

Background and Scientific Objectives

Reasons why you should go to the Amazon in 2014.

And bring good ideas.

And bring lots of equipment.

1. 2014 is different than 2008

Still ideal lab for natural SOA + anthropogenic interactions and fires

2. SOA production rate and yield

3. SOA anthropogenic-biogenic synergism

4. Modern carbon

5. Aqueous phase organic chemistry

6. New particle formation and growth

7. Photochemistry of SOA precursors

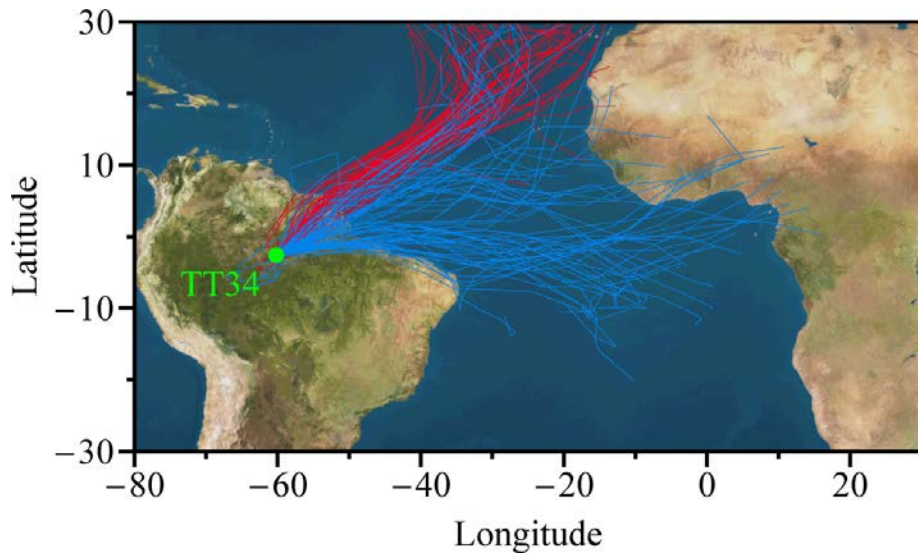
plus aerosol hygroscopicity, CCN, optical properties, budgets, size distributions

plus all the things that the aerosol – cloud interaction group will talk about



Pollution from Manaus not measured in AMAZE-08

Ten-day Back-Trajectories during AMAZE-08



Red: 200 m. **Blue:** 4000 m. Package: HYSPLIT
February 7 – March 14, 2008

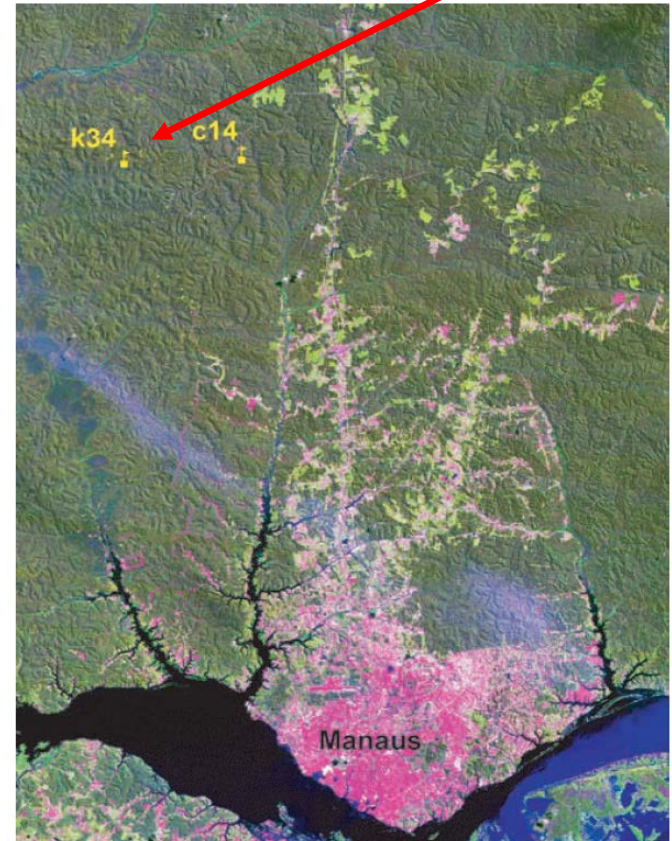
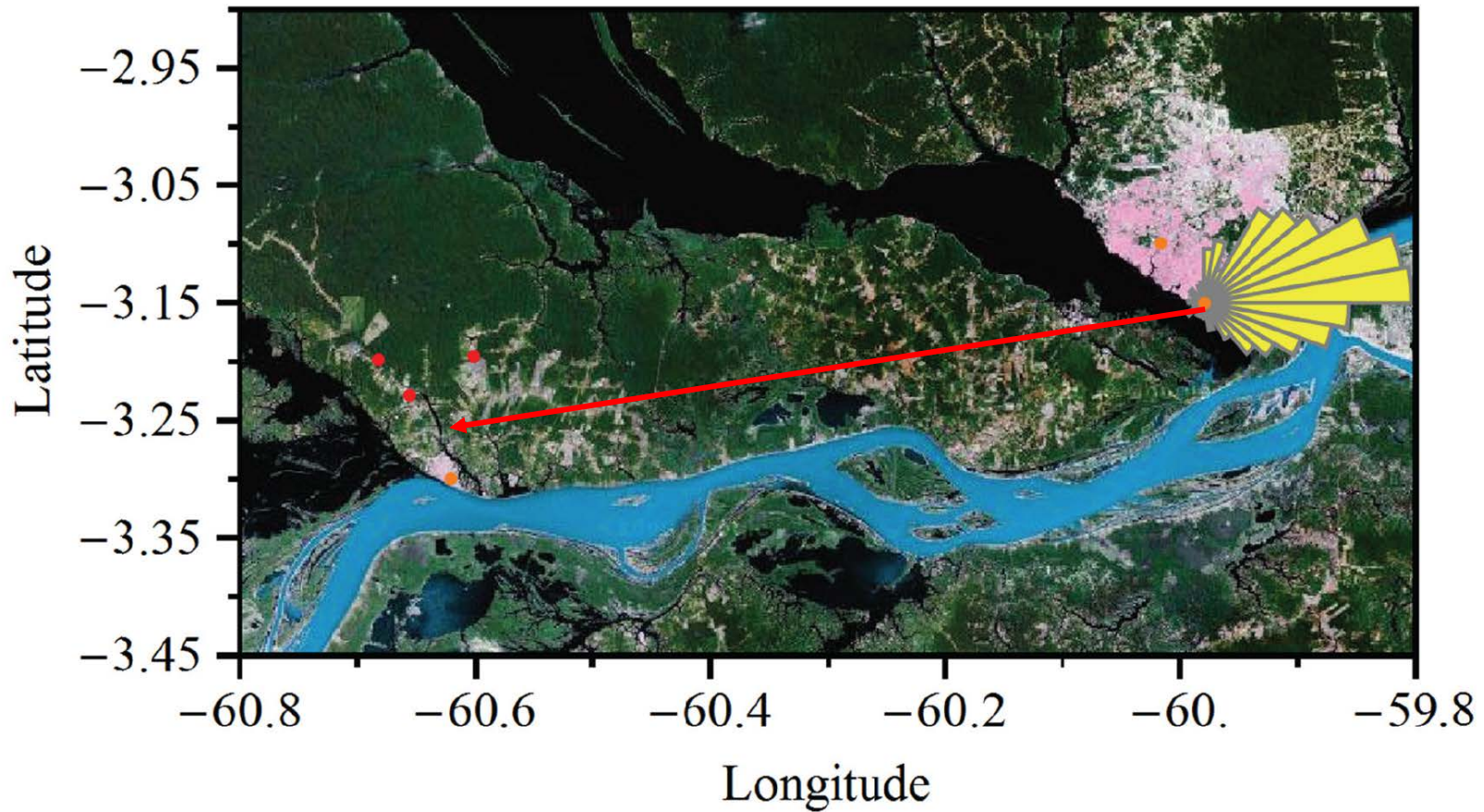


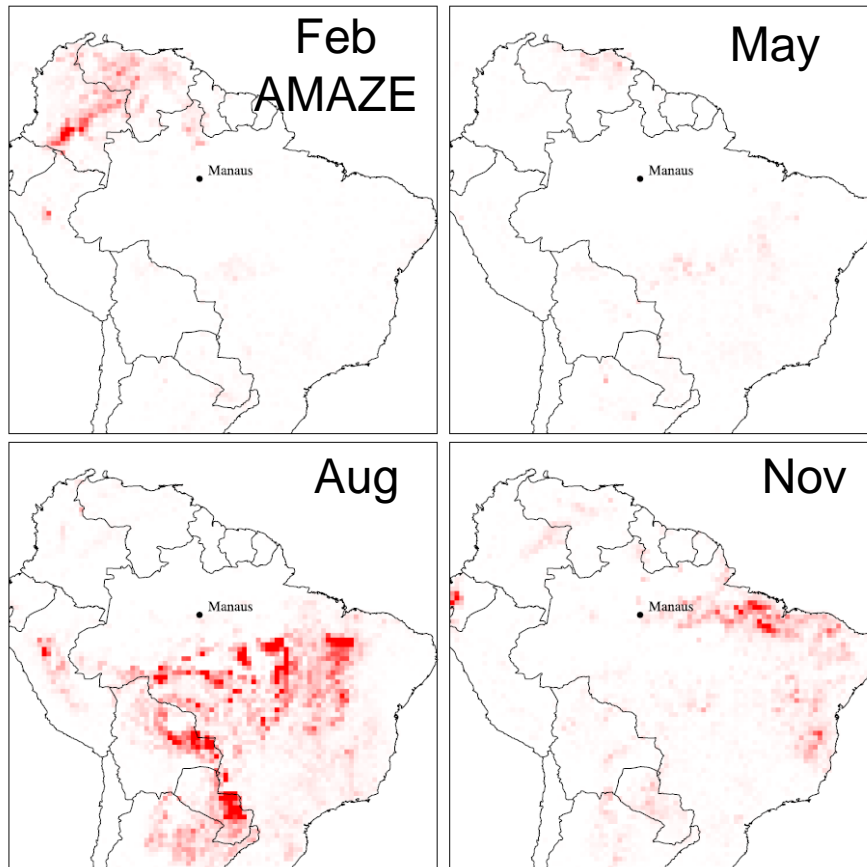
Figure 4. Satellite image showing Manaus, the Reserva Biológica do Cuieiras, and the location of the measurement towers (Landsat TM image courtesy of S. Bergen).

Downwind Site will be in and out of Manaus Plume

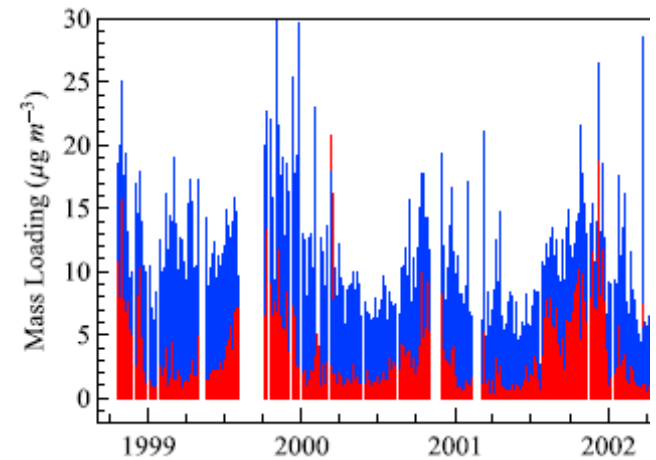


Biomass Burning Low During AMAZE - 08

MODIS Fire Counts, 2007



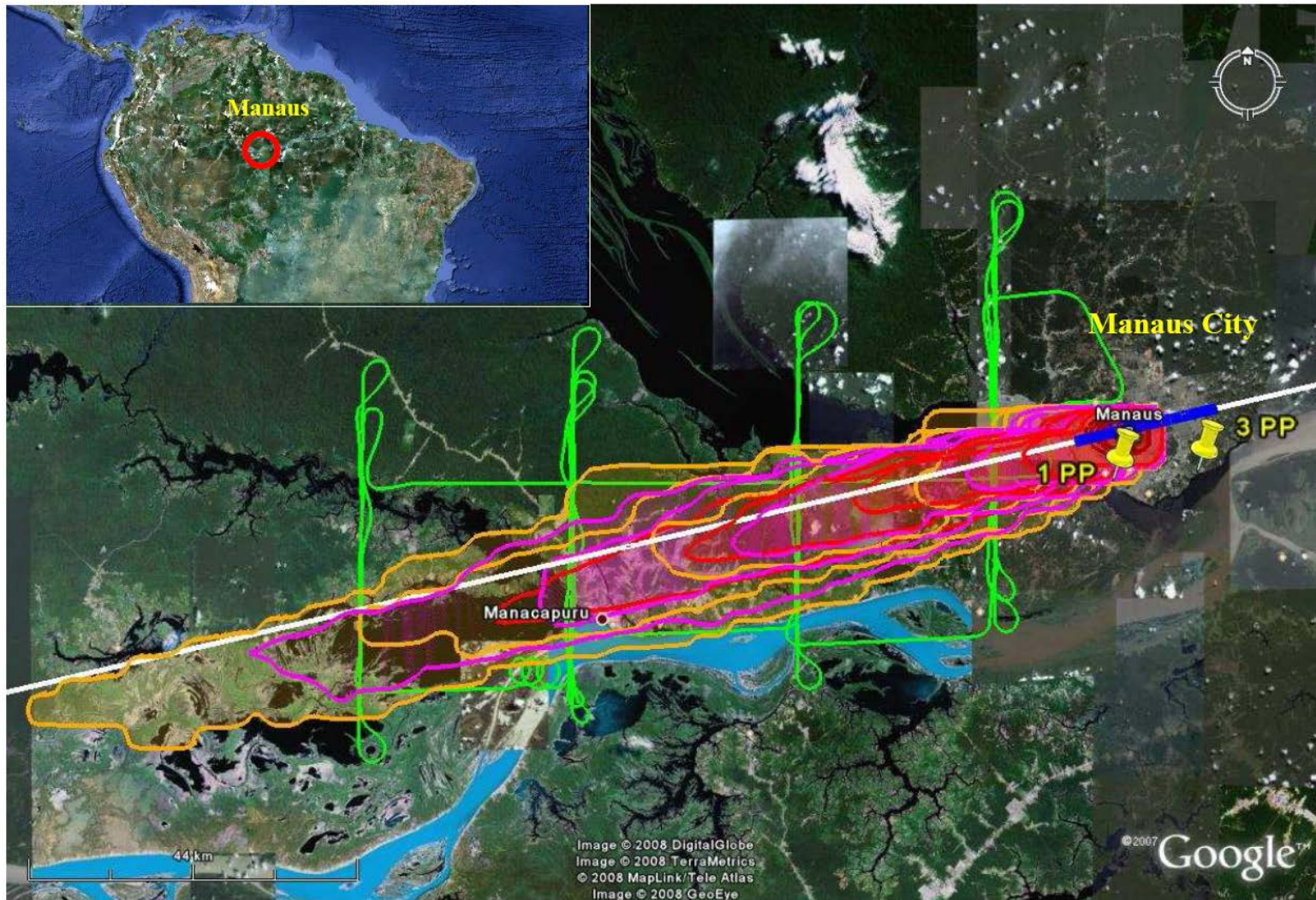
Balbina (N of Manaus)
Fine, Coarse Mode



**Fine Mode greatest
in Dry Season Aug – Dec**

**Lower wet deposition
Dilute fire plumes**

Time Evolution of Manaus Plume

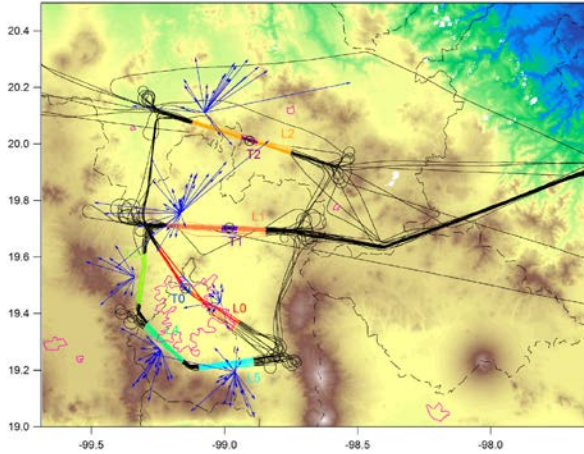


Kuhn et al., ACP 2010
from LBA-CLAIRE-2001

2. SOA production and yield

Aerosol Aging in Mexico City

G-1 flight tracks



Aerosol from AMS, DMA, PCASP

Restrict data to BL urban plume

CO as tracer of urban emissions

Photochemical age = $-\text{Log}_{10}(\text{NO}_x/\text{NO}_y)$
can also use VOC ratios or aerosol O/C

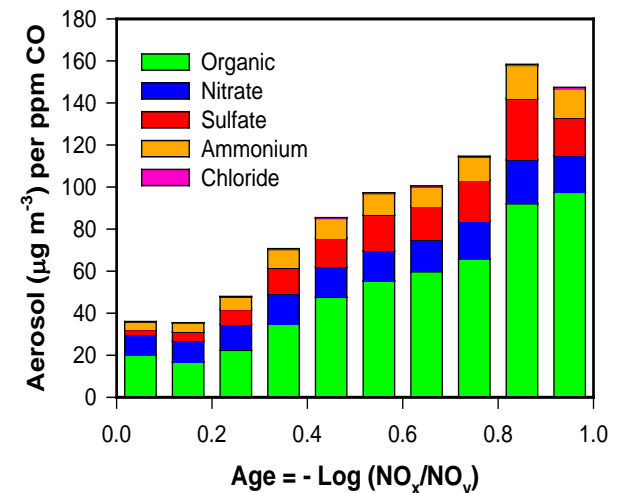


Normalize results to CO to account for dilution

Regression slope of Aerosol vs. CO



**Aerosol / (ppm urban CO)
as a function of photochem age**



Kleinman et al., ACP, 2008 (composition)
2009 (size distribution)

2. SOA production and yield

SOA Anthropogenic - Biogenic Synergism

Effect of biogenic on anthro. OR anthropogenic on bio?

Suppose downwind of Manaus $[OA]/[CO] = 200 \text{ ug/m}^3$ per ppm CO
Mexico City, Atlanta, NE US ~ 80

Are previous urban values dependent on biogenic emissions?

Is there anything special about Manaus $[VOC]/[CO]$?

Is this just a gas - volume partitioning effect?

Effect of NO_x or oxidants on chemistry?

Is “extra” SOA biogenic or anthropogenic?

AMS spectra, precursors, diurnal patterns, calculations?

What else besides the gold standard, ^{14}C ?
which has never fulfilled its potential!

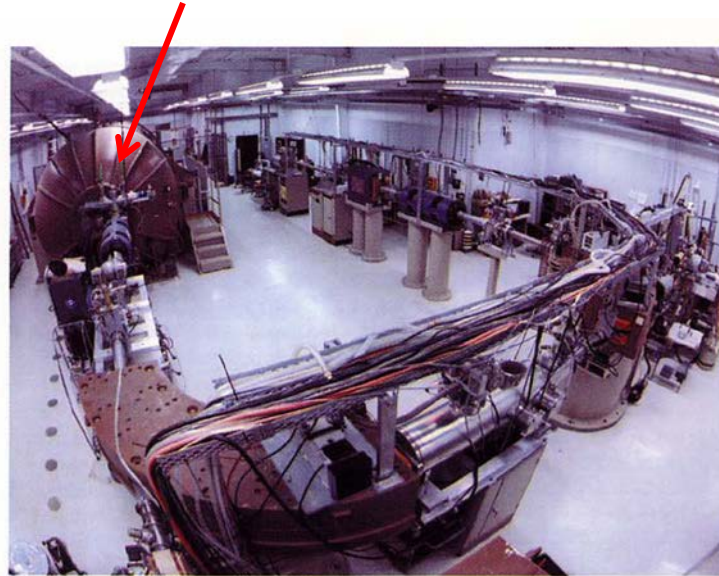
How to do a ^{14}C measurement

Get Stuff from Basement + Tandem Van de Graff accelerator

Enclosure for 2 hi-vol samplers



Pump



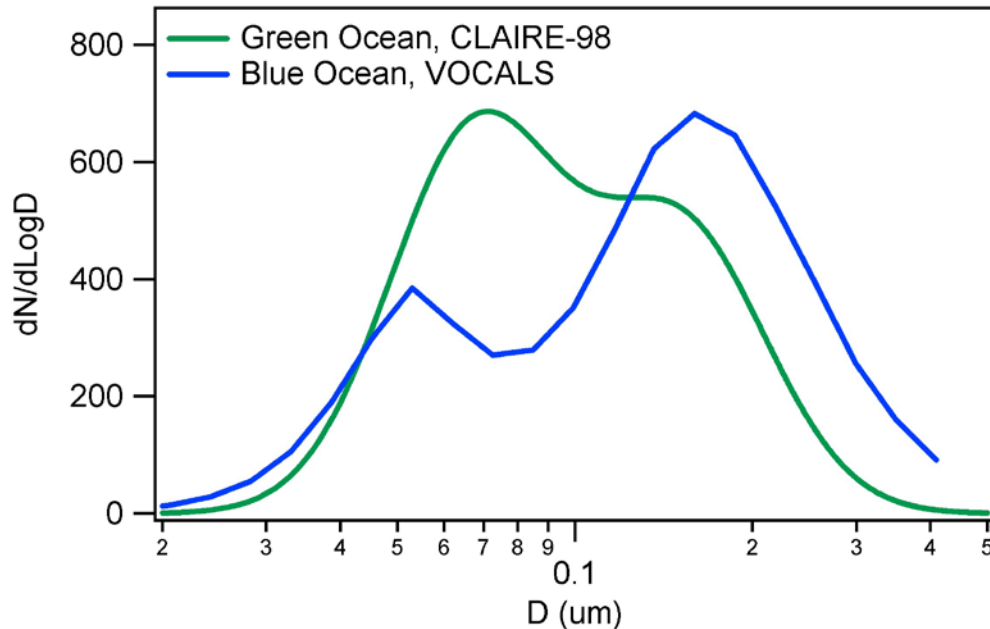
Lawrence Livermore National Laboratory's high-energy spectrometer and particle counter.

**Samples typically collected for 12 hours to days
Need 40 ug C for analysis**

Need time resolution to see ^{14}C correlations!!!

**Switch between Filter A and Filter B according
to anthropogenic tracer**

Aerosol Size Distribution suggests Aqueous Phase Chemistry



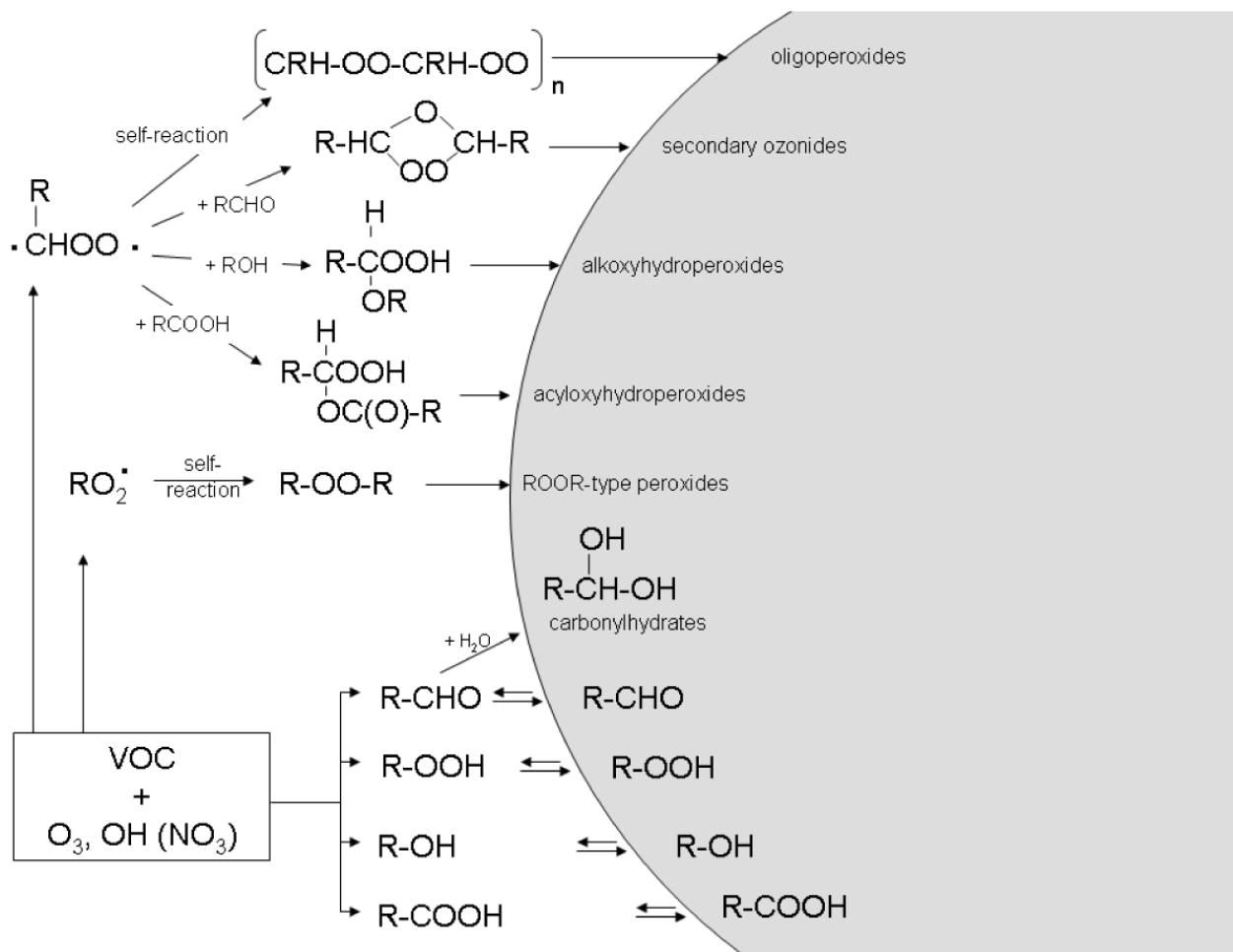
Hoppel minimum in VOCALS (Pacific Ocean) due to aqueous phase oxidation of SO_2 in accumulation mode particles that become CCN.

Similar minimum observed in Amazon “**Green Ocean**” studies

Quantify composition differences between Aitken and Accumulation modes in Amazon. **It is not sulfate.**

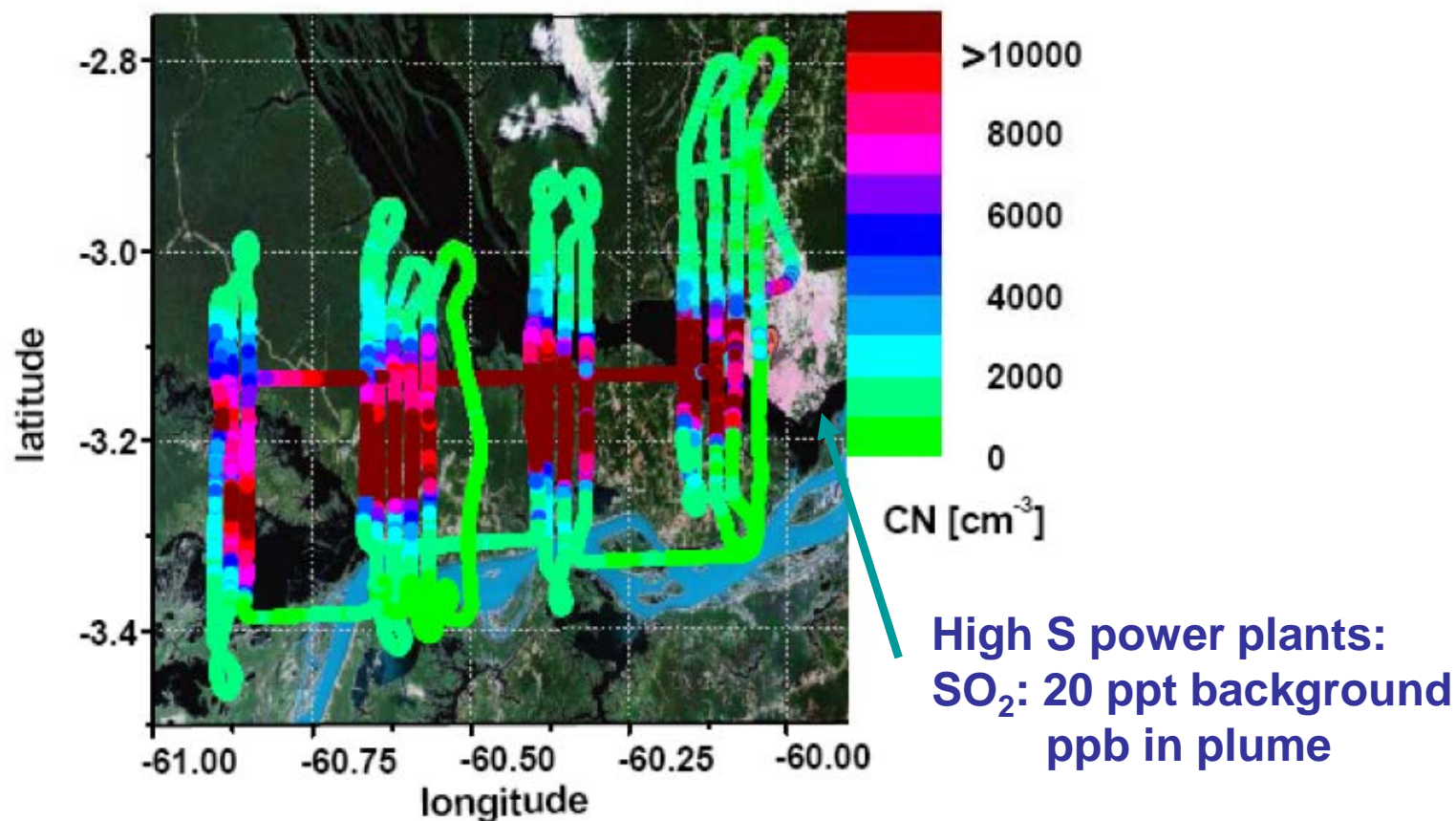
Atmospheric Chemistry of Plant Emissions

Formation of Condensable Organic Material



Adapted from Fig.7 of Hallquist et al., *Atmos. Chem. Phys.*, 9, 5155-5236, 2009.

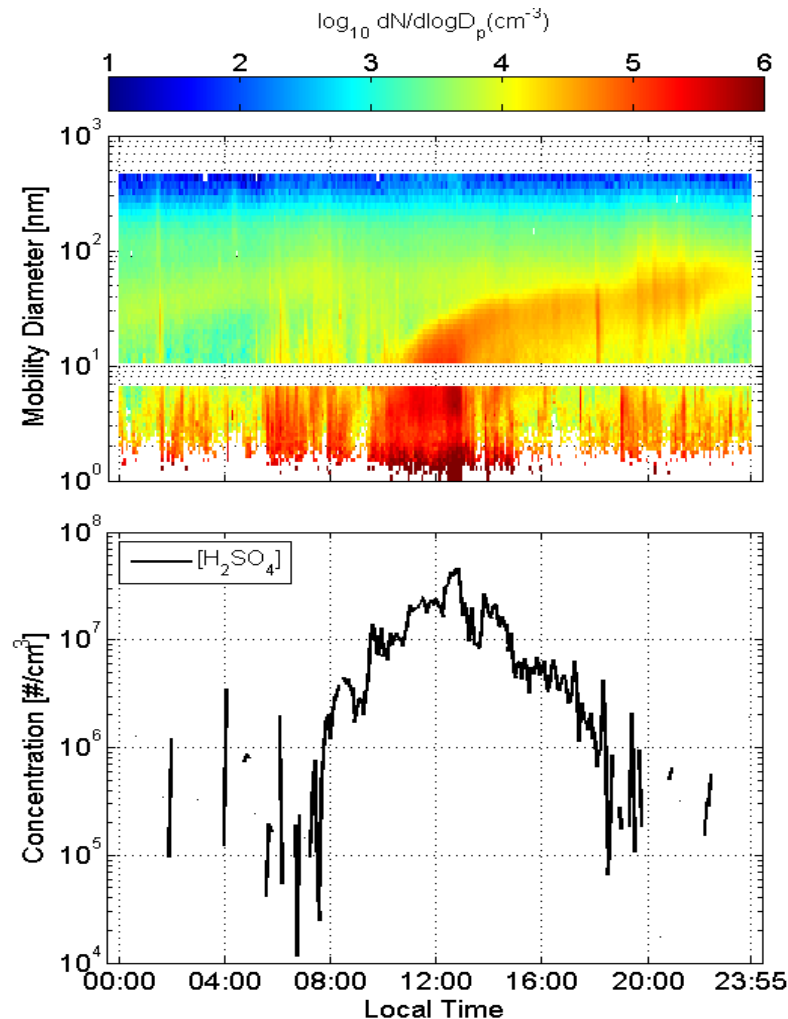
CN are $\sim 300 \text{ cm}^{-3}$ outside Manaus plume (**Green Ocean**)
 $\sim 30,000$ in plume



Kuhn et al., ACP 2010
from LBA-CLAIRE-2001

6. New particle formation and growth

NO New Particle Formation in AMAZE-08 BUT Amazon 2014 is an interesting venue to study NPF



NPF usually requires some S
Background S very low in 2008

2014 site will be in and out of
high S Manaus plume

Establish threshold S for NPF

Establish dependence of particle
growth on precursors

Chongai Kuang (BNL), Jun Zhao (NCAR),
Peter McMurry (U. Minn), Jian Wang (BNL)
Measurements at Boulder with 1nm nano-SMPS

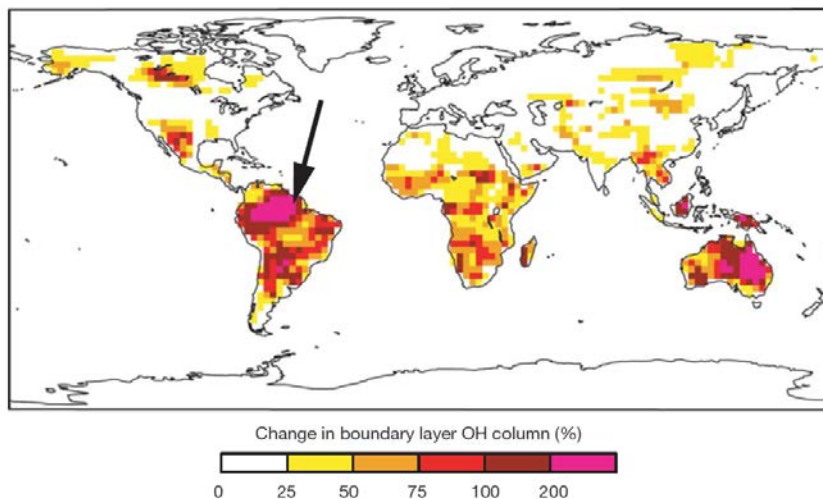
6. New particle formation and growth

Photochemistry forms SOA precursors: Some puzzles

On to gases:

Too much OH

- 1 OH + Isoprene yields OH
- 2 nighttime OH
- 3 Too much OH reactivity
sesquiterpenes?
- 4 NO₂/NO ratio too high
- 5 HO₂ (RO₂) too high at high NO



Lelieveld et al., Nature, 2008

too high means higher than models. sometimes constraints such as $P(O_3) \Delta T \gg \Delta O_3$

Manaus is an Ideal Place to use Photochemical Age for OH

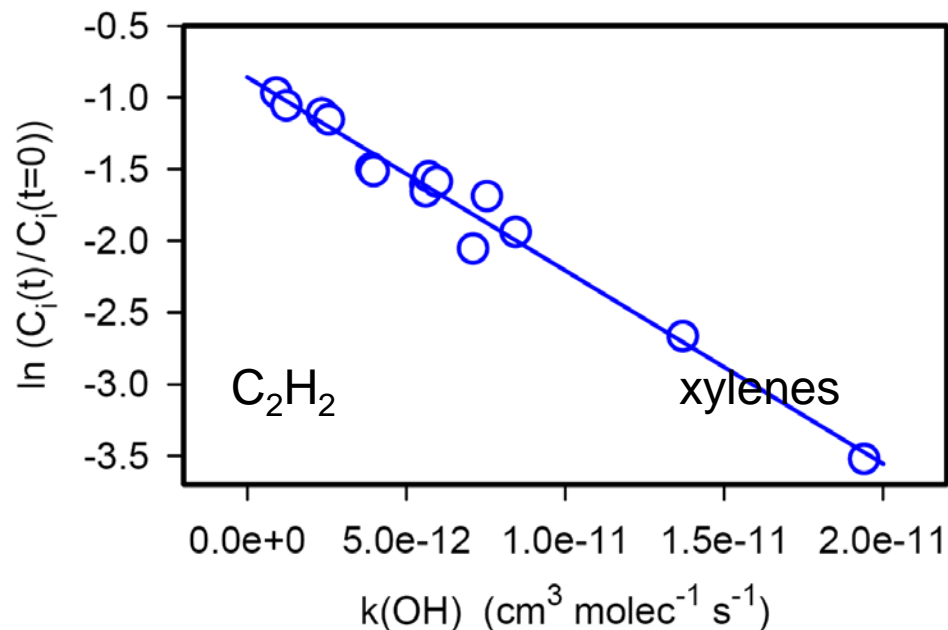
Manaus is like a point source

Spread in air mass travel time small: $|k_i - k_j| [\text{OH}] \Delta t < 1$.

No anthropogenic sources downwind to “reset photochemical clock”



Ratio: [Downwind] / [City] for 15 HCs. Phoenix, 1998



HCs decay from dilution and reaction with OH

Slope \rightarrow photochemical age = $\Delta\text{time} * [\text{OH}]$

Δtime from winds \rightarrow Avg. $[\text{OH}]$

Test of Isoprene + OH chemistry without measuring OH

Kleinman et al., Photochemical age ..., JGR (2003)

7. Photochemistry of SOA precursors

SOA Precursors – New Technology



from Yin-Nan Lee's laboratory

High resolution PTR-MS,
ARRA funding – part of MAOS

Deployment to Summer IOP at BNL
then to GEVAX

Can resolve isobaric VOCs. i.e.
distinguish oxygenated from HCs

**Many good ideas in community for
measuring IVOCs**

7. Photochemistry of SOA precursors

ACRF Deployment and Extras

Surface

- T0 300m tower upwind of Manaus (Mainz, Brazil)
- T1 Center of Manaus
- T2 Western edge: AOS instruments
- T3 70 km downwind: MAOS

Air

G-1, Bandeirante

Manaus plume, unperturbed forest, transition

Within BL, lower free troposphere

Clear air and cloud missions