What have learned from Atmospheric Mass Spectrometry

(1 nanometer to 1 micron)

Douglas R. Worsnop

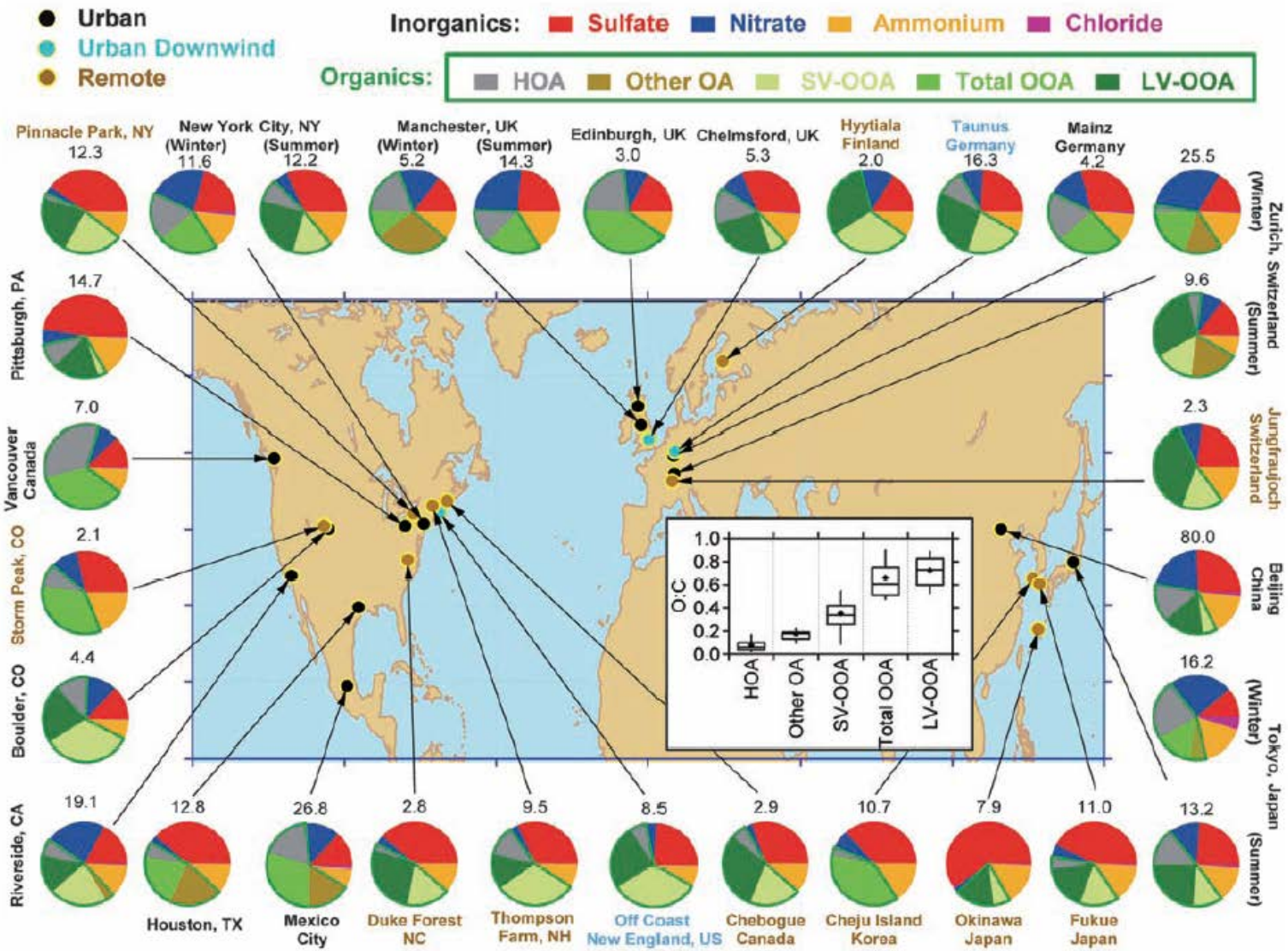
and many collaborators

DoE ASR

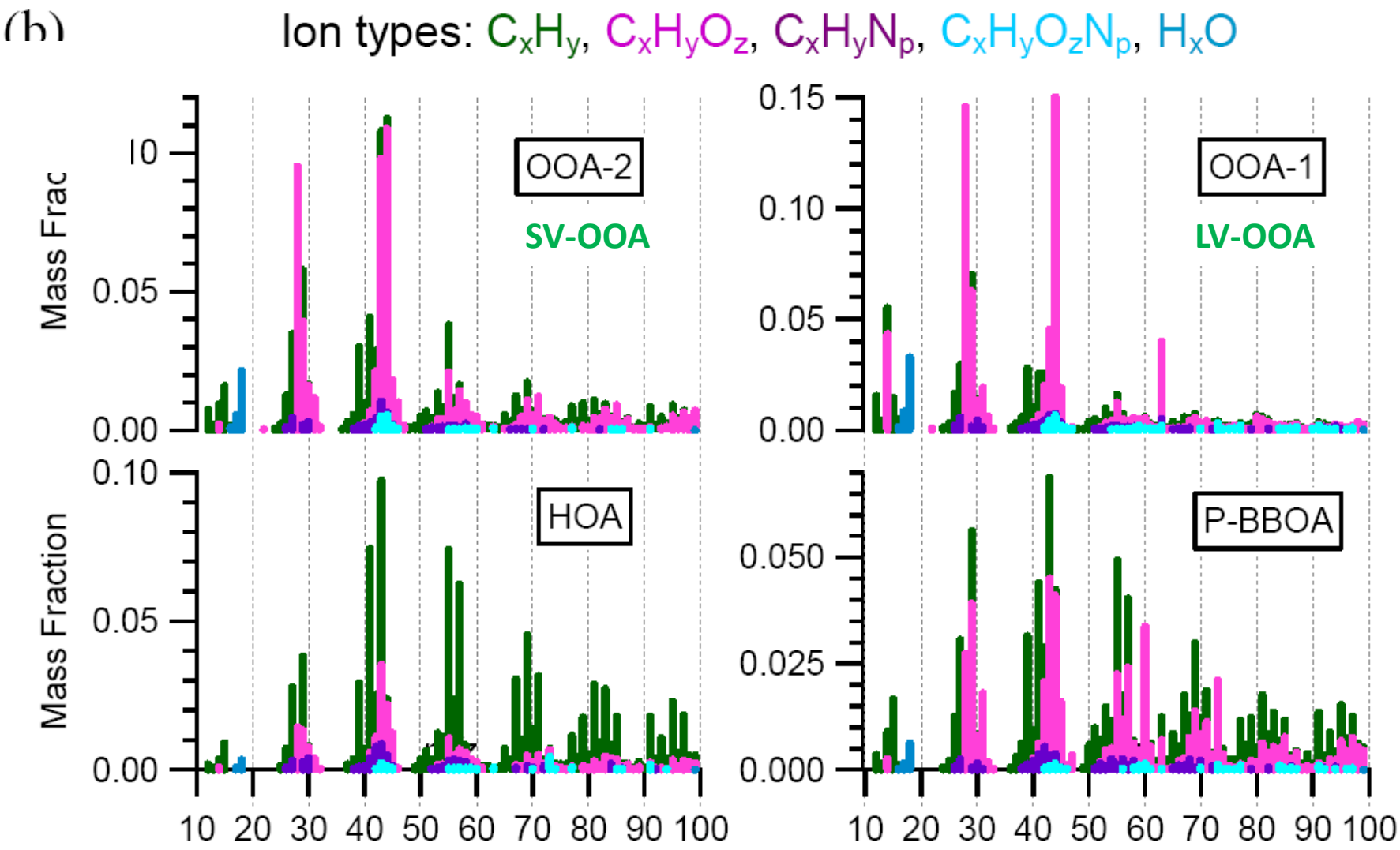
18 March 2015

Inorganic (SO4,NO3) ~ Organic (OOA)

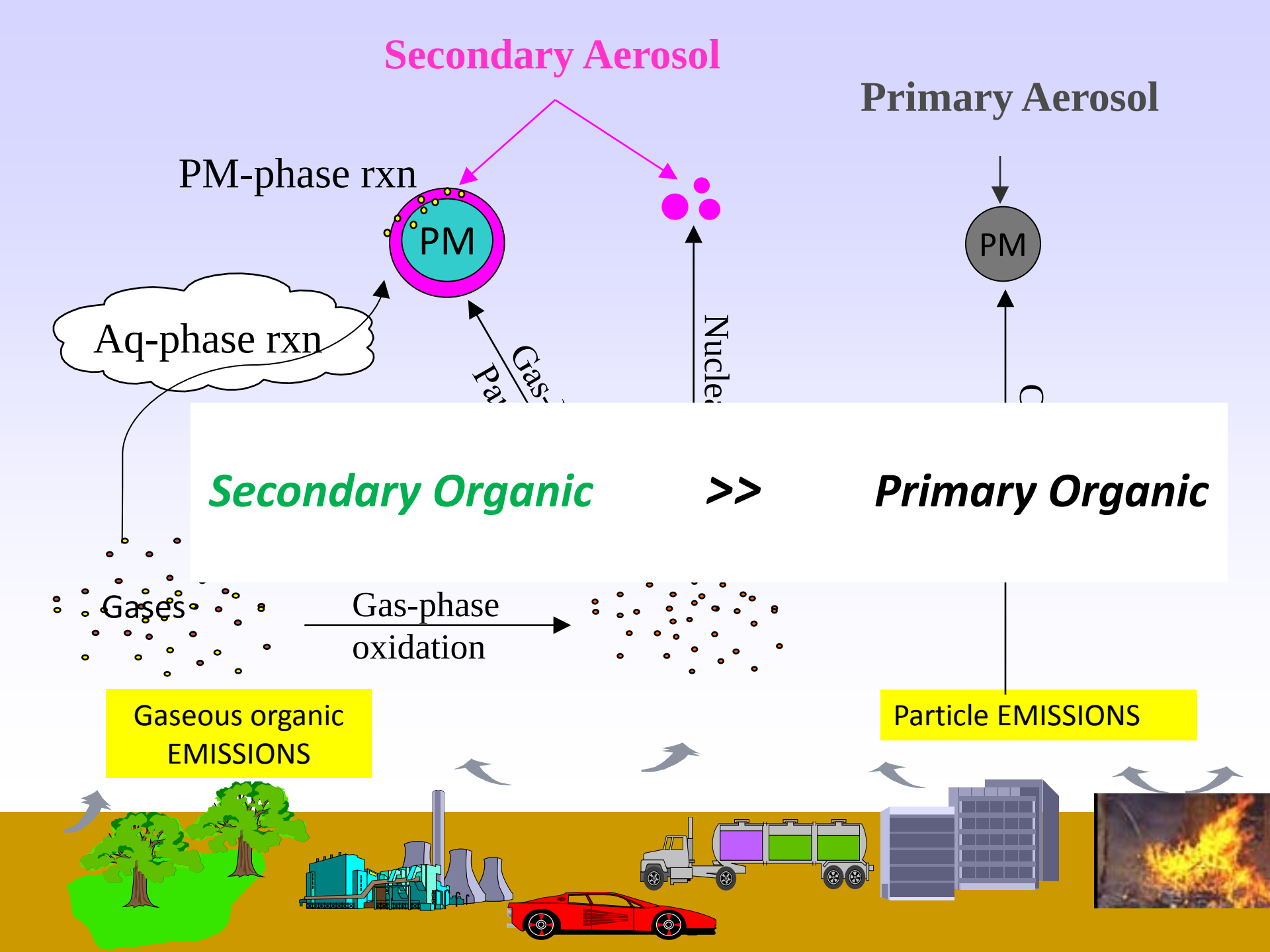
O/C ~ 0.7



Jimenez et al, Science, 2009

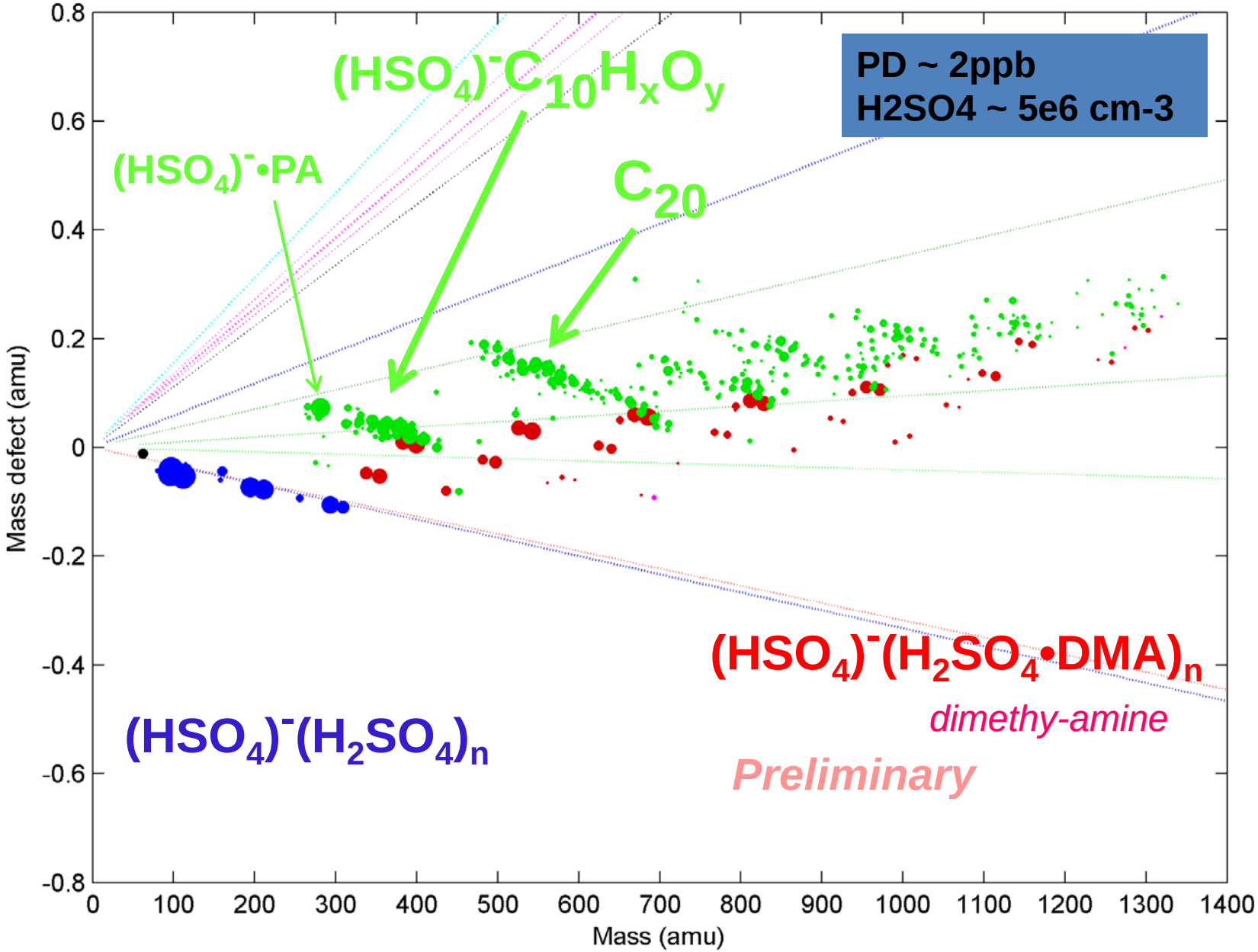


Aiken, DeCarlo & Jimenez, *Anal Chem*, 2007
Aiken et al, *ES&T*, 2008


Secondary Aerosol
Primary Aerosol
PM-phase rxn
PM
PM
Aq-phase rxn
Secondary Organic >> Primary Organic
Gases
Gas-phase oxidation
Gaseous organic EMISSIONS
Particle EMISSIONS

Primary Emission		Secondary Formation
SO_2	→	H_2SO_4
		one compound
VOC	→	OOA
"Volatile Organic Compounds"		*"Oxygenated Organic Aerosol"*
		10,000's compounds

Nucleation and Clusters at the CLOUD Experiment in CERN



Siegfried Schobesberger et al, PNAS, 2013

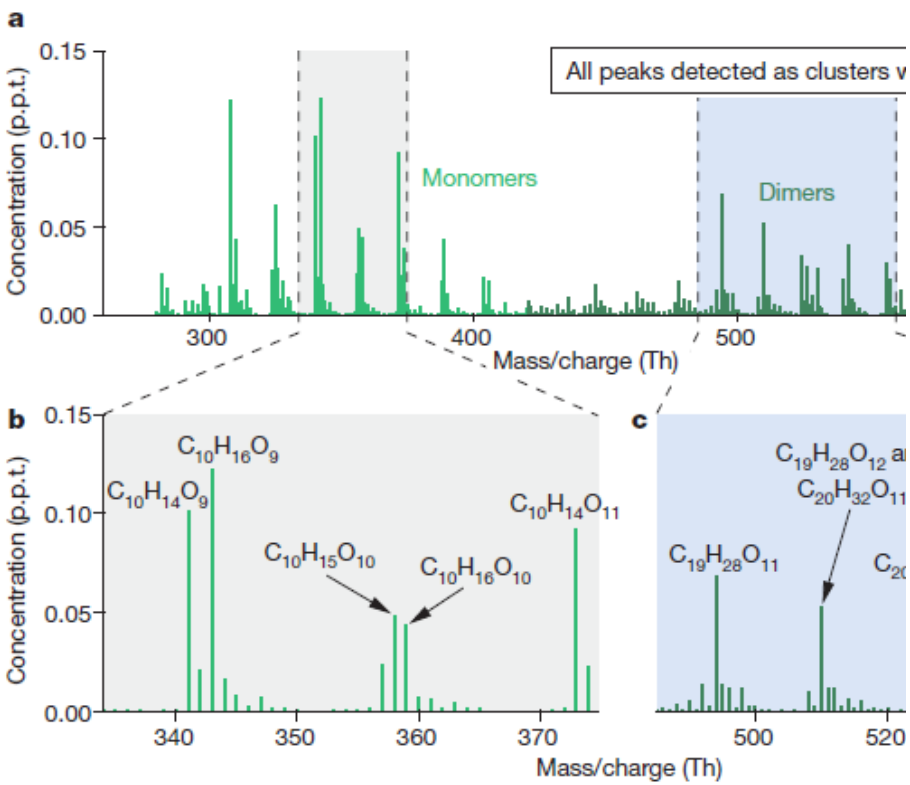
476 | NATURE | VOL 506 | 27 FEBRUARY 2014

LETTER

doi:10.1038/nature13032

A large source of low-volatility secondary organic aerosol

Mikael Ehn[1,2], Joel A. Thornton[2,3], Einhard Kleist[4], Mikko Sipilä[2], Heikki Junninen[2], Iida Pullinen[1], Monika Springer[1], Florian Rubach[1], Ralf Tillmann[1], Ben Lee[3], Felipe Lopez-Hilfiker[3], Stefanie Andres[1], Ismail-Hakki Acir[1], Matti Rissanen[2], Tuija Jokinen[2,5], Siegfried Schobesberger[2], Juha Kangasluoma[2], Jenni Kontkanen[2], Tuomo Nieminen[2,6], Theo Kurtén[7], Lasse B. Nielsen[8], Solvejg Jørgensen[8], Henrik G. Kjaergaard[8], Manjula Canagaratna[9], Miikka Dal Maso[10], Torsten Berndt[5], Tuukka Petäjä[2], Andreas Wahner[1], Veli-Matti Kerminen[2], Markku Kulmala[2], Douglas R. Worsnop[2,9], Jürgen Wildt[4] & Thomas F. Mentel[1]



ELVOC

C10,C20 in the gas phase

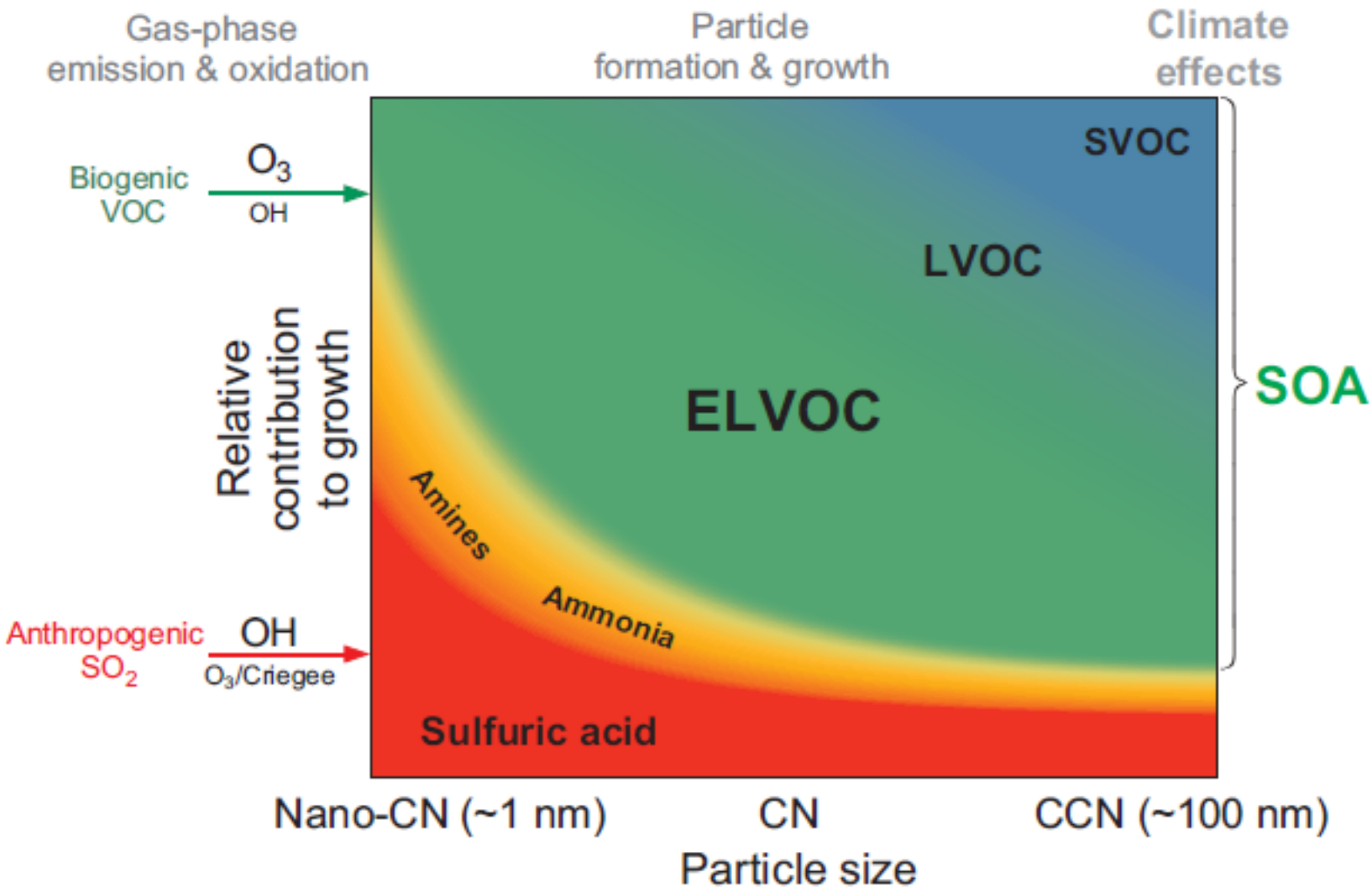
O/C > 0.7

Nucleation, Clusters

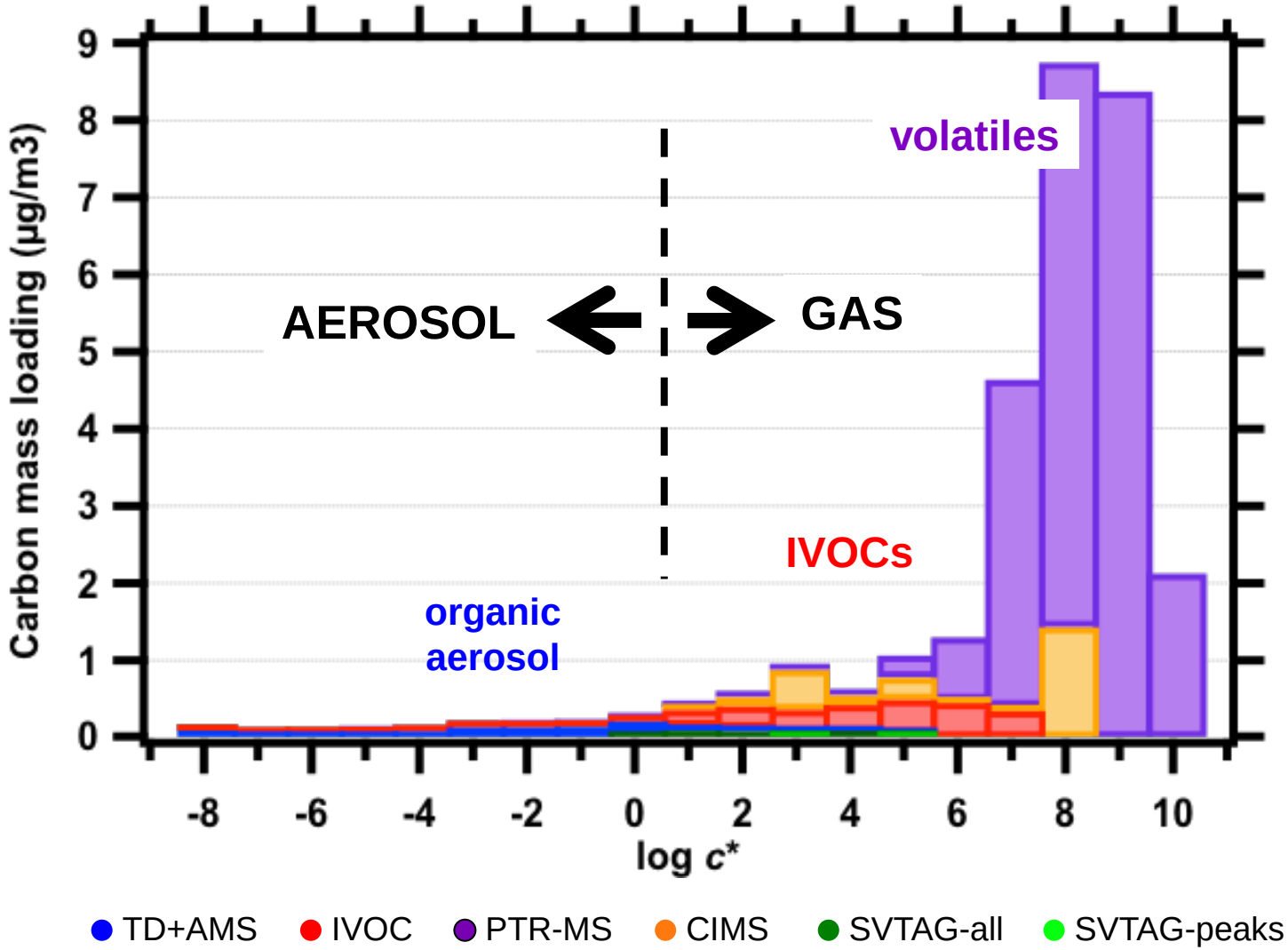
Nanoparticle growth

Nucleation **Growth** **CCN**

1 nm → **~100 nm**



Increasing Volatility →



VOCs >> IVOCs > OA

Jesse Kroll, MIT

Instrumentation developed via DoE SBIR program

Q-AMS, ToF-AMS, ACSM, SP-AMS, ToF-CIMS, FIGAERO SV-TAG, TOC, VAPS, CAPS

MILAGRO, CARES, BBOP, GO-Amazon, BBOP, BAECC

also CalNex, BEACHON, SOAS and many more

Aerodyne Research

Boston College

University of Colorado

UC Berkeley

Aerosol Dynamics

University of Helsinki

University of Washington

Washington University

Caltech

MIT

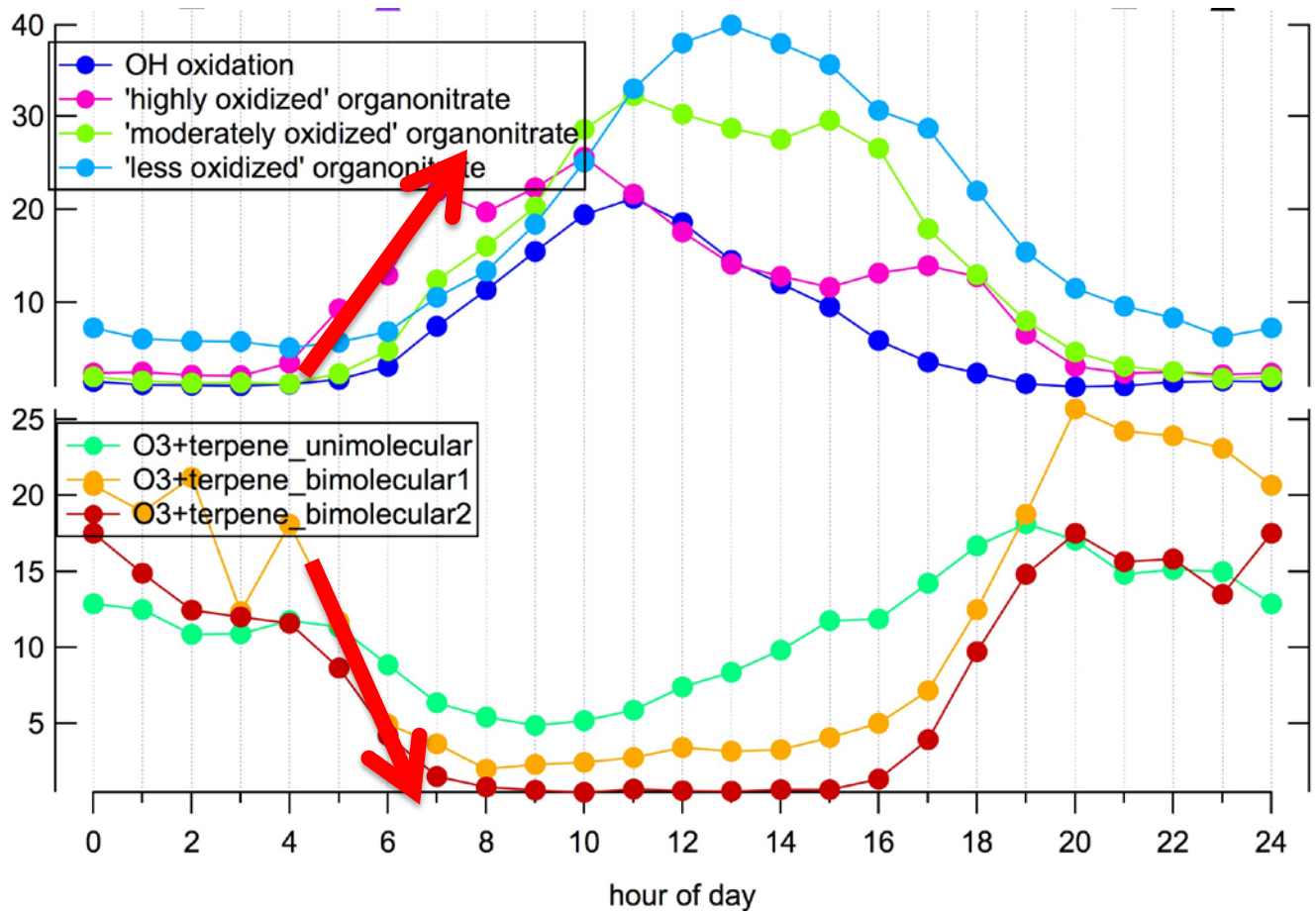
Droplet Measurement Technology

Hyytiälä *NO_3- ToF-CIMS*
PMF Mass Spectral Factors

NO increases

DAY

NIGHT



C10H15O9N
C10H15O10N
C10H15O11N

H2SO4

C10H16O9
C10H16O10
C10H14O11

a-pinene + O3, OH, NO → ELVOC

Global ‘trace gas’ concentrations

H2O	**10,000 ppm**
CO2	**400 ppm**
CH4	**2 ppm**
O3	**50 ppb**
VOC’s	**1->10 ppb**
Aerosol	**1 ppb**
oVOC’s	**1-100ppt**
ELVOC	**1 ppt**
H2SO4	**0.1 ppt**
OH	**0.1 ppt**

Equivalent Climate Impact

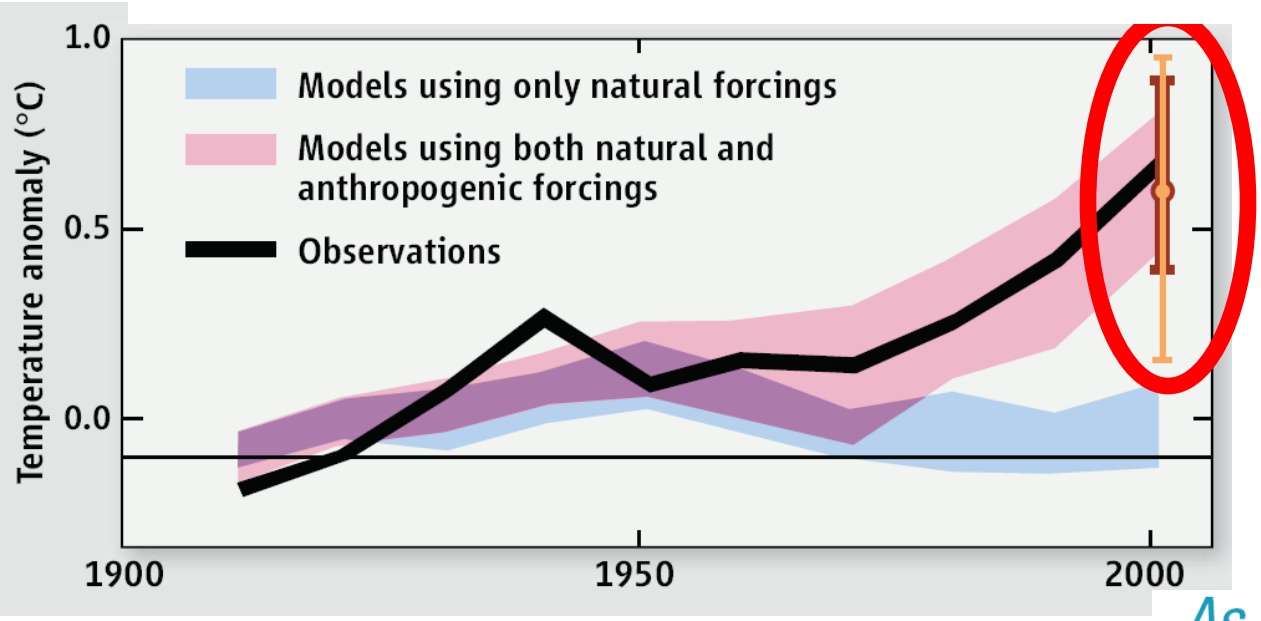
Aerosol Life Cycle required to predict aerosols (clouds) in Current, Past and Future Atmosphere

nature reports climate change | VOL 2 | JULY 2007 |

COMMENTARY

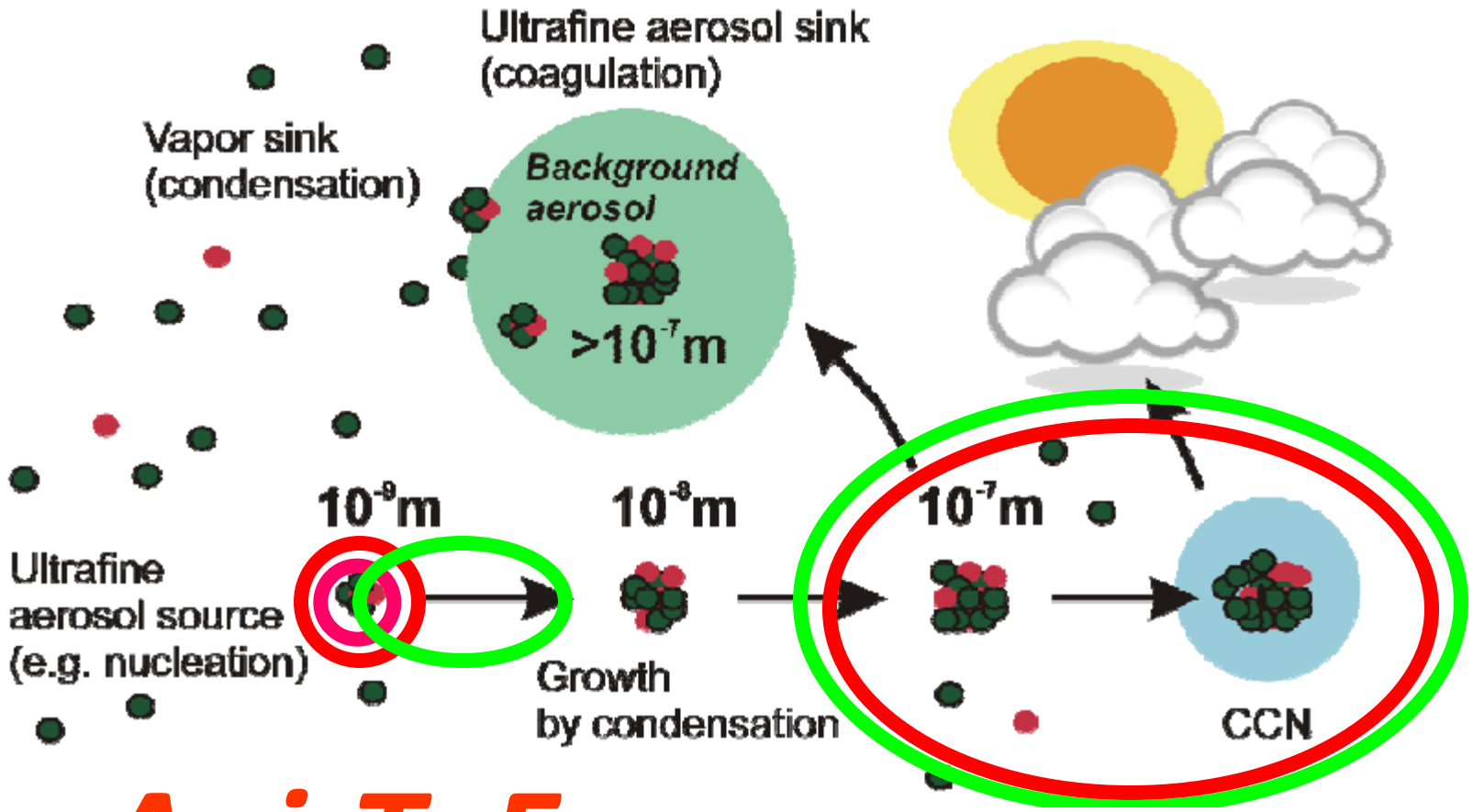
Quantifying climate change — too rosy a picture?

STEPHEN E. SCHWARTZ[1], ROBERT J. CHARLSON[2] AND HENNING RODHE[3]



As it stands, the narrow range of modelled temperatures gives a false sense of the certainty that has been achieved.

< ppt → ppt → ppb (ppm)



Api-ToF-CIMS

AMS

Ilona Riipinen et al

ARTICLE

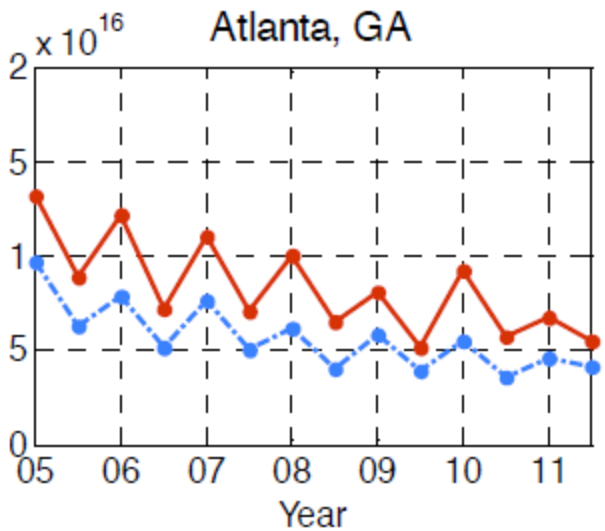
doi:10.1038/nature12674

Large contribution of natural aerosols to uncertainty in indirect forcing

K. S. Carslaw[1], L. A. Lee[1], C. L. Reddington[1], K. J. Pringle[1], A. Rap[1], P. M. Forster[1], G. W. Mann[1,2], D. V. Spracklen[1], M. T. Woodhouse[1]†, L. A. Regayre[1] & J. R. Pierce[3]

The effect of anthropogenic aerosols on cloud droplet concentrations and radiative properties is the source of one of the largest uncertainties in the radiative forcing of climate over the industrial period. This uncertainty affects our ability to estimate how sensitive the climate is to greenhouse gas emissions. Here we perform a sensitivity analysis on a global model to quantify the uncertainty in cloud radiative forcing over the industrial period caused by uncertainties in aerosol emissions and processes. Our results show that 45 per cent of the variance of aerosol forcing since about 1750 arises from uncertainties in natural emissions of volcanic sulphur dioxide, marine dimethylsulphide, biogenic volatile organic carbon, biomass burning and sea spray. Only 34 per cent of the variance is associated with anthropogenic emissions. The results point to the importance of understanding pristine pre-industrial-like environments, with natural aerosols only, and suggest that improved measurements and evaluation of simulated aerosols in polluted present-day conditions will not necessarily result in commensurate reductions in the uncertainty of forcing estimates.

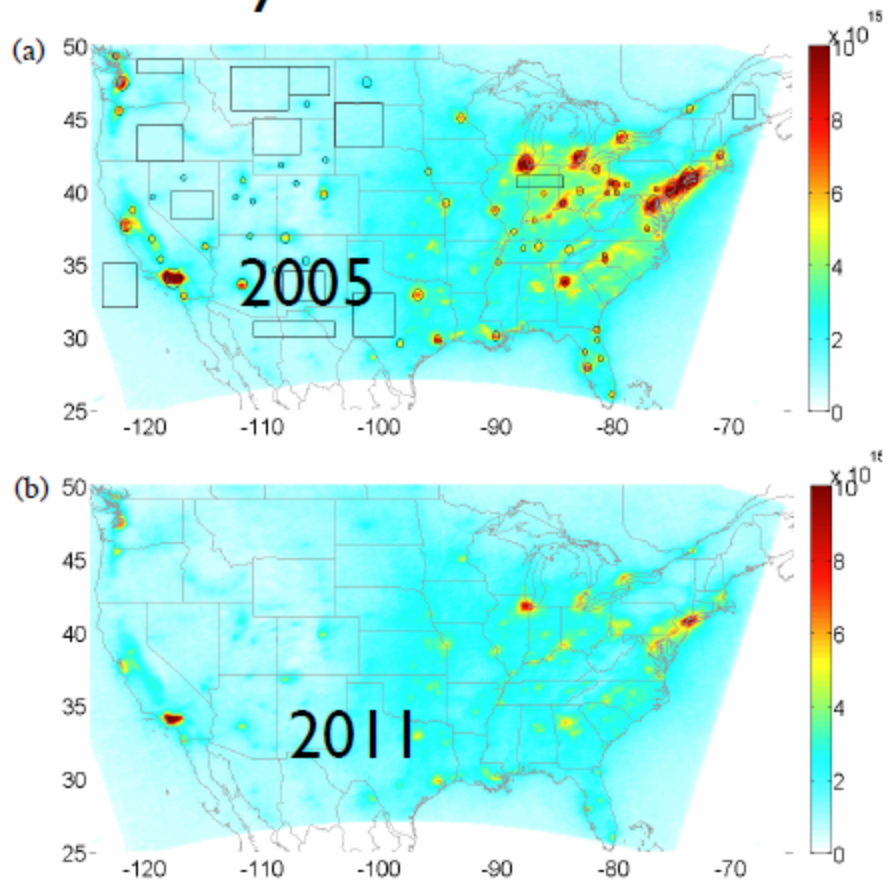
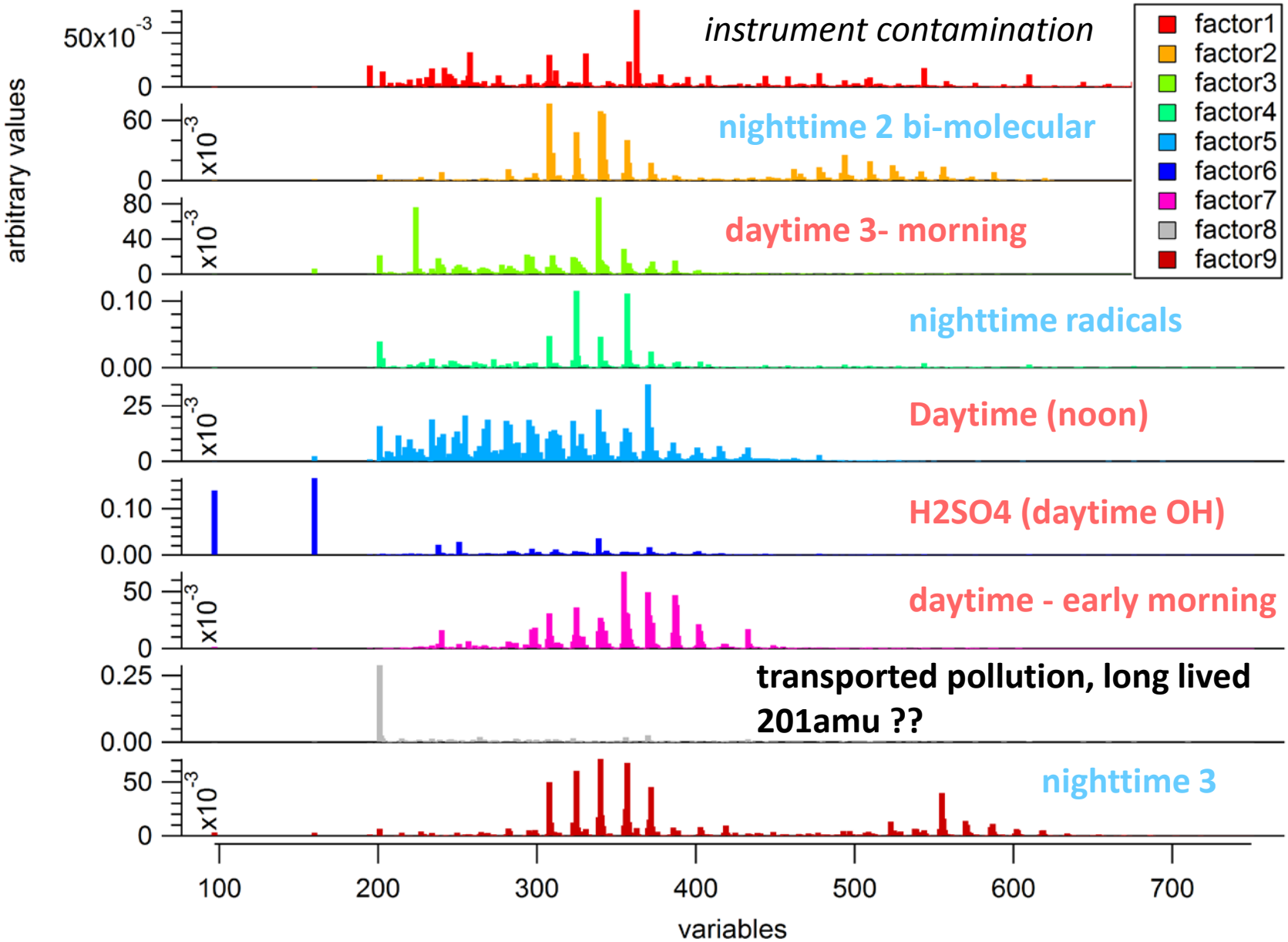
The southeast is transitioning to low NO, oxidant consuming chemistry; southeast Asia is going the other way



Trends in OMI NO_2 observations over the US: effects of emission control technology and the economic recession

A. R. Russell[1], L. C. Valin[1], and R. C. Cohen[1,2]

Atmos. Chem. Phys. Discuss., 12, 15419–15452, 2012



Hyytiälä (BAECC) *NO3- ToF-CIMS*