Investigation of the Los Angeles Basin Atmospheric Sulfur Budget

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Abstract

Airborne sulfur, as gas phase SO_2 and particle phase SO_4^{2-} was measured in Southern California by in situ instruments aboard the NASA DC-8 during the summer 2008 ARCTAS/CARB mission. Using an estimate of CO_2 emissions in the LA basin, we estimate the sulfur emissions in the LA basin to be 6.2 x 10^7 g SO_2 day^{-1}. Emission from on-road traffic and biogenic sources do not account for the amount of sulfur in the LA basin. Emissions from ships appear to be a major contributor to total sulfur.

Motivation

- **Sulfur dioxide is the predominant anthropogenic sulfur-containing air pollutant.**
- **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 and characterize sulfur compounds in and around the Los Angeles basin and to assess their impacts 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**
- **Two independent measurements of SO_2**
  - **California Institute of Technology chemical ionization mass spectrometer. CF_3O^- is used as the reagent ion**
  - **Georgia Institute of Technology chemical ionization mass spectrometer. SF_6^- is used as the reagent ion**
- **Two independent measurements of SO_4^{2-}**
  - **University of Colorado at Boulder high-resolution time-of-flight aerosol mass spectrometer (ToF-AMS)**
  - **University of New Hampshire mist chamber / ion chromatography system**

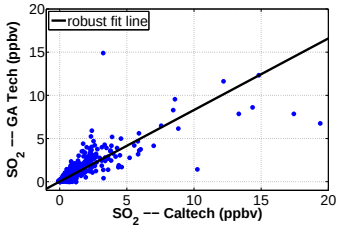

Figure 1. Measurements of SO_2 by GA Tech versus measurements of SO_2 by Caltech for CARB flights June 18 and 26, 2008. The GA Tech instrument reagent ion is SF_6^- while the Caltech instrument uses CF_3O^- as its reagent ion. The slope of the robust fit line is 0.83; intercept is 0.013 ppbv; R^2 is 0.72.

Sulfur in the LA Basin

- **The data presented are measurements made during CARB flights on June 18, 22, and 24 and the transit from Palmdale, California to Cold Lake, Canada on June 26.**
- **In the LA basin away from the coast, there are 8.0 x 10^{-5} moles of sulfur per mole of emitted CO_2 (Figure 2).**
- **For the same data set, CO versus CO_2 yields a slope of 0.011. This is consistent with the CARB inventory (also see Poster B33B-0428).**
- **Using the CARB 2004 estimate of CO_2 emissions for the state of California [CARB 2004] and the percentage of Californians who live in the LA basin [California Census 2000], we estimate the CO_2 emissions in the LA basin to be 194 Tg $year^{-1}$.**
- **Using this estimate of CO_2 emissions and the ratio of total sulfur to CO_2 in the LA basin, we estimate the sulfur budget in the LA basin to be 6.2 x 10^7 g SO_2 day^{-1}**
- **This estimate is close to the CARB inventory of 4.52 x 10^7 g SO_2 day^{-1} in the South Coast Air Basin [CARB 2006].**

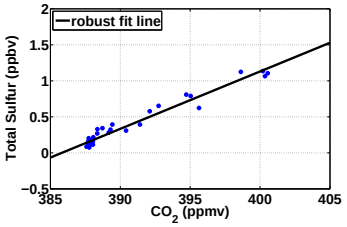

Figure 2. Total sulfur (SO_2 + SO_4^{2-}) versus CO_2. The data shown are those over land (Southern California latitude > N 33° 58' and longitude < W 118 ° 6'). The slope of the robust fit line is 0.08; intercept = -31.

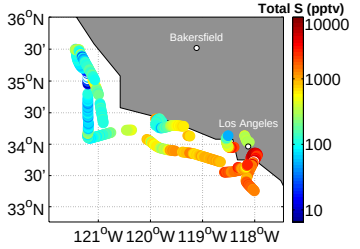

Figure 3. Flight tracks over the Pacific Ocean and LA Basin colored by total sulfur (SO_2 + SO_4^{2-}) for three of the CARB flights and the transit flight from Palmdale, CA to Cold Lake, Canada. Data presented are those when pressure altitude is less than 2 km.

Possible Sources

On-road Traffic Emissions

- **California's sulfur limit for on-road diesel is 15 ppmm**
- **Traffic cannot account for all of the sulfur in the LA basin (The slope of Fig. 2 implies mean S/ CH_2 of 182 ppmm)**

Biogenic Emissions

- **Over the remote ocean, the total sulfur mixing ratio is only 12.6 pptm. Biogenic emissions cannot account for a significant fraction of the sulfur in the LA basin**

Ship Emissions

- **World-wide average sulfur content in marine fuels is 2.7% (27,000 ppmm) [Entec 2002]**
- **Per CO_2 emitted, ship fuel contains 1800 times more sulfur than diesel fuel**
- **Possible ship tracers: 2-methylheptane, 3-methylheptane [Lu 2006]**

Other

- **Petroleum refinery emissions — CARB estimate: 1.14 x 10^7 g SO_2 day^{-1}**
- **Industrial processing emissions — CARB estimate: 2.30 x 10^6 g SO_2 day^{-1}**
- **Aircraft emissions — CARB estimate: 1.17 x 10^6 g SO_2 day^{-1}**

Aging of Sulfur

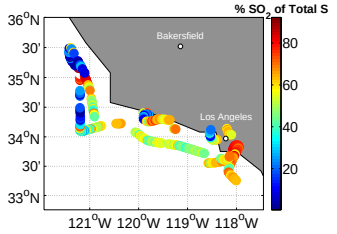

Figure 4. Flight tracks over the Pacific Ocean and LA Basin colored by percent SO_2 of total sulfur (SO_2 + SO_4^{2-}) for three of the CARB flights and the transit flight from Palmdale, CA to Cold Lake, Canada. Data presented are those when pressure altitude is less than 2 km. The ratio of SO_2 to total sulfur can be used as proxy for aging. As SO_2 ages, it is oxidized to H_2SO_4.

SO_2 is emitted from ships and is oxidized over time. As the emission ages, the SO_2 percentage of total sulfur decreases. Measurements of total sulfur indicate that emission plumes are high in SO_2 directly off the coast of southern California.

Conclusions

Two independent measurements of SO_2 were obtained during the CARB intensive in June 2008. These measurements, coupled with measurements of SO_4^{2-}, enable the determination of total sulfur in the LA basin and offshore regions. From the CO_2 budget in the LA basin and the relationship between total sulfur and CO_2 in the LA basin, we estimate the sulfur emissions to the basin to be 6.2 x 10^7 g SO_2 day^{-1}. This estimate is consistent with the CARB 2006 inventory of 4.52 x 10^7 g SO_2 day^{-1}. Given the strict regulations on diesel fuel, on-road traffic accounts for a small fraction of the total sulfur. Biogenic emissions from the ocean is a negligible source. Ship emissions are significant, especially given the high average sulfur content in ship fuel. The pattern of ship emissions indicates a source of sulfur that is occurring in otherwise less polluted areas. Further work will include exploration of ship tracers as a means of clearly identifying sulfur emitted from sea-going vessels.

Acknowledgments

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References

CARB. Almanac Emission Projection Data. http://www.arb.ca.gov/app/emsinv/emssumcat_query, 2006.
CARB. Greenhouse Gas Inventory Data—1990 to 2004. Technical report, http://www.arb.ca.gov/cc/inventory/data/data.htm, 1990–2004.
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/DEMOGRAP/SDC/SDCProducts.php and http://quickfacts.census.gov/qfd/states/06000.html, 2003.
Entec UK Limited. European Commission: quantification of emissions from ships associated with ship movements between ports in the European Community. Final Report, London, UK, 2002.
Lu et al., Identification and characterization of inland ship plumes over Vancouver, BC. Atmospheric Environment, 20, 2767-2782, 2006.