

# Sun photometer and lidar measurements of the plume from the Hawaii Kilauea Volcano Pu'u O'o vent: Aerosol flux and SO<sub>2</sub> lifetime

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[1] Aerosol optical depths and lidar measurements were obtained under the plume of Hawaii Kilauea Volcano on August 17, 2001, ~9 km downwind from the erupting Pu'u O'o vent. Measured aerosol optical depths (at 500 nm) were between 0.2–0.4. Aerosol size distributions inverted from the spectral sun photometer measurements suggest the volcanic aerosol is present in the accumulation mode (0.1–0.5 micron diameter), which is consistent with past in situ optical counter measurements. The aerosol dry mass flux rate was calculated to be 53 Mg d<sup>-1</sup>. The estimated SO<sub>2</sub> emission rate during the aerosol measurements was ~1450 Mg d<sup>-1</sup>. Assuming the sulfur emissions at Pu'u O'o vent are mainly SO<sub>2</sub> (not aerosol), this corresponds to a SO<sub>2</sub> half-life of 6.0 hours in the atmosphere. **INDEX TERMS:** 1035 Geochemistry: Geochronology; 3099 Marine Geology and Geophysics: General or miscellaneous; 8121 Tectonophysics: Dynamics, convection currents and mantle plumes; 9355 Information Related to Geographic Region: Pacific Ocean

## 1. Introduction

[2] Hawaii's Kilauea Volcano has been in semi-continuous eruption since January 1983, consisting of 55 episodes to date, dominated by tube-fed pahoehoe lava [Heliker *et al.*, 1998]. Since the eruption began, Pu'u O'o vent has been the main source of SO<sub>2</sub> gas release, with much lower emission rates from the summit caldera [Sutton *et al.*, 2001]. In the atmosphere, the SO<sub>2</sub> is oxidized and converted to sulfuric acid aerosols through reactions with OH radical and H<sub>2</sub>O in clear sky and cloud reactions [Finlayson-Pitts and Pitts, 1986]. The aerosol and gas mixture comprises a hazy form of air pollution, locally referred to as volcanic smog, or vog [Sutton *et al.*, 1997]. Once formed, in situ measurements suggest the vog aerosols reach an equilibrium accumulation mode size distribution with a peak dry mass distribution from 0.2–0.4 μm diameter [Porter and Clarke, 1997]. Filter samples (Antony Clarke, University of Hawaii, personal communication, 2001) and temperature volatility tests have shown the vog aerosols are typically composed of sulfuric acid with little neutralization.

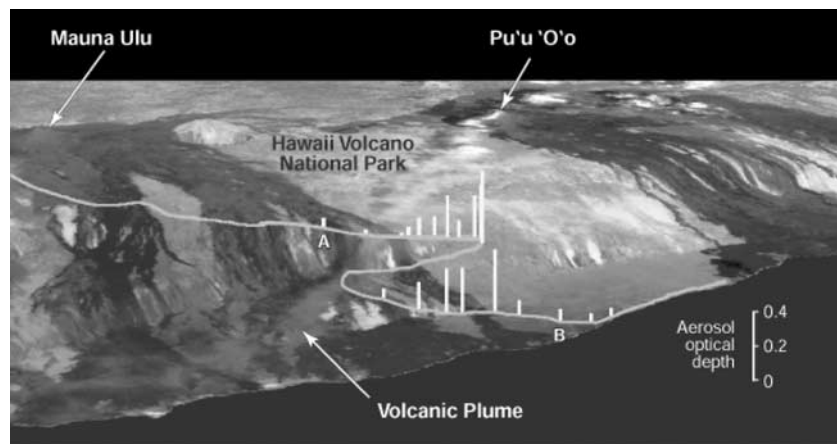
[3] Measurements of volcanic plume sulfur gas and aerosol emission rates can be based on either in situ [Hobbs *et al.*, 1982; Stith *et al.*, 1987; McGee and Gerlach, 1998] or remote sensing

techniques [Andres *et al.*, 1989; Realmuto *et al.*, 1997]. A widely accepted technique to measure SO<sub>2</sub> column abundance is by correlation spectrometer (COSPEC), which employs spectral absorption features of SO<sub>2</sub> gas [Rose *et al.*, 1986; Sutton *et al.*, 2001]. Lidars have also been used to image plume shape [Casadevall *et al.*, 1984; Hobbs *et al.*, 1982]. Sun photometer measurements have also been used to derive volcano aerosol size information [Watson and Oppenheimer, 2000, 2001]. Here we combine three remote sensing techniques, aerosol sun photometry, lidar, and COSPEC measurements to estimate the total oxidized sulfur emissions from the Pu'u O'o plume and the SO<sub>2</sub> lifetime.

## 2. Sun Photometer and Lidar Aerosol Measurements

[4] On August 17, 2001, vehicle-based sun photometer and lidar measurements were made under the Pu'u O'o plume along the Chain of Craters Road within Hawai'i Volcanoes National Park. Sun photometer measurements were made while the vehicle was stationary at different points under the plume. Lidar measurements were made continuously. A portable GPS system and computer recorded time and position of the measurements. The sun photometer used here was a five channel (380, 440, 500, 675, 870 nm) handheld Microtops. The average aerosol optical depths in the volcano plume were 0.38, 0.328, 0.312, 0.214, 0.185 at 380, 440, 500, 675, 870 nm. Calibration for this system is maintained using the Langley plot measurements at the Mauna Loa Observatory. The major errors in making sun photometer measurements are due to pointing, calibration and to a lesser extent sensor thermal drift. Based on theoretical and experimental studies, the error in the aerosol optical depth measurements is expected to be less than 0.01 [Porter *et al.*, 2001]. Figure 1 shows the average aerosol optical depth (at 500 nm) measured at each location along the Chain of Craters road during the third pass. Figure 1 also shows the location of the plume on January 7, 2001, when the Landsat 7 image was taken.

[5] Figure 2 shows a range of lognormal aerosol size distributions, which have spectral scattering coefficients (from Mie theory) that fit the measured aerosol optical depths within their uncertainty. Although a more elegant approach is certainly possible [Lienert *et al.*, 2001], here we have simply tested a range of different size distributions with geometric mean diameters (0.02–0.55 μm) and standard deviations (1.45–3.0) which extend well past those that best fit the data. A real index of refraction of 1.35 with no absorption was assumed here. The uncertainty in the aerosol



**Figure 1.** Landsat 7 satellite image collected on January 7, 2001 (at approximately 10:30 am local time) combined with a digital elevation map showing the location of the Chain of Craters road and the Pu'u O'o vent. Vertical stems show the aerosol optical depths (at 500 nm) measured at each point along the road on August 17, 2001. The points labeled A and B are for reference in Figure 4.

optical depth measurements and the limited range of wavelengths prevents us from further defining the size distribution.

[6] During each pass, lidar measurements were obtained (zenith angle of  $\approx 38^\circ$ ) through the vehicle open door (see Figure 3). The custom lidar system used for this experiment was a co-axial 12.7 cm telescope system using a 15 mJ pulsed frequency doubled (532 nm) Nd-YAG laser with 20 Hz pulse rate. A photomultiplier tube detector equipped with a custom log-amp yielded signal from 90-m out to 3-km. In order to avoid damage to the detector from bright sunlight, we always pointed the lidar away from the sun. The inversion of the lidar data is based on a forward stepping approach similar to the one used by Porter *et al.* [2000] but with different constraints. Here the lidar calibration (which is largely unknown) is adjusted so that the largest lidar integrated optical depths are in agreement with the largest sun photometer measured aerosol optical depths. For the lidar inversion, we also assume the aerosols have no absorption and have an aerosol phase function value (at  $180^\circ$  scattering angle) of 0.3 based on Mie calculations from existing aerosol models of the volcanic aerosol (vog) [Porter and Clarke, 1997]. Based on the lidar measurements, it was seen

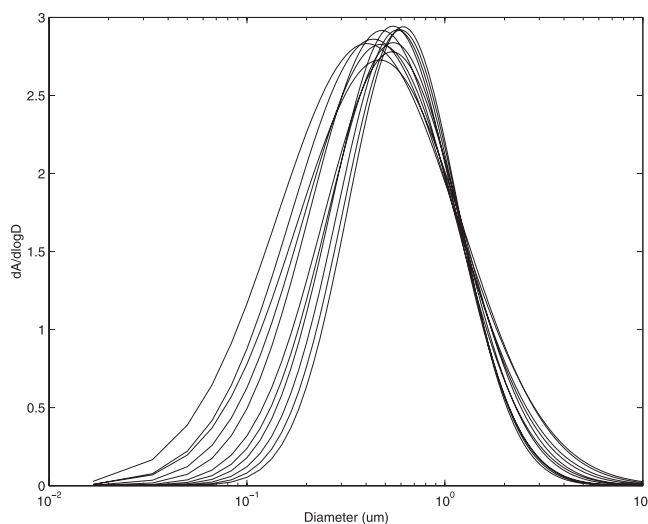
that the majority of the volcano plume was below 500 m height but was irregularly shaped possibly due to atmospheric turbulence.

### 3. Aerosol Flux Rates

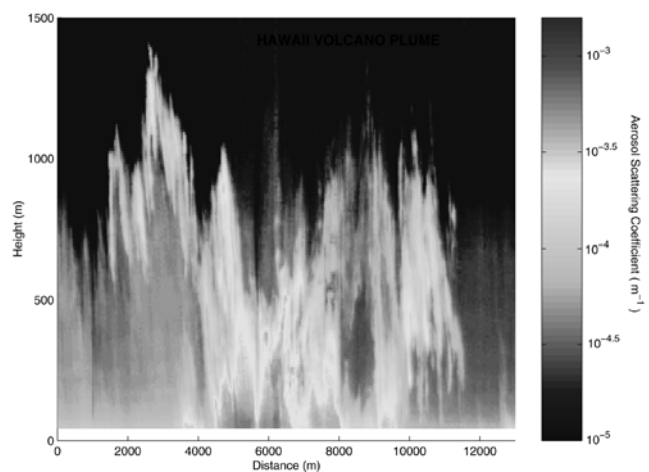
[7] In order to estimate the flux of dry sulfuric acid aerosol we follow equation (1),

$$\text{Flux Rate} = \left( \frac{\text{Wind Speed}}{\gamma} \right) \sum_{i=1}^n [w_i \tau_i] \quad (1)$$

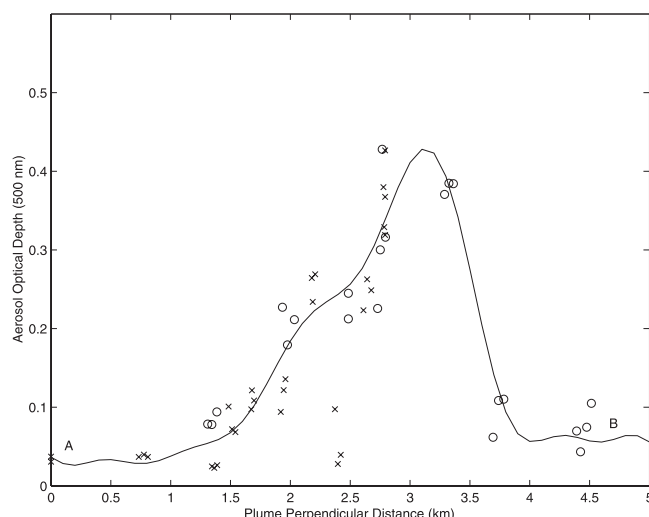
where  $\tau_i$  is the aerosol optical depth for interval  $i$  across the plume,  $w_i$  is the effective width for that interval and  $\gamma$  is the aerosol mass scattering efficiency (in  $\text{m}^2/\text{g}$ ) (discussed below) at the same wavelength as the aerosol optical depth being used (500 nm in this case). An aerosol mass scattering coefficient of  $7.7 \text{ m}^2 \text{ g}^{-1}$  was used for these calculations. This value was based on the average of Mie theory calculations from the size distributions shown in Figure 2 with a standard deviation of  $2.4 \text{ m}^2 \text{ g}^{-1}$ . In obtaining this value we have assumed the hygroscopic aerosols have a water uptake



**Figure 2.** Aerosol size distributions inverted from the aerosol optical depths measurements.



**Figure 3.** Aerosol scattering coefficient (at 500 nm) derived from the lidar while passing under the plume during the third pass. The log of the aerosol scattering coefficient is shown on the right. The data are shown at the height from the surface.



**Figure 4.** Aerosol optical depths (at 500 nm) plotted along a line perpendicular to the volcano plume. The x symbols show measurements made on the upper part of the road while o symbols show the measurements made on the lower part of the road. The plume perpendicular angle was chosen to produce the best overlap. The symbols A and B show the position of the measurements on Figures 1 and 4.

that is slightly less than sulfuric acid [Tang, 1980] due to the presence of small amounts of ammonium [Porter and Clarke, 1997]. An average relative humidity of 65% was assumed for the lowest 500 m based on the Hilo sounding at 2 p.m. Although the Hilo sounding is  $\sim 30$  km away, the cloud base predicted from parcel theory from the sounding data was in good agreement with cloud bases observed by lidar, suggesting similar conditions existed at both sites.

[8] The aerosol optical depth across (perpendicular to) the plume is needed to use equation 1. Unfortunately, the road does not cut straight across the plume (Figure 1) so it was necessary to convert the position of the aerosol optical depth measurements to their position along a line perpendicular to the plume. Figure 4 shows the aerosol optical depths along this perpendicular line. All the measurements at each location are shown in Figure 4 while only the average values at each location are shown in Figure 1. The measurements labeled A and B are indicated in Figures 1 and 4. A curve fit to the measurements was carried out and equation 1 was then used to calculate dry aerosol mass flux rates of 47, 60, and 52 ( $\pm 40\%$ )  $\text{Mg d}^{-1}$  for passes 2, 3 and 4. Background aerosol optical depths (on either side of the plume) were averaged and subtracted from the in-plume optical depths prior to using equation 1. Aerosol flux rates calculated from the lidar data gave very similar values, which is expected since the lidar is calibrated with the sun photometer measurements. The first pass could not be used because part of the plume was beyond the road. Accounting for the difference in molecular weight between  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$ , the formation of 53  $\text{Mg d}^{-1}$  of vog aerosol (the average of the three passes) corresponds to 35  $\text{Mg d}^{-1}$  of  $\text{SO}_2$  loss between the vent and the measurement point. We have assumed that all the S(VI) was derived from S(IV).

#### 4. $\text{SO}_2$ Half Life in the Hawaii Kilauea Volcano Plume

[9] Regular measurements of the  $\text{SO}_2$  column abundance in the Pu'u O'o plume have been made by the U.S. Geological Survey Hawaiian Volcano Observatory since 1992 using vehicle-based COSPEC [Sutton et al., 2001; Elias et al., 1998]. These data are combined with locally recorded wind speeds to estimate  $\text{SO}_2$

emission rates. Based on COSPEC data and field observations of lava effusion rate estimates, which bracketed our aerosol measurements, we estimate that the  $\text{SO}_2$  emissions on August 17, 2001 were 1450  $\text{Mg d}^{-1}$  ( $\pm 300 \text{ Mg d}^{-1}$ ). The boundary layer winds on August 17 ( $12 \text{ m s}^{-1}$ ) resulted in a travel time of 12.5 minutes from the vent to our sample site (9 km downwind). Following Finlayson-Pitts and Pitts [1986]

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (2)$$

where  $C_0$  and  $C$  are the initial and final concentrations, and  $t_{1/2}$  is the half-life (so  $t_{1/2} = \ln(0.5)/k$ ). Assuming that all the S(VI) was derived from S(IV), we obtain a  $\text{SO}_2$  half-life of 6.0 hours in the Pu'u O'o plume. Adding in uncertainty in the aerosol and  $\text{SO}_2$  flux rates results in half-life values ranging from 3.5–10 hours. Here we have assumed the  $\text{SO}_2$  oxidation occurs in the atmosphere but some probably occurs right above the vent. This would make the atmospheric half-life longer than the 6.0 hours estimated here. In comparison, Finlayson-Pitts and Pitts [1986] summarize measurements of  $\text{SO}_2$  oxidation rates and find half life values  $\sim 6.6$  hours have been reported in many studies [Gillani et al., 1981; Newman, 1981], although values up to 69 hours [Lusis et al., 1978] and down to 1.9 hours [Mezaros et al., 1977] have also been reported. The general trend is toward faster conversion rates in low latitudes (more solar irradiance) and when partially cloudy conditions exist where in cloud processes can occur [Eatough et al., 1994].

#### 5. Conclusion

[10] Sun photometer and lidar measurements were made under the Hawaii Kilauea Pu'u O'o Volcano plume to measure aerosol flux rates. Accounting for the wind speed and aerosol hygroscopic properties, average aerosol dry mass flux rates of 53  $\text{Mg d}^{-1}$   $\text{H}_2\text{SO}_4$  were obtained. Using the calculated  $\text{SO}_2$  emission rate, the  $\text{SO}_2$  oxidation half-life was estimated to be 6.0 hours. Further studies are needed to test these results. Combined aerosol and gas measurements at different distances downwind in the plume would be important for helping to access the long-term impact of the Pu'u O'o plume on the local ecosystem and residents. Similar studies at other volcanoes where continuous low-level degassing can continue for years (e.g., Masaya, Nicaragua) also appear warranted.

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