CARBOXYLIC ACIDS, SULFATES, AND ORGANOSULFATES IN PROCESSED CONTINENTAL ORGANIC AEROSOL OVER THE SOUTHEAST PACIFIC OCEAN DURING VOCALS-REX 2008

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Hawkins et al., 2009, in prep.
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AIR MASS SECTORS BY RADON

HYSPLIT 3-day back trajectories (50 masl, 100 masl, and 500 masl)

- **High radon**, recent (< 3 days) continental contact
- **Intermediate radon**
- **Low radon**, > 3 days continental contacts

For radon, see Bates et al., 2008 and references therein
REPORTED SIGNATURES OF FINE PARTICLE SOURCES IN SANTIAGO, CHILE

Particles < 2 µm were analyzed for black carbon and elemental concentrations

- Copper smelting, coal combustion, residual oil combustion
  - sulfur (as $\text{SO}_2$ oxidized to $\text{SO}_4^{2-}$), vanadium, and nickel
- Transportation (buses, cars, etc.)
  - potassium, bromine, and tin
- Resuspended soil dust (“direct traffic emissions are generally mixed with soil dust”)
  - calcium and iron

Artaxo et al., 1999
PM$_1$ generally follows radon
AMS SO$_4^{2-}$ and FTIR OM show similar time trends
AMS OM does not
REDUCED COLLECTION EFFICIENCY (CE) OF ORGANICS ON REFRACTORY PARTICLES (DUST)

Estimated AMS CE of organics = 42%
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Sulfate varied from acidic (no ammonium) to bisulfate.

Estimated AMS CE of sulfate = 100%

Slope = 0.93, r = 0.98
SINGLE PARTICLE MEASUREMENTS FROM STXM-NEXAFS (X-RAY MICROSCOPY)

Below 0.7 µm, “dustlike” particles are 80% dust on average.

Takahama et al., 2007;2009
CONTINENTAL SOURCE OF PM$_1$ TO THE VOCALS STUDY REGION

Positive correlations with radon imply continental source

No (v. weak inverse) correlation with radon implies marine source

Aiken et al., 2007;2008
Low rate of oxidation is consistent with low $O_3$ (25 +/- 4 ppb average, compare to 75 ppb EPA 8-hour standard) measured on board the RHB (away from Santiago).
ORGANOSULFATE FORMATION: TRENDS WITH SO$_4^{2-}$/NH$_4^+$ AND RH

Surratt et al., 2007a,b; Altieri et al., 2009
ORGANOSULFATE FORMATION:
TRENDS WITH $\text{SO}_4^{2-}/\text{NH}_4^+$ AND RH

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Acid-catalyzed reaction

Defined as AMS $\text{SO}_4^{2-}/\text{NH}_4^+$
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Continental outflow of organic, sulfate, and dust components is main PM$_1$ source.

Santiago (and similar cities) are large contributors.

Aging in continental air masses was slow (low ozone).

Organosulfate increases with organics, sulfate, and acidity and decreases with RH.

CONCLUSIONS FROM RHB AEROSOL CHEMISTRY