.

TECO O ₃ (ppbv)	Sonde O ₃ (ppbv)	TECO SO ₂ (ppbv)	Sonde SO ₂ (ppbv)
81.0 ± 2.1	82.7 ± 1.9	-0.009 ± 0.090	-0.98 ± 0.70
82.0 ± 2.8	84.1 ± 2.7	65.85 ± 0.49	65.12 ± 0.68
80.4 ± 2.0	81.5 ± 1.6	47.20 ± 0.46	46.38 ± 0.55
80.8 ± 1.4	81.56 ± 0.92	27.85 ± 0.36	26.43 ± 0.34
79.9 ± 2.6	81.3 ± 2.0	18.85 ± 0.38	17.36 ± 0.51
80.7 ± 1.3	81.7 ± 1.0	9.05 ± 0.29	7.60 ± 0.56
81.7 ± 2.1	82.5 ± 1.5	3.95 ± 0.24	2.45 ± 0.51
80.1 ± 2.6	80.9 ± 2.2	0.02 ± 0.12	-1.24 ± 0.55

(3.45 cc s^{-1}). Thus the laboratory test was equivalent to an SO₂ column of ~ 150 DU. Even after such exposure, the filter performance was still quite good. For the 40-ppbv-level test, we used a new SO₂ filter of the same type as for the 120- and 80-ppbv tests. The same linear regression analysis as above reveals a slope of 0.0458 ± 0.0083 ppbv DU⁻¹ exposure, with most of the change occurring over the last four levels of data [i.e., when SO₂ was lowered from $\sim (20\text{--}2.5)$ ppbv]. While our dual-sonde SO₂ measurement changed more with respect to the TECO SO₂ measurement for this test than the previous two tests, the changes are still < 2 ppbv of SO₂ at a cumulative exposure of the equivalent of nearly 40 DU. Thus, the filters stand up well to high SO₂ concentrations for extended periods of time, consistent with the findings of Saltzman and Wartburg (1965).

Figure 5 shows the filtered ozonesonde reading as a function of the TECO O₃ reading. The regression of the overall data shows a line of best fit with a slope to within 1% of 1.00 and an intercept of less than one-half of one standard deviation from 0.00. Good agreement is seen at all levels: at the 120-ppbv O₃ level, the mean O₃ difference (sonde – TECO) = 0.3 ± 4.8 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.87 ± 2.3 ppbv; at the 80-ppbv O₃ level, the mean O₃ difference

TABLE 1. Individual readings for the ~ 120 ppbv ozone test. The mean ozone difference (sonde – TECO) = 0.3 ± 4.8 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.87 ± 2.3 ppbv.

TECO O ₃ (ppbv)	Sonde O ₃ (ppbv)	TECO SO ₂ (ppbv)	Sonde SO ₂ (ppbv)
121.64 ± 0.97	118.32 ± 0.50	-0.034 ± 0.082	0.49 ± 0.68
120.6 ± 1.2	120.27 ± 0.90	65.35 ± 0.64	66.12 ± 0.64
120.76 ± 0.69	121.13 ± 0.40	46.90 ± 0.49	48.10 ± 0.51
121.27 ± 0.71	121.48 ± 0.64	27.81 ± 0.51	28.54 ± 0.65
121.78 ± 0.68	122.57 ± 0.52	18.04 ± 0.33	18.92 ± 0.61
119.97 ± 0.84	122.3 ± 1.9	9.03 ± 0.28	10.13 ± 0.64
121.5 ± 1.9	122.9 ± 1.7	3.90 ± 0.27	5.03 ± 0.55
122.9 ± 1.3	123.9 ± 1.3	0.03 ± 0.16	0.77 ± 0.72

TABLE 3. Individual readings for the ~ 40 ppbv ozone test. The mean ozone difference (sonde – TECO) = -1.0 ± 5.3 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.74 ± 1.5 ppbv.

TECO O ₃ (ppbv)	Sonde O ₃ (ppbv)	TECO SO ₂ (ppbv)	Sonde SO ₂ (ppbv)
40.9 ± 1.8	40.6 ± 1.7	-0.020 ± 0.080	-1.20 ± 0.18
40.4 ± 1.0	39.44 ± 0.83	34.71 ± 0.35	32.84 ± 0.28
41.2 ± 1.3	40.1 ± 1.1	32.95 ± 0.41	31.68 ± 0.54
39.5 ± 1.9	38.7 ± 1.8	27.92 ± 0.34	26.63 ± 0.26
42.4 ± 1.4	41.0 ± 1.3	18.13 ± 0.49	17.57 ± 0.24
42.2 ± 1.5	40.8 ± 1.2	9.07 ± 0.30	8.95 ± 0.20
38.6 ± 1.3	37.6 ± 1.0	2.48 ± 0.16	2.56 ± 0.21
43.84 ± 0.66	42.68 ± 0.66	0.03 ± 0.12	0.61 ± 0.16

FIG. 5. The EnSci CrO₃ version of the SO₂ filter was tested at the University of Houston at three different O₃ concentrations. Within each O₃ concentration, SO₂ was varied from 0 to 65 ppbv. Shown here is the O₃ reported by the filtered sonde vs that measured by the standard TECO O₃ analyzer. The response is linear, with reasonably high accuracy and precision. See text for details.

(sonde – TECO) = 1.2 ± 8.0 ppbv, while the mean SO₂ difference (sonde – TECO) = -1.2 ± 1.9 ppbv; and at the 40-ppbv O₃ level, the mean O₃ difference (sonde – TECO) = -1.0 ± 5.3 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.74 ± 1.5 ppbv. We note that the uncertainties in the (sonde – TECO) O₃ are rather large, owing to the fact that the O₃ calibrator instrument experienced difficulty in maintaining O₃ at constant concentrations. While we have not made adjustments for the offsets at [SO₂] = 0 for this test, we correct these offsets for flight data. The offsets can be corrected by adjustments in the background cell current of each ECC independently or through a subtraction from the post-flight SO₂ concentrations.

Figure 6 shows the derived SO₂ concentration (filtered – unfiltered) as a function of the TECO SO₂ reading. Again, the regression of the entire dataset shows a line-of-best-fit slope to within 0.1% of 1.00 and an intercept of -0.36 ± 0.14 ppbv. The ~40 ppbv ozone level test was used to examine closely the limits of the SO₂ measurement (data in Table 3). It appears that this technique can distinguish 2.5 ppbv from 0 ppbv of SO₂ at the surface. In flight, the detection limit may be somewhat higher [$\sim(3\text{--}5)$ ppbv] due to differing response time constants of the two ECC instruments.

One final laboratory test at Hokkaido University examined the SO₂ destruction properties of our 4-yr-old filters and used the experimental setup depicted in Fig. 7. The laboratory equipment consisted of a temperature-controlled oven for SO₂ production and a chemical ionization mass spectrometer (CIMS) for measurement

FIG. 6. As in Fig. 5, but here we examine the SO₂ measurements. The dual-sonde response is quite linear, accurately reproducing the measurements made by the standard TECO SO₂ analyzer. See text for details.

of the SO₂ concentration. The details of the CIMS instrument are described in Hirokawa et al. (2009). SO₂ gas was released at a rate of 120 ng min^{-1} from a permeation tube in the oven controlled at 40°C and was diluted by N₂ at a flow rate of $200 \text{ cm}^3 \text{ min}^{-1}$ to prepare a test gas mixture containing approximately 200 ppbv of SO₂. The test gas mixture was sampled in the glass inlet of the CIMS instrument both with and without passing through an SO₂ filter. In the inlet, the SO₂–N₂ was further diluted by N₂ at a flow rate of $1000 \text{ cm}^3 \text{ min}^{-1}$ and then introduced into a chemical ionization region, in which SO₂ was ionized via the following ion–molecule reactions (Huey et al. 1995; Lovejoy and Wilson 1998):

The ions as well as the unreacted SF₆[–] were mass-analyzed by a quadrupole mass filter and detected by a secondary electron multiplier. The SO₂ concentration was measured by monitoring ion signals of SO₂F₂[–] detected at a mass-to-charge ratio (m/z) of 102.

Figure 8 shows the results of this test. The performance of two other tested filters, described in the appendix, is also shown in this figure. Despite their age, the CrO₃ filters resulted in an $(87 \pm 14)\%$ reduction of SO₂ at ~200 ppbv. We do not expect to encounter such high SO₂ levels during our flights, and tests described above (made with Teflon filter paper in 2009) suggest that these new filters are nearly 100% effective at removing SO₂.

FIG. 7. A schematic of the instruments used in the laboratory test of the several different SO_2 filters conducted at Hokkaido University in August 2008.

3. Field observations

a. Ozonesonde background

The example data presented here used the ECC type EnSci 2Z ozonesonde instruments (Komhyr 1986; Komhyr et al. 1995) with 0.5% buffered KI cathode solution. Meteorological measurements (pressure, temperature, and relative humidity) for all dual-sonde flights are provided by Väisälä RS80–15N radiosondes, as described in Thompson et al. (2003, 2007). Onboard global positioning systems (GPS) provided latitude, longitude, altitude, wind speed, and wind direction data. With a typical rise rate of $\sim 5 \text{ m s}^{-1}$ and a measurement time constant of $\sim 25 \text{ s}$, the effective vertical resolution of O_3 features is $\sim 125 \text{ m}$ (see also Smit et al. 2007).

Dual-ozonesonde payloads (Fig. 3) consisted of two such ECC cells, one with the EnSci SO_2 filter on the inlet side and one without, so that, by subtraction, an SO_2 profile was derived. (Note that the circuits of the two sondes have been modified by EnSci so that the data from the two instruments are combined and transmitted to the surface in the same datastream.) Differences in the measurement time constants between the two ECC units can result in the appearance of false SO_2 signals as the sonde moves through air with strong vertical gradients in O_3 . Thus, evaluation of SO_2 profiles requires some care. Nevertheless, we have had good success in producing tropospheric O_3 and SO_2 profiles on 20+ dual-sonde payload balloon flights. (All of our data are available on our project Web sites: <http://physics.valpo.edu/ozone>, www.rice.edu/ozone, and www.imaqs.uh.edu/ozone.)

Before each flight, the dual O_3 – SO_2 payloads are bench tested to make sure the SO_2 filter is properly conditioned and does not destroy O_3 . Inlets from the filtered and unfiltered sonde are connected to the EnSci ozonizer unit, which is set to 0, low (10–40 ppbv), medium (40–80 ppbv), and high (80–300 ppbv) concentrations of O_3 . Figure 9 shows that for the 14 flights from Sapporo in August 2008 and 2009, the O_3 readings reported by the two instruments agree extremely well, indicating that the filter is properly conditioned. The mean offset (secondary–primary) was $-0.4 \pm 2.3 \text{ ppbv}$, with a mean absolute offset (secondary–primary) of $1.5 \pm 1.8 \text{ ppbv}$.

FIG. 8. Results of a laboratory test of different SO_2 filters conducted at Hokkaido University in August 2008. The 4-yr-old EnSci CrO_3 version of the filter removed $\sim 85\%$ of the incident SO_2 , while the KMnO_4 filter removed nearly 100%. However, after high ozone conditioning, the KMnO_4 filter no longer removed SO_2 . See text for details.

FIG. 9. Preflight comparison of O_3 readings from the filtered and unfiltered ozonesondes conducted on the laboratory bench at 0, low (0–40 ppbv), medium (40–80 ppbv), and high (>80 ppbv) O_3 concentrations, with good agreement shown. Data shown are from 4 dual O_3 – SO_2 sonde flights from Hokkaido University in August 2008 (dots) and 10 flights in August 2009 (stars).

Such results suggest that the technique may be able to identify SO_2 features of as little as 3 ppbv. This test should be performed before all dual O_3 – SO_2 flights.

b. Volcanic plume case—Sapporo, 22 August 2008

At 0424 UTC 22 August 2008, we released a dual sonde from the campus of Hokkaido University in Sapporo (43.07°N, 141.35°E; elevation 26 m). Figure 10 shows the SO_2 profile for this flight, with a prominent feature of ~17 ppbv between 0.45 and 0.95 km. Since this flight employed a 4-yr-old SO_2 filter, a correction factor was employed (this filter was determined to be ~65% effective). Newer filters do not require such corrections since they are nearly 100% effective (see above).

Figure 10 also shows that relative humidity (RH) increases steadily from the surface (~38%) to ~1.85 km (87%), with values ~50% in the layer of elevated SO_2 . Potential temperature (theta) is nearly constant at 295 K from the surface to 1.9 km, where the temperature data indicate a strong inversion (not shown). Ozone is nearly constant at ~40 ppbv from the surface to ~2.4 km. Elevated SO_2 is also seen up to ~3 km, but at much lower concentrations. If we integrate the SO_2 column from the surface to 3 km, we find 0.9 DU.

Figure 11 shows the OMI SO_2 map near Hokkaido for 0345–0349 UTC 22 August 2008, with a retrieval assuming a 3-km center for the peak height of the SO_2 cloud. The OMI data show a swath of elevated SO_2 (>2.5 DU) stretching from eastern Siberia across the Tatar Strait to the northeast coast of Hokkaido, then southward into the Pacific, with values ~(0.3–1.0) DU

FIG. 10. Profiles of SO_2 (black dots), O_3 (gray dots), RH (black line), and theta (gray line) from the 22 Aug 2008 dual-sonde released from Hokkaido University in Sapporo, Japan. The SO_2 peak near 0.7 km is most likely a plume from a volcanic eruption that has been transported to Hokkaido. See text for further details.

along the flight path of the dual sonde (due southeast of Sapporo).

There are two possible volcanic sources for the SO_2 plume. Mt. Kasatochi erupted violently three times during 2200 UTC 7 August to 0435 UTC 8 August 2008, sending emissions to >13.5 km. Eruptions continued through ~1800 UTC 9 August. Emissions from the eruption, quickly detected by MODIS and OMI, traveled around the world (see papers in the Okmok–Kasatochi special issue of *J. Geophys. Res.*). The Bezymianny volcano (55.98°N, 160.58°E) erupted at 1030 UTC 19 August 2008, producing an ash plume up to 9 km that drifted west ~1200 km (data available from the Alaskan Volcano Observatory online at <http://www.avo.alaska.edu>). The plume of the former can be followed in the OMI SO_2 data from the time of the eruption until its arrival in the vicinity of Hokkaido 2 weeks later. The arrival of the Kasatochi plume, however, coincides well with the arrival of the plume of the latter as well. Thus, identifying which of the two plumes our sonde actually detected may be difficult.

Back trajectories at 500 and 1500 m for this case (not shown, but found online at physics.valpo.edu/ozone/fulbrightdata.html) were calculated using the NASA Goddard Space Flight Center (GSFC) Trajectory Model (Schoeberl and Sparling 1995) run in kinematic mode (hereafter referred to as the KTM) with National Centers for Environmental Prediction (NCEP) reanalysis ($1^\circ \times 1^\circ \times 6$ h) meteorological fields. The trajectories show the air masses over the previous 3 days arriving from the north-northeast, descending in altitude from ~1.5 to 0.5 km and from ~4 to 1.5 km, respectively, as they passed over the Sea of Okhotsk into Hokkaido. KTM forward trajectories run from the time of the Kasatochi eruption through 22 August 2008 indicate

FIG. 11. OMI SO_2 retrieval assuming a 3-km height for the arriving SO_2 plume shows a 2.5+ DU cloud moving across Hokkaido on 22 Aug 2008. The position of Sapporo is marked by the star in the figure. The balloon flight was due south-southeast from Sapporo, parallel to the high- SO_2 feature seen in the OMI data. See text for further details.

strong descent as the air mass arrived near Hokkaido (these trajectories can be found online at http://physics.valpo.edu/ozone/data/Fulbright/trajectory/kasatochi_simulation/kasatochi_simulation.mov). Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT) model (Draxler and Rolph 2010) trajectories for the Bezymianny eruption are shown in Fig. 12. The air parcel initialized at ~ 5 km altitude arrives nearer to Sapporo than the Kasatochi plume seen in the OMI SO_2 data (Fig. 11).

Despite the theta profile that indicates that the peak was observed within the boundary layer, we believe this SO_2 peak is not of local origin. In particular, we have looked at the dependence of the dual-sonde-measured $[\text{SO}_2]$ in the lower 1.0 km for all of our balloon flights in August 2008 and August 2009 from Sapporo, excluding the 22 August 2008 case. We find that northwesterly, northerly, or northeasterly winds (as was the case for the 22 August 2008 profile) produced mean $[\text{SO}_2] = 1.11 \pm 0.66$ ppbv. Easterly, southeasterly, and southerly winds, on the other hand, produced mean $[\text{SO}_2] = 1.8 \pm 1.2$ ppbv. Although not statistically significant given the limited number of profiles and the typically low local SO_2 concentrations, such differences can be explained by local

geography, with the sea to the north providing cleaner air and the industrial centers to the southeast providing more polluted air. It seems likely, therefore, that the source of the SO_2 peak is different than the usual urban centers southeast of Sapporo and may well be linked to one of the two volcanic eruptions (described above).

c. Houston plume case

The Study of Houston Atmospheric Radical Precursors (SHARP) campaign occurred from 15 April to 31 May 2009. As part of that campaign, 19 ozonesondes were released from the campus of the University of Houston (29.72°N, 95.34°W; el.19 m). On two occasions, dual O_3 – SO_2 sonde balloon payloads were flown to detect plumes emitted from industrial facilities in the Houston ship channel region (east of campus). It was found as part of this study that when light easterly winds were present, monitors on the UH Moody Tower frequently recorded higher levels of SO_2 .

Figure 13 shows the O_3 , SO_2 , RH, and theta profiles for the dual sonde released at 1323 UTC (shortly after dawn) on Saturday, 30 May 2009. Ozone increased from ~ 15 ppbv at the surface to 80 ppbv at 1.3 km. SO_2 increased from ~ 11 ppbv near the surface to ~ 55 ppbv near 400 m. Winds near 400 m as reported by the sonde were light ($< 4 \text{ m s}^{-1}$) and generally from the east-southeast direction. Moody Tower 1-min-average SO_2 readings on this morning peaked at 38 ppbv at 1154 UTC, while the hourly average at the nearby Continuous Ambient Monitoring Station 81 (29.73°N, 95.32°W) peaked at 1300–1400 UTC at 12.4 ppbv [data available online from the Texas Commission for Environmental Quality (TCEQ) at <http://www.tceq.state.tx.us>].

Back trajectories were calculated at 250, 500, and 750 m with the UH Regional Data Assimilation System (UH-RDAS), with winds from the NCEP North America Mesoscale Model (NAM). The domain is interpolated to 12- and 4-km resolution, then adjusted by observations using the objective analysis module in the fifth-generation Pennsylvania State University–National Center for Atmospheric Research Mesoscale Model (MM5) (Grell et al. 1994). These trajectories suggest air arriving at UH from the east-northeast. HYSPLIT back trajectories, calculated at 300, 400, and 500 m, suggest sources to the east or southeast of UH. (A map of the 300- and 400-m HYSPLIT trajectories and the 750-m UH-RDAS trajectory can be accessed online at <http://www.imaqs.uh.edu/ozone/ourdata.html> via a link in the 2009 data table in the row labeled “20090530, 13:23.”) The trajectories suggest that influences from sites along the Houston Ship Channel are possible. Examining the upset inventory maintained by the TCEQ (available online at <http://www.tceq.state.tx.us>), we find that Houston Refining (12000

FIG. 12. HYSPLIT forward trajectories [graphical output described in Rolph (2010)] from Mt. Bezymianny on the Kamchatka Peninsula started at 1100 UTC 19 Aug 2008 at the time of an observed eruption. The trajectories descend rapidly and arrive near Sapporo at the time of the dual-sonde release (data shown in Fig. 10). See text for details.

Lawndale St., very near to the 300-m HYSPLIT back trajectory) reported the emission of ~ 1900 kg of SO_2 between 0200 and 0710 UTC 30 May 2009. Thus, the most likely explanation for this plume is a primary source at this industrial plant along the ship channel.

4. Summary

This work has presented a new technique for inexpensively measuring tropospheric SO_2 plumes using a modified dual-ozonesonde approach. This technique is useful for validation of satellite SO_2 observations as well as transport studies of SO_2 plumes, both from natural (volcanic) and anthropogenic sources.

Laboratory tests found the EnSci SO_2 filter made with CrO_3 most effective at removing SO_2 from the inlet airstream, with $\sim 100\%$ removal by the new Teflon paper filters. These tests further showed that the filters did

not interfere with measurements of O_3 and demonstrated that the filters remained effective at removing SO_2 even after exposure to $\sim 2.8 \times 10^{16}$ molecules.

By flying balloons with two ozonesondes on the same payload, one with an SO_2 filter and one without, O_3 and SO_2 profiles can be measured simultaneously. Laboratory tests and field experience suggest that the detection limit is around 3 ppbv for altitudes below the ozonopause (i.e., $< \sim 8\text{--}10$ km). Readings near and above the ozonopause probably are not robust, as the derived SO_2 concentration becomes the difference between two relatively large numbers. Since reported ozonesonde measurement accuracy is 5%–10%, when O_3 concentrations reach 200 ppbv, these accuracy limitations can result in 10–20-ppbv SO_2 readings at altitudes where no SO_2 is present. Thus, we recommend our dual-sonde approach only for lower- to midtropospheric SO_2 profiles. Care must be taken in deriving the SO_2 profiles for

FIG. 13. As in Fig. 10, but for the dual-sonde from the University of Houston on 30 May 2009. A peak of >60 ppbv of SO_2 was observed near 0.4 km. See text for further details.

sondes with different time constants, particularly when the vertical O_3 gradient is large.

Before flight the SO_2 filters should be conditioned with 2–4 h of high- O_3 air. Furthermore, it is important that the filter paper be dry before high- O_3 conditioning. One hour of baking in an 80°C oven is sufficient to insure that the filter paper is dry.

Two examples demonstrated the effectiveness of the technique in measuring SO_2 plumes. The 22 August 2008 flight from Sapporo, Japan, detected an SO_2 plume near 700 m that most likely was emitted by a volcanic eruption. The 30 May 2009 flight from Houston, Texas, detected an SO_2 plume near 400 m that most likely was emitted by industrial processes.

For ECC sonde operators near SO_2 sources, it is recommended that SO_2 filters be deployed on the inlet to remove SO_2 and accurately retrieve O_3 . If possible, dual sondes as described here should be flown in such locations to provide the most reliable O_3 profiles and simultaneous SO_2 profiles. Before launching the dual-sonde payloads, we recommend reviewing local air traffic regulations and contacting local air safety officials.

Acknowledgments. Funding for this work was provided by NASA's *Aura* Validation Program (D. Considine and E. Hilsentrath, program managers) and by the Japan–U.S. Educational Commission through a Fulbright Scholar grant. Thanks to the OMI team for the SO_2 data and Hokkaido University and the Frontier Research Center for Global Change in Yokohama, Japan, for hosting the lead author of this study, with particular thanks to M. Fujiwara and F. Hasebe at Hokkaido University for assisting with the dual-sonde balloon flights from Sapporo, Japan, and to H. Akimoto for sponsoring my time in Japan. Special thanks also to the students at the University of Houston, in particular

M. Taylor, N. Grossberg, and C. Haman, who helped with dual-sonde balloon flights and/or preparation of laboratory equipment for the SO_2 filter test at UH and to Winston Luke for loaning us the SO_2 analyzer for the laboratory test. Thanks to B. Johnson (NOAA/Earth System Research Laboratory) for preparing the cathode and anode solutions used in this study, and thanks to Valparaiso University colleague Thomas Goyne and to the anonymous reviewers for their helpful comments for improving our manuscript. The authors gratefully acknowledge the NOAA/Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or the READY Web site (<http://www.arl.noaa.gov/ready.php>) used in this publication.

APPENDIX

ECC Filter Tests

Many of the following tests employed the EnSci ozonizer unit to produce ozone and measure the current flowing between the cathode and anode cells, hereafter referred to as the intercell current (IC). The ozonizer consists of a UV lamp with an adjustable shield that produces ozone in a tube of air flowing next to the lamp. High ozone concentrations up to 4 ppmv can be achieved by turning off the ozonizer air pump, pulling the UV shield completely out, and drawing air past the UV lamp at the ozonesonde pump flow rate ($\sim 200 \text{ cc min}^{-1}$). Lower concentrations ($0 - \sim 500$ ppbv) are achieved by running the ozonizer air pump and adjusting the shield until the desired IC is achieved. Descriptions of the ozonizer unit and its operation can be found in Komhyr (1999).

a. Empty cell and filter paper tests

We assessed the impact of the various materials from which our SO_2 filter is constructed. An ECC ozonesonde was run on ozone-free air for 5 min with a background cell current of $0.03 \mu\text{A}$, then run with ozonated air with a resulting $\text{IC} = \sim 5 \mu\text{A}$ for 5 min, with a final reading of $4.98 \mu\text{A}$. An empty Teflon cell of the same type that is used to hold the cathode and anode solutions was inserted between the inlet side of the pump and a constant known O_3 source. For an unconditioned cell, the IC dropped $>50\%$, while for a high- O_3 -conditioned (i.e., 5 h of high O_3 exposure) cell, the IC dropped 5%–12%. The fact that the empty, conditioned Teflon cell itself results in O_3 loss is interesting, as the ECC approach to measuring O_3 profiles has been used worldwide and demonstrated to be accurate and reliable for more than 35 yr.

When measuring ozone with the ECC ozonesonde, the incoming air bubbles through the cathode solution. Reactions in the solution in the presence of the platinum

electrode, therefore, must take place on a time scale smaller than the diffusion of air in the solution to the Teflon cell walls. With a pump flow rate of $\sim 200 \text{ cc min}^{-1}$ and a Teflon cell volume of $\sim 5 \text{ cc}$, this puts an absolute upper limit of $\sim 1.5 \text{ s}$ on the reaction time constant.

We next placed an unshredded, unconditioned, 1.3-cm-diameter Teflon filter paper disk (the same size as the Teflon filter cell inner diameter) over the outlet port on the inside of the filter cell and inserted this filter between the inlet side of the pump and a constant known O_3 source. The IC dropped by 40%. This test was repeated using an unshredded, unconditioned, 2.0-cm glass fiber paper, which when placed between the constant ozone source and the pump led to an IC drop of 60%. It appears, therefore, that use of the Teflon filter paper is preferable to the glass fiber filter paper for construction of the SO_2 filter.

Finally, we shredded one untreated, unconditioned, 3.7-cm Teflon filter paper disk into approximately eight pieces, folded the pieces in half, and placed them inside the Teflon filter cell. When this filter cell was inserted between the inlet side of the pump and a constant known O_3 source, the IC dropped by $>80\%$. The additional surface area provided by the shredded paper left a lot of surfaces for ozone deposition and destruction to take place.

b. H_2O version

We examined the impact of water on the measurement of SO_2 and O_3 . We conditioned a Teflon cell with high O_3 for 30 min, then ran for 10 min on O_3 -free air. Upon insertion of this Teflon cell between the outlet side of the pump and the cathode cell, the IC dropped 30%–40%. Water was added slowly to the Teflon cell until it was about half full; the IC was observed not to change, whether the incoming air was bubbled through the H_2O or cycled through the cell above the water level (i.e., sent through 100% relative humidity air).

We reran the test using a Teflon cell that had been high- O_3 conditioned with dry air for 4 h. As before, when inserted between the pump and the O_3 source, the empty, conditioned Teflon cell resulted in an IC drop of 13%. Water again was slowly added to the Teflon cell. This time, however, the IC dropped by 70% after about 1 min, then slowly rose to a $\sim 24\%$ deficit after 5 min, with the recovery likely due to the increasing dissolved O_3 content in the H_2O slowing its further absorption as saturation was approached.

Measurements by the CIMS (described above) of air after passing through the H_2O filter indicated near-complete destruction of SO_2 . When the SO_2 air was passed through the H_2O filter cell without bubbling through the H_2O , little to no SO_2 was removed.

c. Other filters

We tested filters made from filter paper soaked in NaHCO_3 and KMnO_4 solutions, then dried. In the former case, the IC current dropped 50%, suggesting an interference with the measurement of O_3 . In the latter case, IC current drops were $>12\%$. Initially, the KMnO_4 filter removed nearly 100% of incident SO_2 (as indicated by tests using the apparatus in Fig. 7, described above), but 1 week after its construction, the filter no longer removed SO_2 . Thus, we were unable to create successfully a filter using NaHCO_3 or KMnO_4 .

REFERENCES

- Benkovitz, C. M., S. E. Schwartz, M. P. Jensen, M. A. Miller, R. C. Easter, and T. S. Bates, 2004: Modeling atmospheric sulfur over the Northern Hemisphere during the Aerosol Characterization Experiment 2 experimental period. *J. Geophys. Res.*, **109**, D22207, doi:10.1029/2004JD004939.
- Bovensmann, H., J. P. Burrows, M. Buchwitz, J. Frerick, S. Noël, V. V. Rozanov, K. V. Chance, and A. P. H. Goede, 1999: SCIAMACHY: Mission objectives and measurement modes. *J. Atmos. Sci.*, **56**, 127–150.
- Bramstedt, K., A. Richter, M. Van Roozendaal, and I. De Smedt, 2004: Comparisons of SCIAMACHY sulfur dioxide observations. *Proc. Second Workshop on the Atmospheric Chemistry Validation of Envisat (ACVE-2)*, Frascati, Italy, European Space Agency, ESA SP-562. [Available online at <http://envisat.esa.int/workshops/acve2/papers/ESC02KB.pdf>.]
- Burrows, J. P., and Coauthors, 1999: The Global Ozone Monitoring Experiment (GOME): Mission concept and first scientific results. *J. Atmos. Sci.*, **56**, 151–175.
- Carn, S. A., A. J. Krueger, G. S. J. Bluth, S. J. Schaefer, N. A. Krotkov, I. M. Watson, and S. Datta, 2003: Volcanic eruption detection by the Total Ozone Mapping Spectrometer (TOMS) instruments: A 22-year record of sulfur dioxide and ash emissions. *Volcanic Degassing*, C. Oppenheimer, D. M. Pyle, and J. Barclay, Eds., Special Publication 213, Geological Society of London, 177–202.
- , —, N. A. Krotkov, and M. A. Gray, 2004: Fire at Iraqi sulfur plant emits SO_2 clouds detected by Earth Probe TOMS. *Geophys. Res. Lett.*, **31**, L19105, doi:10.1029/2004GL020719.
- Chin, M., and Coauthors, 2000: Atmospheric sulfur cycle simulated in the global model GOCART: Comparison with field observations and regional budgets. *J. Geophys. Res.*, **105** (D20), 24 689–24 712.
- Dickerson, R. R., and Coauthors, 2007: Aircraft observations of dust and pollutants over northeast China: Insight into the meteorological mechanisms of transport. *J. Geophys. Res.*, **112**, D24S90, doi:10.1029/2007JD008999.
- Draxler, R. R., and G. D. Rolph, cited 2010: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website. NOAA/Air Resources Laboratory, Silver Spring, MD. [Available online at <http://ready.arl.noaa.gov/HYSPLIT.php>.]
- Eisinger, M., and J. P. Burrows, 1998: Tropospheric sulfur dioxide observed by the ERS-2 GOME instrument. *Geophys. Res. Lett.*, **25**, 4177–4180.
- EPA, 2000: National Air Pollutant Emission Trends, 1900–1998. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards Rep. EPA-454/R-00-002, 238 pp.

- [Available online at <http://www.epa.gov/ttn/chief/trends/trends98/trends98.pdf>.]
- Fioletov, V. E., E. Griffioen, J. B. Kerr, D. I. Wardle, and O. Uchino, 1998: Influence of volcanic sulfur dioxide on spectral UV irradiance as measured by Brewer spectrophotometers. *Geophys. Res. Lett.*, **25**, 1665–1668.
- Galle, B., and Coauthors, 2010: Network for Observation of Volcanic and Atmospheric Change (NOVAC)—A global network for volcano gas monitoring: Network layout and instrument description. *J. Geophys. Res.*, **115**, D05304, doi:10.1029/2009JD011823.
- Grell, G. A., J. Dudhia, and D. Stauffer, 1994: A description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5). NCAR Tech. Note NCAR/TN-398+STR, 121 pp.
- Hirokawa, J., T. Kato, and F. Mafuné, 2009: In situ measurements of atmospheric nitrous acid by chemical ionization mass spectrometry using chloride ion transfer reactions. *Anal. Chem.*, **81**, 8380–8386.
- Huey, L. G., D. R. Hanson, and C. J. Howard, 1995: Reactions of SF_6^- and I^- with atmospheric trace gases. *J. Phys. Chem.*, **99**, 5001–5008.
- Kearney, C. S., K. Dean, V. J. Realmuto, I. M. Watson, J. Dehn, and F. Prata, 2008: Observations of SO_2 production and transport from Bezymianny volcano, Kamchatka using the MODerate resolution Infrared Spectroradiometer (MODIS). *Int. J. Remote Sens.*, **29**, 6647–6665.
- Khokhar, M. F., C. Frankenberg, M. Van Roozendaal, S. Beirle, S. Kühl, A. Richter, U. Platt, and T. Wagner, 2005: Satellite observations of atmospheric SO_2 from volcanic eruptions during the time-period of 1996–2002. *Adv. Space Res.*, **36**, 879–887.
- Kloster, S., and Coauthors, 2008: Influence of future air pollution mitigation strategies on total aerosol radiative forcing. *Atmos. Chem. Phys.*, **8**, 6405–6437.
- Komhyr, W. D., 1969: Electrochemical concentration cells for gas analysis. *Ann. Geophys.*, **25**, 203–210.
- , 1986: Operations handbook: Ozone measurements to 40 km altitude with mode 4A electrochemical concentration cell (ECC) ozonesondes (used with 1680-Mhz radiosondes). NOAA Tech. Memo. ERLARL-149, 49 pp.
- , 1999: En-Sci Corporation Model KTU-2A Ozonesonde Ozone Analyzer/Test Unit, 7 pp. [Available online at <http://ready.arl.noaa.gov/>, P.O. Box 3234, Boulder, CO 80303.]
- , R. A. Barnes, G. B. Brothers, J. A. Lathrop, and D. P. Opperman, 1995: Electrochemical concentration cell performance evaluation during STOIC. *J. Geophys. Res.*, **100**, 9231–9244.
- Krotkov, N. A., A. J. Krueger, and P. K. Bhartia, 1997: Ultraviolet optical model of volcanic clouds for remote sensing of ash and sulfur dioxide. *J. Geophys. Res.*, **102** (D18), 21 891–21 904.
- , S. A. Carn, A. J. Krueger, P. K. Bhartia, and K. Yang, 2006: Band residual difference algorithm for retrieval of SO_2 from the aura Ozone Monitoring Instrument (OMI). *IEEE Trans. Geosci. Remote Sens.*, **44**, 1259–1266.
- , K. Yang, A. Krueger, S. A. Carn, P. K. Bhartia, and P. F. Levelt, 2007: SO_2 data from the Ozone Monitoring Instrument. *Proc. ENVISAT Symp. 2007*, Montreux, Switzerland, European Space Agency, ESA SP-636, 509823. [Available online at <http://envisat.esa.int/envisatsymposium/proceedings/sessions/3G2/509823kr.pdf>.]
- , and Coauthors, 2008: Validation of SO_2 retrievals from the Ozone Monitoring Instrument over NE China. *J. Geophys. Res.*, **113**, D16S40, doi:10.1029/2007JD008818.
- Krueger, A. J., 1983: Sighting of El Chichon sulfur dioxide with the Nimbus-7 total ozone mapping spectrometer. *Science*, **220**, 1377–1378.
- , L. S. Walter, P. K. Bhartia, C. C. Schnetzler, N. A. Krotkov, I. Sprod, and G. J. S. Bluth, 1995: Volcanic sulfur-dioxide measurements from the total ozone mapping spectrometer instruments. *J. Geophys. Res.*, **100** (D7), 14 057–14 076.
- , S. J. Schaefer, N. Krotkov, G. Bluth, and S. Barker, 2000: Ultraviolet remote sensing of volcanic emissions. *Remote Sensing of Active Volcanism*, *Geophys. Monogr.*, Vol. 116, Amer. Geophys. Union, 25–43.
- Lee, C., A. Richter, M. Weber, and J. P. Burrows, 2008: SO_2 retrieval from SCIAMACHY using the Weighting Function DOAS (WFDOAS) technique: Comparison with standard DOAS retrieval. *Atmos. Chem. Phys.*, **8**, 6137–6145.
- , R. V. Martin, A. Donkelaar, G. O’Byrne, N. A. Krotkov, A. Richter, L. G. Huey, and J. S. Holloway, 2009: Retrieval of vertical columns of sulfur dioxide from SCIAMACHY and OMI: Air mass factor algorithm development, validation, and error analysis. *J. Geophys. Res.*, **114**, D22303, doi:10.1029/2009JD012123.
- Levelt, P. F., E. Hilsenrath, G. W. Leppelmeier, G. B. J. van den Oord, P. K. Bhartia, J. Tamminen, J. F. de Haan, and J. P. Veefkind, 2006a: Science objectives of the Ozone Monitoring Instrument. *IEEE Trans. Geosci. Remote Sens.*, **44**, 1199–1208.
- , and Coauthors, 2006b: The Ozone Monitoring Instrument. *IEEE Trans. Geosci. Remote Sens.*, **44**, 1093–1101.
- Lovejoy, E. R., and R. R. Wilson, 1998: Kinetic studies of negative ion reactions in a quadrupole ion trap: Absolute rate coefficients and ion energies. *J. Phys. Chem. A*, **102**, 2309–2315.
- Luke, W. T., 1997: Evaluation of a commercial pulsed fluorescence detector for the measurement of low-level SO_2 concentrations during the Gas-Phase Sulfur Intercomparison Experiment. *J. Geophys. Res.*, **102**, 16 255–16 265.
- Richter, A., F. Wittrock, and J. P. Burrows, 2006: SO_2 measurements with SCIAMACHY. *Proc. Atmospheric Science Conf.*, Frascati, Italy, European Space Agency, ESA SP-628, 6 pp. [Available online at http://earth.esa.int/workshops/atmos2006/participants/804/paper_richter_esa_06.pdf.]
- Rolph, G. D., cited 2010: Real-time Environmental Applications and Display sYstem (READY). NOAA/Air Resources Laboratory, Silver Spring, MD. [Available online at <http://ready.arl.noaa.gov/>.]
- Saltzman, B. E., and A. F. Wartburg, 1965: Absorption tube for removal of interfering sulfur dioxide in analysis of atmospheric oxidant. *Anal. Chem.*, **37**, 779–782.
- Schoeberl, M. R., and Coauthors, 2006: Overview of the EOS Aura Mission. *IEEE Trans. Geosci. Remote Sens.*, **44**, 1066–1074.
- , and L. Sparling, 1995: Trajectory Modeling, in *Diagnostic Tools in Atmospheric Physics*. *Proc. Int. Sch. Phys. “Enrico Fermi,”* **124**, 289–306.
- Seinfeld, J. H., and S. N. Pandis, 1998: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley and Sons, 1326 pp.
- Smit, H. G., and Coauthors, 2007: Assessment of the performance of ECC-ozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Jülich Ozone Sonde Intercomparison Experiment (JOSIE). *J. Geophys. Res.*, **112**, D19306, doi:10.1029/2006JD007308.
- Soloman, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller, Eds., 2007: *Climate Change 2007: The Physical Science Basis*. Cambridge University Press, 996 pp.
- Taubman, B. F., J. C. Hains, A. M. Thompson, L. T. Marufu, B. G. Doddridge, J. W. Stehr, C. A. Piety, and R. R. Dickerson,

- 2006: Aircraft vertical profiles of trace gas and aerosol pollution over the mid-Atlantic United States: Statistics and meteorological cluster analysis. *J. Geophys. Res.*, **111**, D10S07, doi:10.1029/2005JD006196.
- Thomas, W., T. Erbertseder, T. Ruppert, M. van Roozendaal, J. Verdebout, D. Balis, C. Meleti, and C. Zerefos, 2005: On the retrieval of volcanic sulfur dioxide emissions from GOME backscatter measurements. *J. Atmos. Chem.*, **50**, 295–320.
- Thompson, A. M., and Coauthors, 2003: Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998–2000 tropical ozone climatology 1. Comparison with Total Ozone Mapping Spectrometer (TOMS) and ground-based measurements. *J. Geophys. Res.*, **108**, 8238, doi:10.1029/2001JD000967.
- , and Coauthors, 2007: IONS (INTEX Ozone-sonde Network Study, 2004). 1. Summertime UT/LS (upper troposphere/lower stratosphere) ozone over northeastern North America. *J. Geophys. Res.*, **112**, D12S12, doi:10.1029/2006JD007441.
- Warmbt, W., and G. Herrmann, 1977: Surface ozone measurements utilizing chromium trioxide filters. *Proc. Joint Symposium Atmospheric Ozone*, Vol. 1, Dresden, Germany, 179–188.
- Yang, K., N. A. Krotkov, A. J. Krueger, S. A. Carn, P. K. Bhartia, and P. F. Levelt, 2007: Retrieval of large volcanic SO₂ columns from the Aura Ozone Monitoring Instrument (OMI): Comparison and limitations. *J. Geophys. Res.*, **112**, D24S43, doi:10.1029/2007JD008825.
- , —, —, —, —, and —, 2009a: Improving retrieval of volcanic sulfur dioxide from backscattered UV satellite observations. *Geophys. Res. Lett.*, **36**, L03102, doi:10.1029/2008GL036036.
- , X. Liu, N. A. Krotkov, A. J. Krueger, and S. A. Carn, 2009b: Estimating the altitude of volcanic sulfur dioxide plumes from space borne hyper-spectral UV measurements. *Geophys. Res. Lett.*, **36**, L10803, doi:10.1029/2009GL038025.

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