

# Remote measurement of high pre-eruptive water vapor emissions at Sabancaya volcano by passive differential optical absorption spectroscopy

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## Key Points

- Volcanic water vapor emissions were measured with passive differential optical absorption spectroscopy (DOAS) for the first time.
- Exceptionally high water vapor emissions were detected at Sabancaya, most likely due to boiling-off of the hydrothermal system.
- The DOAS method could be used to detect similar, pre-eruptive water vapor plumes at other volcanoes, thus improving eruption forecasts.

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## Abstract

Water ( $\text{H}_2\text{O}$ ) is by far the most abundant volcanic volatile species and plays a predominant role in driving volcanic eruptions. However, numerous difficulties associated with making accurate measurements of water vapor in volcanic plumes have limited their use as a diagnostic tool. Here we present the first detection of water vapor in a volcanic plume using passive visible-light differential optical absorption spectroscopy (DOAS). Ultraviolet and visible-light DOAS measurements were made on 21 May 2016 at Sabancaya Volcano, Peru. We find that Sabancaya's plume contained an exceptionally high relative water vapor abundance six months prior to its November 2016 eruption. Our measurements yielded average sulfur dioxide ( $\text{SO}_2$ ) emission rates of 800-900 metric tons per day (t/d),  $\text{H}_2\text{O}$  emission rates of around 250,000 t/d, and an  $\text{H}_2\text{O}/\text{SO}_2$  molecular ratio of 1,000 which is about an order of magnitude larger than typically found in high-temperature volcanic gases. We attribute the high water vapor emissions to a boiling-off of Sabancaya's hydrothermal system caused by intrusion of magma to shallow depths. This hypothesis is supported by a significant increase in the thermal output of the volcanic edifice detected in infrared satellite imagery leading up to and after our measurements. Though the measurement conditions encountered at Sabancaya were very favorable for our experiment, we show that visible-light DOAS systems could be used to measure water vapor emissions at numerous other high-elevation volcanoes. Such measurements would provide observatories with additional information particularly useful for forecasting eruptions at volcanoes harboring significant hydrothermal systems.

## 1. Introduction

Water ( $\text{H}_2\text{O}$ ) is by far the most abundant volcanic volatile species. In fact, high-temperature volcanic gases from arc volcanoes typically contain at least an order of magnitude more  $\text{H}_2\text{O}$  than any other species [Giggenbach, 1996; Gerlach, 2004]. Besides  $\text{H}_2\text{O}$ , high-temperature volcanic gases are mostly made up of carbon dioxide ( $\text{CO}_2$ ), sulfur dioxide ( $\text{SO}_2$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ), along with a number of minor constituents that together typically make up less than 2% of emissions [Gerlach, 2004]. Despite its abundance, there are a number of challenges associated with accurately determining volcanic  $\text{H}_2\text{O}$  emission rates, and measurements of  $\text{H}_2\text{O}$  output are therefore relatively seldom reported.

Here we show how we were able to overcome these difficulties and present a novel approach to measuring water vapor in volcanic plumes using passive, visible-light differential optical absorption spectroscopy (DOAS). With this new method, we were able to capture unexpectedly high  $\text{H}_2\text{O}$  emissions from Sabancaya Volcano (Peru) in May 2016. We interpret our measurements in the context of subsequent activity at Sabancaya and explain why monitoring  $\text{H}_2\text{O}$  emissions with DOAS could provide valuable information for eruption forecasting at high-elevation volcanoes in the future.

## 1.1 Water vapor in volcanic plumes

As the most abundant volatile, H<sub>2</sub>O controls many aspects of volcanic eruptions. Eruptions can be initiated by excess pressure developing in a magma chamber due to accumulation of water-rich magma at the chamber top [Blake, 1984]. As magma rises and the hydrostatic pressure decreases, water vapor is exsolved, expands, and accelerates the rising column [Sparks, 1978; Woods, 1995]. When magma reaches the surface, dissolved H<sub>2</sub>O has largely partitioned to the gas phase and controls the explosivity of the eruption [Wilson *et al.*, 1980]. Water can also influence the generation of pyroclastic flows [Carey and Sigurdsson, 1989]. As the eruption progresses, the volatile content of the primitive melt critically impacts the total erupted mass required to relieve overpressure [Bower and Woods, 1997], thereby affecting when the eruption will end. Clearly, a lot can be learned about volcanic systems by analyzing their water vapor emissions during periods of effusive degassing and eruption.

Volcanogenic water vapor emitted into the lower atmosphere has negligible environmental impact due to the high natural tropospheric H<sub>2</sub>O background. However, large eruptions, particularly those occurring at mid-latitudes, can inject water vapor into the stratosphere. Here, it acts as a strong greenhouse gas [Solomon *et al.*, 2010]. Though recent satellite observations indicate that direct injection of volcanic H<sub>2</sub>O is not an efficient mechanism for stratospheric hydration [Sioris *et al.*, 2016], it is possible that very large eruptions (VEI > 5) could influence the entrainment of tropospheric water vapor, or even seawater, into the stratosphere [Joshi and Shine, 2003; Joshi and Jones, 2009; Löffler *et al.*, 2016] and thus impact climate. Perhaps more importantly, the water content of an eruption column clearly impacts its thermal energy budget and vertical development [Herzog *et al.*, 1998], thus also affecting the downwind transport of erupted products.

Despite its importance in driving volcanic processes and its possible role as a diagnostic tool for detecting volcanic unrest, water vapor measurements are relatively underreported in the literature when compared with other major volatile components of volcanic gases such as CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S. In part, this is because water vapor emissions from volcanoes are often difficult to interpret due to the fact that not all water vapor emitted by volcanoes actually originates in the magma. Many volcanoes host hydrothermal systems, and magmatic fluids passing through these can incorporate meteoric water [Hinkley *et al.*, 1995; Goff and McMurtry, 2000; Botcharnikov *et al.*, 2003]. At some volcanoes, additional H<sub>2</sub>O might originate from heated local seawater incorporated in the conduit [Symonds *et al.*, 1990].

Another complicating factor stems from difficulties in accurately measuring water vapor in volcanic plumes. Any form of direct sampling or direct analysis of volcanic water vapor is subject to errors induced by the pressure and temperature-dependency of the H<sub>2</sub>O vapor pressure inside the sampling system [Symonds *et al.*, 1994; Wiederhold, 1997]. Changes in pressure and temperature often lead to condensation which, if not carefully accounted for, can skew a sample or buffer a direct measurement in an undesirable manner. There is also always the potential for contamination of a measurement or sample by atmospheric water vapor.

Many of these difficulties can be overcome by using a contact-free method of detection. Volcanic water vapor has been successfully measured using Fourier Transform Infrared

(FTIR) spectroscopy. *Naughton et al.* [1969] first measured the infrared absorption of volcanic volatiles by aiming an infrared spectrometer at a lava fountain during the 1968 Kilauea eruption. *Burton et al.* [2000] measured H<sub>2</sub>O/SO<sub>2</sub> ratios at Masaya Volcano, Nicaragua, using active-source open path FTIR. These ratios can then be multiplied by SO<sub>2</sub> emission rates obtained from Correlation Spectrometer (COSPEC) or DOAS measurements to obtain H<sub>2</sub>O emission rates. In 2004, *Oppenheimer and Kyle* [2008] were able to measure the relative abundances of a wide range of volcanic gases including H<sub>2</sub>O emitted from Erebus Volcano, Antarctica, by pointing an FTIR spectrometer at the hot lava lake, and similar experiments have been conducted here and elsewhere since then. The main challenge with these types of measurements is finding an adequate source of infrared radiation – a lamp, lava lake or lava flow is required. Passive FTIR measurements using either the sun or solar radiation scattered in the atmosphere would be preferable, but are significantly more difficult due to the fact that the entire atmospheric column is probed (see next section). To our knowledge, the only scattered-light FTIR measurements of volcanic water vapor in the literature were reported by [*Love et al.*, 2000], but these relied on several relatively uncertain assumptions regarding the vertical atmospheric water vapor and temperature profiles, and have yet to be reproduced.

Besides measuring volcanic H<sub>2</sub>O in infrared absorption, several studies have recently attempted to quantify water emissions by measuring the scattering of radiation on water droplets suspended in volcanic gas plumes [*Matsushima and Shinohara*, 2006; *Girona et al.*, 2015; *Pering et al.*, 2017]. These techniques attempt to relate the scattering efficiency of liquid water droplets in the plume to the abundance of water vapor or total water. However, this relationship depends on numerous parameters such as the vent exit temperature, the volcanic gas composition, the concentration of sulfate aerosols and other condensation nuclei in the plume, the temperature and relative humidity of the background air that is mixed into the plume, and the observation geometry (e.g. solar zenith and azimuth angles). Though potentially viable for detecting relative variability on short time scales, these techniques are difficult to implement quantitatively and require very frequent calibration using other methods.

## 1.2 Water vapor in the atmosphere

A major difficulty in measuring volcanic H<sub>2</sub>O degassing stems from the fact that the atmospheric water vapor background is quite large. In fact, the volcanic H<sub>2</sub>O contribution to the global atmospheric budget is negligible compared to the current natural background concentration, which mainly stems from evaporation of large water bodies. Averaged globally, the vertical atmospheric water vapor column density (VCD) is approximately  $8 \times 10^{22}$  molecules/cm<sup>2</sup> [*Randel et al.*, 1996]. If all water vapor in this column were condensed and precipitated, its depth would amount to about 2.5 cm. However, due to the fact that the vapor pressure of water in liquid and solid state increases exponentially with temperature (Clausius-Clapeyron relation), the atmosphere's ability to hold water vapor is strongly dependent on air temperature. Therefore, the atmospheric water vapor distribution is highly variable on both vertical and latitudinal spatial scales. Latitudinal cross-sections of the total

water vapor column often show VCDs of less than  $1 \times 10^{22}$  molecules/cm<sup>2</sup> (equivalent to 3 mm liquid water) at the poles but at least an order of magnitude more than that at the equator [Maurellis *et al.*, 2000; Ye *et al.*, 2007]. Likewise, the water vapor VCD above a given location will typically vary with season as the air temperature changes [Gaffen *et al.*, 1992]. The water vapor concentration decreases rapidly with altitude in the troposphere [COESA, 1976; Cahen *et al.*, 1982; Palchetti *et al.*, 2007], as temperature also decreases. Strikingly, a temporary decrease in global average H<sub>2</sub>O VCDs was even observed ensuing the 1991 eruption of Mt. Pinatubo, as global-mean lower tropospheric temperature cooled by about a half degree C for several years [Soden *et al.*, 2002].

As mentioned before, the vertical water vapor distribution can be approximated by an exponential decrease in concentration with altitude. The so-called ‘scale height’  $H$  of this distribution gives the altitude at which the concentration has dropped to  $1/e$  times the concentration present at sea level. The water vapor scale height in the atmosphere typically varies between about 1 and 3 km, with the highest values observed in close proximity to large, high-temperature bodies of water where evaporation is most efficient [Tomasi, 1984; Turner *et al.*, 2001; Wagner *et al.*, 2013]. Away from major water vapor sources and sinks, a scale height of 2 km usually represents a good estimate [ITU, 2012]. Since the scale height of oxygen and nitrogen, the major constituents of the atmosphere, is approximately 8 km, by far the majority of the water vapor is located in the lowermost part of the atmosphere.

An approximation for the atmospheric H<sub>2</sub>O VCD above a given altitude or topographic elevation  $h$  can be obtained by integrating the exponential concentration profile  $c_{H_2O}(z)$  from  $h$  to infinity.

$$VCD(h) = \int_h^{\infty} c_{H_2O}(z) dz = \int_h^{\infty} c_0 e^{-\left(\frac{z}{H}\right)} dz = c_0 H e^{-\left(\frac{h}{H}\right)}$$

(Eq. 1)

At sea level, the VCD is therefore simply the concentration of water vapor  $c_0$  times the scale height. The vertical column decreases very rapidly as the observer ascends in elevation. At 5,000 m, for example, the VCD is less than 10% of the VCD measured at sea level for a scale height  $H$  of 2 km.

Based on these considerations, we will refer to a ‘standard atmosphere’ throughout this manuscript as one that has an H<sub>2</sub>O VCD of  $8 \times 10^{22}$  molecules/cm<sup>2</sup>, an H<sub>2</sub>O scale height of 2 km, an air scale height of 8 km and an air concentration of  $2.6 \times 10^{19}$  molecules/cm<sup>3</sup> at sea level.

### 1.3 The challenge of measuring water vapor in volcanic plumes with scattered-light remote sensing

The global volcanic flux of water vapor into the atmosphere remains relatively poorly constrained [Textor *et al.*, 2004]. One reason for this is the fact that accurately quantifying volcanic H<sub>2</sub>O emission rates is challenging. Up to now, all measurements of volcanic H<sub>2</sub>O output have been based on an indirect measurement scheme. First, the relative chemical



composition of volatile output is determined, either by petrologic analysis of relative volatile concentrations in extruded lava or by laboratory or direct analysis of the H<sub>2</sub>O/SO<sub>2</sub> ratio in the emitted gases. In a second step, the H<sub>2</sub>O flux is then derived from this composition and the lava extrusion rate or SO<sub>2</sub> emission rate measured by another technique. Methods measuring light scattered on condensed water droplets can derive the emission rate directly, but then rely on an indirect relationship between light-scattering and H<sub>2</sub>O abundance.

Constraining the SO<sub>2</sub> emission rate is relatively straightforward because this species can readily be measured using scattered-light remote sensing and its atmospheric background is negligible. Today, DOAS is commonly used to measure the absorption of ultraviolet solar radiation as it passes through the volcanic plume. By scanning a DOAS instrument field of view across the plume or passing an upward-looking instrument under the plume, the number of SO<sub>2</sub> molecules in a 1 m-wide plume cross-section can be determined (e.g., in molecules/m). This number, multiplied by the plume speed (e.g., in m/s), gives the SO<sub>2</sub> emission rate (e.g., in molecules/s).

The main difficulty in measuring volcanic H<sub>2</sub>O and CO<sub>2</sub> in the same way lies in the non-negligible atmospheric background concentrations of these gases. Since all scattered solar radiation has already passed through the entire atmospheric column to reach the detecting instrument, H<sub>2</sub>O and CO<sub>2</sub> absorption signals are present regardless of whether the radiation has passed through a volcanic plume or not. In fact, the signal enhancement expected from a volcanic plume will normally be very small. A typical high-temperature plume from an active, quiescently degassing volcano might contain an SO<sub>2</sub> VCD of about 10<sup>18</sup> molecules/cm<sup>2</sup>. That same plume might contain 10<sup>20</sup> H<sub>2</sub>O molecules/cm<sup>2</sup>, but this is only about 0.1% of the average atmospheric H<sub>2</sub>O background VCD at sea level.

In this study, we aim to show that, though difficult, measuring H<sub>2</sub>O with scattered-light DOAS is not actually impossible. By selecting a favorable, very high volcano located in an unusually dry region with an above-average H<sub>2</sub>O flux, we were able to measure the volcanic H<sub>2</sub>O emission rate with DOAS for the first time. Though clearly a special case study, we argue that the technique is indeed applicable to a number of high-altitude volcanoes around the world, and that the additional insights we stand to gain make the task well worth pursuing.

## **2. Instrument setup and study site**

In this section, the instrumentation and methods that were used to perform DOAS measurements of H<sub>2</sub>O are described. DOAS measurements were made in both vehicle-based traverse and stationary scanning geometries at Sabancaya Volcano, Peru. In addition to the visible spectral range (Vis) used for H<sub>2</sub>O analysis, all measurements also included the ultraviolet (UV) spectral region so that SO<sub>2</sub> column densities and emission rates could be retrieved. The SO<sub>2</sub> emissions give background information on Sabancaya's level of activity during the measurements and provide context for comparing the H<sub>2</sub>O retrievals and results presented later on in sections 3 and 4.

## 2.1 Sabancaya Volcano, Peru

Sabancaya Volcano is an active stratovolcano located in the central Andean volcanic zone in southern Peru (Figure 1). With a summit elevation of 5967 m, it is slightly lower than the 6288 m dormant Ampato Volcano located just 4 km to its immediate southwest and part of the same complex [*Samaniego et al.*, 2016]. Prior to its current crisis, Sabancaya last experienced a violent eruption in May-June 1990 followed by a period of 8 years with frequent vulcanian and phreatomagmatic events. The small volumes of juvenile tephra erupted during this time period were of andesitic to dacitic composition [*Gerbe and Thouret*, 2004].

Small explosions emitted gas and ash in 2000 and 2003, but the volcano then became quiet for a decade. This period of quiescence ended in February 2013, when an earthquake swarm damaged walls and bridges in an irrigation canal network on the Majes drainage. Around this time, gases also began emitting from fumaroles in the summit crater area, and SO<sub>2</sub> emissions picked up from essentially zero to several tens of metric tons per day (t/d) in 2013 and up to 1,000 t/d in 2014, as measured by vehicle-based DOAS traverses of the plume. Beginning in 2016, a scanning DOAS network was installed as part of the Network for Observation of Volcanic and Atmospheric Change (NOVAC, Galle et al. 2010), and emissions have since climbed to maximum values of over 6,000 t/d. A number of fumaroles located away from the volcano's summit vent began visibly steaming in summer of 2016, with emissions appearing to increase in vigor over time. Finally, a series of minor explosions and continuous low-level ash emissions began 6 November 2016, and on 11 November 2016, Sabancaya experienced an explosive eruption that sent an ash column up to 3 km above the volcano's summit. Unrest continues through the time of this writing.

The current crisis at Sabancaya poses limited hazards of ashfall to small communities surrounding the volcano. In particular, local alpaca and llama farmers are concerned for the health of their animals given the ashfall on grazing land. There are reports of cattle dying in proximal areas during the lead-up to the 1990 eruption, either from breathing noxious fumarolic gases or eating contaminated foliage (de Silva and Francis 1990 and references therein). If larger eruptions were to occur, the main associated hazards would stem from lahars, mudflows and, to a lesser degree, pyroclastic and lava flows down the Rio Colca, Sihuas and Majes drainages [*de Silva and Francis*, 1991]. The Observatorio Vulcanológico del Instituto Geológico, Minero y Metalúrgico (OVI) closely monitors Sabancaya. Hazard maps and reports on current activity can be found on their website (<http://ovi.ingemmet.gob.pe>).

## 2.2 DOAS traverse measurements

The measurements we report on in this study were recorded on 21 May 2016, when SO<sub>2</sub> emissions had not yet reached their current levels and the plume was still free of ash. Light winds carried the plume emitted from Sabancaya's summit towards the southeast. Access to the volcano is by unpaved dirt track from the east, so our vehicle passed beneath the plume during our approach of the volcano between 11:43 and 12:39 local time (Figure 1). During

this time, the solar zenith and azimuth angles ranged from 36 to 39 and from 0 to 339 deg, respectively. Two zenith-looking telescopes were mounted on the truck, each coupling scattered solar radiation from a narrow 1-degree field of view into separate fiber optic cables and into two different spectrometers. An Ocean Optics SD2000 UV spectrometer was used to measure the spectral radiance between 280 and 420 nm at a spectral resolution of 0.6 nm, and an Ocean Optics USB2000+ Vis spectrometer was used to measure the spectral radiance between 450 and 780 nm at a resolution of 1.2 nm. Using a compiled MATLAB code written for this purpose, data was acquired at 1 s integration time on two laptop computers, and GPS receivers were used to record the time and location of each acquisition.

### **2.3 Scanning DOAS measurements**

After the plume traverse was completed, scanning DOAS measurements were set up at a site 5 km south of Sabancaya's summit at 5040 m elevation (Figure 1). A small scanner was set on a tripod such that its scanning plane was approximately perpendicular to the direction of plume propagation (Figure 2). In the scanning unit, a servo motor successively positioned an aluminum-coated right-angle mirror such that scattered radiation was collected from elevation angles between 4 and 82 deg above the horizontal in steps of 3 deg. A 40 mm focal length fused silica lens coupled scattered radiation into a  $2 \times 600 \mu\text{m}$  diameter bifurcated fiber, thus collecting radiation from an  $\sim 0.9$  deg field of view. The fibers led to two separate Ocean Optics USB2000+ spectrometers (Figure 2). Similar to the traverse setup, the two spectrometers covered the spectral ranges 280–430 nm and 450–780 nm at optical resolutions of 0.6 nm and 1.2 nm, respectively. Two laptops were again used to acquire data through the spectrometers' USB interfaces.

Prior to spectral analysis, the data acquired on the two separate spectrometer systems was synchronized according to the time stamps provided by GPS receivers connected to each laptop. The computer controlling the Vis spectrometer also controlled the scanner, positioning the latter such that a Vis spectrum with 5 s integration time could be recorded at each elevation angle. The start and stop time of each Vis measurement was saved. UV spectra were recorded coincidentally on the other system at 1 s integration times. These were later sorted such that successive UV spectra recorded during a particular Vis acquisition were co-added and UV spectra recorded while the scanner was moving were discarded. This procedure resulted in a time-series of UV and Vis spectra recorded at coincident times and viewing geometries.

The scanning measurements ran from 14:11 to 16:11 local time. During this interval, measurement conditions were ideal for UV/Vis remote sensing. The solar zenith and azimuth angles ranged from 51 to 75 deg and 314 to 297 deg, respectively. Only very few, very small meteorological clouds were in the area and did not interfere with measurements. Perceptible visibilities were in excess of 80 km based on the discernibility of surrounding topography when viewed from the measurement site.



## 2.4 SO<sub>2</sub> emissions from Sabancaya

For the traverse measurements, the SO<sub>2</sub> VCD above the vehicle was retrieved from the collected UV spectra by performing a standard DOAS evaluation [Galle *et al.*, 2002; Platt and Stutz, 2008]. For this, the measurement spectra were first corrected for detector dark current and electronic offset. The optical depth was calculated by dividing by a clear-sky reference and taking the negative of the logarithm of this ratio. Then, a number of pre-calculated reference spectra were fit to the measurement spectra in the 314-330 nm wavelength interval: (1) the high-resolution absorption cross-sections of SO<sub>2</sub> [Vandaele *et al.*, 2009] and O<sub>3</sub> [Bogumil *et al.*, 2003] were convolved with the UV spectrometer's instrument line shape (obtained from a laboratory measurement of a mercury calibration lamp) to account for the spectrometer's optical resolution; (2) a Ring spectrum [Grainger and Ring, 1962] was calculated from the clear sky spectrum using the DOASIS software [Kraus, 2006] to account for a variable contribution of Raman scattering to the measured spectra; (3) two references were prepared to correct for minor changes in the spectrometer's wavelength calibration during the course of the measurements following the recommendations of [Beirle *et al.*, 2013]; and (4) a third-order polynomial was included in the fit to describe broadband variations in the spectrum. Table 1 summarizes this procedure as well as the similar retrievals of O<sub>4</sub> and H<sub>2</sub>O discussed later on.

When applied to the spectra recorded during the vehicle traverse of the plume, the DOAS analysis yielded SO<sub>2</sub> column densities of up to  $1 \times 10^{18}$  molecules/cm<sup>2</sup>. Measurement errors derived from the fit residual [Stutz and Platt, 1996] averaged  $1 \times 10^{17}$  molecules/cm<sup>2</sup>. Though traces of SO<sub>2</sub> were encountered east of the vent, perhaps from swirling distal winds, the highest columns were clearly found at a location 10 km southeast of the active summit (Figure 1). From these, the near-field wind direction can be estimated at  $300 \pm 10$  deg off north. Integrating the column densities obtained while traversing the main plume and multiplying by a wind speed of  $(4.1 \pm 0.8)$  m/s (derived from video sequences recorded later at the scanning site, see below) yields an SO<sub>2</sub> emission rate of  $800 \pm 180$  t/d. The error indicated here is calculated based on independent propagation of errors in the individual column densities, the plume direction and the plume speed.

The UV spectral data collected during our plume scans were analyzed for SO<sub>2</sub> absorption according to the same methodology. The results show that gas emissions from the summit and wind conditions were both relatively stable throughout the measurement period. The plume was generally detected in a swath of about 15 deg width. During the course of the measurements, its center position varied between 8 and 20 deg elevation. The plume reached all the way down to the horizon in a few scans but not the majority. Variations in plume center position appeared to stem from small changes in the altitude of the lofting plume.

The wind direction of  $(300 \pm 10)$  deg was previously determined by a DOAS traverse conducted while approaching the scanning location (section 2.2). The wind speed was determined by recording a video of the plume from the DOAS scanner location at 15:11 local time. Though virtually invisible at the location of the scanning plane, it was possible to track visible plume features in closer proximity to the vent (Figure 2). Several features were tracked in video frames separated by 10 seconds each, and their location relative to stationary landmarks was determined. The hand-picked plume displacement averaged  $(1.57 \pm 0.34)$  pixels per second which, when combined with an assumed plume distance of 3.4 km, a total sensor width of 1644 pixels and a camera horizontal viewing angle of 64.6 deg, yielded a wind speed of  $(4.1 \pm 0.8)$  m/s.

SO<sub>2</sub> emission rates were obtained for the scanning measurements using the standard approach of integrating each scan and multiplying the retrieved SO<sub>2</sub> burdens with the wind speed [Galle *et al.*, 2002]. During the period of scanning measurements, the SO<sub>2</sub> emission rate averaged 890 t/d, with a standard deviation for individual scans of 240 t/d. Rather than assume a constant plume height for our calculations, we assumed a constant plume distance and integrated radially across the plume. We deem this approach to be less susceptible to errors given the apparent variability of plume height but relative stability of wind direction, though these observations stem solely from visual estimation of the plume geometry over time.

Analogous to the methods presented by Kern *et al.* [2009], the radiative transfer model McArtim [Deutschmann *et al.*, 2011] was used to examine the influence of light dilution on our measurements. In the absence of scattering aerosols, an assumption justified by the pristine atmospheric conditions observed during our measurement period, we found that our retrieved SO<sub>2</sub> column densities likely underestimate the true values by an average of ~10% due to light entering the instrument field of view without having passed through the plume. However, we chose not to correct our emission estimates because the correction would depend on the exact measurement geometry at a given time and would therefore vary over the course of the measurements as the plume height varies. We also found that the influence of light dilution on the H<sub>2</sub>O column densities, measured in the visible region and discussed in the next section, was almost identical. Therefore, the H<sub>2</sub>O/SO<sub>2</sub> ratios are not significantly affected and need not be corrected.

We estimate the variation of the plume height over time and the measurement error stemming from our assumption of a constant plume distance to be about ~10% as well. Furthermore, the spectroscopic error derived from the DOAS fit residual was also ~10% and independent of

the other errors. However, the largest source of error for the emission rate stems from the uncertainty of the wind speed (~20%, see above). Taking all of these error sources into consideration, we estimate the total error on our derived SO<sub>2</sub> emission rate to be about 230 t/d, or 26% of the average value. Therefore, the recorded variability of emissions (240 t/d standard deviation) may simply be the result of variability in the plume geometry and wind speed during our measurement interval.

### 3. Measuring water vapor with DOAS

Though, to our knowledge, volcanic water vapor emissions have never before been measured by DOAS, the technique has been used extensively to measure total atmospheric water vapor column densities from both ground-based and satellite platforms [Noël *et al.*, 1999, 2004, Wagner *et al.*, 2003, 2013; Sierk *et al.*, 2004; Lampel *et al.*, 2015]. In the following, we discuss the geometric considerations that are necessary for evaluating passive DOAS measurements of localized water vapor plumes in the atmosphere. Then, the details of our spectral H<sub>2</sub>O retrieval are outlined and the differences to evaluation schemes targeting atmospheric H<sub>2</sub>O are discussed.

#### 3.1 Geometric approximation of atmospheric radiative transfer

In comparison to the relatively straightforward evaluation of spectroscopic SO<sub>2</sub> measurements, the analysis of water vapor absorption measurements is complicated by the fact that the atmospheric background of water vapor is significant. In fact, any H<sub>2</sub>O absorption signals measured with DOAS will typically be mainly associated with the natural background rather than a localized plume. Perhaps even more importantly, any change in the atmospheric radiative transfer, i.e. the distribution of light paths between the sun and the instrument, has the potential to affect the measured H<sub>2</sub>O absorbance. Therefore, any spectroscopic measurements of water vapor can only be interpreted in the context of the measurement geometry.

For these discussions it is useful to define a number of terms typically used in the Multi-Axis DOAS (MAX-DOAS) community. The water vapor vertical column density (VCD) has already been defined as the total number of gas-phase H<sub>2</sub>O molecules per unit area along a vertical path above the instrument. The water vapor slant column density (SCD) gives the number of gas-phase H<sub>2</sub>O molecules per unit area along the effective light path through the atmosphere. The atmospheric light path is generally not a vertical column, which is particularly obvious when the instrument field of view is aimed at a non-zenith elevation angle  $\alpha$  (Figure 3). The extension of the effective light path in the atmosphere over the vertical column is given by the so-called air mass factor (AMF).

$$SCD = AMF \cdot VCD \quad (\text{Eq. 2})$$

In DOAS analyses, a given measurement spectrum is always evaluated relative to a reference spectrum. In the case of our scanning measurements, we evaluated all spectra in a particular scan relative to the most upward-looking spectrum recorded in that scan. Therefore, we are

measuring the enhancement of water vapor absorption over what is already contained in the reference spectrum. This value is called the differential slant column density (DSCD).

All the measurements collected in this study use scattered solar radiation as a light source. The interpretation of our measured DSCDs is aided by knowledge of where the recorded radiation was last scattered before arriving at the instrument. Due to the pristine nature of the atmosphere at the time of our measurements and the relatively low albedo of the terrain surrounding our study site, we can approximate atmospheric radiative transfer by assuming a pure Rayleigh atmosphere, i.e. an atmosphere in which radiative transfer is governed by scattering on air molecules. In this approximation, the atmospheric scattering coefficient is proportional to the density of air molecules, which decreases exponentially with altitude. Therefore, scattering will be most efficient close to the ground. However, if we compare the number of air molecules in the lowermost 2 km layer above the instrument with the number of molecules in the rest of the atmospheric column, we find that about 80% of molecules are located above 2 km, regardless of the altitude of the instrument. In single scattering approximation, this means that ~80% of the detected radiation has passed through the lowermost 2 km of the atmosphere in a straight line along the instrument's viewing direction, regardless of the measurement elevation angle  $\alpha$ . Since the water vapor scale height is only 2 km, by far the majority of the detected radiation has passed through the relatively thin water vapor layer in a straight line.

In cases like this, where the detected scattered radiation mainly passes through a proximal trace gas layer along a straight path, the respective AMF is given by a simple geometric approximation and depends only on the elevation angle  $\alpha$  of the measurement.

$$AMF = 1/\sin(\alpha) \quad (\text{Eq. 3})$$

This geometrical approximation of the AMF greatly simplifies the interpretation of scattered-light DOAS data. We verified its applicability to our measurements by comparing the geometrical AMFs (equation 3) to AMFs calculated using the McArtim radiative transfer model [Deutschmann *et al.*, 2011] initialized with our approximate measurement geometry (see Supporting Information). The geometric AMFs were within 20% of the model results for all elevation angles, and within 13% for elevation angles between 8 and 20 deg where the volcanic plume was located. We expect the associated errors of the retrieved H<sub>2</sub>O VCD and SCDs presented in the following section to be < 10%, and therefore choose to adopt the geometrical approximation throughout this study, as has commonly been done by others in the past [e.g., Hönninger *et al.*, 2004; Wagner *et al.*, 2013].

One result of the geometric relationship is that the H<sub>2</sub>O VCD equals the SCD detected while aimed at the zenith (see equation **Error! Reference source not found.**). In other words, the light measured while pointing upwards has passed through the vertical water vapor column exactly once, regardless of the solar zenith angle  $\theta$  (see Figure 3). Though our scans unfortunately did not include an exact 90 degree measurement, equation 3 indicates that the

light path of the 82 degree measurement was within 1% of the straight vertical column and can therefore be considered vertical for practical purposes.

Also, since the reference spectra contain absorption features associated with the VCD, the DSCDs that we obtain from our differential analyses of scanning spectra are actually representative of the difference between SCD and VCD

$$DSCD = SCD - VCD = VCD (AMF - 1) \quad (\text{Eq. 4})$$

### 3.2 Saturation of water vapor absorption lines

Water vapor is different than most atmospheric trace gases that are commonly measured by DOAS in that instrument sensitivity is not usually an issue. The abundance of water vapor in the atmosphere and the relatively strong spectral absorption features throughout the visible and near-infrared spectral regions combine to produce large optical depths which are easily detected. The difficulties associated with these measurements instead stem from the fact that individual absorption lines are too narrow to be resolved by grating spectrometers deployed to the field or on satellite platforms. Figure 4 shows the absorption cross-section of water vapor taken from the HITRAN2012 molecular spectroscopic database [Rothman *et al.*, 2013] between 713 and 748 nm. Convolution of this cross-section with our Vis spectrometer's slit function yields our expected spectral response (red line in Figure 4) when measuring weak water vapor absorption [Platt and Stutz, 2008].

However, if the water vapor optical depth increases beyond about 0.1, the depth increase of individual water vapor absorption lines becomes non-linear according to the Beer-Lambert-Bouguer law. This is sometimes called 'saturation' of absorption lines. The result is that the low resolution absorption spectrum measured by our spectrometer begins to change shape and the measured optical depth no longer scales linearly with the H<sub>2</sub>O SCD. Since the maximum value of the H<sub>2</sub>O absorption cross-section in our selected wavelength interval is about  $1 \times 10^{-22}$  cm<sup>2</sup>/molecule, this saturation threshold is attained if the measured H<sub>2</sub>O SCD exceeds  $1 \times 10^{21}$  molecules/cm<sup>2</sup>, a value which is almost two orders of magnitude below the average atmospheric H<sub>2</sub>O VCD (see section 1.2).

For this reason, conventional DOAS measurements targeting the atmospheric H<sub>2</sub>O VCD typically utilize the H<sub>2</sub>O absorption bands at 590 or 650 nm [Wagner *et al.*, 2003, 2013] which are about an order of magnitude weaker than the 720 nm band we have selected. More recently, even weaker bands in the blue and UV spectral regions were explored [Lampel *et al.*, 2015]. But two factors led us to choose a stronger absorption band. For one, the water vapor VCD above our 5,000 m measurement location is anticipated to be at least an order of magnitude lower than the atmospheric VCD at sea level. Secondly, our measurements are targeting a subtle increase in total atmospheric H<sub>2</sub>O column caused by the volcanic plume rather than the total column itself. A stronger absorption band will provide greater sensitivity to that expectedly small enhancement.

Luckily, the effect of saturation on the spectrometer's sensitivity to water vapor SCD can be modelled relatively easily [Wagner *et al.*, 2003]. First, some value for the H<sub>2</sub>O SCD is



assumed. This SCD is then used to calculate a transmittance spectrum according to the Beer-Lambert-Bouguer law using the high-resolution absorption-cross section of H<sub>2</sub>O. Next, this spectrum is convolved with our instrument slit function and down-sampled to the pixel resolution of our spectrometer. Finally, a DOAS fit is applied using the convolved H<sub>2</sub>O cross-section (red line in Figure 4) as a reference. Due to the saturation effect, the fit returns an SCD that is lower than the SCD assumed when generating the transmittance spectrum. This process can be repeated for various H<sub>2</sub>O SCDs in the expected measurement range, thus characterizing the sensitivity of a given spectrometer to various true H<sub>2</sub>O SCDs.

The characterization of our spectrometer for DOAS H<sub>2</sub>O retrievals performed on the 720 nm absorption band is shown in Figure 5. The non-linearity of the instrument response is clearly visible. Note that we have plotted the DSCD rather than the SCD here. Since we are not using a top-of-atmosphere reference, all of our differential measurements are relative to zenith-looking reference spectra. As per our discussion above, these already contain the absorption associated with the H<sub>2</sub>O VCD over the instrument. Therefore, the described sensitivity study was performed multiple times using clear-sky reference spectra containing varying amounts of H<sub>2</sub>O VCDs. Two examples are shown in Figure 5: H<sub>2</sub>O VCD =  $1 \times 10^{21}$  molecules/cm<sup>2</sup> (solid line) and H<sub>2</sub>O VCD =  $5 \times 10^{21}$  molecules/cm<sup>2</sup> (dashed line). After determining the actual H<sub>2</sub>O VCD present during the scanning measurements (see section 4.1), the appropriate curve was used to correct all H<sub>2</sub>O DSCD measurements presented in this study for the effect of line saturation.

### 3.3 Spectral retrieval of water vapor

The DOAS retrieval of water vapor was performed in the same manner for both the scanning and the vehicle traverse measurements. The spectral range between 713 and 748 nm was chosen for the retrieval. The pre-processing and correction of spectra was analogous to the procedure described for the SO<sub>2</sub> analysis (section 2.4). The fit parameters used in the DOAS evaluation are summarized in Table 1.

Figure 6 depicts two example DOAS fits (a) for a scanning measurement and (b) for a traverse measurement. In both cases, the result of the DOAS fit (red, top panel) appears to explain the measurements well (black, top panel) as is evidenced by the relatively small fit residual. Water vapor was detected in both of the two measurement spectra. Since the scanning spectrum shown in (a) was recorded at an elevation angle  $\alpha$  of 19 deg and evaluated against a zenith-looking reference, it is not surprising that a positive water vapor DSCD was retrieved, and at least part of it must stem from the atmospheric H<sub>2</sub>O background. The retrieved value of  $4.7 \times 10^{21}$  molecules/cm<sup>2</sup> corresponds to  $5.2 \times 10^{21}$  molecules/cm<sup>2</sup> after saturation correction (see section 3.2). As will be shown later on, this is about twice as high as the expected atmospheric background DSCD at that elevation angle due to the presence of additional water vapor inside the Sabancaya plume. The retrieval shown in Figure 6 (b) resulted in an H<sub>2</sub>O DSCD of  $9.0 \times 10^{20}$  molecules/cm<sup>2</sup>. Saturation correction yielded  $9.2 \times 10^{20}$  molecules/cm<sup>2</sup>. Since this spectrum was recorded in zenith-looking direction while passing under the volcanic plume and evaluated relative to a zenith-looking clear-sky

spectrum, this DSCD is actually a direct measurement of the enhancement in H<sub>2</sub>O VCD by the volcanic plume (see section 4.3).

#### 4. Water vapor measurement results

In this section, we describe the results of our DOAS measurements of water vapor in the plume of Sabancaya Volcano. The measurements presented here were all recorded on 21 May 2016. Both upward-looking traverse and scanning DOAS geometries were employed (see section 2 for details).

##### 4.1 Atmospheric water vapor column

As described in section 3.2, a correction must be applied to the H<sub>2</sub>O DSCD values obtained from our DOAS fits to account for the influence of saturated H<sub>2</sub>O absorption lines. This correction depends on the H<sub>2</sub>O VCD present in our clear-sky reference spectra. Therefore, the first step in evaluating our spectral data is to determine the atmospheric H<sub>2</sub>O VCD above our instrument at the time of the measurements.

For this purpose, the scanning UV measurements were first analyzed for SO<sub>2</sub>. All Vis spectra for which the corresponding SO<sub>2</sub> column density was greater than  $6 \times 10^{17}$  molecules/cm<sup>2</sup> were initially filtered out. The remaining spectra can be considered largely uninfluenced by the volcanic plume and therefore representative of the atmospheric H<sub>2</sub>O background. This is confirmed by the fact that the H<sub>2</sub>O DSCDs retrieved from these spectra closely follow the trend expected for the geometric AMF. Figure 7 shows that the plume-free H<sub>2</sub>O DSCDs are proportional to  $1/\sin(\alpha)-1$ , as expected from equations 3 and 4. Plotting the DSCDs against  $\text{AMF}-1$  yields a linear trend, the slope of which gives the H<sub>2</sub>O VCD. A very high coefficient of determination  $R^2 = 0.96$  was obtained, though it should be noted that the elevation angles initially associated with each scanner position had to be corrected by 4 deg to achieve this value. It is not surprising that the absolute determination of elevation angle was initially imperfect as no means for achieving absolute alignment of the scanner were available in the field.

A complicating factor in this determination of H<sub>2</sub>O VCD stems from the need to correct the retrieved DSCDs for the saturation effect. Because this correction is itself dependent on the VCD (see section 3.2), a recursive method must be applied. An initial guess for the H<sub>2</sub>O VCD is used to correct the clear-sky DSCDs for saturation. A new VCD is derived from the corrected DSCDs according to the method shown in Figure 7. This new H<sub>2</sub>O VCD is then used for saturation correction in the next iteration. Starting with an a-priori VCD of  $1 \times 10^{21}$  molecules/cm<sup>2</sup>, we found that only two iterations were needed to constrain the atmospheric H<sub>2</sub>O VCD to within 10% which is sufficiently precise for use in the saturation correction (see Figure 5). Using this method, we determined that the atmospheric H<sub>2</sub>O VCD above our measurement location was  $(1.5 \pm 0.1) \times 10^{21}$  molecules/cm<sup>2</sup>.

## 4.2 Testing for scattering on plume aerosols

After establishing that the background water vapor profile did indeed closely follow the expected trends for our radiative transfer assumptions, we checked for one other potential pitfall. Though the plume was clearly optically thin in the visible spectral range at the location of the scanning plane (Figure 2), there is still a potential for some amount of scattering to occur on aerosols within the plume. If the contribution of radiation scattered in the plume to our measurement spectra is significant, the geometrical approximation of AMF would no longer be valid for the in-plume measurements. As depicted by path C in Figure 3, this is due to the fact that the plume was located within the proximal atmospheric water vapor layer. Scattering of visible radiation on aerosols in the plume would therefore change the effective path length in this layer, thus affecting the measured water vapor DSCD without the need for an H<sub>2</sub>O enhancement (or deficit) within the plume. In our particular case, the most likely effect would be a reduction in near-surface light path length, as the plume was located at elevation angles  $\alpha$  smaller than the solar elevation angle ( $90 - \theta$ ) during the measurement timeframe. To test for aerosol scattering, a DOAS analysis of O<sub>4</sub> was performed on the Vis spectra. O<sub>4</sub> is shorthand for the (O<sub>2</sub>)<sub>2</sub> collision complex. Atmospheric O<sub>4</sub> forms when two oxygen molecules collide and thus its vertical concentration profile is proportional to the square of the oxygen profile and has a  $\sim 4$  km scale height. DOAS measurements of O<sub>4</sub> are commonly used as a source of additional information on atmospheric radiative transfer [Wagner *et al.*, 2002, 2004; Frieß *et al.*, 2006]. The idea is that, since the concentration profile is known, measured O<sub>4</sub> DSCDs are actually indicative of the radiative transfer between the sun and the instrument rather than variations in the O<sub>4</sub> concentration.

We evaluated our measured spectra for O<sub>4</sub> absorption in the 560-610 nm spectral region. The details of the DOAS analysis are listed in Table 1. Figure 8 shows three exemplary scans through the Sabancaya plume measured between 14:50 and 15:06 local time on 21 May 2016. Plotted in red, the retrieved SO<sub>2</sub> DSCD clearly shows that the plume center was located at approximately 20 deg elevation during this period. The plume width was about 15 deg which, at the plume distance of 3.4 km, corresponds to about 900 m. In the plume center, SO<sub>2</sub> DSCDs of up to  $2.8 \times 10^{18}$  molecules/cm<sup>2</sup> were obtained. Assuming a circular plume cross-section, this corresponds to an average SO<sub>2</sub> concentration of about  $3 \times 10^{13}$  molecules/cm<sup>3</sup>.

The black points in Figure 8 depict the retrieved O<sub>4</sub> DSCDs from the same plume scans. According to equation 3, a  $1/\sin(\alpha)$  trend should describe the O<sub>4</sub> DSCDs well as long as the geometric approximation for AMF holds true. This progression was fit to the O<sub>4</sub> DSCDs obtained in each of the scans. Elevation angles within the main bounds of the plume, i.e. with more than  $6 \times 10^{17}$  molecules/cm<sup>2</sup> SO<sub>2</sub>, were not included in the fit. The fit results (shown as dotted black lines in Figure 8) generally describe the DSCDs well, with no systematic deviation from the expected atmospheric background trend visible at the location of the volcanic plume. In particular, there is no apparent dip in O<sub>4</sub> DSCDs at the plume location which is what we might expect if scattering of visible radiation on plume aerosols were occurring. Therefore, we find no evidence for a significant impact of plume aerosols on the radiative transfer of our scene in the red spectral region.

### 4.3 Water vapor in the Sabancaya plume

Since plume aerosols do not appear to be affecting radiative transfer, any enhancement of H<sub>2</sub>O absorption over the atmospheric background found while scanning through the plume can be attributed to water vapor within the plume itself. Figure 9 shows the results of the water vapor DOAS retrieval, the details of which are described in section 3.3, for the same three exemplary scans shown in Figure 8. The SO<sub>2</sub> column density is again plotted in red, and the H<sub>2</sub>O DSCD is now plotted in black. The atmospheric water vapor background is again expected to follow a  $1/\sin(\alpha)$  relationship as per equation 3. As was previously done for O<sub>4</sub>, this trend was fit to the H<sub>2</sub>O DSCDs for each scan, again exempting H<sub>2</sub>O values recorded within the main bounds of the plume ( $\text{SO}_2 > 6 \times 10^{17}$  molecules/cm<sup>2</sup>) from the fit.

The H<sub>2</sub>O DSCD trends expected for the background atmosphere are shown as dotted lines in Figure 9. The difference between our retrieved H<sub>2</sub>O DSCDs and these trends is plotted in blue as a function of elevation angle. Here, there does appear to be a significant systematic enhancement of the H<sub>2</sub>O DSCDs over the atmospheric background at the exact location of the volcanic plume. This enhancement stems from light absorption by additional water vapor contained within the volcanic plume. The H<sub>2</sub>O excess is significantly larger than the spectroscopic errors derived from the DOAS fit errors [Stutz and Platt, 1996], the mean values of which are shown in the top right corner of Figure 9. Up to  $(2.7 \pm 0.4) \times 10^{21}$  molecules/cm<sup>2</sup> of excess water vapor were found when the scanner was aimed at the plume center. Again assuming a circular plume cross-section with a 900 m diameter, this corresponds to a concentration of about  $(3.0 \pm 0.4) \times 10^{16}$  H<sub>2</sub>O molecules/cm<sup>3</sup>.

Integration across each of the three scans shown in Figure 9 yields the SO<sub>2</sub> and H<sub>2</sub>O burden in the scanning plane. Multiplication of this burden with the 4.1 m/s wind speed gives a volcanic emission rate for each scan. The calculated emission rates for SO<sub>2</sub> and H<sub>2</sub>O are noted next to each peak in Figure 9. The SO<sub>2</sub> emission rate declined from 11.7 kg/s to 4.9 kg/s during the depicted 15-minute measurement interval. This change is greater than the estimated uncertainty of our measurements (~26%, see section 2.4). At the same time, the H<sub>2</sub>O emission rate decreased from 2750 kg/s to 860 kg/s. The change in measured emissions may be caused by a short-term change in volcanic output, but the dynamics of the turbulent diffusion processes transporting the volcanic gas from the vent to the scanning plane are complex. Without detailed knowledge of the shape of the summit crater, the location of the main vent within it, and the locations of any additional fumaroles that may be contributing to the measured H<sub>2</sub>O emissions, we cannot rule out the possibility that the measured drop in emissions was simply a result of turbulent atmospheric dispersion.

The accuracy and precision of these emission rates is mainly determined by (1) the accuracy and precision of the wind speed measurement and (2) the ability to accurately correct the measured DSCD for atmospheric water vapor. This atmospheric correction becomes increasingly sensitive to the accuracy of the elevation angle as the plume moves closer to the horizon because the correction term can become much larger than the plume-induced enhancement of the DSCD. We performed a sensitivity analysis by varying the elevation angle of each measurement by  $\pm 0.5$  deg. We estimate this to be our angular precision based

on the fact that larger variations significantly reduce the quality of the linear fit to the clear-sky DSCDs shown in Figure 7. For the scans shown here, a half degree uncertainty in elevation angle is on average associated with a  $\pm 27\%$  error in the  $\text{H}_2\text{O}$  emission rates. Combined with the independent 20% relative error of the wind speed, we estimate the errors of each of the  $\text{H}_2\text{O}$  emission rates shown in Figure 9 and determined from individual scans to be  $\pm 35\%$ . More accurate measurements would be possible if the plume were intersected at higher elevation angles, but unfortunately our measurement geometry did not allow for that, and the depicted scans are examples taken from a time when the plume was intersected relatively high above the horizon compared to some of the other scans.

In an alternate approach, the  $\text{H}_2\text{O}$  emission rate can be derived by multiplying the measured  $\text{H}_2\text{O}/\text{SO}_2$  ratio with the  $\text{SO}_2$  emission rate. The blue circles in Figure 10 depict the excess  $\text{H}_2\text{O}$  DSCDs retrieved from all 24 plume scans recorded between 14:11 and 16:11 local time plotted against the  $\text{SO}_2$  DSCDs measured coincidentally. For this plot, all data recorded at elevation angles of less than 15 deg have been removed. The data is thus limited to measurements in which the plume excess  $\text{H}_2\text{O}$  DSCD is at least comparable to the atmospheric background DSCD, thereby reducing the uncertainty related to the atmospheric corrections. Fitting a linear trend to this data yields a molecular  $\text{H}_2\text{O}/\text{SO}_2$  ratio of  $1.0 \times 10^3$ . In other words, water vapor was found to be 1,000 times more abundant than  $\text{SO}_2$  in the plume. The coefficient of determination was 0.83, and the standard error of the slope was  $\pm 20\%$  based on the standard deviation of individual DSCDs from the best fit. The calculated  $\text{H}_2\text{O}/\text{SO}_2$  ratio is thus expected to be accurate to within  $\pm 20\%$  and our  $\text{SO}_2$  emission rate measurements, for which no atmospheric corrections are needed, can now be scaled by this ratio. We thus obtain an  $\text{H}_2\text{O}$  emission rate of  $(2,900 \pm 870)$  kg/s or  $(250,000 \pm 75,000)$  t/d from our scanning measurements.

The vehicle traverse measurements mentioned in section 2.2 were also analyzed for water vapor absorption. Interpretation of these measurements is simpler, as all spectra were recorded in zenith-looking direction. Therefore, the DSCDs retrieved relative to the zenith-pointing, clear-sky reference already represent the excess  $\text{H}_2\text{O}$  associated with the volcanic plume, and no further atmospheric correction is needed. However, note that determination of the atmospheric  $\text{H}_2\text{O}$  VCD, as was described in section 4.1, is still necessary in order to properly perform the saturation correction of the DOAS fit results (section 3.2).

Figure 11 shows the  $\text{H}_2\text{O}$  and  $\text{SO}_2$  DSCDs retrieved from spectra recorded while passing under the highest  $\text{SO}_2$  burden and then exiting out from under the plume. The DSCD progression for both species is well-correlated, though the relative measurement errors are larger here due to (1) the shorter 1 s integration time used during the traverse and (2) the lower absolute DSCDs associated with greater distance from the vent. The results of this measurement are plotted as red crosses in Figure 10. The larger errors and lower dynamic range yield a lower coefficient of determination for the linear regression, but the retrieved  $\text{H}_2\text{O}/\text{SO}_2$  ratio of  $1.0 \times 10^3$  is exactly the same as that obtained from the scans. Multiplication with the 800 t/d  $\text{SO}_2$  emission rate retrieved for the traverse yields an  $\text{H}_2\text{O}$  emission rate of  $(225,000 \pm 68,000)$  t/d, which is well within the range of values obtained from the scanning measurements.



#### 4.4 Potential sources for additional error

The H<sub>2</sub>O emission rate from Sabancaya Volcano is larger than one might expect based on volcanic gas compositions reported in the literature (see next section). Before interpreting these results, a few additional potential error sources should be discussed.

One relatively obvious potential error source is the effect of condensation in the plume. Besides affecting the atmospheric light path of radiation that reaches the instrument (see section 4.2), any H<sub>2</sub>O present in the condensed, liquid or solid phase would be invisible to our spectroscopic approach. A simple, back-of-the-envelope calculation can shed some light onto the significance of condensation in the Sabancaya plume. If we assume that the plume was well mixed with the atmospheric background in the scanning plane of the measurements, the absolute humidity inside the plume can be obtained by adding the plume and background water vapor concentrations. Our scanning measurements yielded an atmospheric background H<sub>2</sub>O VCD of  $1.5 \times 10^{21}$  molecules/cm<sup>2</sup> over our instrument (see section 4.1). Taking into account the ~2 km scale height of H<sub>2</sub>O in the atmosphere, this corresponds to an atmospheric water vapor concentration at the plume's altitude of about  $5 \times 10^{15}$  molecules/cm<sup>3</sup>. Adding this to the enhanced H<sub>2</sub>O concentration emitted from the volcano ( $\sim 3 \times 10^{16}$  molecules/cm<sup>3</sup>, section 4.3) yields an absolute humidity of about  $3.5 \times 10^{16}$  H<sub>2</sub>O molecules/cm<sup>3</sup> ( $\sim 1$  g/m<sup>3</sup>) within the plume. This concentration is equivalent to an H<sub>2</sub>O partial pressure of about 1.3 hPa.

For a given temperature, the H<sub>2</sub>O saturation vapor pressure can be easily and quite accurately approximated using the August-Roche-Magnus formula [August, 1828; Alduchov and Eskridge, 1996]. During our measurements, the ambient temperature is estimated to have been between 5 and 10 °C (based on the vehicle's thermometer). The temperature at plume height was likely several °C cooler, between about -5 and 0 °C. This puts the in-plume H<sub>2</sub>O saturation vapor pressure between about 4 and 6 hPa. Our measured water vapor concentration therefore corresponds to a relative humidity in the range of about 20-35%. Condensation is not efficient at such low relative humidity, which explains the relative transparency of the plume in the scanning plane. Despite the substantial H<sub>2</sub>O output, we therefore expect the fraction of the H<sub>2</sub>O present in the condensed phase and invisible to our measurements to have been negligible, though this will clearly not be the case for less favorable conditions (see [Matsushima and Shinohara, 2006] and section 5.2).

Another potential error source comes from the need for an accurate correction of the atmospheric background. In our background correction, we implicitly assumed an atmospheric H<sub>2</sub>O concentration profile that varies only with altitude and is otherwise homogeneous on the scale of our measurements. In principle, it is possible that a water-rich air parcel could be lofted to an altitude at which its H<sub>2</sub>O concentration is higher than that of the surrounding air, thus giving the appearance of a water vapor plume. We see no evidence for this in our data and it is unlikely to have influenced our measurements. For one, such 'false' plumes would equilibrate relatively quickly with surrounding air, particularly in an environment as dry as that found at Sabancaya. Also, our background atmospheric

measurements followed the geometric AMF approximation very closely, only deviating from the expected profile exactly at the location of the volcanic SO<sub>2</sub> plume.

Another explanation for a water vapor plume around Sabancaya Volcano could come from the presence of snow and ice around its summit. Sublimation of ice and snow is known to introduce water vapor into air passing over frozen terrain. Interestingly, though dry air does favor sublimation processes, the main controls on sublimation rate are the wind speed and porosity of the snowpack, neither of which are expected to be unusually high in our case. *Reba et al.* [2012] report sublimation rates of less than 1 mm / day as typical for mountainous terrain. Even when considering several square km of snow-covered area around Sabancaya's summit, this value yields a maximum of only a few thousand t/d of H<sub>2</sub>O introduced into the atmosphere by sublimation, orders of magnitude less than we detected in the volcanic plume.

Finally, though spectroscopic measurements have the clear advantage of being contact-free and thus avoid many of the problems faced when using in-situ sampling techniques, there are some potential error sources associated with them as well. For one, the saturation correction (section 3.2) depends on the resolution of the instrument. If the instrument line shape changed over time, e.g. due to a temperature drift, this could impact the spectrometer's sensitivity to H<sub>2</sub>O absorption. However, this effect would only be on the order of a few percent. Also, it is difficult to assess the magnitude of stray light in the visible-light spectra as, in contrast to the UV measurements, there is no measured spectral region that is expected to stay completely dark. The effect of stray light would be a filling-in of absorption lines, thereby reducing the measured H<sub>2</sub>O column densities. However, if this effect were significant, a systematic misfit of the H<sub>2</sub>O band would appear as a function of the absolute radiance measured in a given spectrum. Such a misfit was not observed in our measurements, so stray light was likely insignificant.

## 5. Discussion

### 5.1 Implications for activity at Sabancaya Volcano

In an environmental context, the 250,000 t/d H<sub>2</sub>O emission rate from Sabancaya is fairly modest when compared to natural evaporation from open water. For example, evaporation rates from nearby Lake Titicaca are estimated to be around 5 mm/day [*Declaux et al.*, 2007] which, when scaled with its surface area of 8,560 km<sup>2</sup>, makes for an atmospheric input more than an order of magnitude greater than Sabancaya's H<sub>2</sub>O emission rate. Therefore, the volcanic H<sub>2</sub>O emissions are not expected to have a significant environmental impact other than perhaps in direct proximity to the vent.

In the context of volcanic activity, however, the measured water vapor emissions from Sabancaya are extremely high. For example, *Aiuppa et al.* [2008] report the average H<sub>2</sub>O emissions from Mt. Etna, one of the most prodigiously degassing volcanoes in the world, to lie around 13,000 t/d. The measured H<sub>2</sub>O/SO<sub>2</sub> molecular ratio of 1,000 is also much higher than typical H<sub>2</sub>O/S ratios measured in andesitic melt. *Giggenbach* [1996] reports volatile compositions with molar ratios between 60 and 330 measured in melt inclusions of various

andesitic magmas, with a mean value of 160. There are several possible explanations for our observations. For one, it is possible that the magma from which the gases originate is at a critical depth and temperature such that H<sub>2</sub>O dissolution is favored over that of S. The solubility of H<sub>2</sub>O in a melt is given by a relatively simple relationship between its partial pressure and concentration in the melt [Holloway and Blank, 1994]. The SO<sub>2</sub> solubility is more complex and depends on pressure, temperature, magma composition and oxygen fugacity [Scaillet *et al.*, 1998; Oppenheimer *et al.*, 2011]. This complicates the process of evaluating the expected gas composition without additional information about the source region. However, based on comparison with gas emissions from other volcanoes around the world, it is improbable that preferential degassing of H<sub>2</sub>O alone is responsible for the observed high H<sub>2</sub>O/SO<sub>2</sub> ratio.

Instead, the interaction of magmatic gases with hydrothermal fluids together with a boiling-off of meteoric water provides a more likely explanation for our observations. Due to the relatively long period of repose since the last explosive eruption at Sabancaya in 1990, the hydrothermal system harbored by the volcanic edifice is likely to have been completely reestablished prior to the current episode of unrest. Therefore, gases exsolved from magma at depth will need to pass through this system prior to emission into the atmosphere. While interacting with meteoric water in the hydrothermal system, sulfur-bearing gases can be scrubbed and removed from the bulk plume [Symonds *et al.*, 2001]. Sulfur that does pass through the hydrothermal system will be at least partially reduced to H<sub>2</sub>S and thus become invisible to our measurements.

Scrubbing would increase the measured H<sub>2</sub>O/SO<sub>2</sub> ratio in the downwind plume over that of the relative volatile composition in the degassing magma. However, the significant SO<sub>2</sub> emission rate (800-900 t/d) observed during our measurements indicates that the scrubbing of sulfur gases is unlikely to be the only explanation for the high H<sub>2</sub>O/SO<sub>2</sub> ratio. Instead, we believe that our measurements captured the boiling-off of Sabancaya's hydrothermal system. As magma moves to shallower depths in the volcanic edifice and the thermal flux into the hydrothermal system increases, additional water can be added to the magmatic gas emissions through boiling-off of hydrothermal fluids.

The boiling of hydrothermal fluids is likely to occur not only directly at the location of the volcanic conduit, thus adding H<sub>2</sub>O to the bulk plume emitted from the main vent, but also in other areas throughout the volcanic edifice. The boiling process would then release water vapor through the porous cone and into the atmosphere, where it would mix with the bulk plume prior to reaching our measurement scanning plane. Locally, this process would manifest itself in water-rich, sulfur-poor gases diffusively degassing through soils and low-temperature (boiling point) fumaroles around the main high-temperature vent from which most of the SO<sub>2</sub> is emitted. The appearance of visibly steaming fumaroles observed away from the volcano's summit vent shortly after our measurements in May 2016 could be a manifestation of these processes. The relatively large short-term variability of the H<sub>2</sub>O/SO<sub>2</sub> ratio observed at times during our measurement period also corroborates our hypothesis. For example, the H<sub>2</sub>O/SO<sub>2</sub> ratio decreased by about 35% in only 15 minutes during the scans shown in Figure 9. Such short-term variability is consistent with heterogeneous mixing of

gases with different compositions being emitted from spatially separate (but potentially overlapping) sources.

To provide some temporal context for our measurements, we analyzed thermal infrared (TIR) imagery from the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) collected at Sabancaya before and after our measurement period. ASTER's TIR subsystem acquires pixels with a 90 m spatial resolution over five different channels within the spectral range of 8 to 12  $\mu\text{m}$  [Yamaguchi *et al.*, 1998]. Figure 12 shows TIR scenes from October 2015, June 2016, and November 2016. For each image, level 2 atmospherically-corrected surface-leaving radiance (AST\_09T, [Abrams, 2000]) was converted to temperature above background using an emissivity normalization approach wherein radiance data are separated into surface emissivity and surface kinetic temperature [Gillespie, 1986]. The reported temperatures have an approximate radiometric accuracy of  $\pm 2^\circ\text{C}$  [Thome *et al.*, 1998].

A thermal anomaly is identified as any pixel that has been elevated as the result of thermal activity [Pieri and Abrams, 2005; Reath *et al.*, 2016]. A background temperature was established from the average temperature of a  $10 \times 10$  pixel area adjacent to the potentially active area, but not included in the thermal anomalies. Due to the radiometric accuracy of these data, a  $2^\circ\text{C}$  threshold was established to identify thermally anomalous pixels within the potentially active area. This threshold was then applied to a region of interest containing all potential thermal anomalies, and the area of these anomalies was tracked over time. The total area increased consistently from October 23, 2015 until November 3, 2016, the last scene acquired before the eruption on November 11, 2016.

Figure 12 demonstrates the expansion of the thermal anomaly from 12 pixels on 23 October 2015, to 33 pixels on 19 June 2016, to 77 pixels on 3 November 2016. Starting with the June image (b) and the corresponding oblique view (d), three areas with anomalous temperatures outside the summit crater can be identified. These coincide with the location of visibly steaming fumaroles appearing around the same time, and appear to grow in size and radiative output between June and November. Though the satellite-derived temperatures in the anomalous pixels range from 2 to  $30^\circ\text{C}$  above background, the actual temperatures were likely significantly higher, as the 90 m spatial resolution of the TIR sensor is insufficient to fully resolve these thermal features. Reported temperature values are thus obtained by averaging over both hot and cool areas. This also makes a quantitative analysis of the absolute thermal energy release difficult, but these data clearly point to an expansion and intensification of the thermal features over time. Presumably as areas surrounding the summit heat up, hydrothermal fluids are boiled off, and hot volcanic gases are eventually able find new pathways through faults, cracks and pore spaces. We believe our DOAS measurements captured the water vapor emissions associated with this pre-eruptive boiling.

## 5.2 Applicability of the technique to other volcanoes

Though previously difficult to observe, it is likely that many volcanoes harboring hydrothermal systems experience periods of enhanced water vapor emissions prior to

magmatic eruptions as hydrothermal fluids are boiled off. However, as we mentioned early on, the success of the DOAS measurements presented here was in part due to the very favorable conditions encountered at Sabancaya. Two important factors that led to the success of our measurements were (1) the relatively high H<sub>2</sub>O emission rate at the time of the measurements and (2) the very high elevation of the volcano and, associated with this, the low atmospheric H<sub>2</sub>O column above the instruments. Though these factors helped make our results particularly convincing, a few considerations can help determine how applicable our technique would be at other volcanoes with less ideal conditions.

The detection limit of DOAS systems is given by the shot statistics of the spectral radiance measurements themselves. A conservative estimate of the minimum detectable column density of a given absorbing trace gas can be obtained by assuming that, for a positive detection, its measured optical depth must exceed the standard deviation of the overlaying noise by a factor of two. In our case, the standard deviation of the measurement noise was about  $2.5 \times 10^{-3}$  (see residual plots in Figure 6) meaning that H<sub>2</sub>O optical depths of  $> 5 \times 10^{-3}$  were detectable. Dividing this value by the amplitude of the convolved H<sub>2</sub>O absorption cross section ( $\sim 7.5 \times 10^{-24}$  cm<sup>2</sup>/molecule, see Figure 4) and correcting for the saturation effect (see section 3.2) yields a minimum detectable H<sub>2</sub>O DSCD of about  $7 \times 10^{20}$  molecules/cm<sup>2</sup>. Note that this is the detection limit for a single measurement spectrum. The H<sub>2</sub>O DSCDs detected in our traverse measurement were not much higher than this limit, but the measurements become more and more convincing as an increasing number of spectra are recorded and an H<sub>2</sub>O enhancement is detected in each.

Since our achieved detection limit was about 4 times below the maximum H<sub>2</sub>O columns measured in the Sabancaya plume, we can estimate that the minimum detectable H<sub>2</sub>O emission rate would have been about 700 kg/s or 60,000 t/d for the specific geometry and conditions of our measurements. In the same measurement conditions, a volcano emitting a pure, high-temperature magmatic gas with a typical H<sub>2</sub>O/SO<sub>2</sub> ratio of 160 [Giggenbach, 1996] would need to emit about 1,300 t/d of SO<sub>2</sub> to have a detectable, volcanogenic water vapor plume. This is not an uncommon SO<sub>2</sub> emission rate for active, open-vent volcanic systems, so it is likely that, using our method, water vapor could be detected in volcanic plumes even if no additional meteoric water were entrained, though the measurement conditions would have to be close to ideal.

The more problematic limitation of the DOAS technique for measuring volcanic H<sub>2</sub>O output is associated with the relatively high atmospheric H<sub>2</sub>O background. Clearly, the high elevation of our measurement site will not be achievable at most active volcanoes. When going to lower elevations, the accuracy of the atmospheric background correction will gain in importance. As long as the geometric approximation for the AMF holds, the technique will work. However, even slight deviations from the geometric approximation can potentially cause relatively large errors for plumes at lower altitudes.

The greatest potential source of error comes from the fact that a fraction of the measured light may have been scattered in the plume. Most large volcanic plumes will contain some amount of aerosols on which light can be scattered. When analyzed relative to a zenith-looking



plume-free spectrum, the measured H<sub>2</sub>O DSCD<sub>meas</sub> would then be given by the sum of the plume H<sub>2</sub>O DSCD<sub>plume</sub> and an additional contribution from the atmosphere above the plume DSCD<sub>atm</sub>. If we assume a volcanic plume directly above our instrument and a simple, single-scattering model for atmospheric radiative transfer, any light that is scattered in the plume would have an additional path in the atmosphere that is inversely proportional to the cosine of the solar zenith angle  $\theta$  (path C in Figure 3).

$$DSCD_{meas} = DSCD_{plume} + DSCD_{atm} = DSCD_{plume} + f \cdot VCD(h) \cdot \left( \frac{1}{\cos(\theta)} - 1 \right)$$

(Eq. 5)

Here,  $f$  is the fraction of detected light (between 0 and 1) that was scattered in the plume and has therefore passed through the lower atmosphere at the solar zenith angle. Equation 5 shows that, in addition to H<sub>2</sub>O in the volcanic plume, atmospheric water vapor will contribute to the measured DSCD unless (1) aerosol scattering is negligible, ( $f \approx 0$ ) or, (2) the sun and the plume are straight overhead ( $\theta \approx 0$ ) or, (3) the H<sub>2</sub>O VCD above the plume is negligible compared to the DSCD within the plume ( $VCD(h) \ll DSCD_{plume}$ ). Our O<sub>4</sub> measurements and the transparent appearance of the Sabancaya plume indicate that aerosol scattering was negligible in our study and, for our 6 km plume height, we estimate  $VCD(h)$  to have been approximately 3 times smaller than  $DSCD_{plume}$ . Thus, for our measurements,  $DSCD_{atm}$  can be neglected in equation 5.

However, this will not generally be the case. Clearly, DOAS measurements of H<sub>2</sub>O will need to be limited to mostly transparent plumes. Measurements of opaque or condensing plumes with large aerosol optical depths will almost certainly be subject to large uncertainties induced by unknown radiative transfer. If we limit observations to plumes with  $f < 0.1$  and require that the atmospheric contribution to the measured DSCD be less than 10% of the in-plume H<sub>2</sub>O signal ( $DSCD_{atm} < 0.1 \cdot DSCD_{plume}$ ), we find

$$VCD(h) < DSCD_{plume} \left( \frac{1}{\cos(\theta)} - 1 \right)^{-1}$$

(Eq. 6)

For solar zenith angles  $\theta$  of around 30 deg, this means that  $VCD(h)$  should not exceed ~6 times  $DSCD_{plume}$ . In a standard atmosphere, a plume comparable to that emitted from Sabancaya would thereby be accessible to DOAS measurements down to altitudes of approximately 3,000 m. DOAS measurements of similar H<sub>2</sub>O plumes emitted below that level would be subject to large uncertainties due to subtle variations in radiative transfer unless the parameters  $f$ ,  $\theta$  and  $VCD(h)$  in equation 5 are all very well constrained. Less vigorous H<sub>2</sub>O plumes will only be reliably measured at higher altitudes or smaller solar zenith angles, according to equation 6. Still, a significant number of active volcanoes emit plumes above 3 km altitude and, according to these admittedly rough estimates, our method should be applicable to these.

### 5.3 Potential use of water vapor measurements as a forecasting tool

Though only applicable to a subset of the world's most active volcanoes, DOAS measurements of water vapor could potentially provide valuable information for eruption

forecasting. The measurements do suffer from ambivalence introduced by the likely interaction of volcanogenic volatiles with meteoric water, but this is a known issue and is not limited to H<sub>2</sub>O/SO<sub>2</sub> ratios alone. Recent studies have shown that geochemical measurements can provide eruption precursors despite, or even because of the varying degrees of interaction of magmatic gas with a hydrothermal system or volcanic lake [de Moor *et al.*, 2016a, 2016b]. The DOAS technique described in this study could offer continuous, reliable measurements of volcanic water vapor output that, when interpreted in the context of other processes occurring at a given active volcano, could provide volcano observatories with valuable information on the stage of activity.

To date, geochemical information used in eruption forecasts has largely been limited to compositional plume data (CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub>O) measured by MultiGAS or similar instrumentation [Aiuppa *et al.*, 2007; Werner *et al.*, 2013; de Moor *et al.*, 2016a] and SO<sub>2</sub> emission rate data obtained from scanning DOAS measurements (for example, [Olmos *et al.*, 2007]). Recent findings suggest that the abundance of bromine monoxide (BrO) and chlorine dioxide (ClO) in high-temperature volcanic gases might also be sensitive to shallow magmatic recharge [Bobrowski and Giuffrida, 2012; Lübcke *et al.*, 2013], which is interesting mainly due to our ability to measure these species with scanning DOAS.

However, with the notable exception of CO<sub>2</sub>, all of these parameters suffer from the difficulties involved with interaction of magmatic gases with volcanic hydrothermal systems. Sulfur and halogen species are particularly soluble in water and hydrothermal fluids, and thus emissions associated with shallow magmatic recharge can easily be masked by scrubbing processes unless a relatively dry pathway exists for gases to escape. Such dry pathways often exist at volcanoes with persistent high-temperature degassing activity, but are unlikely to exist in the initial phase of reactivation at long-dormant volcanoes.

Water vapor emissions, on the other hand, may provide valuable information about shallow magmatic recharge in wet volcanic systems. As magma is intruded to shallow depths, the associated thermal input will generally cause hydrothermal systems to boil off. If the evaporated water cannot easily escape, pressure can build and culminate in phreatic explosions. On the other hand, more permeable systems will allow water vapor to escape effusively. In such systems, large pulses of water vapor emission could precede the first magmatic eruptions, as the hydrothermal fluids are boiled off. In fact, such water vapor exhalations might easily precede changes in most other geochemical parameters. In our case, for example, high H<sub>2</sub>O emissions were detected months before the SO<sub>2</sub> emissions had reached their maximum pre-eruptive values (~6,000 t/d). Elevated CO<sub>2</sub> emissions might provide more advanced warning, but currently CO<sub>2</sub> can only be monitored in a continuous manner by placing instruments directly at the suspected source location of future degassing. Visible-light DOAS measurements, on the other hand, could be implemented at high altitude volcanoes with relative ease, for example by collocating visible spectrometers with existing scanning DOAS infrastructure. At volcanoes harboring hydrothermal systems, visible-light DOAS measurements could thus provide a new, largely independent geochemical parameter that, when used in combination with complimentary geophysical information, could help improve eruption forecasts.

## 6. Conclusions

In this study, we first describe a novel method for measuring volcanic H<sub>2</sub>O emissions. These are the first measurements of volcanic water vapor using the DOAS remote sensing technique and, to our knowledge, the first direct measurements of water vapor emission rates from a passively degassing volcano. We find that the main difficulty in passive remote sensing of volcanic water vapor is performing a sufficiently accurate correction of the atmospheric background H<sub>2</sub>O column. As discussed in section 5.2, the keys to successful measurements are (1) avoiding plumes with scattering aerosols and/or condensed water droplets, (2) performing measurements at high elevations to minimize the overhead background water vapor column, and (3) limiting measurements to low solar zenith angles around solar noon.

Our measurements at Sabancaya volcano yielded interesting and unprecedented results. The favorable timing of our experiment and nearly ideal measurement conditions allowed us to detect an extremely high pre-eruptive H<sub>2</sub>O emission rate six months prior to the first explosive activity at Sabancaya during its current eruptive crisis. As the detected H<sub>2</sub>O/SO<sub>2</sub> ratio is much higher than expected from the relative composition of these species in the magma, we believe the large H<sub>2</sub>O emissions stem from the boiling-off of Sabancaya's shallow hydrothermal system. This hypothesis is corroborated by the coincident appearance of fumaroles and anomalous thermal features around the volcano's main summit crater (section 5.1). We speculate that similarly high pre-eruptive water vapor emissions are likely to occur at other 'wet' volcanoes harboring significant hydrothermal systems, and that visible-light DOAS monitoring could help identify these events and thus inform eruption forecasts.

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All DOAS spectral data collected at Sabancaya Volcano and evaluated and interpreted as part of this study are available for download from the USGS ScienceBase-Catalog:

Kern, C, P. Masias, and F. Apaza (2017) Differential Optical Absorption Spectroscopy data acquired at Sabancaya Volcano (Peru) on 21 May 2016: U.S. Geological Survey data release, <https://doi.org/10.5066/F7VH5M1B>.

ASTER L2\_TIR data can be accessed and ordered through the USGS Global Visualization Viewer (GloVis) website. <https://glovis.usgs.gov/>

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**Table 1** – Retrieval parameters used in this study for the DOAS analysis of SO<sub>2</sub>, O<sub>4</sub>, and H<sub>2</sub>O. All spectral analyses were performed using the DOASIS software [Kraus, 2006]. All literature reference cross-sections were convolved with the respective spectrometers' instrument line shape prior to fitting.

DOAS retrieval parameter	Value
<b>All evaluations</b>	
Spectral corrections	Subtract dark current Subtract electronics offset
Calculation of optical depth	Divide by clear-sky or zenith spectrum Logarithm
<b>SO<sub>2</sub> analysis</b>	
Fit wavelength range	314-330 nm
Fit references	SO <sub>2</sub> [Vandaele <i>et al.</i> , 2009] O <sub>3</sub> [Bogumil <i>et al.</i> , 2003] Ring correction [Grainger and Ring, 1962] Wavelength calibration correction [Beirle <i>et al.</i> , 2013] Polynomial (3 <sup>rd</sup> order)
<b>O<sub>4</sub> analysis</b>	
Fit wavelength range	560-610 nm
Fit references	O <sub>4</sub> [Hermans, 2010] O <sub>3</sub> [Bogumil <i>et al.</i> , 2003] H <sub>2</sub> O [Rothman <i>et al.</i> , 2013] Ring correction [Grainger and Ring, 1962] Wavelength calibration correction [Beirle <i>et al.</i> , 2013] Polynomial (3 <sup>rd</sup> order)
<b>H<sub>2</sub>O analysis</b>	
Fit wavelength range	713-748 nm
Fit references	H <sub>2</sub> O [Rothman <i>et al.</i> , 2013] Ring correction [Grainger and Ring, 1962] Wavelength calibration correction [Beirle <i>et al.</i> , 2013] Polynomial (3 <sup>rd</sup> order)

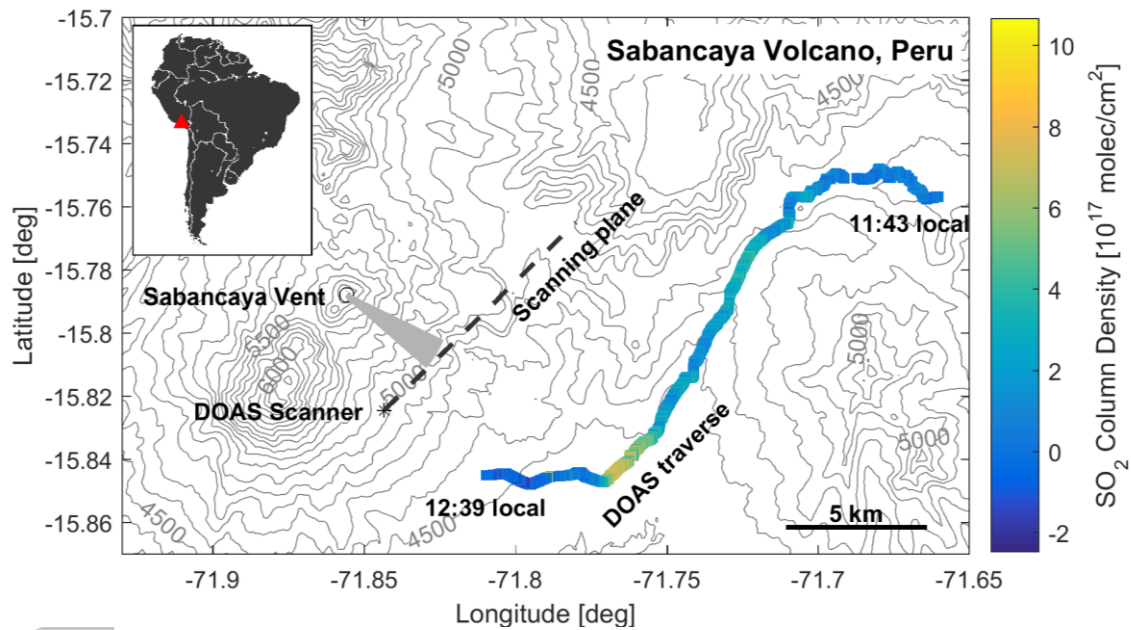


Figure 1 – Topographic map of Sabancaya Volcano, Peru, and the surrounding area. A DOAS traverse beneath the gas plume was performed between 11:43 and 12:39 local time on May 21, 2016. The SO<sub>2</sub> column density measured above the vehicle during this traverse is shown. Up to about  $1 \times 10^{18}$  SO<sub>2</sub> molecules/cm<sup>2</sup> were detected. Also shown is the approximate plume direction (shaded area) and where the scanning measurements performed later that afternoon intersected the plume (dashed line). Topographic data from [USGS, 2006]

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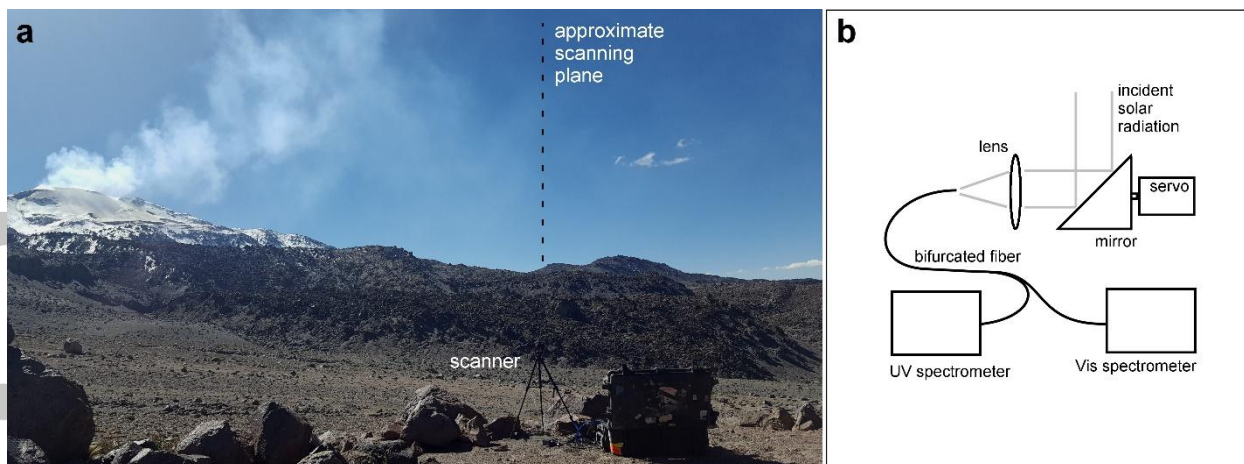


Figure 2 – (a) Photograph of the scanning DOAS measurement setup on 21 May 2016. Mounted on a tripod, a scanner was used to scan across the plume emitted from Sabancaya in approximately perpendicular direction. The elevation angles of between 4 and 82 deg were stepped through in 3 degree increments. (b) Schematic of the optical setup. Light reflected on the scanner’s mirror was coupled into a bifurcated fiber leading to UV and Vis spectrometers.

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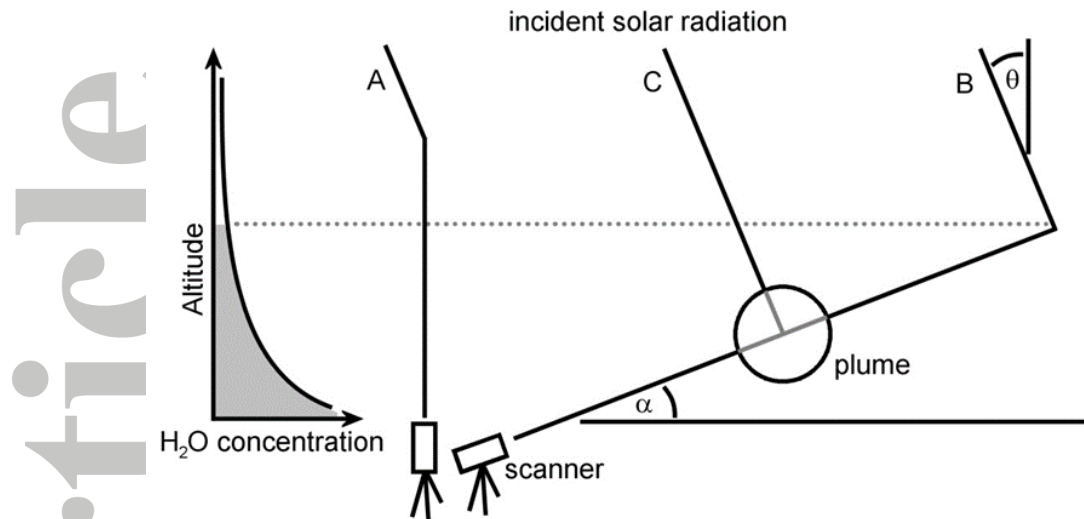


Figure 3 – Schematic of the radiative transfer in the scanning DOAS measurements. Since the atmospheric concentration of H<sub>2</sub>O decreases very rapidly with altitude, a zenith-looking instrument sees the VCD regardless of the solar zenith angle  $\theta$  (path A). In geometrical approximation, all H<sub>2</sub>O is close enough to the ground such that an instrument aimed at elevation angle  $\alpha$  measures radiation last scattered above the H<sub>2</sub>O layer (path B). The light path length in the H<sub>2</sub>O layer is then proportional to  $1/\sin(\alpha)$ . This geometrical approximation could become inaccurate if light were scattered on aerosols in the plume (path C), as this last scattering event would potentially lie within the atmospheric H<sub>2</sub>O layer.



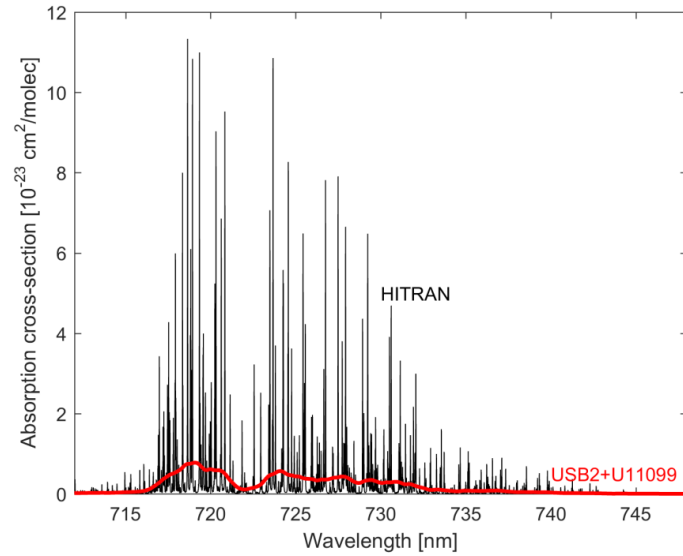


Figure 4 – The water vapor absorption band around 720 nm was chosen for our spectral retrieval. Convolution of the HITRAN2012 absorption cross-section (black, [Rothman *et al.*, 2013]) with our instrument slit function yields the expected response of our spectrometer (red). Because individual absorption lines cannot be resolved, the instrument response is slightly non-linear in water vapor column density (see text for details).

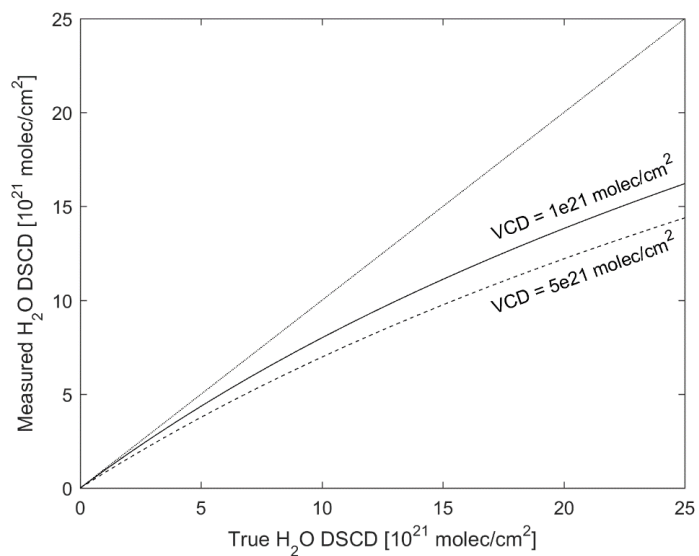


Figure 5 – Modeled instrument response over the range of expected H<sub>2</sub>O DSCDs. The non-linearity of the instrument response stems from the inability of our spectrometer to resolve individual H<sub>2</sub>O absorption lines. Since the zenith-pointing measurements contain the H<sub>2</sub>O absorption associated with the atmospheric H<sub>2</sub>O VCD, all measurements are relative to this value. The model results show that the H<sub>2</sub>O VCD slightly influences the instrument response and 2 exemplary VCD scenarios are depicted here.

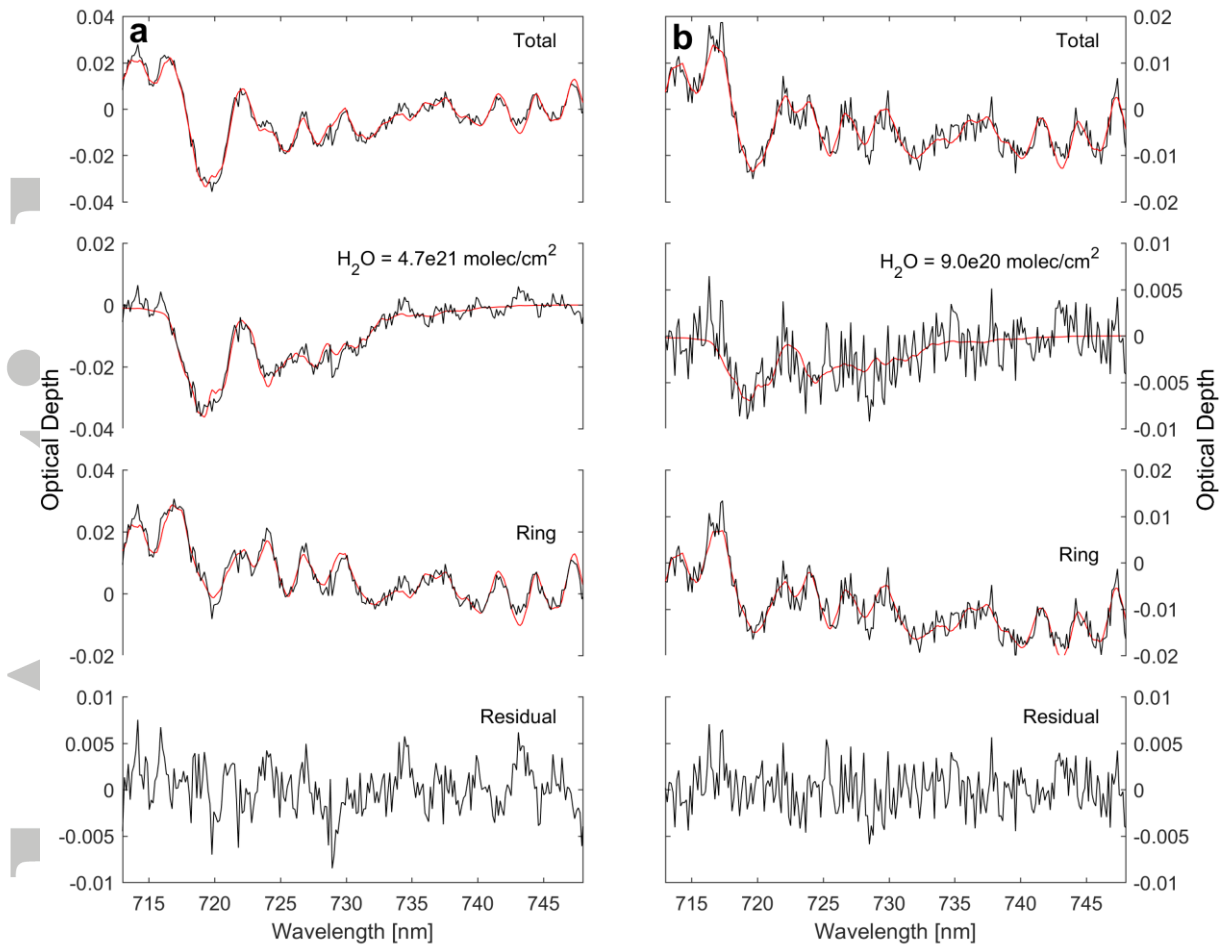


Figure 6 – Spectral retrieval of H<sub>2</sub>O between 713 and 748 nm. (a) Data collected during a scan of the Sabancaya plume. The DOAS fit yields an H<sub>2</sub>O DSCD of  $4.7 \times 10^{21}$  molecules/cm<sup>2</sup>. Applying the saturation correction yields  $5.2 \times 10^{21}$  molecules/cm<sup>2</sup>. This column is  $2.5 \times 10^{21}$  molecules/cm<sup>2</sup> higher than the atmospheric column expected for plume-free conditions (see section 4). (b) Data collected during a vehicle traverse beneath the Sabancaya plume. The retrieved H<sub>2</sub>O DSCD is  $9.0 \times 10^{20}$  molecules/cm<sup>2</sup> higher than the reference value measured after exiting from under the plume (compare Figure 11). Correction of the saturation effect yields an H<sub>2</sub>O DSCD of  $9.2 \times 10^{20}$  molecules/cm<sup>2</sup>.

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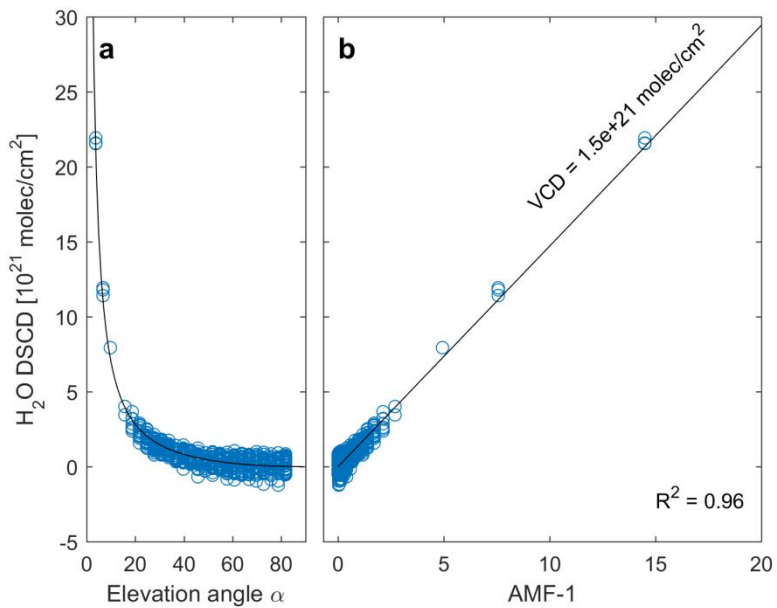


Figure 7 – (a) When the H<sub>2</sub>O DSCDs retrieved from all plume-free spectra during the measurement period are plotted against elevation angle  $\alpha$ , they follow a clear  $1/\sin(\alpha)$  trend (black line). (b) Plotting the same H<sub>2</sub>O DSCDs against AMF-1, where AMF is the geometrical approximation for the air mass factor (equation 3), yields the vertical column density (slope of black line, see text for derivation).

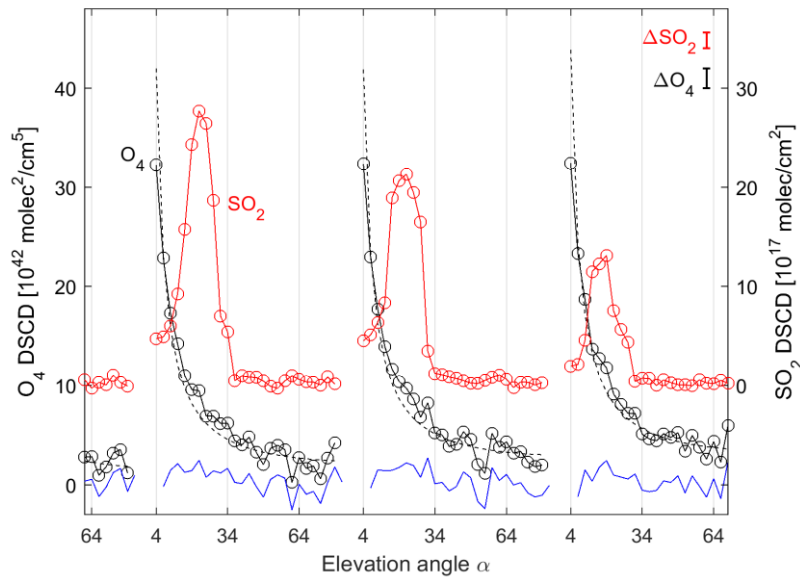


Figure 8 – Three exemplary scans through the Sabancaya plume collected on 21 May 2016 between 14:54 and 15:11 local time. For each scan, the elevation angle  $\alpha$  was stepped from 4 to 82 deg in increments of 3 deg. The  $\text{SO}_2$  differential column density was retrieved from spectra collected with a UV spectrometer. It is depicted in red and shows the location of the volcanic gas plume in each scan. The black points represent the retrieved  $\text{O}_4$  differential column density. The mean errors for  $\text{SO}_2$  and  $\text{O}_4$  are shown at top right. There is no systematic deviation from the  $1/\sin(\alpha)$  trend expected for the geometrical air mass factor (dotted black line, difference shown in blue). Therefore, we find no evidence of the plume significantly affecting the light path distribution of incident radiation in the red spectral region.



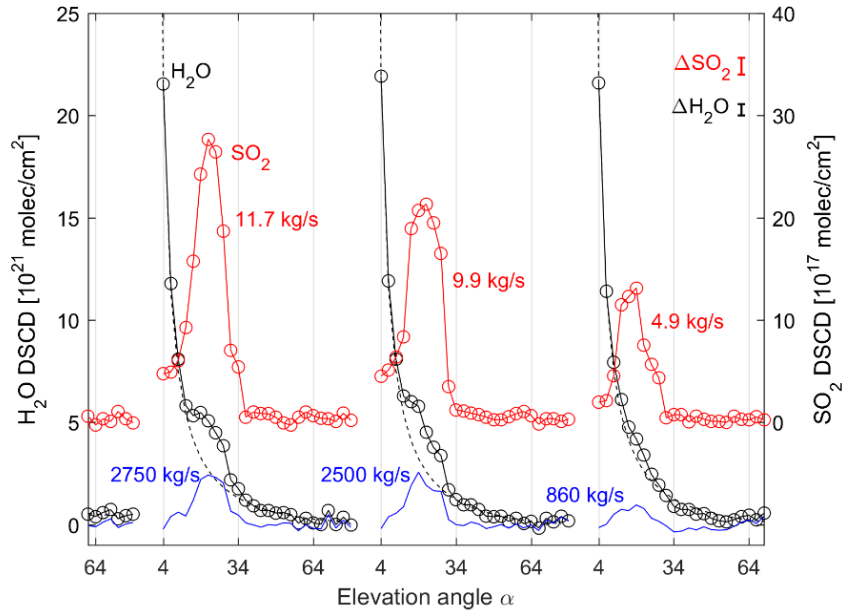


Figure 9 – Black points depict H<sub>2</sub>O DSCDs measured while scanning through the Sabancaya plume. All H<sub>2</sub>O DSCDs have been corrected for the saturation effect. The SO<sub>2</sub> DSCDs measured in the UV spectral region are again shown in red for reference. The H<sub>2</sub>O DSCDs show a systematic excess above the 1/sin( $\alpha$ ) behavior expected for the background atmosphere (dotted black line) at the location of the volcanic gas plume. The difference between measured DSCD and expected atmospheric DSCD is shown in blue and reaches up to  $2.6 \times 10^{21}$  H<sub>2</sub>O molecules/cm<sup>2</sup> in the plume center. Integration over the individual scans and multiplication by the 4.1 m/s wind speed yields the SO<sub>2</sub> and H<sub>2</sub>O emission rates for each scan.

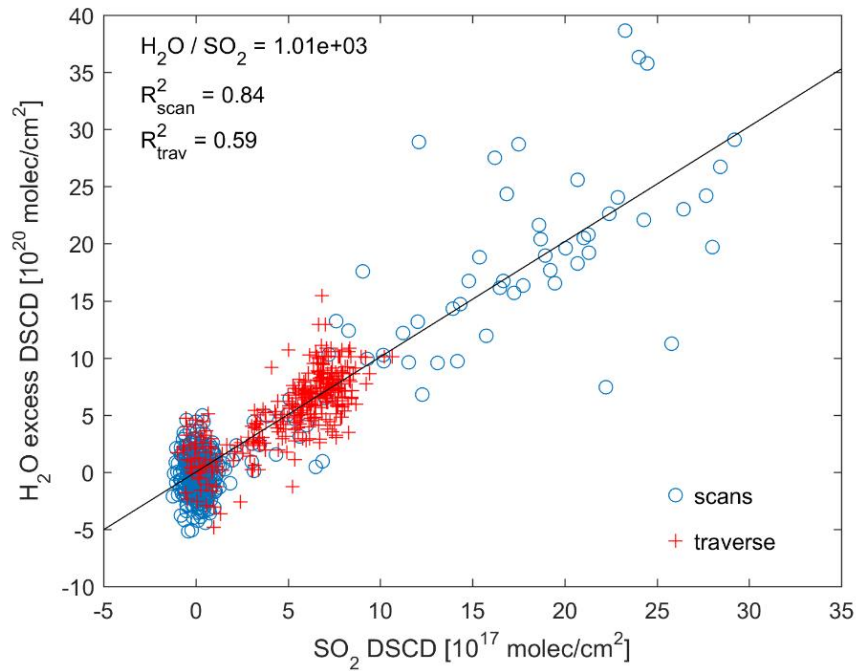


Figure 10 – The excess H<sub>2</sub>O DSCDs above the atmospheric background retrieved from plume scans (blue circles) and traverse measurements (red crosses) performed at Sabancaya volcano on 21 May 2016 are correlated with the SO<sub>2</sub> DSCDs retrieved from simultaneously recorded UV spectra. Both measurements found a molecular ratio of H<sub>2</sub>O to SO<sub>2</sub> of  $1.01 \times 10^3$  in the volcanic plume (black line).

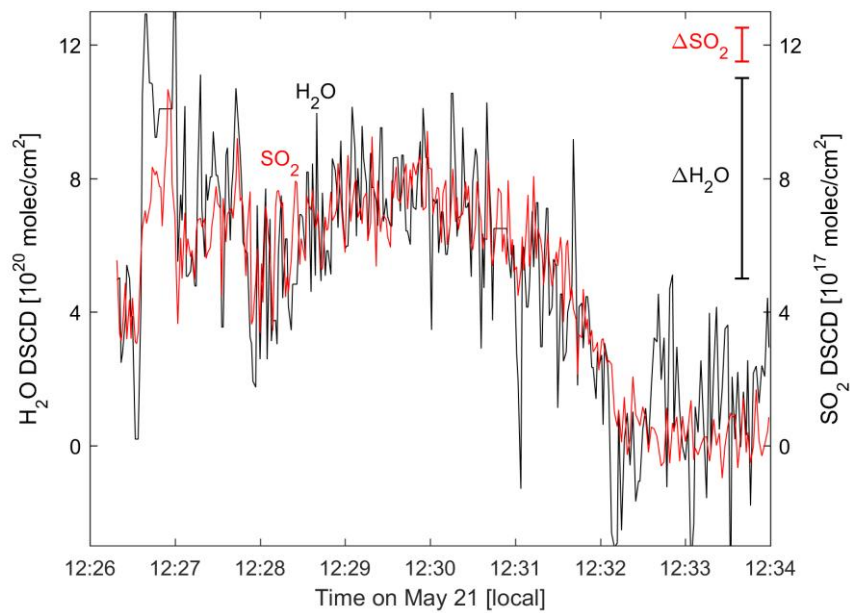


Figure 11 – H<sub>2</sub>O and SO<sub>2</sub> DSCDs retrieved from upward-looking plume traverse measurements in the visible and UV spectral regions. The 300 spectra recorded while passing under the highest SO<sub>2</sub> column densities and then exiting out from under the plume are shown. H<sub>2</sub>O and SO<sub>2</sub> are clearly correlated (also see Figure 10). The mean measurement errors derived from the DOAS fits are represented in the top right corner.

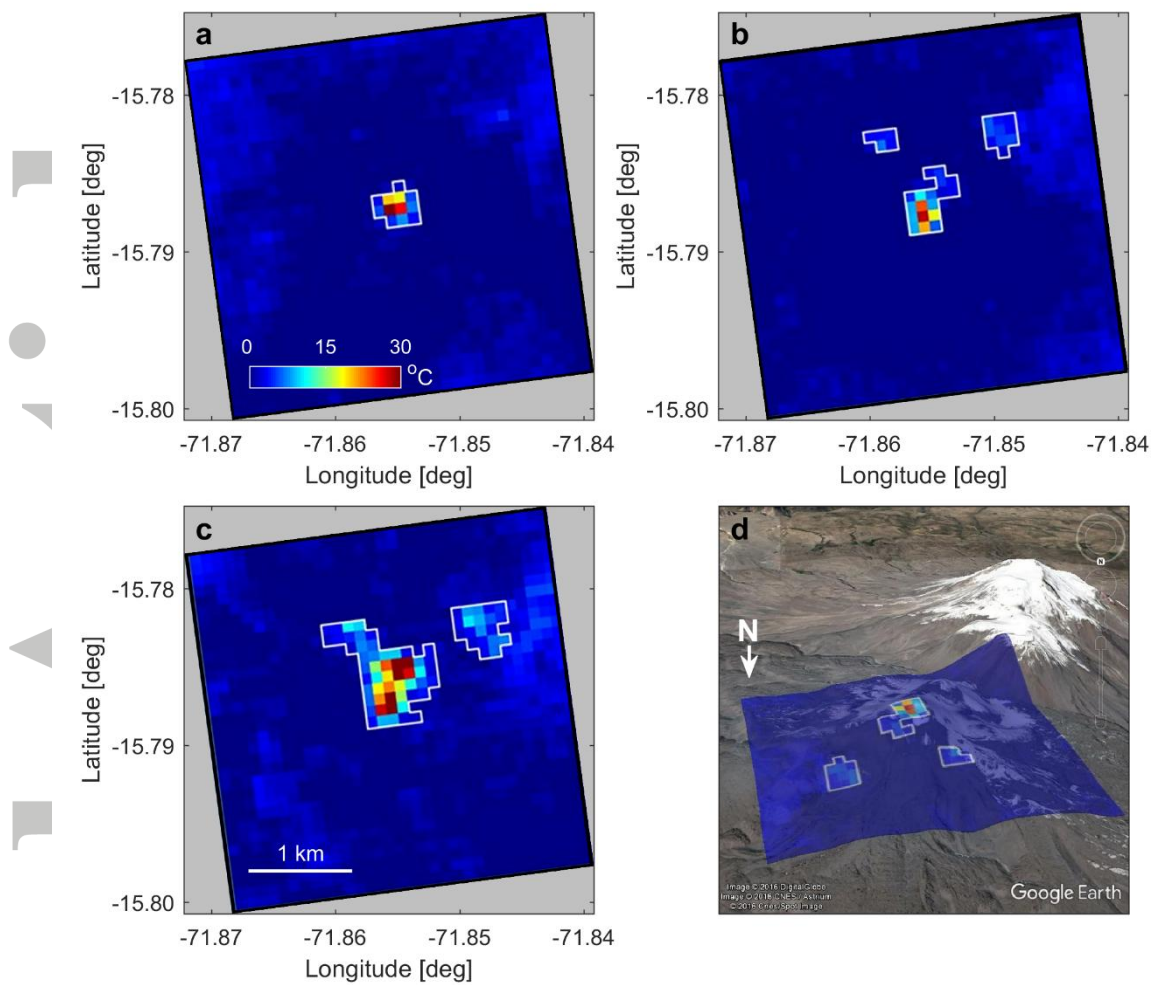


Figure 12 - Thermal Infrared (TIR) scene from ASTER acquired over the summit of Sabancaya Volcano on (a) 23 October 2015, 03:30:39 UTC, (b) 19 June 2016, 03:31:06 UTC, and (c) 3 November 2016, 03:24:16 UTC. Pixels exceeding 2°C above background have been outlined in white and are considered thermally anomalous. In (d), an oblique view of the June 19 2016 TIR scene, as seen from the north, is overlaid on a satellite image and digital elevation model. Ampato Volcano is in the background. Three areas with anomalous temperatures away from the summit vent are clearly visible. The location of these areas coincides with locations at which fumaroles were observed to become visibly active shortly after our measurements in May 2016.