## National Oceanic and Atmospheric Administration





## Regional Aerosol Properties: Shipboard Intensives and Long-term Measurements

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## PMEL Atmospheric Chemistry Data Server: Shipboard Measurements

http://saga.pmel.noaa.gov/data/



## **Project/Cruise: ICEALOT 2008**

#### ACTION

Plot Time or Space Series

Plot One Variable vs. Another

Download data file

View Parameter Info

Plot Particle Size Distributions

Aerosol Chemistry

Distributions

Plot Radiosonde Data

Go to Another Cruise

- •VESSEL: R/V Knorr
- •DEPARTED: Woods Hole,

Massachusetts on 19 March, 2008

- •ARRIVED: Tromso, Norway on 12 April 2008
- •DEPARTED: Tromso, Norway on 13 April 2008
- •ARRIVED: Reykjavik, Iceland on 24 April 2008
- <u>Link to more</u> ICEALOT 2008 pages



http://saga.pmel.noaa.gov/data/

Shipboard Data Available for Download

http://saga.pmel.noaa.gov/data/

Aerosol

- Chemical composition
  - Impactors (2 or 7 stage) inorganic ions, OC, EC, trace elements, mass
  - AMS NR SO4, NO3, NH4, POM
- Number concentration
- Size distribution
- Optical properties (sub 1 um and sub 10 um)
  - Scattering, backscattering, and absorption at 3 wavelengths
- CCN concentration
- Optical Depth
- Gas phase
  - DMS, SO2, O3
- Seawater
  - DMS
- Met parameters



## PMEL Atmospheric Chemistry Data Server: Station Measurements

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## Comparison of measured and modeled (STEM) concentrations from INDOEX, ACE-Asia, and ICARTT



Model was driven by analyzed met data and sampled at the times and locations of the measurements every 30 min along the cruise track.

• Best agreement was found for submicron SO4 due to accuracy in emissions, chemical conversion, and removal.

• Underestimation of supermicron sea salt most likely due to errors in emissions.

Bates et al., ACP, 2006

Use of field measurements to parameterize the impact of particulate organic matter on the relative humidity dependence of light scattering



$$\gamma_{s} = \ln \left( f \sigma_{sp} \left( RH, RH_{ref} \right) \right) / \ln \left( \frac{100 - RH_{ref}}{100 - RH} \right)$$
$$F_{o} = POM / \left( POM + SO4 \right)$$

$$\gamma_s = 0.9(\pm 0.003) - 0.6(\pm 0.01)F_o$$

Quinn et al., GRL, 2005.

## Humidity Dependence of Light Extinction and Aerosol Age



Quinn et al., JGR. 2006

## 2006 TexAQS: Effect of Organics on CCN Activation



Increasing mass fraction of HOA leads to an increase in the critical diameter for particle activation

Quinn et al., ACP, 2008

# Decadal trends in aerosol chemical composition at Barrow, AK: 1976 - 2008

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#### nss Sulfate 1.8 nss $SO_4^{\text{F}}$ , ug m<sup>-3</sup> Nitrate nss Potassium 1.2 -MSA 0.6 0.0 0.20 -<sup>(\*)</sup> E 0.15 -<sup>(\*)</sup> 0.10 -<sup>(\*)</sup> 0.05 -0.00 80x10<sup>-3</sup> 80x10<sup>-3</sup> nss K<sup>+</sup>, ug m<sup>-3</sup> MSA, ug m<sup>-3</sup> 60 -60 40 -40 20 20 0 0 1/98 1/99 1/00 1/01 1/02 1/03 1/04 1/05 1/06 1/07 1/08 • nss $SO_4^{=}$ , $NO_3^{-}$ , nss $K^+ \rightarrow$ long range transport • MSA $\rightarrow$ local biogenic production

## Seasonality of Aerosol Composition at Barrow (1997 – 2008)

Aerosol tracer species measured at Barrow during the past 30 years

Species	Winter/Spring Source	Summer Source	Measured 1976 - 1977?	Measured 1997 – 2008?
Non-seasalt $SO_4^=$ (nss $SO_4^=$ )	Fossil fuel combustion	DMS (biogenic)	Yes	Yes
Non-crustal <sup>*</sup> Vanadium (nc V)	Mid-latitude combustion of heavy residual oil		Yes	Yes (2003 – 2008)
Non-crustal <sup>*</sup> Manganese (nc Mn)	Iron, steel, and ferro-alloy mfg, coal and oil combustion, mining		Yes	Yes (2003 – 2008)
Methanesulfonic acid (MSA)		DMS (biogenic)	No	Yes

\* Excess V or Mn above that due to crustal rock

Comparison of monthly averaged values of nss  $SO_4^=$  and nc V 1976 – 1977 vs. 1997 - 2008



## nss $SO_4^=$ and nc V averaged over the haze season (Jan – Apr): Then and Now



• Linear regression of concentrations averaged over the haze season reveals a 60% decrease over the past 30 years for both species Haze season ratio of nss SO<sub>4</sub><sup>=</sup> to nc V as a tracer for mid-latitude pollution

nss SO<sub>4</sub>= / nc V secondary / primary component



• Ratios within the Arctic were over an order of magnitude larger than those measured in midlatitude source regions

 N. Norway was mid-way between mid-latitude and Arctic sites

• Higher Arctic ratios were attributed to oxidation of mid-latitude SO<sub>2</sub> while enroute to Barrow resulting in an aged version of mid-latitude aerosol Haze season ratio of nss  $SO_4^{=}$  to nc V as a tracer for mid-latitude pollution: Then and Now



• Concentrations of nss SO<sub>4</sub>= and nc V have decreased but the ratio has not changed significantly

- Emissions are decreasing
- Measuring the same source as 30 years ago.

## Winter time ratio of particulate nc Mn to nc V as a regional tracer



## Winter time ratio of particulate nc Mn to nc V as a regional tracer



(1985).

## Ratio of nc Mn to nc V as a regional tracer Then and Now



• 2003 – 2008 Barrow ratios are consistent with those from 1976 – 1978.

• The nc Mn / nc V ratio has remained the same at Barrow and distinct from the Norwegian Arctic.

• Emissions in the source regions to the Arctic have decreased over the past 3 decades but source regions themselves have not changed. Changes in aerosol composition at Barrow during the haze season: 1997 - 2008



• Concentrations of nss  $SO_4^=$ have decreased by about 2% per year over the past decade – consistent with 1976 – 2008 trend.

• Concentrations of  $NH_4^+$ have decreased by 6% per year over the same time period.

- Why the difference?
  - Data show both components are decreasing in source regions to the Arctic
  - Emissions for Russia and EU as used in EMEP models show  $SO_x$ decreasing faster than  $NH_4^+$  between 1997 and 2008.

Changes in aerosol composition at Barrow during the haze season: 1997 - 2008



•  $NH_4^+$  / nss  $SO_4^=$  molar ratio has decreased by about 6% per year.

• The mid-latitude aerosol reaching the Arctic during the haze season is becoming more acidic.



Changes in aerosol composition at Barrow during the haze season: 1997 - 2008



CI<sup>-</sup> / Na<sup>+</sup> ratio is decreasing
3% per year. Why?

• The decreasing NH<sub>4</sub>+/nss SO<sub>4</sub>= molar ratio results in an increasingly acidic anthropogenic aerosol that is available to react with sea salt in the Barrow boundary layer.

• The less neutralized SO<sub>4</sub><sup>=</sup> aerosol transported to Barrow may be resulting in more HCI displacement from the sea salt aerosol.

- Reduction in VOC lifetimes including CH4
- Impact reactions that produce and destroy O3
- Increase the production of highly reactive CI containing gases other than HCI such as CINO2

Changes in aerosol composition at Barrow during the summer: 1997 - 2008



• Over the past decade, there has been a 12% per year increase in MSA during the summer months

• And an 8% per year increase in SO<sub>4</sub>=

• Why?

Methanesulfonic acid in a Svalbard ice core as an indicator of ocean climate

O'Dwyer et al., GRL, 2000

"MSA may be a useful proxy for past climate."

Ocean climate may be an indicator of current and future aerosol composition (biogenic, anyway).



Flexpart-predicted SO<sub>2</sub> and Measured SO<sub>4</sub><sup>=</sup> at Barrow



SO<sub>2</sub> is overpredicted relative to SO<sub>4</sub><sup>=</sup> by about an order of magnitude
Still, this level of agreement in trends of predicted SO<sub>2</sub> and measured SO<sub>4</sub><sup>=</sup> says Flexpart is getting transport to Barrow right.







#### EDGAR Map: Sulphur oxide (SO2)



## Predicted SO<sub>2</sub> for January and February 2005



What fraction of  $SO_4^{=}$  is due to transport from Norilsk vs. other sources?

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• NOAA PMEL Atmospheric Chemistry Group data can be found at:

http://saga.pmel.noaa.gov/data/

• Empirical parameterizations for relating f(RH) to composition are available in

Quinn et al., GRL, 2005; Quinn et al., JGR, 2006

• We have a great interest in combining data with models to explain seasonality of Barrow data as well as sources and decadal scale trends.

