Sulfur dioxide emissions from Peruvian copper smelters detected by the Ozone Monitoring Instrument

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[1] We report the first daily observations of sulfur dioxide (SO₂) emissions from copper smelters by a satellite-borne sensor - the Ozone Monitoring Instrument (OMI) on NASA’s EOS/Aura spacecraft. Emissions from two Peruvian smelters (La Oroya and Ilo) were detected in up to 80% of OMI overpasses between September 2004 and June 2005. SO₂ production by each smelter in this period is assessed and compared with contemporaneous emissions from active volcanoes in Ecuador and southern Colombia. Annual SO₂ discharge from the Ilo smelter, La Oroya smelter, and volcanoes in 2004–2005 is estimated and amounts to 0.3 ± 0.1, 0.07 ± 0.03, and 1.2 ± 0.5 Tg, respectively. This study confirms OMI’s potential as an effective tool for evaluation of anthropogenic and natural SO₂ emissions. Smelter plumes transport an array of toxic metals in addition to SO₂ and continued monitoring to mitigate health and environmental impacts is recommended.


1. Introduction

[2] Anthropogenic activities over the last century (mainly fossil fuel burning and metal smelting) have raised atmospheric SO₂ concentrations by up to 3 orders of magnitude [Pham et al., 1996]. Of potentially greater significance is the concomitant increase in production of derived sulfate aerosol, which indirectly affects the climate system and water cycle by supplying cloud condensation nuclei, enhancing cloud albedo, and suppressing precipitation [Twomey, 1977; Charlson et al., 1992; Rosenfeld, 2000]. An inventory of anthropogenic SO₂ source strengths is therefore a crucial component of global atmospheric models, but to date emissions from major source regions such as East Asia have typically been estimated using complex algorithms that rely on large input datasets, enumerating parameters such as fuel use and the removal efficiency of emission abatement systems [e.g., Streets et al., 2003].

[3] As a viable alternative to these “bottom-up” estimates of emissions, the ultraviolet (UV) GOME and SCIAMACHY satellite sensors have demonstrated that anthropogenic SO₂ emissions can be detected from space [e.g., Eisinger and Burrows, 1998]. However, the efficacy of GOME and SCIAMACHY data for detailed studies of SO₂ emissions is restricted by poor spatial or temporal sampling. On July 15, 2004, NASA launched the Ozone Monitoring Instrument (OMI) as part of the EOS-Aura mission (http://aura.gsfc.nasa.gov). OMI has a unique combination of footprint size (13 × 24 km at nadir), spectral resolution (0.45 nm) and global contiguous coverage for space-based UV measurements of SO₂, surpassing the sensitivity of the Earth Probe Total Ozone Mapping Spectrometer (EP-TOMS), which could only detect anthropogenic SO₂ emissions when atmospheric loadings were exceptional [Carn et al., 2004]. Using algorithms developed for retrieval of SO₂ from OMI, the noise level of SO₂ measurements has been reduced by an order of magnitude compared to the TOMS instruments [Krotkov et al., 2006]. As we demonstrate here, these improvements permit detection of SO₂ discharge from specific industrial sources on a daily basis.

2. OMI Instrument and SO₂ Algorithm

[4] OMI is a hyperspectral UV/Visible spectrometer with a 2600 km swath for daily, contiguous global mapping of ozone and trace gases including SO₂, NO₂ and BrO. It was contributed to the 6-year Aura mission by the Royal Netherlands Meteorological Institute (KNMI) and the Netherlands Agency for Aerospace Programs (NIVR), in collaboration with the Finnish Meteorological Institute (FMI). Operational data flow from OMI began in September 2004. The Aura spacecraft is in a sun-synchronous orbit at 705 km altitude and crosses the equator at 1:45 pm ± 15 minutes local time each day (ascending node).

[5] Most OMI data products are currently produced using radiances at a subset of UV wavelengths calibrated with post-launch data. We have developed a scheme termed the Band Residual Difference (BRD) algorithm, which retrieves total column SO₂ using four OMI wavelengths situated at SO₂ band extrema between 310.8 and 314.4 nm [Krotkov et al., 2006]. As described above, the BRD retrieval noise is an order of magnitude lower than achieved with EP-TOMS, permitting detection of weaker SO₂ sources and smaller SO₂ clouds with OMI. We have also developed time-averaging techniques which further improve the signal to noise ratio. All SO₂ data in this paper were produced using the BRD algorithm, the derivation of which is described by Krotkov et al. [2006].

[6] We caution that OMI SO₂ algorithms are subject to ongoing development and refinement, and that OMI SO₂ data have not yet been rigorously validated using correlative measurements. Retrieval of anthropogenic SO₂ in the planetary boundary layer (PBL) is particularly challenging due...
Note the diffuse region of elevated SO$_2$ such as As, Cd, Cu, Pb, Se and Zn) [e.g., L09801]. Volcanoes (triangles), from north to south, are: Nevado del Ruiz, Galeras, Reventador, Guagua Pichincha, Tungurahua, Sangay, and Sabancaya. Peruvian copper smelters are also not accounted for in the BRD algorithm. Although we endeavor to place realistic error bounds on the SO$_2$ of OMI rather than the quantitative results. For the current status of OMI SO$_2$ algorithms and publicly released data, and associated documentation, the reader is referred to http://so2.umbc.edu/omi.

Figure 1. Average SO$_2$ column amounts measured by OMI over southern Colombia (Co), Ecuador (Ec), and Peru (Pe) between 1 September 2004 and 30 June 2005. Volcanoes (triangles), from north to south, are: Nevado del Ruiz, Galeras, Reventador, Guagua Pichincha, Tungurahua, Sangay, and Sabancaya. Peruvian copper smelters (diamonds; symbol size proportional to capacity) are located at La Oroya (11.53°S, 75.9°W) and Ilo (17.63°S, 71.33°W). Note the diffuse region of elevated SO$_2$ over the Pacific Ocean region.

3. Sulfur Dioxide Emissions From Copper Smelters

Copper smelting, involving extraction of copper from chalcopyrite (CuFeS$_2$), liberates large quantities of sulfur gases: ~2 tons of SO$_2$ are discharged in flue gases (which also contain CO$_2$ and NO$_x$) per ton of copper produced. Smelters have long been recognized as significant sources of SO$_2$ and other pollutants (including toxic heavy metals such as As, Cd, Cu, Pb, Se and Zn) [e.g., Gidhagen et al., 2002]; for example, the environmental crisis associated with Ni-Cu smelting on NW Russia’s Kola Peninsula is well known [Simonetti et al., 2004]. Most polluting smelters are now situated in developing countries, where modern sulfur capture technology may be unavailable or unaffordable. Approximately 50% of smelters capture <84% of emitted SO$_2$, whilst 10% capture none at all [Boon et al., 2001]. Most of the latter are situated in Australasia, South America, Africa and China.

Analysis of early OMI SO$_2$ data revealed two persistent sources of SO$_2$ in Peru that did not correspond to the locations of active volcanoes (Figure 1). These were subsequently identified as copper smelters situated in Ilo (at sea level in southern Peru; owned by the Southern Peru Copper Company) and La Oroya (112 miles north-east of Lima; alt. 12,385 ft; operated by The Doe Run Company, La Oroya, Peru, http://www.doeun.com/whatwedolauraya.aspx). Annual capacities of these smelters in 2002 were reportedly 300 and 80 thousand metric tons, respectively [Feliciano and González, 2003], making Ilo one of the ten largest copper smelters in the world. This output would yield annual SO$_2$ emissions of 0.6 and 0.16 Tg, respectively, assuming 2 tons of SO$_2$ emitted per ton of copper produced, operation at maximum capacity, and no SO$_2$ capture. Boon et al. [2001] report annual SO$_2$ emissions amounting to 0.42 Tg from the Ilo smelter (several times larger than the total output of many European nations), which at the time captured 30% of its SO$_2$ yield for sulfuric acid production. These amounts are commensurate with SO$_2$ production reported for these smelters in the Global Emissions Inventory Activity (GEIA) database for 1985 (http://www.geiacenter.org). Boon et al. [2001] also note that a 250 MW coal-fired power plant is located 25 km south of Ilo, although the SO$_2$ emissions are significantly lower than those from the smelter.

Both Peruvian copper smelters are implicated in poor local air quality and health crises and are aiming to reduce pollution by increasing SO$_2$ capture [Boon et al., 2001; Centers for Disease Control, 2005]. Modernization of the Ilo smelter was scheduled for completion in 2006 and will result in capture of 93% of SO$_2$ emissions [Boon et al., 2001]. As a demonstration of OMI’s capabilities, we report here OMI measurements of SO$_2$ burdens over Peruvian smelters from September 2004–June 2005, and compare them with contemporaneous SO$_2$ emissions from active volcanoes in Ecuador and S. Colombia.

4. OMI SO$_2$ Data Analysis

We calculated daily mean SO$_2$ burdens measured by OMI over three regions for each month (Table 1). Regions were delineated according to the maximum extent of SO$_2$ plumes observed from each source in a single day of OMI data. BRD algorithm SO$_2$ retrievals assumed an SO$_2$ layer altitude of 5 km for the La Oroya smelter and the high-altitude volcanoes of Ecuador/S. Colombia, and <3 km (PBL) for the coastal Ilo smelter. Total SO$_2$ amounts in Table 1 were calculated by summing all the SO$_2$ retrieved in the region during each month and applying a background correction using an adjacent box of similar dimensions containing no significant SO$_2$ sources. Mean burdens were then derived in two ways (M$_{\text{OBS}}$ and M$_{\text{D}}$; Table 1); M$_{\text{OBS}}$ (based on observed SO$_2$ plumes) being an attempt to compensate for inevitable masking of SO$_2$ by cloud on certain days. Figure 2 depicts raw daily SO$_2$ burdens for each region without a background correction.

The map in Figure 1 depicts the long-term average distribution of SO$_2$ measured by OMI in 2004–2005. Dispersal of SO$_2$ from La Oroya occurs predominantly to the southwest (towards Lima), whilst the SO$_2$ plume from Ilo, clearly the stronger source, typically hugs the coastline.
northwest of the smelter and is traceable for ~300 km. No other strong point sources of SO$_2$ are apparent in Peru.

[12] SO$_2$ emissions from active volcanoes in Ecuador and Colombia are clearly visible in Figure 1. In the timeframe studied, Reventador and Tungurahua (Ecuador) and Galeras (Colombia) were the most active (e.g., see archived volcanic ash advisories issued for the region at http://www.ssd.noaa.gov/VAAC/messages.html). Note that although a small SO$_2$ anomaly appears to be associated with Nevado del Ruiz volcano (Colombia; Figure 1), this was not included in the SO$_2$ burden calculations given in Table 1 and Figure 2. A spike in the SO$_2$ burden over Ecuador/S. Colombia in mid-May (Figure 2) was due to the transit of an SO$_2$ cloud from an eruption of Fernandina (Galapagos Is) across the region. We cannot rule out a contribution to the SO$_2$ burden measured over Ecuador/S. Colombia from anthropogenic sources along the coastal plain, and there is possible evidence for such sources in the OMI data (Figure 1). However, the 1985 GEIA database indicates that these sources would contribute on the order of 0.01 Gg/day or less of SO$_2$, which is <1% of the total amounts measured by OMI (Table 1). OMI does not currently provide information on the vertical distribution of SO$_2$ and therefore cannot

![Figure 2](image-url)

**Figure 2.** Daily SO$_2$ burdens (vertical bars) measured by OMI over (a) Ecuador and southern Colombia, (b) Ilo, and (c) La Oroya. Some of the variability in these burdens is due to cross-track variations in OMI ground pixel size, from 13 × 24 km at nadir to an estimated 41 × 140 km at the swath edge. Thus, sensitivity to SO$_2$ is reduced when the target is located at the swath edge. A 14-day centered moving average (grey curve) shows the general trend in the data. See Table 1 for the bounds of each region. Note the OMI data gaps listed in Table 1 (which produce false minima in the smoothed data), and varying scale on the ordinate.
measurements at or near-nadir, but that the BRD algorithm may underestimate PBL SO$_2$ uncertainty on PBL SO$_2$ extremes off-nadir viewing geometry, which occurs approximately once every 6 days. This result holds for model aerosol vertical distributions with half-widths of 1 km (aerosol closer to the ground) and 2 km (larger vertical extent of aerosol). Errors on the Ilo SO$_2$ emissions reported below reflect this tendency to underestimate PBL SO$_2$ amounts; the effect is less significant for SO$_2$ located at higher altitudes. We stress that these conclusions are particular to the Ilo site, and that aerosol parameters and vertical profiles of SO$_2$ and aerosols specific to each location are needed to assess these effects more accurately.

5. Discussion

The Ilo smelter was the most persistent SO$_2$ source in the 10-month period studied, with emissions detected in ~80% of OMI observations (Table 1). In terms of source strength, the volcanoes of Ecuador/S. Colombia were dominant (particularly during a period of elevated activity at Reventador in June 2005; Figure 2), followed by Ilo and La Oroya, with mean $M_{\text{O}_{2}}$ ($\pm 1\sigma$) of $3.2 \pm 1.4$, $0.8^{+0.3}_{-0.25}$ and $0.2 \pm 0.08$ Gg, respectively. The volcanic signal showed most variability, whilst SO$_2$ burdens over Ilo were the most consistent.

Based on average observed burdens, and assuming an SO$_2$ lifetime of 1 day, annual SO$_2$ discharge from the Ilo and La Oroya smelters is currently on the order of $0.3^{+0.2}_{-0.1}$ and $0.07 \pm 0.03$ Tg, which for Ilo compares well with published data [Boon et al., 2001], given the higher uncertainty on PBL SO$_2$ columns. The annual volcanic flux for Ecuador and S. Colombia amounts to $1.2 \pm 0.5$ Tg. We caution that conversion rates lower than 100% SO$_2$ day$^{-1}$ would reduce these values. We note a significant decline in daily SO$_2$ burdens at the Ilo smelter, from ~1 Gg or more in September–November 2004 to an average of ~0.6 Gg from January 2005 onwards (Table 1; Figure 2). Although we cannot exclude factors such as a reduction in smelter operating capacity or a change in the aerosol regime at this stage, this may reflect ongoing modernization of the smelter and increased SO$_2$ capture. SO$_2$ burdens over the La Oroya smelter were ostensibly lower between December 2004 and April 2005 (Table 1), but this coincides with the Andean wet season, and we therefore attribute this trend to increased cloudiness and/or wet deposition of SO$_2$ in this period. The Peruvian coast around Ilo is, in contrast, rather arid year-round.

Uncertainty on actual SO$_2$ emissions arises from inadequate constraints on SO$_2$ conversion rates and their temporal variability. Concentrations of SO$_2$ near the smelters vary diurnally, peaking at night or in the morning at both plants [Boon et al., 2001; Dirección General de Salud Ambiental, 1999]. This is probably a result of the temperature dependence of the rate constant for the SO$_2$ (g) to sulfate conversion [Eatough et al., 1994], and the exhaustion of oxidants (primarily the OH radical, derived from photolysis of O$_3$) at night. Studies of copper smelter plumes document gas-phase homogeneous SO$_2$ conversion rates of $\sim 1$–$8$% hr$^{-1}$, peaking in hot (~30°C), sunny conditions [Eatough et al., 1982], which are similar to reported rates in power plant plumes, suggesting that the trace metal content of smelter emissions has no appreciable catalytic effect [Hewitt, 2001].

Aqueous-phase conversion of SO$_2$ to sulfate (e.g., plumes entrained into cloud or fog) can proceed at rates up to 100% hr$^{-1}$ but is also dependent on the availability of oxidants (principally H$_2$O$_3$ and O$_3$) [Eatough et al., 1984; Eatough et al., 1994]. Fog (garua) affects the coast of Peru from May – November, but we see no clear artifacts in the Ilo data (Table 1), possibly because the plume is not emitted into fog or because the supply of the necessary oxidants is inadequate. Given the anisotropic dispersal of the emissions (Figure 1) the supply of oxidants in the plume might become limiting at times, which could explain the surprisingly large extent of the SO$_2$ plume from Ilo in Figure 1.

The potential impacts of Ilo smelter pollution on fog acidity warrant further study, since in this arid region the water supply is augmented by harvesting (condensing) fog.

The early afternoon OMI overpass therefore likely coincides with peak SO$_2$ conversion rates and minimum ambient SO$_2$ concentrations, but the SO$_2$ plume mapped in an OMI snapshot is the cumulative product of emission, transport and conversion over a 24-hour period. Conversion rates depend on temperature, relative humidity, droplet size, oxidant abundance, meteorology and the relative significance of gas-phase and aqueous-phase reactions [Eatough et al., 1994]. Constant conversion at 8% hr$^{-1}$ would result in a SO$_2$ lifetime of <1 day and a potential underestimate of SO$_2$ emissions by OMI, whereas removal of 1% SO$_2$ hr$^{-1}$ in daylight could produce daily residuals of over 80% of the previous day’s discharge, and overestimated emissions. The reality probably falls between these extremes, but would require a complex model for resolution and is beyond the scope of this paper. We also note that any diurnal variation in smelter emissions (for which data are unavailable) would not be captured by the OMI measurements, particularly if the SO$_2$ lifetime were <1 day. Emissions might be significantly underestimated if the smelters only operate at night.

Although the smelter emissions are undoubtedly significant, regional average SO$_2$ column amounts (Figure 1) highlight the more widespread impact of volcanic emissions in 2004–2005. A diffuse zone of elevated SO$_2$ can be seen extending west from the region across the Pacific (Figure 1), and most likely reflects the higher altitude and source strength of the volcanic emissions. Continued analysis of OMI SO$_2$ data throughout the Aura mission will establish whether this is typical, or a result of above-average levels of volcanic unrest in 2004–2005.

6. Conclusions

We have demonstrated that the UV OMI sensor on Aura can detect daily tropospheric emissions from anthro-
pogenic and natural sources of SO₂. Due to its relatively short tropospheric residence time \[ \text{[Eatough et al., 1994]} \], SO₂ is not a significant greenhouse gas, but it is easier to measure than longer-lived species such as CO₂, CH₄ and N₂O and hence can be used to pinpoint major sources of pollution and quantify source strengths.

[21] Numerous other anthropogenic SO₂ sources have been sensed by OMI. Smelter and power plant pollution in Chile, Eastern Europe, Russia, China and Uzbekistan has also been detected. The recognized health impacts of the array of toxic metals released in smelter plumes warrant increased efforts to monitor and map such emissions, though Boon et al. [2001] note that access to environmental monitoring data is often difficult in Latin America, Asia and Africa. Space-based monitoring of emissions with instruments such as OMI offers an economical solution to this problem.

[22] An irrefutable contribution of anthropogenic activities to global warming over the last century is now widely acknowledged [Intergovernmental Panel on Climate Change (IPCC), 2001]. Quantification of the negative forcing by atmospheric sulfate aerosol, plus indirect aerosol effects, is a critical, yet poorly constrained, aspect of climate models [IPCC, 2001]. Accurate mapping of the spatial and temporal variability of SO₂ emissions using OMI will therefore contribute to improved modeling of the climate system. OMI measurements could also facilitate mitigation of health and environmental impacts of SO₂ and sulfate aerosol (e.g., visibility impairment, acid rain) close to sources.

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References


Eatough, D. J., et al. (1982), Sulfur chemistry in a copper smelter plume, \textit{Atmos. Environ.}, 16, 1001–1015.


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