Fire at Iraqi sulfur plant emits SO_2 clouds detected by Earth Probe TOMS

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[1] A fire started at the Al-Mishraq State Sulfur plant near Mosul, Iraq on 24 June 2003 and burned for almost a month. Combustion of elemental sulfur in the fire produced dense clouds of sulfur dioxide (SO_2) that were detected from space by the Earth Probe Total Ozone Mapping Spectrometer (EP TOMS) on 18 days. Estimated daily SO_2 production from the continuously emitting source closely mirrors contemporaneous thermal infrared radiance from the fire sensed in the 3.96 μm band of the Moderate Resolution Imaging Spectroradiometer (MODIS). We calculate total SO_2 production during the blaze amounting to ~600 kilotons, which is roughly commensurate with the predicted SO_2 yield from the inventory of elemental sulfur allegedly destroyed by the fire when potential SO_2 losses are considered. This event is the largest non-volcanic SO_2 emission incident measured to date by any TOMS instrument. *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques. **Citation:** Carn, S. A., A. J. Krueger, N. A. Krotkov, and M. A. Gray (2004), Fire at Iraqi sulfur plant emits SO_2 clouds detected by Earth Probe TOMS, *Geophys. Res. Lett.*, *31*, L19105, doi:10.1029/2004GL020719.

1. Introduction

[2] The Total Ozone Mapping Spectrometer (TOMS) instrument has been measuring volcanic sulfur dioxide (SO_2) clouds from space since 1982 [*Krueger*, 1983], and the SO_2 emissions record derived from the four TOMS missions covers over 25 years [*Carn et al.*, 2003]. However, the SO_2 sensitivity of TOMS is usually limited to stratospheric and upper tropospheric clouds and it is seldom able to detect SO_2 emitted by non-volcanic sources, which typically resides in the lower troposphere or boundary layer. Only exceptionally strong anthropogenic SO_2 emissions, such as those produced by the Nadezhda nickel smelting plant in Norilsk, Siberia, are resolvable using the coarse spatial and spectral resolution of TOMS. Emissions from Norilsk were often apparent in ultraviolet (UV) Nimbus-7 and Earth Probe (EP) TOMS data in springtime during the 1980s and 1990s, when UV light levels at Siberian latitudes were adequate and a covering of snow increased ground reflectivity, thereby enhancing the tropospheric signal. In this paper we document the most significant non-volcanic SO_2 discharge measured to date by any TOMS instrument, produced by a fire at an Iraqi sulfur plant in 2003 (NASA Earth Observatory Newsroom, Sulfur dioxide plume lingers over Iraq, 2003, available at http://earthobservatory.nasa.gov/Newsroom/NewImages/images.php3?img_id=15349).

[3] The fire, believed to be an act of arson, started in late June 2003 at a facility owned by the Al-Mishraq State Company for Sulfur, located ~40 km southeast of Mosul and ~315 km north of Baghdad in northern Iraq (36.0°N, 43.3°E; elevation 200–300 m a.s.l.), at the confluence of the Tigris and Great Zab rivers (Figure 1). This plant extracts and refines sulfur from the Mishraq native sulfur deposit, which is the largest known occurrence of stratiform bioepigenetic sulfur in the world [*Barker et al.*, 1979], containing an estimated 500 million tons of elemental sulfur worth ~US$25 billion (Iraq Coalition Provisional Authority (ICPA), State-owned enterprise company profiles, 2004, available at http://cpa-iraq.org/business/industries/, hereinafter referred to as ICPA, 2004). Refined sulfur is used to produce sulfuric acid, aluminum sulfate ($Al_2(SO_4)_3$) and sulfur powder for industrial, water treatment and agricultural use. Available data indicate that the Iraqi mineral industry currently produces 100 kilotons (kt) of elemental sulfur per year, of which 98% is derived from deposits such as the Mishraq orebody and 2% is a by-product of petroleum processing (U.S. Geological Survey Mineral Resources Program, USGS minerals information: Africa and the Middle East, 2004, available at http://minerals.usgs.gov/minerals/pubs/country/africa.html). Continued extraction coupled with export restrictions due to sanctions imposed on Iraq after the Gulf War have resulted in large accumulations of processed sulfur at the Al-Mishraq plant (Iraq Press, Sulfur mining works still on fire, available at http://www.iraqpress.org/english.asp?

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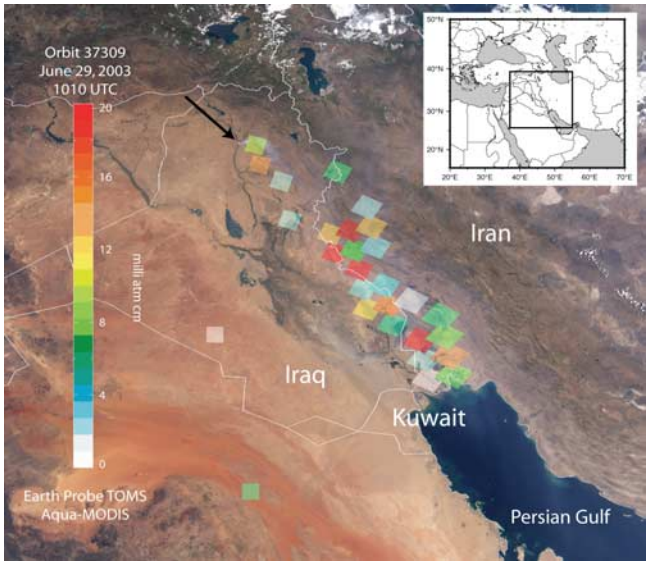

Figure 1. Composite image showing EP TOMS SO_2 column amounts in milli atm cm (*large color-coded pixels*) at 0752UT on 29 June 2003 plotted over a true-color image captured by Aqua-MODIS at 1010UT on the same day. *Inset* map indicates the area covered by the MODIS scene. The *black arrow* indicates the location of the Mishraq sulfur plant fire; aerosols in the emerging plume are faintly visible in the MODIS data (*white haze*). The observed SO_2 cloud, stretching ~900 km SE from the fire towards the Persian Gulf, contained an estimated SO_2 mass of ~100 kt.

fname=ipenglish\2003-07-11\02.htm, 2003, hereinafter referred to as Iraq Press, 2003).

[4] Reports indicate that the fire began on 25 June 2003 and burned for almost a month (Oregon National Guard Bravo 52nd Engineers, B52 HQ messages history (7/27/2003), 2003, available at http://www.rainbowmarketing.com/b52nd/b52hqmessages.htm), although it was apparently under control by 8 July (T. Sawyer, Engineers assault chemical plant fire in Iraq, McGraw-Hill Construction Engineering News-Record, 10 July 2003, available at http://www.enr.com/news/front2003/archives/030710.asp, hereinafter referred to as Sawyer, 2003). A total of 400 kt of finished product, worth ~US$20 million (~33% of total inventory), was destroyed by the fire and the resulting fumes also polluted a local wheat crop worth ~US$40 million, rendering it unusable (ICPA, 2004). Actual production in 2002 amounted to 8 kt sulfur powder, 300 kt sulfur and 7 kt $Al_2(SO_4)_3$ (ICPA, 2004) so we assume that ~98% of the inventory burned in 2003 was elemental sulfur. The environmental and health effects of the plume produced by the fire were significant; with fumes enveloping at least 100 square kilometers, reaching the Kurdish city of Arbil (~100 km from the fire) and covering the skies in Mosul (Iraq's 3rd largest city) (Iraq Press, 2003). Many cases of respiratory disease were reported and two residents of nearby villages were killed; with SO_2 concentrations near the fire reaching 52 ppm shortly after it began (Sawyer, 2003) (the U.S. national air quality SO_2 standard for a 24-hour period is 0.14 ppm) (Environmental Protection Agency, EPA air trends: Sulfur dioxide, 2004, available at http://www.epa.gov/airtrends/sulfur.html, hereinafter referred to as EPA, 2004).

2. Satellite Data

[5] We have used data from EP TOMS and the Moderate Resolution Imaging Spectroradiometer (MODIS) instruments on the EOS Terra and Aqua satellites to track emissions from the Mishraq fire. Daily EP TOMS overpasses of the fire site occurred at 0700–0800UT (1100–1200 local time) and the sensor detected SO_2 clouds over Iraq and neighboring countries on 18 days between 25 June and 15 July (e.g., Figure 1 and Table 1). Strong negative Aerosol Index (AI) signals, indicative of sulfate aerosol, were also recorded after 27 June (Figure 2) but TOMS detected no absorbing aerosol emissions (e.g., soot; which produces a positive AI) during the fire. Emitted SO_2 was tracked into Syria, Iran, Turkey, Azerbaijan and the southern Caspian Sea and, at its furthest extent on 30 June, over the southern Persian Gulf ~1350 km from the sulfur plant. On most days the SO_2 was transported south or southeast of the fire.

[6] EP TOMS data were processed using our standard 4-band inversion technique for volcanic SO_2 clouds [*Krueger et al.*, 1995]. Estimated errors for this low solar zenith angle case are +10%/−22% assuming moderate optical depths of sulfate aerosol collocated with the SO_2, which would lead to an overestimate of SO_2 burdens [*Krueger et al.*, 1995]. Absorbing aerosol (e.g., soot, dust) would also bias retrievals but AI data indicated that sulfate was the dominant species (e.g., Figure 2). High surface reflectivity (e.g., low meteorological cloud, snow/ice)

Table 1. SO_2 Emissions During the 2003 Mishraq Fire

Date – Time (UT)	EP TOMS SO_2 (Observed, kt)	SO_2 Production (kt)
24 June - 0703	0	2.7[a]
25 June - 0752	17.8	17.8
26 June - 0703	26.2	22
27 June - 0752	50.3	44.1
28 June - 0703	49.5	37.6
29 June - 0752	102	90.3
30 June - 0703	74.3	50.2
1 July - 0752	116	116
2 July - 0702	36.4	1.6
3 July - 0751	41.6	41.6
4 July - 0702	58.2	48.4
5 July - 0751	57	43.3
6 July - 0702	18.8	5.3
7 July - 0752	34.7	30.3
8 July - 0701	6.9	0
9 July - 0750	1.5	1.5
10 July - 0701	0	2.7[a]
11 July - 0750	0	0.5[a]
12 July - 0701	0	2.7[a]
13 July - 0751	9.5	9.5
14 July - 0700	5.9	3.7
15 July - 0749	11.6	10.2
16 July - 0700	0	3.8[a]
17 July - 0749	0	0.5[a]
18 July - 0700	0	3.8[a]
19 July - 0749	0	0.5[a]
20 July - 0700	0	3.8[a]
21 July - 0749	0	0.5[a]
TOTAL:	718.2	594.9

[a]On days when TOMS detected no SO_2, the detection limit for the pixel containing the fire was used.

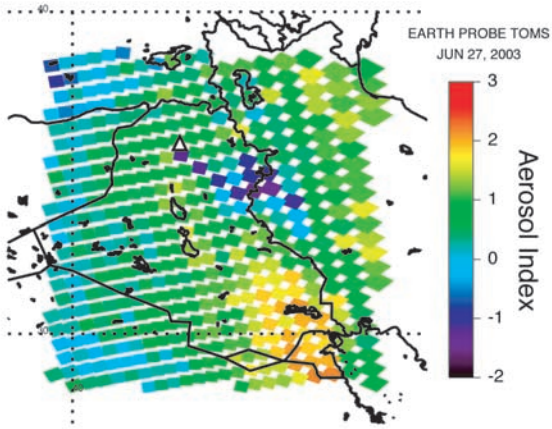

Figure 2. EP TOMS Aerosol Index (AI) over Iraq and W. Iran on 27 June 2003. Negative AI values are indicative of sulfate aerosol. Note the plume of sulfate emanating from the Mishraq fire (*triangle*) into Iran.

enhances the lower tropospheric signal in UV TOMS data, but in the cloud-free, desert environment of Iraq reflectivity is low. No independent estimate of plume height is available for the Mishraq fire but our experience with volcanic SO_2 plumes leads us to conclude that the SO_2 must have risen to $\geq$3–4 km, which is the lowest altitude at which EP TOMS has detected SO_2 from the most prodigious volcanic sources [e.g., *Carn*, 2004]. Comparison of SO_2 cloud trajectories and radiosonde wind profiles from Diyarbakir (S.E. Turkey, 37.9°N, 40.2°E, ~350 km from the fire) indicate that the SO_2 was mostly below 7 km altitude, perhaps rising to 10–15 km on 1 July. It is unlikely that EP TOMS detected SO_2 located close to the ground; hence our SO_2 loading estimates are probably minima.

[7] To chart the evolution of the fire we have used hot-spot data generated from MODIS thermal infrared (TIR) radiances by the operational MODVOLC algorithm [*Wright et al.*, 2002; Hawai'i Institute of Geophysics and Planetology, MODVOLC: Near-real-time thermal monitoring of global hot-spots, 2004, available at http://modis.higp.hawaii.edu]. MODIS hot-spots at the location of the fire commenced on 24 June, with none apparent on 23 June. Assuming that there is no other major source of TIR radiance in the vicinity, it therefore appears that the fire started on 24 June, contrary to available press reports. Hot-spots were visible at the site every day until 21 July. In subsequent analysis, we therefore assume that the fire was burning continuously from 24 June–21 July inclusive.

3. SO_2 and Thermal Emissions From the Mishraq Fire

[8] SO_2 tonnages retrieved from EP TOMS data on each day of the fire are given in Table 1. Peak SO_2 column amounts measured by EP TOMS remained high (~35–55 milli atm cm) until 7–8 July, after which emissions were reduced (Figure 3 and Table 1). This corresponds to the date on which the fire was reportedly brought 'under control' by firefighters (Sawyer, 2003). On several days, particularly towards the end of the incident, EP TOMS was unable to detect any SO_2 and in this case we use the detection limit for the TOMS ground-pixel containing the fire as an estimate of minimum emissions for that day (Table 1).

[9] To estimate daily SO_2 production we have treated the fire as a continuously emitting source of SO_2, analogous to an effusive volcanic eruption [*Krueger et al.*, 1996]. This procedure involves separating 'new' from 'old' SO_2 on each day, although in practice this was only possible on 30 June and 2 July. Data from these two days suggest a daily SO_2 loss rate of 70–75%, and adopting a value of 75% day^{-1} for the remaining days yields the production estimates in Table 1 and Figure 3. The resulting cumulative SO_2 emission is ~600 kt (464–655 kt accounting for errors) for the 28 days, or an average of ~21 kt day^{-1}. We justify using a TOMS-derived SO_2 loss rate by stressing the wide range of reported values for power plant emissions in the troposphere (~24–240% day^{-1} and ~50–12000% day^{-1} for gas and aqueous phase reactions, respectively), and their dependence on temperature, relative humidity, particle density, droplet size and oxidant abundance [*Eatough et al.*, 1994; *Hewitt*, 2001]. Neither these parameters nor the SO_2 chemistry are known for the Mishraq plumes, hence we adopt our observed value, which is within the range of prior determinations.

[10] Our SO_2 production estimates are corroborated when plotted with total spectral radiance recorded by the low-gain 3.96 μm band (channel 21) of MODIS (Figure 3). The high-gain MODIS band at the same wavelength (channel 22) was often saturated by IR emission from the fire. Assuming that the 3.96 μm spectral radiance is a reasonable proxy for the vigor of the fire (and hence for the amount of combusting sulfur), close correspondence between SO_2 release and IR spectral radiance suggests that our production trends are realistic (Figure 3). Reduced SO_2 output and a gradual decline in IR emission after 8 July probably represent the smoldering phase of the fire after it was brought under control.

4. Discussion

[11] The EP TOMS-derived estimate of total SO_2 emission from the Mishraq fire is consistent with the

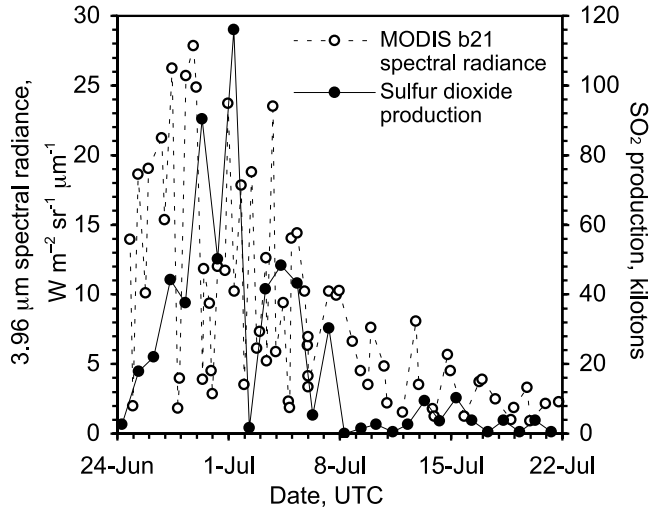

Figure 3. SO_2 production estimated from EP TOMS data plotted with total spectral radiance recorded in Terra/Aqua MODIS thermal infrared band 21 (3.96 μm) for all fire pixels during the Mishraq fire.

combustion of ~300 kt of elemental sulfur via the reaction:

$$S + O_2 \rightarrow SO_2 \quad (1)$$

Reports document the loss of 400 kt of finished product (ICPA, 2004) and, as explained above, we assume that ~391 kt (~98%) of this was elemental sulfur, implying a negligible contribution from $Al_2(SO_4)_3$. Likely causes for the discrepancy are that some SO_2 was removed by oxidation to sulfate or dry/wet deposition before detection by EP TOMS, that EP TOMS failed to detect emissions close to ground level or that the estimate of lost inventory is inaccurate. Our adopted SO_2 loss rate (75% day^{-1}) could also be too low or not representative of the average rate during the fire (note that using a 100% day^{-1} loss rate raises the estimate of combusted sulfur to ~360 kt; Table 1). Loss of SO_2 during combustion of sulfur is also possible via the secondary reaction:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \quad (2)$$

This can prevail at low combustion temperatures, and continuous dowsing of the blaze by firefighters may also have removed some SO_2. All the above factors probably contributed to the apparent minor underestimate of SO_2 emissions by EP TOMS. EP TOMS data indicate that substantial amounts of sulfate aerosol formed in the clouds very close to the source (e.g., Figure 2), rather than downwind, and thus SO_2 sequestration was clearly occurring at an early stage.

[12] In terms of cumulative tonnage, the Mishraq fire ranks among the 20 largest volcanic SO_2 emissions detected by TOMS since 1978 [*Carn et al.*, 2003] and the average SO_2 emission of ~21 kt day^{-1} is rarely exceeded by passively degassing volcanoes. Highly polluting power plants in the United States emit on the order of 20 kt SO_2 yr^{-1}, and hence the Mishraq fire was an exceptionally strong point source of pollution. As mentioned earlier, the nickel smelting plant at Norilsk on Russia's Kola Peninsula is the only other non-volcanic source of SO_2 known to have been consistently detected by any TOMS instrument. The full Norilsk dataset has yet to be analyzed in detail, but emissions of SO_2 from Norilsk are variously reported as being on the order of 2–3 Megatons (Mt) per year (e.g., Foreign and Commonwealth Office, Environmental problems in the Russian federation, 2000, available at http://www.fco.gov.uk/Files/kfile/russiaenviro.pdf), or ~5.5–8.2 kt day^{-1} on average. For comparison, total SO_2 emissions from all sources (fuel combustion, industrial and transportation) in the United States amounted to ~13.6 Mt in 2002 (EPA, 2004), or ~37.3 kt day^{-1} on average.

[13] Monitoring of SO_2 pollution events using UV satellite data is set to improve following the launch of the Ozone Monitoring Instrument (OMI) on the EOS-Aura satellite on 15 July 2004 (http://aura.gsfc.nasa.gov). EOS-Aura forms the tail-end of a procession of satellites termed the 'A-Train', lead by EOS-Aqua (carrying MODIS and the Atmospheric Infrared Sounder [AIRS]) with Aura following 15 minutes later. OMI is a CCD-based hyperspectral UV/VIS imaging spectrometer with 740 channels (compared to 6 on TOMS) and a spatial resolution of 13 × 24 km (compared to 39 × 39 km on EP TOMS). These specifications will permit retrievals of SO_2 in the lower troposphere and boundary layer with detection limits over two orders of magnitude lower than TOMS. A spatial zoom feature will provide 13 × 13 km resolution OMI data for tracking of small-scale pollution events.

[14] **Acknowledgments.** The MODIS Thermal Alert Team at the Hawai'i Institute of Geophysics and Planetology, University of Hawai'i, are thanked for providing an excellent online resource (http://modis.higp.hawaii.edu). We acknowledge NASA's Office of Earth Science (Code YS) for continued support through the TOMS and OMI Science Teams, and thank two reviewers for suggesting improvements to the paper.

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