Current issues in Atmospheric Chemistry and Climate
Aktuelle Problemstellungen in Atmosphärenchemie/physik in Bezug auf den Klimawandel

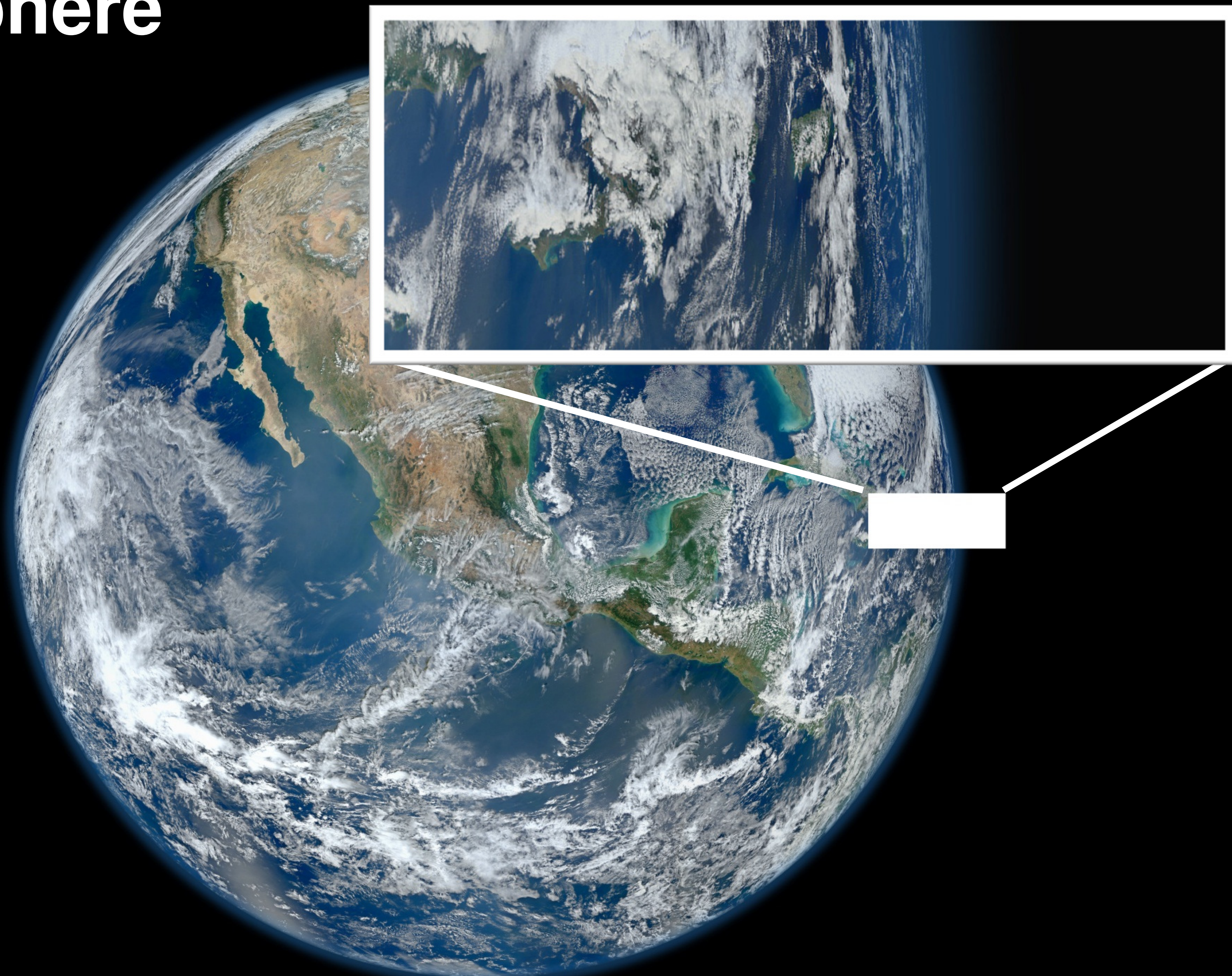
universität innsbruck

Institute for Meteorology and Geophysics

Thomas Karl

Institute for Meteorology and Geophysics – University of Innsbruck

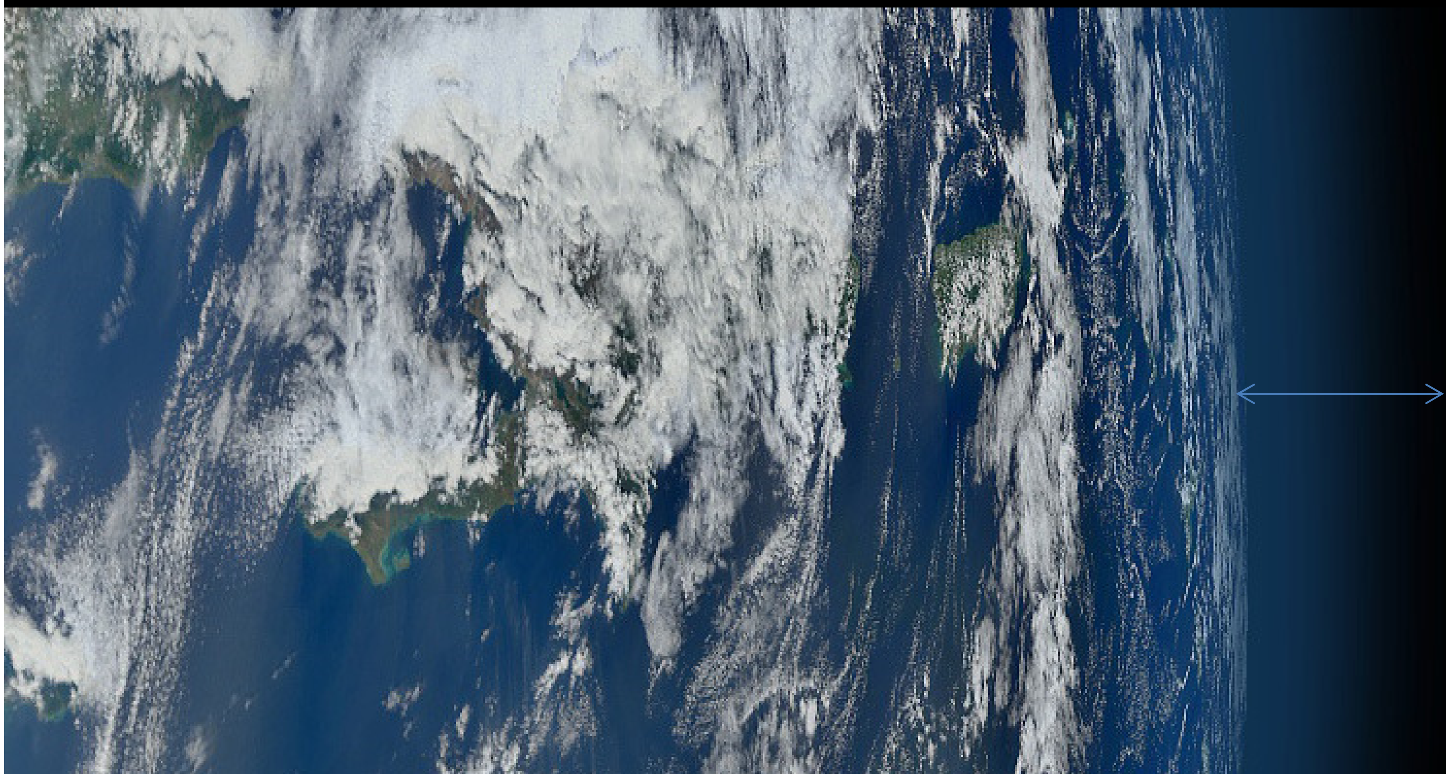
Atmosphere



Diameter of the atmosphere: 1999 km (p = 1 atm)
Mass: 5140 Trillion tons

PhotoCredit: NASA

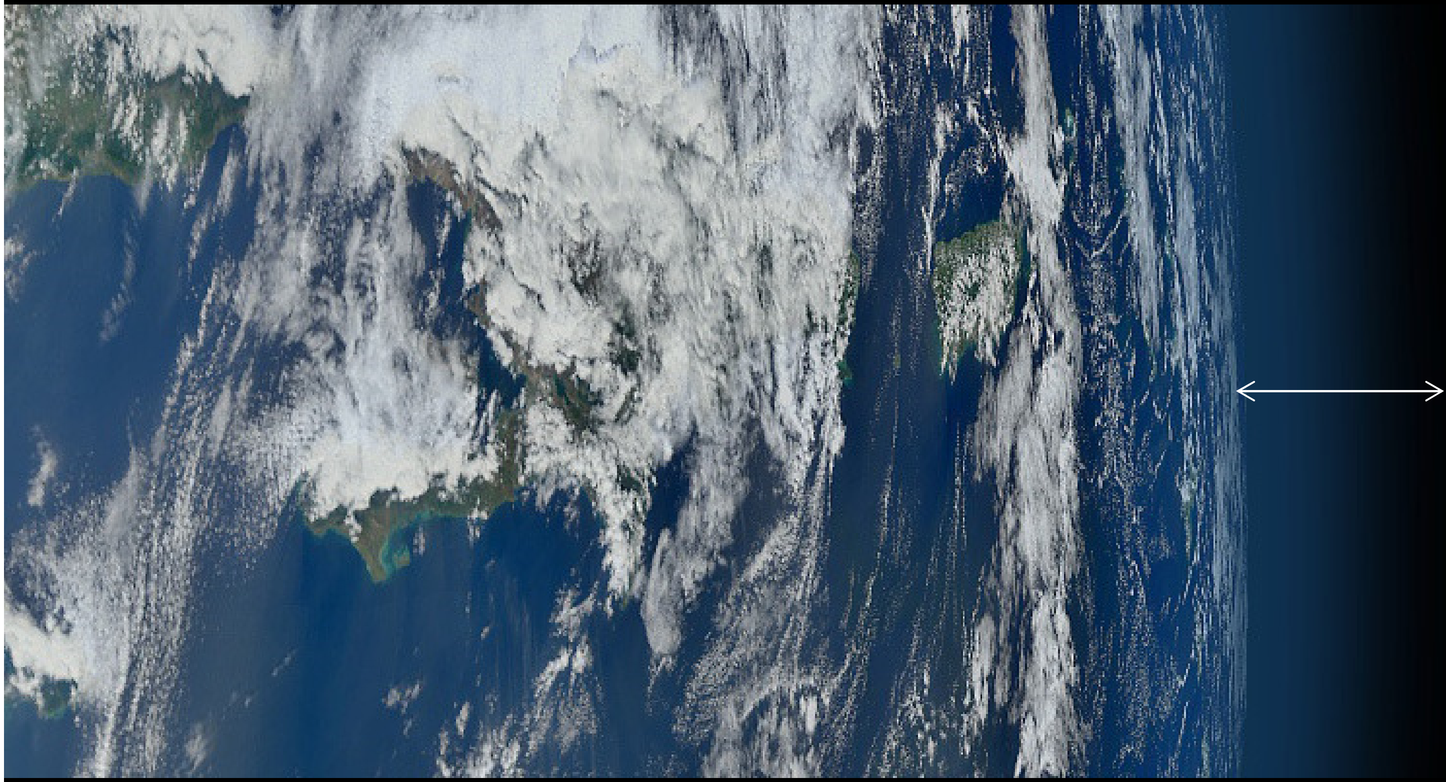
Atmosphere



Volume: approx. 3% compared to planet (p = 1 atm)
Mass: only 0.00009 % of the Earth's mass

PhotoCredit: NASA

Atmosphere



due to it's *small reservoir* the atmosphere is the most *vulnerable* part of the planet – any environmental changes on the planet manifest themselves fastest in the atmosphere

PhotoCredit: NASA

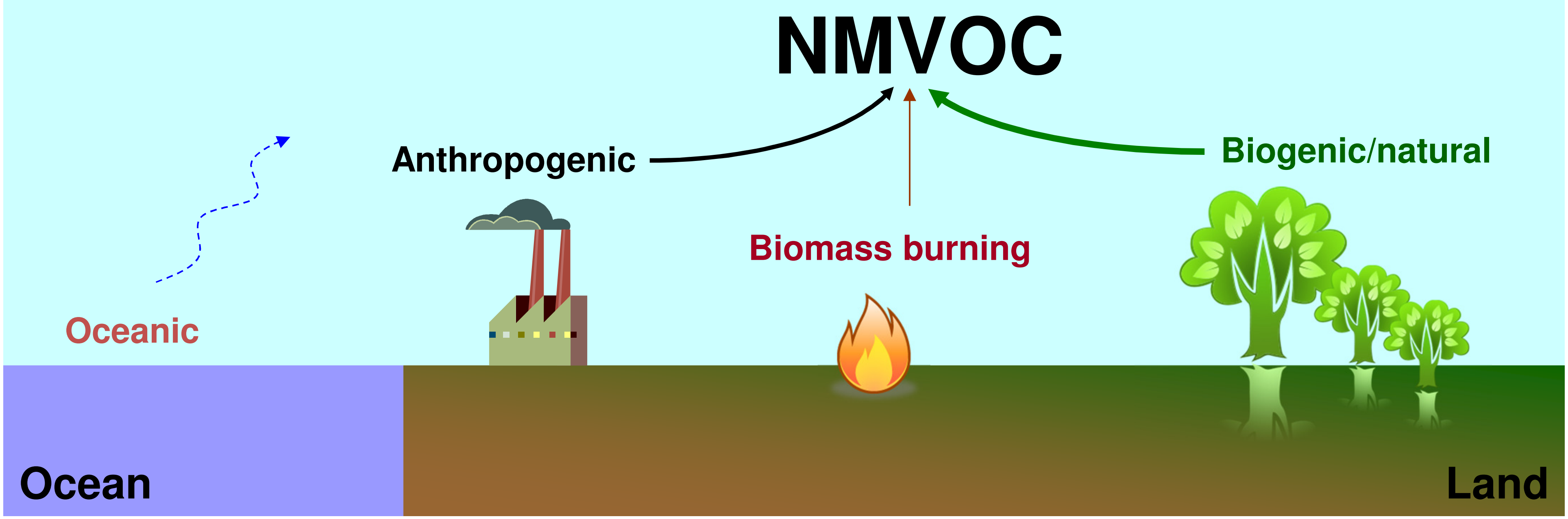
NMVOC

Definition:

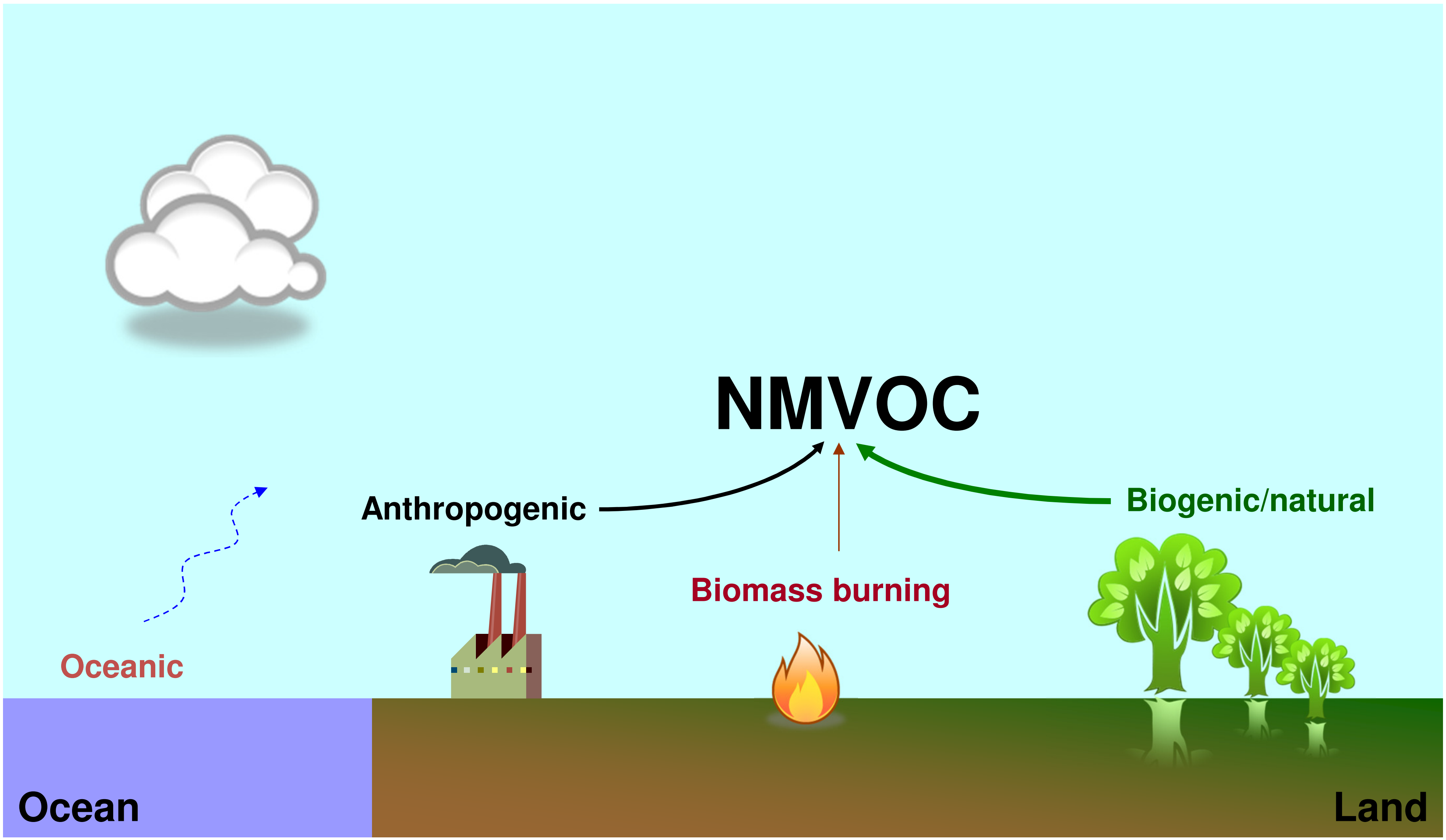
NMVOC: non methane volatile organic compounds (often also termed VOC)

Other subcategories used:

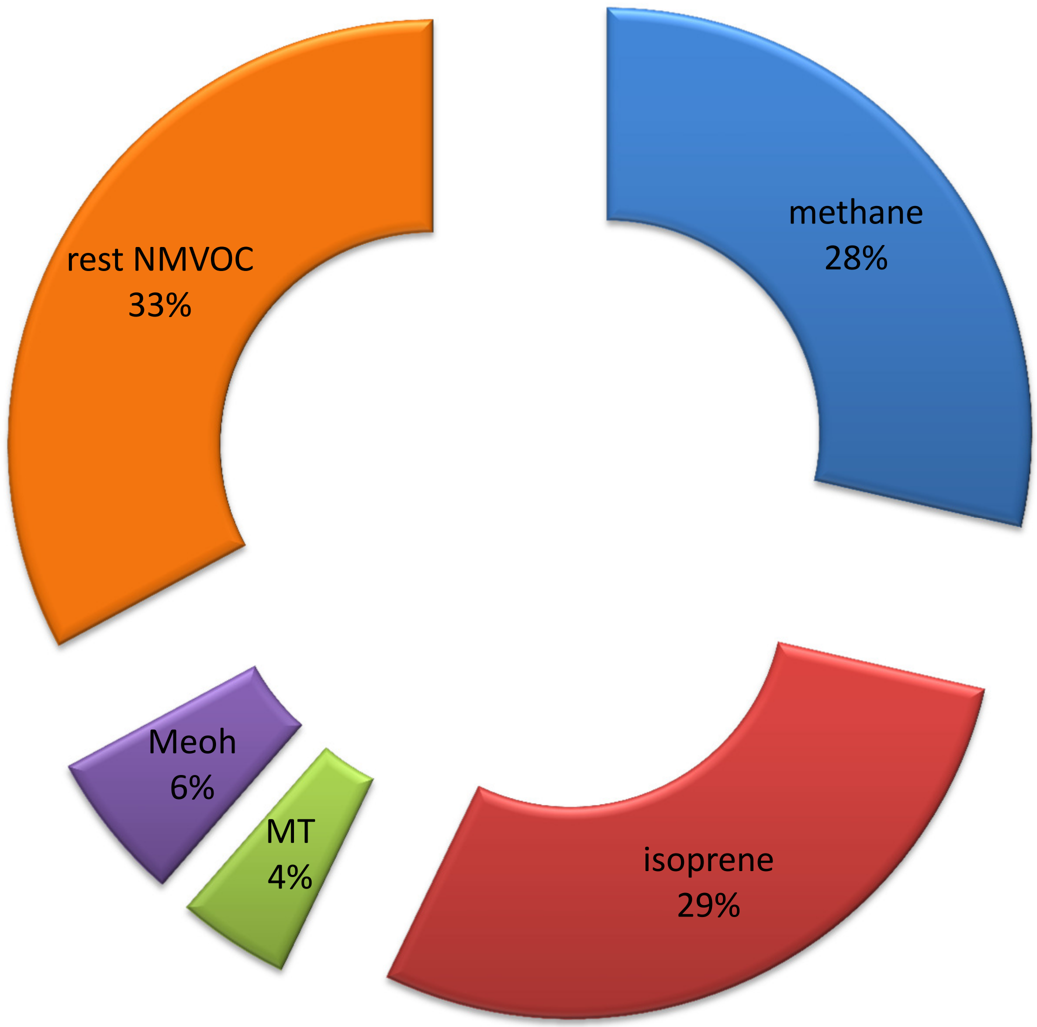
- BVOC: biogenic volatile organic compounds
- oVOC: oxygenated volatile organic compounds
- NMHC: non methane hydrocarbons (old terminology)



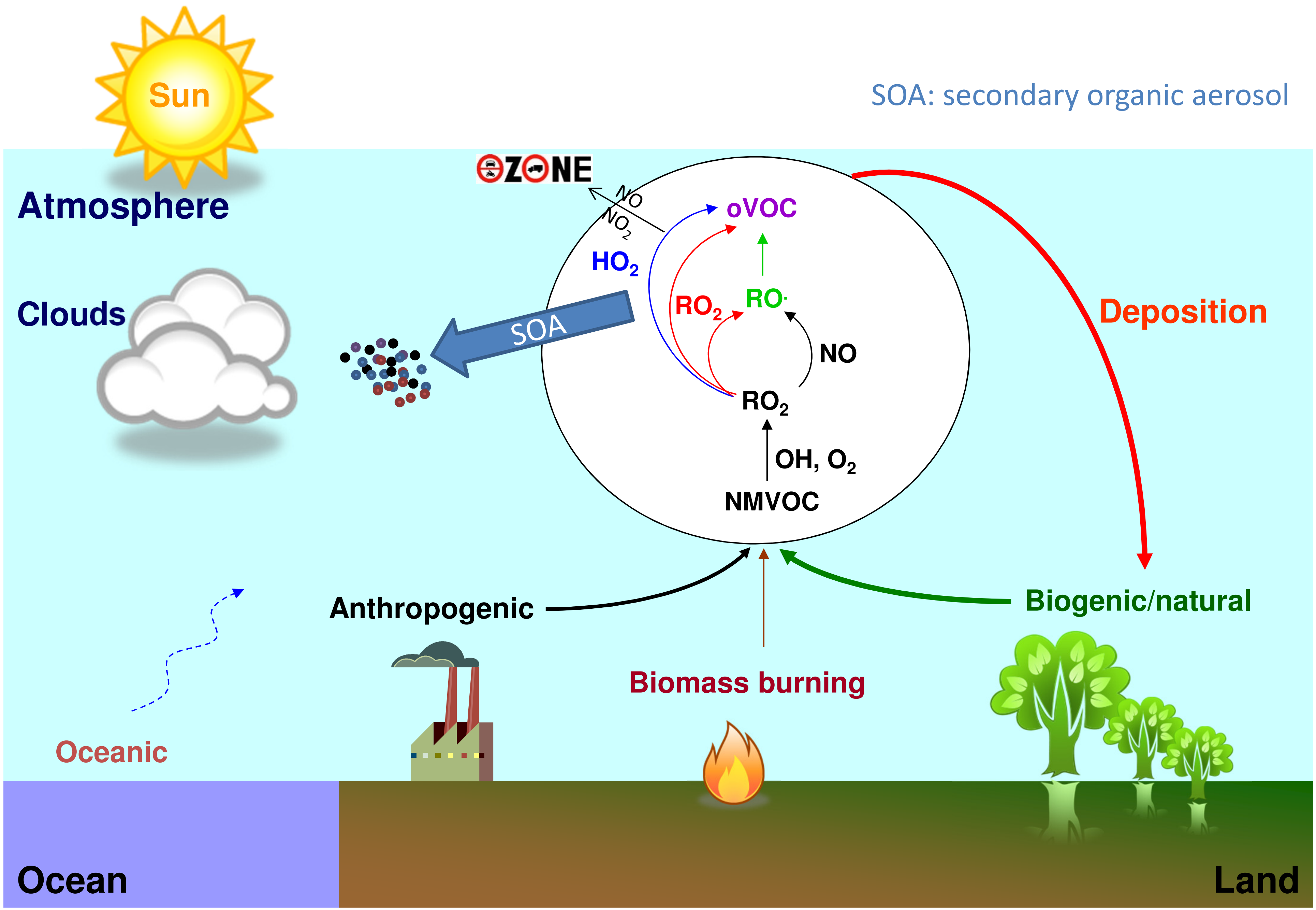
Budgets of NMVOC

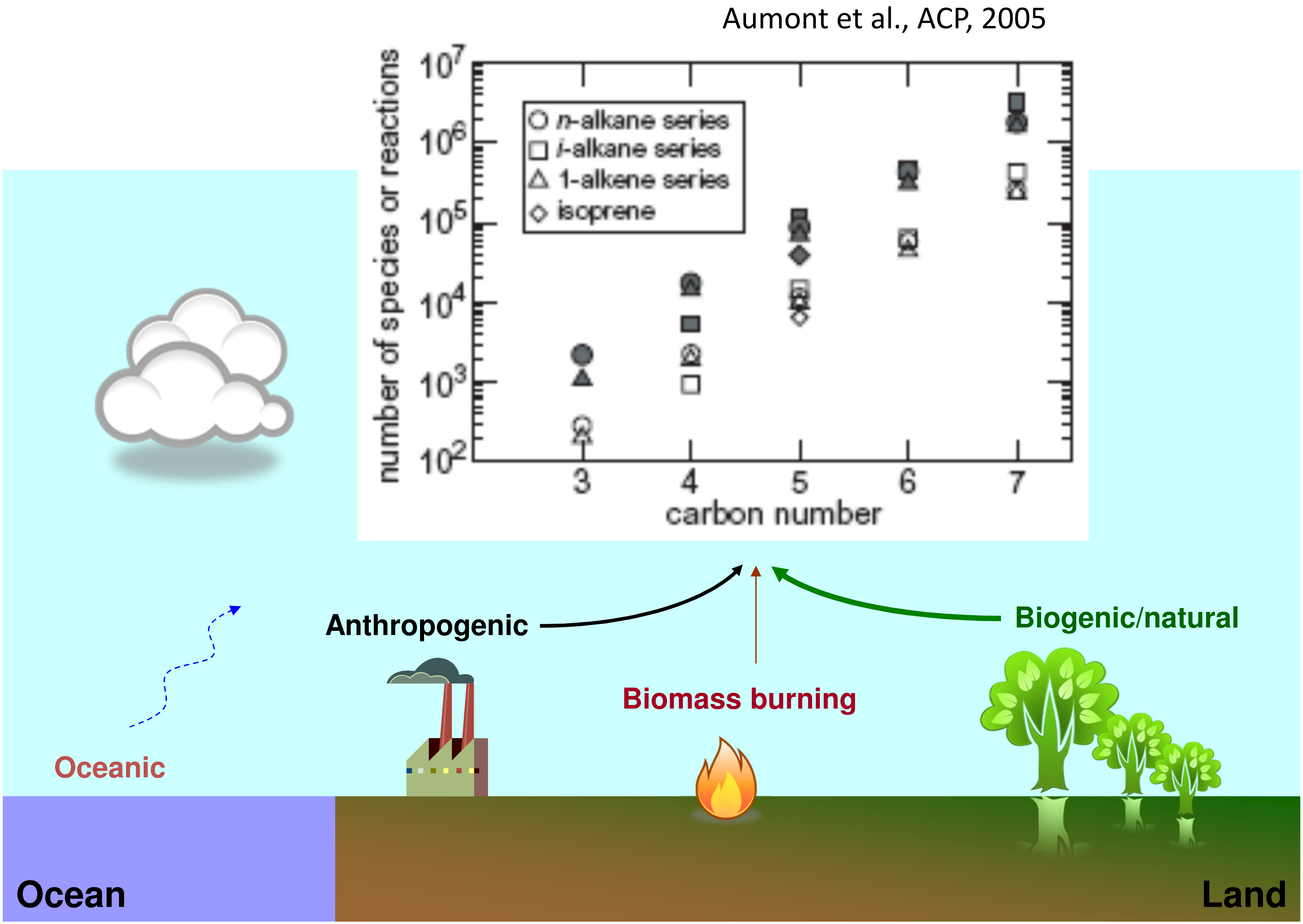


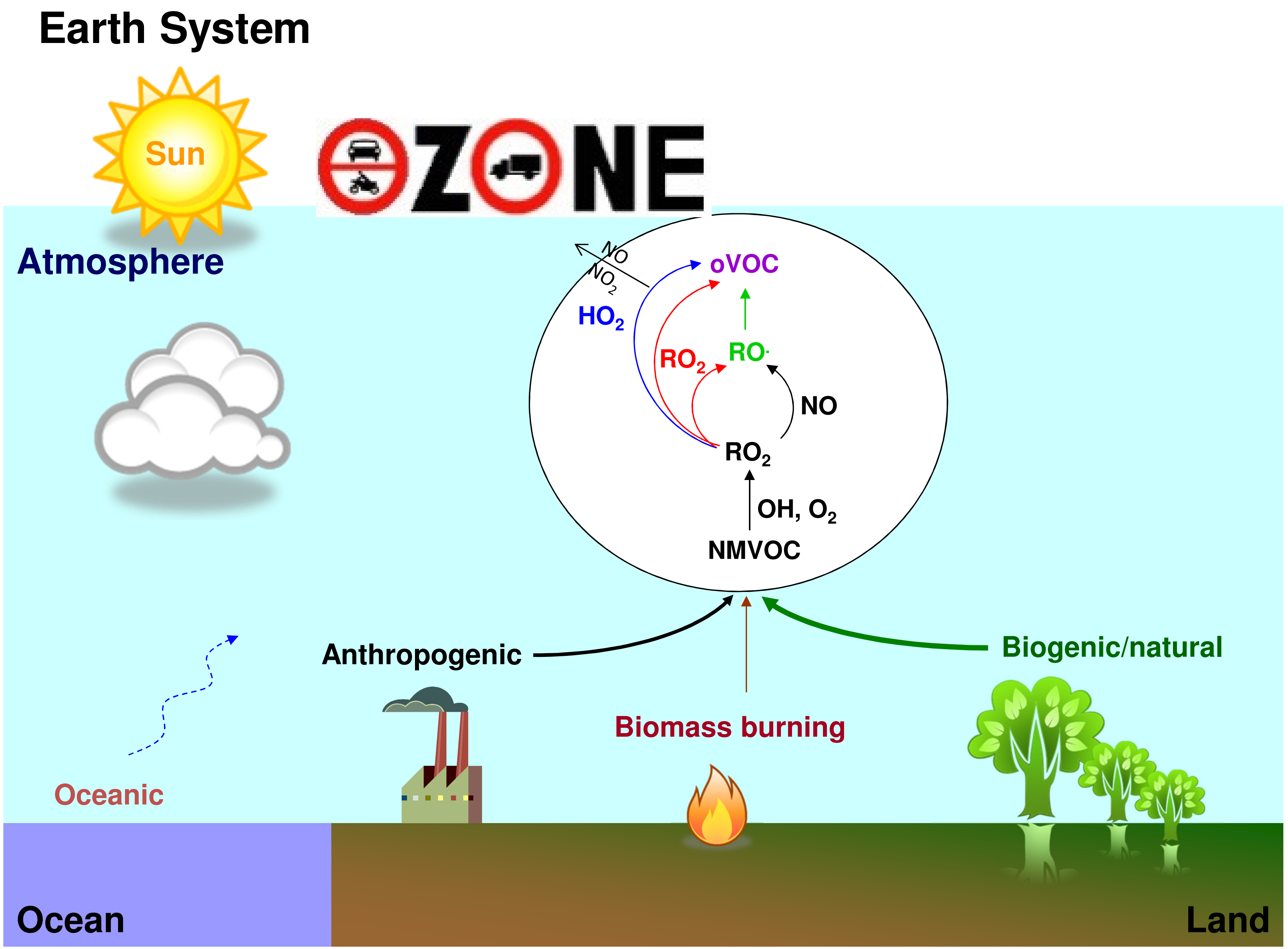
Budgets of Methane and NMVOC Fluxes



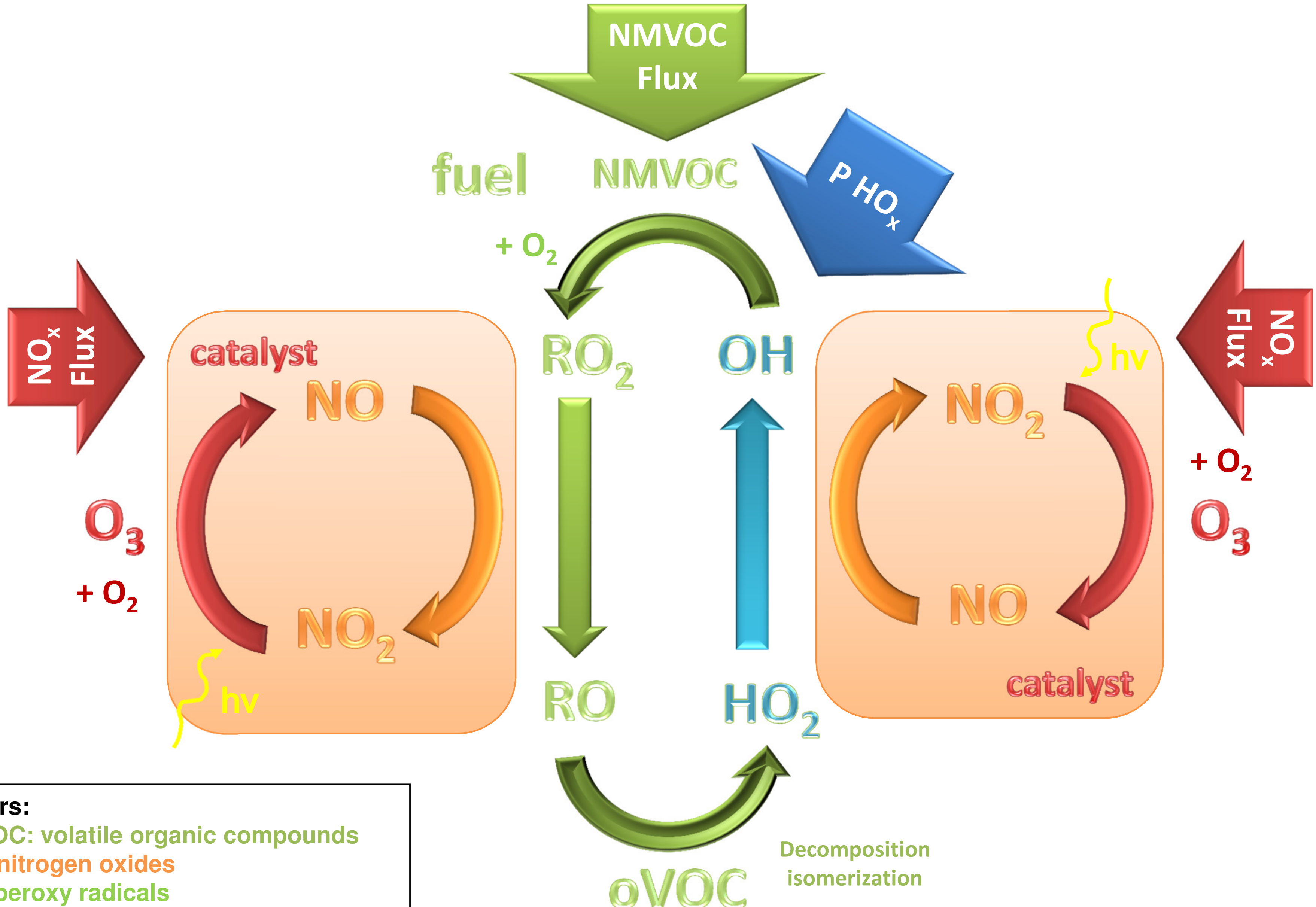
Earth System




Aumont et al., ACP, 2005
number of species or reactions
10^7
10^6
10^5
10^4
10^3
10^2
n-alkane series
i-alkane series
1-alkene series
isoprene
3
4
5
6
7
carbon number
Anthropogenic
Biogenic/natural
Biomass burning
Oceanic
Ocean
Land


Earth System
Sun
OZONE
Atmosphere
NO
NO_2
HO_2
oVOC
RO_2
RO·
NO
RO_2
OH, O_2
NMVOC
Anthropogenic
Biogenic/natural
Biomass burning
Oceanic
Ocean
Land

The photochemical engine



Players:
NMVOC: volatile organic compounds
NO_x: nitrogen oxides
RO_x: peroxy radicals
HO_x: hydroxy radicals
hv: radiation

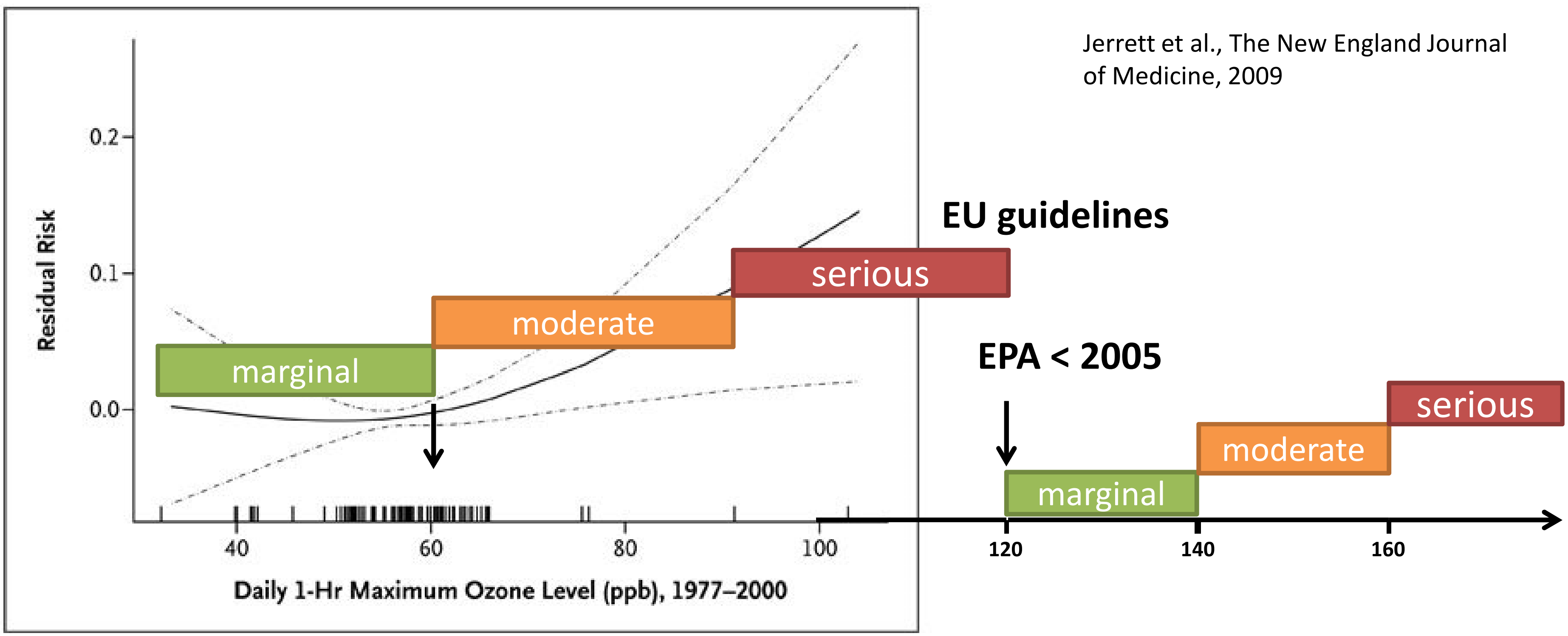
Elevated Ozone Causes Health Problems and Damages Plants/Crops

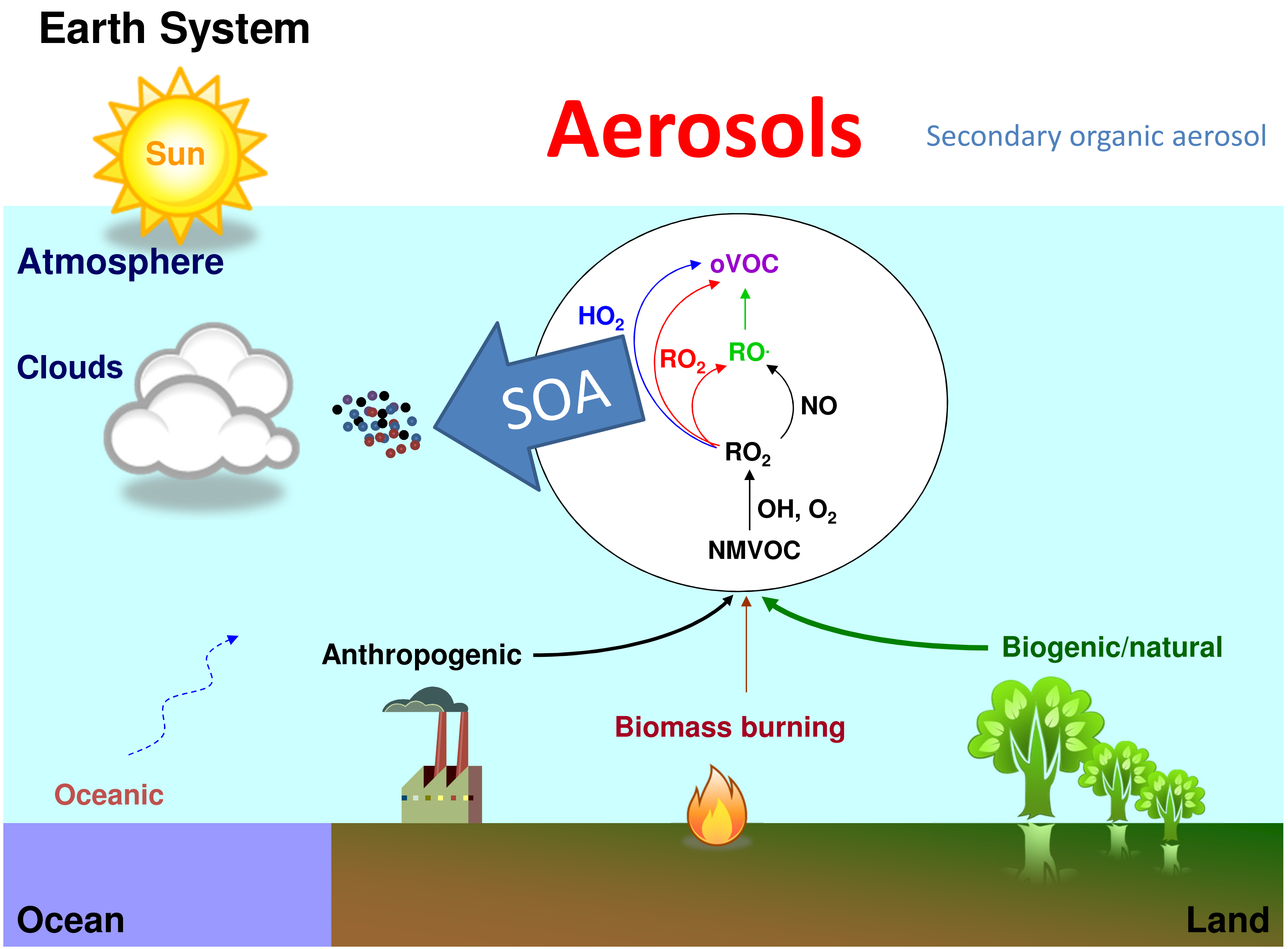
e.g. in US: ~14-55 billion U$ health care costs / year

NMVOCs fuel an oxidizing atmosphere

Long –Term Ozone Exposure and Mortality

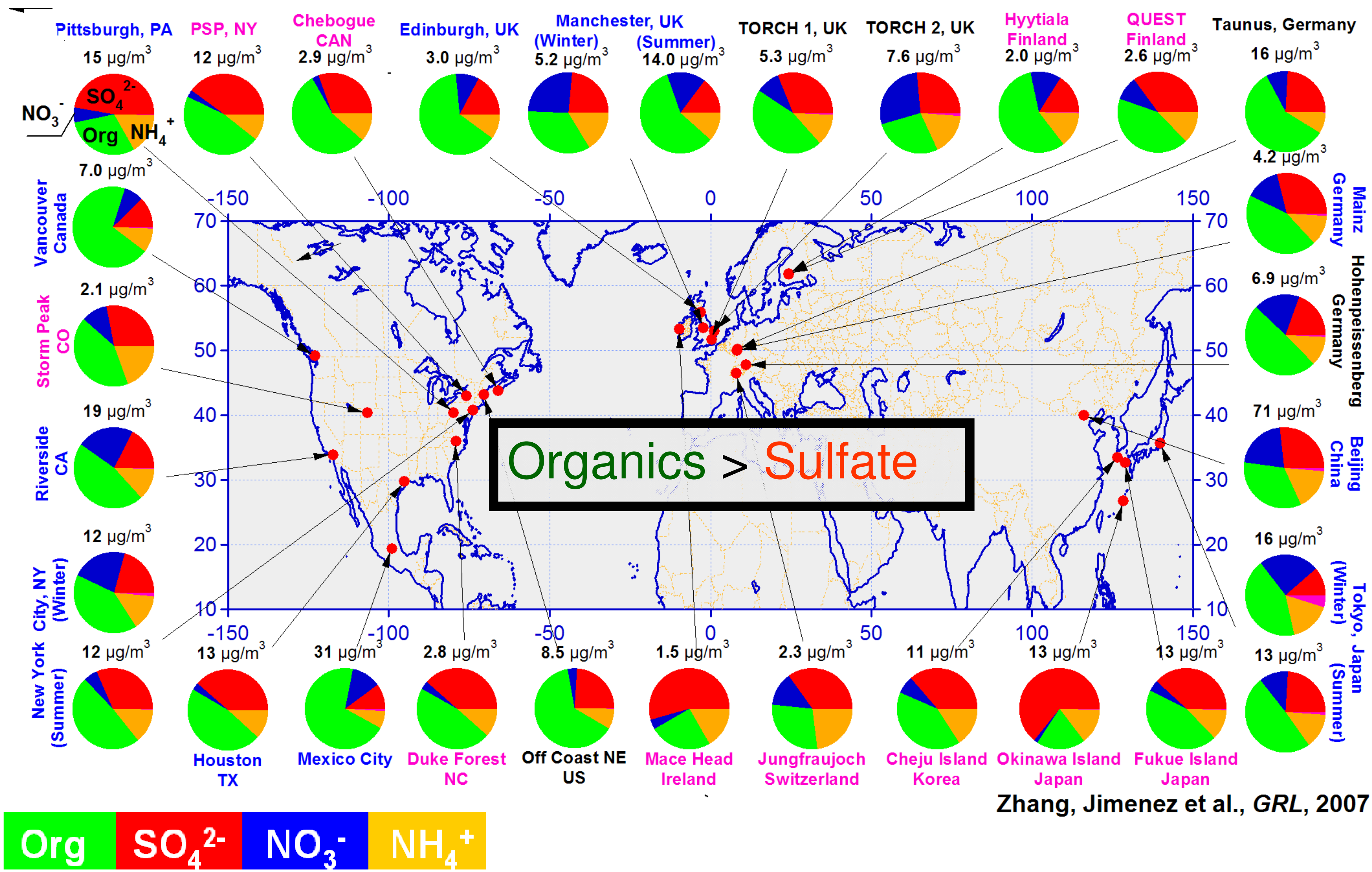
Jerrett et al., The New England Journal of Medicine, 2009




Earth System
Sun
Aerosols
Secondary organic aerosol
Atmosphere
Clouds
SOA
oVOC
HO_2
RO_2
RO·
NO
RO_2
OH, O_2
NMVOC
Anthropogenic
Biogenic/natural
Biomass burning
Oceanic
Ocean
Land

Atmospheric oxidation of NMVOCs leads to organic aerosol formation

Accumulation Mode ≈ 1 µm



Zhang, Jimenez et al., *GRL*, 2007

Dominant aerosol sources

- Dust
- Sea Salt
- Organic Carbon (POA+SOA)
- Black carbon (BC)
- Sulfur

POA: primary organic aerosol

SOA: secondary organic aerosol

Source*	Total (Tg/y)
Dust	1000-3000
Sea salt	8000-16000
SOA	100-1500?
POA	~1000[x]
BC	6-8
Sulfur	16-45

* IPCC 4/5

[x] Jaenicke et al., Science, 2005

Dominant aerosol sources

- Dust
- Sea Salt
- Organic Carbon (POA+SOA)
- Black carbon (BC)
- Sulfur

POA: primary organic aerosol

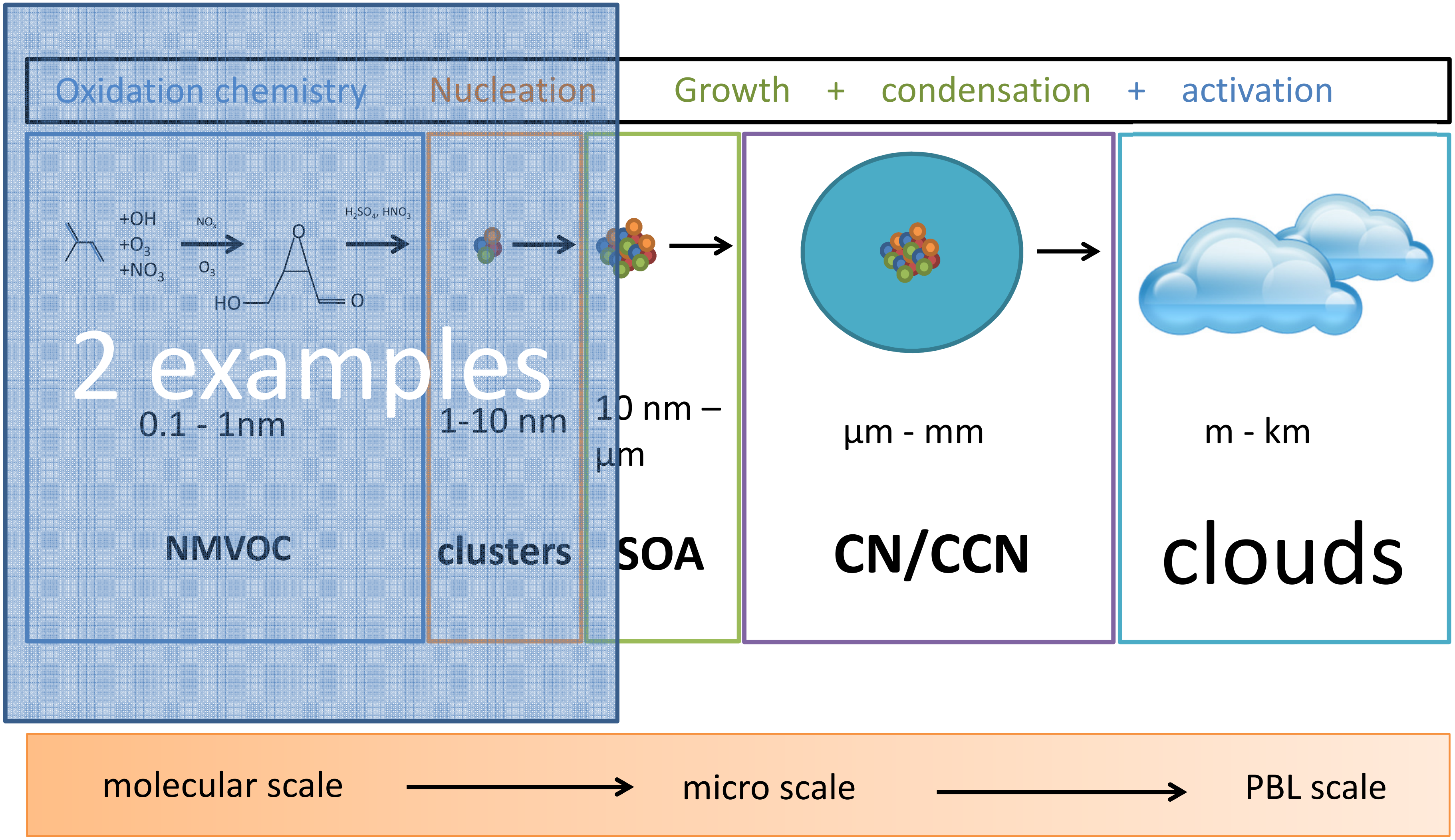
SOA: secondary organic aerosol

Source[*]	Total (Tg/y)	Accumulation mode <2.5µm (Tg/y)
Dust	1000-3000	70-700 (270)
Sea salt	8000-16000	1200-2400 ??
SOA	100-1500?	100-1500 (850??)
POA	~1000[x]	<<
BC	6-8	<6 (?)
Sulfur	16-45	16-45

[*] IPCC 4/5

[x] Jaenicke et al., Science, 2005

From molecules to clouds



Example 1 of biogenically enhanced SOA in ultrafine mode

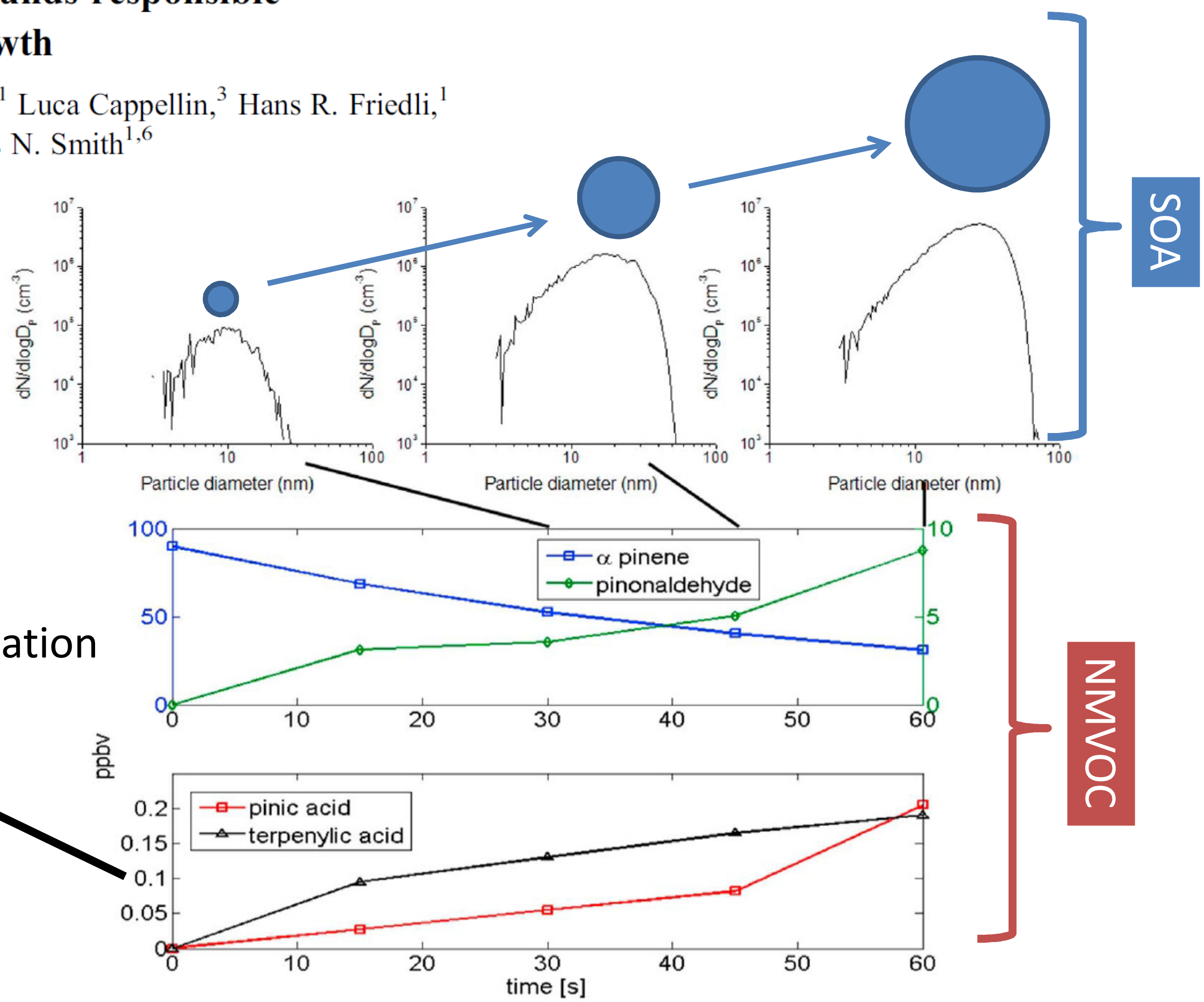
Identification of the biogenic compounds responsible for size-dependent nanoparticle growth

Paul M. Winkler,[1,2] John Ortega,[1] Thomas Karl,[1] Luca Cappellin,[3] Hans R. Friedli,[1] Kelley Barsanti,[4] Peter H. McMurry,[5] and James N. Smith[1,6]

GRL, 2012

Evolution of particle size

Organic acids from Terpene Oxidation



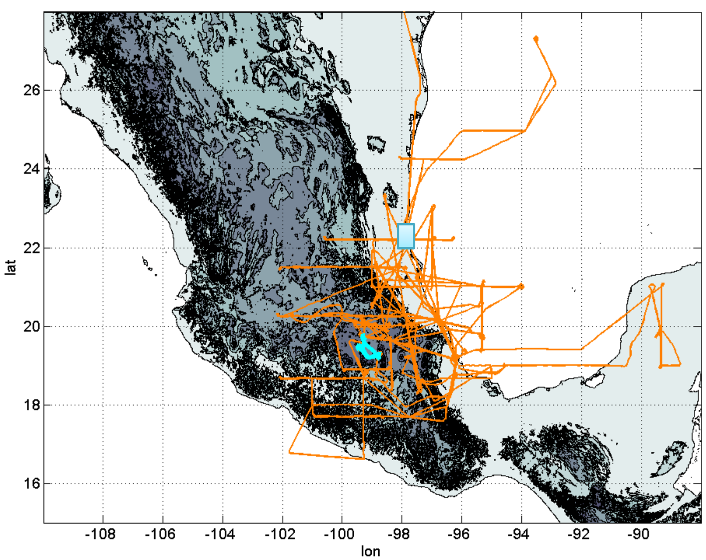
Example 2: Studying the influence of GCR (galactic cosmic rays) on aerosol production and cloud formation at CERN

The CLOUD project at CERN

http://cloud.web.cern.ch/cloud/Physics/modulation.html

Results: GCR can not explain the formation rate of ultrafine aerosols in the lower atmosphere!
NEED precursor gases

Brown Haze over Mexico City

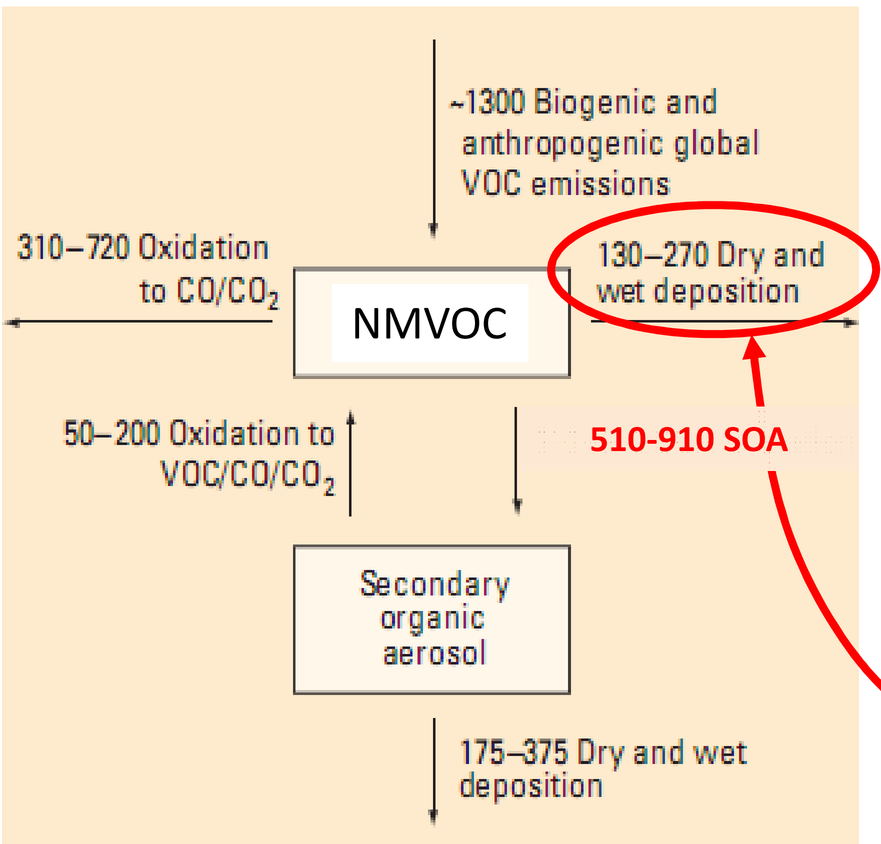


MIRAGE, 2006

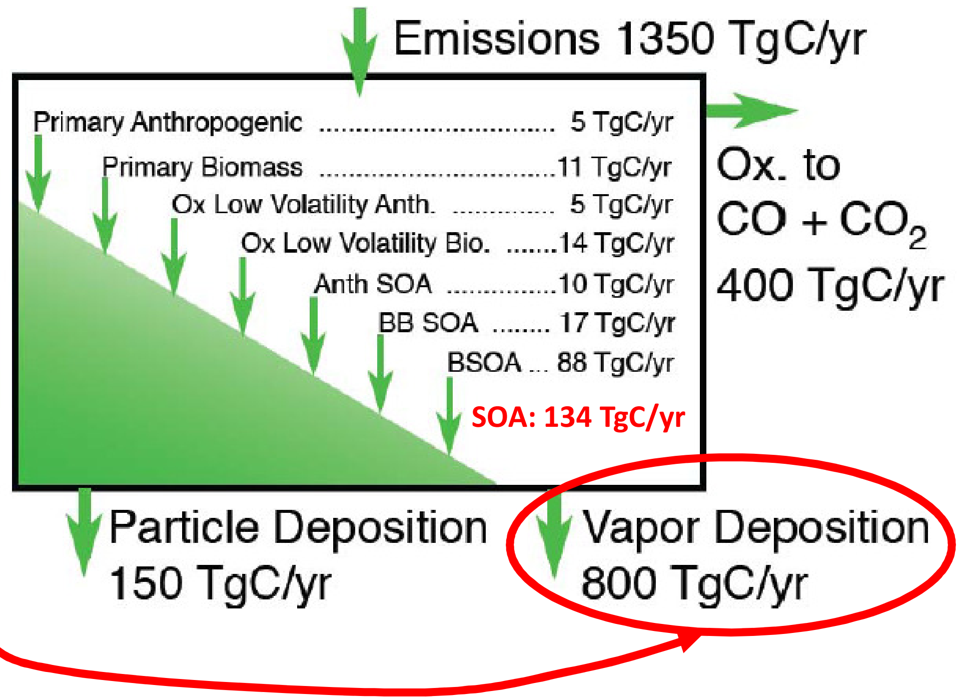
Blue Haze

Two different estimates of SOA: 710 TgC/y vs 134 TgC/y

Goldstein and Galbally, ES&T, 2007

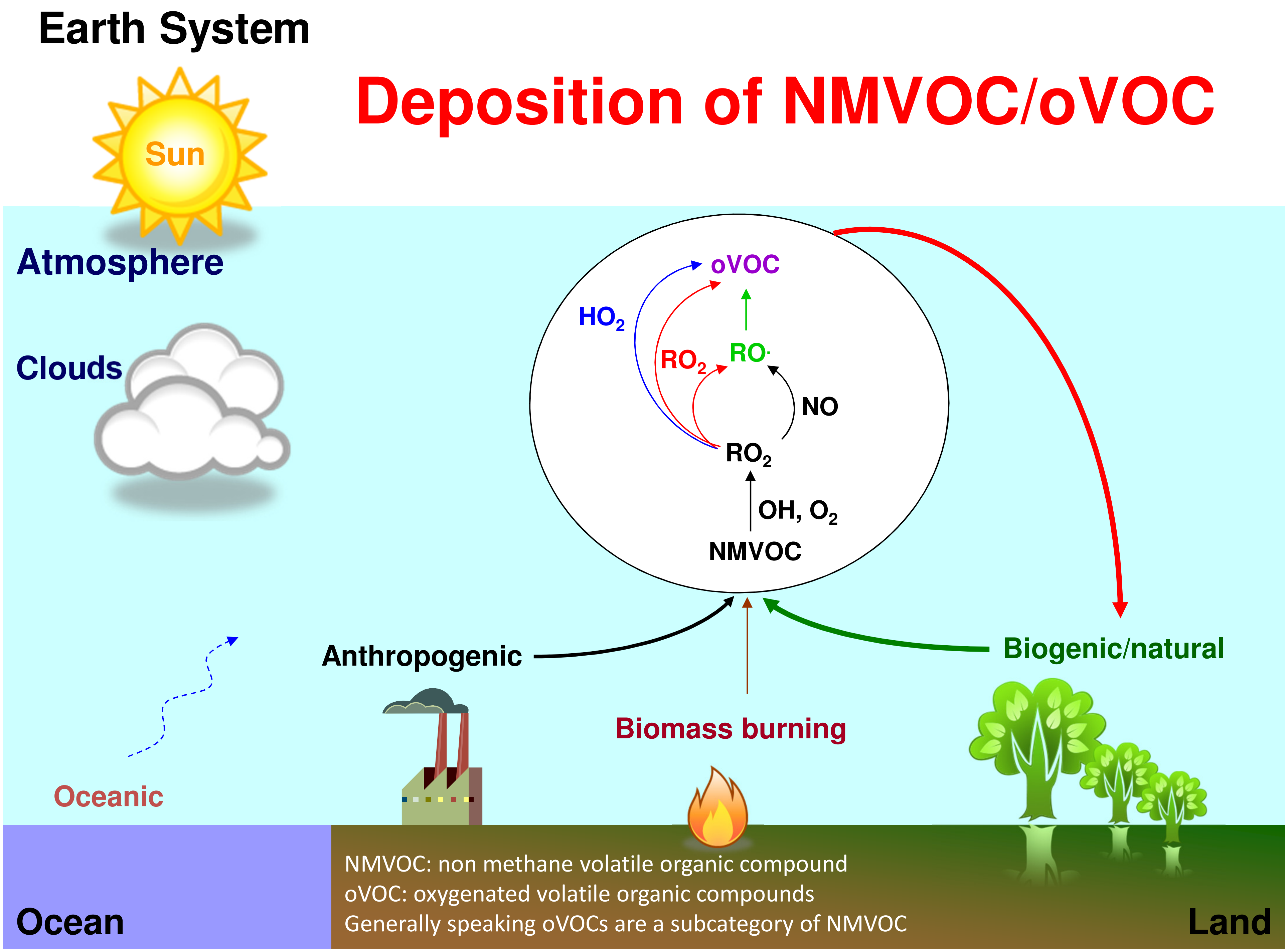


Hallquist et al., ACP, 2009



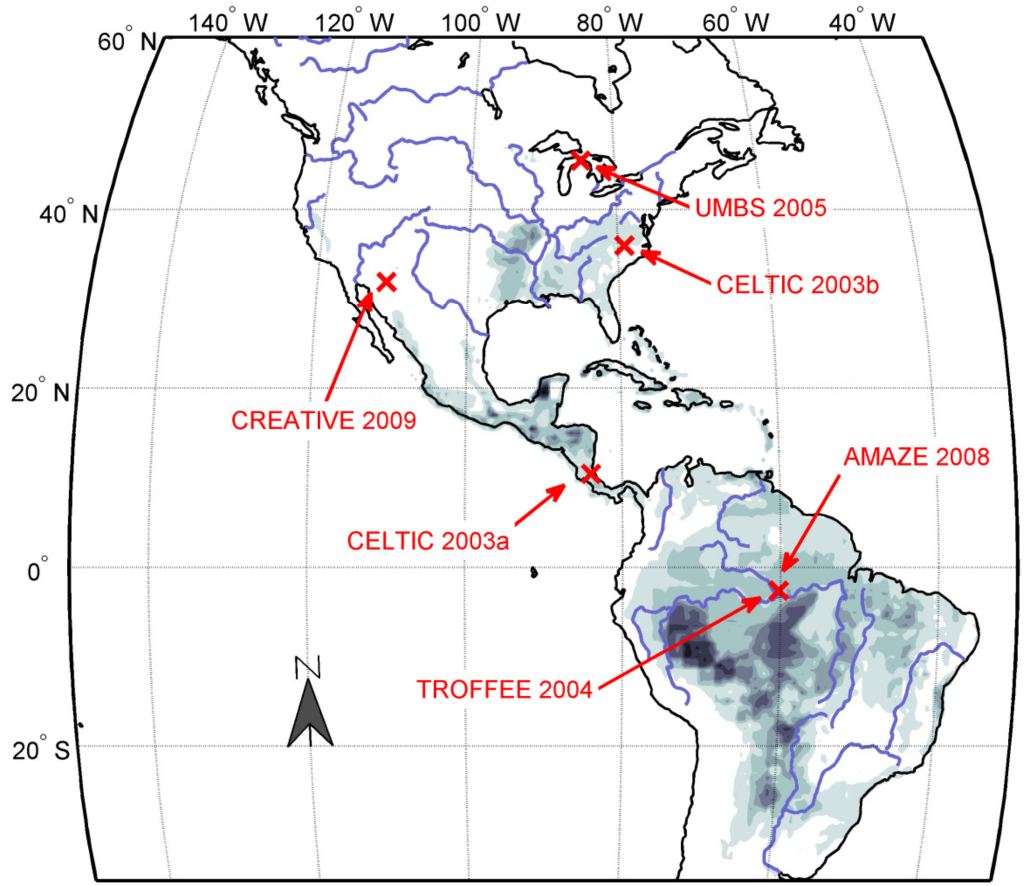
large uncertainty in deposition assumptions

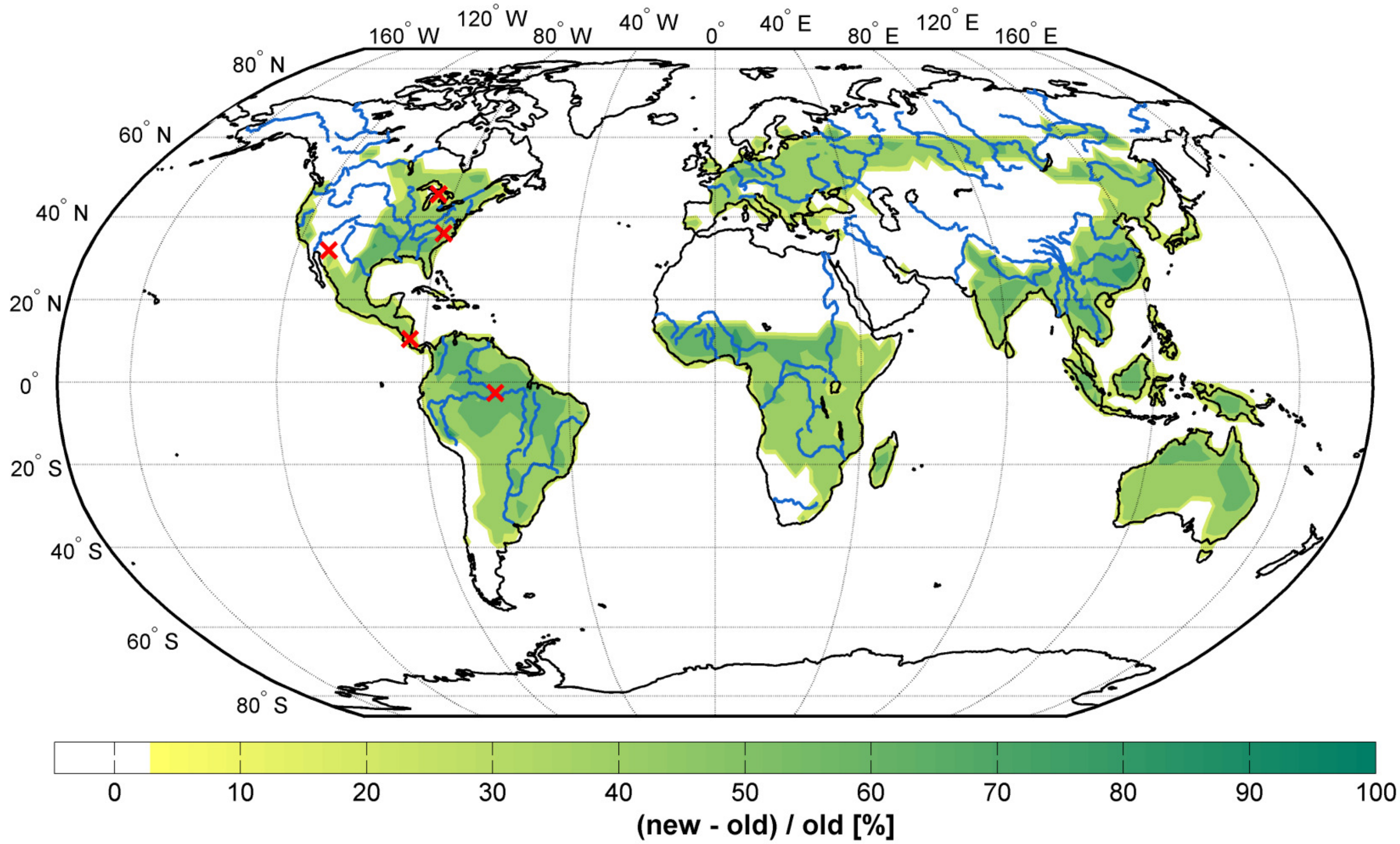
Deposition of NMVOC/oVOC



NMVOC: non methane volatile organic compound
oVOC: oxygenated volatile organic compounds
Generally speaking oVOCs are a subcategory of NMVOC

Field campaigns 2003-2009





1300 TgC/a primary VOC input

	Mean [TgC/a]	Comments
this study	**590±130**	**Dry and wet deposition (vapors)**
Goldstein and Galbally (2007)	200±100	Dry and wet deposition (vapors)
Hallquist et al., 2009	800	Dry and wet deposition (vapors)
Willey et al. (2000)	430±150	Wet deposition (vapors+particles)

US Environmental Protection Agency

202 comments

Summer of 2013 among coolest on record in Alabama, continues cooling trend, climatologist says

The cool temperatures this summer were perhaps best epitomized by the more than 4 inches of rain that fell on July 4 in Huntsville. (The Huntsville Times file photo)

Print

By Paul Gattis | pgattis@al.com
Email the author | Follow on Twitter
on August 29, 2013 at 4:39 PM, updated August 31, 2013 at 11:46 AM

Entertainment Listings
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Region
Event Type
Next 7 Days
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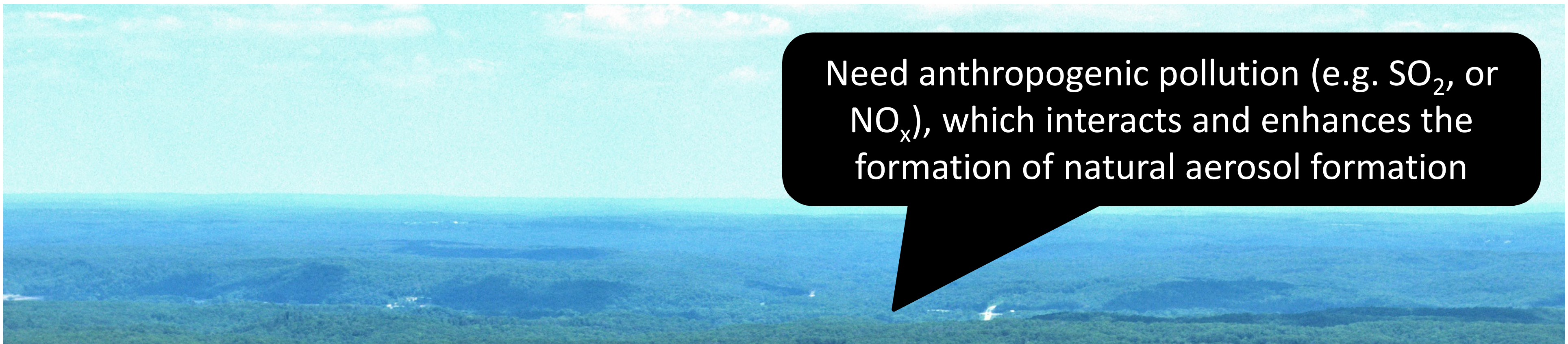
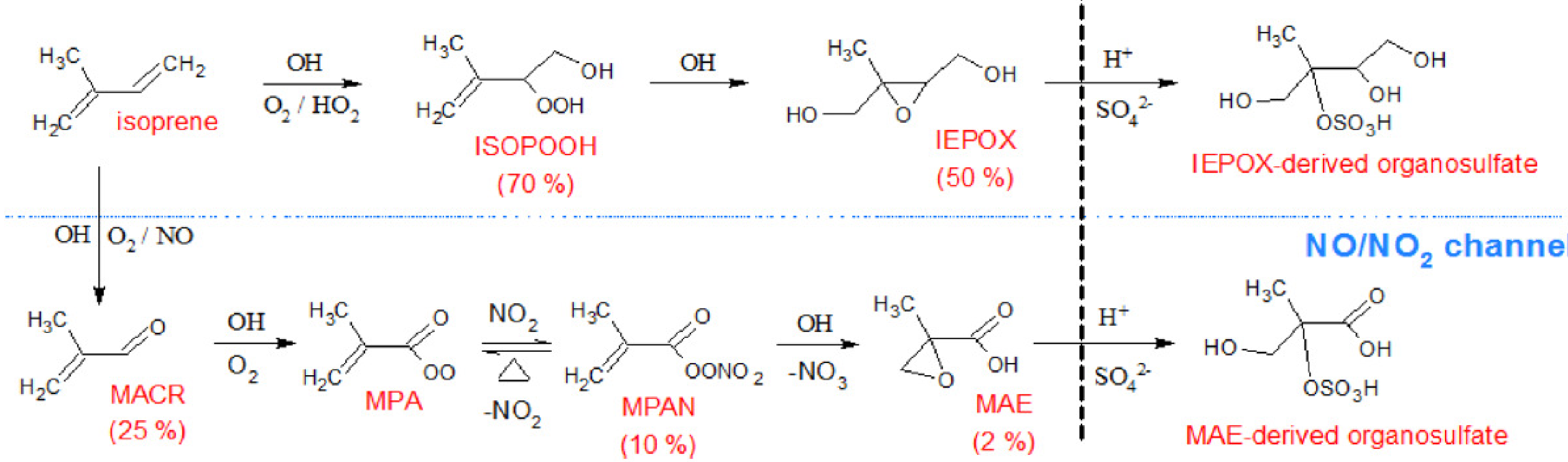
973 Live updates: No. 1 Alabama vs. Virginia Tech (chat)
884 Live at 9 with Kevin Scarbinsky: Nick Marshall leads AJ McCarron in quarterback rating

…armed like …S.

Blue Haze formation via terpene derived organosulfates?



Worton et al, ES&T, 2013



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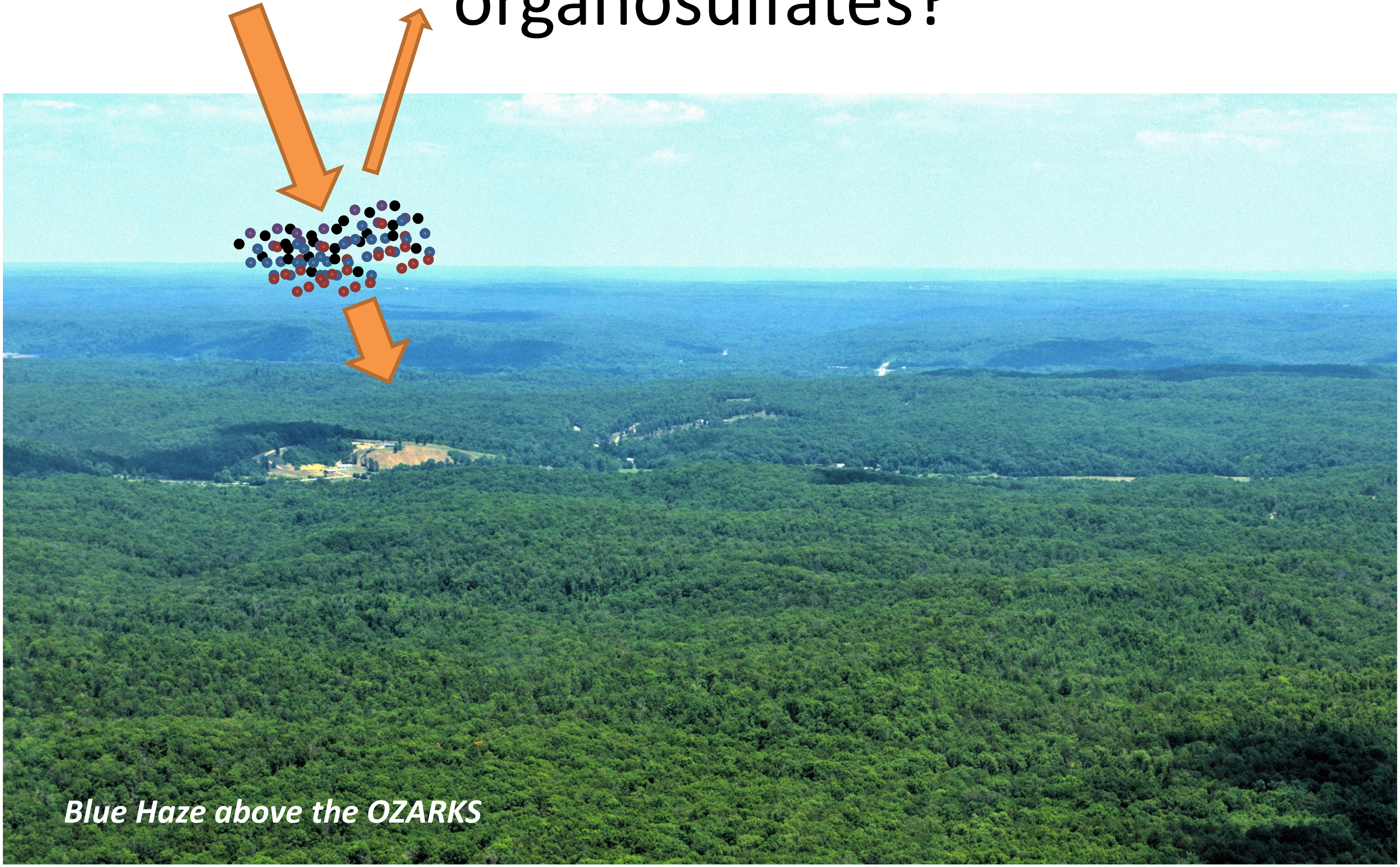
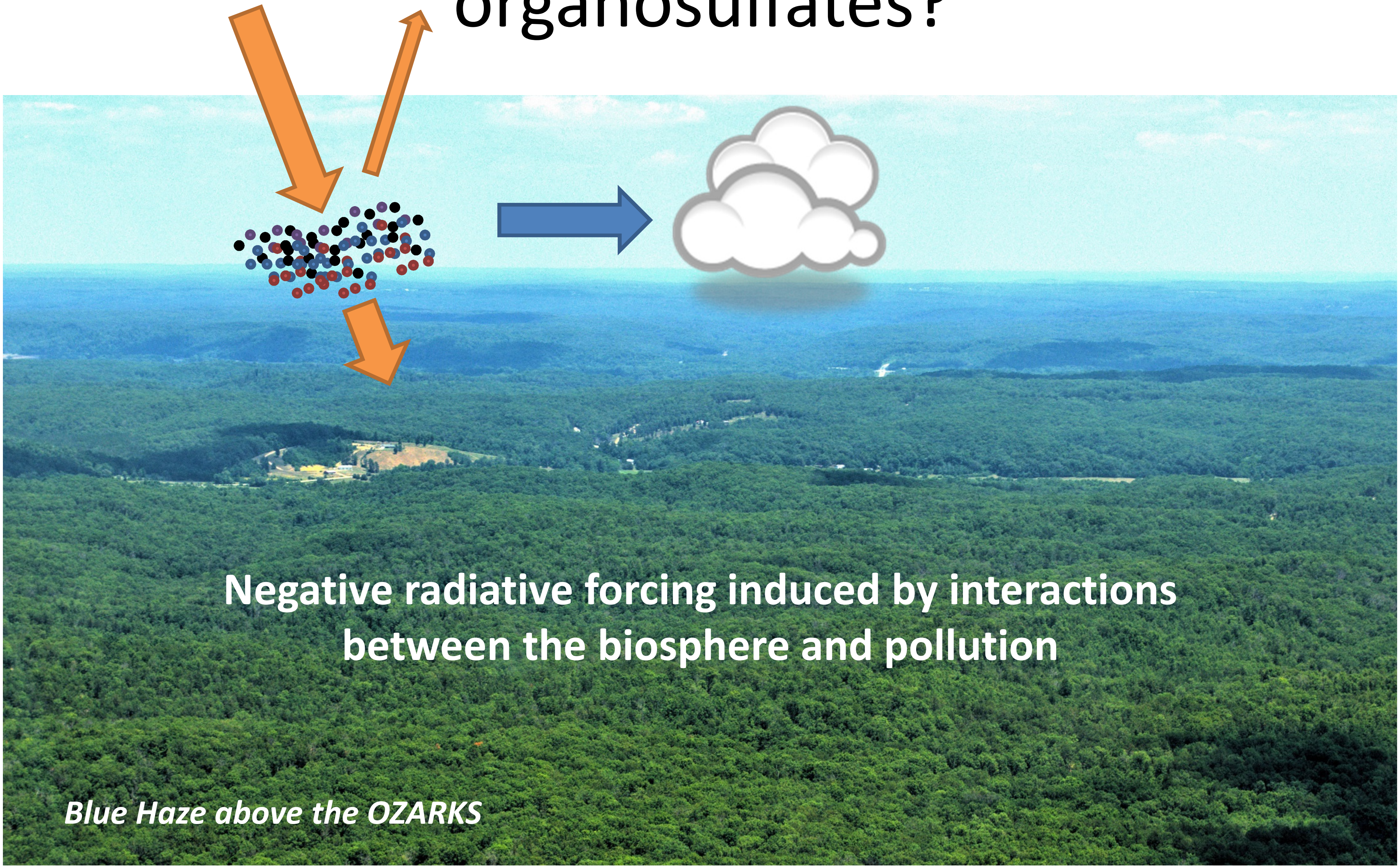
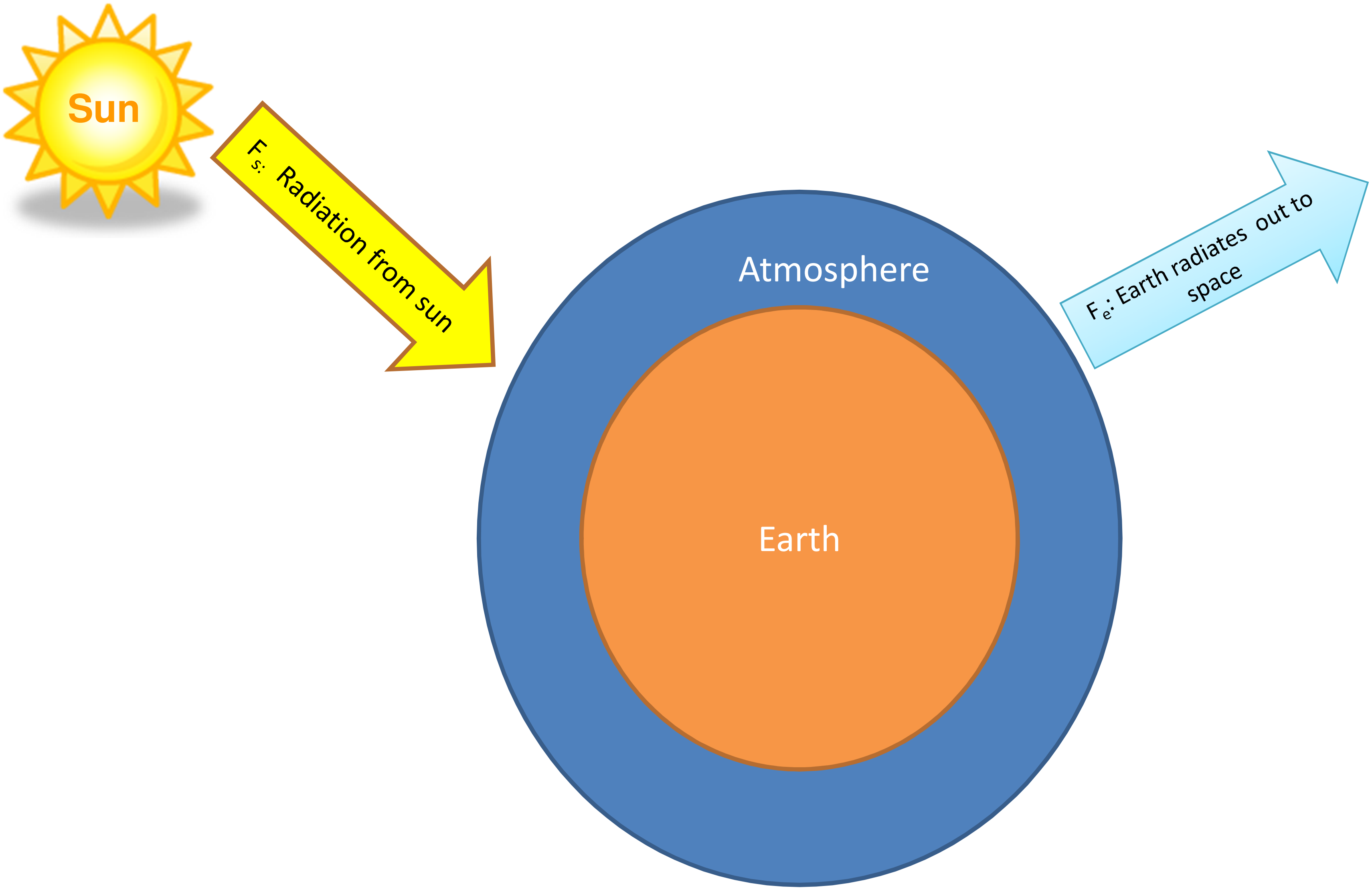


Blue Haze formation via terpene derived organosulfates?

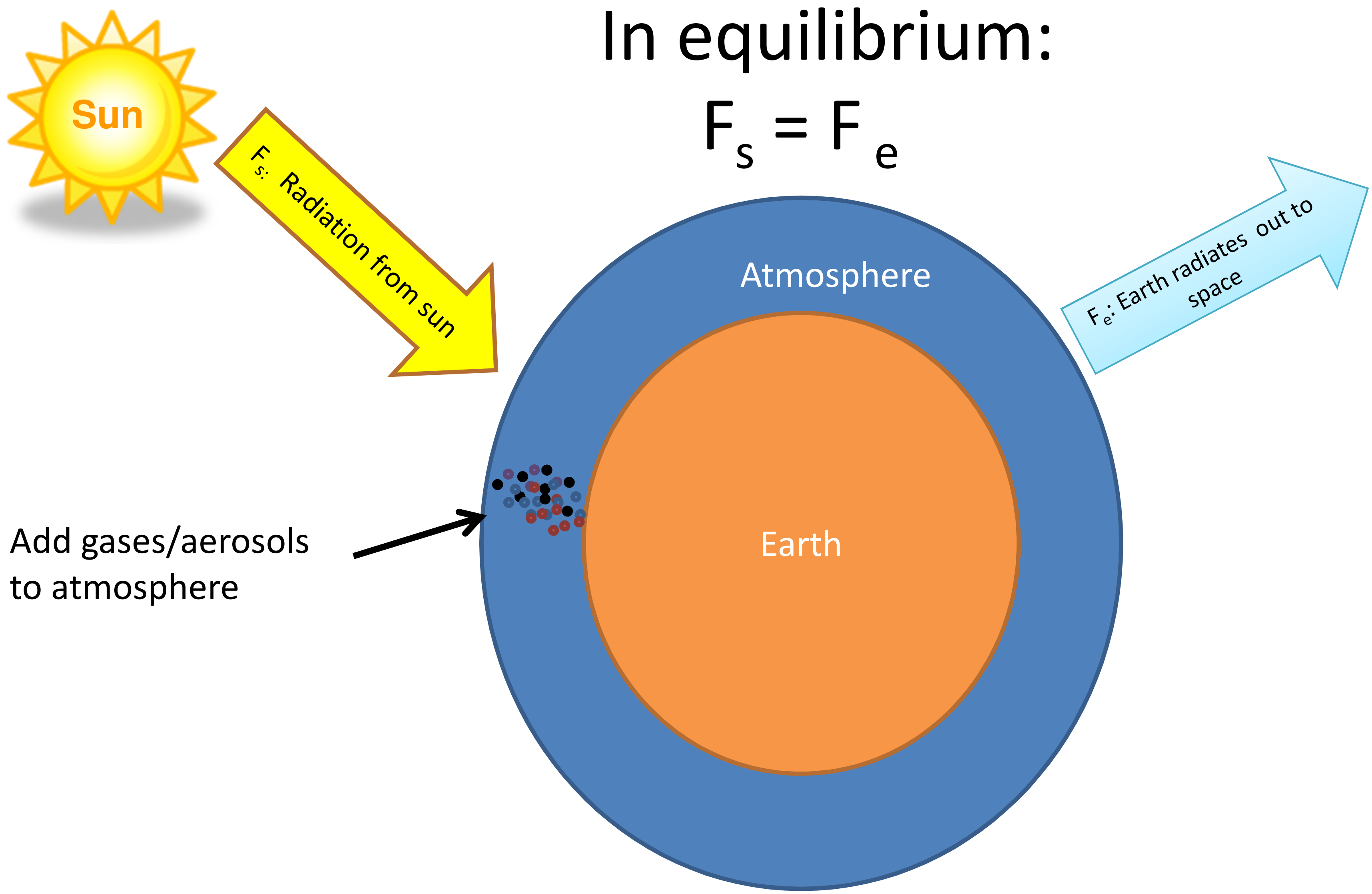


What is radiative forcing in a nutshell?

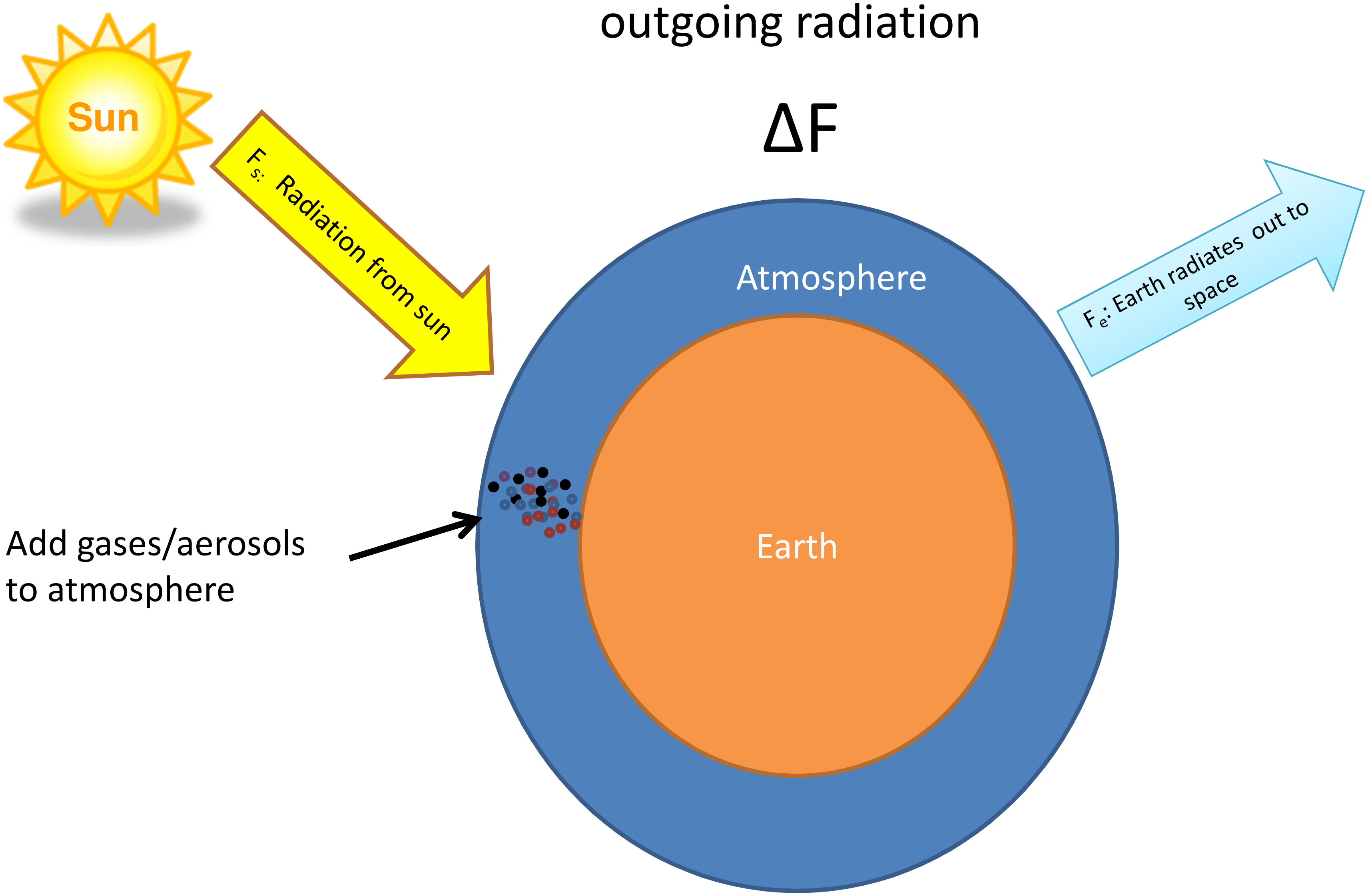


In equilibrium:

$$F_s = F_e$$

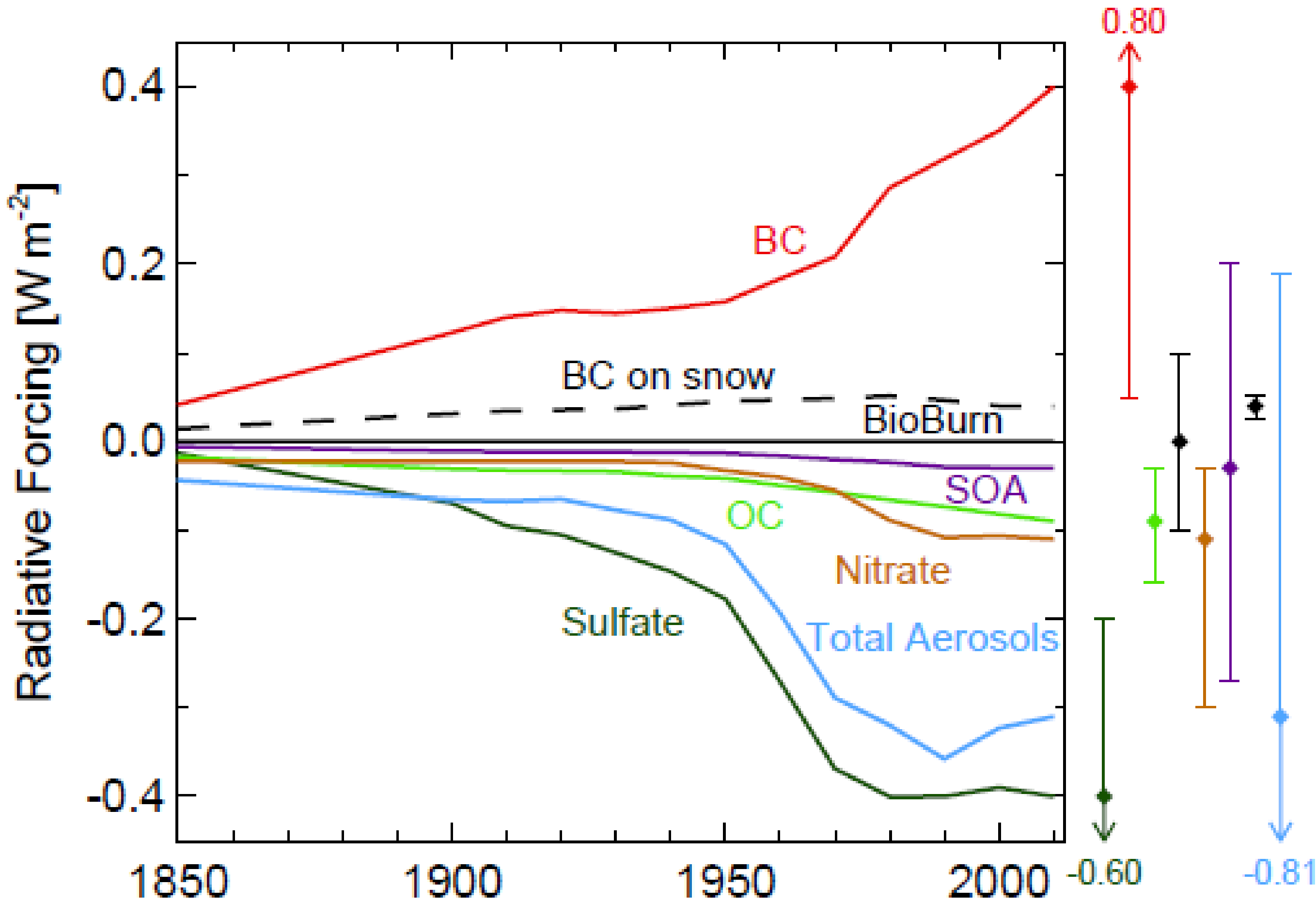


Imbalance between incoming and outgoing radiation



…. until new equilibrium is reached

Radiative forcing of aerosols, IPCC, 5AR, 2013



Aerosols and Climate Sensitivity

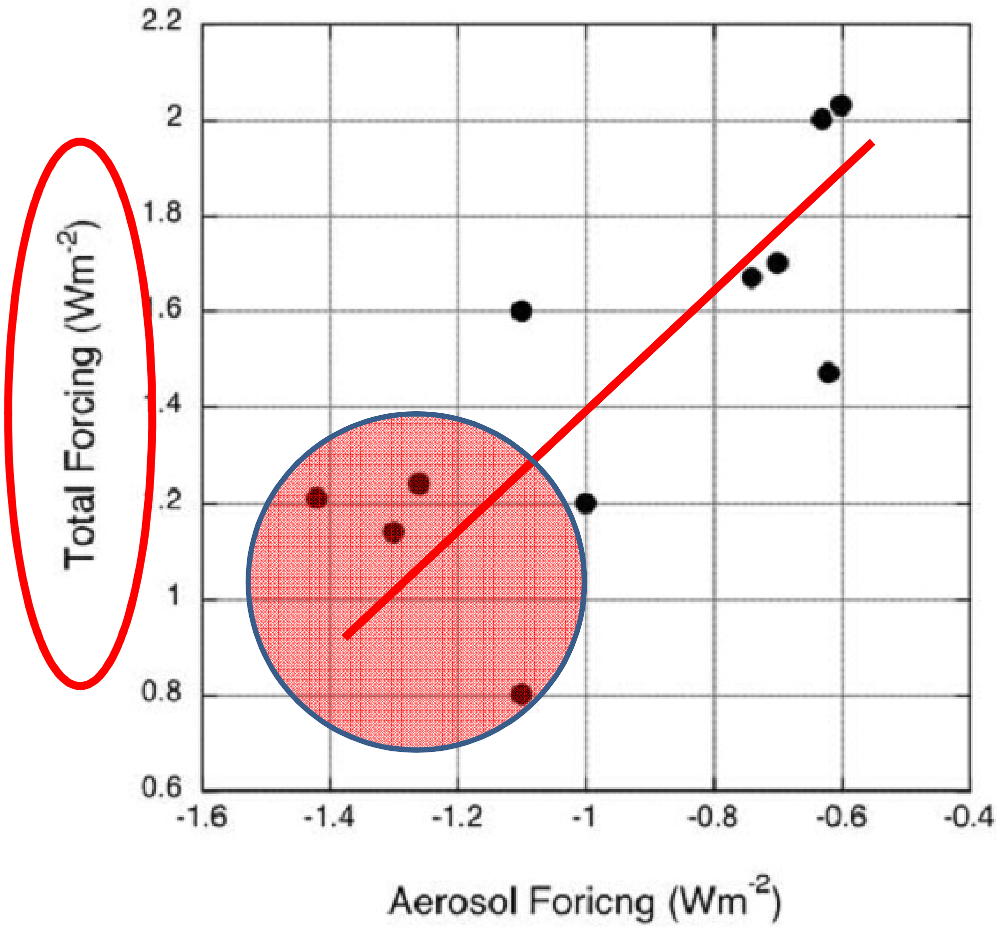


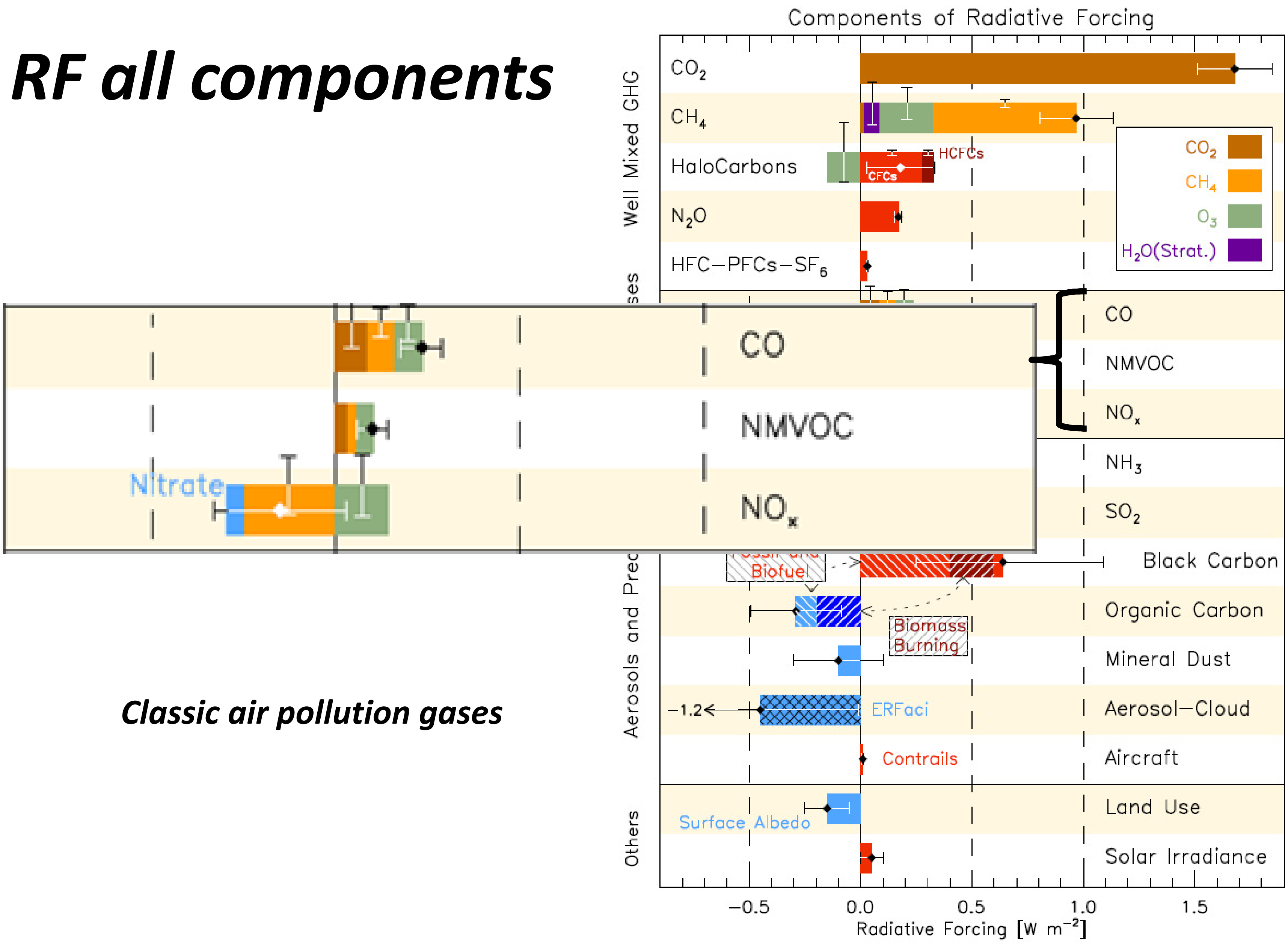
Figure 2. Total anthropogenic forcing (Wm^{-2}) versus aerosol forcing (Wm^{-2}) from nine fully coupled climate models and two energy balance models used to simulate the 20th century.

Climate Models are tuned by adjusting aerosol forcing, a poorly constrained process

Models with large climate sensitivity need large aerosol forcing

Kiehl, GRL, 2007

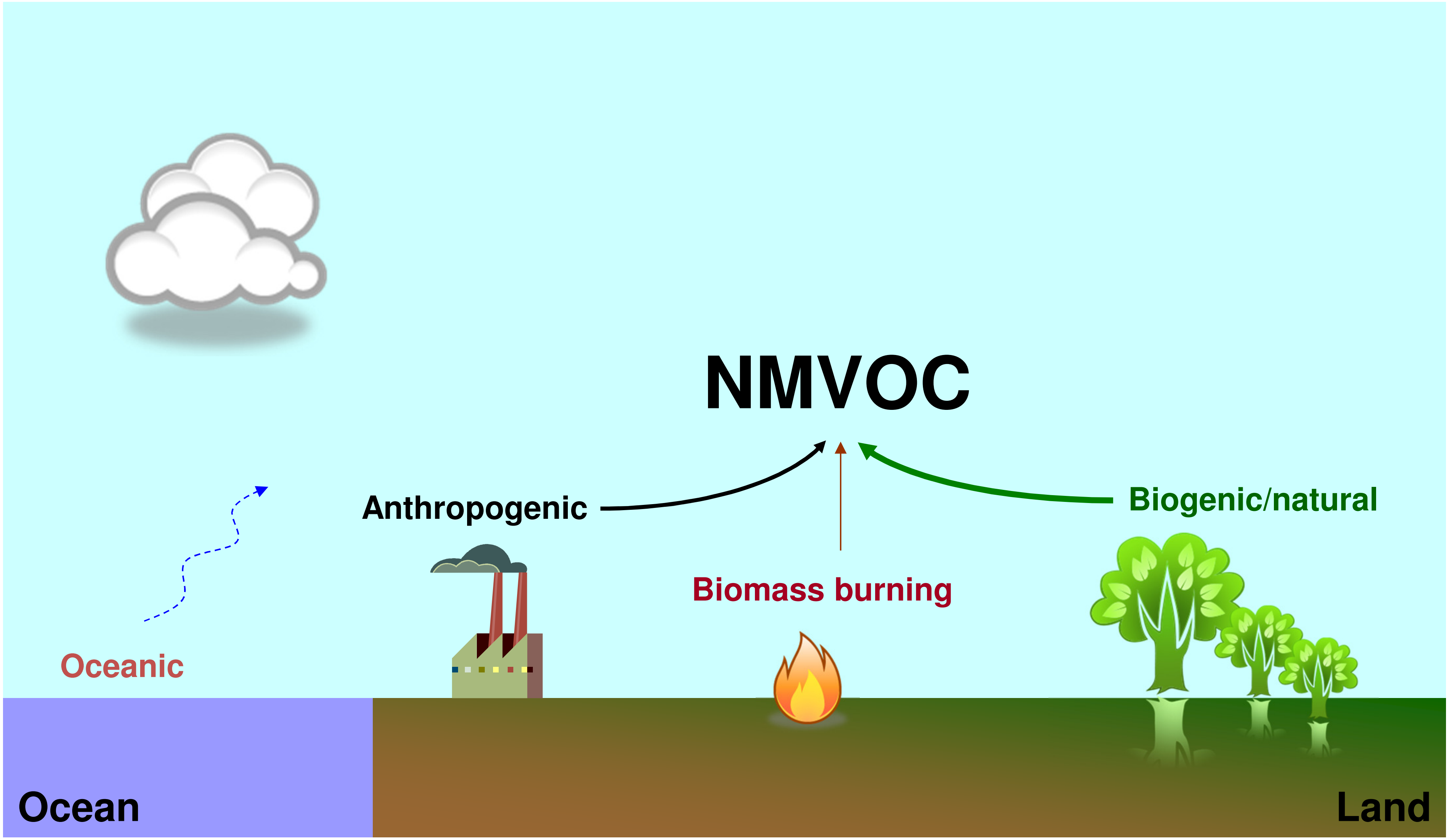
RF all components



Classic air pollution gases

5AR, IPCC, 2013

Emission of NMVOC

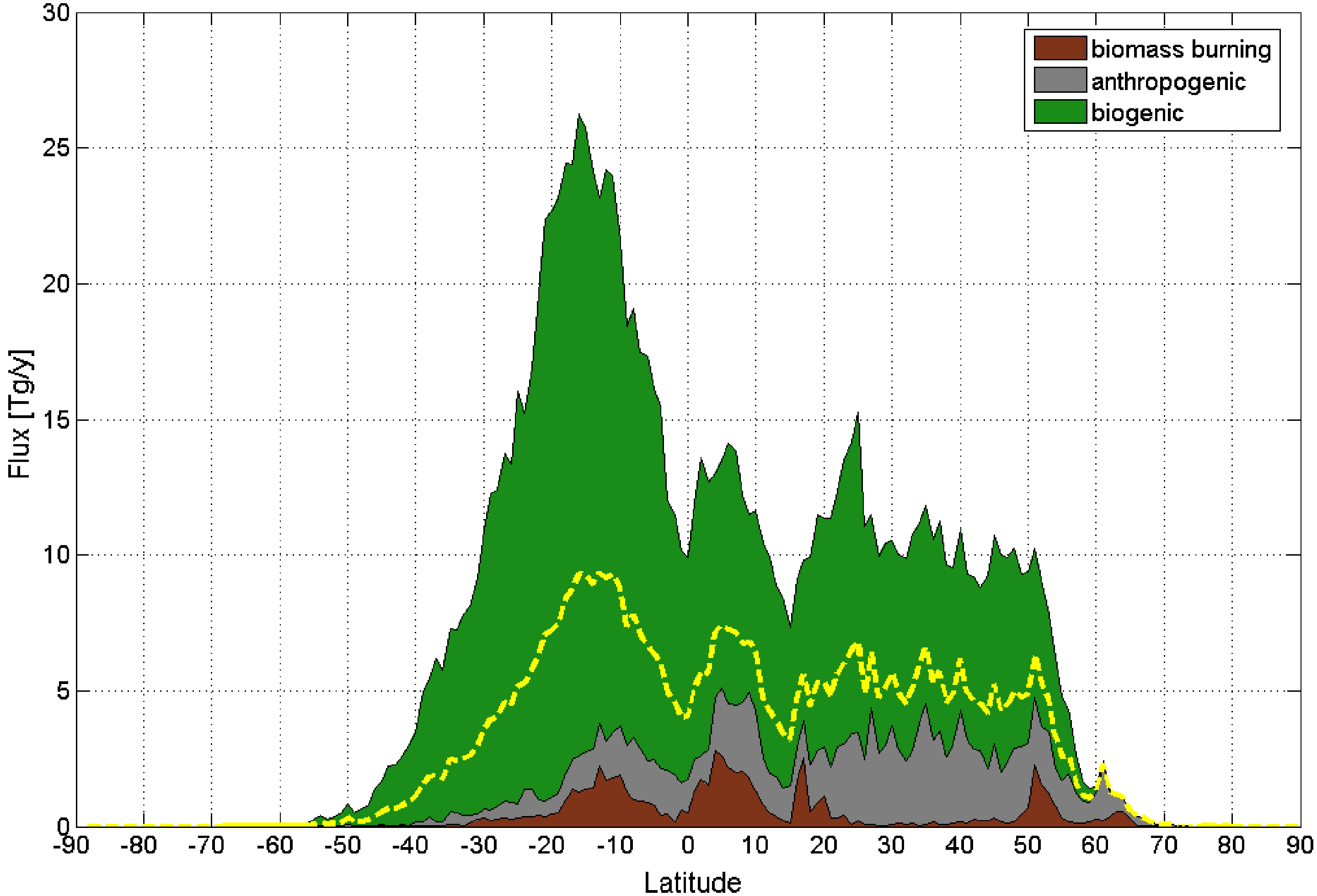


Latitudinal Distribution of NMVOC

Bottom-up (total): 1580 Tg/y

IPCC2001, 2007: 450 Tg/y

Compare to CH_4: about 500-600 Tg/y
Isoprene: about 500-700 Tg/y



GFEDv2, 2000 x2, EDGAR 2000; Guenther et al., 1995, 2007

A multi-investigator field mission in the SE USA in 2013

NitrogenOxidantsMercuryAerosolDistributionSourcesandSinks

SouthEastNEXus

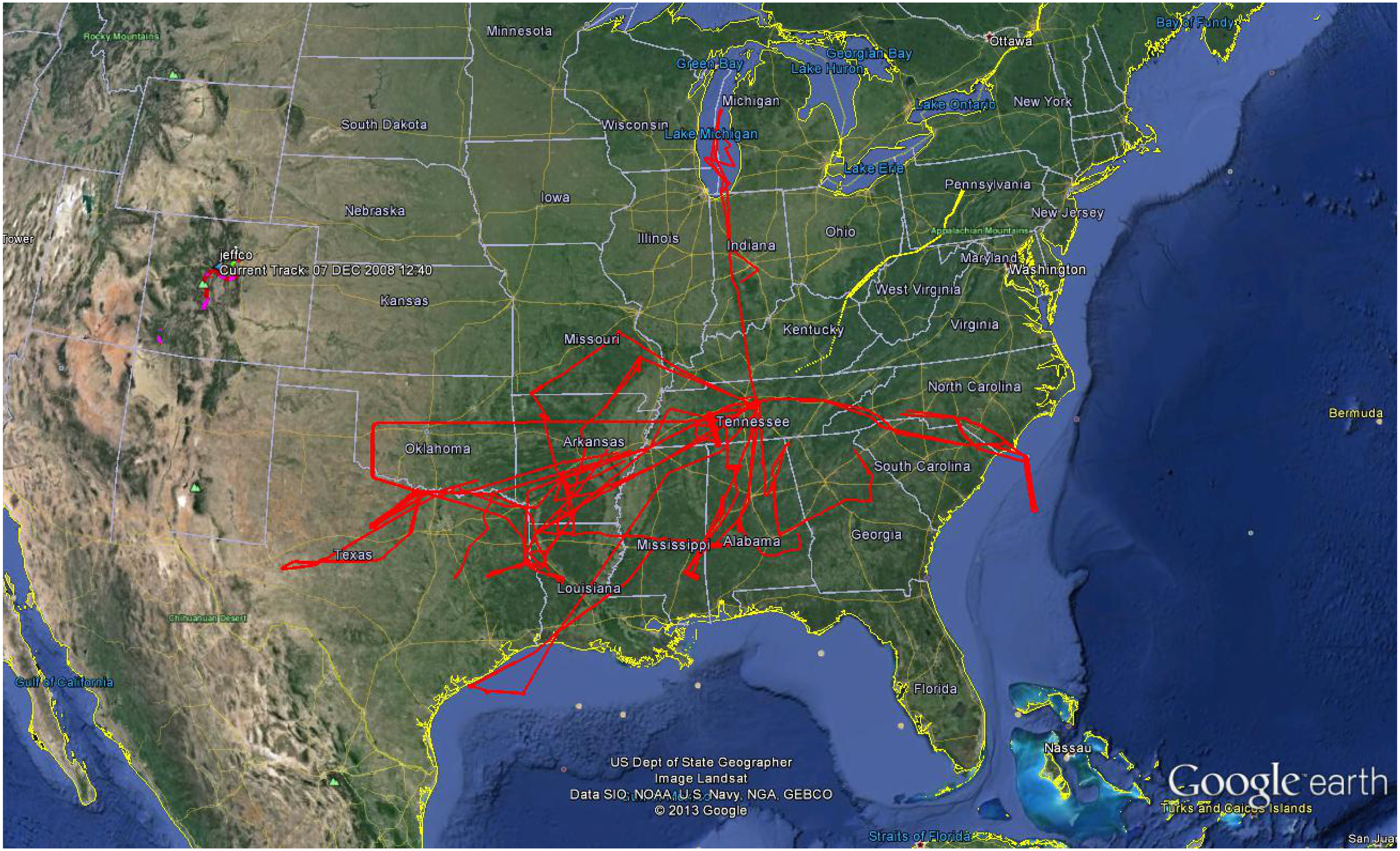
SouthernOxidantsandAerosolStudy

funded by NSF, NOAA, EPA

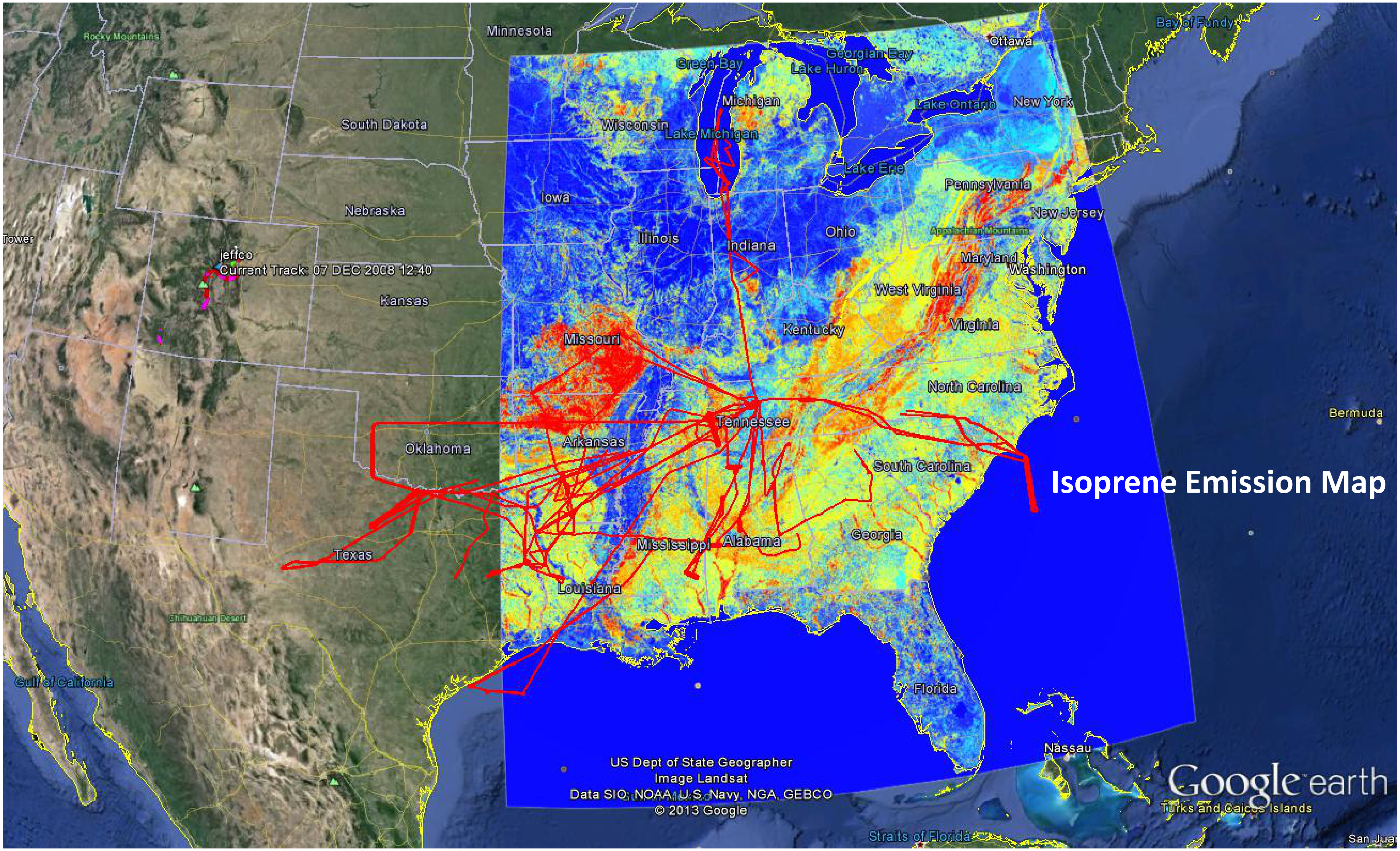
http://catalog.eol.ucar.edu/sas

2013

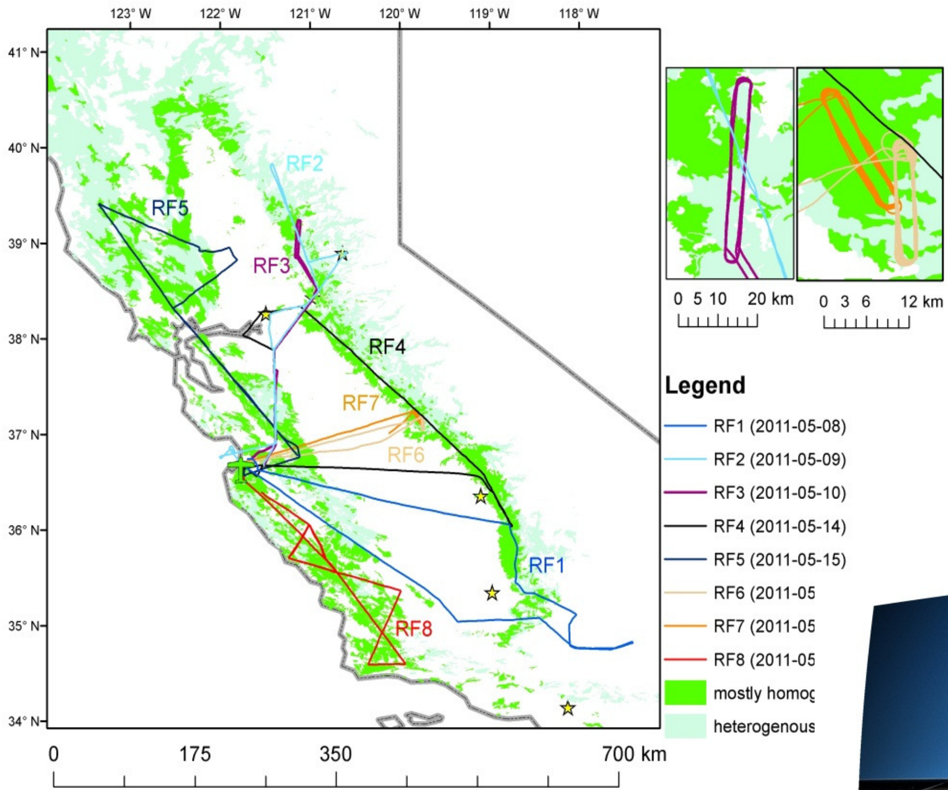
NOMADSS (Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks
SAS (Southeast Atmosphere Study) – ***All flights***



NOMADSS (Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks
SAS (Southeast Atmosphere Study) – ***MEGAN Emission Factor MAP***



California Airborne NMVOC Emission Research in Natural Ecosystem Transects (CABERNET) experiment, 2011



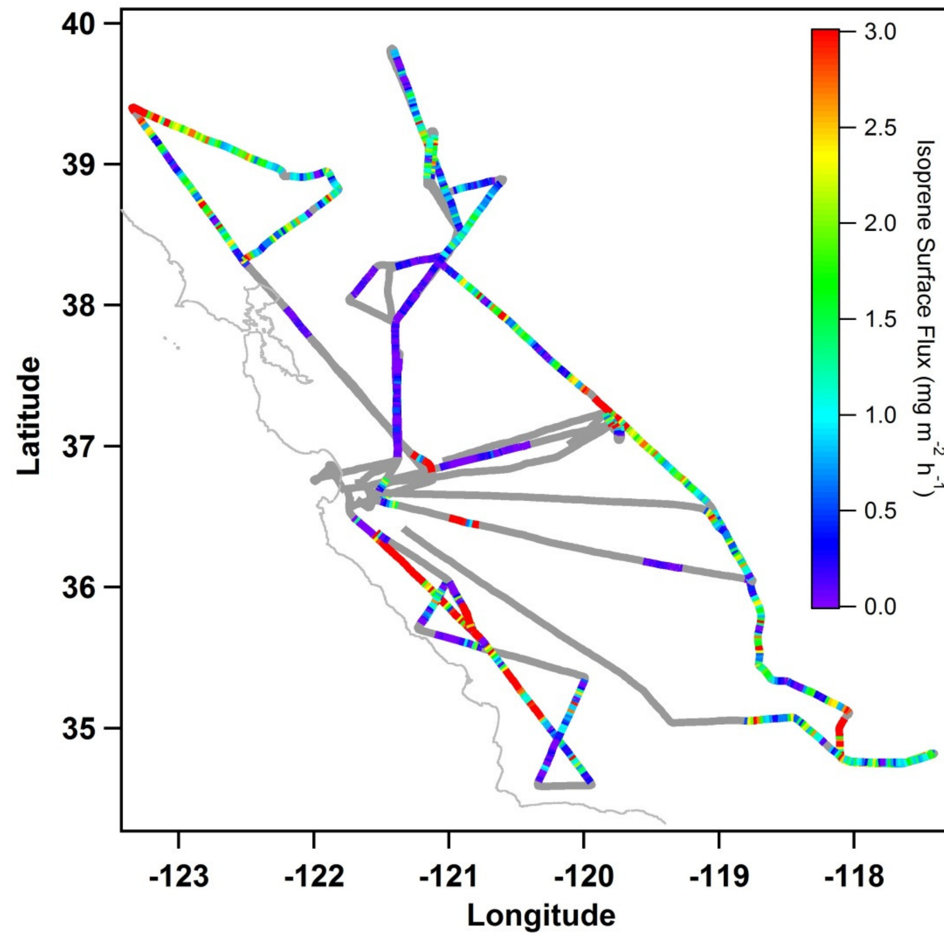
Investigating Isoprene Fluxes

Karl et al., JAS, 2013

Observationally derived spatially segregated NMVOC emission maps

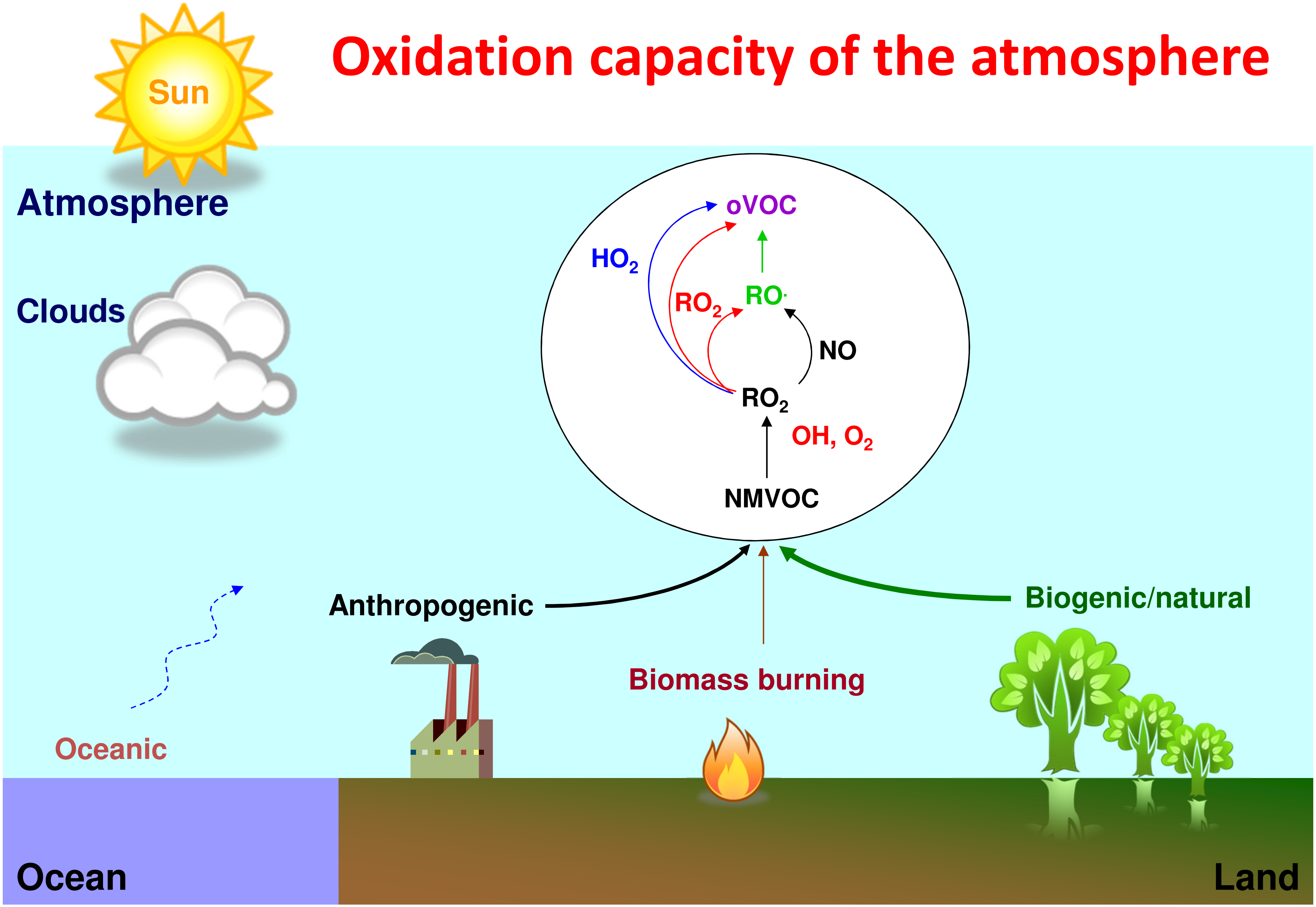
Goal:

Dataset will be used to improve process based NMVOC models by constraining landscape level emission factors

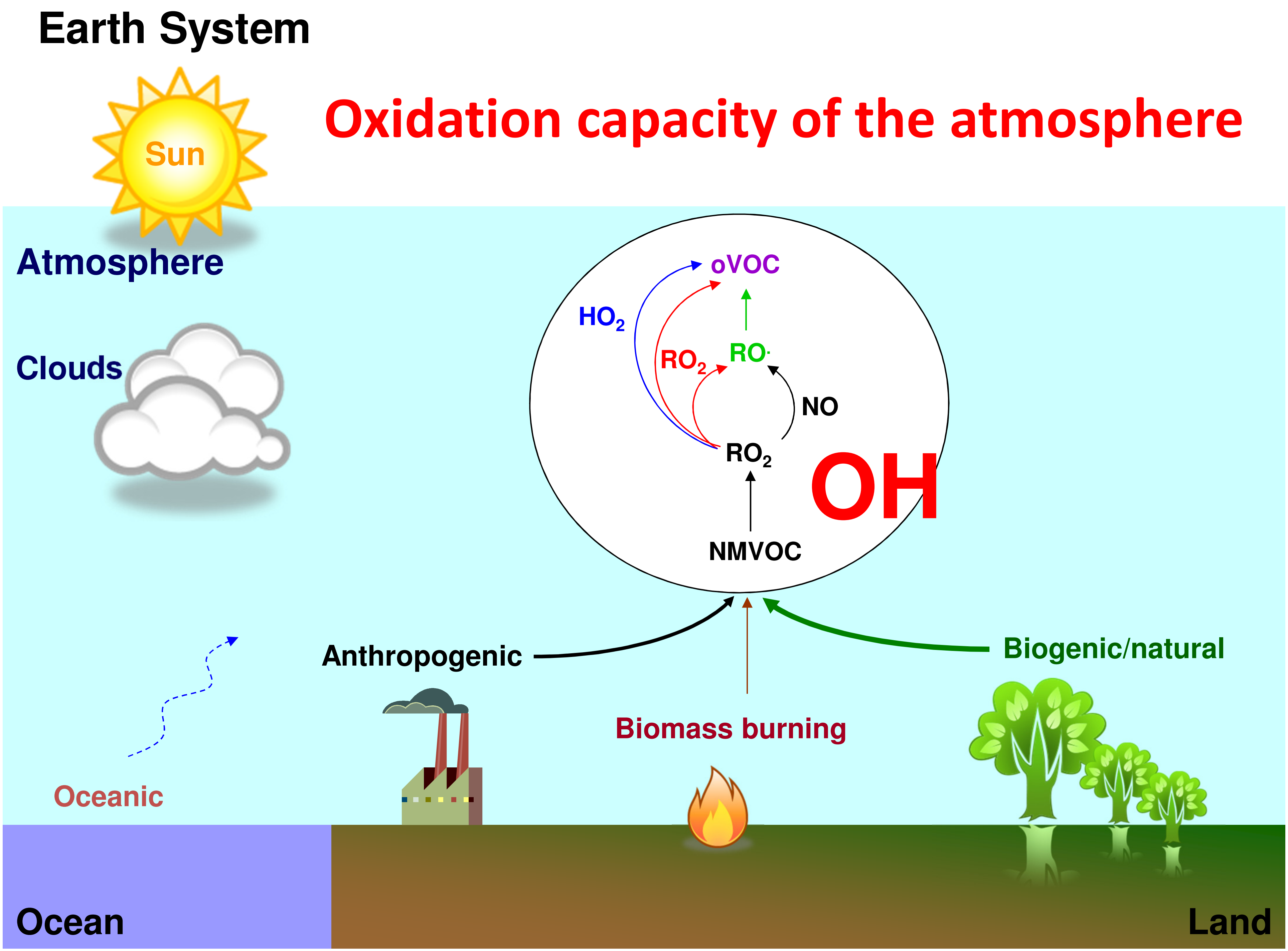


Earth System

Oxidation capacity of the atmosphere



Oxidation capacity of the atmosphere



OH – The Detergent of the Atmosphere

$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$

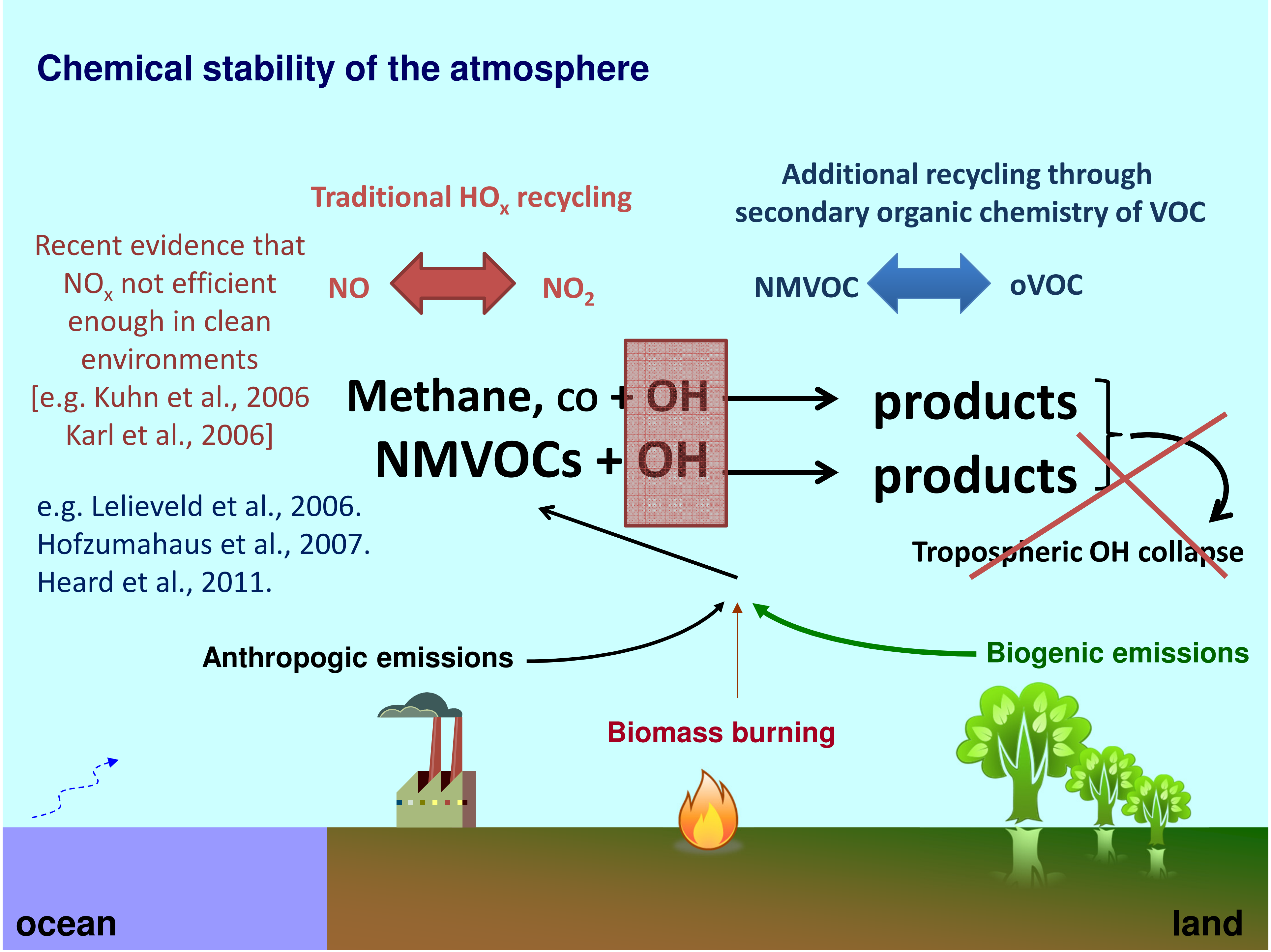
$$O(^1D) + H_2O \longrightarrow OH + OH$$

other HOx sources: photolysis of carbonyls, ozonolysis of hydrocarbons, OH+peroxides, O_3 +HO_2

Very low mixing ratios: 1 - 4 x 10^{-14} (ppqv range)

Very reactive free radical – together with H and HO_2 it forms the HO_x pool (= H + HO + HO_2)

UV radiation can not dissociate O_2 for HO_x production in the troposphere anymore


Chemical stability of the atmosphere
Traditional HO_x recycling
Additional recycling through secondary organic chemistry of VOC
Recent evidence that NO_x not efficient enough in clean environments [e.g. Kuhn et al., 2006 Karl et al., 2006]
NO
NO_2
NMVOC
oVOC
Methane, co + OH
NMVOCs + OH
products
products
Tropospheric OH collapse
e.g. Lelieveld et al., 2006.
Hofzumahaus et al., 2007.
Heard et al., 2011.
Anthropogic emissions
Biogenic emissions
Biomass burning
ocean
land

Methane and isoprene (+monoterpenes) are the among the most important reactive carbon containing trace gases to understand paleoclimate

Enhanced chemistry-climate feedbacks in past greenhouse worlds

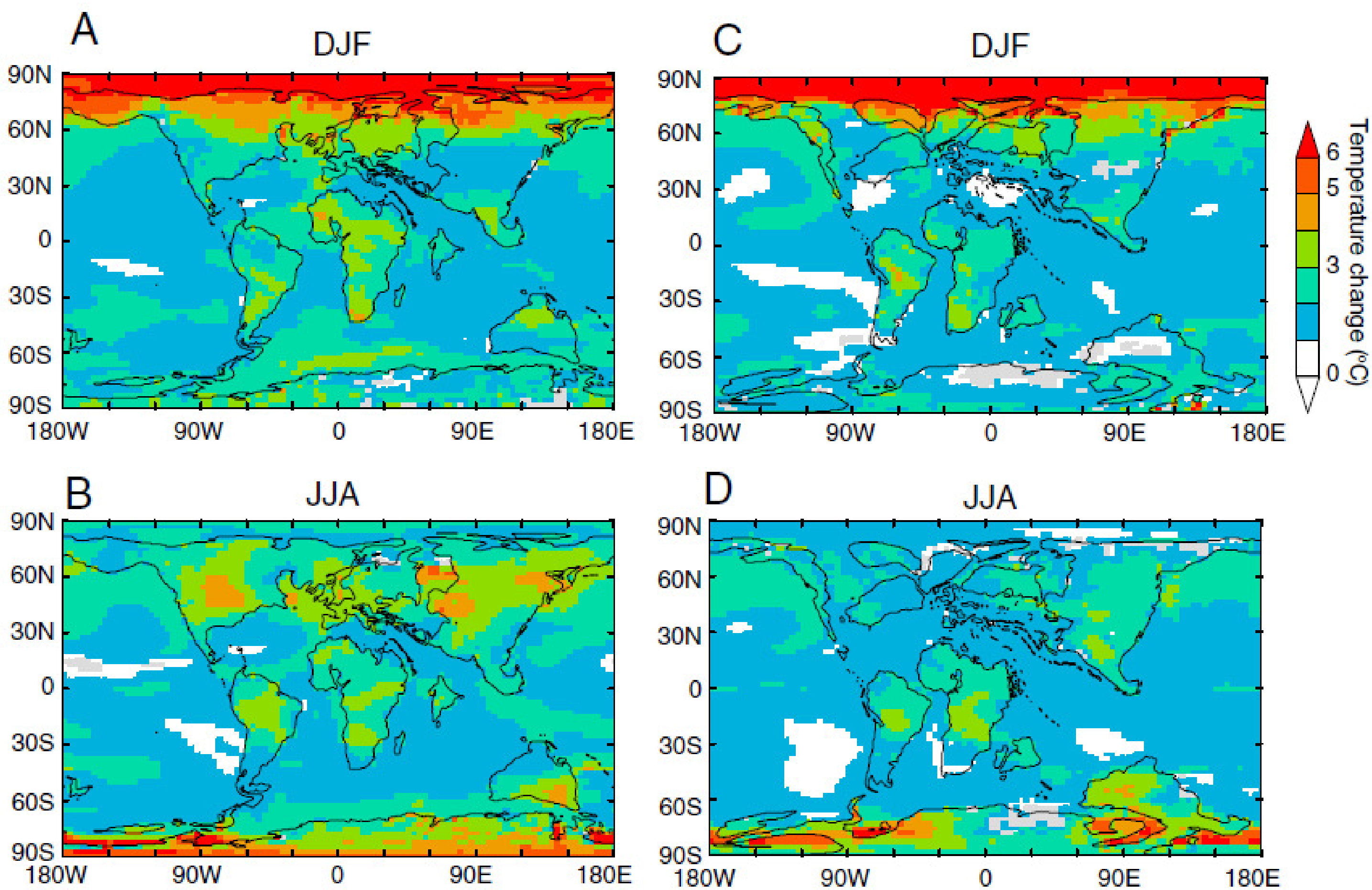
PNAS

David J. Beerling[a,1], Andrew Fox[a,2], David S. Stevenson[b], and Paul J. Valdes[c]

[a]Department of Animal and Plant Sciences, University of Sheffield, Sheffield S10 2TN, United Kingdom; [b]School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JN, United Kingdom; and [c]Department of Geographical Sciences, University of Bristol, Bristol BS8 1SS, United Kingdom

Edited by Ralph J. Cicerone, National Academy of Sciences, Washington, DC, and approved April 26, 2011 (received for review February 11, 2011)

Isoprene controls the lifetime of methane – both emissions are much higher than pre industrial levels – this system causes a high climate sensitivity due to it‘s impact on OH



Eocene

55 Ma

Cretaceous

90 Ma

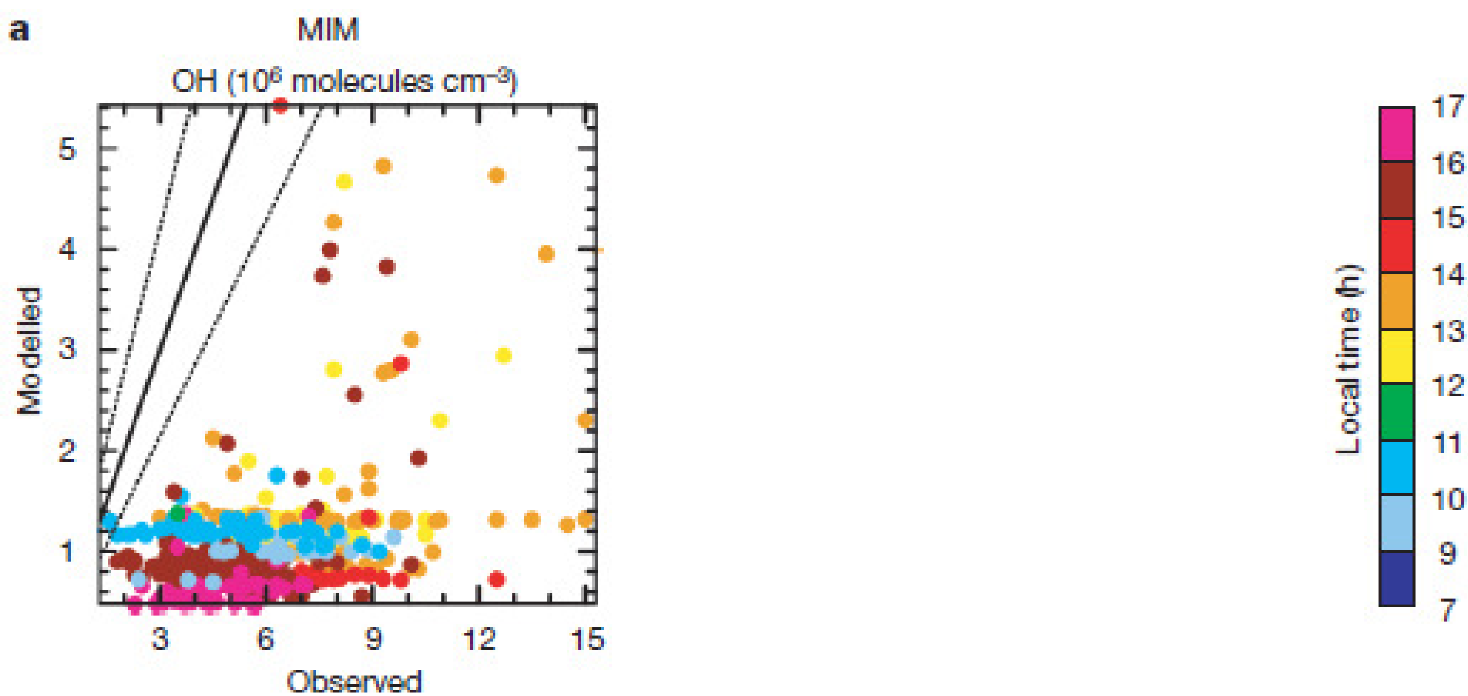
High climate sensitivity through chemistry – climate interactions

First assessment of the performance of a global CT Model

Atmospheric oxidation capacity sustained by a tropical forest

Nature, 2008

J. Lelieveld[1], T. M. Butler[1], J. N. Crowley[1], T. J. Dillon[1], H. Fischer[1], L. Ganzeveld[1], H. Harder[1], M. G. Lawrence[1], M. Martinez[1], D. Taraborrelli[1] & J. Williams[1]



Also: Hofzumahaus et al. , Science, 2009. Paulot et al. , Science, 2009.

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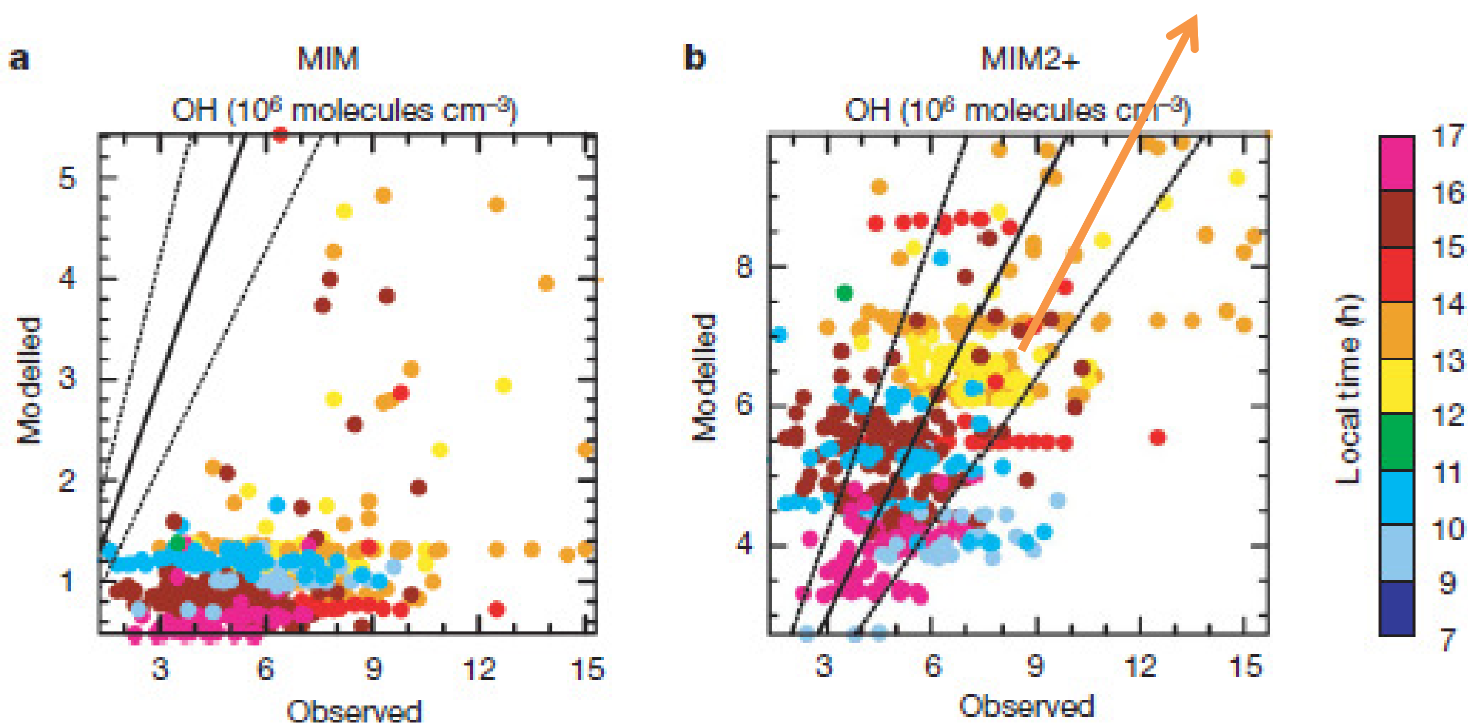
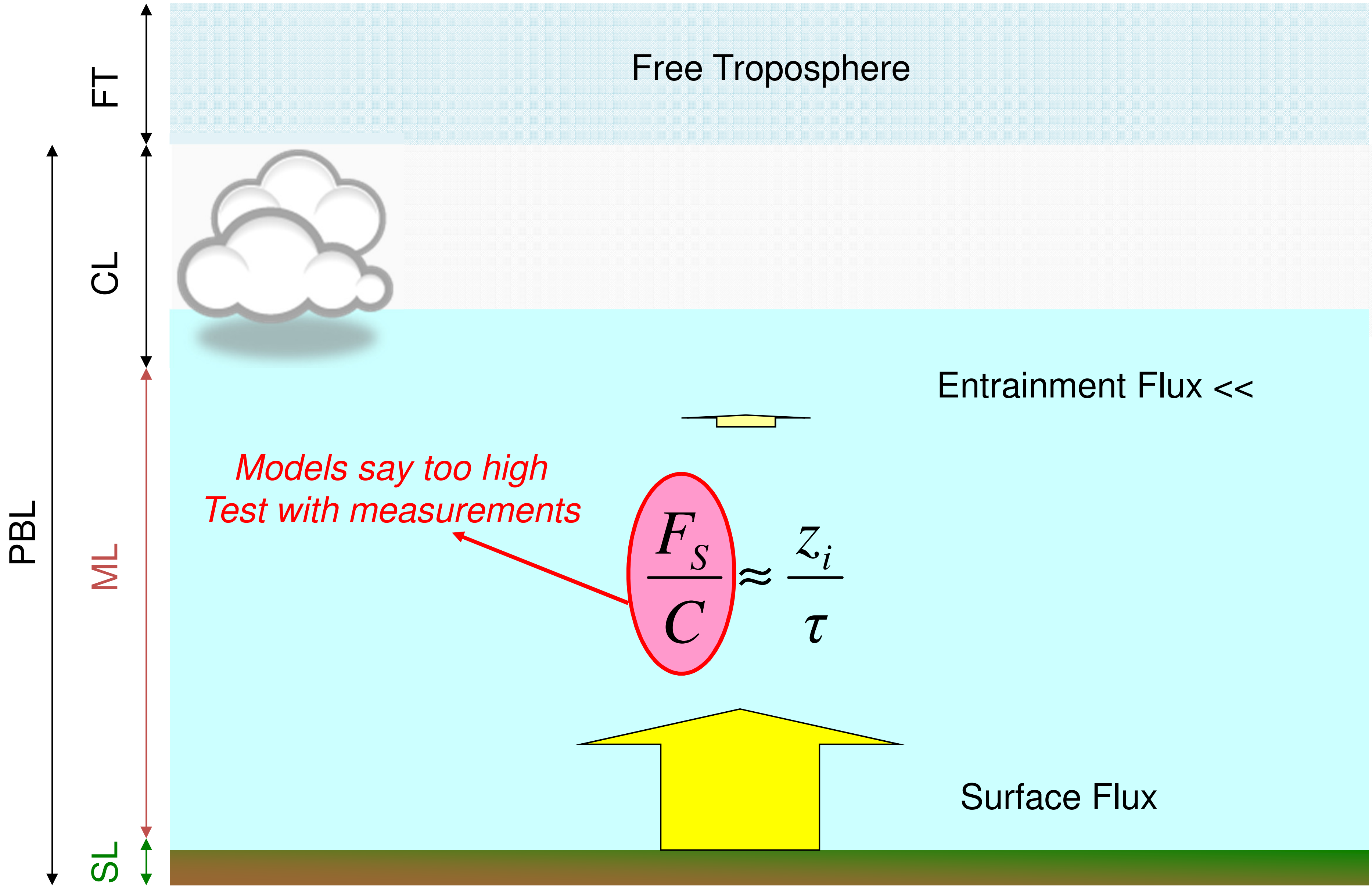
Model chemistry „tuned“

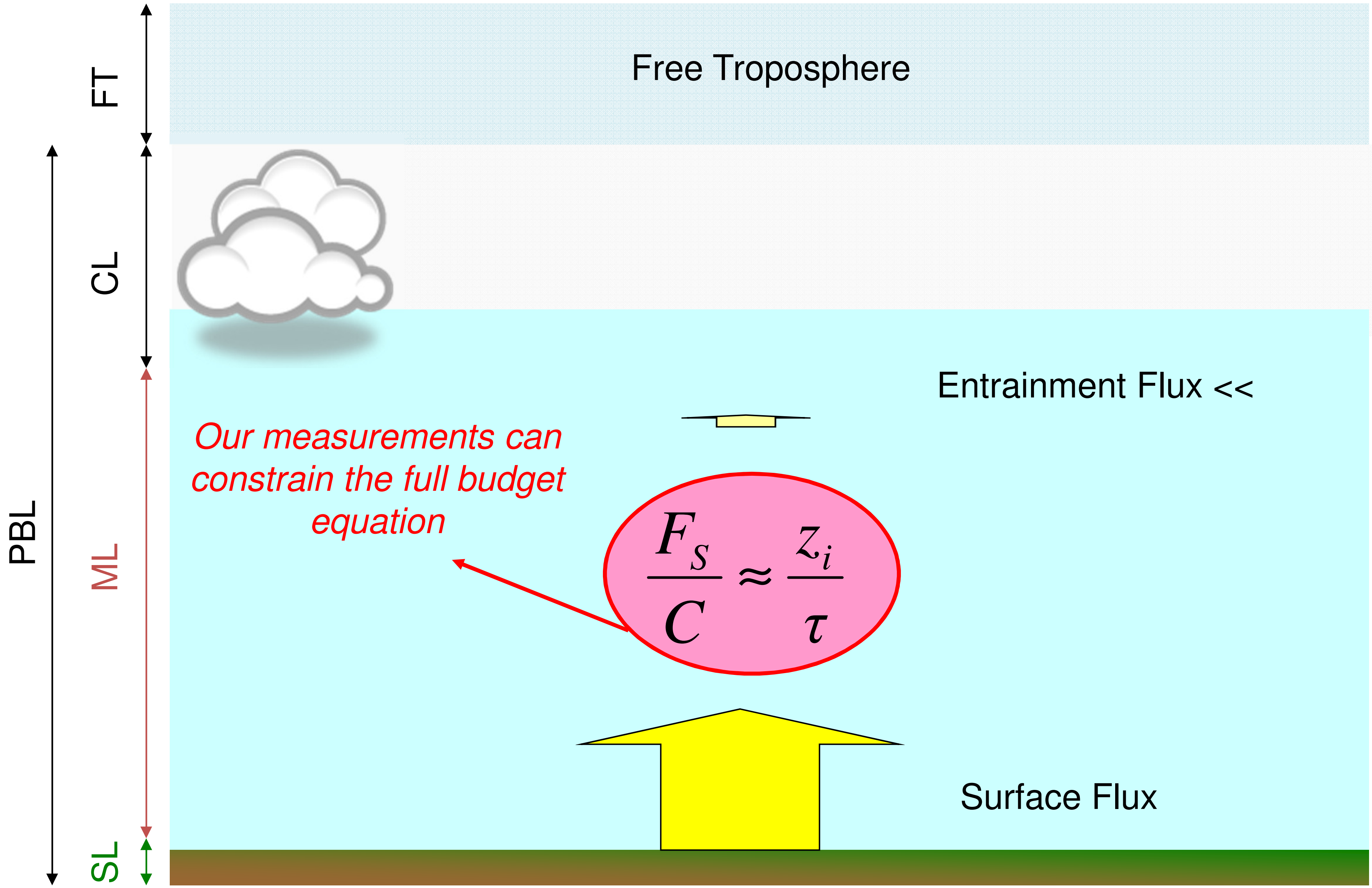


Also:

Hofzumahaus et al. , Science, 2009. Paulot et al. , Science, 2009. Taraborelli et al., Nat. Geo., 2012



Free Troposphere
FT
CL
PBL
ML
SL
Entrainment Flux <<
Models say too high
Test with measurements
$\frac{F_S}{C} \approx \frac{z_i}{\tau}$
Surface Flux



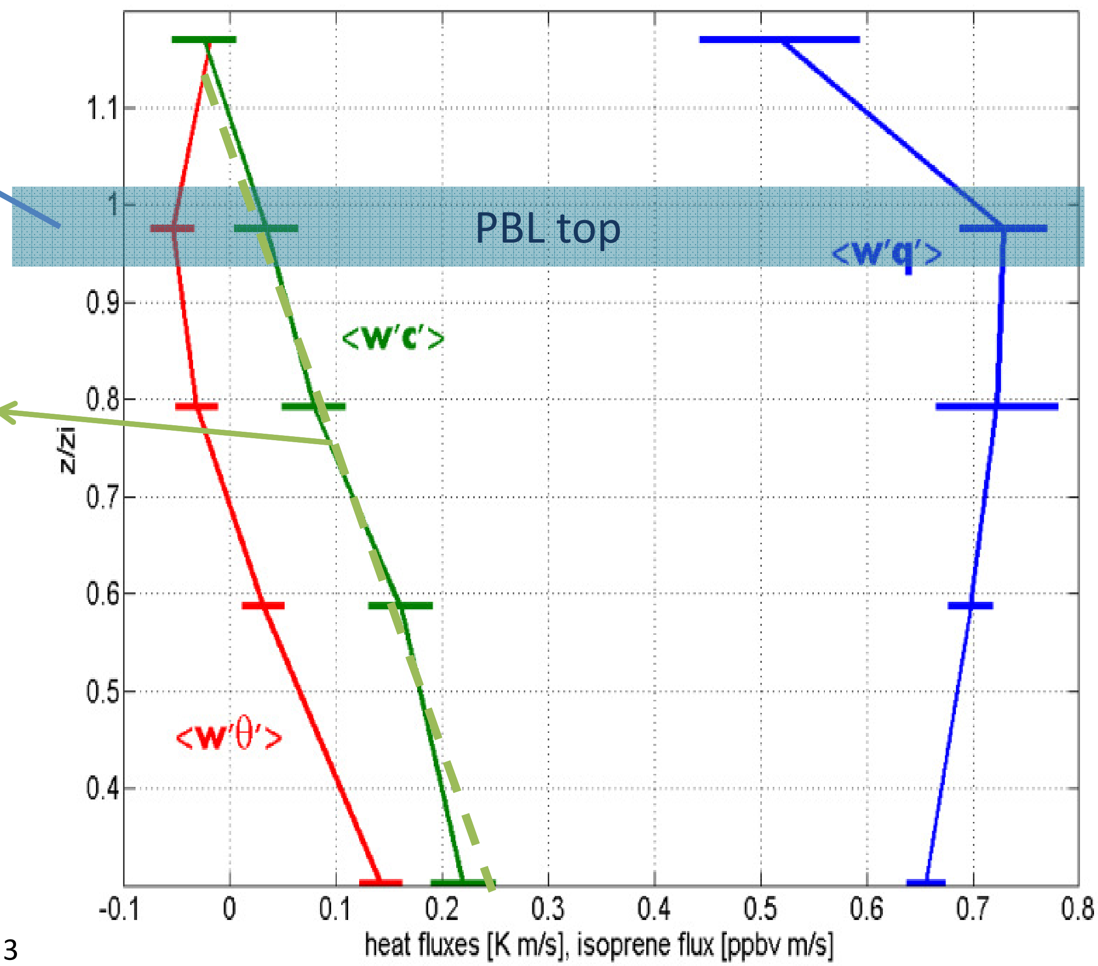
Free Troposphere
FT
CL
PBL
ML
SL
Entrainment Flux <<
Our measurements can constrain the full budget equation
$\frac{F_S}{C} \approx \frac{z_i}{\tau}$
Surface Flux

CABERNET - results

Minimum of sensible heat flux

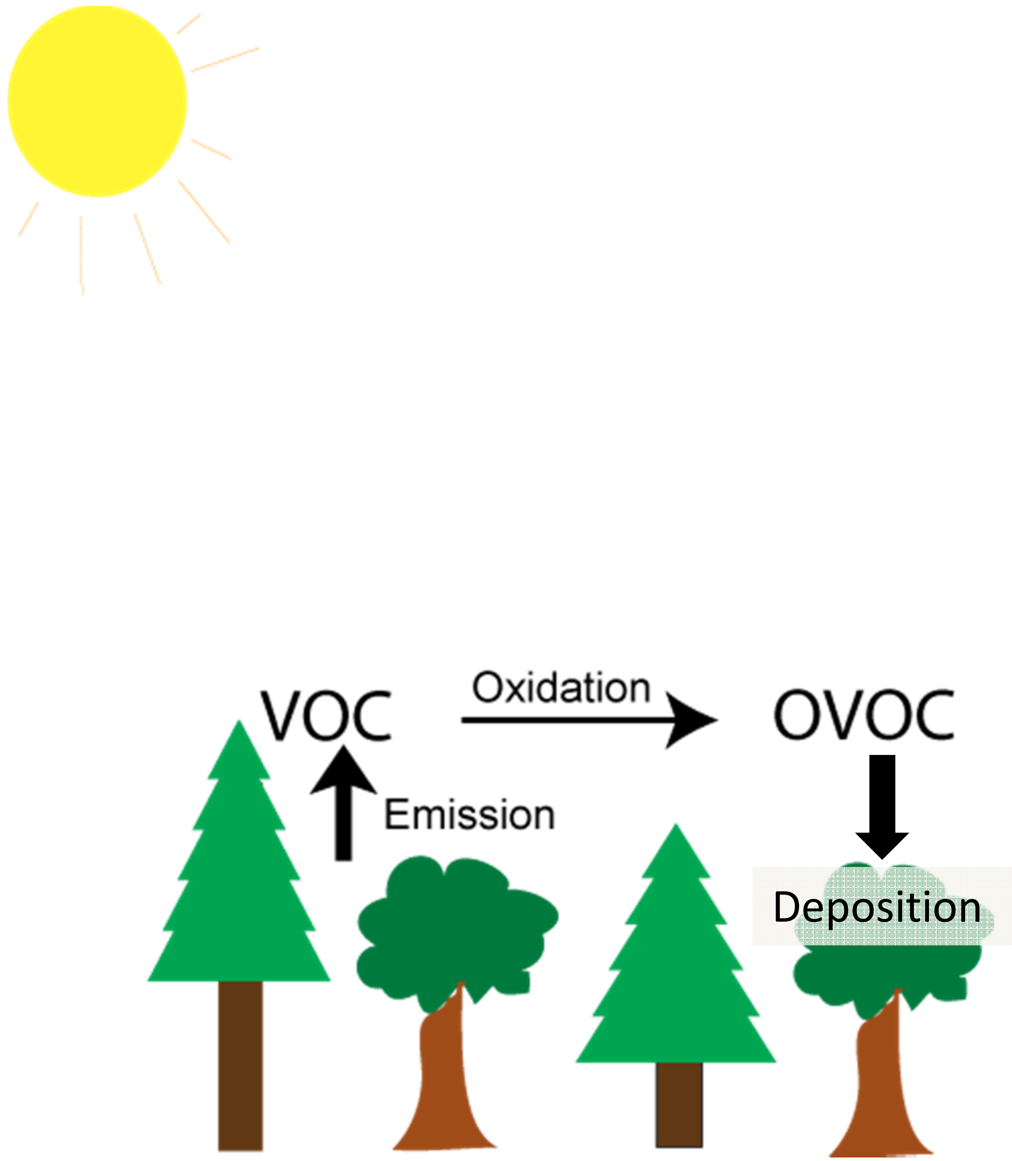
Slope of Isoprene flux divergence is proportional to Dahmkoehler (Da) number and the ***lifetime*** imposed by the ***OH radical***

3 research flights:
Da: 0.2 – 0.9
v_e : 1.5 – 9.6 cm/s
OH: 4.4 – 7.2 x 10^6 molecules/cm^3

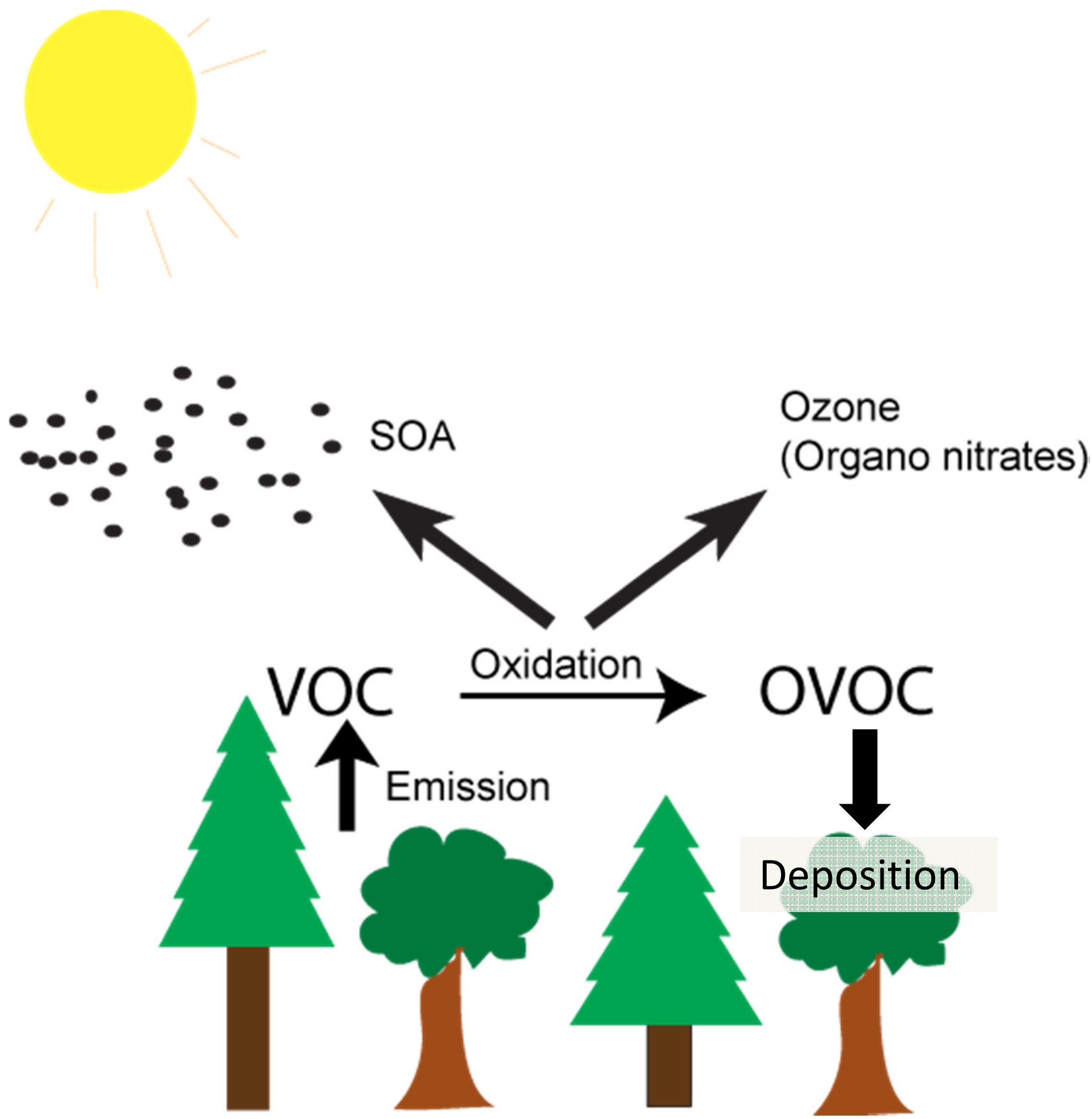


Karl et al., JAS, 2013

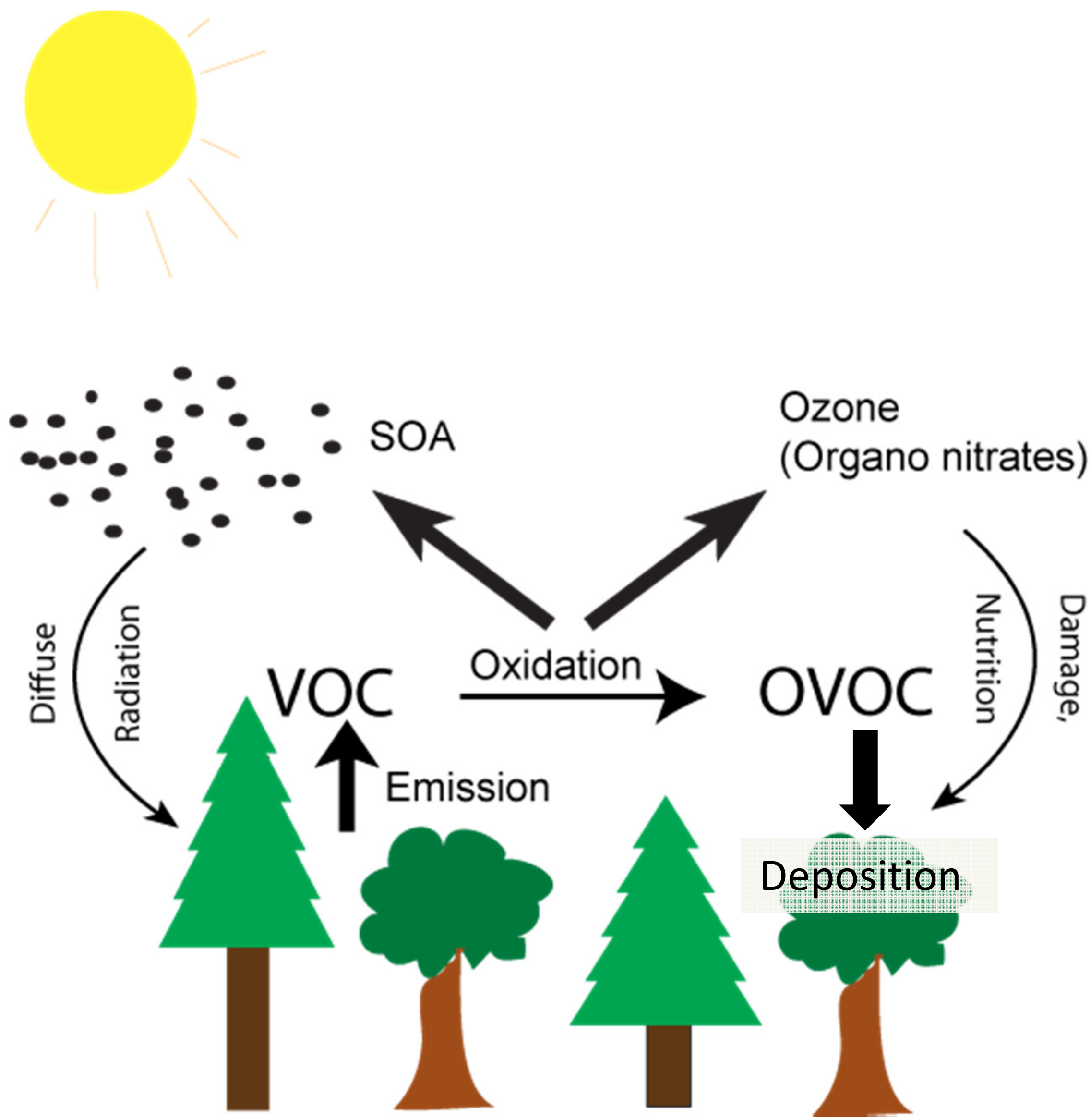
NMVOC Oxidation, Ozone and SOA Formation: Air pollution-Atmosphere Feedbacks



NMVOC Oxidation, Ozone and SOA Formation: Air pollution-Atmosphere Feedbacks



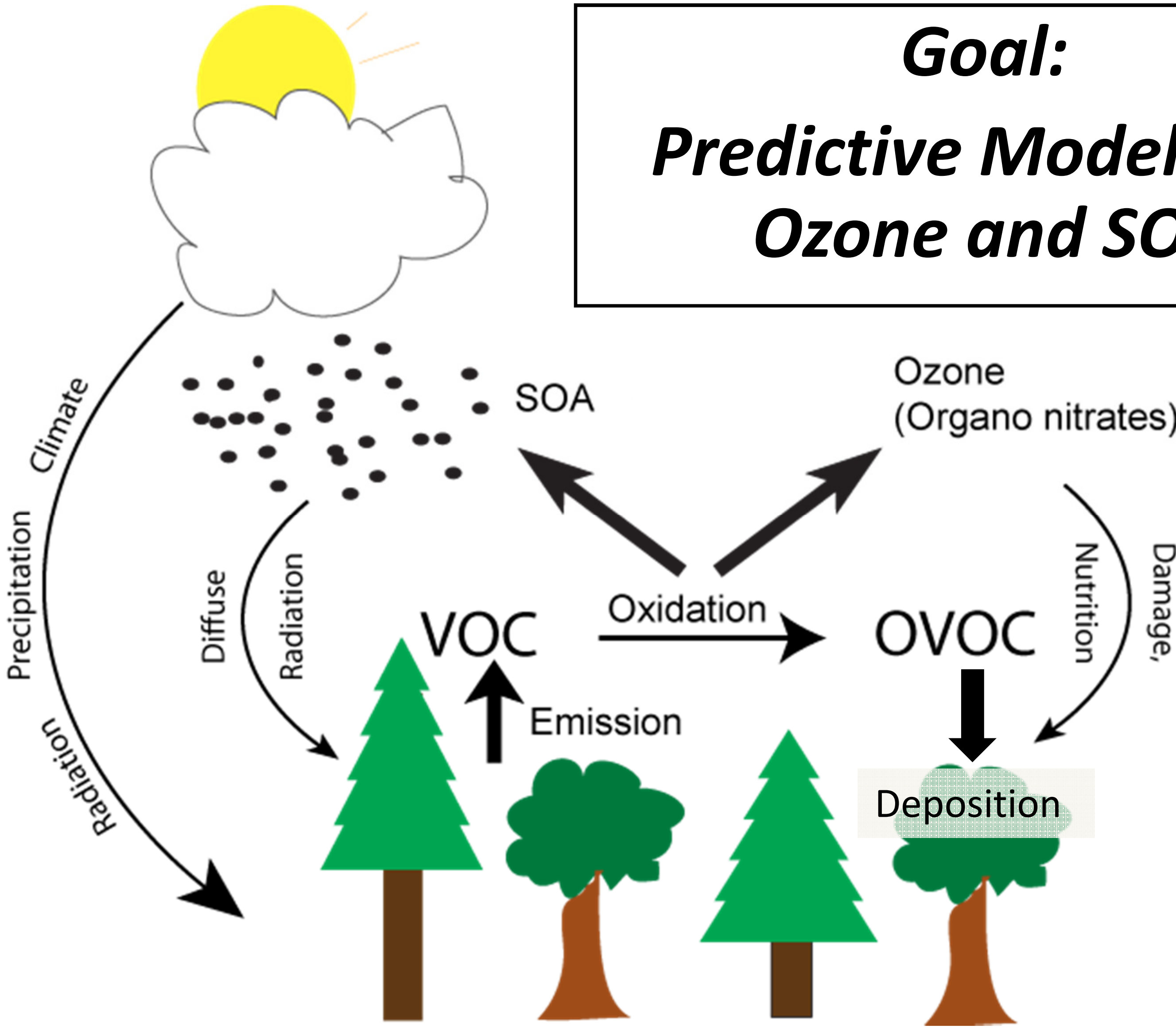
NMVOC Oxidation, Ozone and SOA Formation: Air pollution-Atmosphere Feedbacks



NMVOC Oxidation, Ozone and SOA Formation: Air pollution-Atmosphere Feedbacks

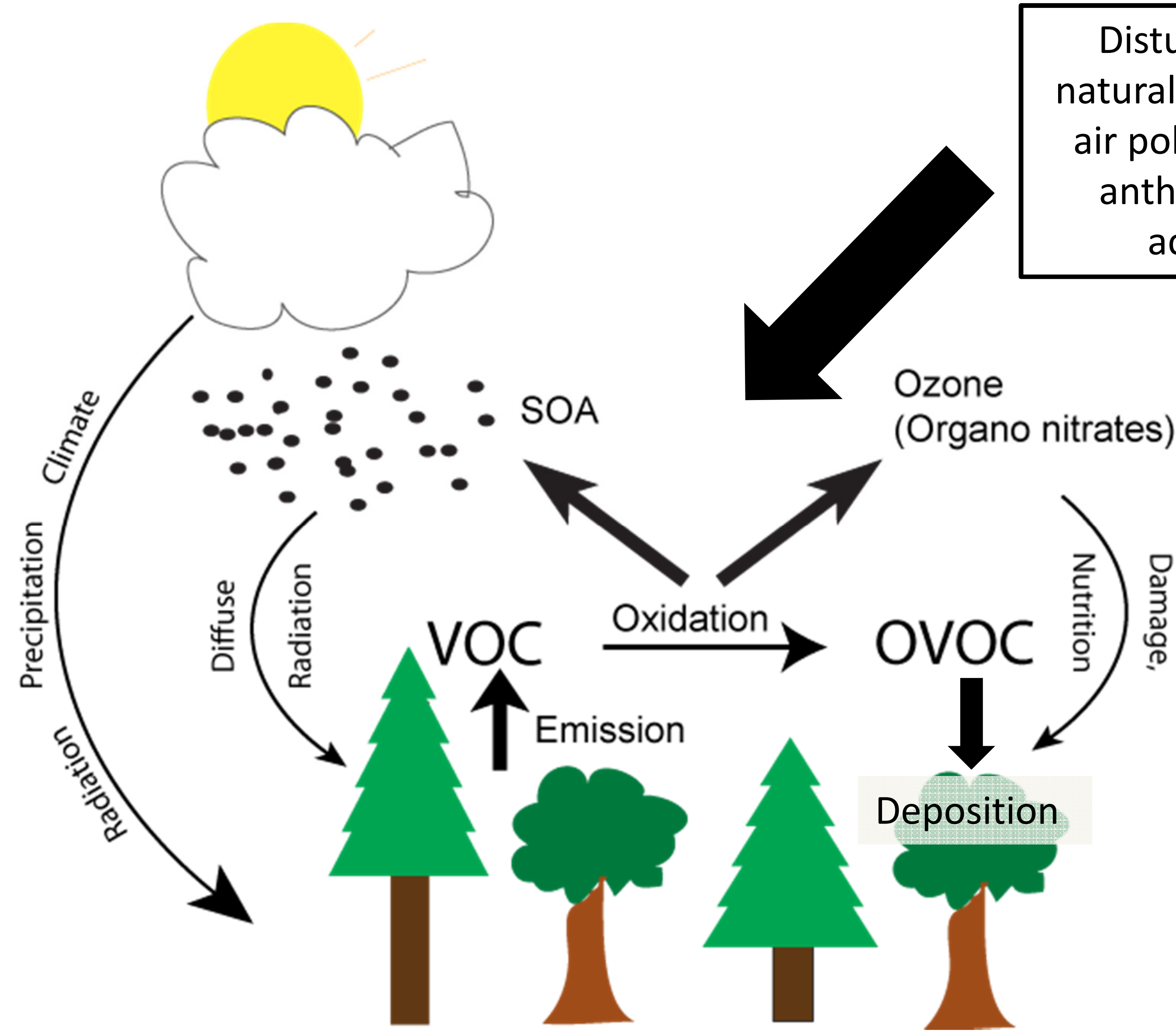
Goal:

Predictive Models for Ozone and SOA

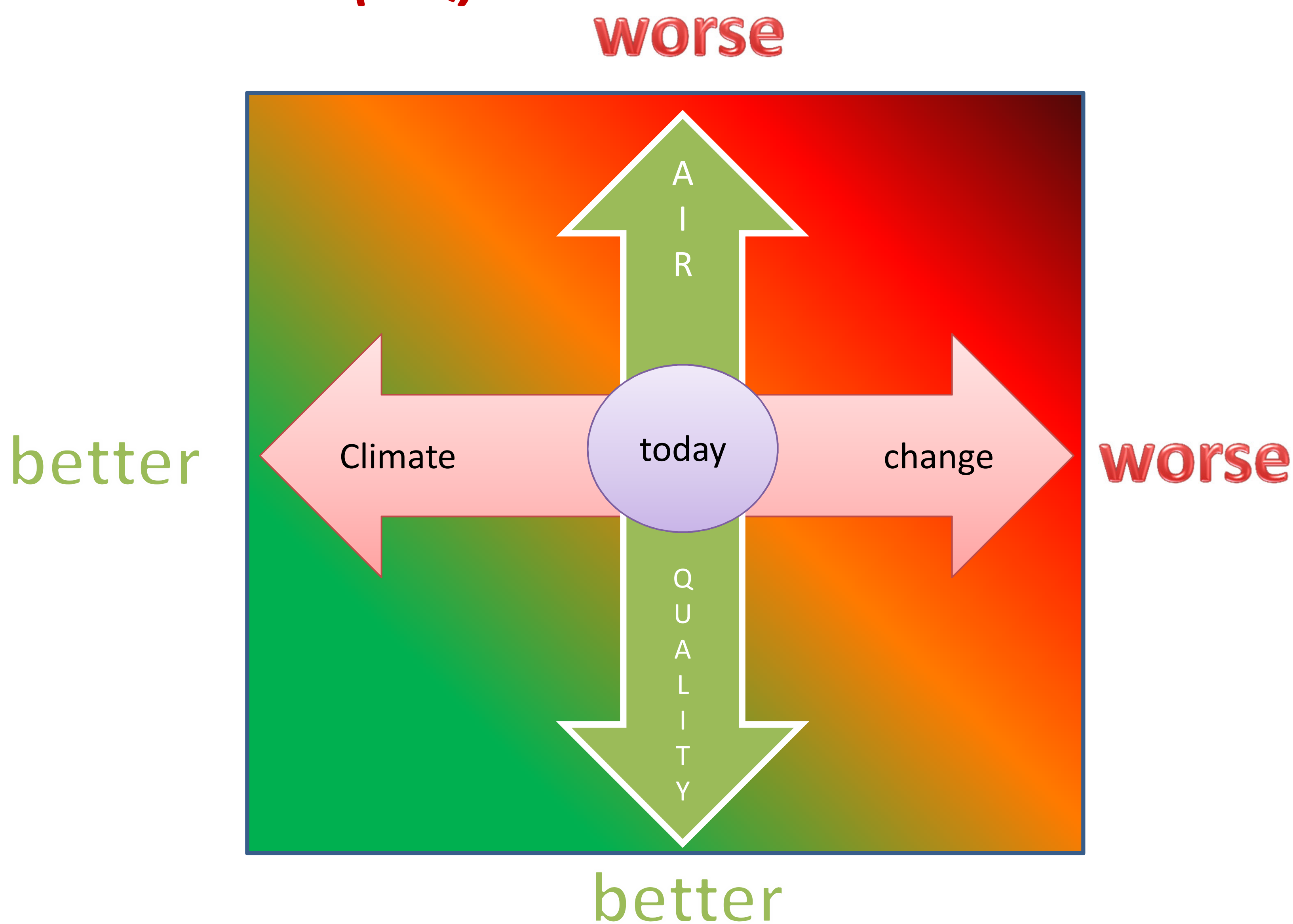


NMVOC Oxidation, Ozone and SOA Formation: Air pollution-Atmosphere Feedbacks

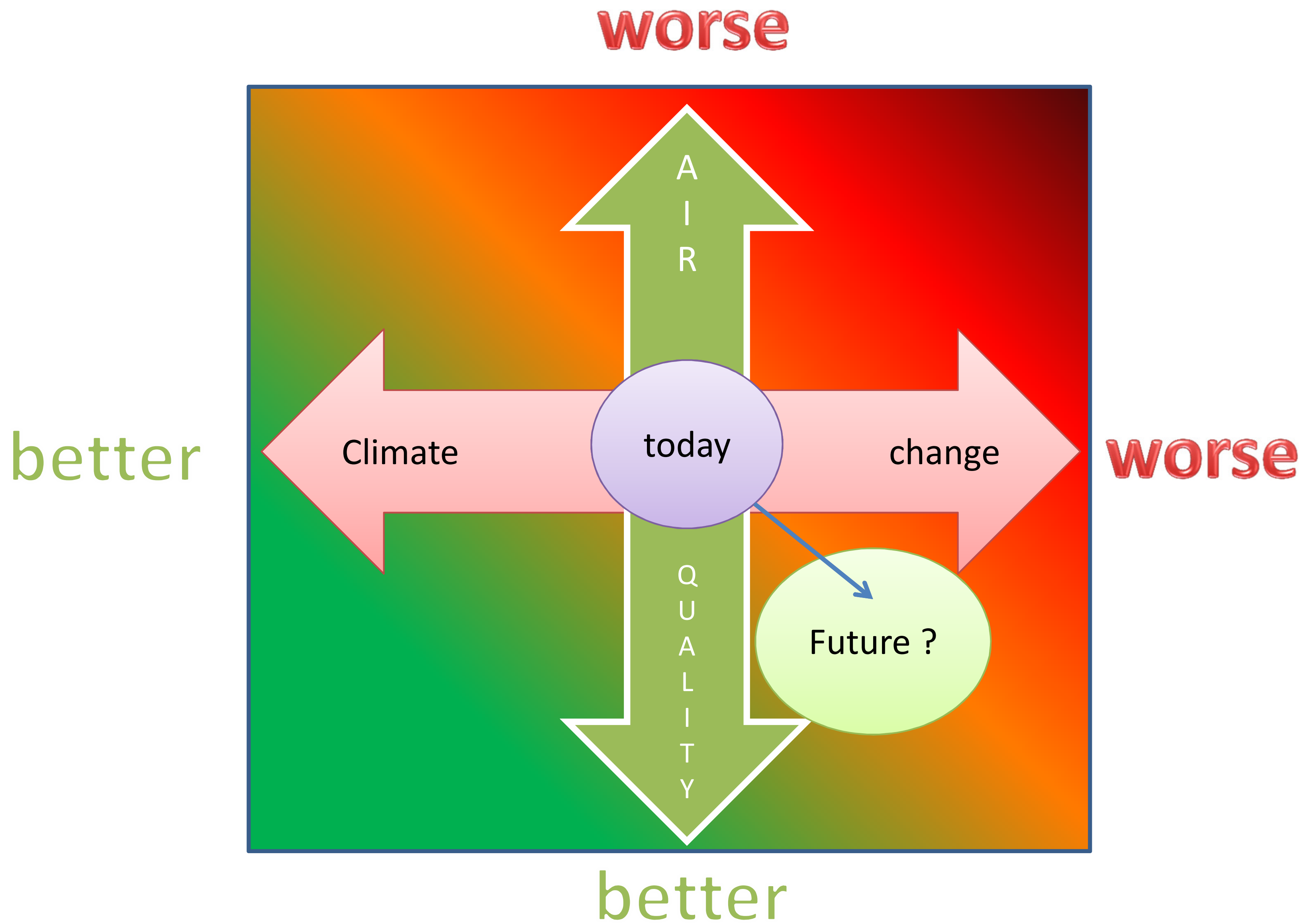
Disturbance of natural cycle due to air pollution from anthropogenic activities



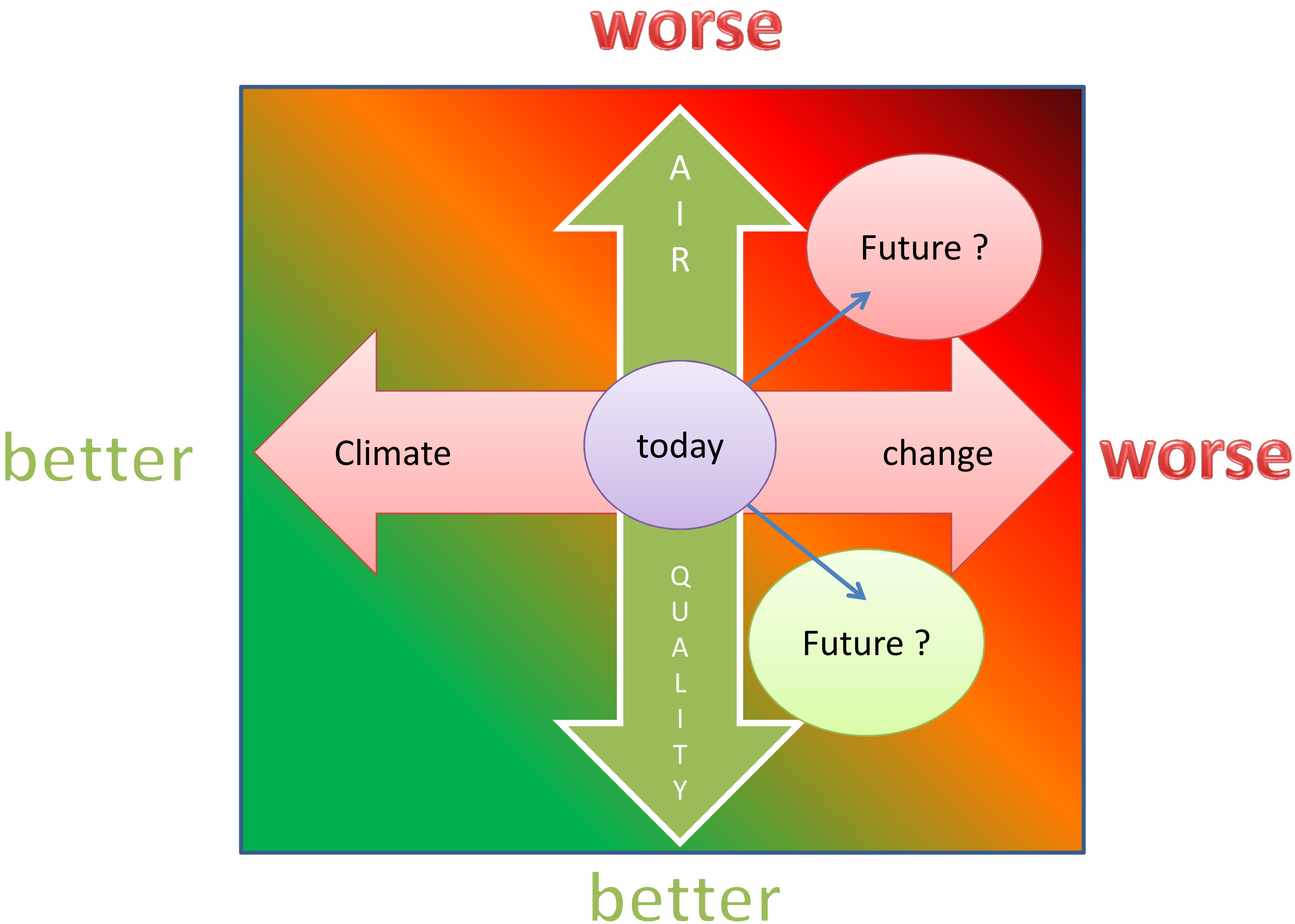
Science to support decisions: Climate vs Air Quality (AQ) – at a cross roads

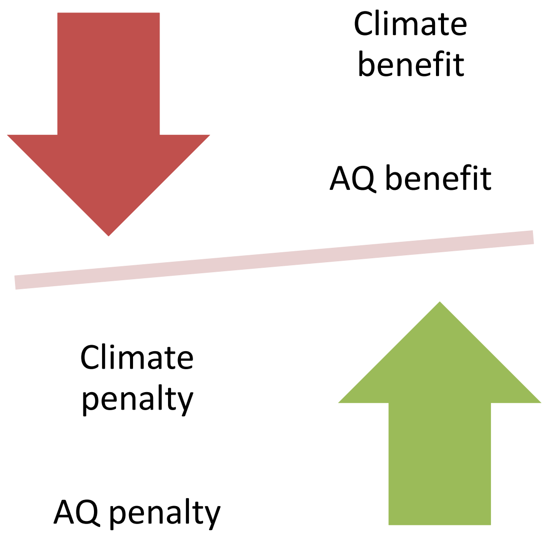


Science to support decisions: Climate vs Air Quality (AQ) – at a cross roads

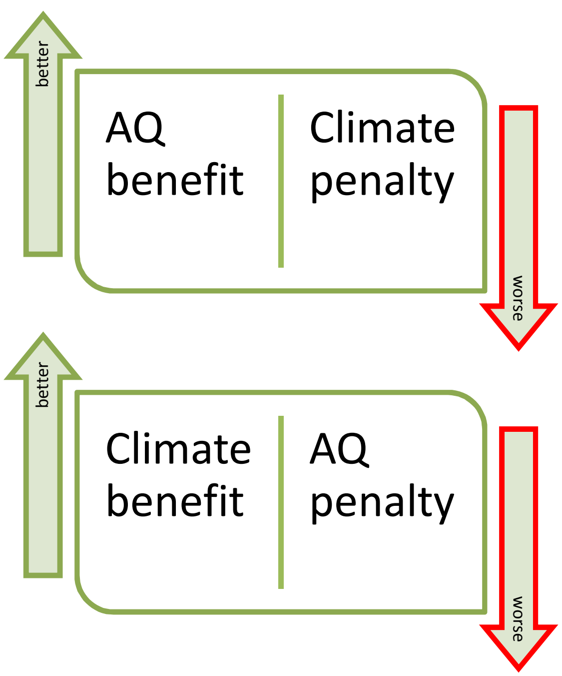


Science to support decisions: Climate vs Air Quality (AQ) – at a cross roads





Win-win: AQ and climate mitigation strategies benefit from each other: an ideal scenario for policy makers



However relationships between AQ and climate can also behave antagonistically

AQ-climate interaction

Climate mitigation exhibits a complex interaction with air quality control measures

As an example the National Academy of Sciences (NAS) recommended in its 2004 report, Air Quality Management in the United States, that air pollution and climate change policies be developed through an integrated approach.

Climate penalty on Air Quality

- ***Rising temperature*** will result in enhanced emissions of biogenic ***NMVOCs*** (volatile organic compounds) -> increase in ozone and SOA

- Longer stagnant periods/heat waves will ***accumulate pollutants***

- Biomass fuels: increase in black carbon and SOA – could also increase in regional NMVOC
- ……

Air Quality penalty on Climate

- Reduction of aerosols
  - Reduction of primary aerosols (other than black carbon)
  - Reduction of anthropogenically enhanced biogenic SOA formation
  - Reduction of SO_2

Summary

- Reducing some short-lived constituents have a strong immediate climate benefit

- AQ-climate interactions can be complex and need to be considered for policy making

- Feedbacks can dampen or enhance response processes in the climate system (e.g. higher temperatures -> higher natural NMVOC emissions - > more SOA -> negative forcing - more cooling?)

- Overall it is expected that AQ will increasingly suffer due to climate change (e.g. longer stagnant periods such as the 2003 heat wave in Europe)
  - This might mandate stricter AQ measures to maintain the current status (Climate penalty on AQ)

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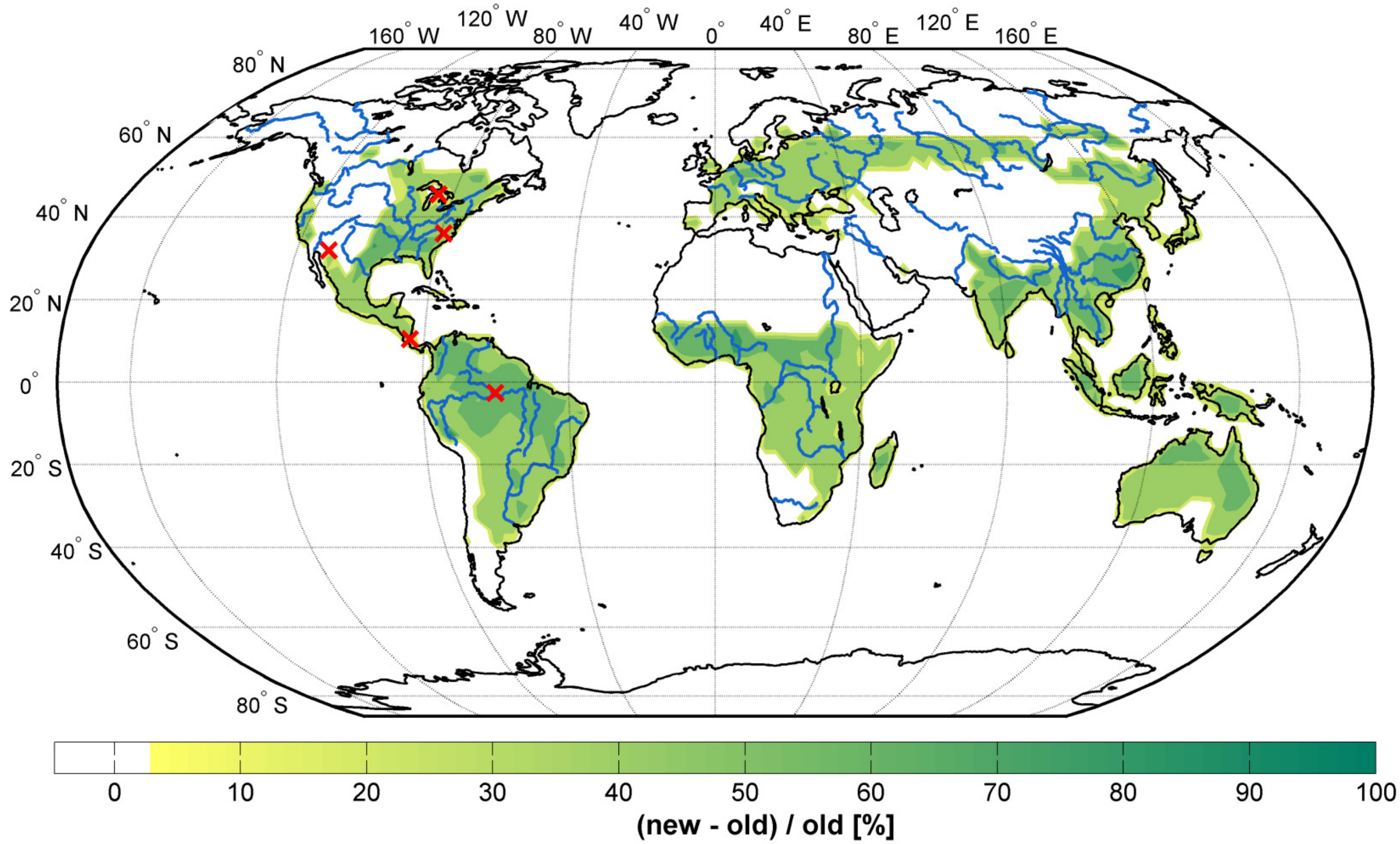
ADDITIONAL SLIDES



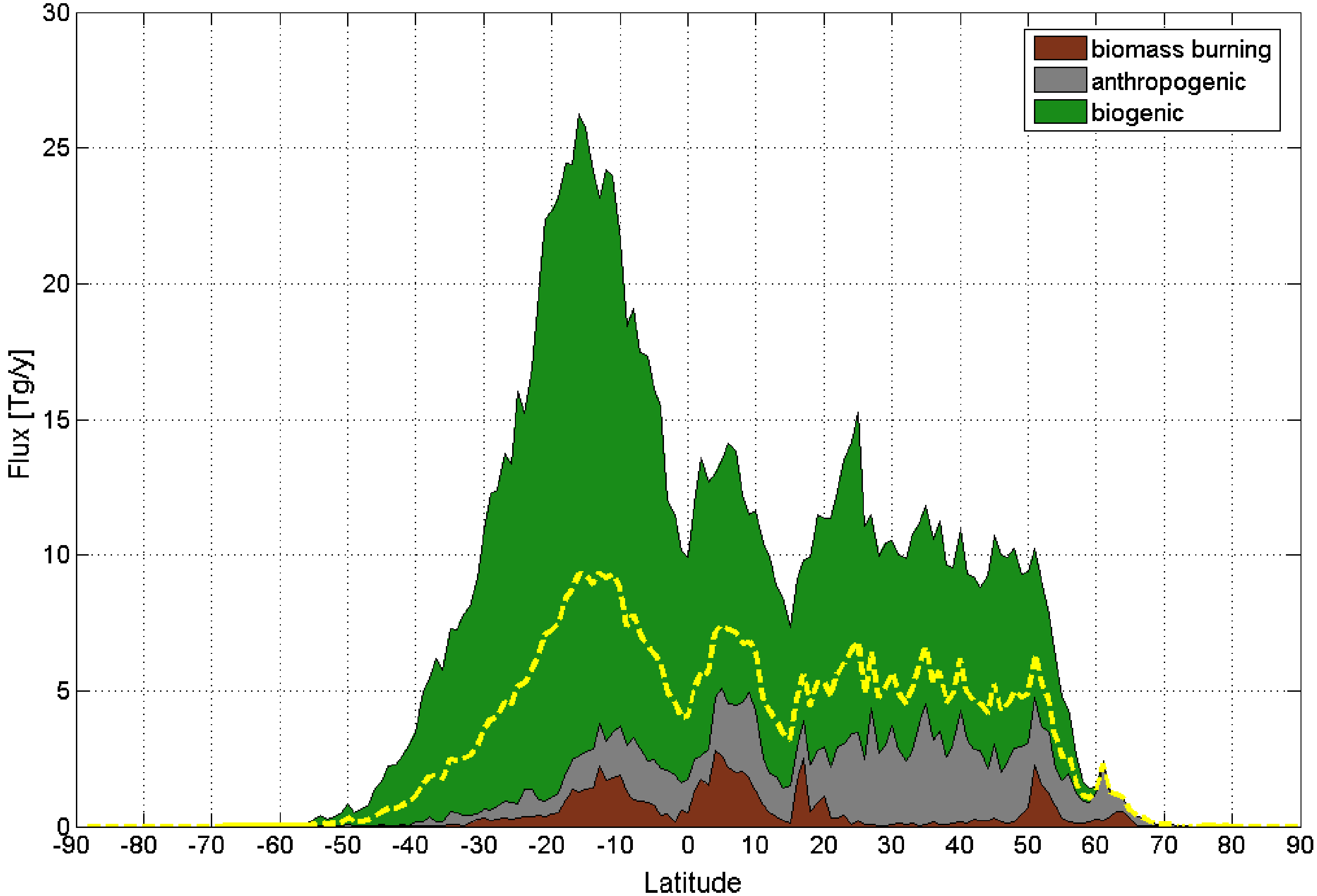
Deposition

	Mean [TgC/a]	Comments
this study	**590±130**	**Dry and wet deposition (vapors)**
Goldstein and Galbally (2007)	200±100	Dry and wet deposition (vapors)
Hallquist et al., 2009	800	Dry and wet deposition (vapors)
Willey et al. (2000)	430±150	Wet deposition (vapors+particles)

Latitudinal Distribution of NMVOCs

Bottom-up (total): 1580 Tg/y
IPCC2001, 2007: 450 Tg/y

Compare to CH_4: about 500-600 Tg/y
Isoprene: about 500-700 Tg/y



GFEDv2, 2000 x2, EDGAR 2000; Guenther et al., 1995, 2007

Biogenically enhanced secondary organic aerosol formation?

Some studies suggest (e.g. Jacobson, JGR, 2010) that a reduction of methane and black carbon aerosol might be an effective short-term climate mitigation strategy. This would be an example of a *win – win situation* (air quality and climate benefit).

AQ-climate interaction

- Changes in NO_y (***loose?-win?***)
  - increases in reactive nitrogen leads to increases in ozone (***climate penalty/AQ penalty***) and increases in the oxidation capacity of the atmosphere (via primary OH production and NO_x recycling) (***climate benefit/AQ impact ? – (AQ penalty if it leads to more SOA)***) – this in turn would lead to a decrease in atmospheric lifetimes of reactive climate active gases (methane, HFC) (***climate benefit/AQ benefit***)

  - increase in scattering aerosols (enhanced SOA formation) (***climate benefit/AQ penalty***)

Reduction of aerosols

Aerosols are predominantly thought to exhibit a negative forcing on climate (exception black soot – positive forcing)

Win-loose: cleaning the air from aerosols can have a climate penalty, but result in an air quality benefit

Win-Win (black soot, methane): reduction in black carbon and methane (air quality and climate benefit).