

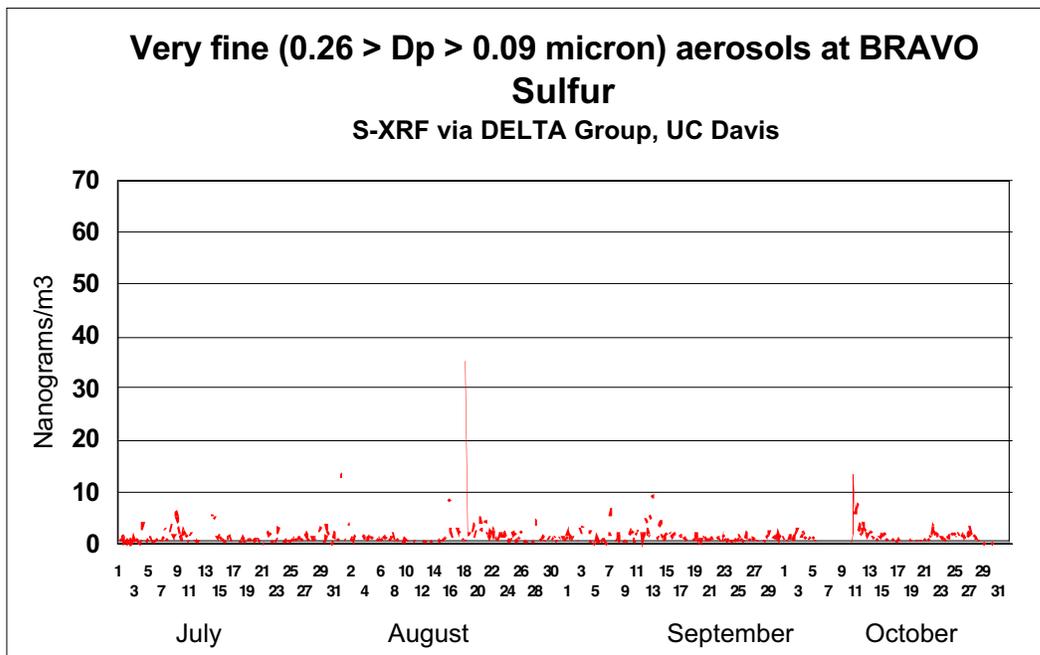
Very fine ($0.26 > D_p > 0.09 \mu\text{m}$) Silicon plus Sulfur as a Tracer of Coal Fired Power Plants during BRAVO

Thomas A. Cahill, Steve S. Cliff, Michael Jimenez-Cruz, Kevin D. Perry,
DELTA Group, University of California, Davis, and
Scott McHugo, Advanced Light Source, Lawrence Berkeley NL

Primary particles from high temperature sources tend to form very fine and ultra-fine particles that reflect the source materials (EPA 1996). Normally, very fine ($D_p < 0.26 \mu\text{m}$) and ultra fine ($D_p < 0.1 \mu\text{m}$) particles have a short life time due to high diffusion rates, but under cases, such as rapid dilution into the clean, dry conditions seen in the southwest US, they can persist and become an important component of the ambient aerosol (Cahill et al, 1993). Near Big Bend NP, there are many such potential sources including coal fired power plants and industrial sources in both the US and Mexico. Such large point sources, however, often produce relatively narrow plumes of aerosols that may affect a receptor site for a limited duration, requiring highly time resolved as well as size resolved data. In order to establish transport patterns into Big Bend NP during BRAVO, we initiated a study to collect and analyze very fine particles by size, time, and composition.

Particles were collected in an 8 stage rotating drum impactor (Raabe et al, 1988) modified to a slotted configuration and with cut points of 12 to 5, 2.5, 1.15, 0.75, 0.56, 0.34, 0.26, and $0.09 \mu\text{m}$ aerodynamic diameter (DELTA 8 DRUM). The flow was held at 10 L/min by the final slot which was a critical orifice. The rotation rate was 6 mm/day, which for 4 weeks gave 8 Apiezon greased Mylar strips each 168 mm long. The finest of these strips, representing particles $0.26 > D_p > 0.09 \mu\text{m}$, were analyzed on the DELTA Group synchrotron x-ray fluorescence (S-XRF) microprobe on ALS beam line 10.3.1. (Bench et al, 2002). The extremely high x-ray flux and 100% polarization allowed highly sensitive measurements of all elements sodium and heavier, to a few 10^3 's of pg/m^3 , although elements heavier than molybdenum and lighter than gold are often interfered with by more abundant light elements. The seven larger DRUM strips were archived.

The results for two of the most abundant elements, silicon and sulfur, are shown for August, 1999. Generally, the average concentrations of these particles are very low, ($\text{Si} = 0.14 \mu\text{g}/\text{m}^3$, $\text{S} = 1.88 \mu\text{g}/\text{m}^3$) with the very fine sulfur (presumably sulfate) a small fraction of $\text{PM}_{2.5}$ sulfate. However on occasion sharp increases in both Si and S occur, always in correlation ($r^2 = 0.95$ for August, for example). Comparison with high resolution $\text{PM}_{2.5}$ sulfate data show that on one occasion, August 18, there were three hours in which almost all the $\text{PM}_{2.5}$ sulfate was in the very fine size range. The silicon is not accompanied by other crustal elements (enrichment factor vs aluminum, ~ 20) but is probably derived from the same processes as the "large glassy plerospheres" long associated with coal fired power plants; $\text{SiO}_2 \rightarrow \text{SiO}$ in the reducing fuel rich region of combustion, followed by oxidation to SiO_2 in the flame and rapid condensation to very fine glassy mist that can form very fine particles, some of which agglomerate into the large "plerospheres". The sulfur in the largest peaks is probably H_2SO_4 , based on hydrated droplets seen even after vacuum, which argues against long range transport.



HYSPLIT4 (NOAA ARL READY 2002) isentropic backward trajectory analysis was performed at 500, 1000, and 2000 m AGL for these events and shows that the largest of these events in early and late August occur on slow southeast winds up the Rio Grande Valley, in many cases passing within a few kilometers of the Carbon II power plant. HYSPLIT analysis was also used to study the vertical stability of the atmosphere and examine the conditions under which the elevated plume could ventilate down to ground level. It is unlikely that these very fine particles could long survive in high humidity conditions such as over the Gulf of Mexico or the eastern US. On one occasion, and only for one hour, August 4, 11 AM, we saw a complex mixture of very fine elements, a plume containing a complex mixture of elements Si, S, Ca, Fe, As, K, Cu, Zn, and Se, the latter 7 elements missing from the typical pure Si/S plumes. We interpret this as indicating an additional high temperature source or sources that, from trajectory analysis, could be the city of Monterrey, Mexico.

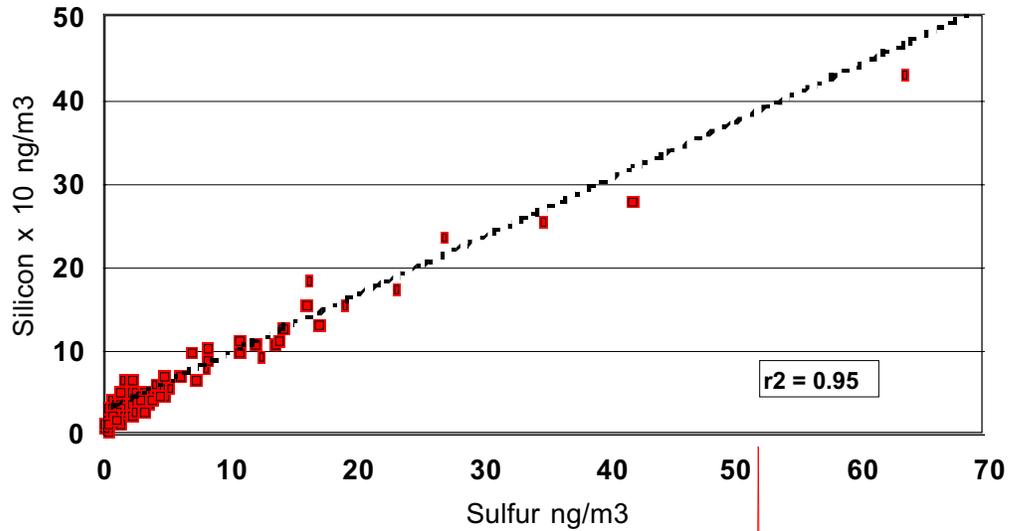
The high $PM_{2.5}$ sulfate episodes of September and October did not have strong Si/S signatures. Thus, if they were from coal fired power plants, they were much farther away than Carbon II or the meteorology had changed and resulted in destruction of the very fine plume, perhaps by particle growth in high humidity. The latter explanation is less plausible than the former since the silicon, almost certainly in non-hydrophilic glassy particles, was also missing from the aerosol.

In summary, we propose that if very fine and highly correlated Si/S is present, without other trace elements, coal power plant influence is assured. Absence of these particles does not, however, infer no power plant influence, as these very fine particles would not survive long range transport in humid conditions.

Very fine ($0.26 > D_p > 0.09$ micron) Aerosols during BRAVO

UCD DELTA Group S-XRF of DRUM Samples

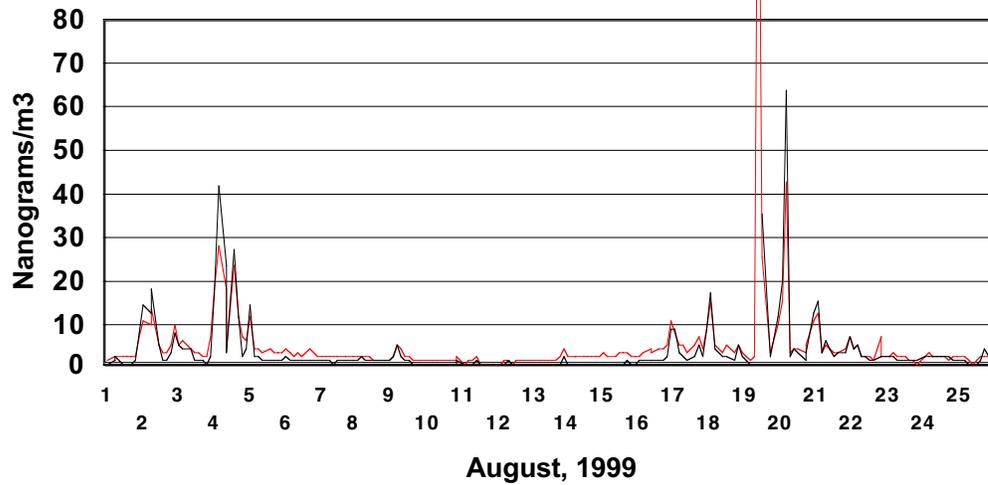
August, 2000



Very Fine ($0.26 > D_p > 0.09$ micron) Aerosols at BRAVO

UCD DELTA Group S-XRF of DRUM Impactor Samples

— Silicon x 25 — Sulfur



References

- Barone, J.B., T.A. Cahill, R.A. Eldred, R.G. Flocchini, D.J. Shadoan, and T.M. Dietz. A multivariate statistical analysis of visibility degradation at four California cities. *Atmospheric Environment*. 12:2213-2221 (1978).
- Graham Bench, P.G. Grant, D. Ueda, S.S. Cliff, K.D. Perry, and T. A. Cahill. The use of STIM and PESA to respectively measure profiles of aerosol mass and hydrogen content across Mylar rotating drum impactor samples. (2002) *Aerosol Science and Technology* 36:642-651.
- Braaten, D.A. and T.A. Cahill. Size and composition of Asian dust transported to Hawaii. *Atmospheric Environment* (Great Britain). 20:1105-1109 (1986).
- Cahill, Thomas A. Comments on surface coatings for Lundgren-type impactors. *Aerosol Measurement*. Dale A. Lundgren, Editor. University Presses of Florida, Pp. 131-134 (1979).
- Buser, Michael D., Thesis, Inherent Errors Associated with EPA's Particular Matter Regulation Guidelines when Applied to Rural Sources, Texas A& M (2002).
- Cahill, T.A. Proton microprobes and particle-induced x-ray analytical systems. *Annual Reviews Nuclear and Particle Science*. 30:211-252 (1980).
- Cahill, T.A., B.H. Kusko, L.L. Ashbaugh, J.B. Barone, R.A. Eldred, and E.G. Walther. Regional and local determinations of particulate matter and visibility in the southwestern United States during June and July, 1979. Symposium on Plumes and Visibility. Grand Canyon, AZ, 1980. *Atmospheric Environment*. 15:2011-2016 (1981).
- Cahill, T.A., C. Goodart, J.W. Nelson, R.A. Eldred, J.S. Nasstrom, and P.J. Feeney. Design and evaluation of the drum impactor. *Proceedings of International Symposium on Particulate and Multi-phase Processes*. Teoman Ariman and T. Nejat Veziroglu, Editors. Hemisphere Publishing Corporation, Washington, D.C. 2:319-325. (1985).
- Cahill, Thomas A., Marcelle Surovik, and Ian Wittmeyer. Visibility and aerosols during the 1986 carbonaceous species methods comparison study. *Aerosol Science and Technology*. 12:149-160 (1990).
- Cahill, Thomas A. and Paul Wakabayashi. Compositional analysis of size-segregated aerosol samples. Chapter in the ACS book *Measurement Challenges in Atmospheric Chemistry*. Leonard Newman, Editor. Chapter 7, Pp. 211-228 (1993).
- Cahill, Thomas A., Kent Wilkinson, and Russ Schnell. Composition analyses of size-resolved aerosol samples taken from aircraft downwind of Kuwait, Spring, 1991. *Journal of Geophysical Research*. Vol. 97, No. D13, Paper no. 92JD01373, Pp. 14513914520, September 20 (1992).

T.A. Cahill, P. Wakabayashi, T. James. Chemical State of Sulfate at Shenandoah National Park During Summer 1991 *Nuclear Instruments and Methods in Physics Research B: Beam Interactions with Materials and Atoms*, 109/110 (1996) 542-547.

EPA/600/P-95/001aF, Volume 1, 6-177 to 6-206 (1996)

Feeney, P.J., T.A. Cahill, R.G. Flocchini, R.A. Eldred, D.J. Shadoan, and T. Dunn. Effect of roadbed configuration on traffic derived aerosols. *Journal of the Air Pollution Control Association*. 25:1145-1147 (1975).

Flocchini, Robert G., Thomas A. Cahill, Danny J. Shadoan, Sandra J. Lange, Robert A. Eldred, Patrick J. Feeney, Gordon W. Wolfe, Dean C. Simmeroth, and Jack K. Suder. Monitoring California's aerosols by size and elemental composition. *Environmental Science and Technology*. 10:76-82 (1976).

Hering, Susanne V., Bruce R. Appel, W. Cheng, F. Salaymeh, Steven H. Cadle, Patricia A. Mulawa, Thomas A. Cahill, Robert A. Eldred, Marcelle Surovik, Dennis Fitz, James E. Howes, Kenneth T. Knapp, Leonard Stockburger, Barbara J. Turpin, James J. Huntzicker, Xin-Qui Zhang, and Peter H. McMurry. Comparison of sampling methods for carbonaceous aerosols in ambient air. *Aerosol Science and Technology*. 12:200-213 (1990).

Malm, W.C., Sisler, J.F., Huffman, D., Eldred, R.A. and Cahill, T.A.. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research*, VOL. 99, No. D1, 1347-1370, January 20, 1994

Motallebi, Nehzat, Robert G. Flocchini, Leonard O. Myrup, and Thomas A. Cahill. A principal component analysis of visibility and air pollution in six California cities. *Atmosfera*. Pp. 127-141 (1990).

Devel. of a Modular System for Acidic Deposition Monit., Contr.No.A132-102, July,1993

Perry, Kevin D., Thomas A. Cahill, Russell C. Schnell, and Joyce M. Harris. Long-range transport of anthropogenic aerosols to the NOAA Baseline Station at Mauna Loa Observatory, Hawaii. 1999 *Journal of Geophysical Research Atmospheres*. Vol. 104, No. D15, Pages 18,521-18,533.

Perry, Kevin, Cahill, T.A., Eldred, R. A., Dutcher, D.D, Gill, T.E. Long-range transport of North African dust to the eastern United States. 1996 *Journal of Geophysical Research-Atmospheres*, 102, D10, 11,225-11,238.

Raabe, Otto G., David A. Braaten, Richard L. Axelbaum, Stephen V. Teague, and Thomas A. Cahill. Calibration Studies of the DRUM Impactor. *Journal of Aerosol Science*. 19.2:183-195 (1988).