

Changes in the South Coast Air Basin Atmospheric Sulfur Budget Between 2002 and 2008

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Abstract

Airborne sulfur, as gas phase SO₂ and particle phase SO₂^{*}, was measured in the South Coast Air Basin (SCB) by in situ instruments aboard the NASA DC-8 during the summer 2008 ARCTAS-CARB campaign. Using an estimate of CO₂ emissions in the SCB, we estimate the sulfur emissions in the SCB to be (8 ± 4) × 10⁷ g SO₂ day⁻¹. This is compared to the CARB 2008 SCB inventory of 3.6 × 10⁷ g SO₂ day⁻¹. In 2008, localized sulfur sources were observed in the SCB. Large sulfur contributions were seen from sources along the coast and offshore, indicating potentially significant emissions from marine vessels and refineries. These observations are in contrast to those obtained in 2002 from the NOAA WP-3D during the ITCT campaign. In 2002, broad sulfur sources were observed, and there was no clear impact of marine vessels. Total sulfur levels observed in 2008 were five times lower than SO₂ levels observed in 2002. SO₂ total vertical column data obtained from the OMI instrument aboard the NASA Aura satellite seem to indicate a decrease in SO₂ between 2007 and 2008. Ground-based observations from the San Gabriel site of the IMPROVE network do not indicate a decrease in fine SO₂^{*} between 2002 and 2008.

Motivation

- Sulfur dioxide is the predominant anthropogenic sulfur-containing air pollutant.
- Sulfate aerosols are an important component of the particulate matter in the SCB. In 2007, there were 273 days in which the State of California 24-hour PM₁₀ standard was exceeded [CARB 2009].
- Sulfate aerosols directly and indirectly affect climate by influencing Earth's albedo and increasing the number of particles and cloud condensation nuclei in the atmosphere.
- The goal of this research is to investigate changes in airborne sulfur compounds observed in the SCB between 2002 and 2008 and to assess the impact of these compounds on air quality and climate.
- Improved understanding of sulfur sources and subsequent chemistry will lead to better informed, more effective policy decisions.

Method

- California Air Resources Board (CARB) / NASA collaboration in 2008 based in Southern California
- NASA DC-8 aircraft platform, altitude range of ~12 km
- SO₂ measurements: California Institute of Technology chemical ionization mass spectrometer with reagent ion CF₃O⁺ and Georgia Institute of Technology chemical ionization mass spectrometer with reagent ion SF₆⁺. SO₂ used for analysis is the average of the two independent measurements.
- SO₂^{*} measurements: University of Colorado at Boulder high-resolution time-of-flight aerosol mass spectrometer (ToF-AMS). University of New Hampshire mist chamber / ion chromatography system.
- CARB flights: 18, 20, 22, 24, 26 June 2008
- SCB is defined as 33 – 35° N latitude and 117 – 119° W longitude
- Region of interest for sulfur budget: Area within SCB that is removed from industrial ports. This was done to avoid oversampling the emissions on the west side of the basin relative to the basin-wide emissions in our sulfur budget analysis.
- 13 May 2002 flight of the ITCT campaign focused on the SCB
- 2002 SO₂ measurement: NOAA UV Pulsed Fluorescence instrument aboard the NOAA WP-3D

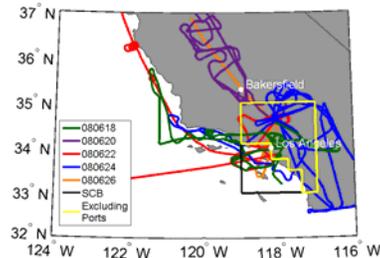


Figure 1. 2008 DC-8 flight tracks of the ARCTAS-CARB flights. The South Coast Air Basin (SCB) is outlined in black. To avoid oversampling the emissions on the west side of the basin relative to the basin-wide emissions in our sulfur budget analysis, we focused on a region within the SCB that is removed from industrial ports. This region is outlined in yellow.

Sulfur Budget

- In the SCB away from industrial ports (Fig. 1) in 2008, there were (8.8 ± 0.6) × 10³ moles of CO per mole of CO₂. This is in good agreement with the CARB 2008 inventory of 8.6 × 10³ moles of CO per mole of CO₂.
- For the same subset of data, there were (6 ± 3) × 10⁵ moles of total sulfur (SO₂ + SO₂^{*}) per mole of CO₂.
- Using the CARB 2004 estimate of CO₂ emissions for the state of California [CARB 2006] and the percentage of Californians (43%) who live in the SCB [California Census 2000], we estimate the CO₂ emissions in the SCB to be 194 Tg year⁻¹.
- Using this estimate of CO₂ emissions and the ratio of total sulfur to CO₂ in the SCB, we estimate the sulfur budget in the SCB to be (8 ± 4) × 10⁷ g SO₂ day⁻¹. This is compared to the CARB inventory of 3.6 × 10⁷ g SO₂ day⁻¹ in the SCB [CARB 2008].
- In 2002 in the SCB away from industrial ports, there were (2.1 ± 0.1) × 10⁴ moles of SO₂ per mole of CO₂ (Fig. 2). This is compared to the 2000 CARB inventory of 6.0 × 10⁵ moles of S per mole of CO₂ [CARB 2008].

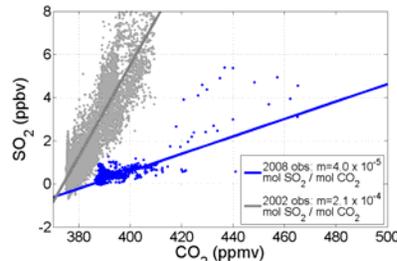


Figure 2. SO₂ versus CO₂. The data shown are those within the SCB that are removed from industrial ports. The 2008 observations are shown in blue. The 2002 observations are shown in grey.

2008 and 2002 Observations

- 2008: Localized sulfur sources are observed. Large sulfur contributions from sources along the coast and offshore are seen, indicating potentially significant emissions from marine vessels and refineries. On-road traffic emissions appear to be small.
- 2002: Broad sulfur sources are observed. No clear impact of marine vessel emissions.

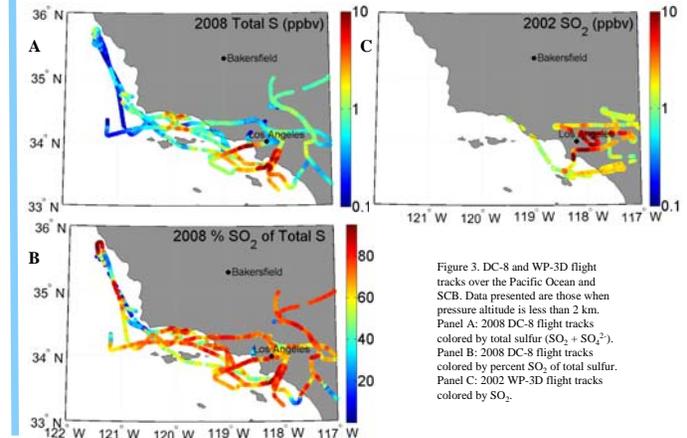


Figure 3. DC-8 and WP-3D flight tracks over the Pacific Ocean and SCB. Data presented are those when pressure altitude is less than 2 km. Panel A: 2008 DC-8 flight tracks color-coded by total sulfur (SO₂ + SO₂^{*}). Panel B: 2008 DC-8 flight tracks color-coded by percent SO₂ of total sulfur. Panel C: 2002 WP-3D flight tracks color-coded by SO₂.

2008 ARCTAS-CARB vs. 2002 ITCT

2008	2002
Large contributions from sources along the coast and offshore	No clear impact of marine vessels
On-road traffic emissions appear to be small (stricter regulations on sulfur content in fuel than in previous years)	
(4 ± 2) × 10 ⁵ mol SO ₂ per mol CO ₂	(2.1 ± 0.1) × 10 ⁴ mol SO ₂ per mol CO ₂
(6 ± 3) × 10 ⁵ mol S per mol CO ₂	
CARB inventory: 4.7 × 10 ⁵ mol S per mol CO ₂	CARB inventory (2000): 6.0 × 10 ⁵ mol S per mol CO ₂

The observed decrease in SO₂ is consistent with OMI total vertical column SO₂ data.

OMI and IMPROVE Observations

- SO₂ total vertical column data were obtained from the Ozone Monitoring Instrument (OMI) aboard the NASA Aura satellite.
- An empirical monthly reference sector background correction was applied to Level 2G Planetary Boundary Layer SO₂ data product. Monthly averages of total vertical column SO₂ in the SCB were calculated.
- Largest difference in monthly average SO₂ total vertical column occurs between 2007 and 2008.
- Ground-based measurements of fine SO₂^{*} were obtained from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network.
- Monthly averages of fine SO₂^{*} concentrations at the San Gabriel site were calculated for years 2002 – 2008.
- No indication of a decrease in fine SO₂^{*} between 2002 and 2008.

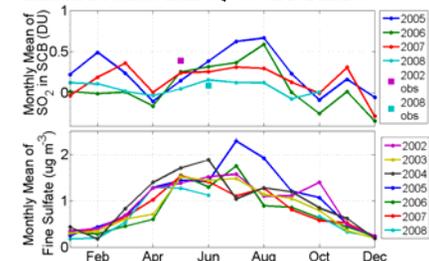


Figure 4. Top panel: Monthly averages of OMI total vertical column SO₂ data in the SCB. Estimated SO₂ total vertical columns were calculated from the 2002 and 2008 aircraft-observed ratios of SO₂ to CO₂. Bottom panel: Monthly averages of fine SO₂^{*} concentrations at the San Gabriel site of the IMPROVE network.

Conclusions

Two independent measurements of SO₂ were obtained during the CARB intensive in June 2008. These measurements, coupled with measurements of SO₂^{*}, enabled the determination of total sulfur in the SCB and offshore regions. In 2008 in the SCB, the observed ratio of sulfur to CO₂ was (6 ± 3) × 10⁵ moles of S per mole of CO₂. The 2008 CARB inventory was 4.7 × 10⁵ moles of S per mole of CO₂ in the SCB. These 2008 total sulfur levels were five times lower than SO₂ levels observed in 2002. In May 2002, (2.1 ± 0.1) × 10⁴ moles of SO₂ per mole of CO₂ were observed, compared to the 2000 CARB inventory of 6.0 × 10⁵ moles of S per mole of CO₂. From the CO₂ emissions in the SCB and the relationship between total sulfur and CO₂ in the SCB, we estimated the sulfur emissions to the SCB to be (8 ± 4) × 10⁷ g SO₂ day⁻¹ in 2008. This estimate is compared to the 2008 CARB inventory of 3.6 × 10⁷ g SO₂ day⁻¹. In 2002, broad sulfur sources were observed while in 2008, localized sources along the coast and offshore were seen. OMI SO₂ total vertical column data corroborate the observed decrease in SO₂ between 2002 and 2008. Ground-based measurements of fine SO₂^{*} at the San Gabriel site of the IMPROVE network do not indicate a decrease in SO₂^{*} between 2002 and 2008.

Acknowledgments

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References

- CARB. Almanac Emission Projection Data. <http://www.arb.ca.gov/app/emsinv/emssumcat.php>, 2008.
- CARB. The California Almanac of Emissions and Air Quality - 2009 Edition. <http://www.arb.ca.gov/aqd/almanac/almanac09/almanac09.htm>, 2009.
- CARB. Greenhouse Gas Inventory Data—2000 to 2006. Technical report, <http://www.arb.ca.gov/cc/inventory/data/data.htm>, 2006.
- CSDC. California State Data Center. Census 2000 Summary File 4. Technical report, U.S. Census Bureau, www.census.gov.
- <http://www.dof.ca.gov/HTML/DEMOCRAT/SDC/SDCProducts.php> and <http://quickfacts.census.gov/qfd/states/06000.html>, 2003.