Organics in the atmosphere from air pollution to biogeochemical cycles and climate

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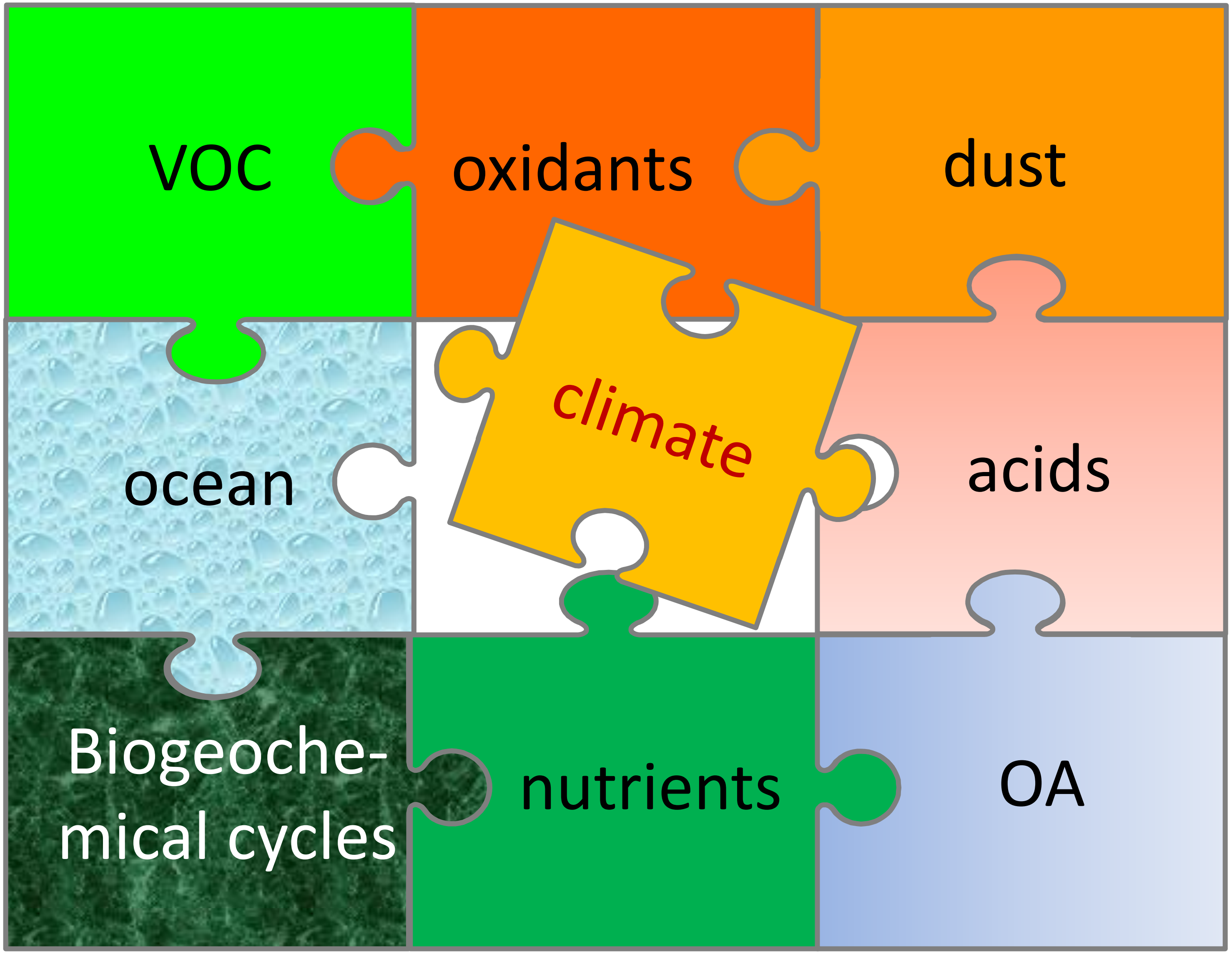
Sao Paolo, 1 August 2019

Organics : key players in the Earth System



VOC

oxidants

dust

ocean

climate

acids

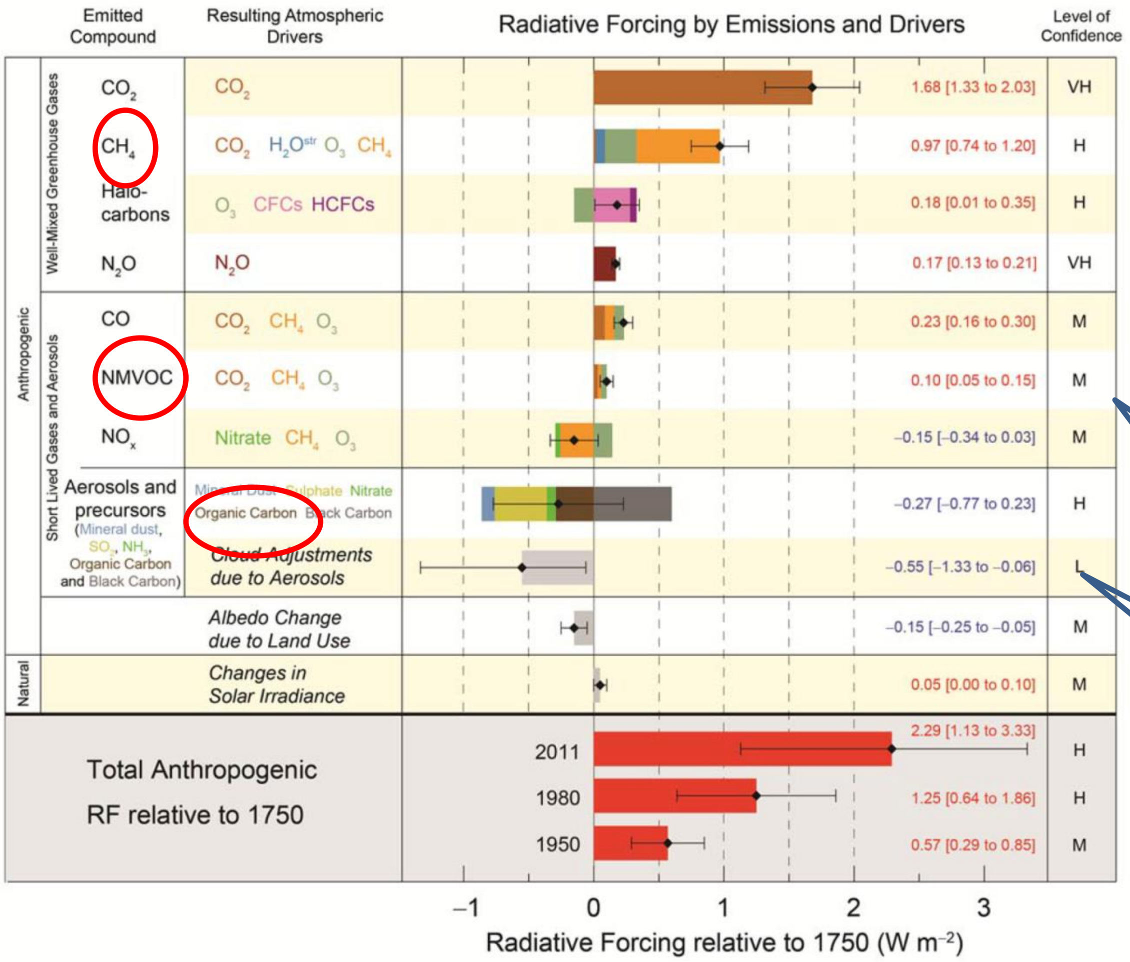
Biogeochemical cycles

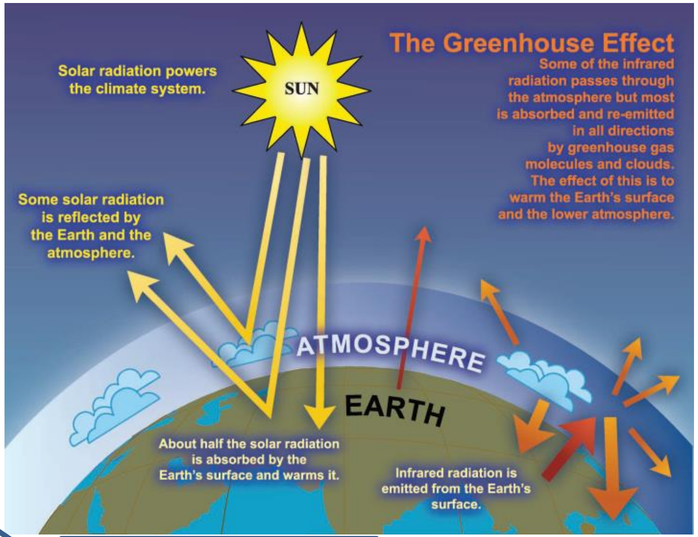
nutrients

OA

Organics affect Earth’s climate

Cooling | warming





Important role for chemistry

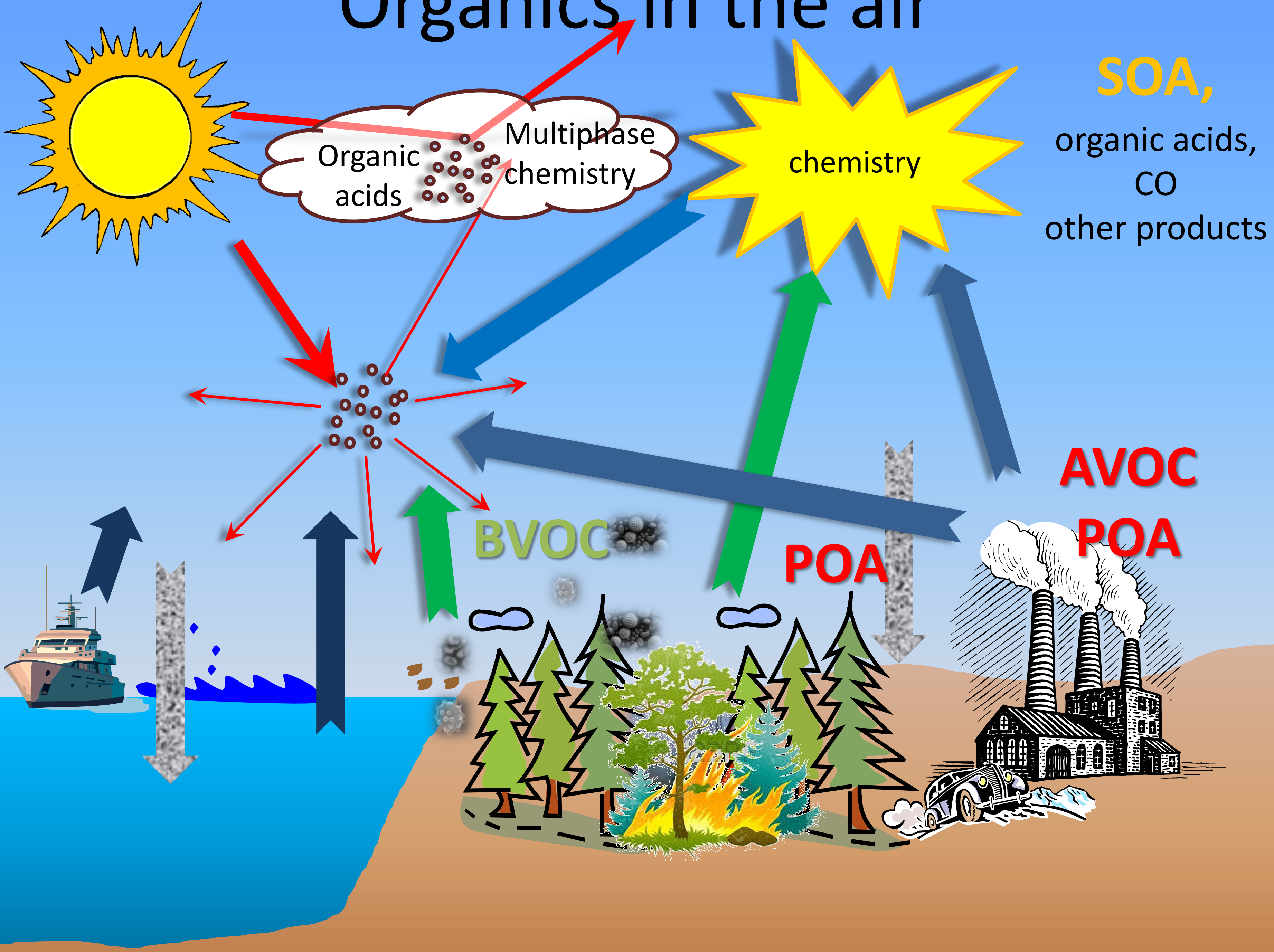
Large uncertainty on aerosol clouds interactions

@IPCC2013

Glossary

- VOC → Volatile organic compounds (attention CO is not organic)
- BVOC→ biogenic VOC (commonly used excluding CH4)
- AVOC → anthropogenic VOC (commonly used excluding CH4)
- NMVOC → non methane VOC
- NMOC → non methane organic carbon (gases+ particles)
- OC ➔ organic carbon (dual use : 1) organic particles expressed in C ; 2) sum of all organics in the atmosphere expressed in C
- OA, OM →organic aerosol or organic matter → particulate organic mass counting all mass and not only the C (i.e. H, O, N etc)
- SOA → secondary organic aerosol
- BSOA → SOA from biogenic precursors
- ASOA → SOA from anthropogenic precursors
- ELVOC → Extremely Low volatility VOC
- HOM → Highly Oxygenated Matter

Organics in the air



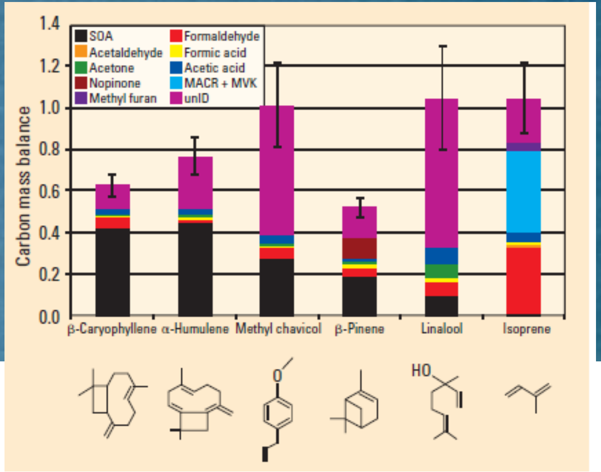
The challenge

Known *and* Unexplored ORGANIC CONSTITUENTS *in the* Earth's Atmosphere

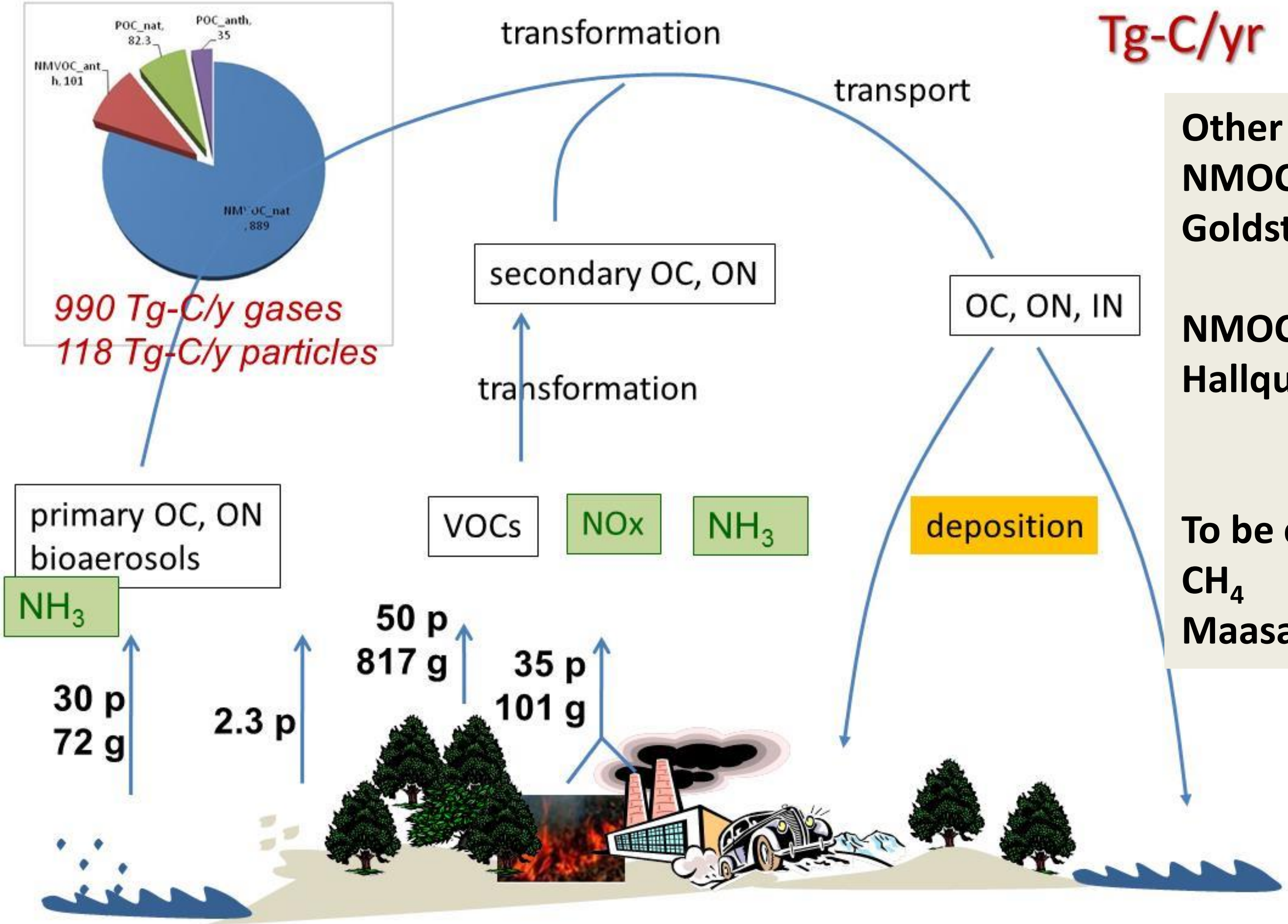
Much remains to be learned about the sources, structure, chemistry, and fate of gas-phase and aerosol organic compounds.

ALLEN H. GOLDSTEIN
UNIVERSITY OF CALIFORNIA, BERKELEY
IAN E. GALBALLY
CSIRO MARINE AND ATMOSPHERIC RESEARCH (AUSTRALIA)

Environ Science Techno, 2007



Organic Carbon in the global atmosphere



Tg-C/yr

990 Tg-C/y gases
118 Tg-C/y particles

transformation

transport

secondary OC, ON

OC, ON, IN

transformation

primary OC, ON
bioaerosols

NH$_3$

VOCs

NOx

NH$_3$

deposition

30 p
72 g

2.3 p

50 p
817 g

35 p
101 g

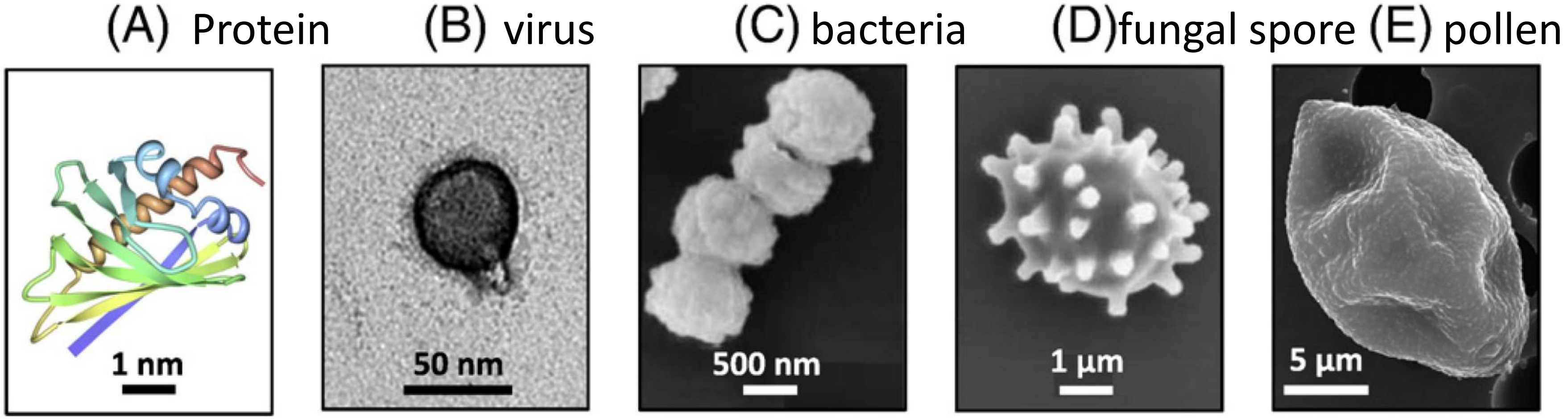
Other estimates
NMOC 1300 (g)
Goldstein & Galbally 2007

NMOC 1334 (g)+16(p)
Hallquist ACP 2009

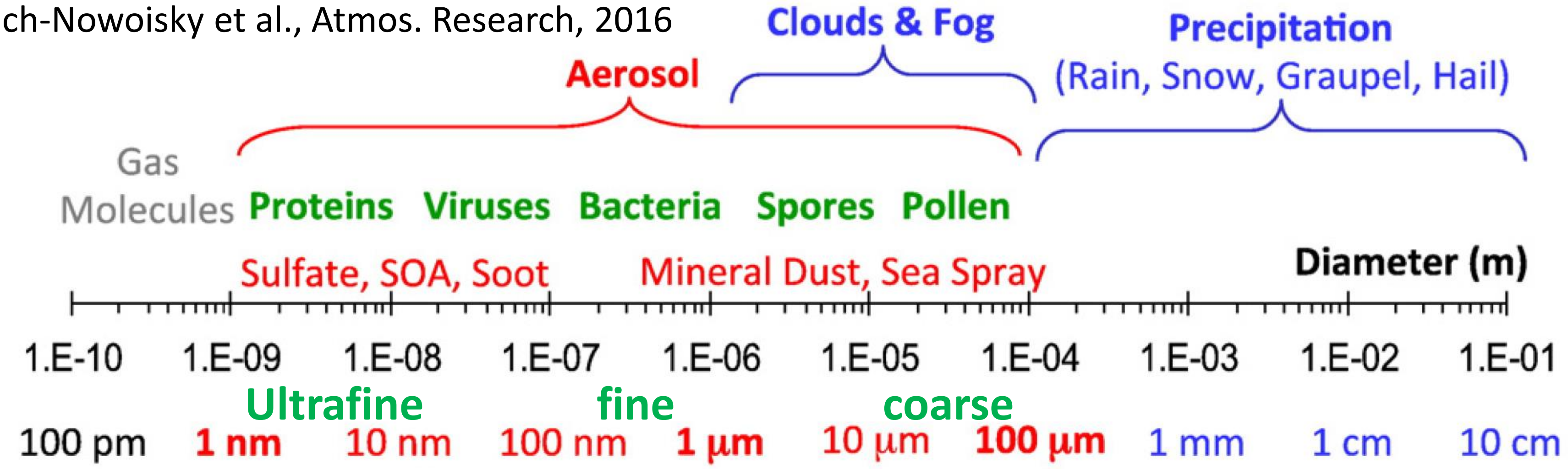
To be compared with
CH$_4$ 410
Maasakkers et al., ACP 2019

Kanakidou, Duce, Prospero, Baker et al., GBC, 2012, doi 10.10.1029/2011GB004277

Large variety in Organic Aerosol morphology



Fröhlich-Nowoisky et al., Atmos. Research, 2016



Clouds & Fog

Precipitation

(Rain, Snow, Graupel, Hail)

Aerosol

Gas Molecules

Proteins Viruses Bacteria Spores Pollen

Sulfate, SOA, Soot

Mineral Dust, Sea Spray

Diameter (m)

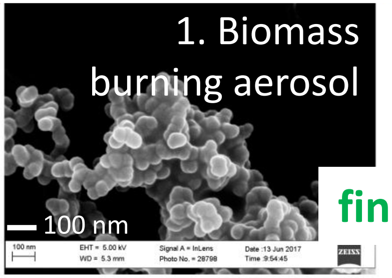
1.E-10 1.E-09 1.E-08 1.E-07 1.E-06 1.E-05 1.E-04 1.E-03 1.E-02 1.E-01

Ultrafine **fine** **coarse**

100 pm **1 nm** 10 nm 100 nm **1 µm** 10 µm **100 µm** 1 mm 1 cm 10 cm

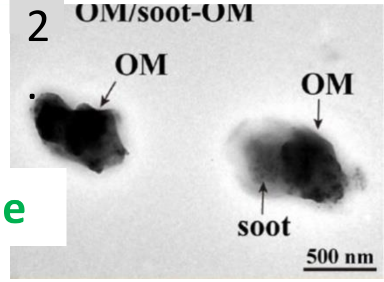
1. Poudel et al, Atmosphere, 2017

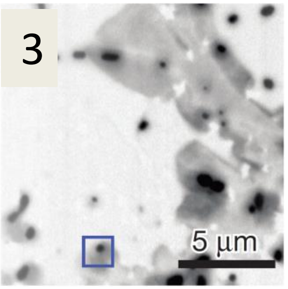
2. Liu et al., Scientific Reports, 2017



1. Biomass burning aerosol

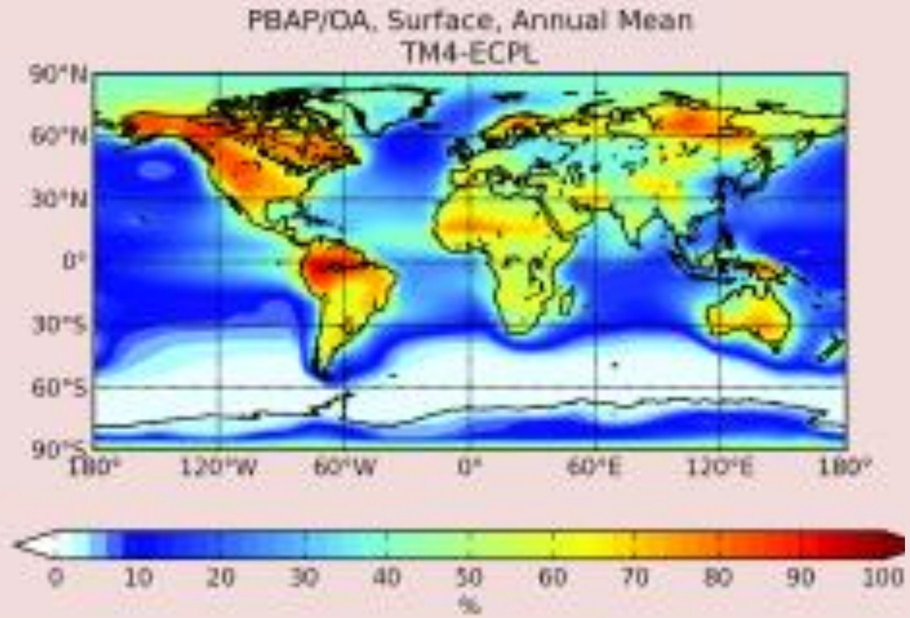
fine

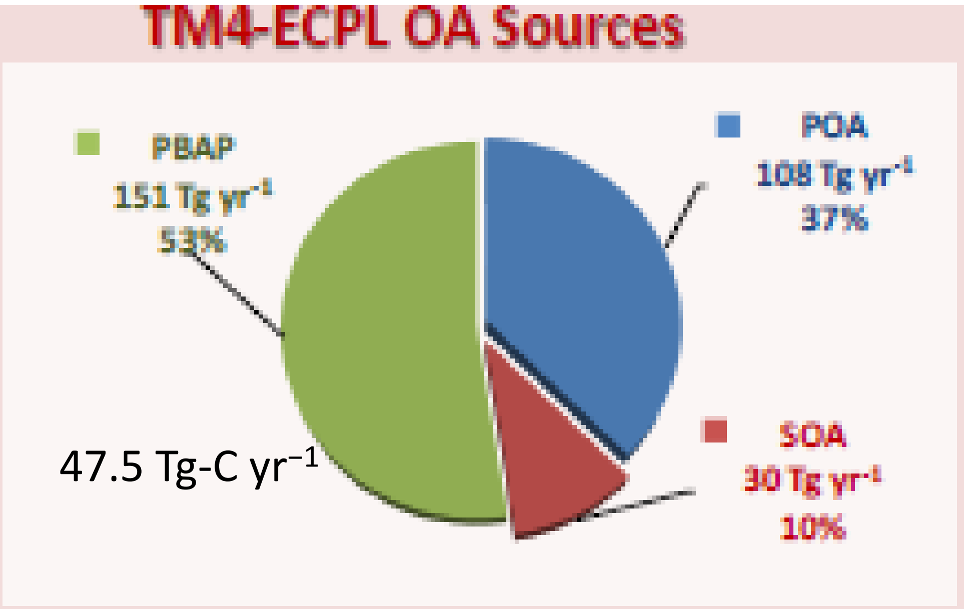




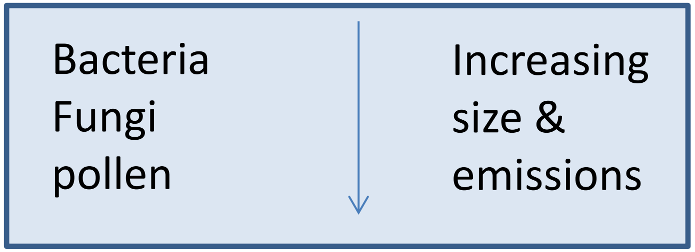
3. Marine Surface Layer Wilson et al. Nature, 2015

Bioaerosols
are important fraction of POA





Myriokefalitakis, et al in Perspectives on Atmospheric Sciences, DOI 10.1007/978-3-319-35095-0_121, *2017 update in Myriokefalitakis et al, Biogeoscience, 2016*



Bacteria
Fungi
pollen

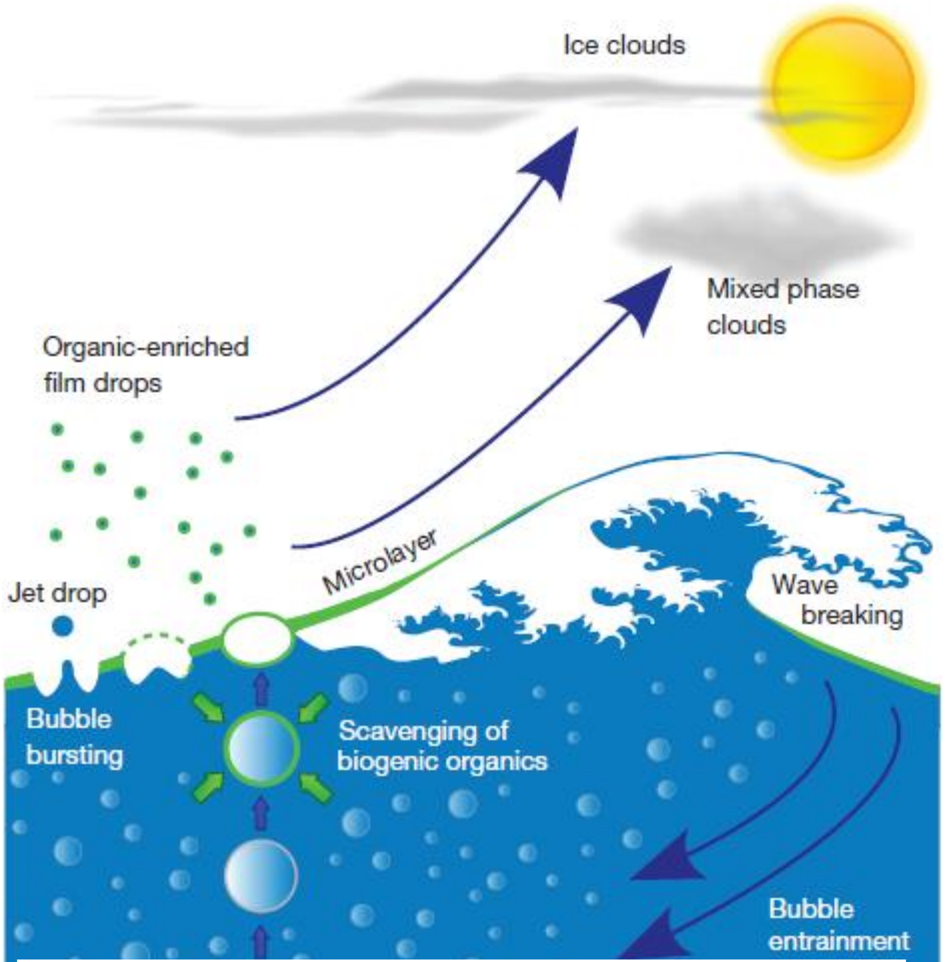
Increasing
size &
emissions

Large uncertainty with estimates up to 1000 Tg-C.y $^{-1}$ *Jaenicke Science 2005*

See Review article by Fröhlich-Nowoisky et al., Atmospheric Research 182 (2016) 346–376

Marine source of

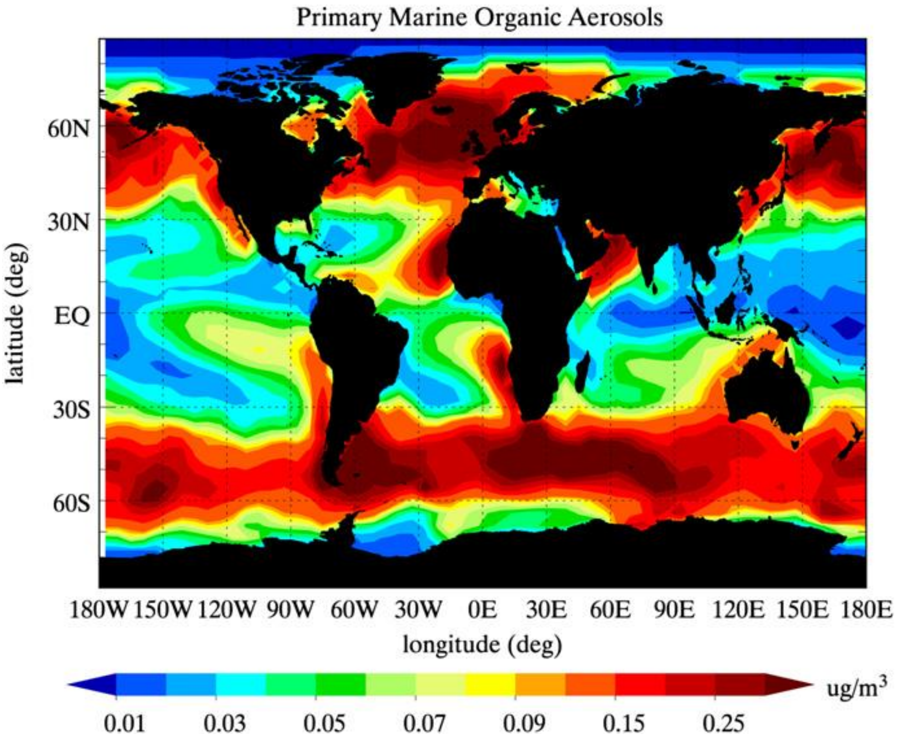
bacteria



A marine biogenic source of atmospheric ice-nucleating particles doi:10.1038/nature14986

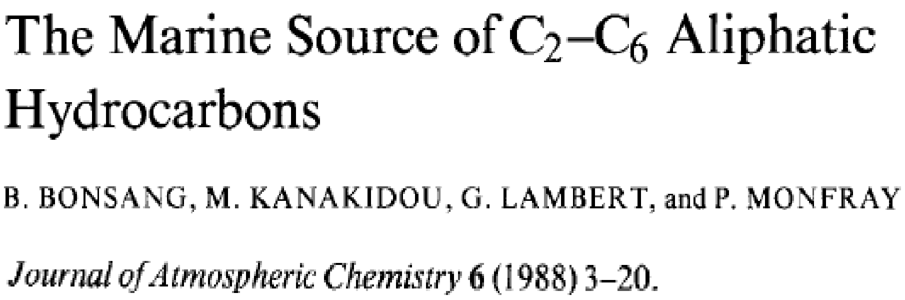
Wilson et al., Nature, 2015

primary organic aerosol



Vignati et al., Atmospheric Environment 44 (2010) 670-677

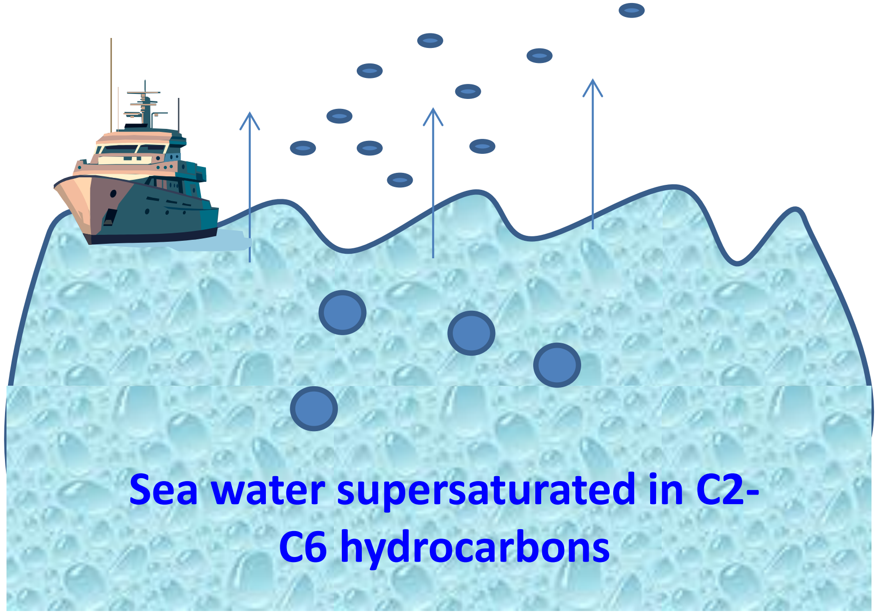
Marine source of VOC and isoprene



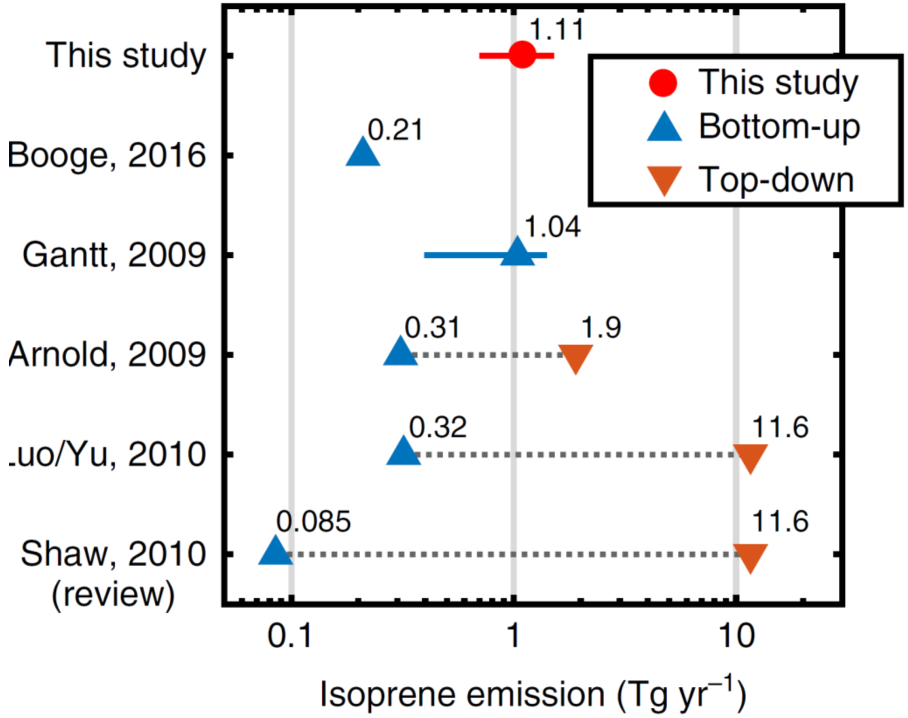
The Marine Source of C_2–C_6 Aliphatic Hydrocarbons

B. BONSANG, M. KANAKIDOU, G. LAMBERT, and P. MONFRAY

Journal of Atmospheric Chemistry 6 (1988) 3–20.



Sea water supersaturated in C2-C6 hydrocarbons



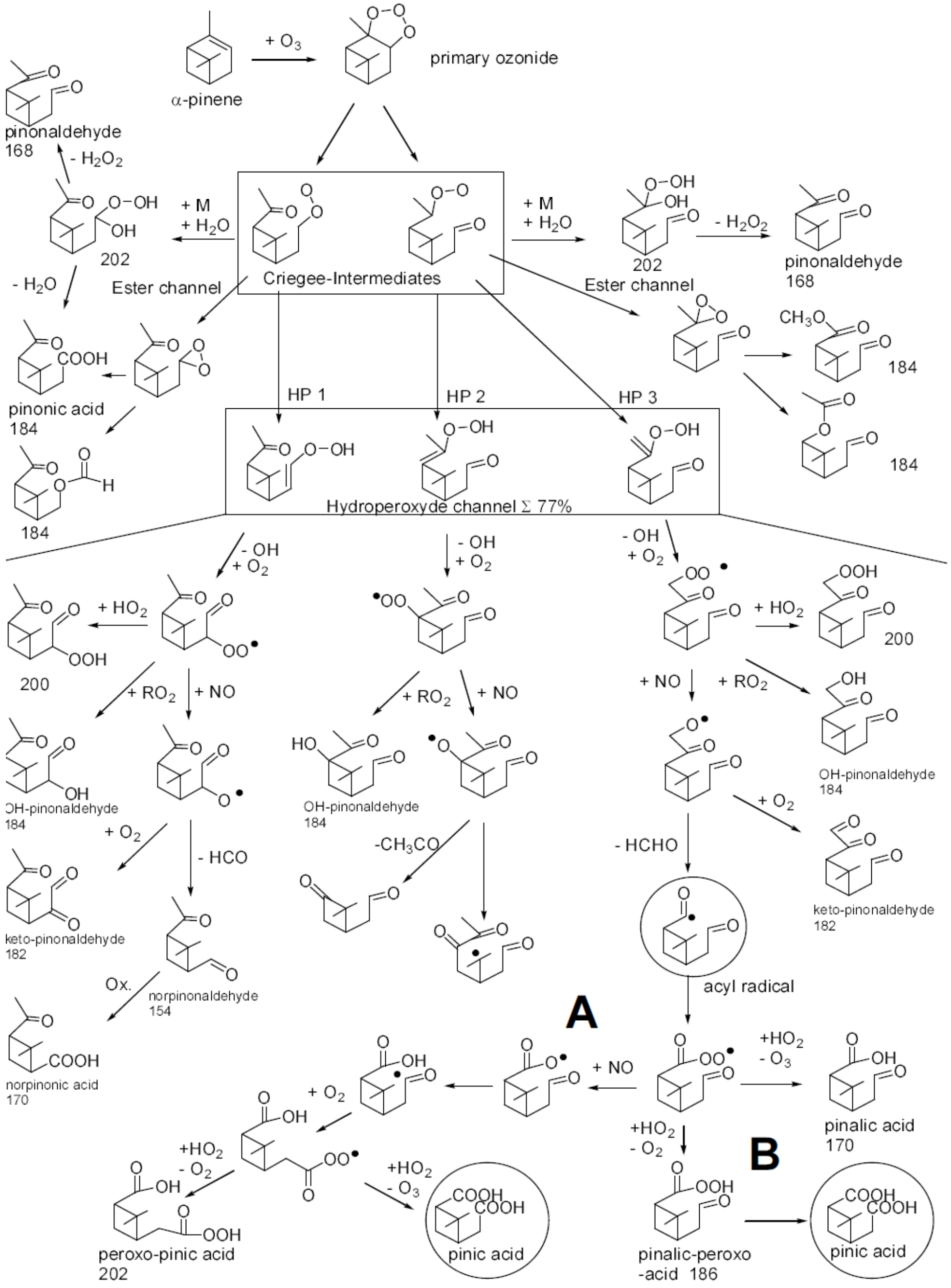
interfacial photochemistry of biogenic sufractants: global emissions of 23.2–91.9 TgC yr^{-1} of VOC from the oceans

Bruggemann et al., Nature Communications, 2018

DOI: 10.1038/s41467-018-04528-7

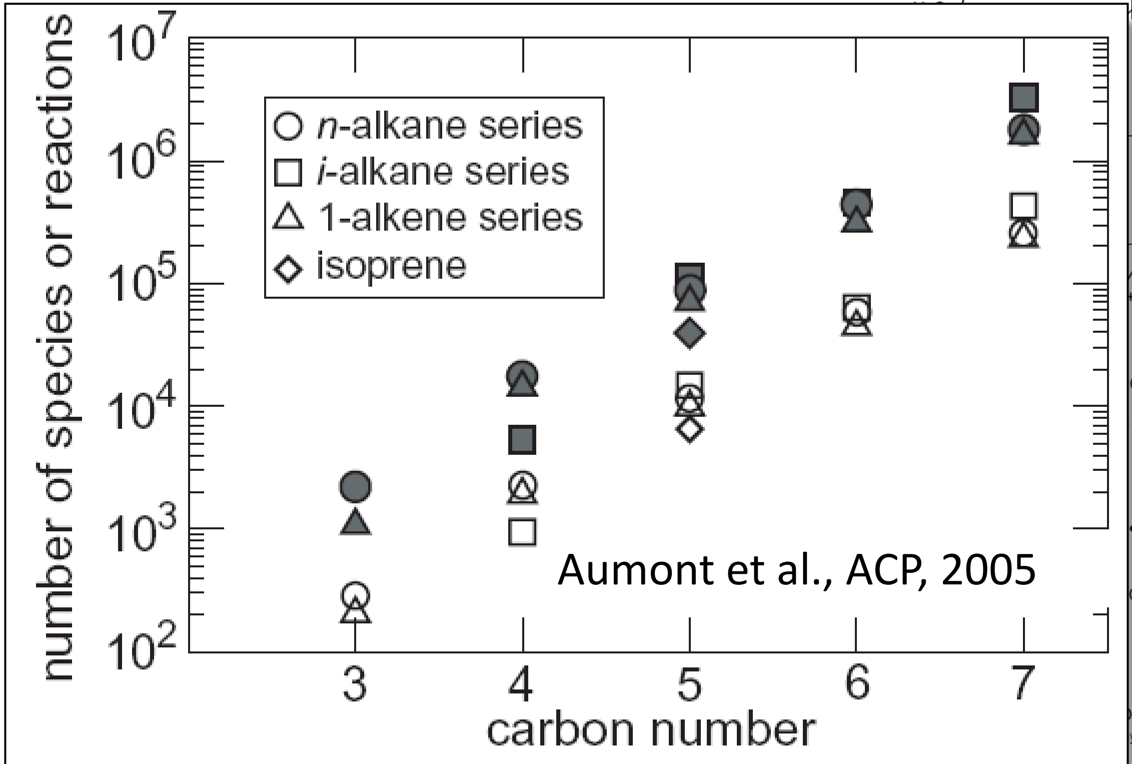
Chemistry

Example of a-pinene oxidation by O_3 to understand SOA production



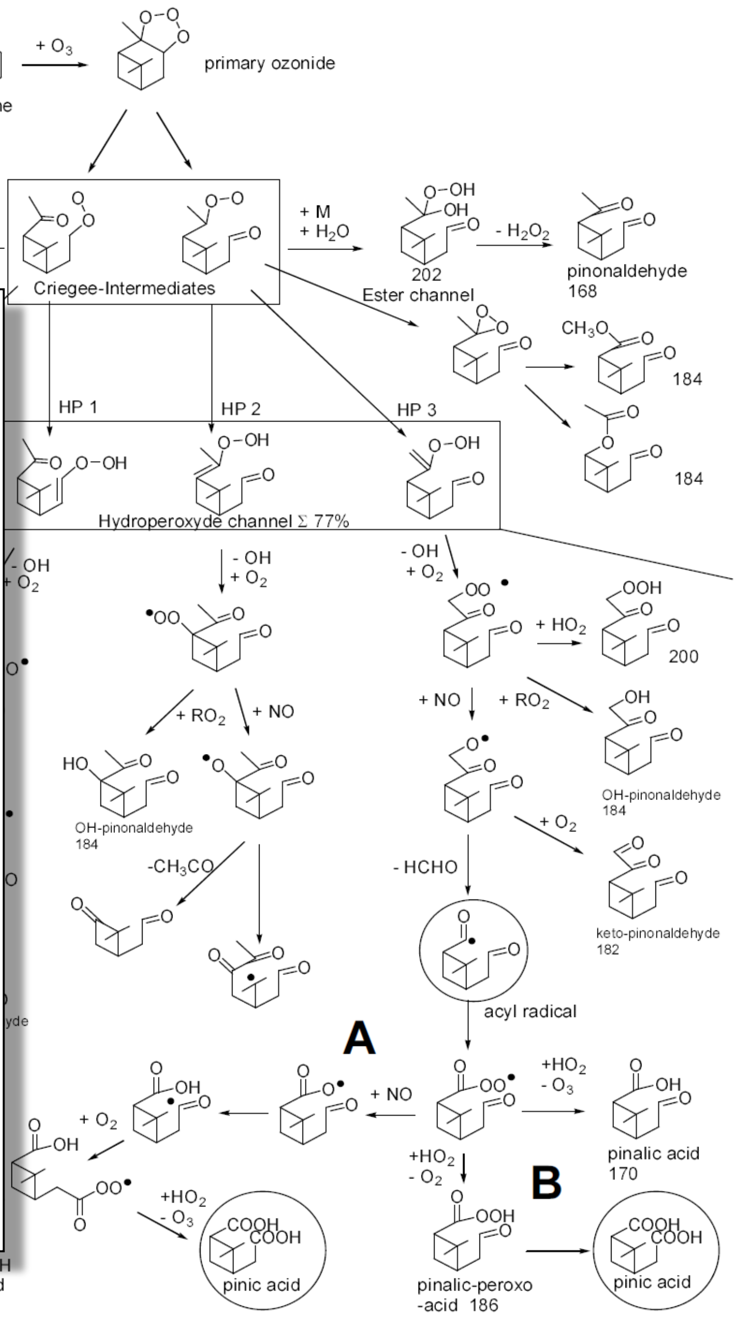
Kanakidou et al., ACP 2005 adopted from Winterhalter et al ACP 2003

Chemistry



Aumont et al., ACP, 2005

Fig. 5. Number of species (open symbols) and reactions (grey symbols) created by the generator for various series (using a 5% threshold for selecting reactions).



Kanakidou et al., ACP 2005 adopted from Winterhalter et al ACP 2003

The magic and challenge of organics

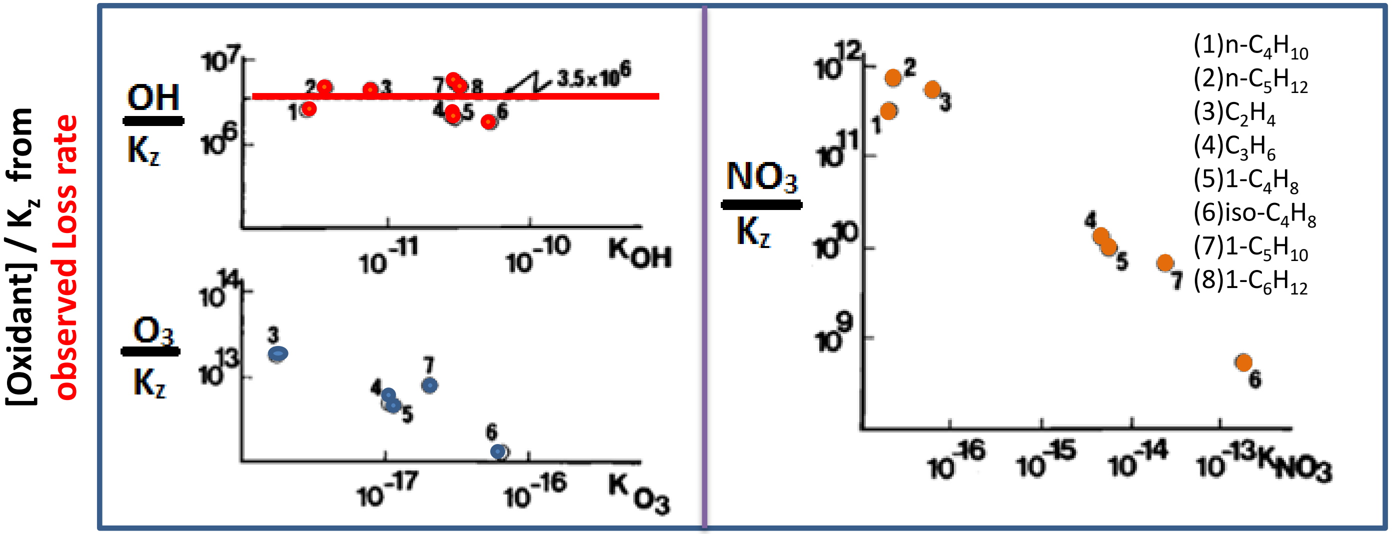
Variety of molecules with

- (g) Different lifetimes with regard to the same oxidant (hydrocarbon clock → chemical age of air masses)
- (g) Different reactivity against different oxidants (O_3, OH, NO_3, Cl → indicators of oxidant levels)
- Sources with different fingerprints (chemical markers)
- (g) Different aerosol forming potential
- (a) composition, properties, impacts …

Hydrocarbon profiles and fluxes

Profiles in Guyana tropical forest

indicators of oxidant levels



Hydrocarbon reactivity →

K_z : vertical diffusion coefficient

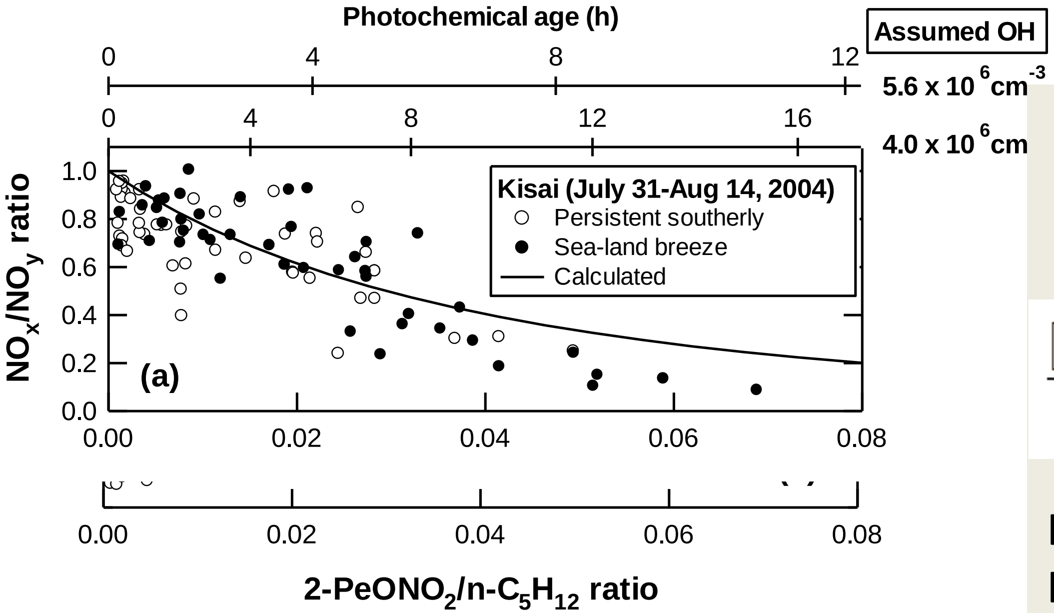
In conclusion, the measurements reported in this study, despite their small number, strongly suggest the existence, in the Guyana tropical forest, of an indirect photochemical process of OH radicals production, which could be important in similar areas.

Bonsang, Kanakidou, Lambert, NMHC Chemistry in an Equatorial Forest, GRL, **1987**

CFR contribution N° 889

Ageing of air masses and Photochemical ageing time

Hydrocarbon clock



Time estimated from the ratio of organic nitrate to its parent hydrocarbon

$$\frac{[2-\mathrm{PeONO_2}]}{[n-\mathrm{C_5H_{12}}]} = \frac{\beta k_A}{(k_B - k_A)}\left(1 - e^{(k_A - k_B)t}\right)$$

K_A formation rate

K_B destruction rate

β fractional yield of the organic nitrate

Assumptions:

OH constant with time, $[2\text{-PeONO}_2]=0$, nC5H12+OH rate limiting step of nitrate formation, dilution/mixing effects are distinguishable.

Tagekawa GRL 2006

Impact of volatile organic oxidation on Tropospheric Ozone & Organic Aerosol formation

VOC + light + NOx

90% biogenic

70% anthropogenic

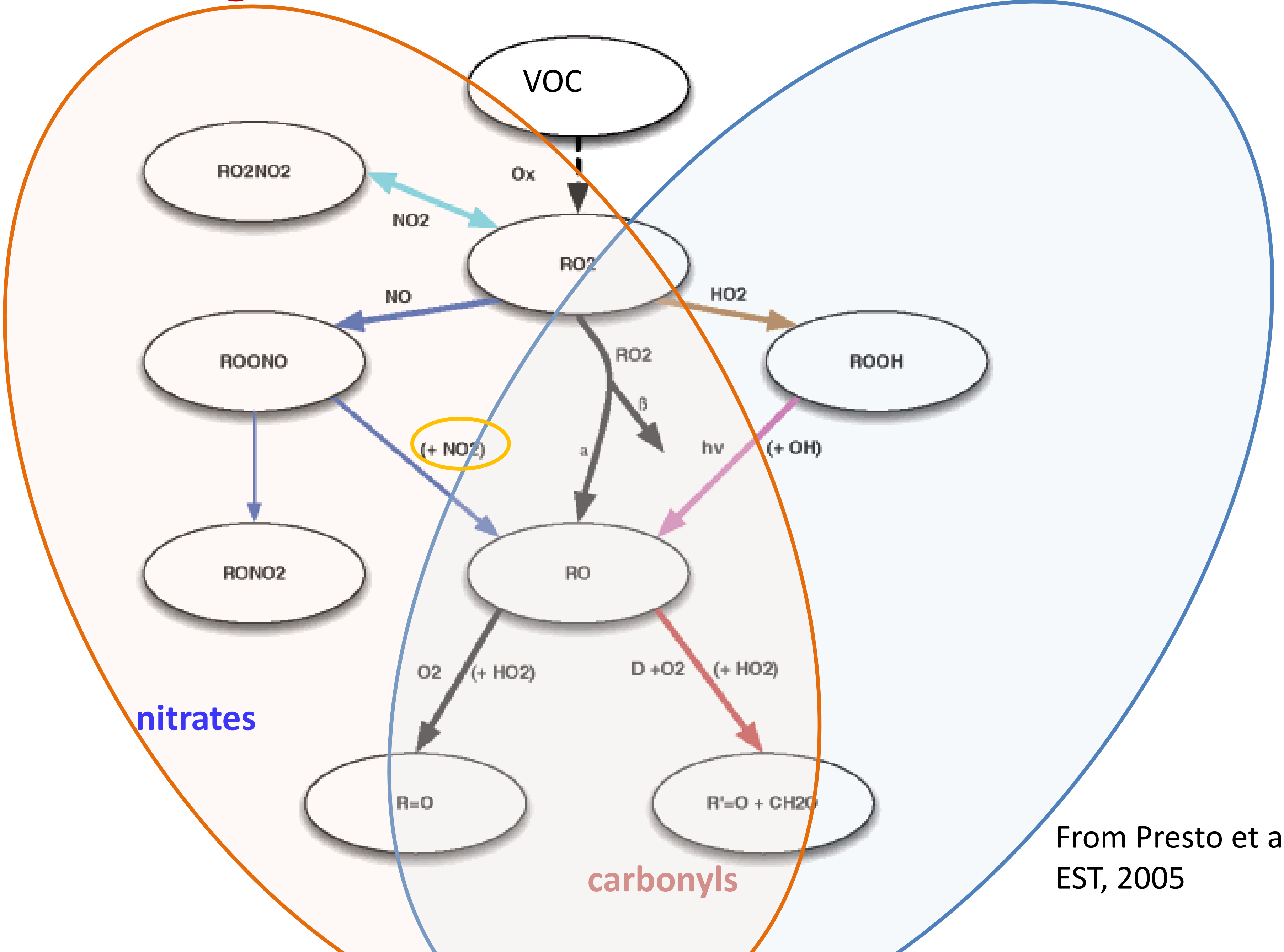
- O_3
- other photo-oxidants
- CO
- Organic nitrates (PAN)
- Aerosols (SOA), including organic nitrogen
- HNO_3/NO_3^- Acid/aerosol

Complex chemistry

5 simple VOC : >15 000 reactions *reduced to* ~200 reactions for air quality modeling –even less for climate models

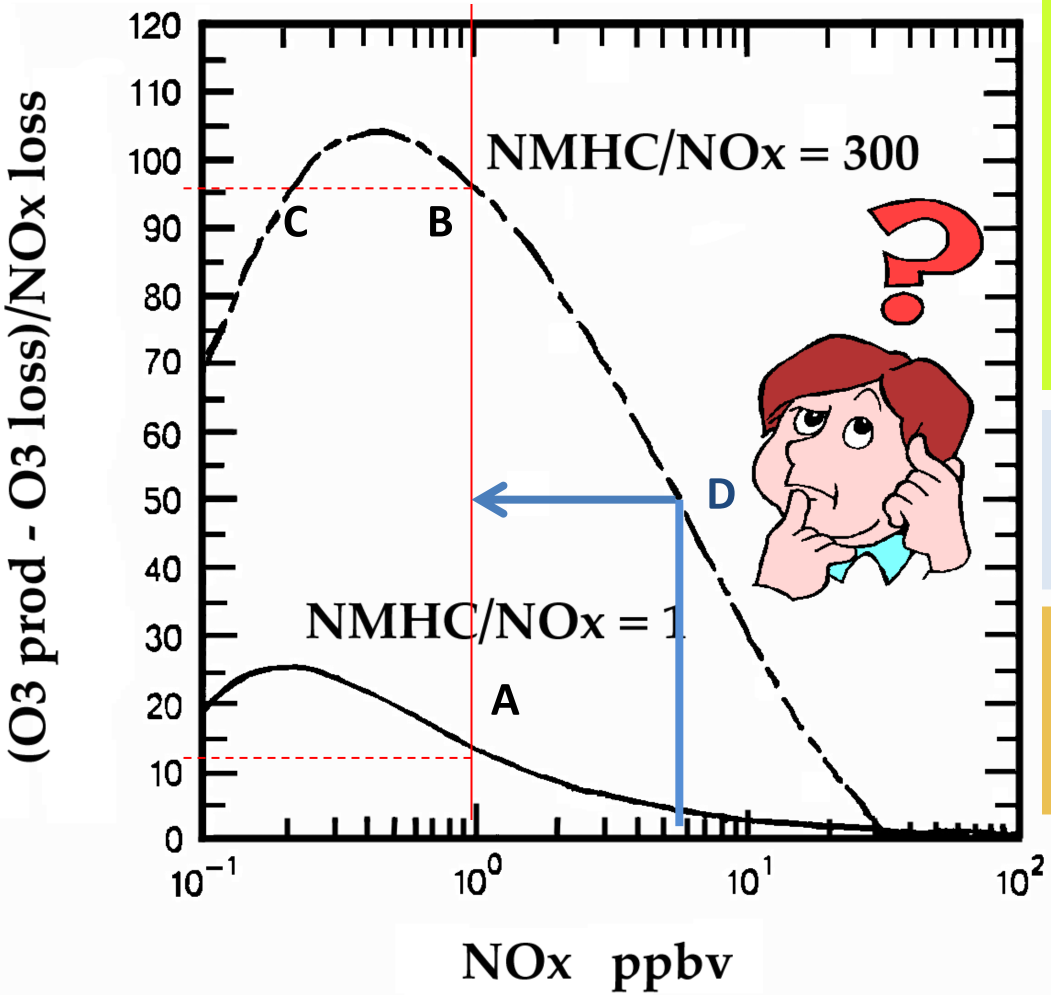
High NOx

Low NOx

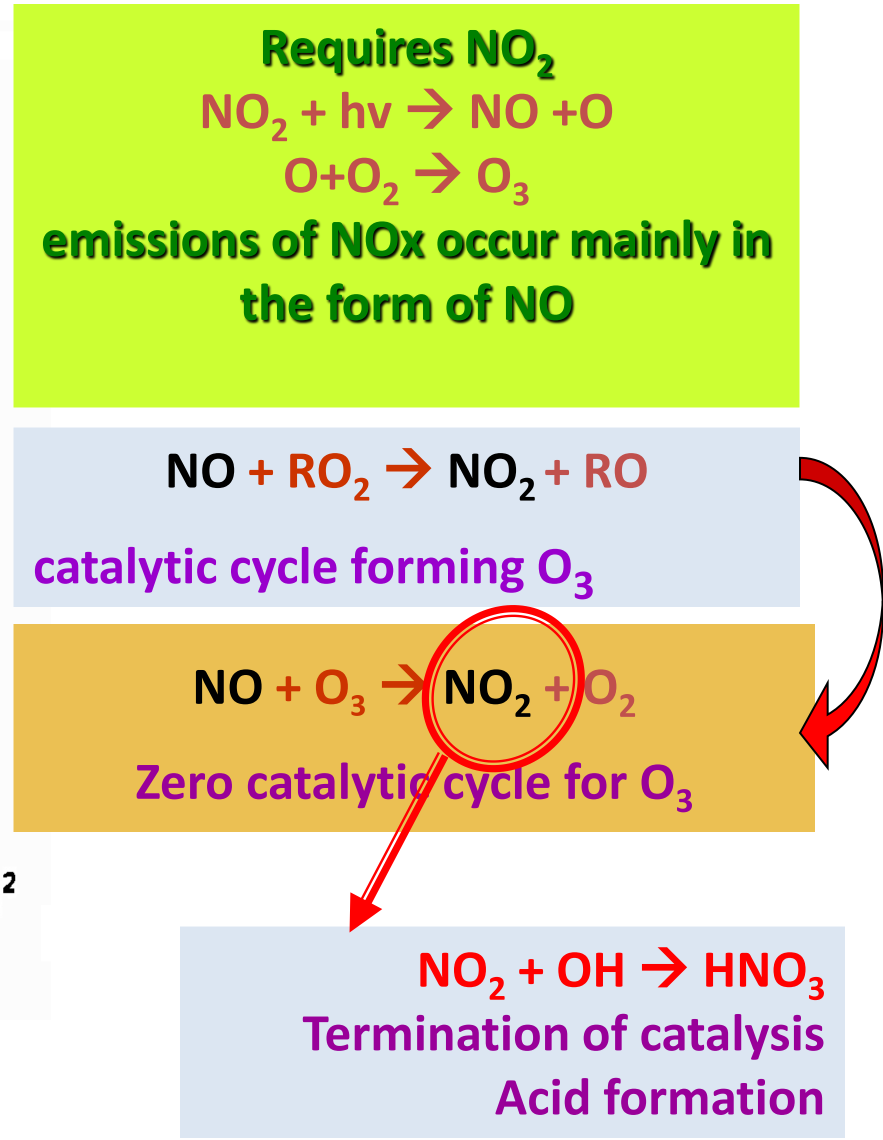


From Presto et al., EST, 2005

Non-linearity in chemical processes
O3 chemical production in the troposphere



Ageing pollution plume



Requires NO_2

NO_2 + hv → NO +O

$O+O_2$ → O_3

emissions of NOx occur mainly in the form of NO

NO + RO_2 → NO_2 + RO

catalytic cycle forming O_3

NO + O_3 → NO_2 + O_2

Zero catalytic cycle for O_3

NO_2 + OH → HNO_3

Termination of catalysis

Acid formation

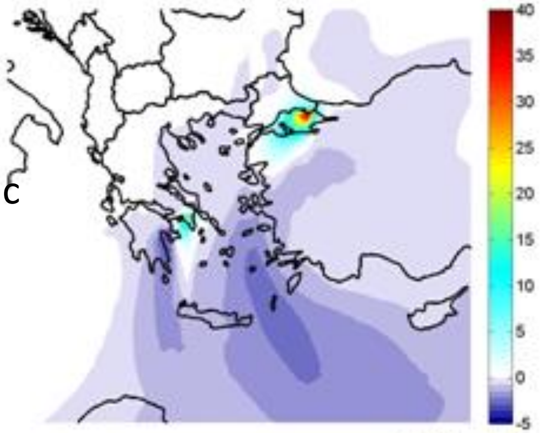
Calculated O3 production efficiency as a function of the concentration of NOx for NMHC/NOx =1 and for NMHC/NOx=100 (NMHC=non methane hydrocarbon). Lin et al. JGR. 1988.

Impact of megacities on air quality

→ can we improve air quality?

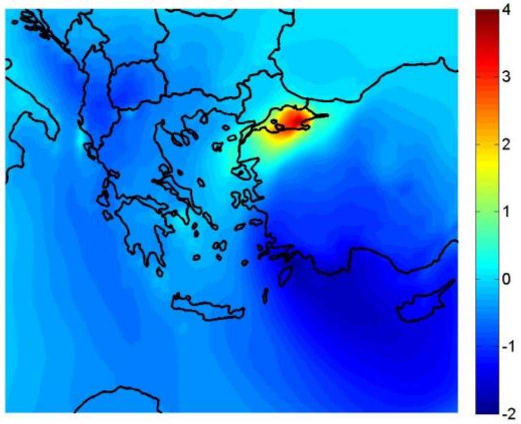
No Istanbul No Athens | Mitigation

Reduction of anthropogenic emissions ➔ O_3 is increasing in the cities



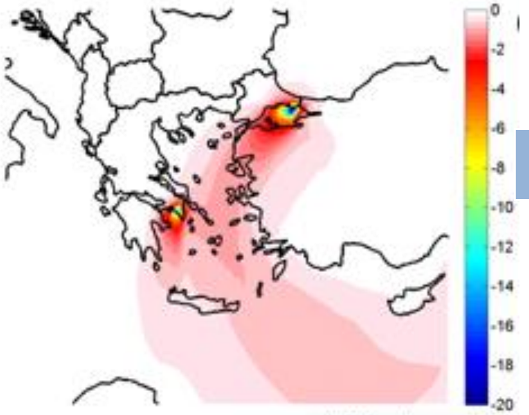
Δ O₃ (ppb)

ΔO_3 (ppbv)



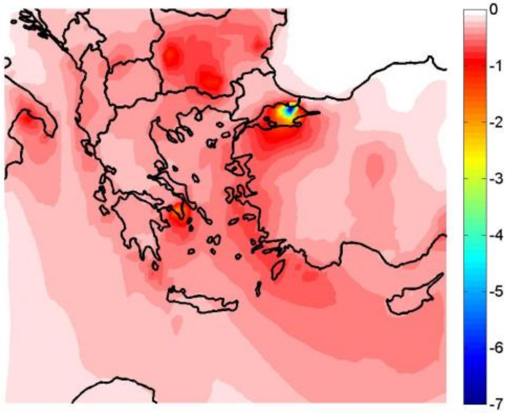
Δ O₃ (ppb)

PM2.5 is reduced everywhere



$\Delta PM_{2.5}$ (µg m⁻³)

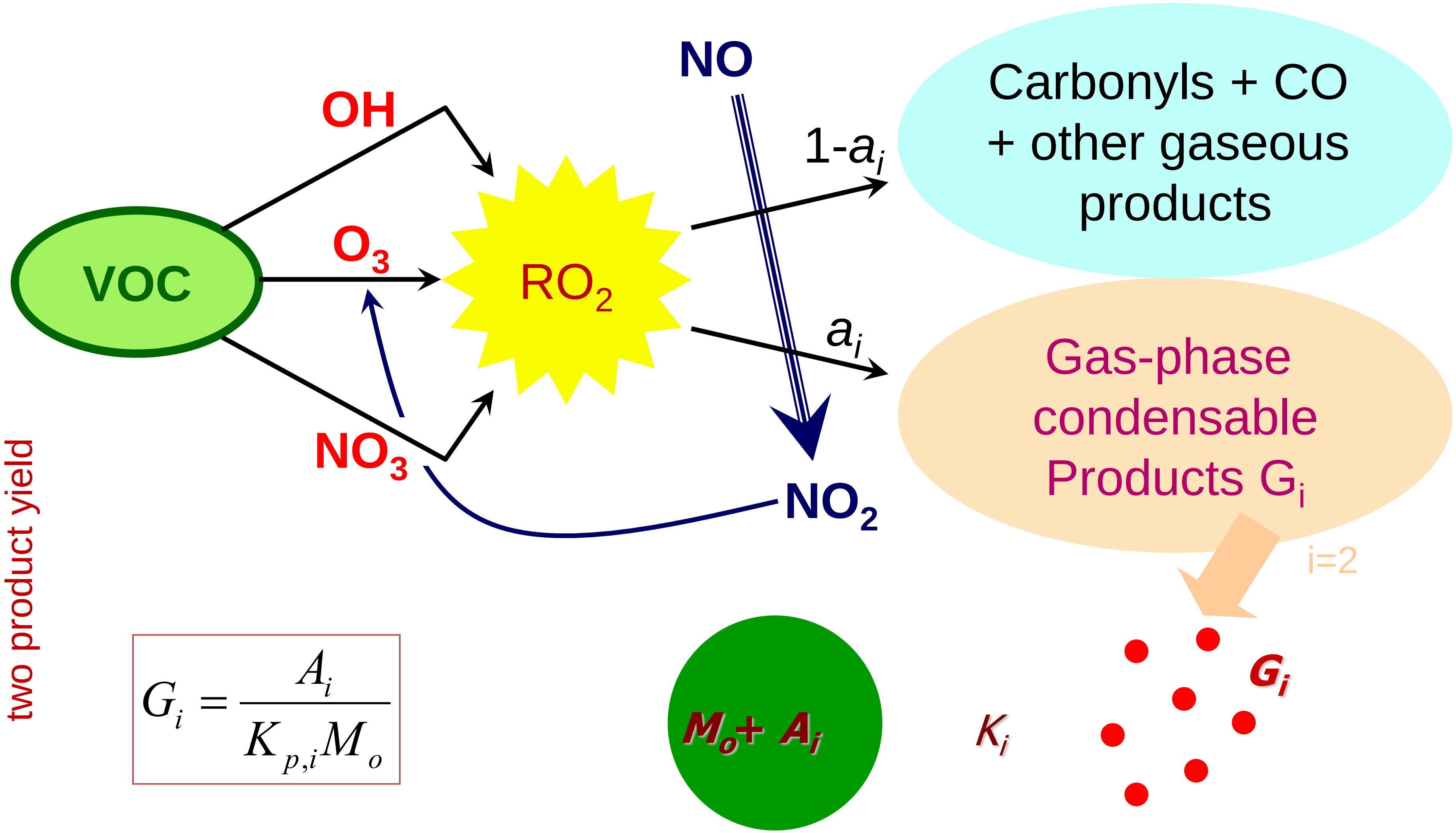
Δ $PM_{2.5}$ ($\mu g/m^3$)



$\Delta PM_{2.5}$ (µg m⁻³)

Im and Kanakidou, ACP 2012

SOA formation in the gas phase



VOC

OH

O_3

NO_3

RO_2

NO

NO_2

1-a_i

a_i

Carbonyls + CO + other gaseous products

Gas-phase condensable Products G_i

i=2

G_i

K_i

$M_o + A_i$

two product yield

$$G_i = \frac{A_i}{K_{p,i} M_o}$$

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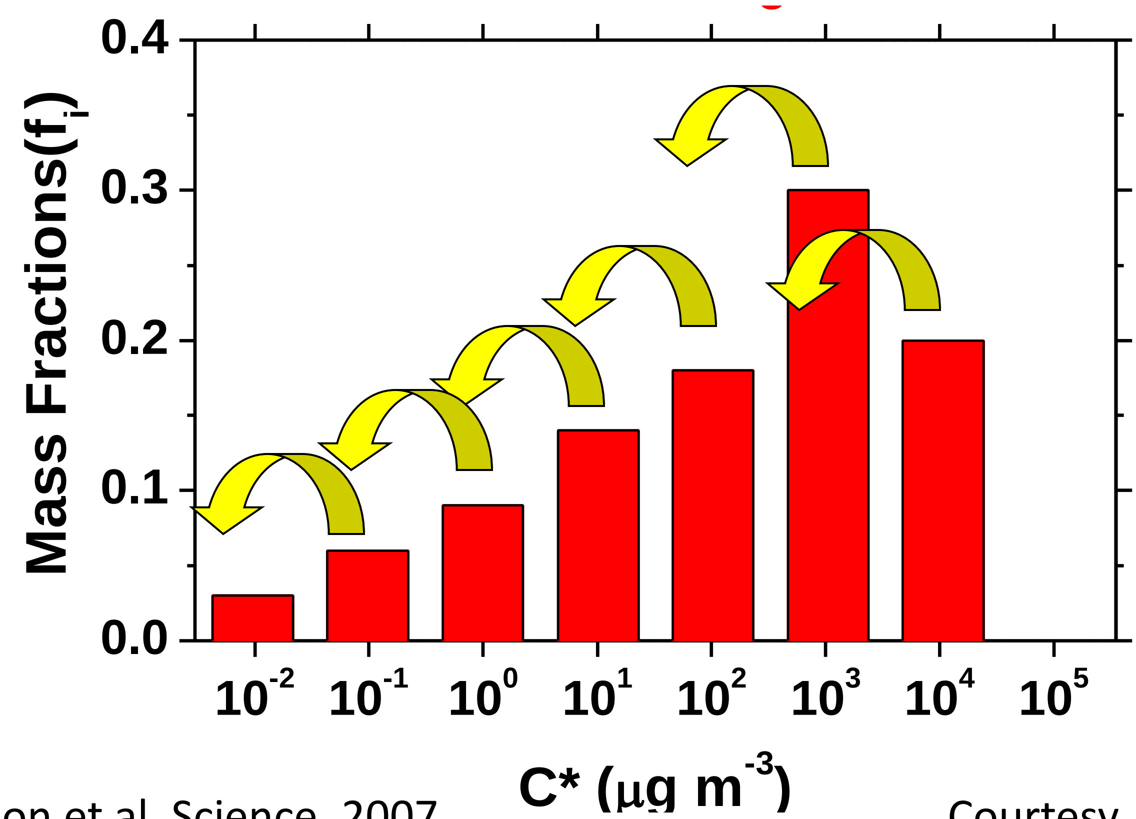
Organic Aerosol and its Chemical Aging

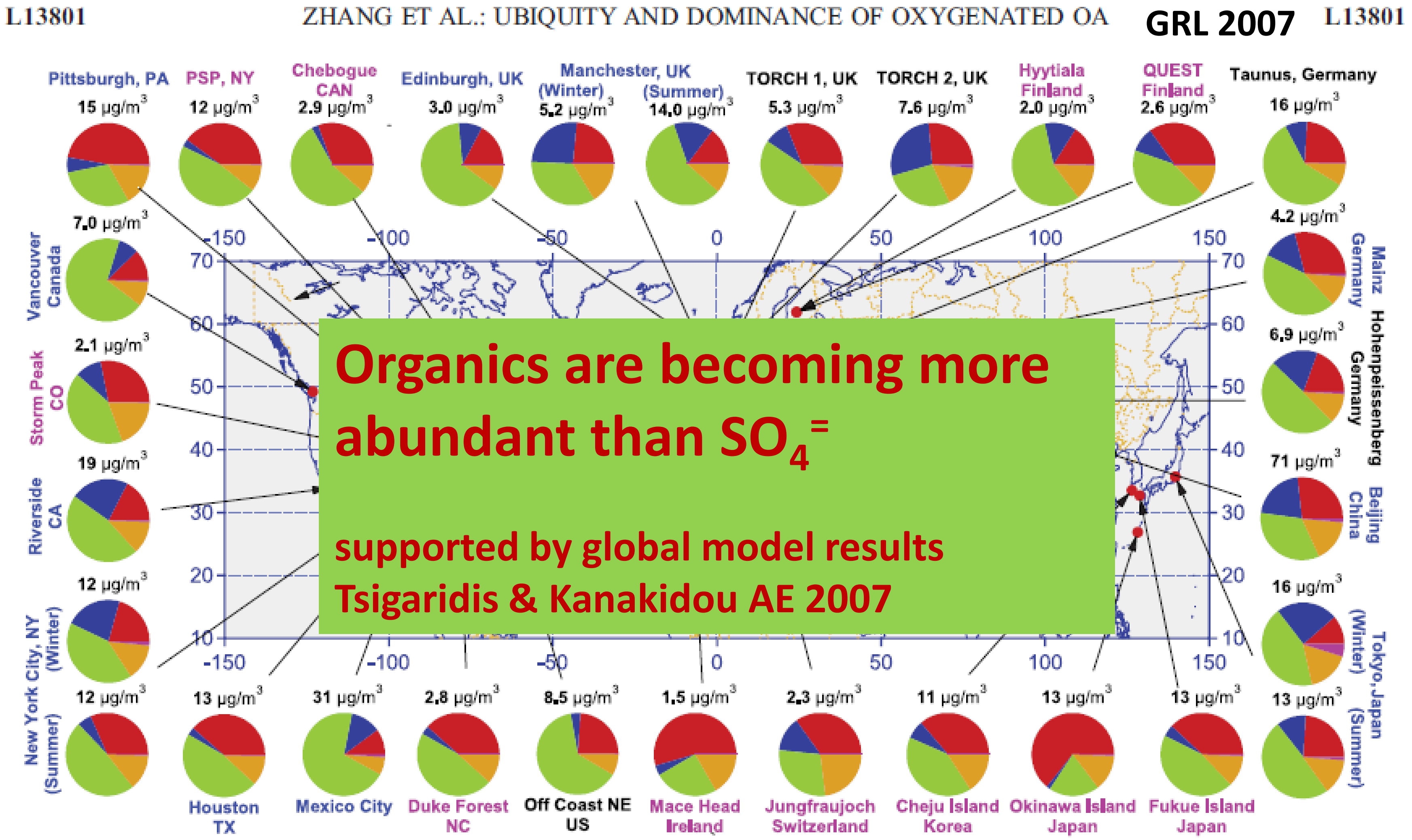
- Primary and secondary organics in the atmosphere also cover a wide range of volatilities
- Compounds react in the gas phase with OH producing material with lower volatility . Formation of very low volatility material (10^{-5} µg m^3 from aging of semivolatile material assumed)



Concept in Robinson et al, Science, 2007

Courtesy Spyros Pandis

Fast evolution of aerosol PM1 characterization with AMS



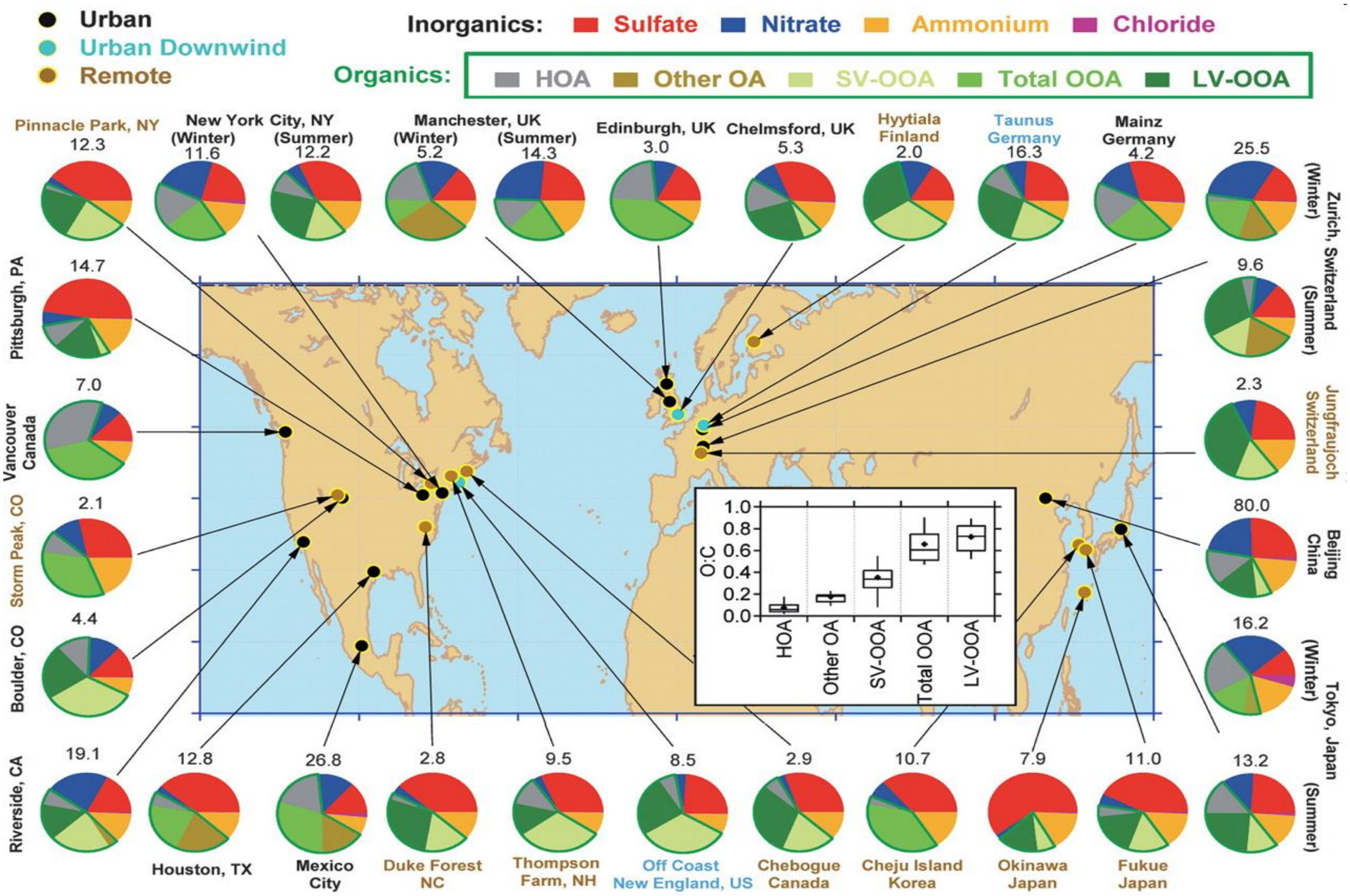
GRL 2007

Organics are becoming more abundant than $SO_4^=$

supported by global model results
Tsigaridis & Kanakidou AE 2007

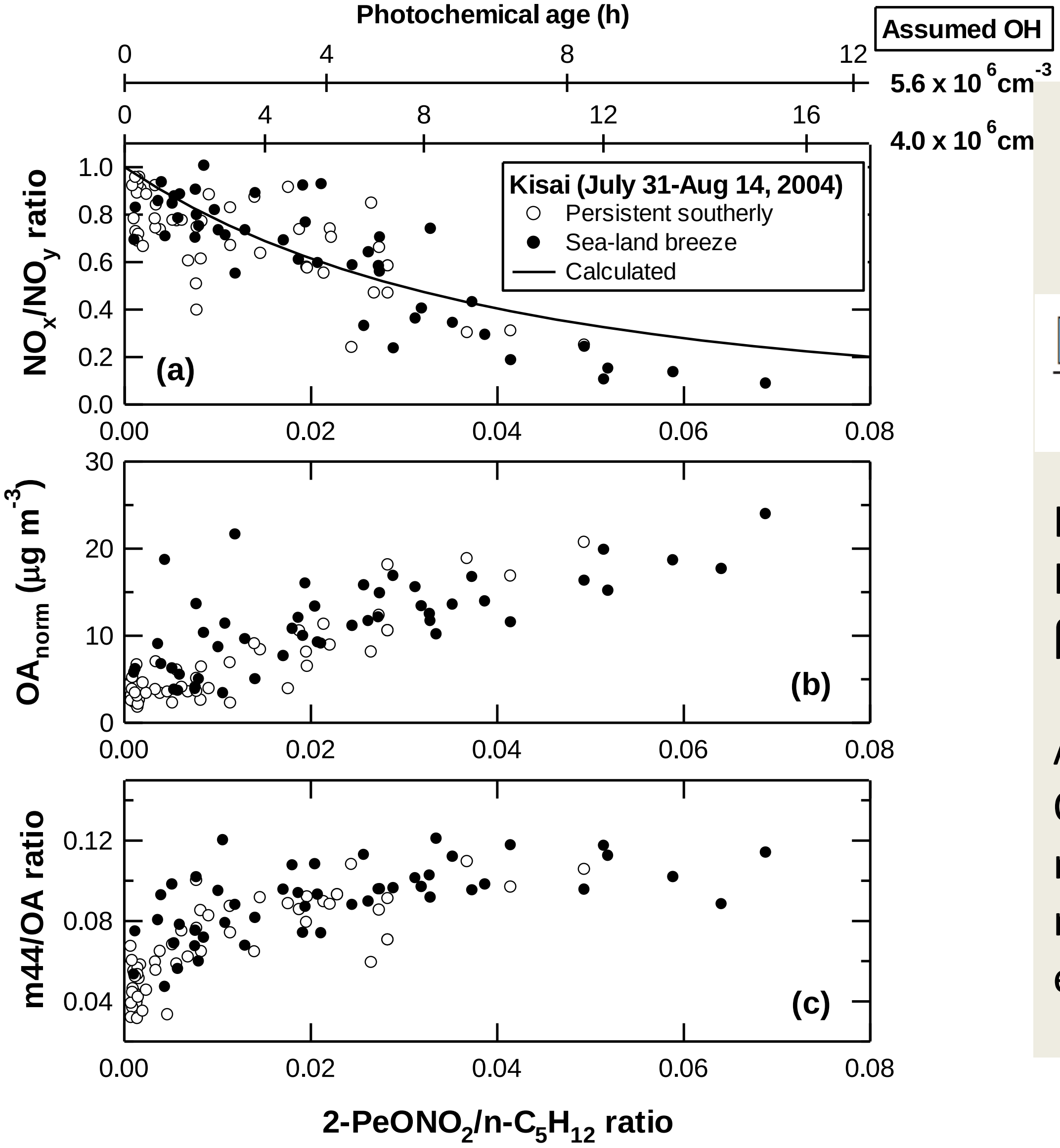
Organic aerosol, sulfate, nitrate, chlorine

PM1 Aerosol Composition



Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

Aging of air masses and outflow of Asia



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K_A formation rate

K_B destruction rate

β fractional yield of the organic nitrate

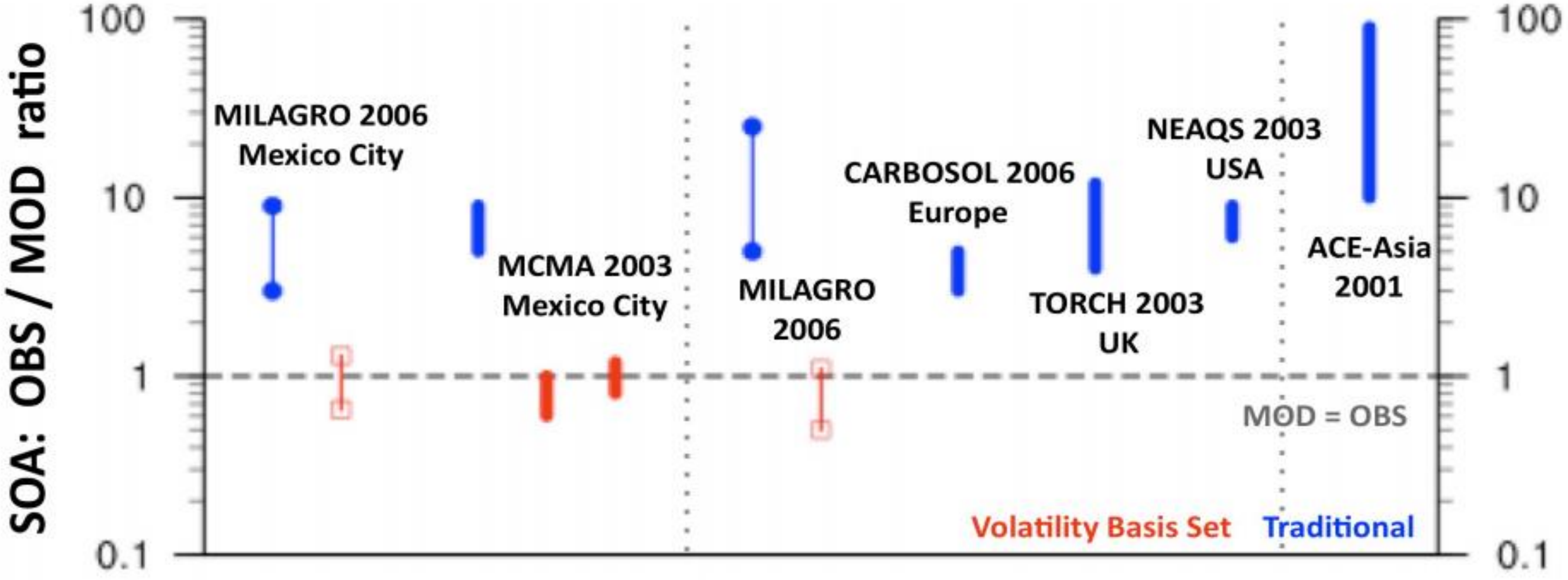
Assumptions:

OH constant with time, $[2\text{-}PeONO_2]=0$, nC5H12+OH rate limiting step of nitrate formation, dilution/mixing effects are distinguishable.

Tagekawa GRL 2006

Underestimate of observations by models & distance from the source

comparison of models to observations



Urban/ Near Source

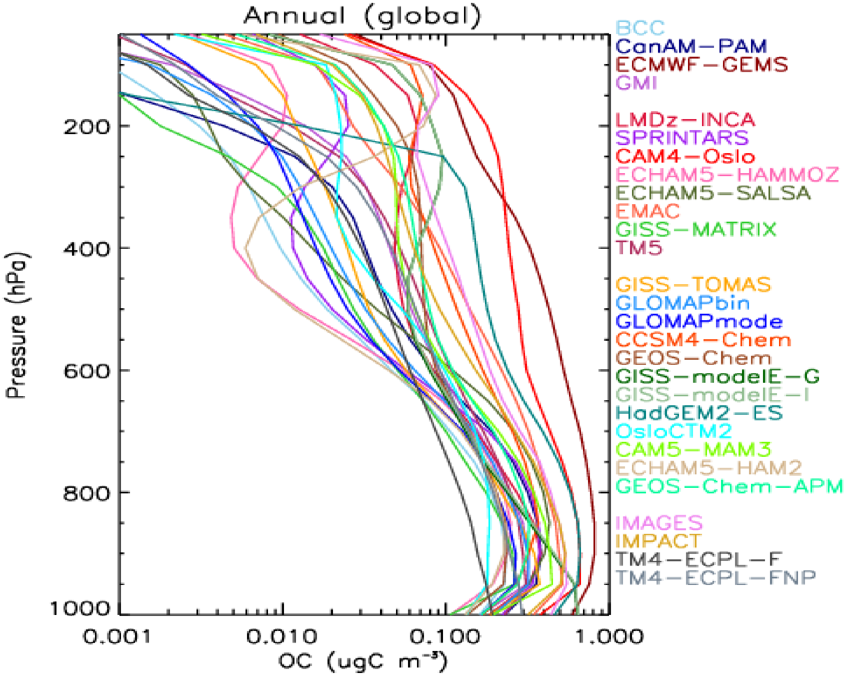
Outflow region/ Regional

Remote

Hodzic et al., ACP, 2010

Distribution of OA : large uncertainty

AEROCOM – comparison of 31 global models



Temperature dependence??

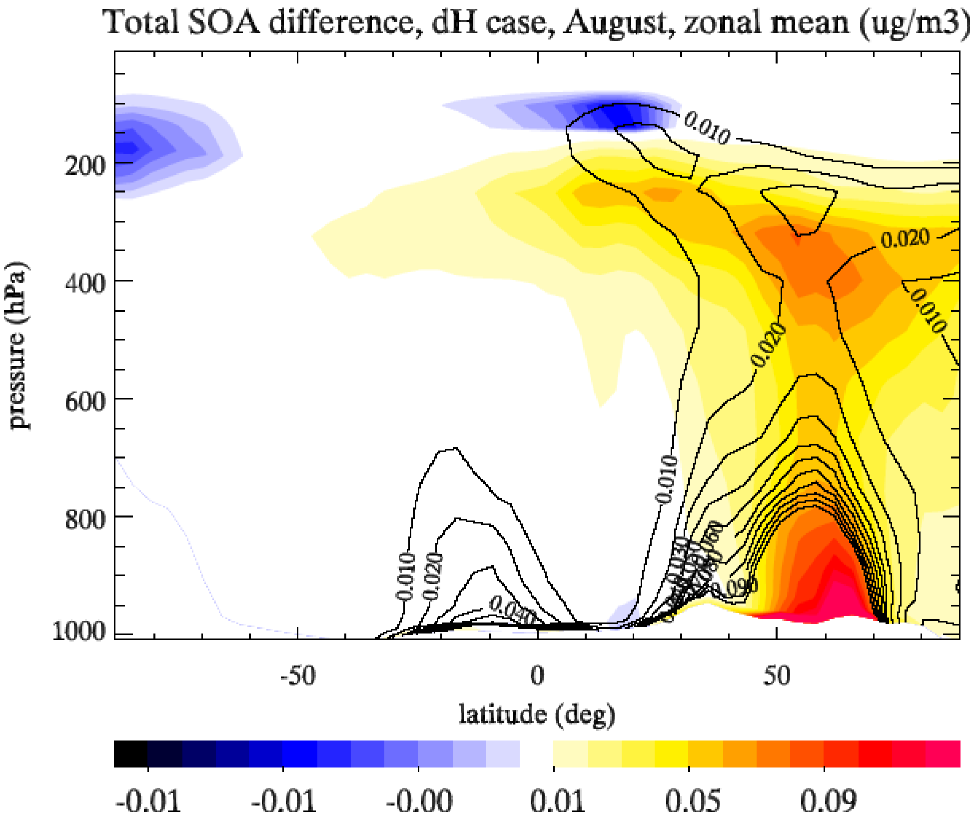
Atmospheric ageing ??

Missing formation pathway??

Missing sources??

Tsigaridis et al., ACP, 14, 10845, 2014

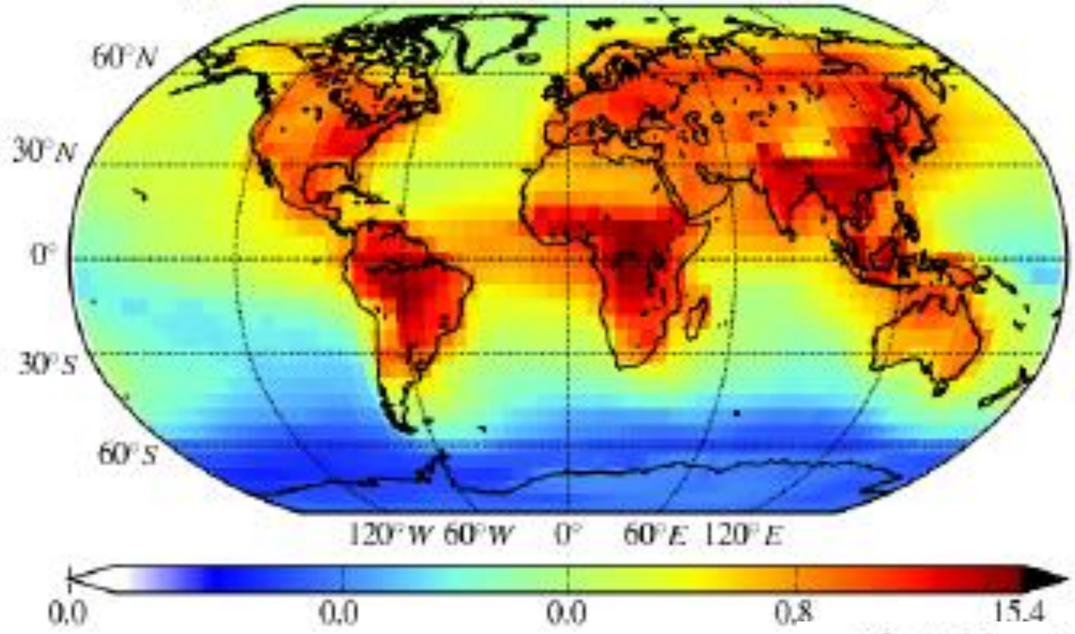
Enthalpy of vaporization



Tsigaridis and Kanakidou, ACP, 2003

ΔH = 79 Kj mol^{-1} vs 49 Kj mol^{-1}

Organic aerosol in global models

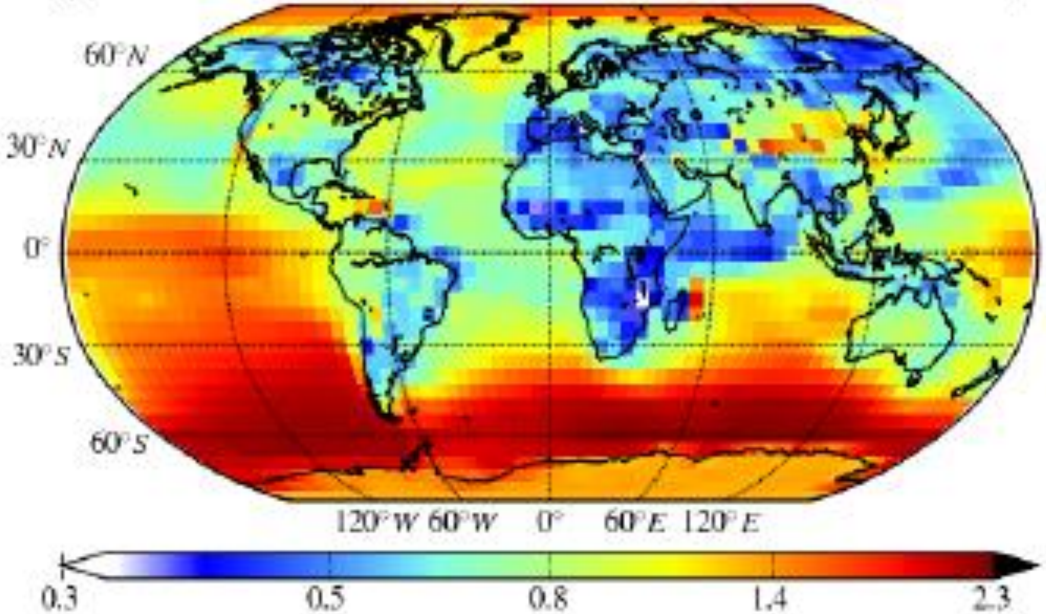

(e) Median model (5x5) - ORG (Annual)

Large differences between models over the oceans

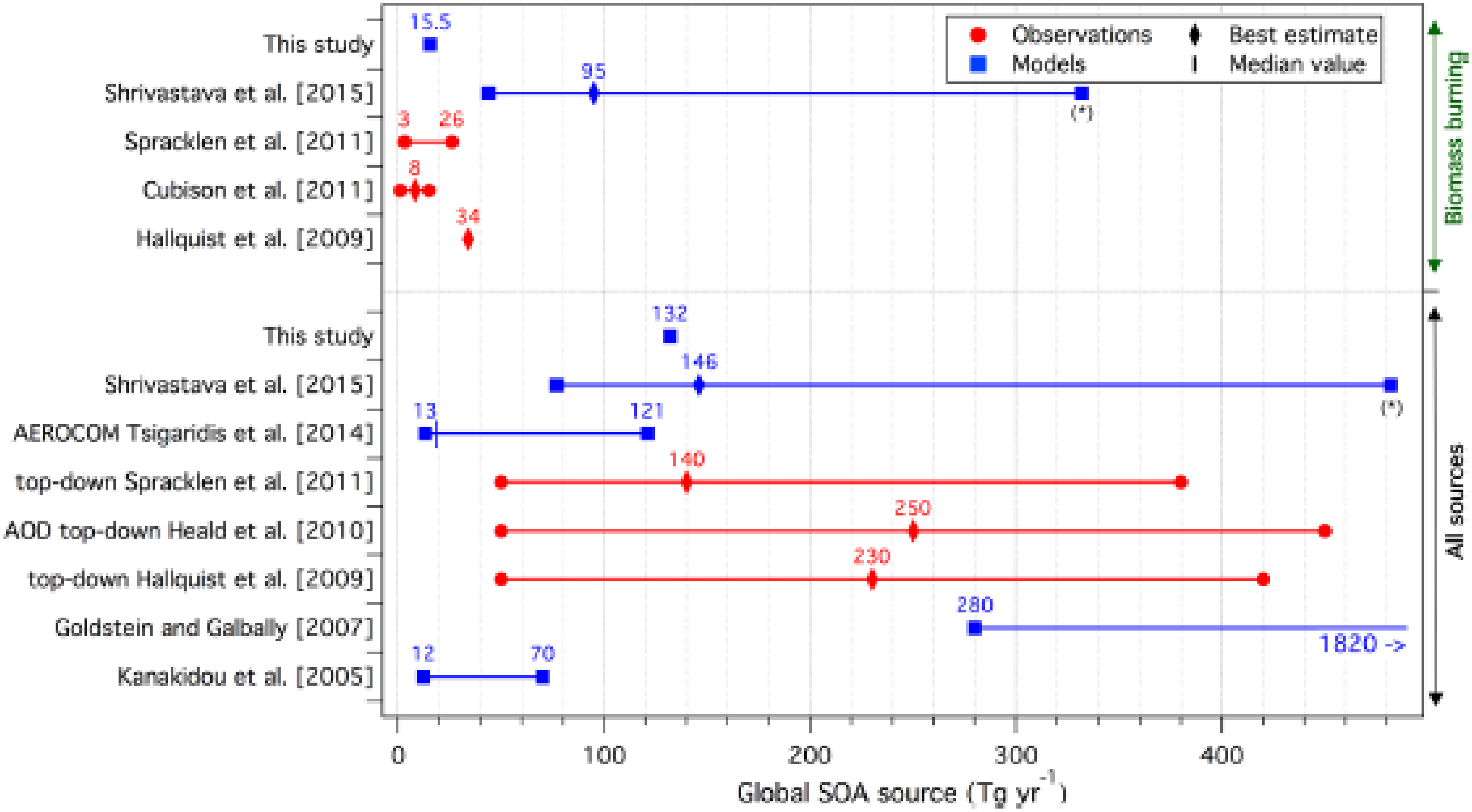
as earlier in
Tsigaridis et al., ACP, 2014

Bacchus-AEROCOM CCN intercomparison exercise

Fanourgakis et al, ACP 2019

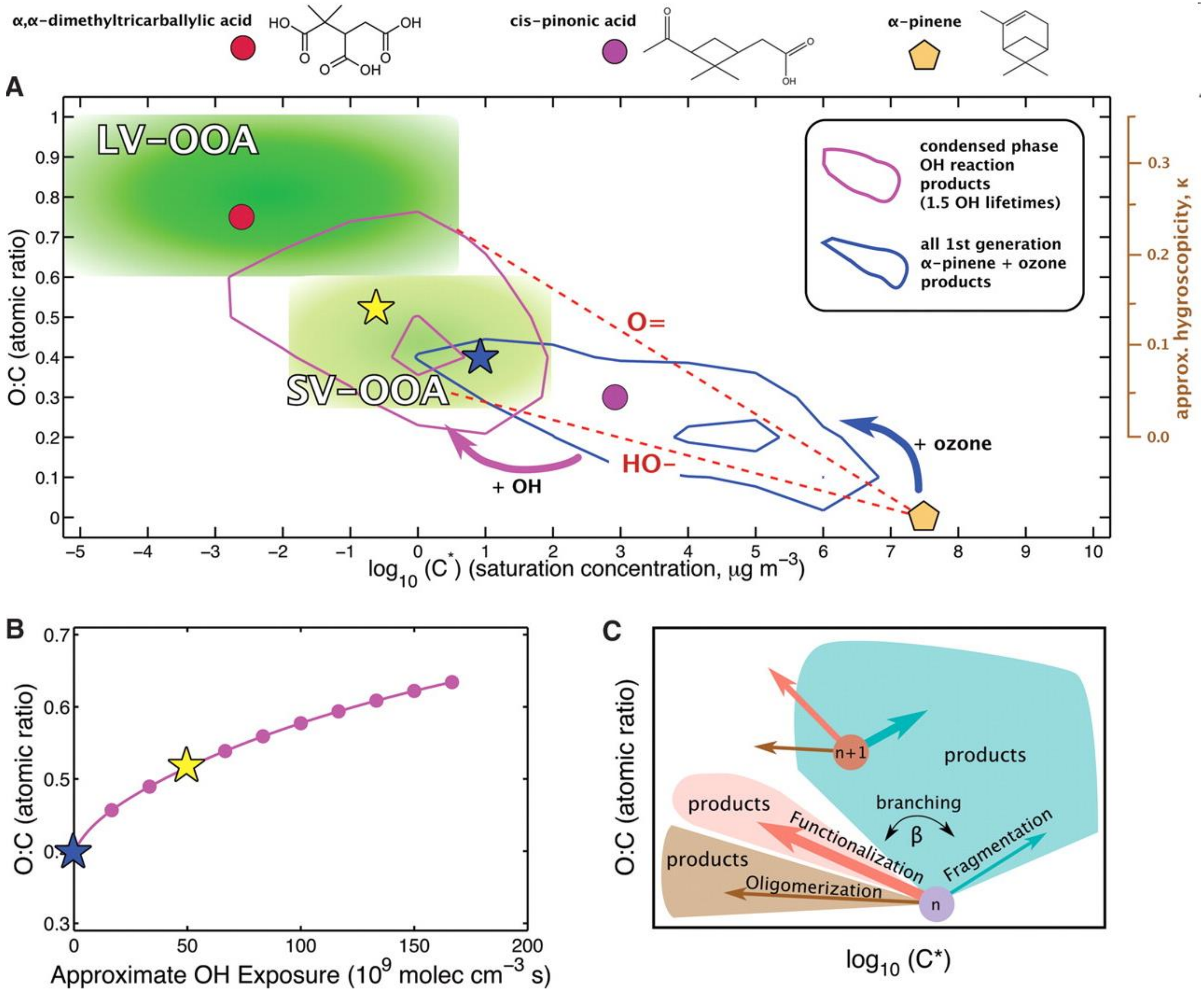

(f) stddev-to-mean of models (5x5) - ORG (Annual)

Estimates of global SOA source



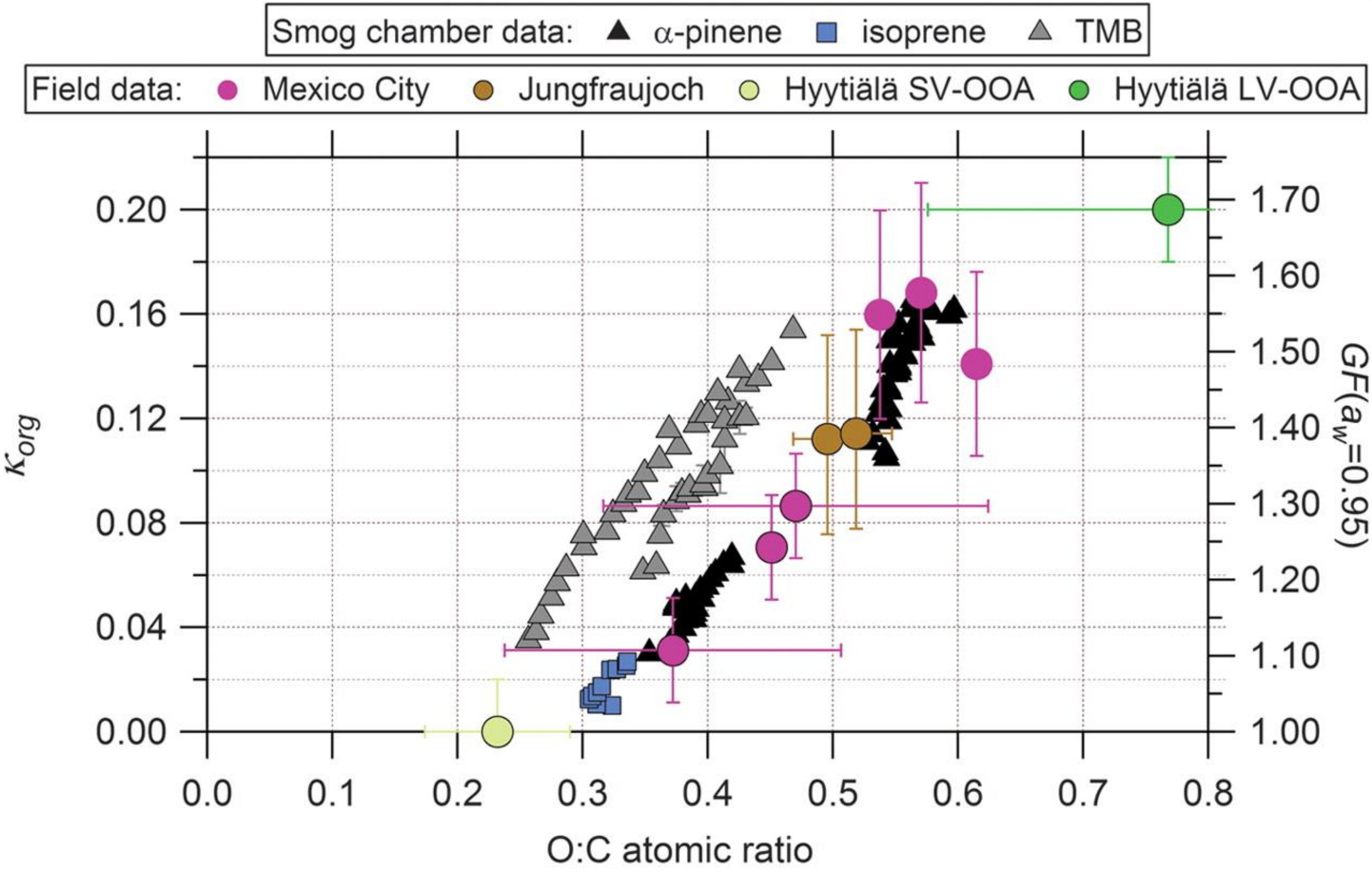
Hodzic et al., ACP, 2016

2D Basis Set: Volatility and O/C



Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

Hygroscopicity (κ_{org}) vs Organic O/C



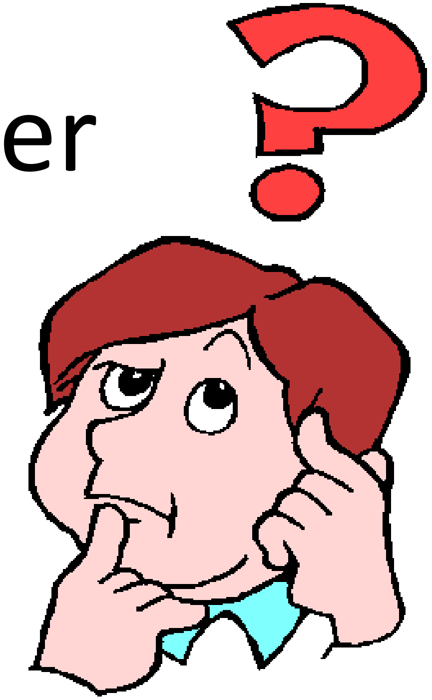
Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

Need to increase predictability of OA by global models

since OA is susceptible to become even more important in the future

Need to long term observations + information on source apportionment

Interactions with water



Interactions with water

Transformation of organics → formation of SOA, organic acids/ligands

Dissolution of WSVOC in aerosol water

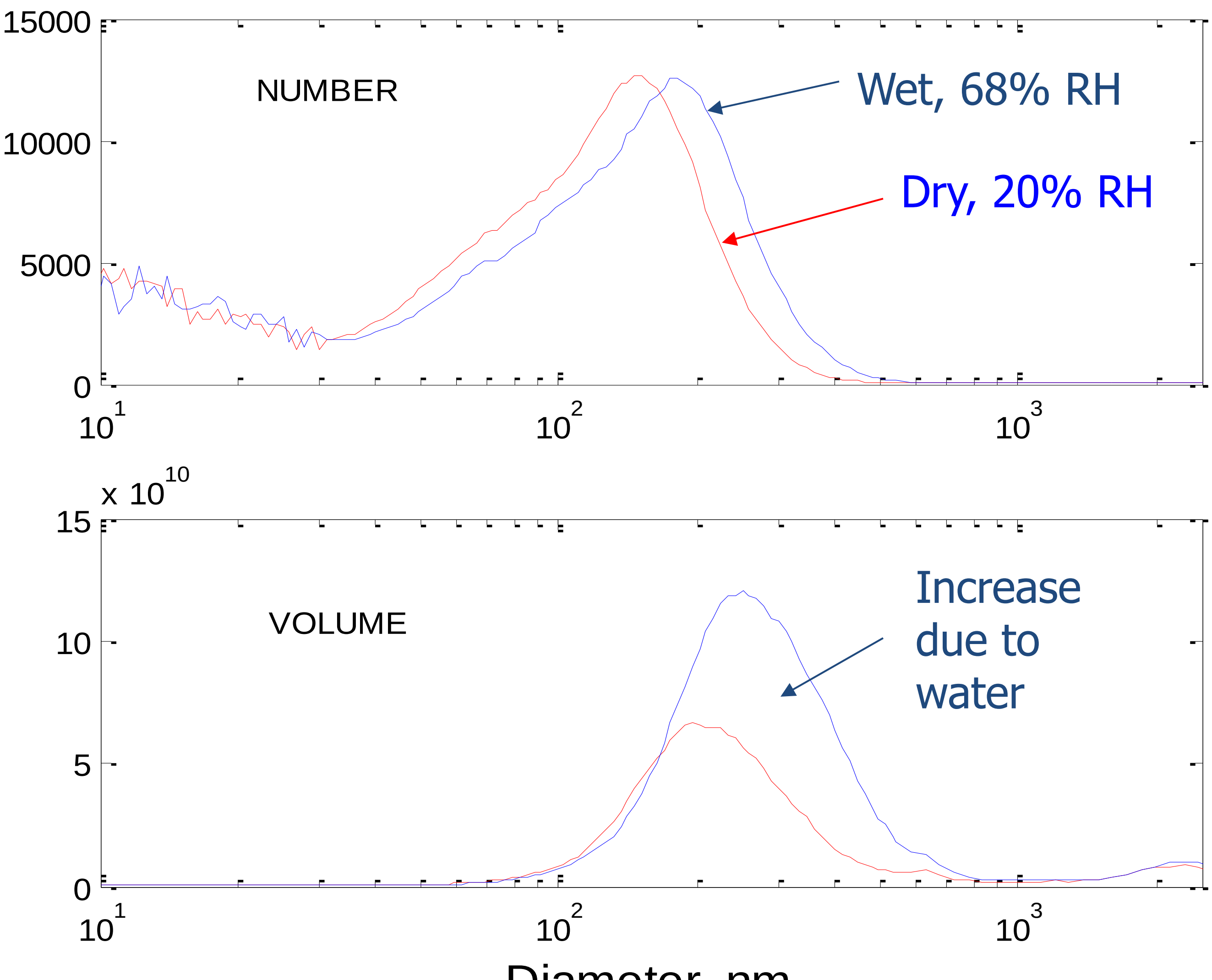
Degradation of SOA → formation of OH, increase of oxidative stress

Aerosol water associated to organics
Impact on pH

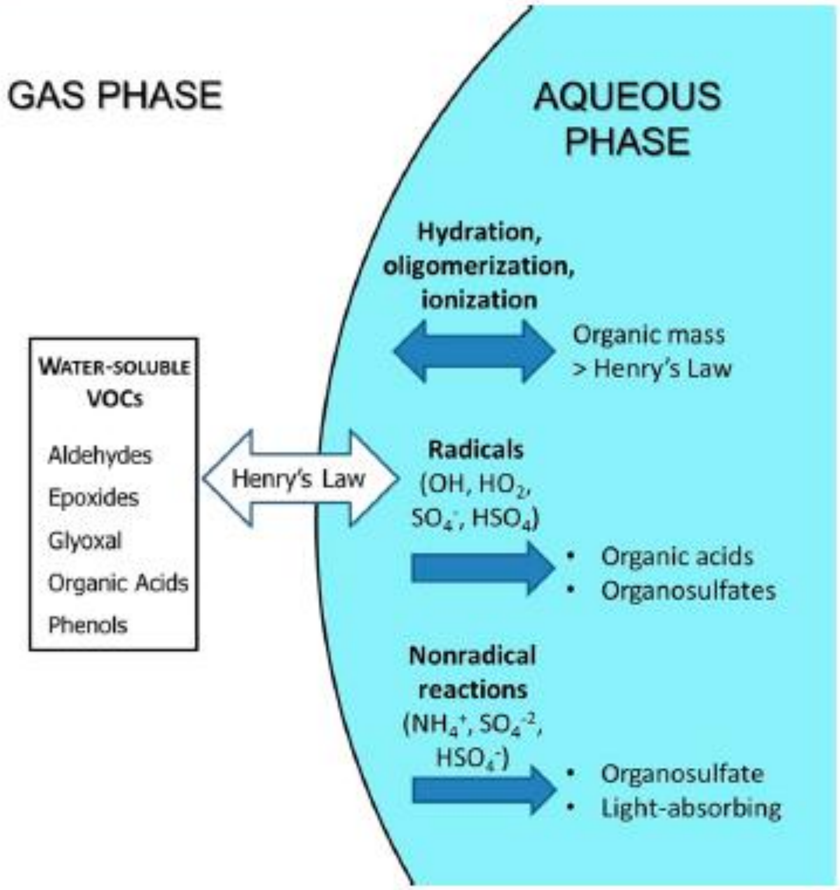
Evidence of aerosol water

Aerosol water =

$\rho_w(V_{wet}-V_{dry})$



reactions


GAS PHASE

AQUEOUS PHASE

Water-soluble VOCs
- Aldehydes
- Epoxides
- Glyoxal
- Organic Acids
- Phenols

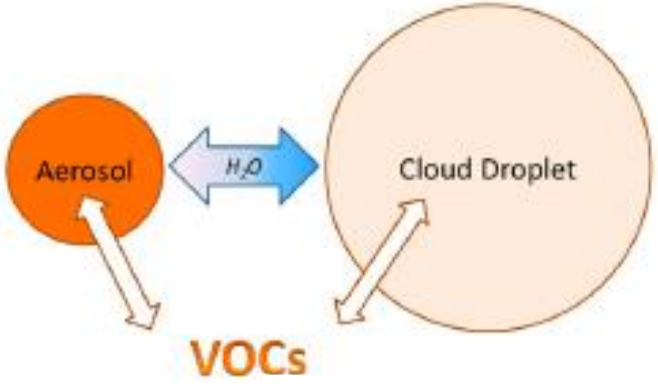
Henry's Law

Hydration, oligomerization, ionization

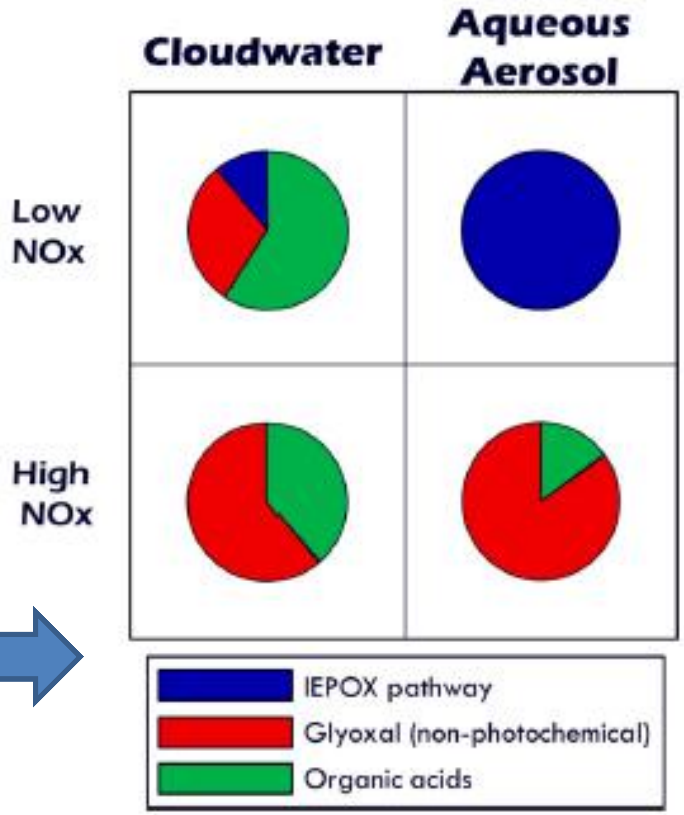
Organic mass > Henry's Law

Radicals (OH, HO_2, SO_4^-, HSO_4)
- Organic acids
- Organosulfates

Nonradical reactions (NH_4^+, SO_4^{-2}, HSO_4^-)
- Organosulfate
- Light-absorbing



result



🟦 IEPOX pathway
🟥 Glyoxal (non-photochemical)
🟩 Organic acids

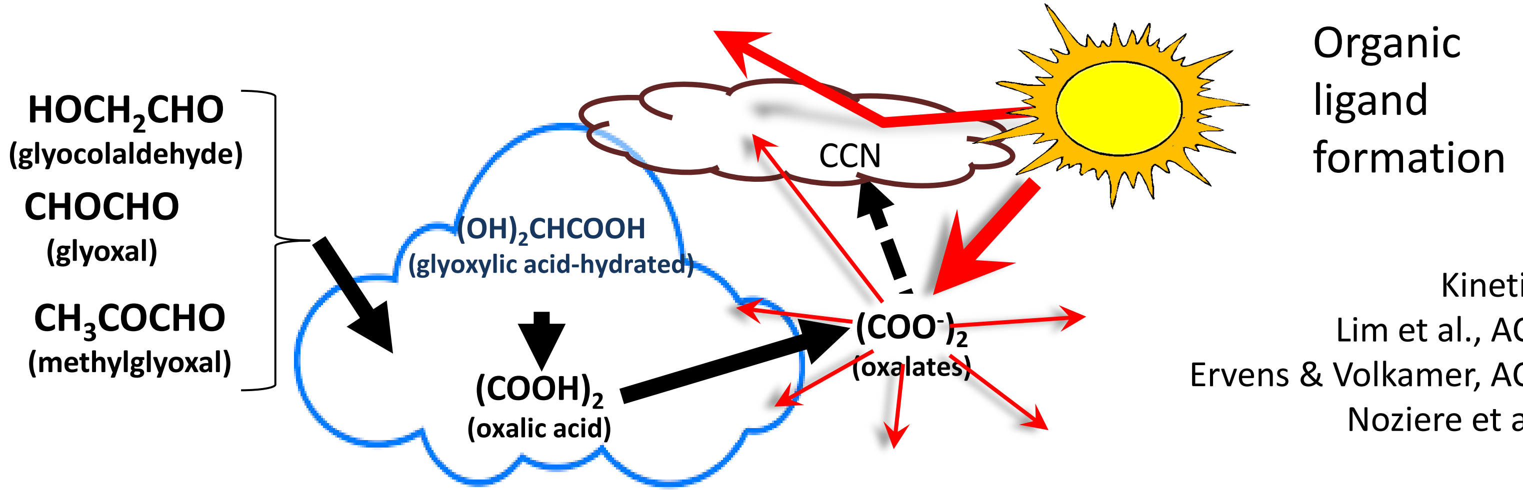
Environmental Science & Technology

2016

Aqueous Organic Chemistry in the Atmosphere: Sources and Chemical Processing of Organic Aerosols

V. Faye McNeill*

Multiphase chemistry in the global troposphere



$HOCH_2CHO$
(glycolaldehyde)
$CHOCHO$
(glyoxal)
CH_3COCHO
(methylglyoxal)

$(OH)_2CHCOOH$
(glyoxylic acid-hydrated)

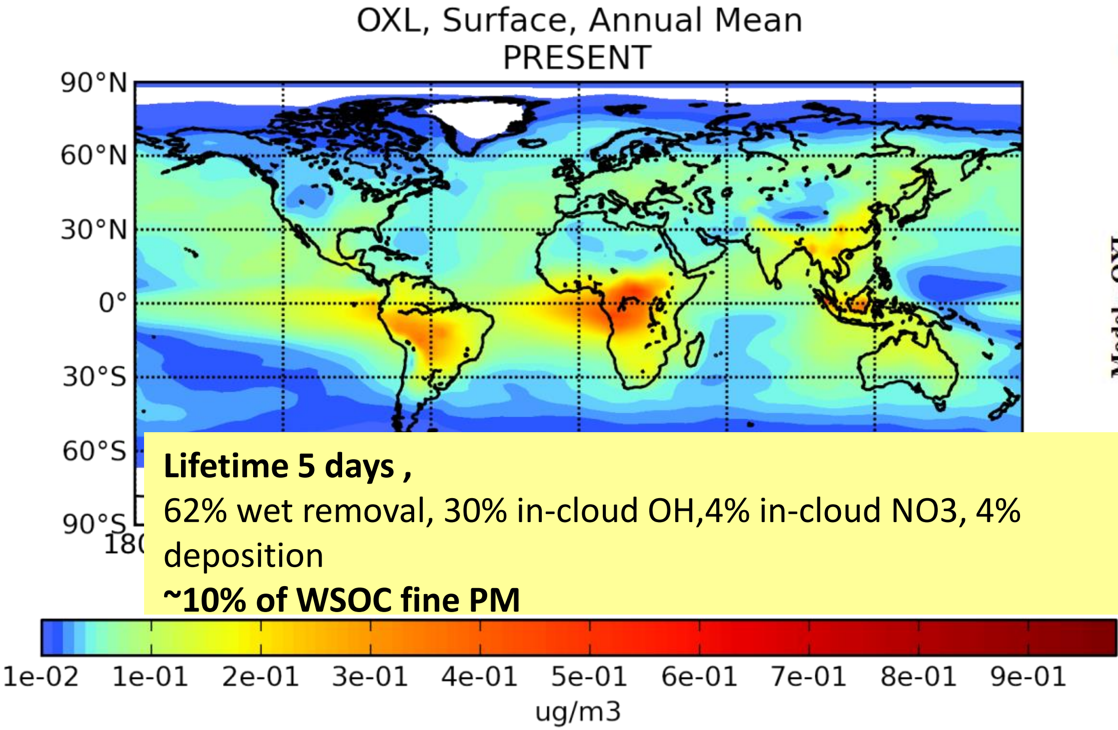
$(COOH)_2$
(oxalic acid)

$(COO^-)_2$
(oxalates)

CCN

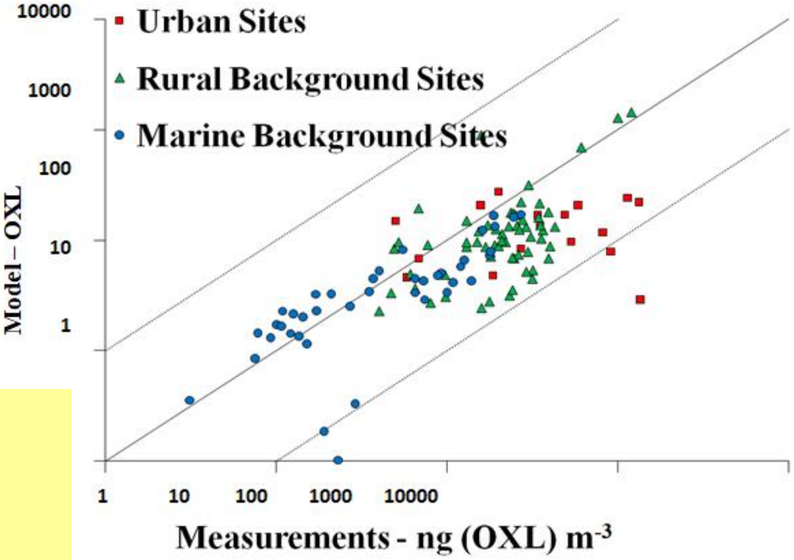
Organic
ligand
formation

Kinetics from
Lim et al., ACP, 2010
Ervens & Volkamer, ACP, 2010
Noziere et al., 2009



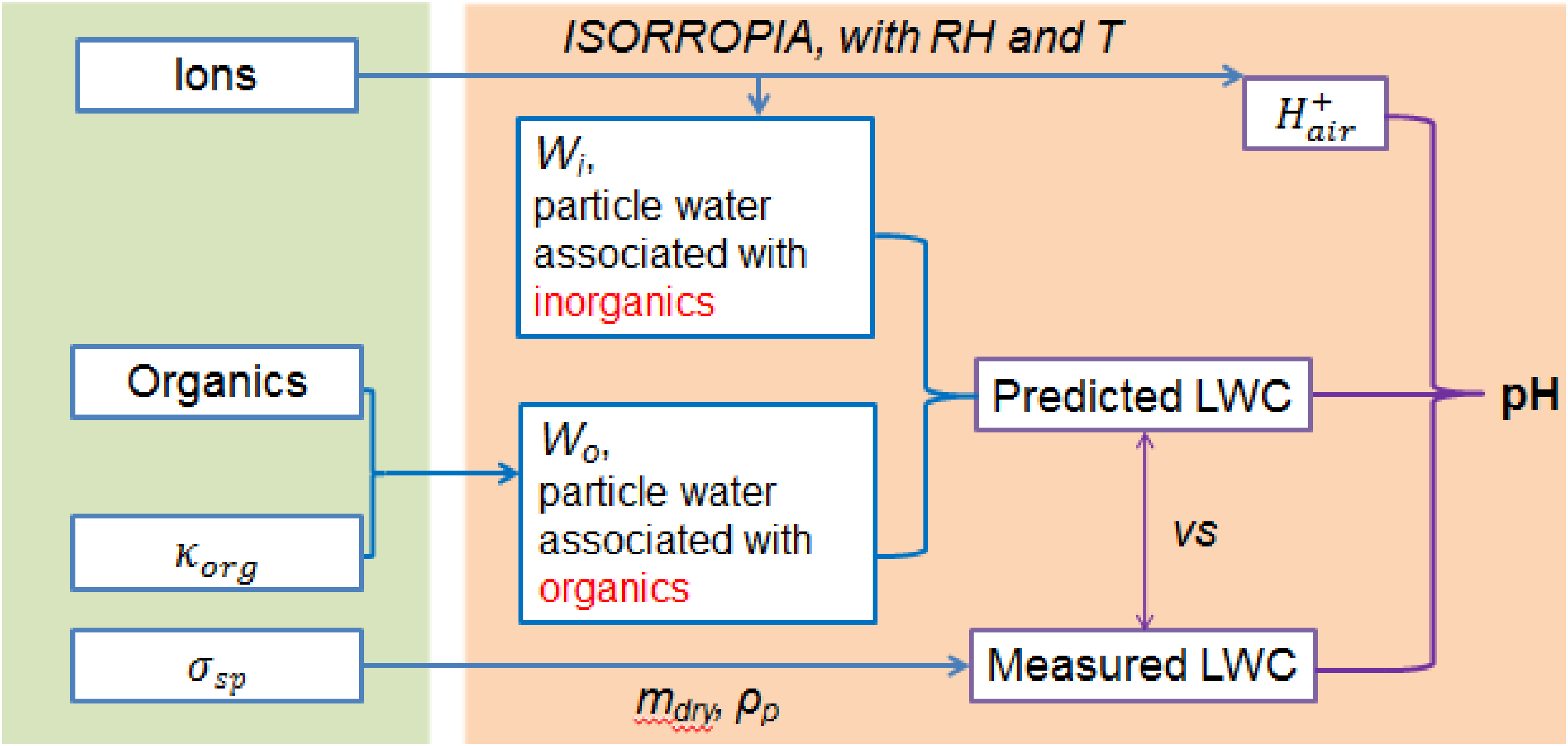
OXL, Surface, Annual Mean
PRESENT

Lifetime 5 days ,
62% wet removal, 30% in-cloud OH,4% in-cloud NO3, 4% deposition
~10% of WSOC fine PM



Myriokefalitakis et al., ACP, 2011

Organics contribute to the aerosol water



Ions

Organics

κ_{org}

σ_{sp}

ISORROPIA, with RH and T

H^{+}_{air}

W_i, particle water associated with inorganics

W_o, particle water associated with organics

Predicted LWC

vs

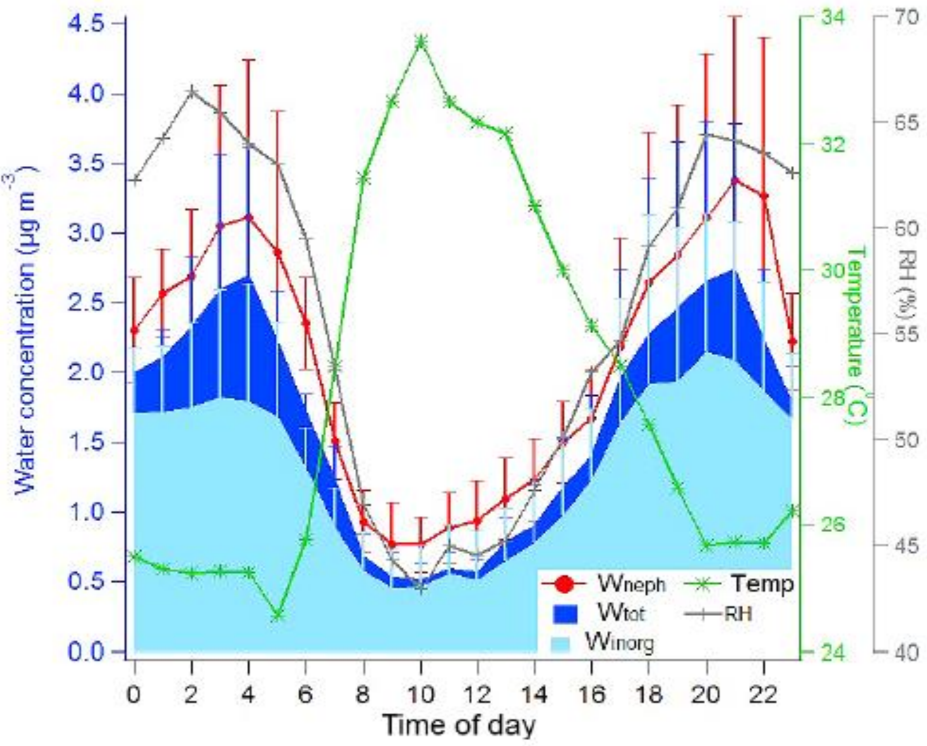
Measured LWC

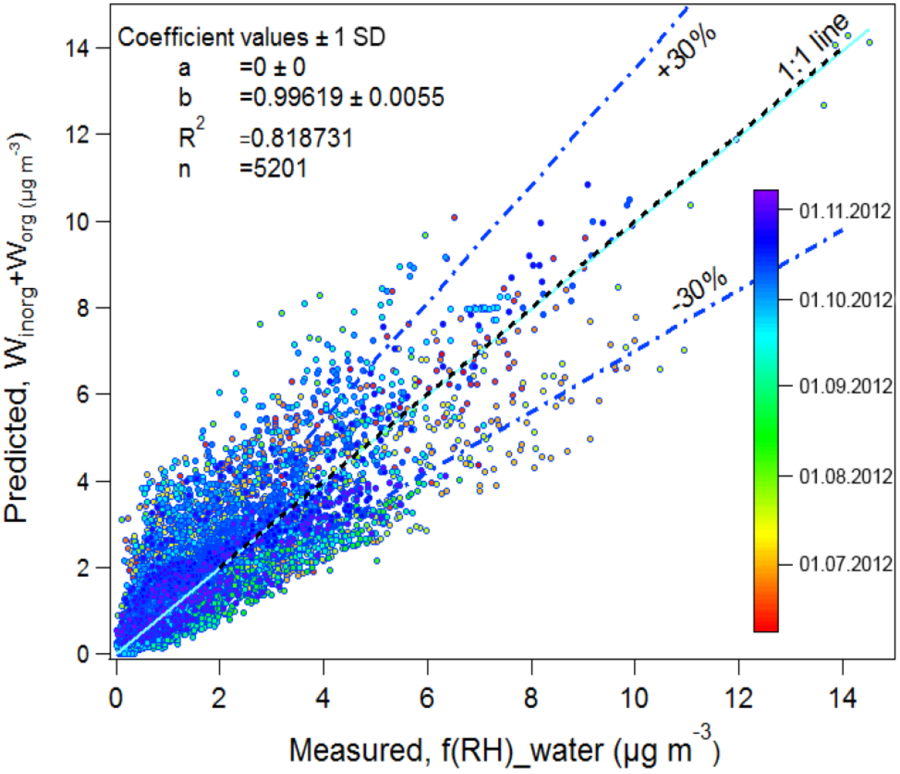
pH

m_{dry}, ρ_p

Guo et al. ACP 2015; Bougiatioti et al., ACP, 2016

Contribution of OA to aerosol water based on experimental data from Finokalia, Greece



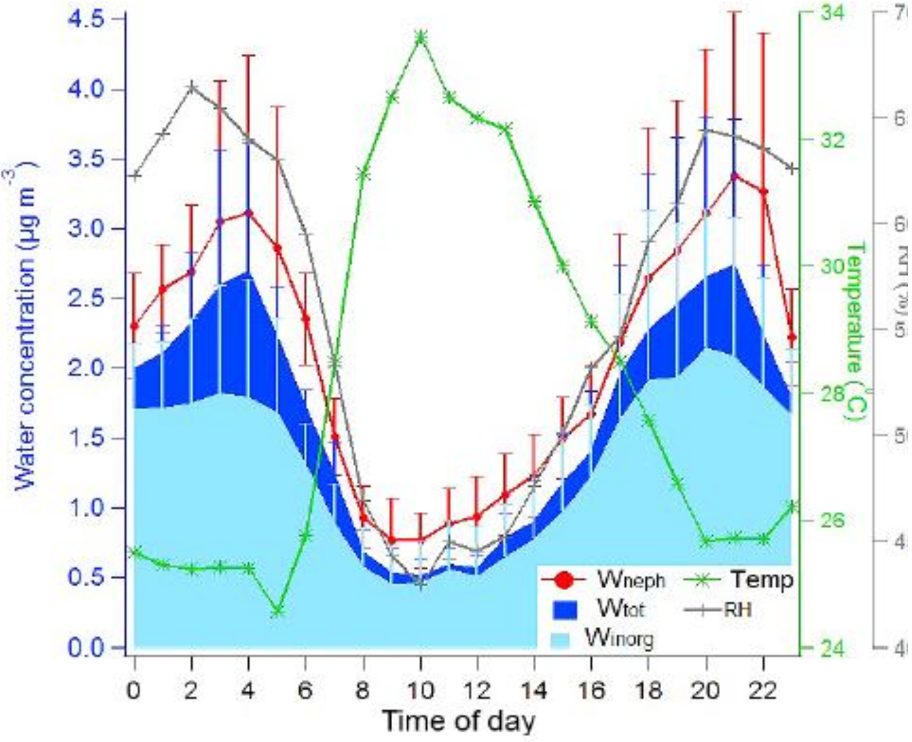


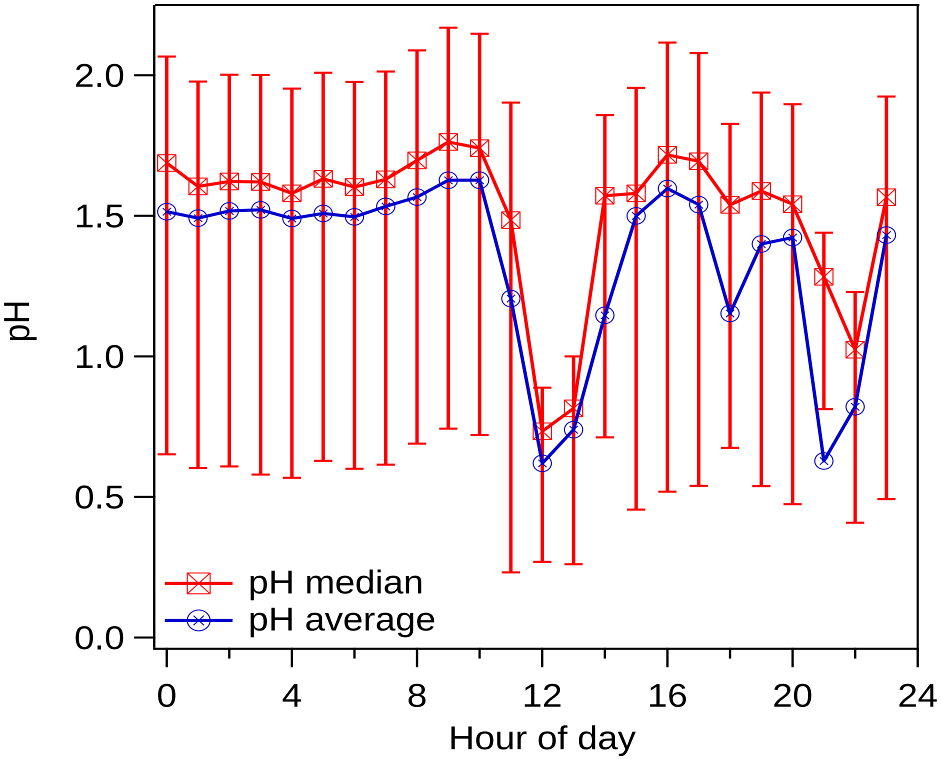
ISORROPIA II → W_{inorg},
κ → W_{org}

Maria Kanakidou, University of Crete

Bougiatioti et al., ACP, 2016

Contribution of OA to aerosol water based on experimental data from Finokalia, Greece



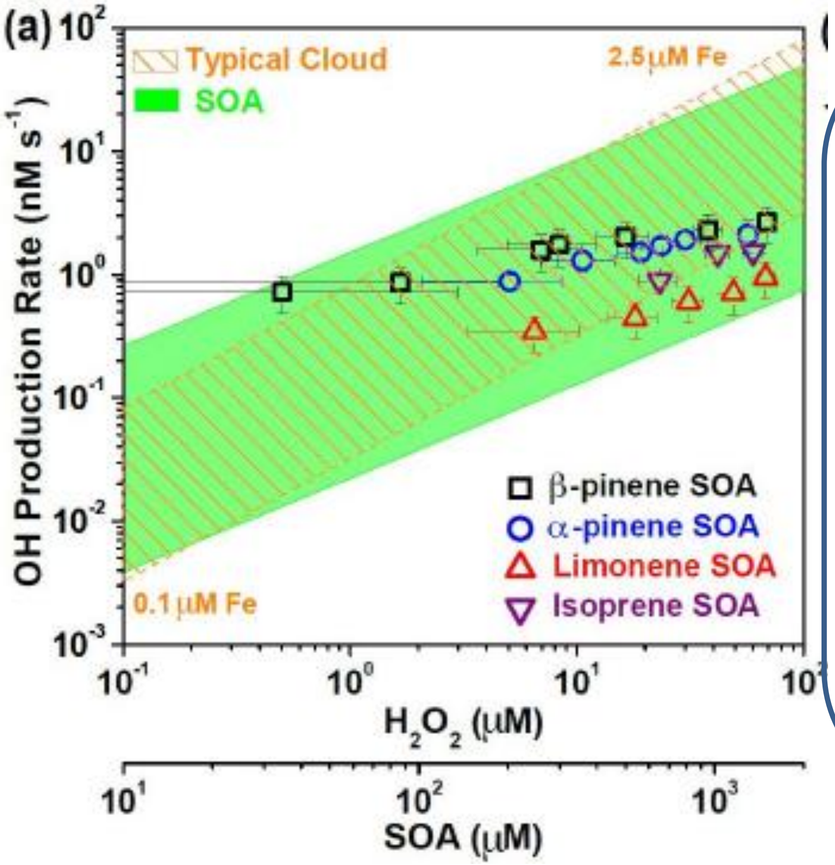


ISORROPIA II → W_{inorg},

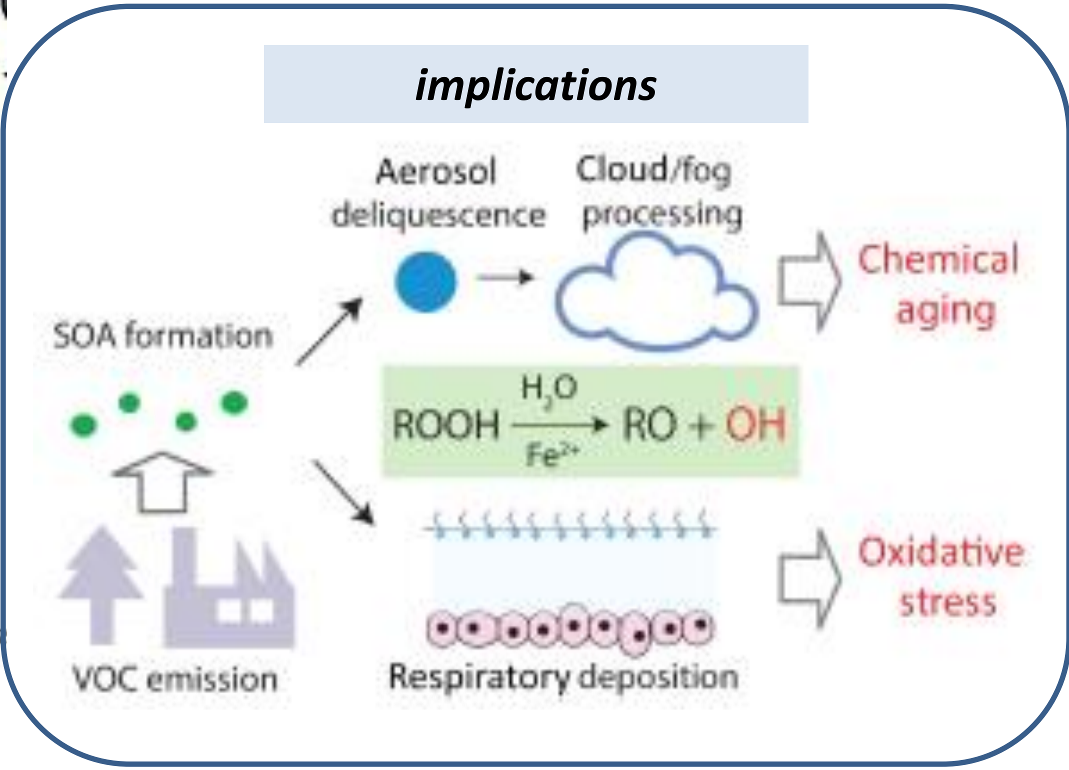
κ → W_{org}

Bougiatioti et al., ACP, 2016

H. Tong et al.: Hydroxyl radicals from SOA decomposition in water in the presence of Fe^{2+} ions due to Fenton-like reactions.



cloud droplets under dark conditions.


implications

→ chemical reactivity and aging of SOA particles is strongly enhanced upon interaction with water and iron

Atmos. Chem. Phys., 16, 1761–1771, 2016

Influence of human activity on BSOA

1- through aerosol water and partitioning of organics to the water phase (Carlton and Turpin, ACP 2013)

2- through increased oxidants and pre-existing particles (Kanakidou et al., JGR 2000)

3- through increased oxidants (Shrivastava et al., Nature Commun. 2015)

Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation

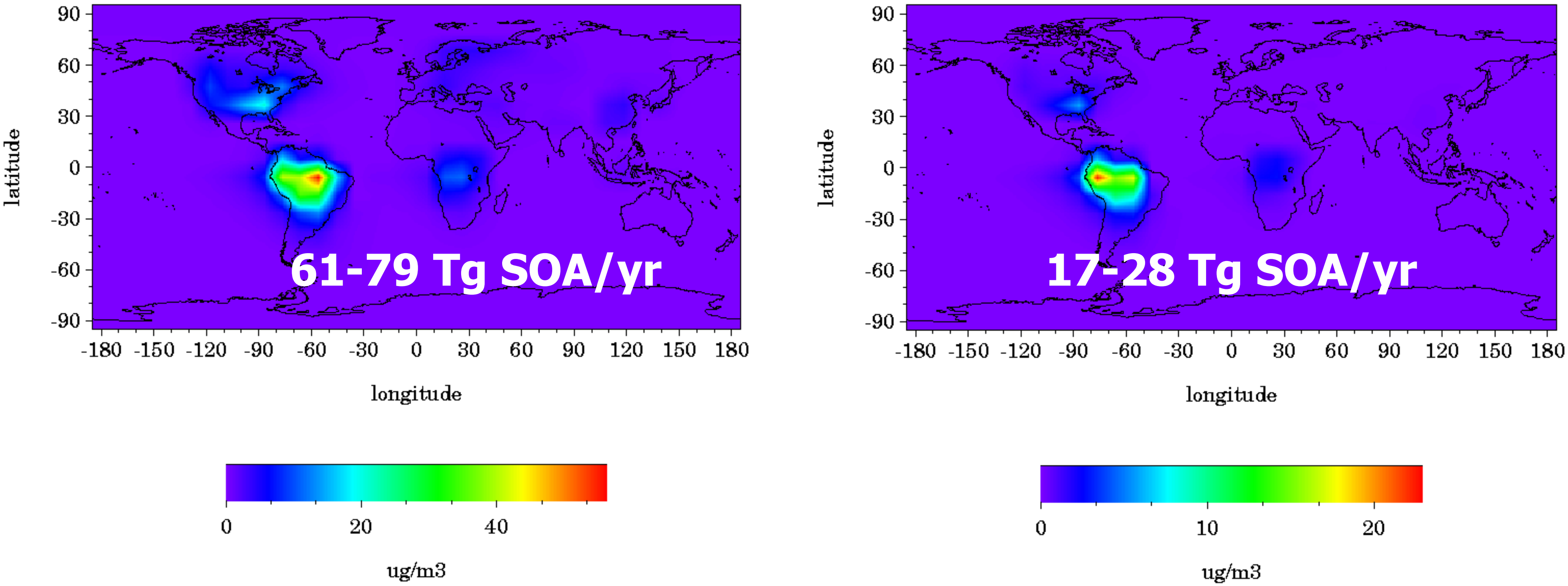
Kanakidou et al., JGR, 105,9243, 2000

First global modeling study of BSOA

INDUSTRIAL

August surface

PRE-INDUSTRIAL

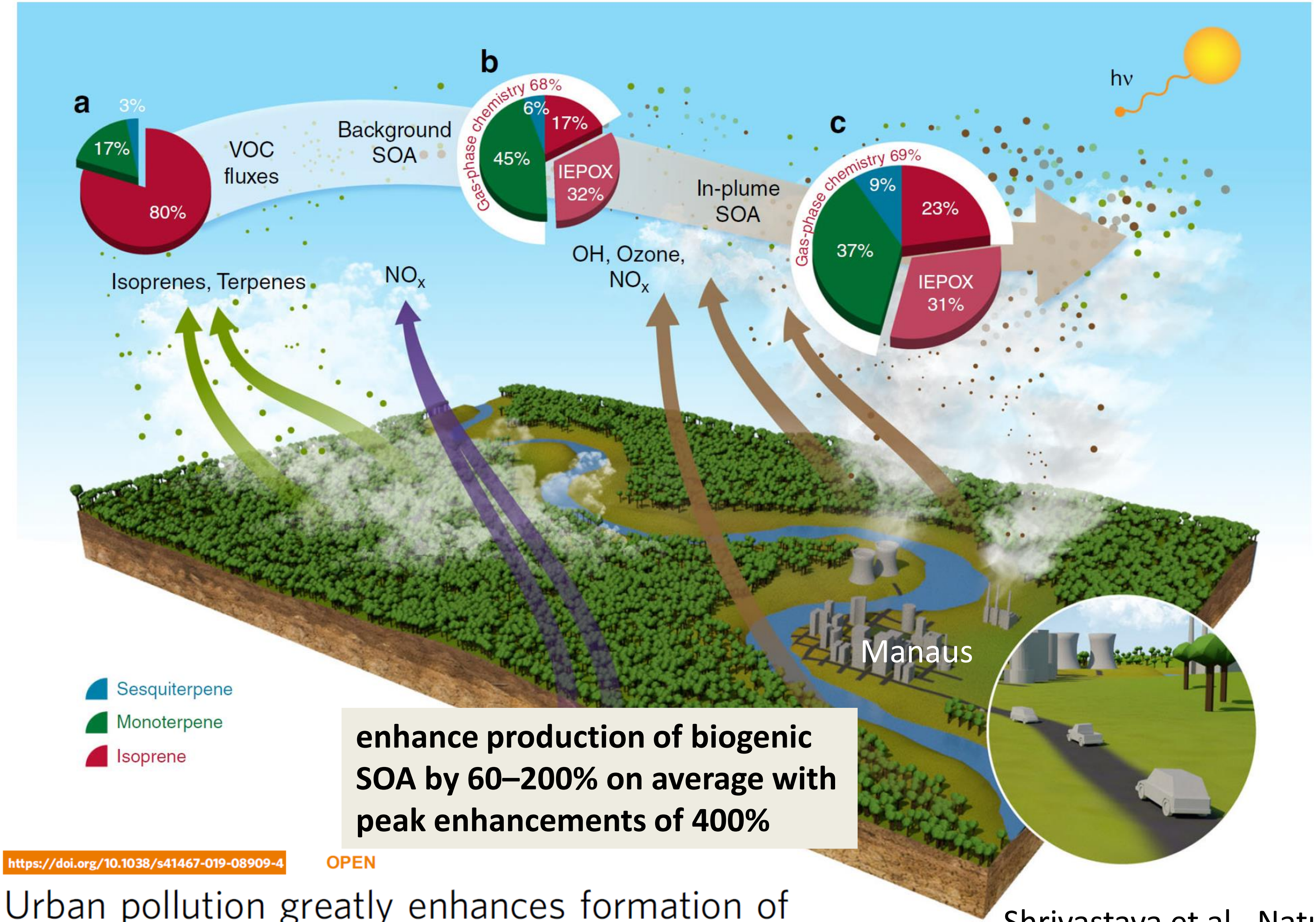


61-79 Tg SOA/yr

17-28 Tg SOA/yr

Human activity enhanced BSOA formation by a factor of about 3 due to increases in

- **oxidant levels**
- **Pre-existing particles**



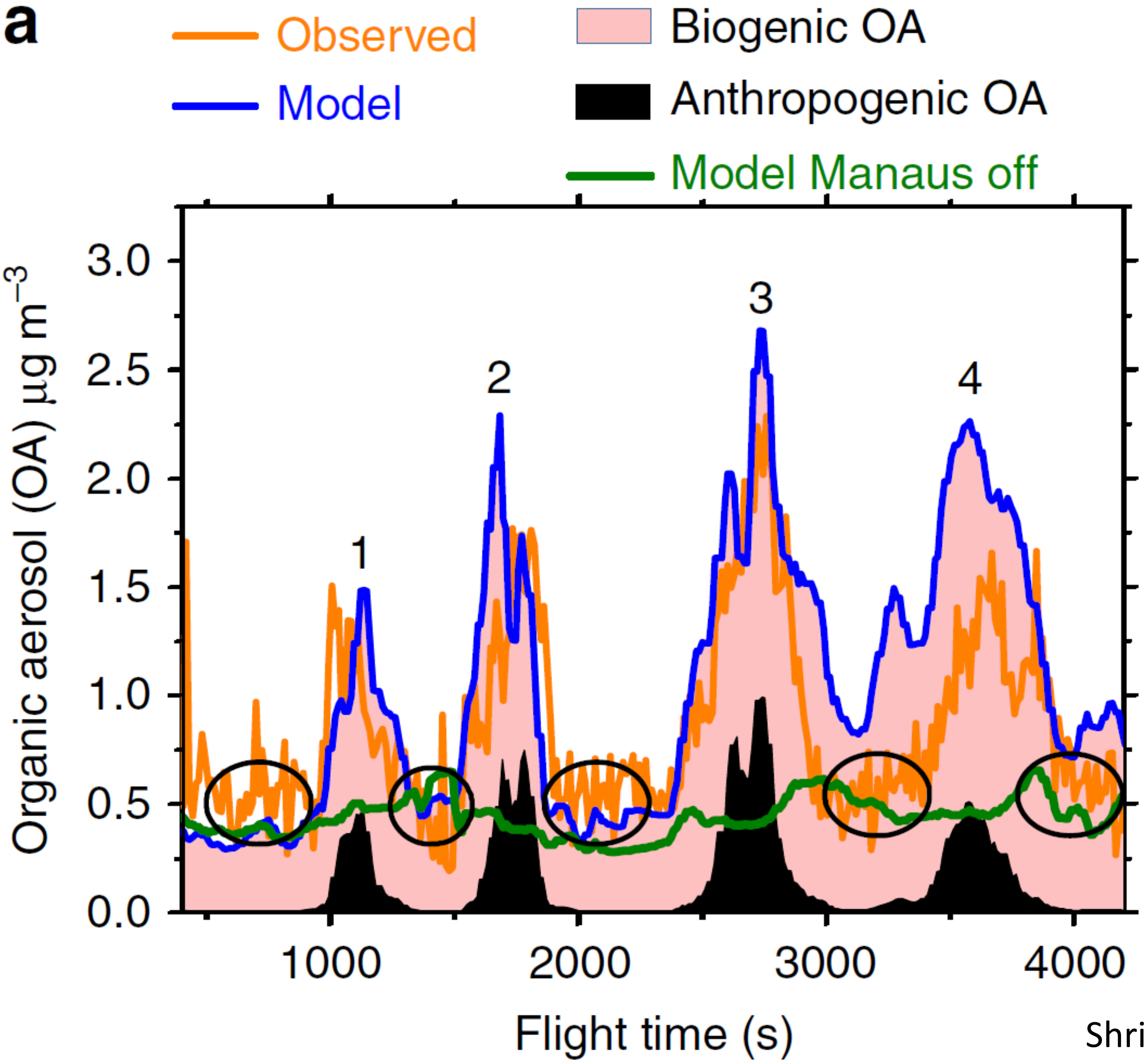
enhance production of biogenic SOA by 60–200% on average with peak enhancements of 400%

https://doi.org/10.1038/s41467-019-08909-4

OPEN

Urban pollution greatly enhances formation of natural aerosols over the Amazon rainforest

Shrivastava et al., Nature Communications 2019

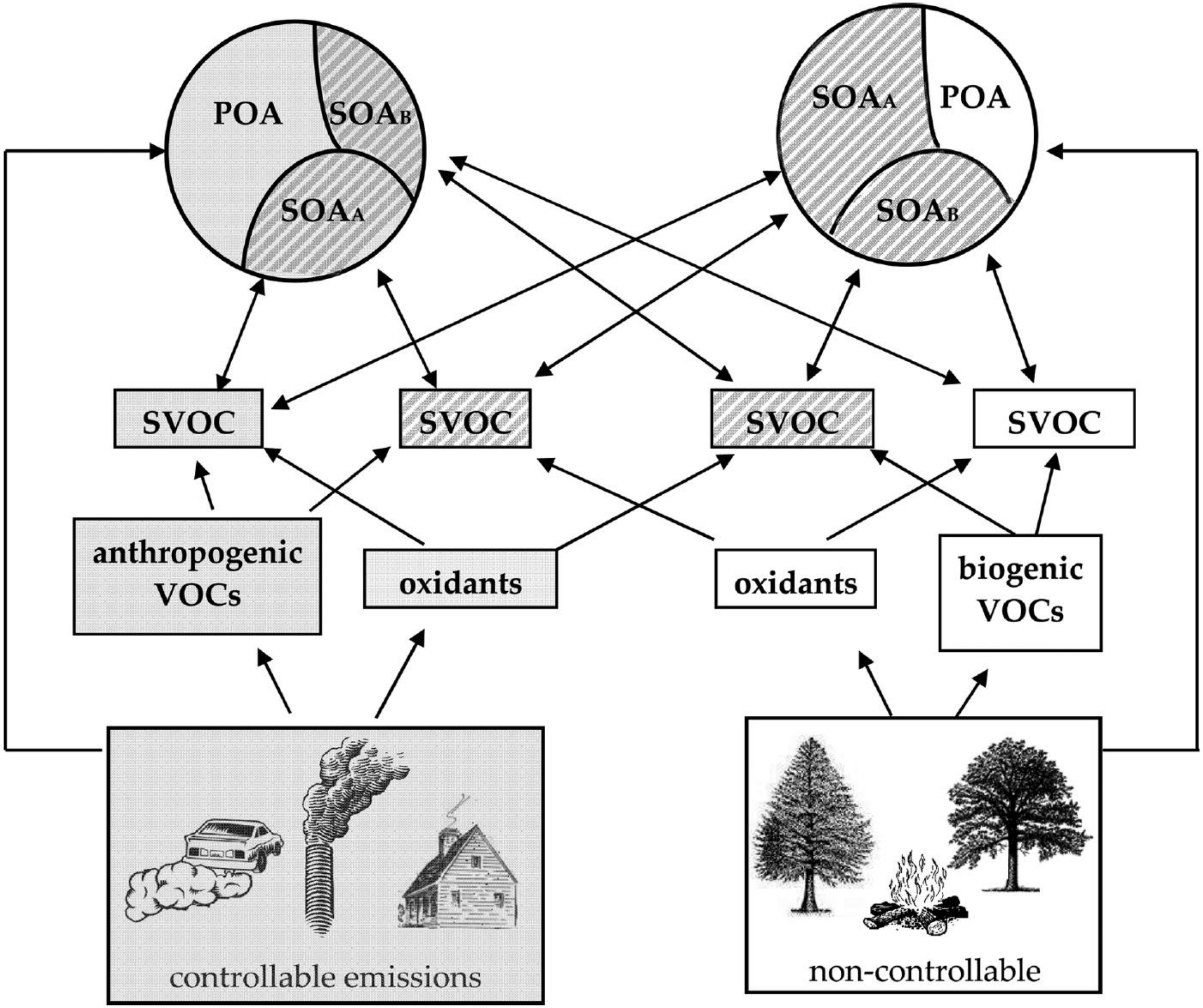


Shrivastava et al., Nature Communications 2019

To What Extent Can Biogenic SOA be Controlled?

Carlton et al. 2010

Environ. Sci. Technol. **2010**, *44*, 3376–3380



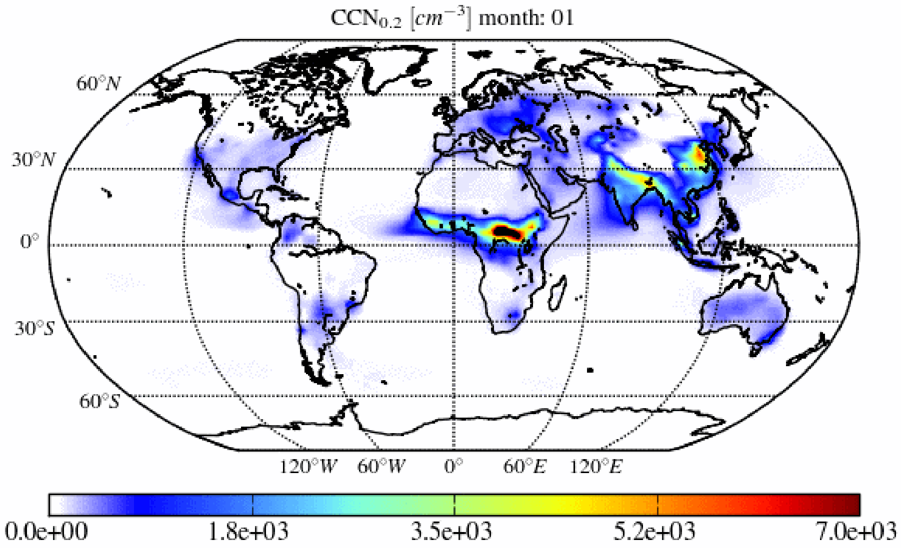
CMAQ Model simulations

Strong dependence of BSOA on anthropogenic emissions

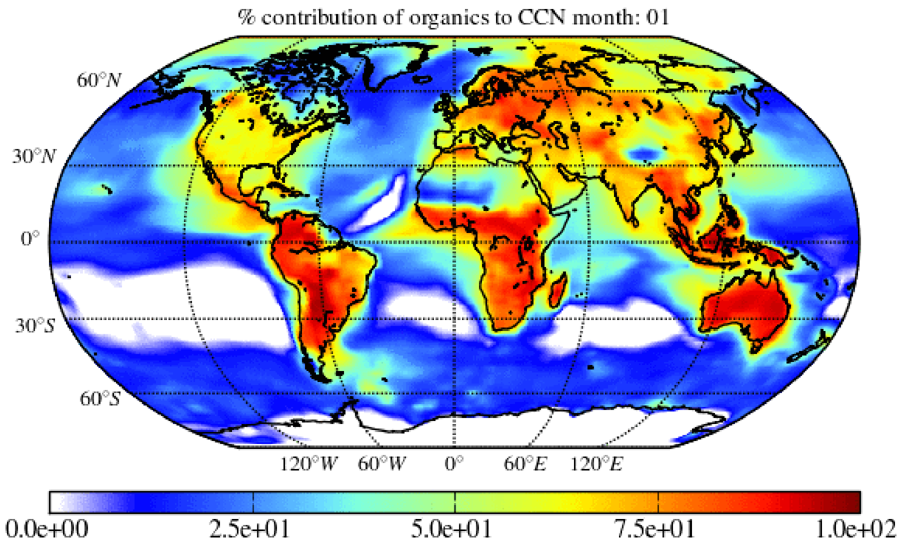
More than 50% of biogenic SOA in the Eastern USA can be controlled

Seasonal variability of CCN at 0.2% ss

CCN with organics



% contribution of organics



Near the surface

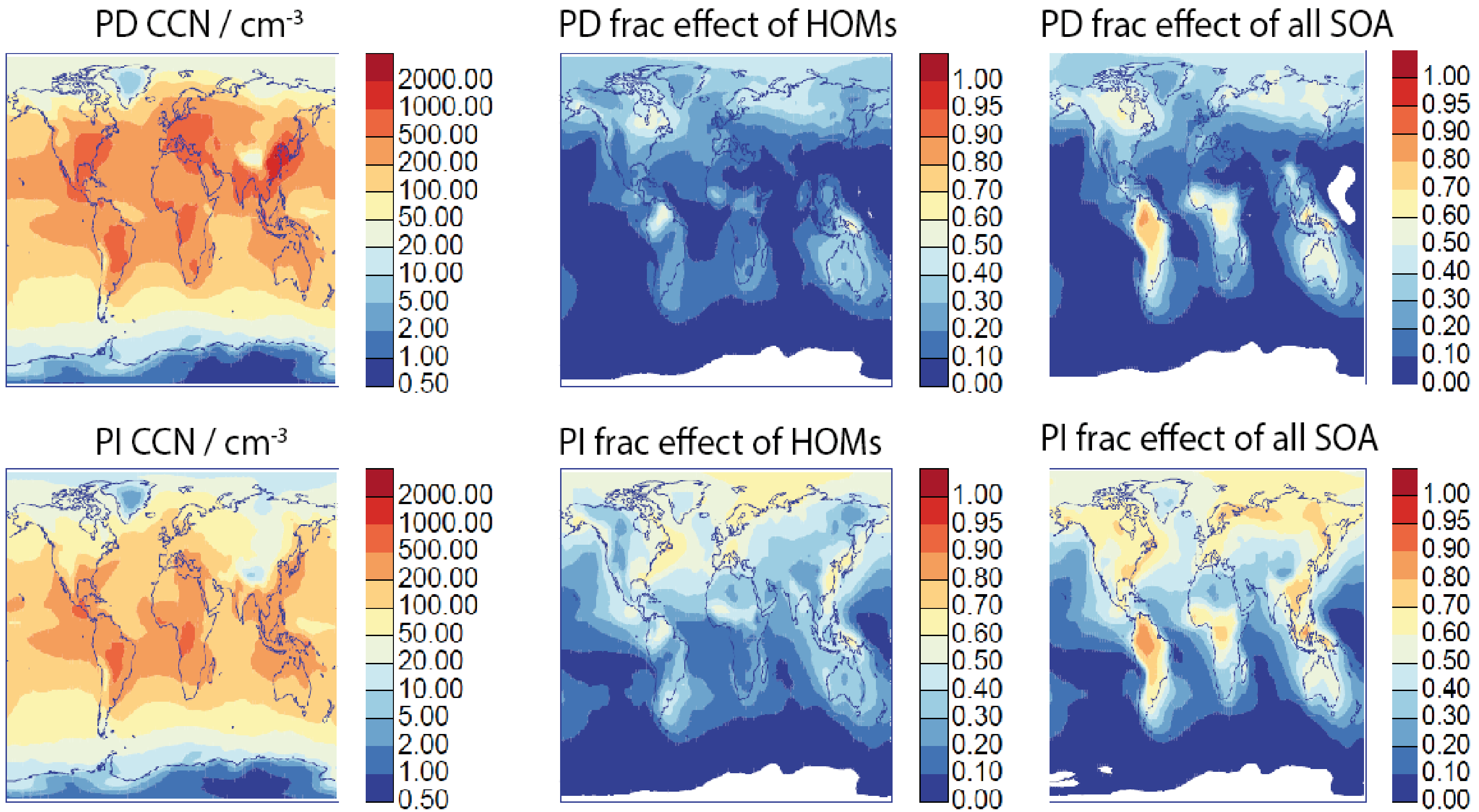
These results are in general agreement with Gordon et al. JGR 2017 who estimated on annual mean basis the contribution of biogenic SOA at ~41% of CCN during the preindustrial period and at 26% of CCN at present day

How OA affect CCN:

- Primary emissions
- New particle formation
- Growth to critical size
- Ageing to hygroscopic material

Fanourgakis et al., 2018 in the proceedings of 36th ITM on Air Pollution Modelling and its Application

Role of organics in CCN & NPF

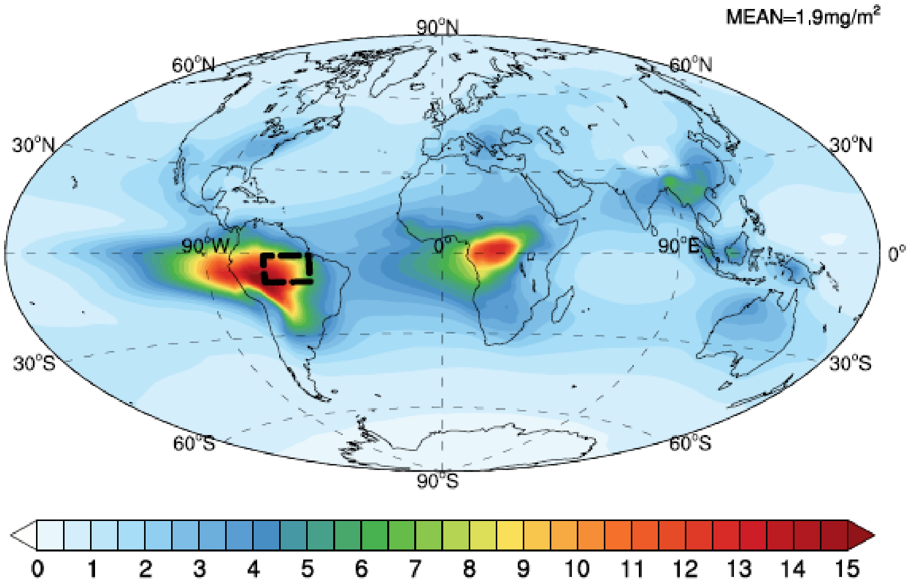


Gordon et al., JGR 2017

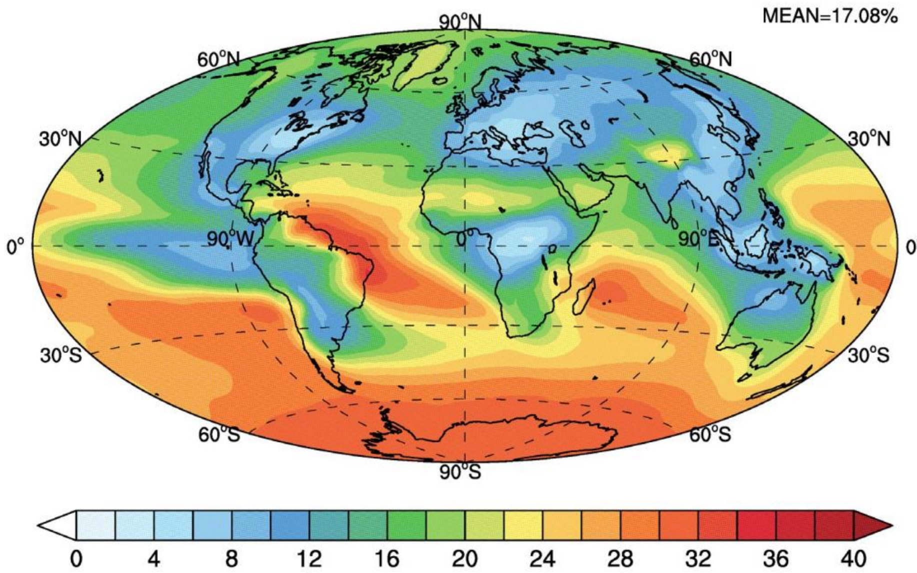
Organic nucleation & growth
~29% of CCN Pre-industrial (PI)
~15% of CCN Present day (PD)

Modelled effect of SOA on annual mean CCN at ss=0.2% in the boundary layer

SOA ~40% of CCN PI; 24% of CCN PD



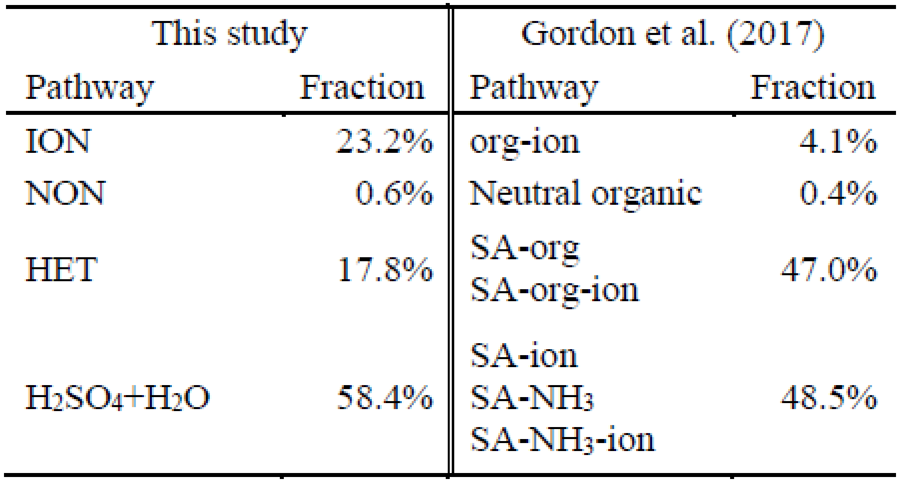
Present day SOA - column



Percentage of ‘new SOA’ to total SOA

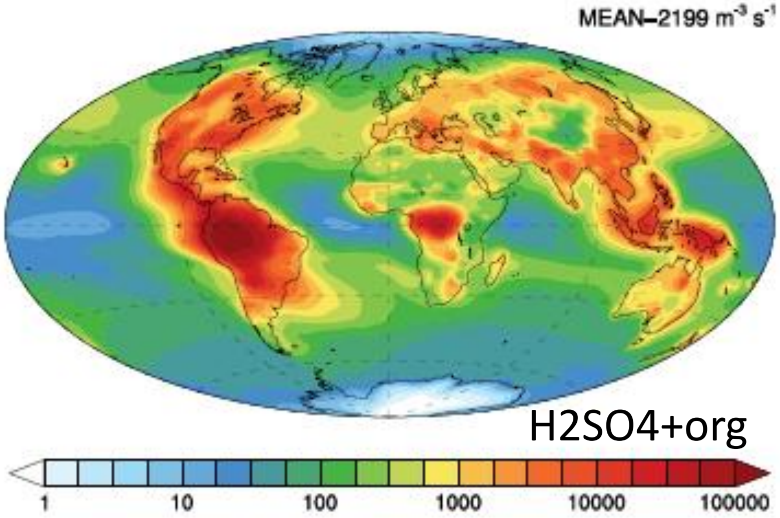
‘new SOA’ and growth explains 17% of total global SOA burden (>30% over some ocean & remote regions)

Organics and nucleation

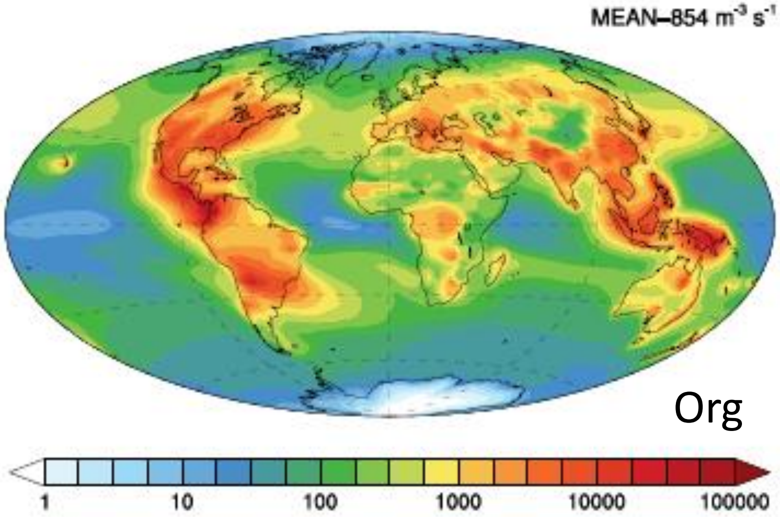


This study		Gordon et al. (2017)	
Pathway	Fraction	Pathway	Fraction
ION	23.2%	org-ion	4.1%
NON	0.6%	Neutral organic	0.4%
HET	17.8%	SA-org SA-org-ion	47.0%
H_2SO_4+H_2O	58.4%	SA-ion SA-NH_3 SA-NH_3-ion	48.5%

Zhu et al Nature Communications, 2019

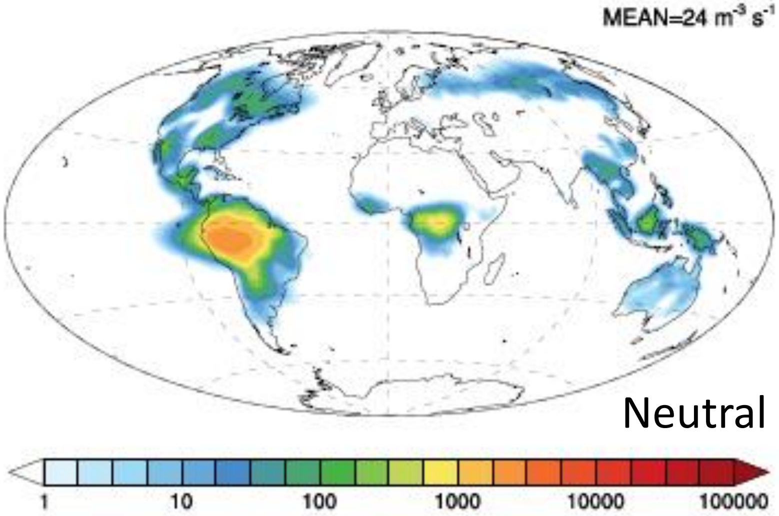


H2SO4+org



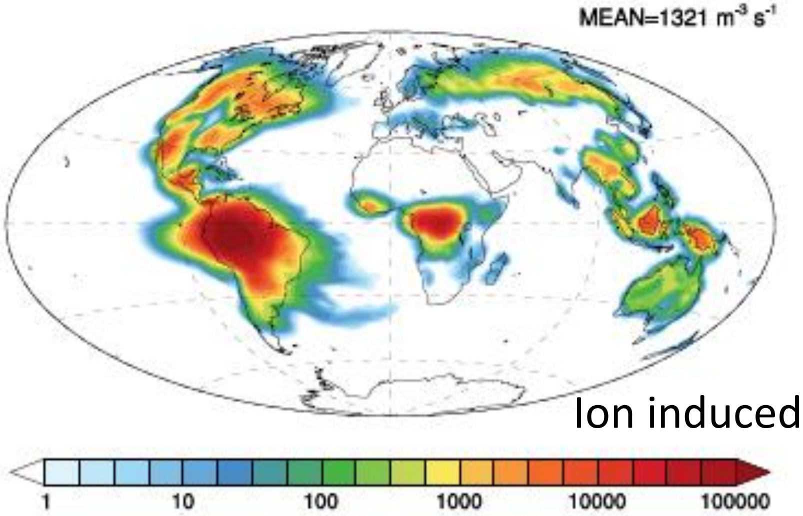
Org

(c)



Neutral Org

(d)

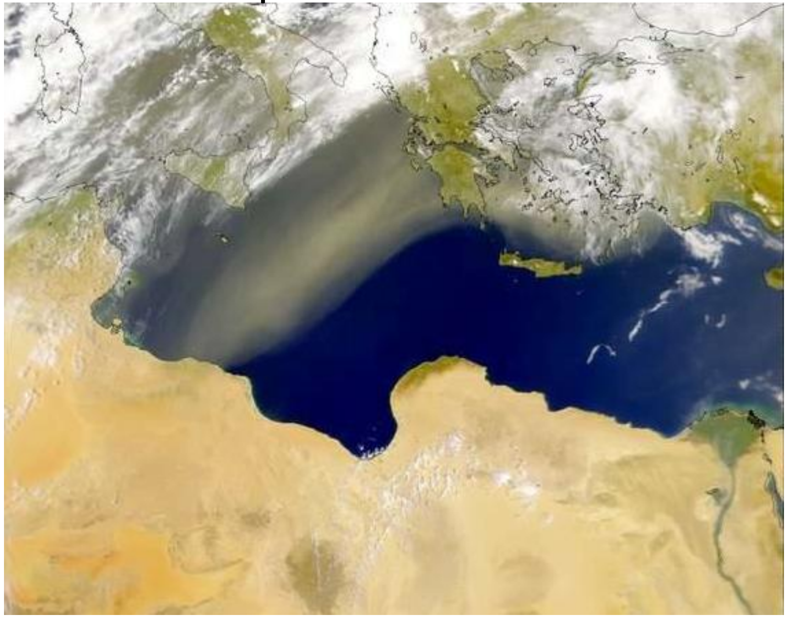


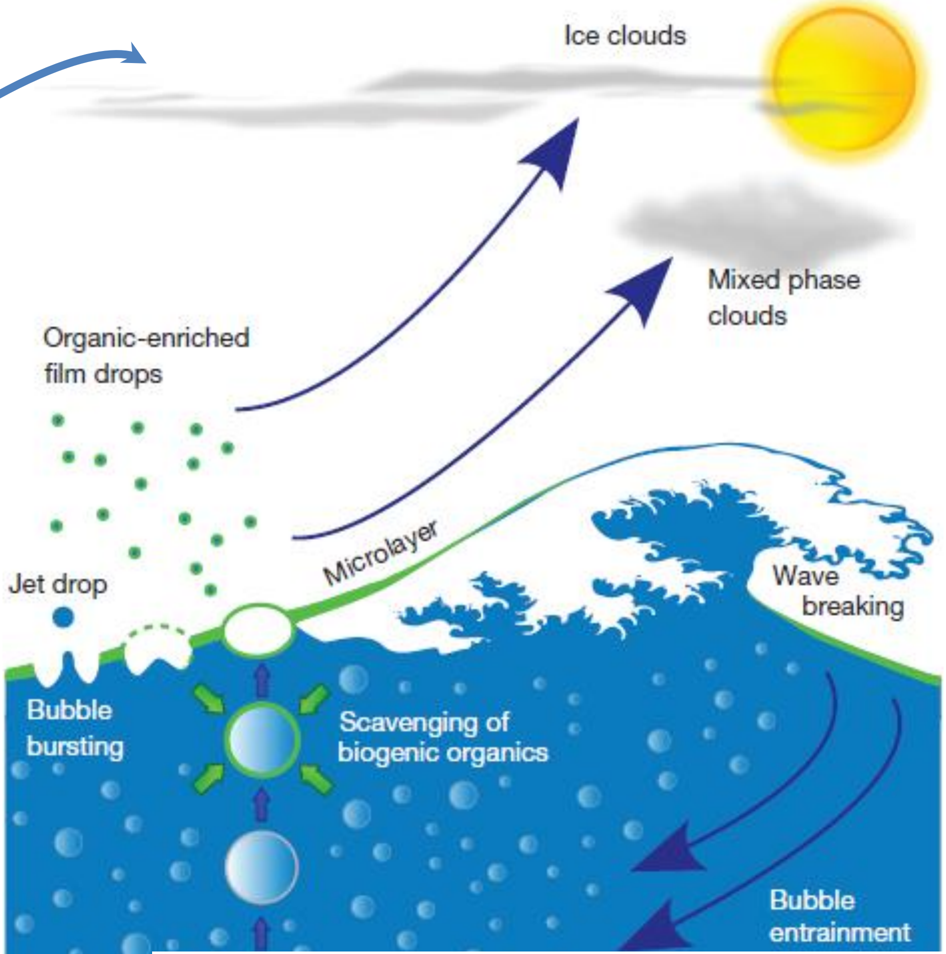
Ion induced Org

Zhu et al Nature Communications, 2019

Contribution to IN

Fledspart



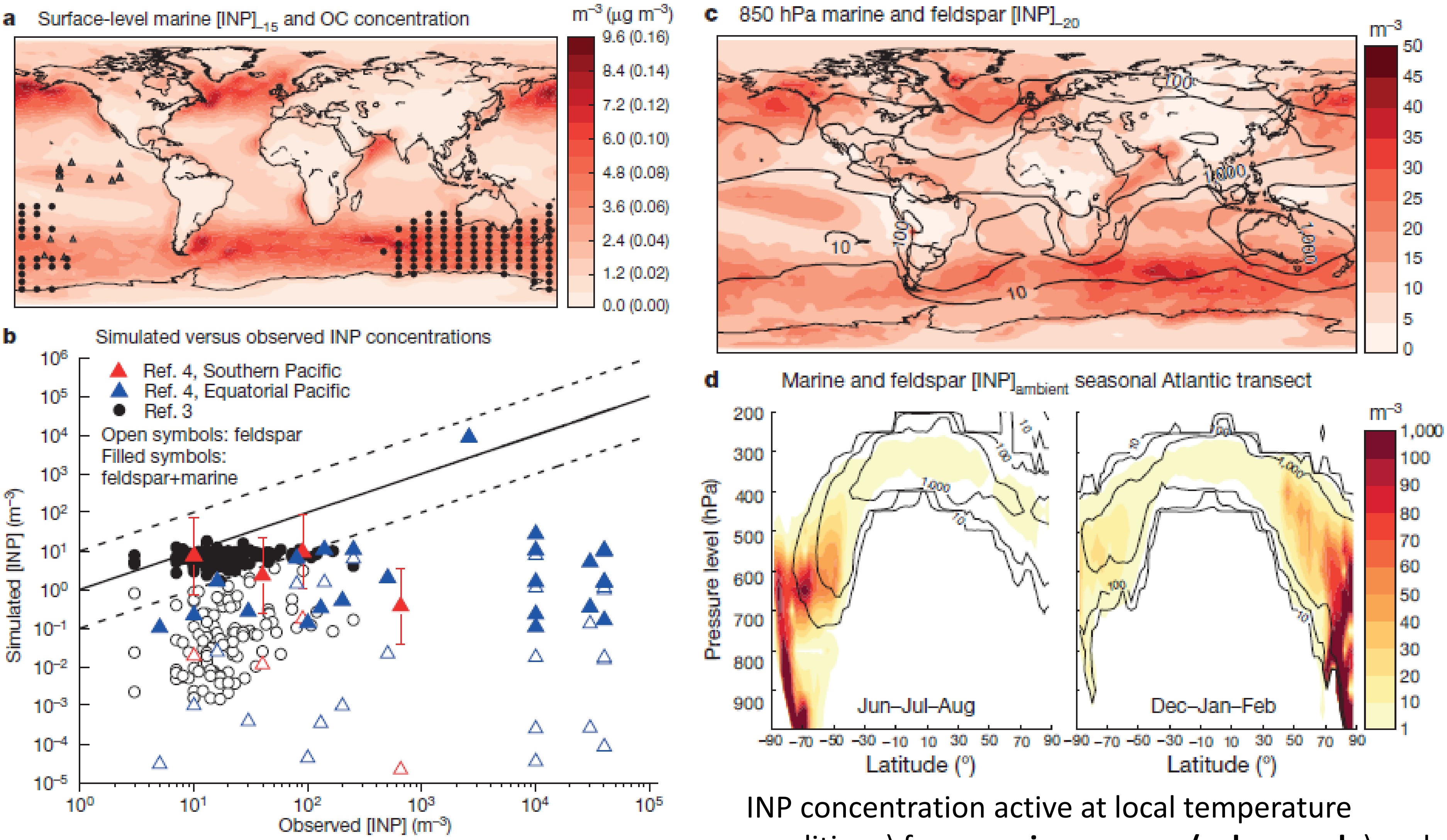


A marine biogenic source of atmospheric ice-nucleating particles

doi:10.1038/nature14986

Wilson et al., Nature, 2015

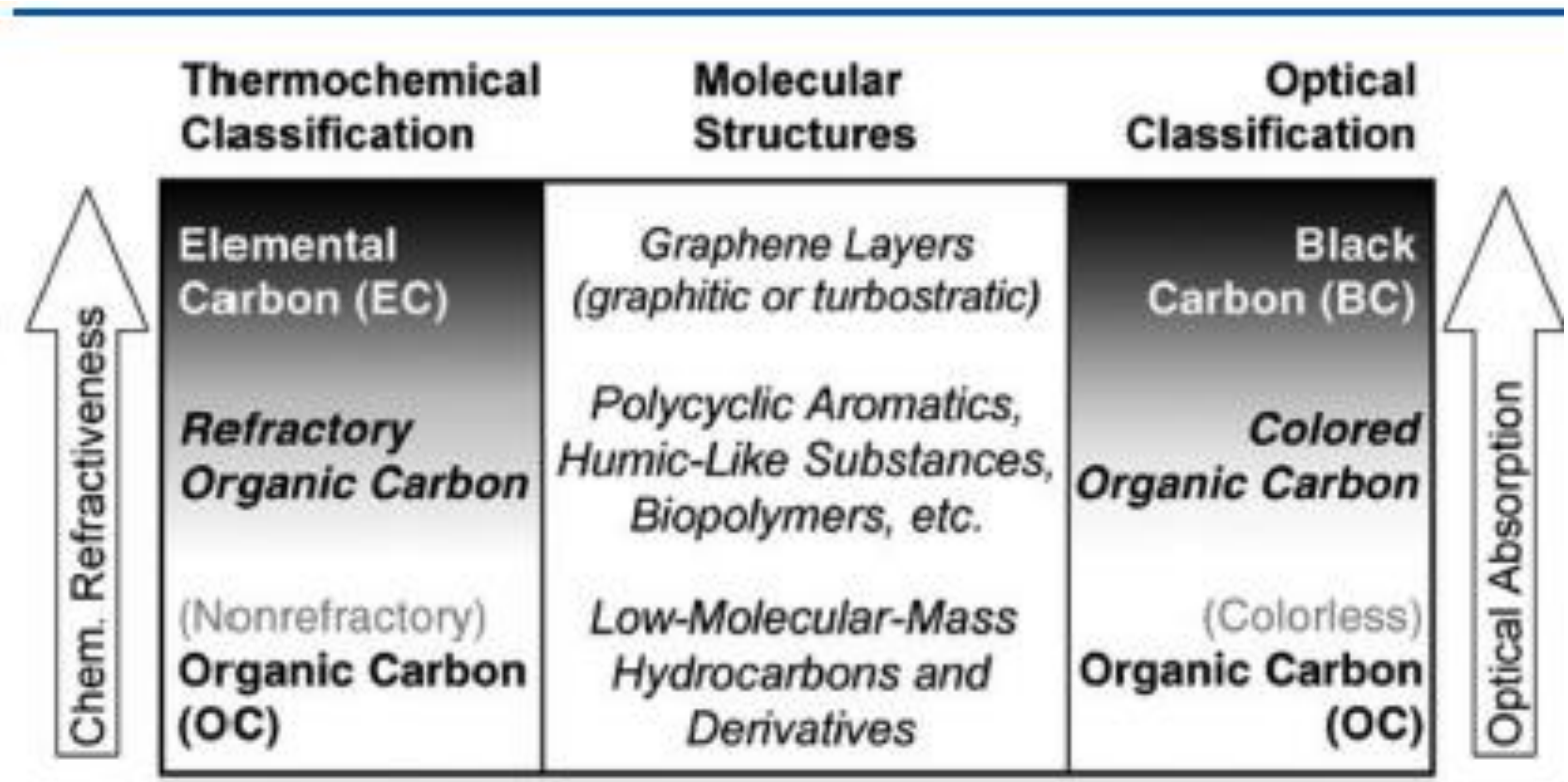
Contribution of OA to IN



Wilson et al. Nature 2015

INP concentration active at local temperature conditions) from **marine sources (colour scale**) and **K-feldspar (black contours)**, for a transect from the South to North poles through the Atlantic (30 W)

Optical properties of organics



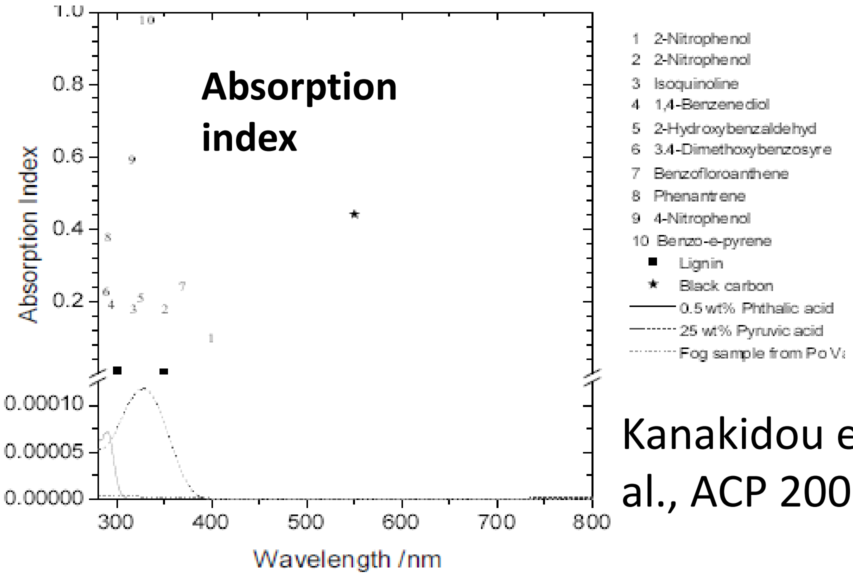
Thermochemical Classification	Molecular Structures	Optical Classification
Elemental Carbon (EC)	*Graphene Layers (graphitic or turbostratic)*	**Black Carbon (BC)**
Refractory Organic Carbon	*Polycyclic Aromatics, Humic-Like Substances, Biopolymers, etc.*	***Colored Organic Carbon***
(Nonrefractory) **Organic Carbon (OC)**	*Low-Molecular-Mass Hydrocarbons and Derivatives*	(Colorless) **Organic Carbon (OC)**

Chem. Refractiveness

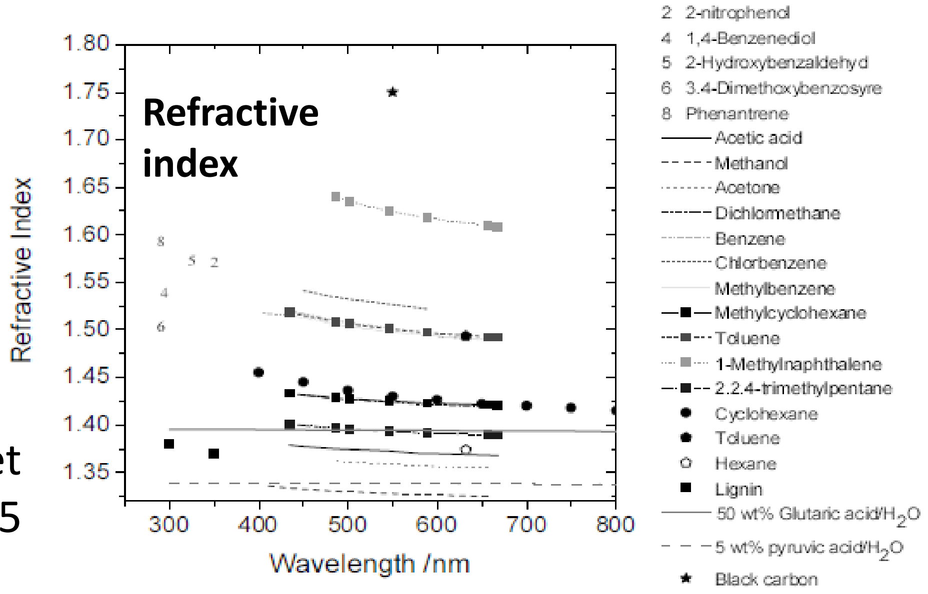
Optical Absorption

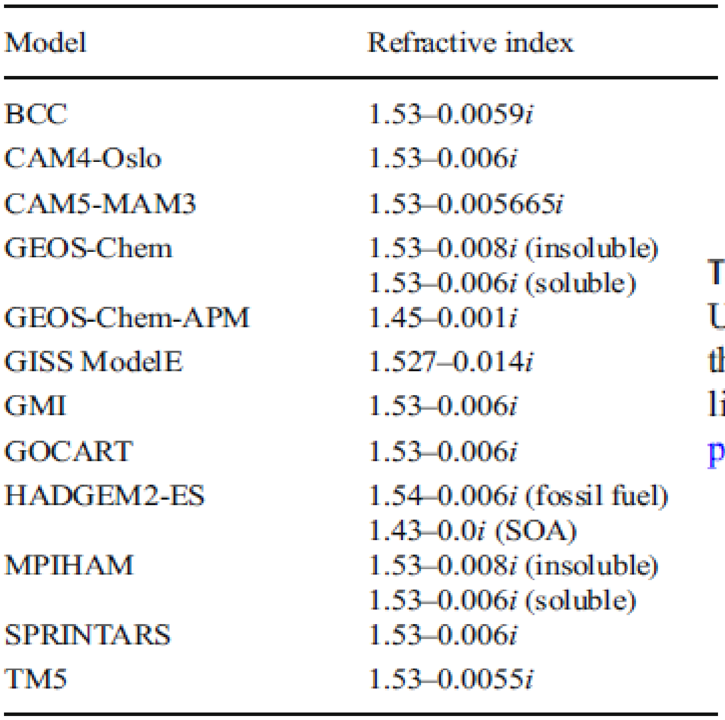
Pöschl U., Angew. Chem. Int. Ed. 2005, 44, 7520 – 7540

Optical properties of OA



Kanakidou et al., ACP 2005





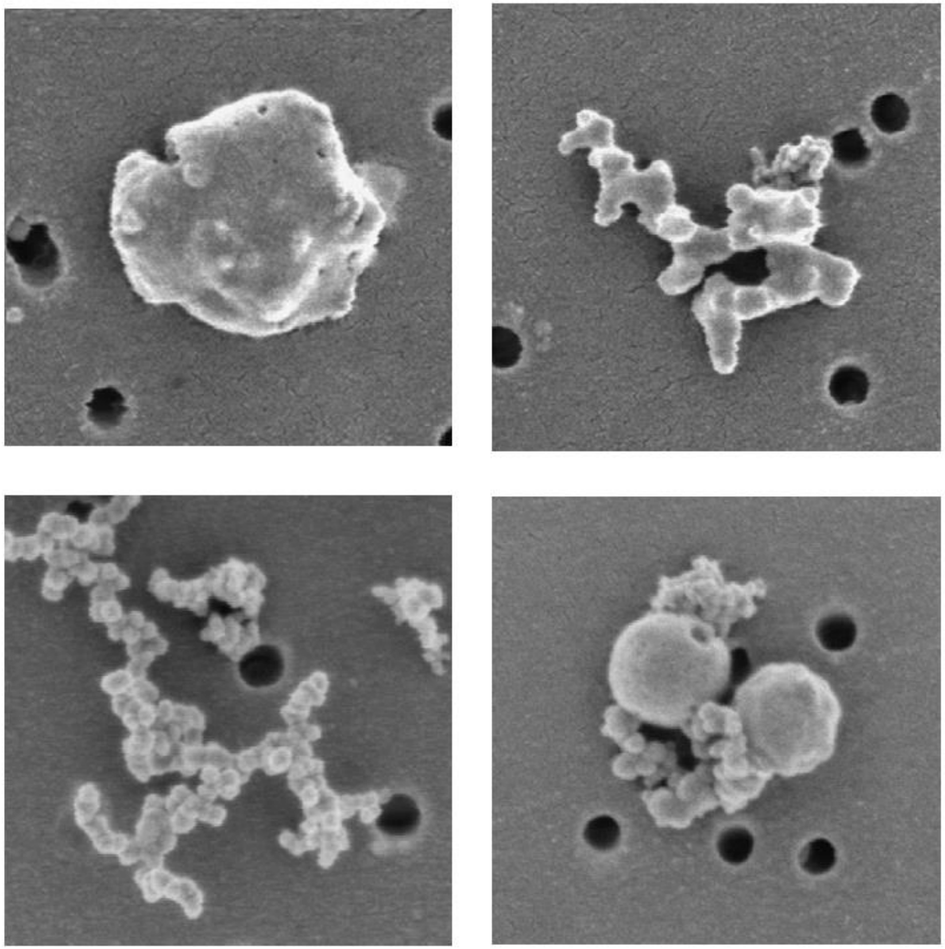
Model	Refractive index
BCC	1.53–0.0059*i*
CAM4-Oslo	1.53–0.006*i*
CAM5-MAM3	1.53–0.005665*i*
GEOS-Chem	1.53–0.008*i* (insoluble) 1.53–0.006*i* (soluble)
GEOS-Chem-APM	1.45–0.001*i*
GISS ModelE	1.527–0.014*i*
GMI	1.53–0.006*i*
GOCART	1.53–0.006*i*
HADGEM2-ES	1.54–0.006*i* (fossil fuel) 1.43–0.0*i* (SOA)
MPIHAM	1.53–0.008*i* (insoluble) 1.53–0.006*i* (soluble)
SPRINTARS	1.53–0.006*i*
TM5	1.53–0.0055*i*

Table 1 Refractive indices of OA at 550 nm used in selected models. Unless BrC is explicitly simulated, POA and SOA are assumed to have the same refractive index, except for one model. Data from the references listed and from AeroCom (https://wiki.met.no/aerocom/optical_properties)

Tsigaridis & Kanakidou, Curr Clim. Change Rep., 2018

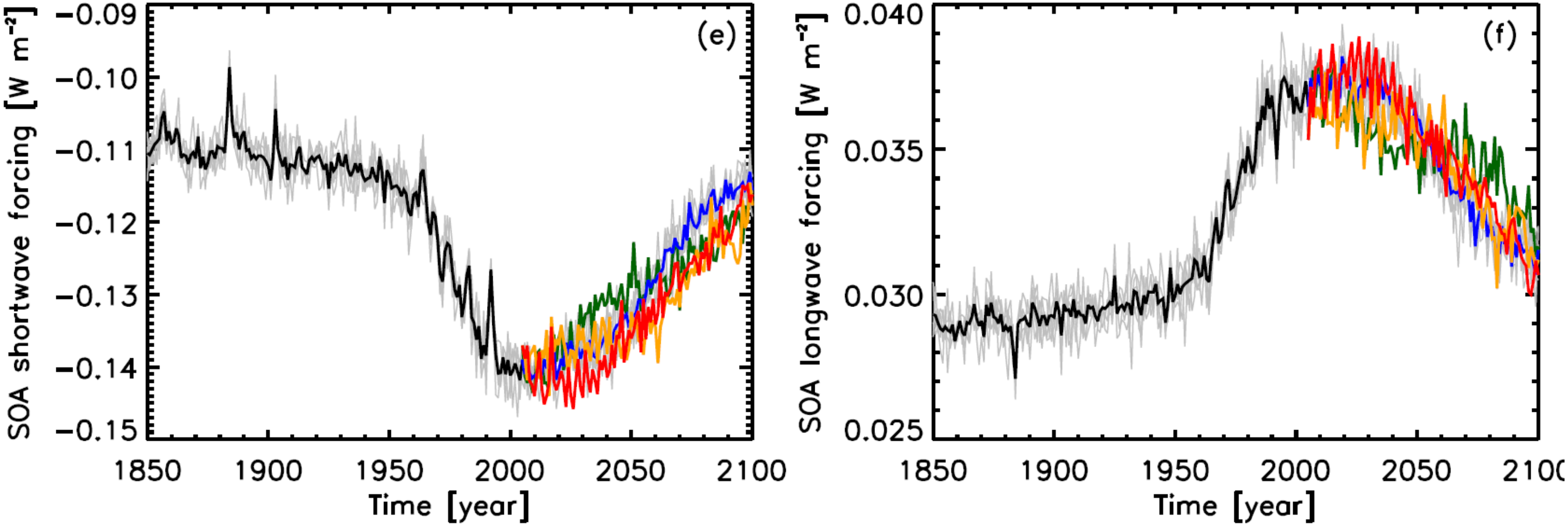
Coating of BC by OA, BrC

Theoretical modelling and laboratory experiments demonstrate that coatings on BC can enhance BC's light absorption, therefore many climate models simply assume enhanced BC absorption by a factor of ~ 1.5 (Liu et al., Nature Communications, 2015)



GISS-E2-R model results

Direct effect of SOA



RCP CMIP5 scenarios (2006–2100; RCP2.6: green; RCP4.5: blue; RCP6.0: orange; RCP8.5: red), and the first 250 years of the preindustrial control (dark gray).

roughly the same with that of POA
4 times smaller than that of SO4
3 times smaller than BC (opposite sign)

~50% higher than that of SO4
almost an order of magnitude higher than that of POA and BC

POA stays mostly in the lower part of the troposphere, SOA can extend all the way to the tropopause

Tsigaridis and Kanakidou Current Climate Change Reports, 2018

Coupling of biogeochemical cycles

- C/N/P cycles are coupled, mainly through photosynthetic fixation of these elements by biological activity.
- C, N and P are main constituent of proteins and living organisms.
- *Biological productivity relies on the availability of these nutrients*
- There is increasing evidence that a significant fraction of N and P deposition occurs as ON and OP.
- *Human activities have modified the atmospheric content and deposition fluxes of OC, ON and OP*
- Critical biochemical feedbacks might exist between chemistry/climate/ terrestrial and marine biosphere that involve the coupling of the C/N/P cycles.

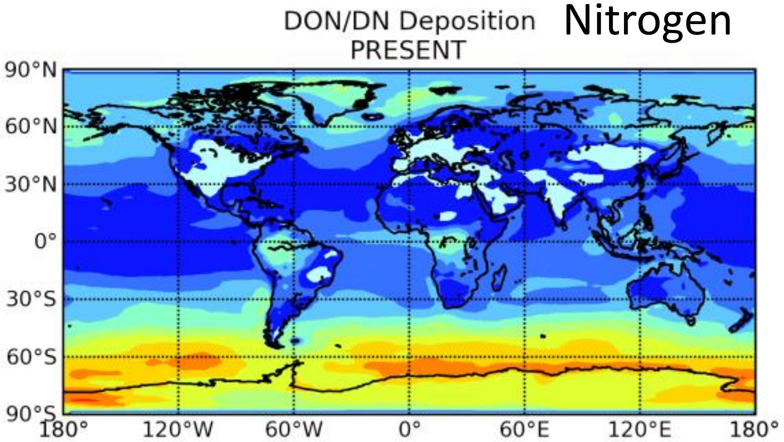
BNMOC (+) → Dep ON (+) + dep OP(+) +SOA (+) + CO_2 uptake (+) → T (-) → BNMOC (- or +) SOA(-) →

T(+) + dep ON (-) + dep OP (-) → ?

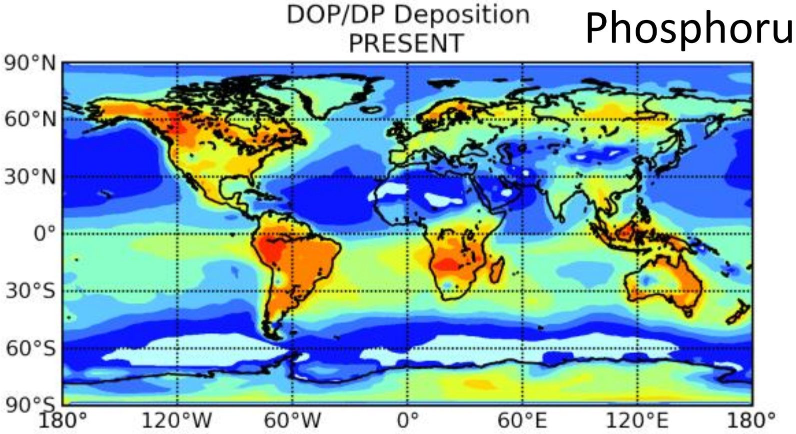
mariak@uoc.gr

Organic fraction of soluble nutrient deposition

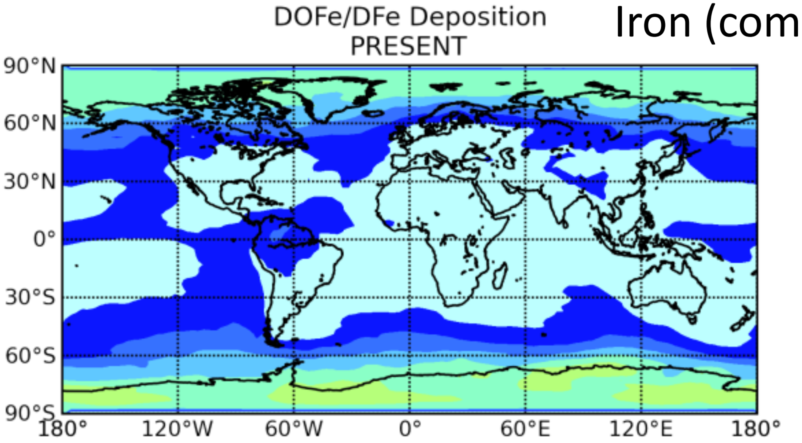
Nitrogen



Phosphorus



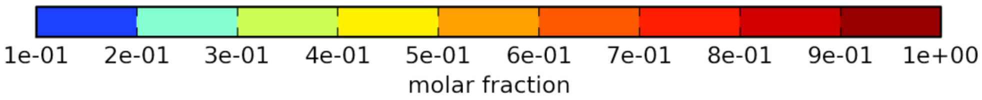
Iron (complexes)



Important contribution of organic nitrogen, organic phosphorus and organic complexes of iron to the respective nutrient total soluble deposition

20-40% (nitrogen)
35-45% (phosphorus)
7-18% (iron)

Important contribution of bioaerosols to ON and OP



Kanakidou et al. , *Environ. Res. Lett.* 13 (2018) 063004