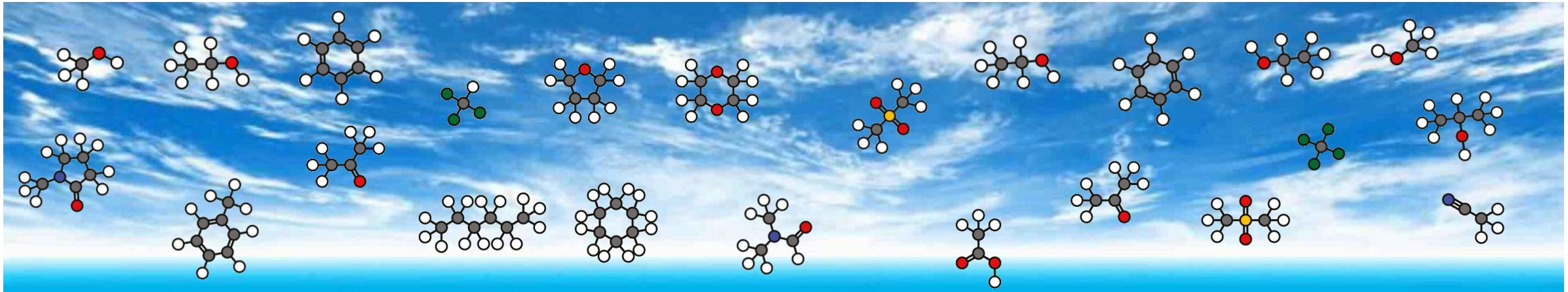


Trace gases in the Earth's system

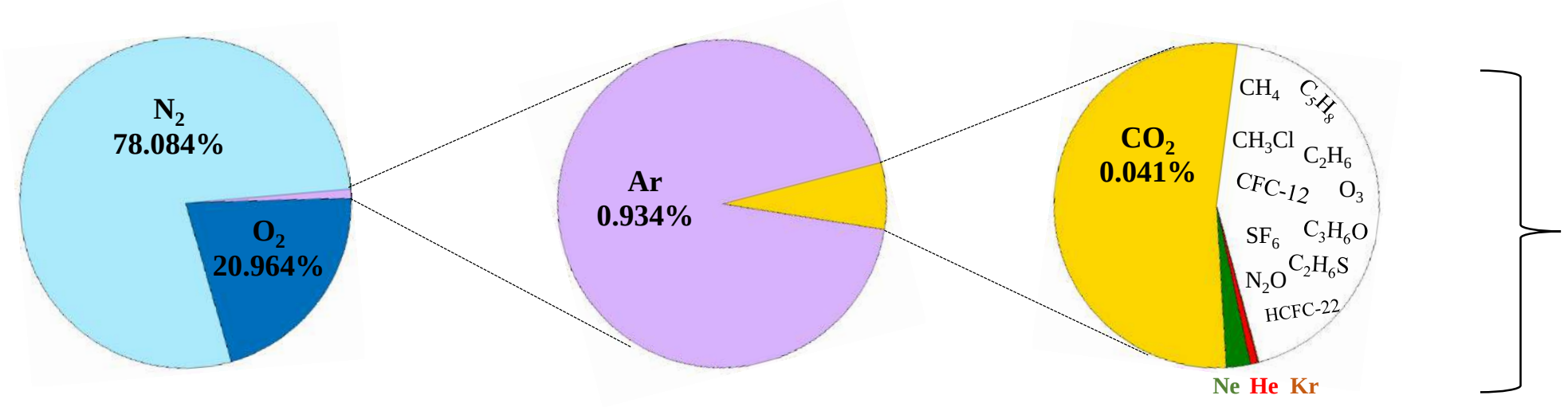
Efstratios Bourtsoukidis

The Cyprus Institute

2 November 2022

EMME-CARE
EASTERN MEDITERRANEAN MIDDLE EAST – CLIMATE & ATMOSPHERE RESEARCH CENTRE

Atmospheric composition



Trace gases

- 99.9% of the atmosphere is chemically inert

- The remaining atmospheric gases are termed as "trace gases" with very small atmospheric mixing ratios: ppm – ppq (0. 0001% - 0.000000001%)

- Trace gases are not chemically inert. They react with atmospheric radicals such as OH, O_3, NO_3… (Free radicals are highly reactive atoms that have one unpaired electron)

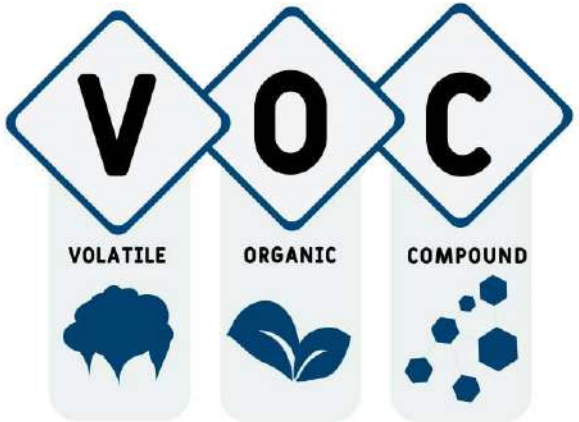
What are the Volatile Organic Compounds?

- Trace gases with very small concentrations and high reactivity: ppb – ppq (0.0000001% - 0.000000001%)

Volatile : Vapor pressure > 0.27 kPa at 20°C.
Organic : Carbon containing
Compound : Stable entity, distinct from radicals

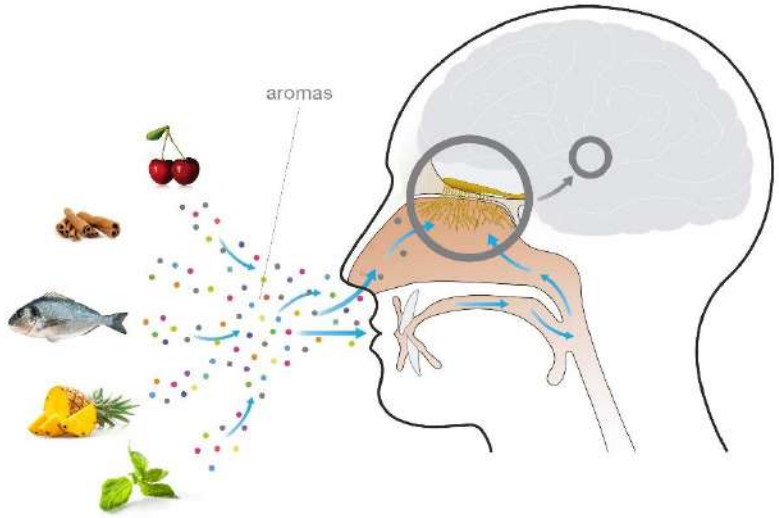
NMHC : Non Methane Hydrocarbons
OVOC : Oxygenated Volatile Organic Compounds
SVOC : Semi-volatile Organic Compounds

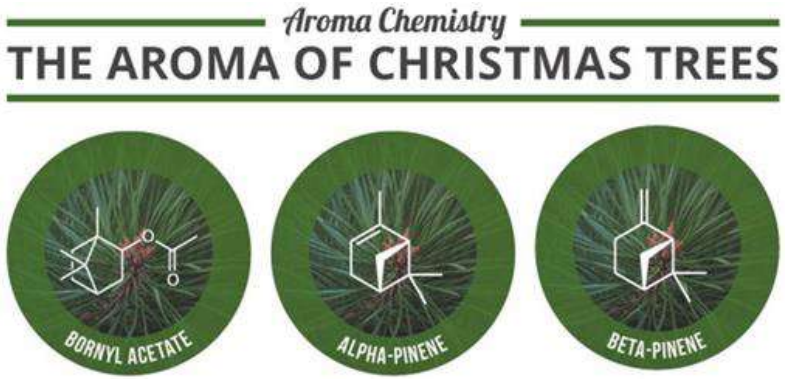
> 10000 compounds

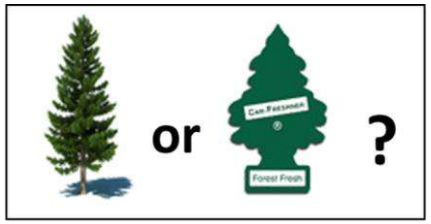


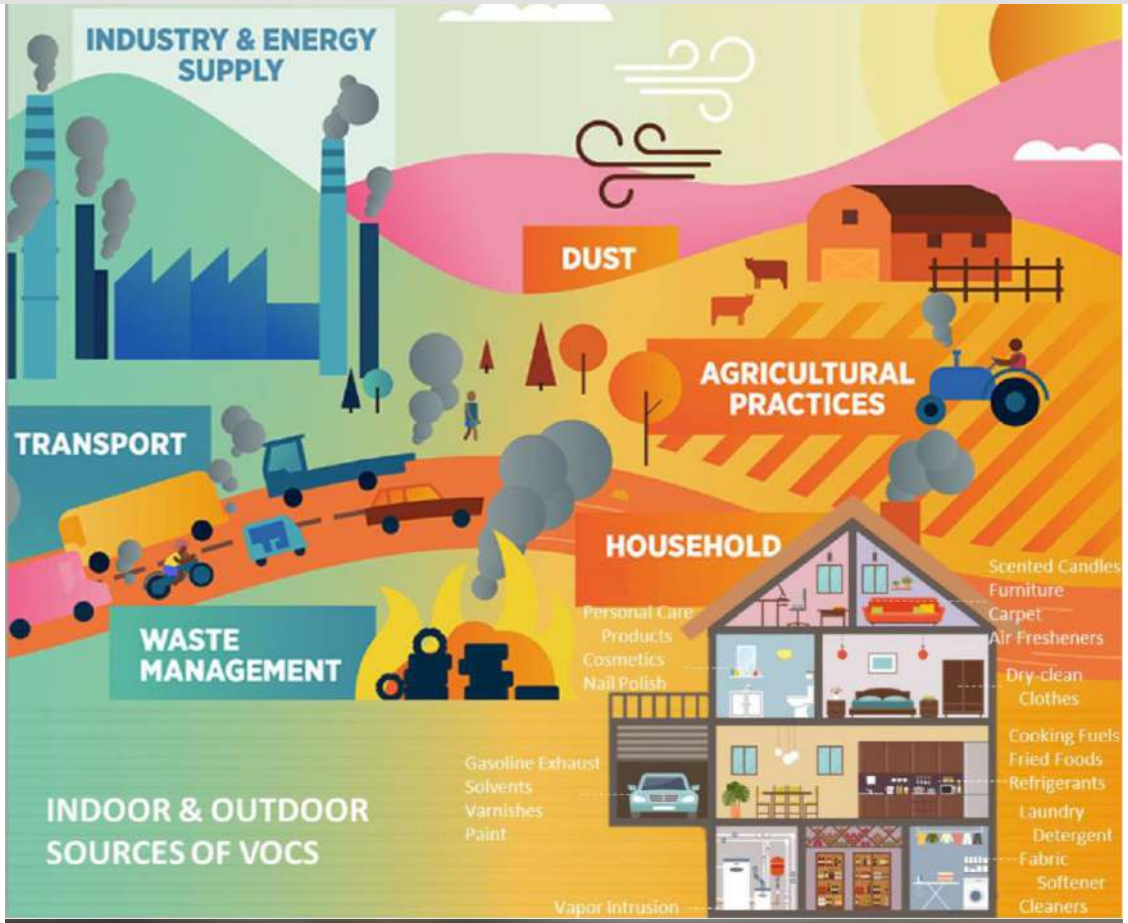
- *This excludes the big 3:*
  1. $CO_2 \approx 410\ ppm$
  2. $CH_4 \approx 1.8\ ppm$
  3. $CO \approx 0.1\ ppm$

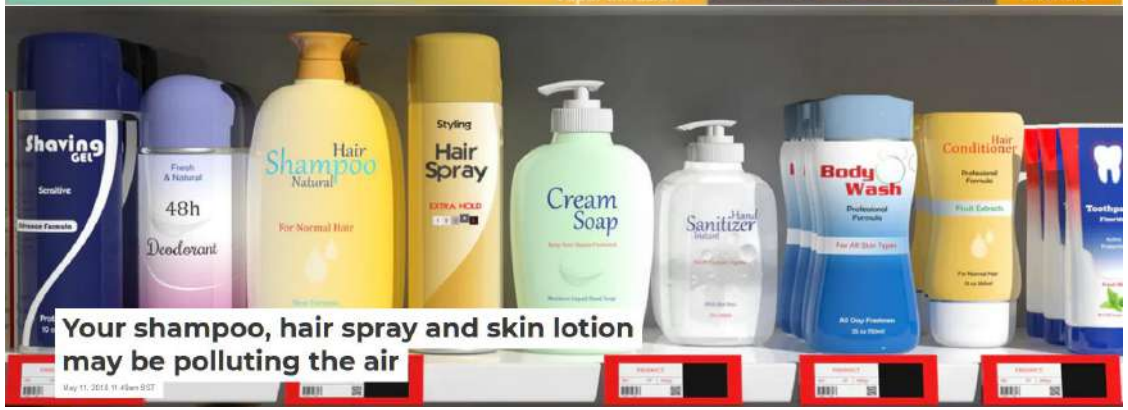
Something to relate…



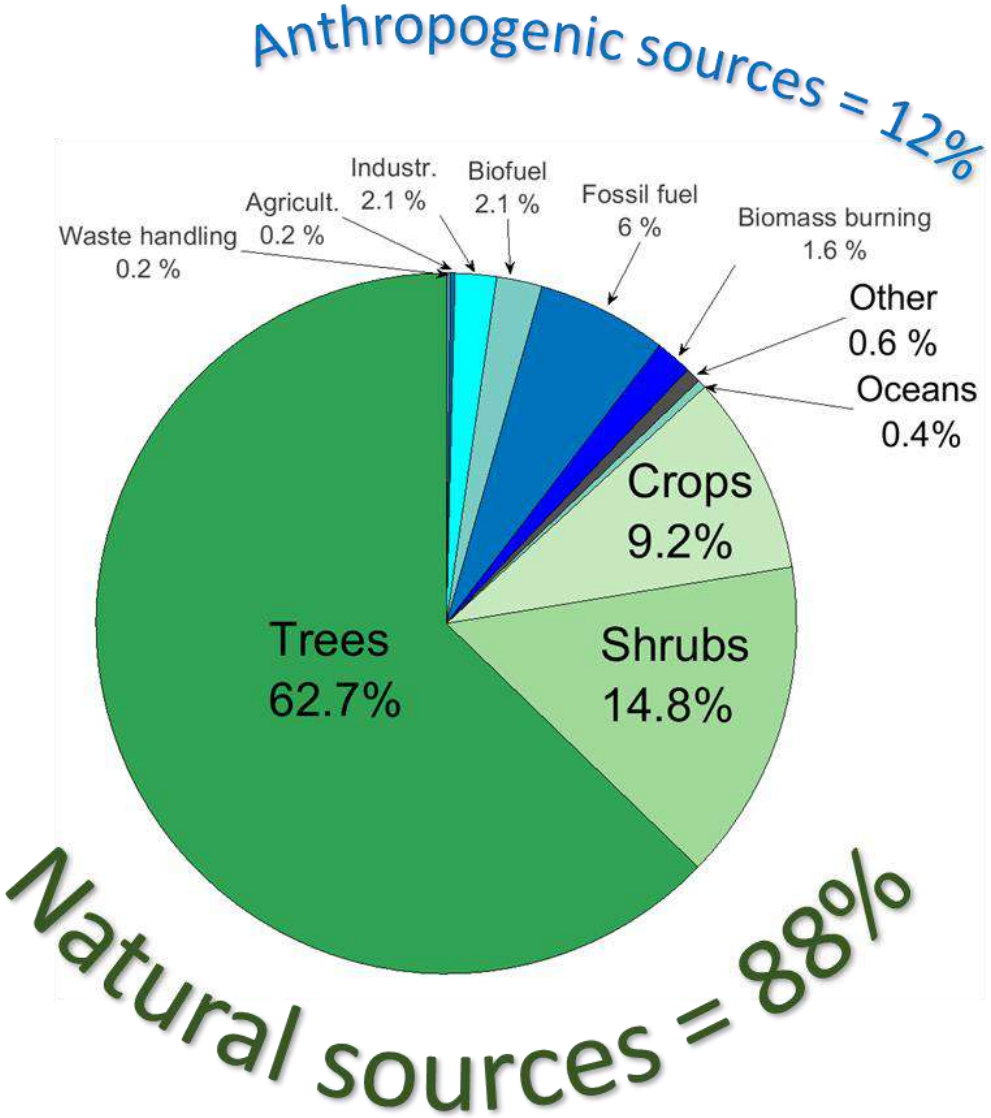




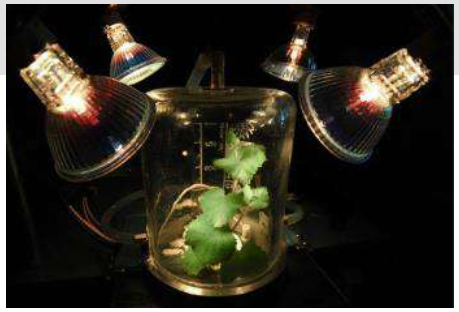




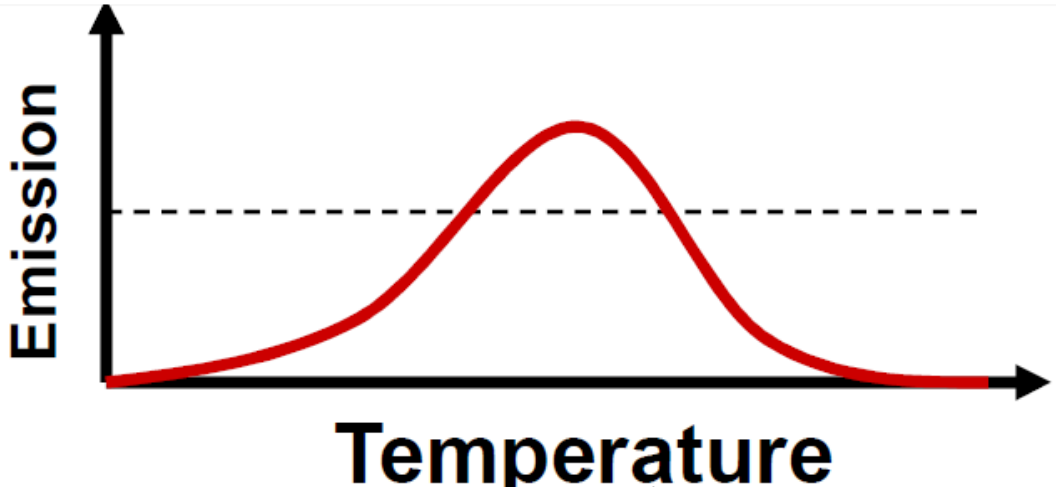
VOC sources

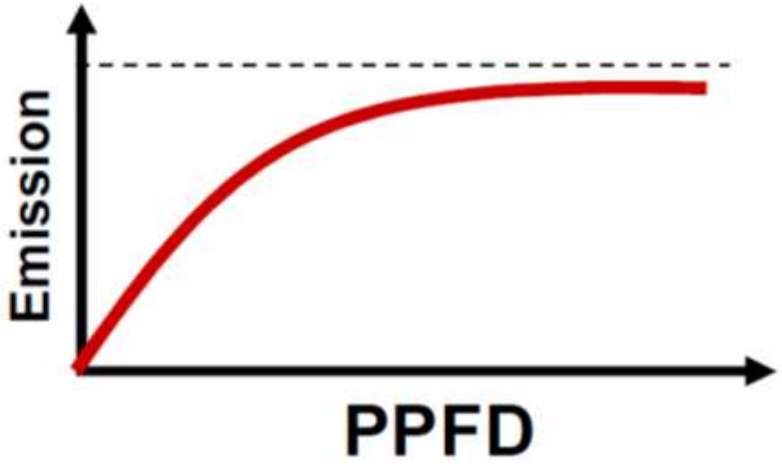

Anthropogenic sources = 12%
Industr. 2.1 %
Biofuel 2.1 %
Agricult. 0.2 %
Fossil fuel 6 %
Waste handling 0.2 %
Biomass burning 1.6 %
Other 0.6 %
Oceans 0.4%
Crops 9.2%
Trees 62.7%
Shrubs 14.8%
Natural sources = 88%

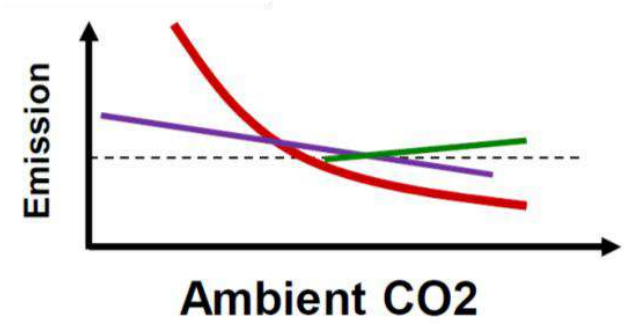
Biogenic VOC sources

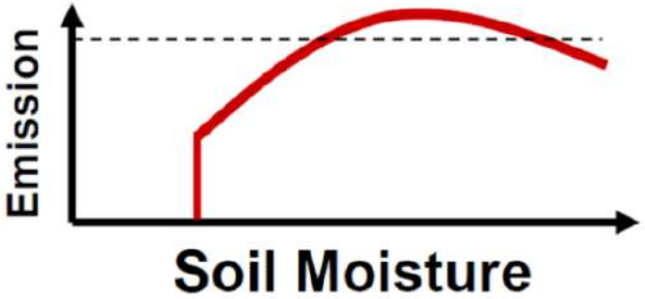


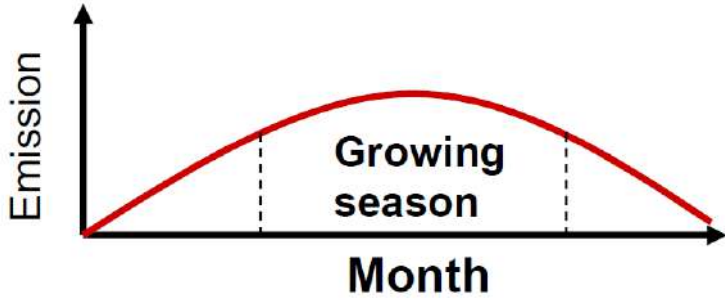
$$\gamma = C_{CE}\ LAI\ \gamma_T\ \gamma_P\ \gamma_A\ \gamma_{SM}\ \gamma_C$$





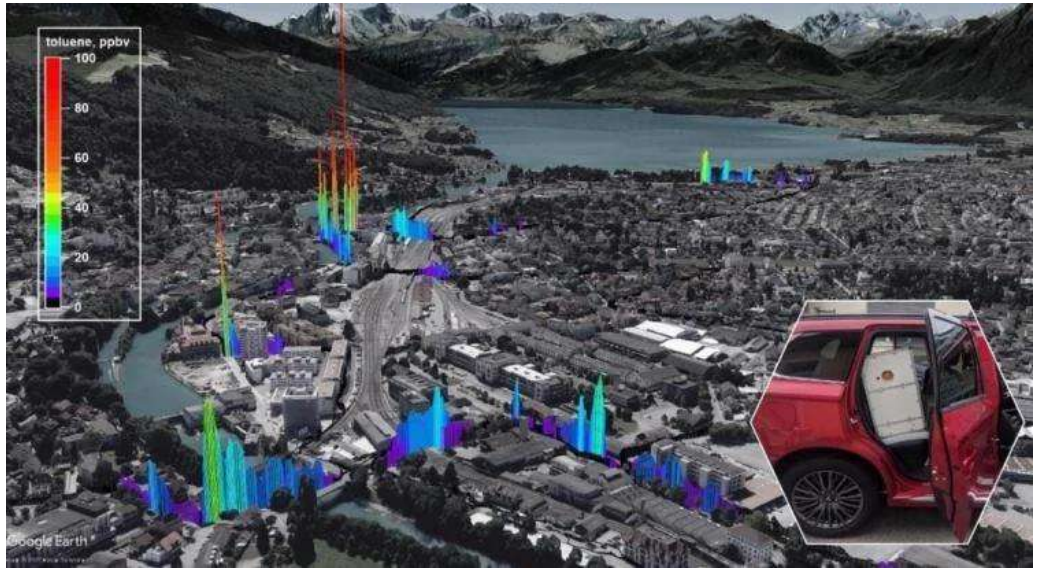




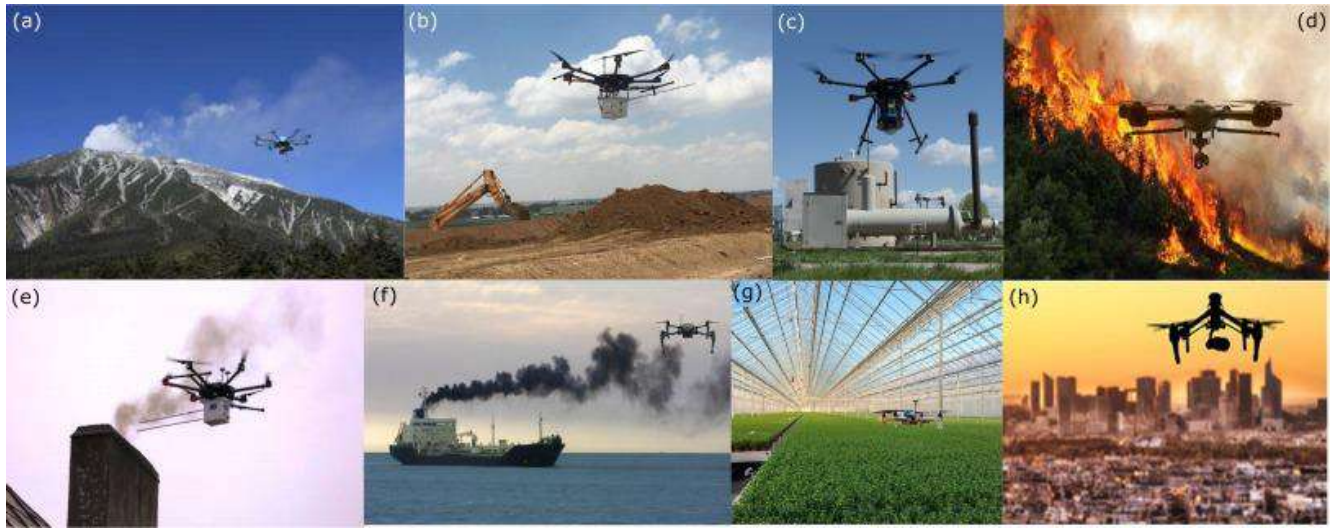


Courtesy: A. Guenther

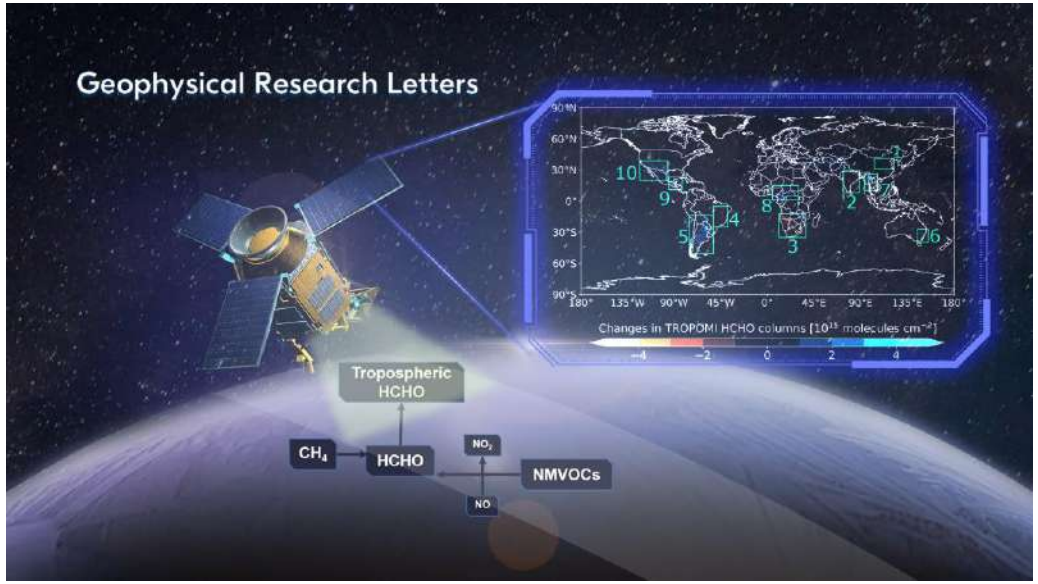
Anthropogenic VOC sources



Credit: TOFWERK

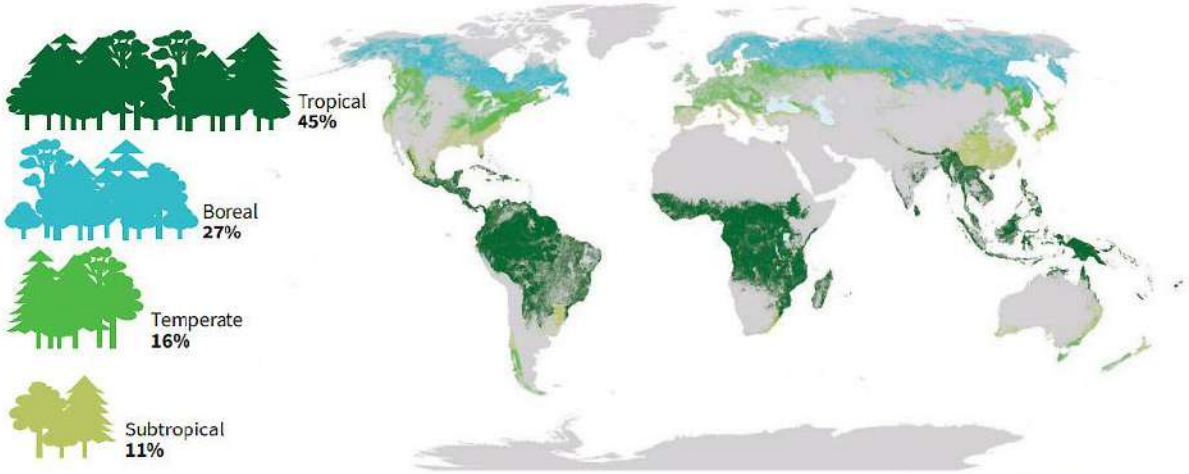


Burgues & Marco, STOTEN, 2020

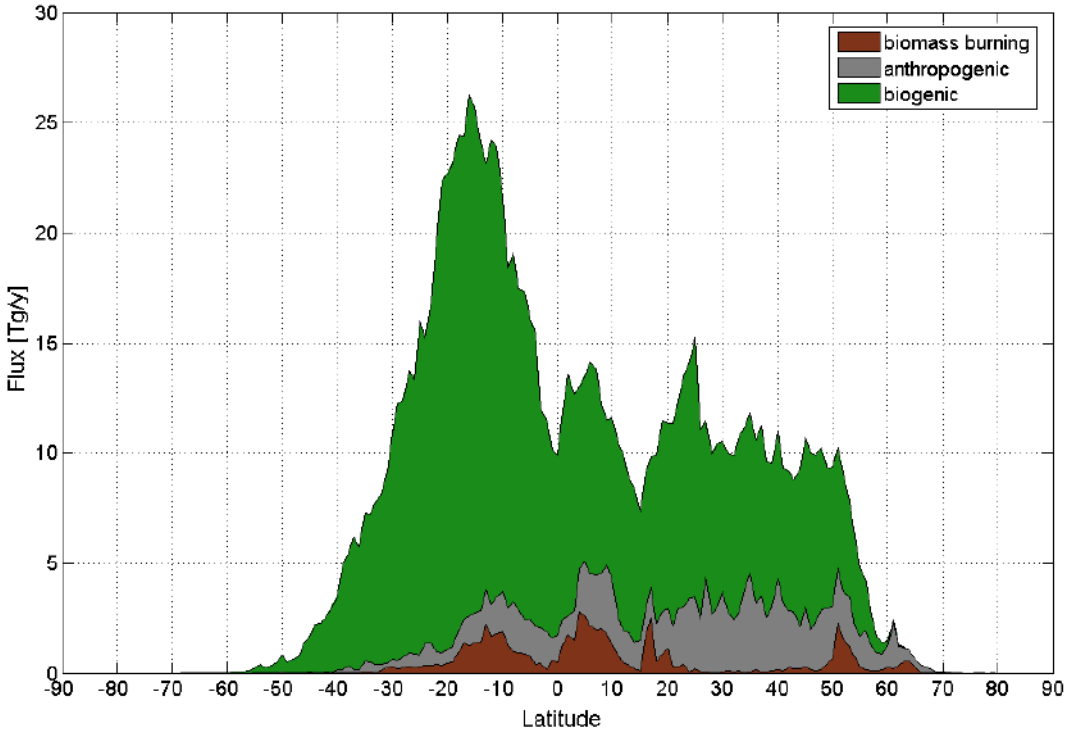


Sun et al., GRL, 2021

Spatial distribution of VOC sources



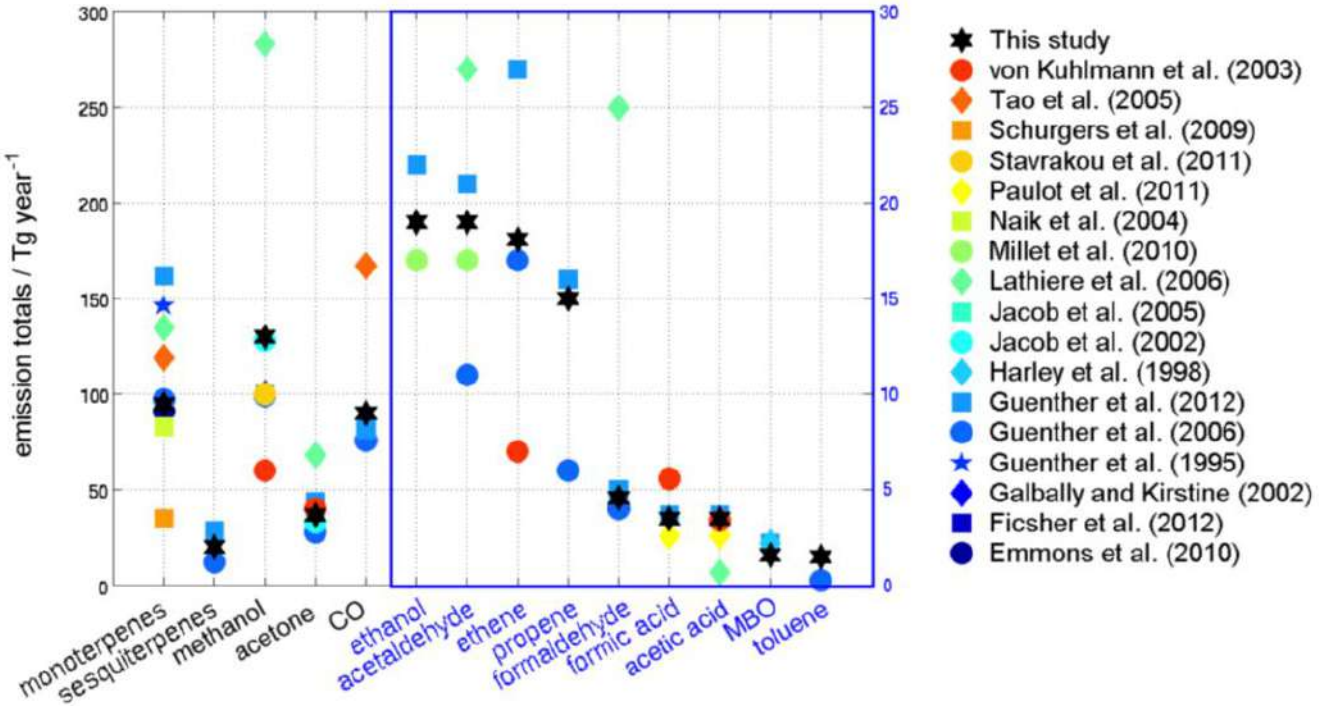
Source: Adapted from United Nations World map, 2020.



Emission uncertainties

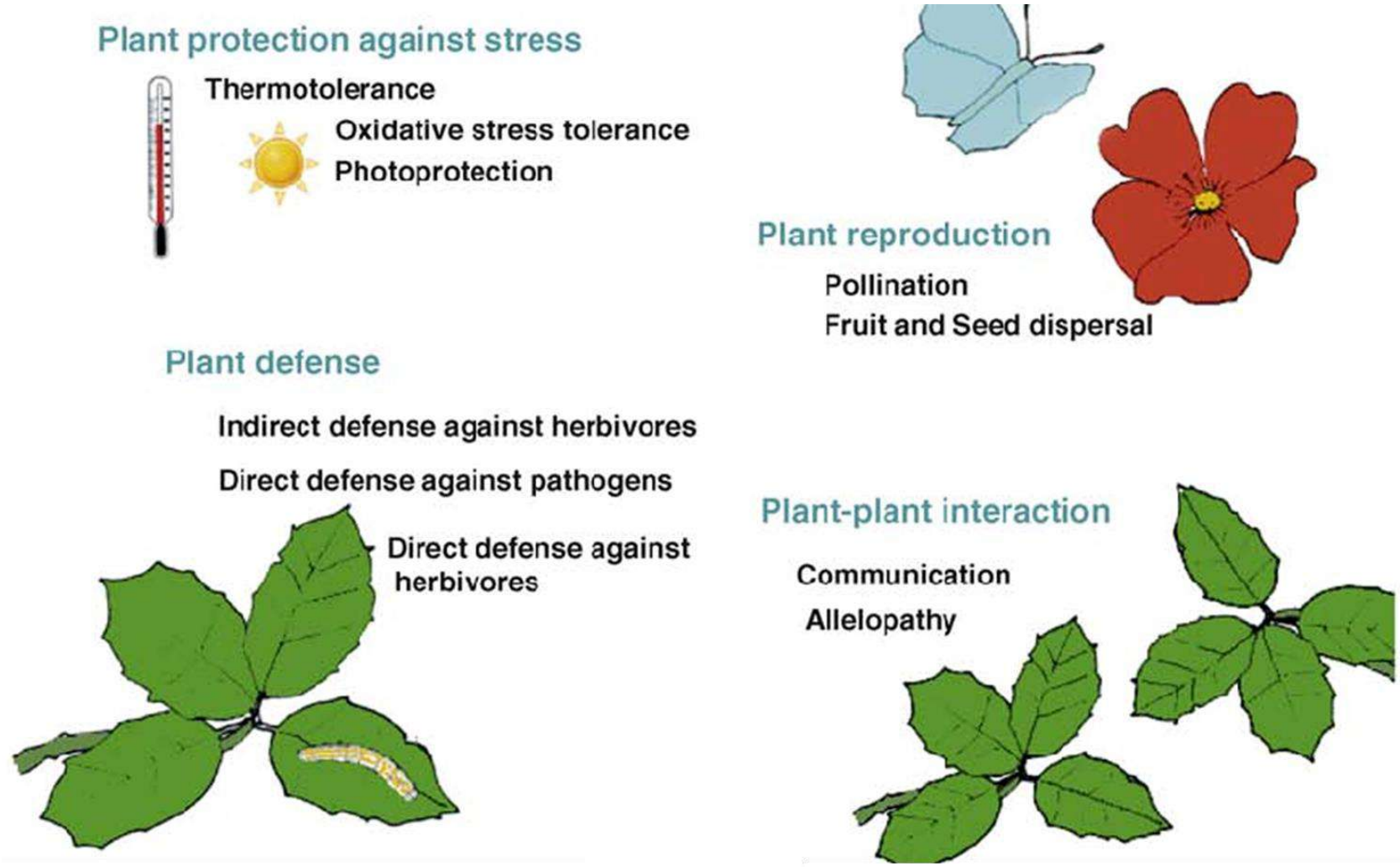
	Emission rate	Uncertainty range
Fossil fuel use		
Alkanes	28	15–60
Alkenes	12	5–25
Aromatic compounds	20	10–30
Biomass burning		
Alkanes	15	7–30
Alkenes	20	10–30
Aromatic compounds	5	2–10
Terrestrial plants		
Isoprene	460	200–1 800
Sum of monoterpenes	140	50–400
Sum of other VOC	580	150–2 400
Oceans		
Alkanes	1	0–2
Alkenes	6	3–12
Sum of anthropogenic and oceanic emissions		
Alkanes	44	
Alkenes	38	
Aromatic compounds	25	
Terrestrial plants	1 180	
Total	1 287	

Koppmann et al., 2007



Sinderalova et al., 2014

VOC importance : Ecology and Biology

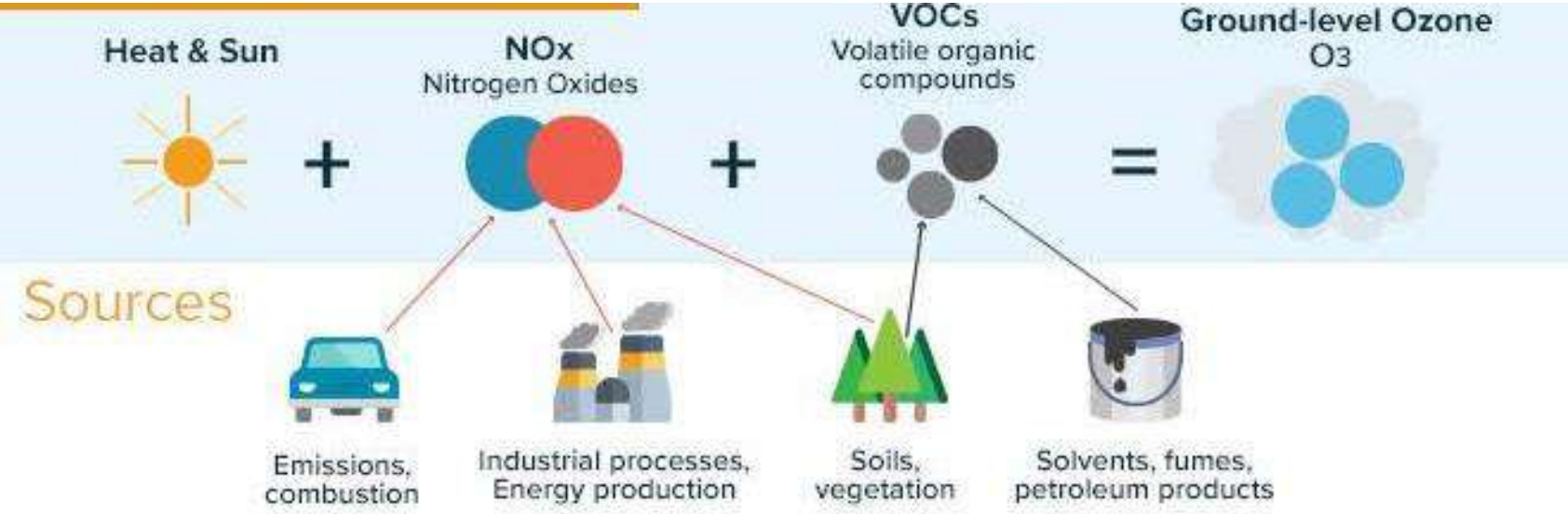


Penuelas and Staudt, 2010

- Biogenic VOCs : The doctor, arsenal and language of ecosystems

VOC importance: Ozone (O_3) formation

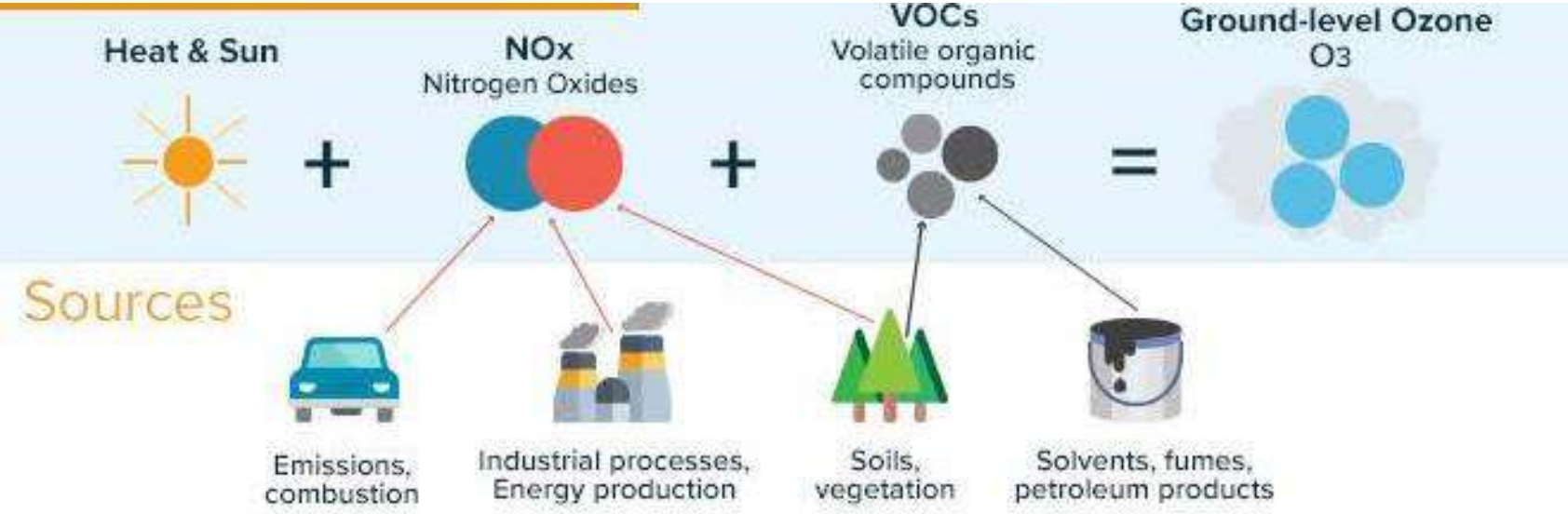
Photochemical smog

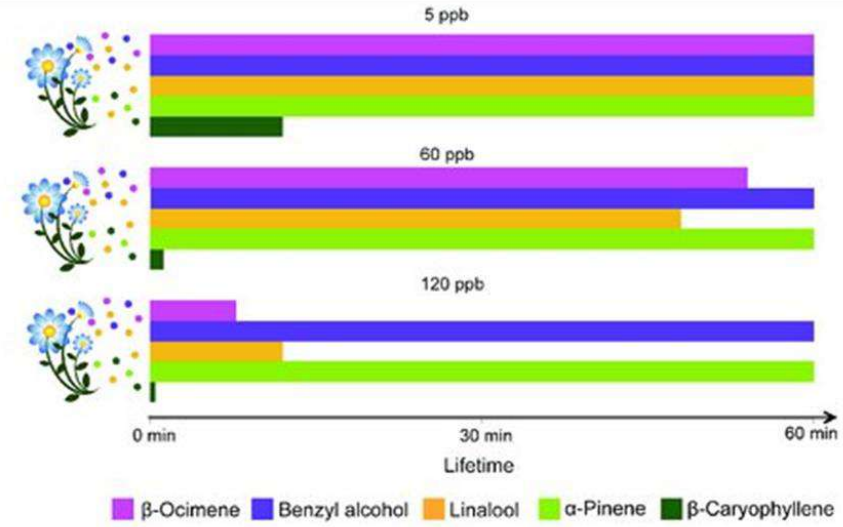


- Leads to poor air quality for human health
- Reduces forests growth and habitat quality
- Reduces species diversity
- Ozone negatively impacts vegetation

VOC importance: Ozone (O_3) formation

Photochemical smog





- Leads to poor air quality for human health
- Reduces forests growth and habitat quality
- Reduces species diversity
- Ozone negatively impacts vegetation
- Disturbs ecosystem signals between plants and insects

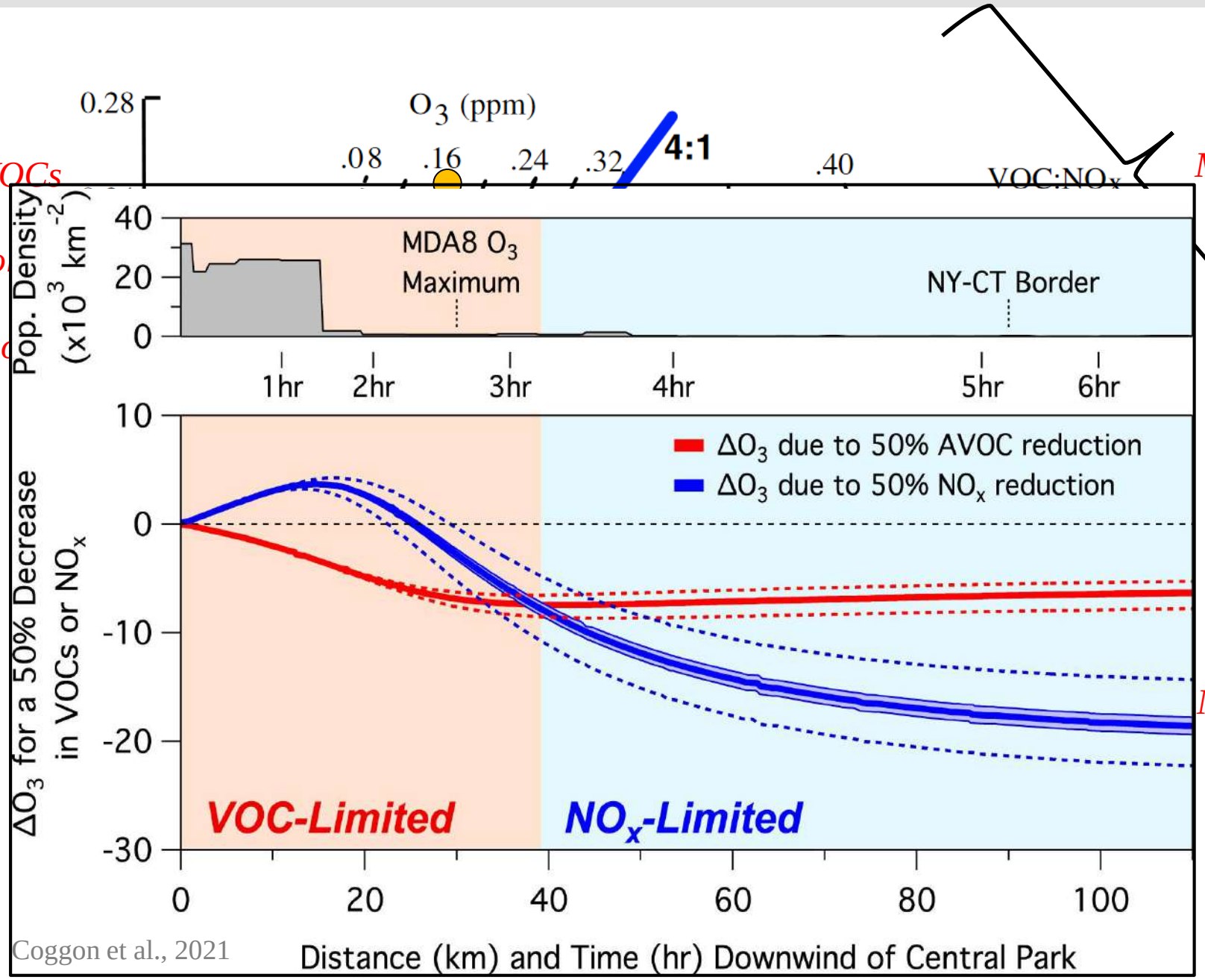
Renu et al., Front. Physiol., 2019

A more complex relationship

Little oxidation of VOCs
=
Counterproductive po
&
Long-range transpo

The spine

Maximum ozone formation
=
Not a nice place to be



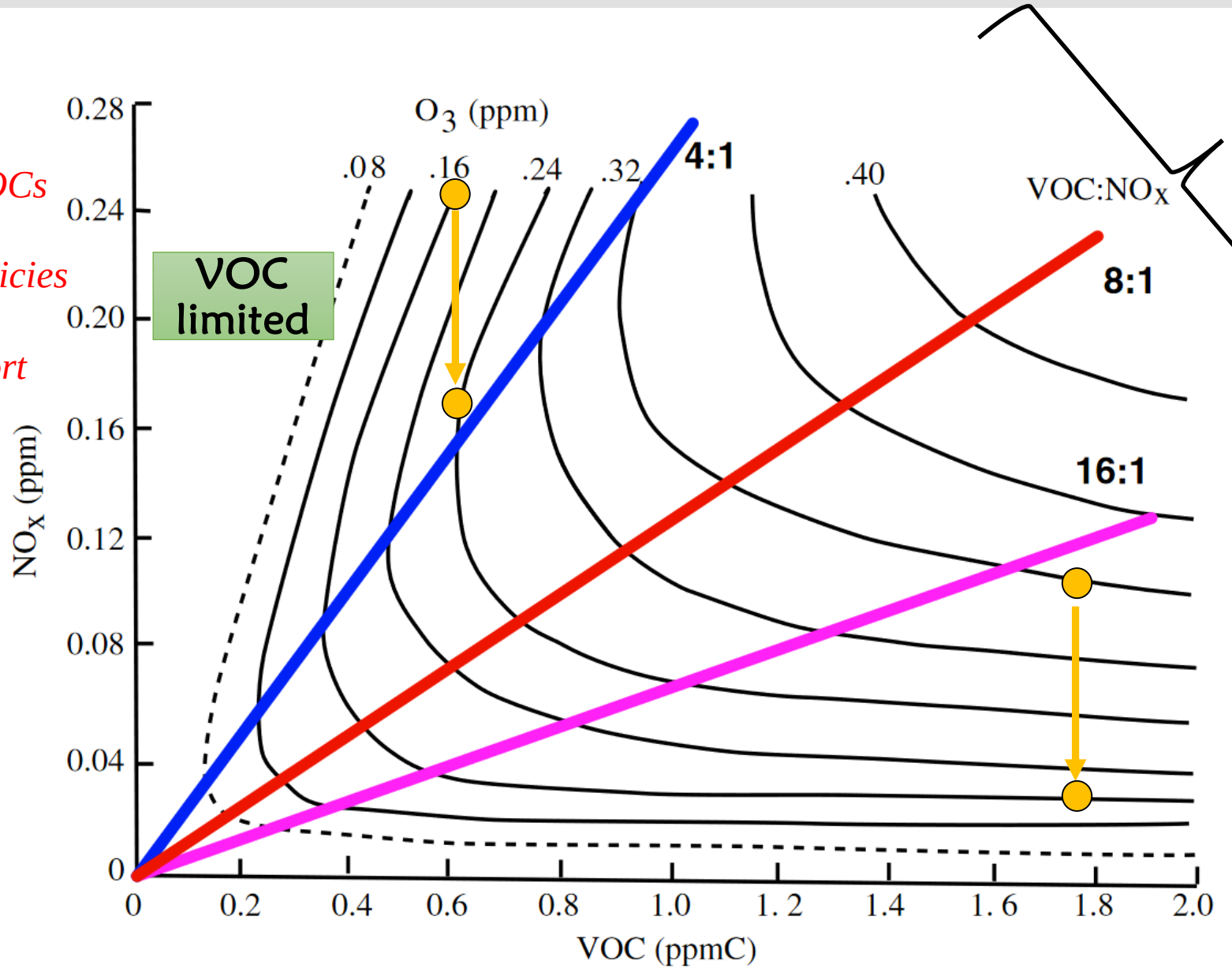
Coggon et al., 2021

NOx limited

NOx reduction is effective

A more complex relationship

Little oxidation of VOCs
=
Counterproductive policies
&
Long-range transport



The spine

Maximum ozone formation
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NOx limited

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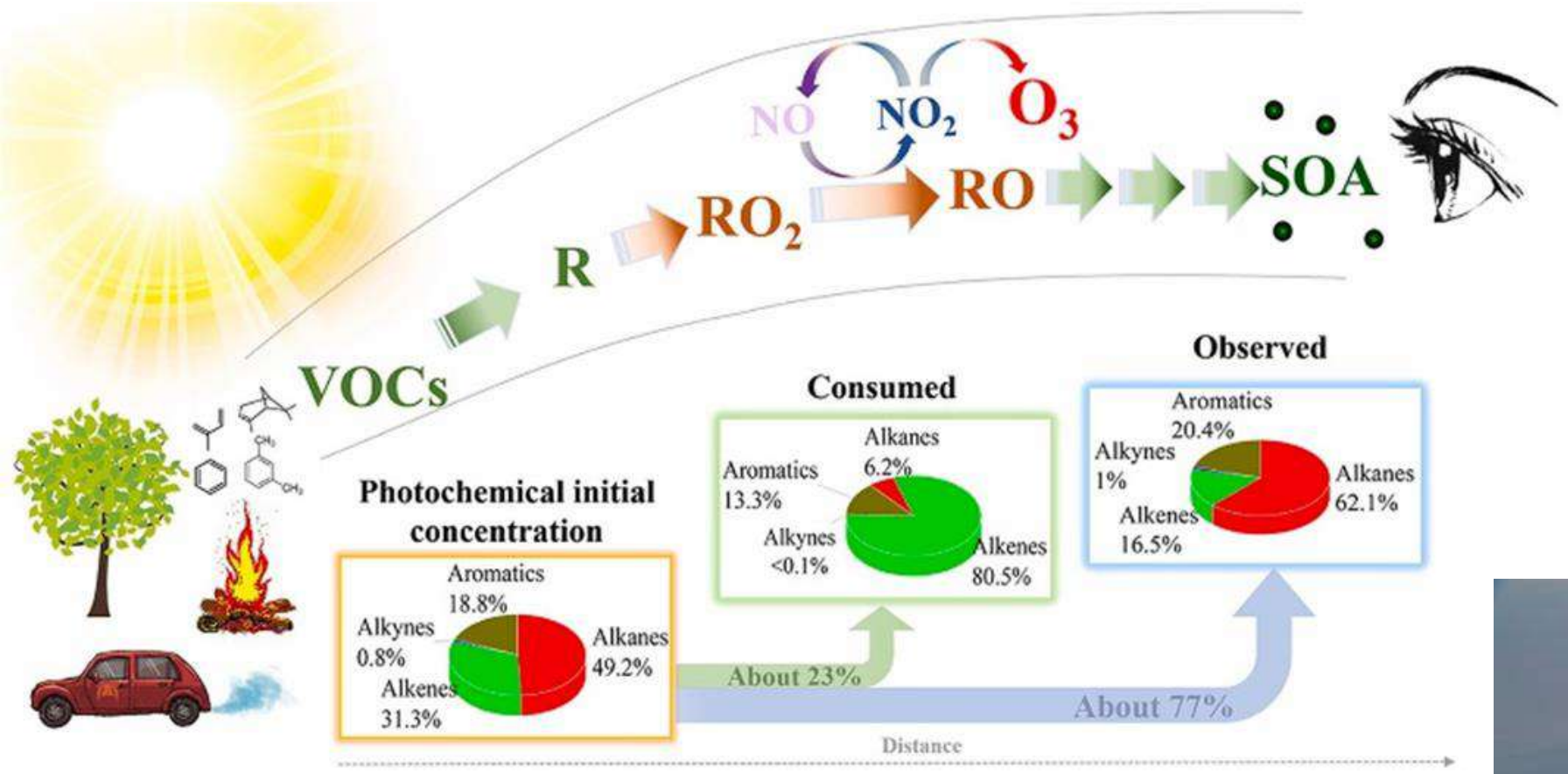
Coggon et al., 2021

Donahiue, Green Chem., 2018

VOC importance : Atmospheric Physics

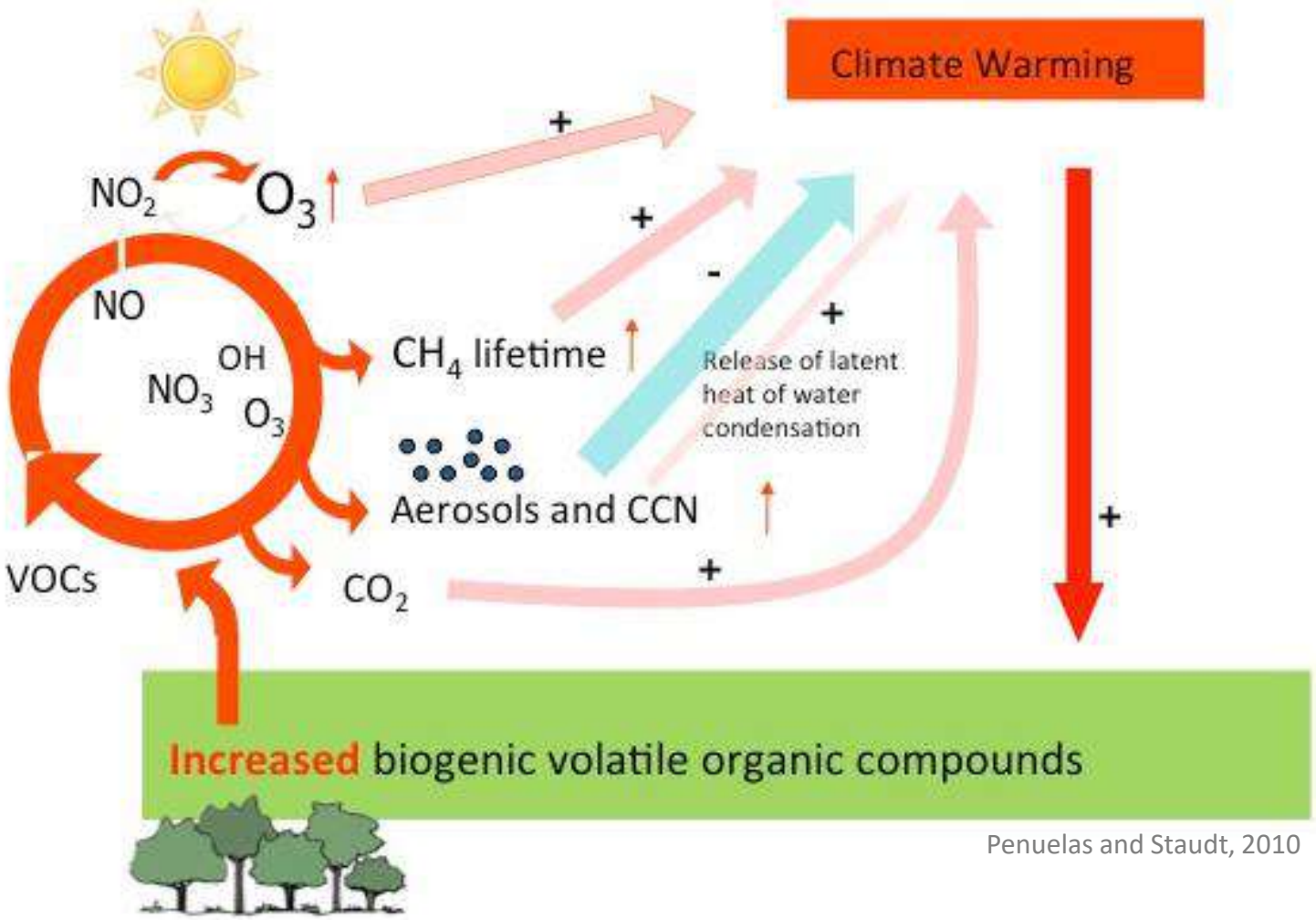


Zhan et al., Environ.Pol., 2021

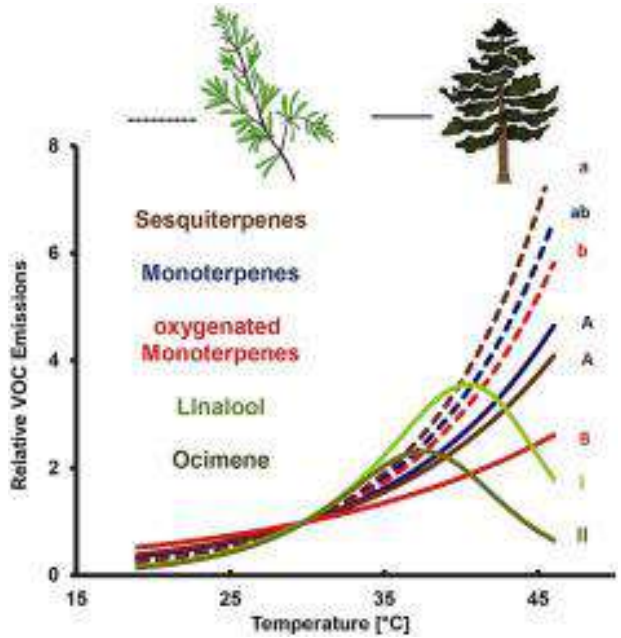
- VOC oxidation products contribute to the growth of Secondary Organic Aerosols
  - Alter cloud properties and precipitation patterns
  - Have an indirect radiation effect
  - Offer beautiful views (‘‘blue haze’’)

Mt. Troodos (credit: Ya Tshey)

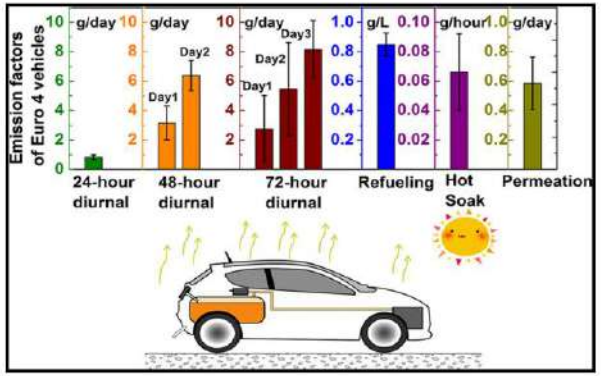
The ‘big picture’



Penuelas and Staudt, 2010



Staudt et al., 2010



Liu et al., 2015

Increased anthropogenic volatile organic compounds

The datasets

NMHC data (CAO-INEIA, CAO-NIC):

- Alkanes (ethane, propane, butanes, pentanes)
- Alkenes (ethene, 1-butane)
- Aromatics (benzene, toluene, xylenes)

VOC data (CAO-AMX, CAO-INEIA):

- Terpenes(isoprene, monoterpenes, sesquiterpenes)
- Aromatics (benzene, toluene, xylenes, naphtalene)
- oxVOC (Methanol, acetone, acetaldehyde, MVK, furan…)
- Acids(formic acid, acetic acid, fulminic acid)
- Nitrogen containing (acetonitrile)
- Sulfur containing (DMS, DMDS)

Trace gases (all stations):

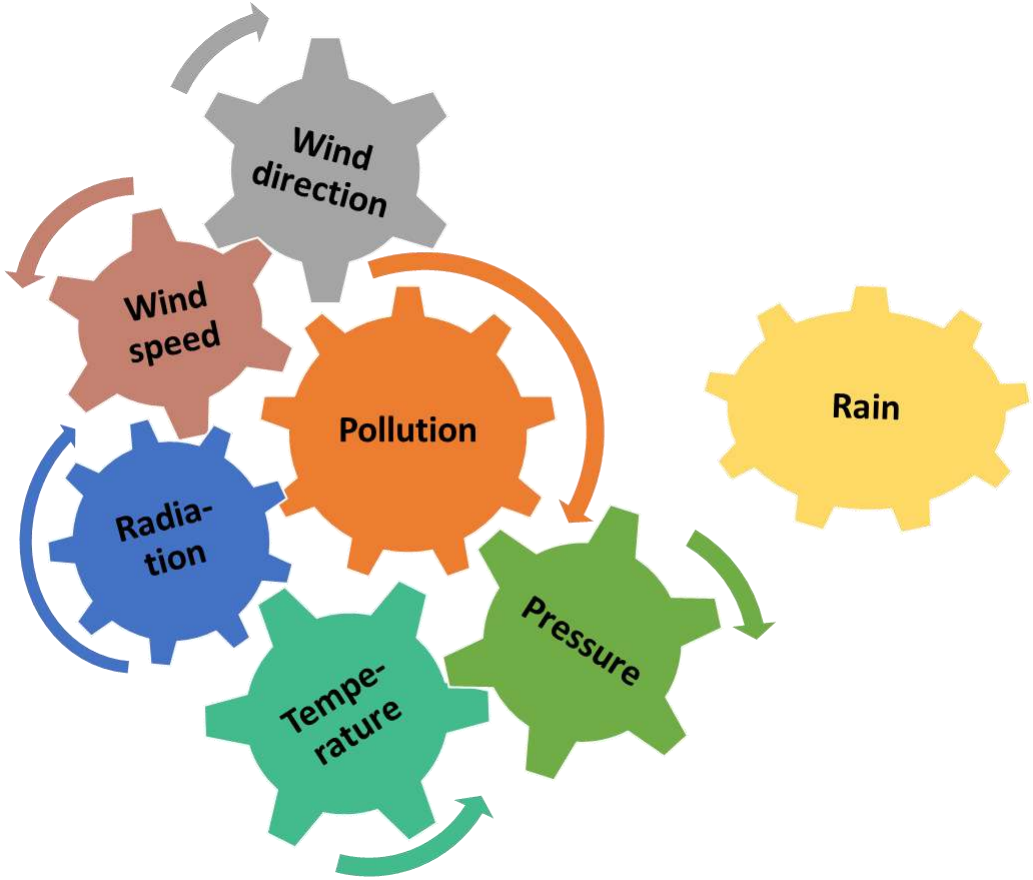
- O_3, NOx, CO, SO_2

GHGs (all stations):

- CO_2, CH_4

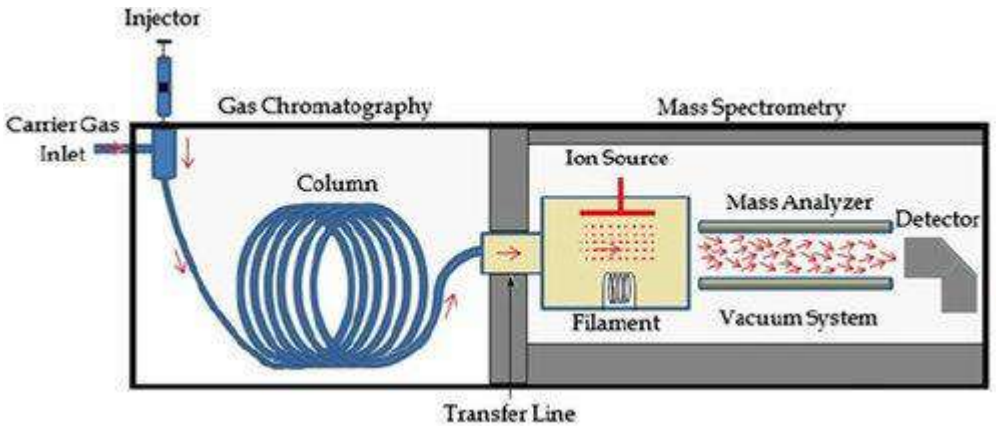
Weather data:

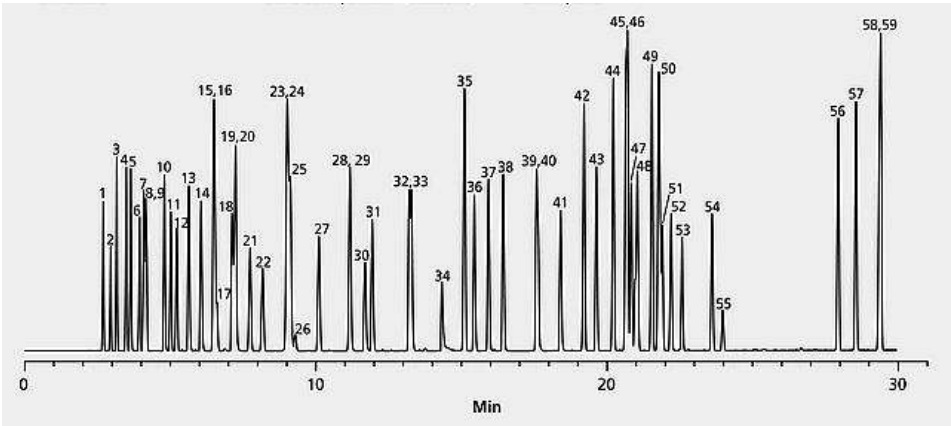
- Temperature, radiation, wind speed and direction, pressure…



Behind the VOC datasets

Chromatography
Ionization with electrons



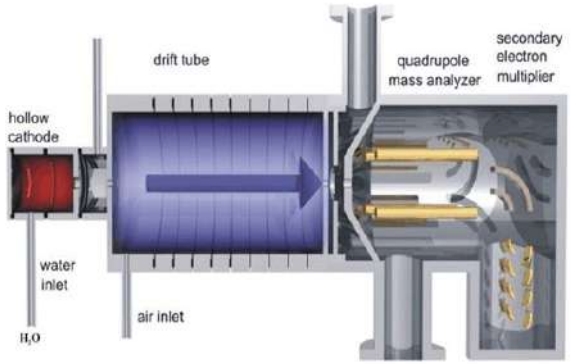


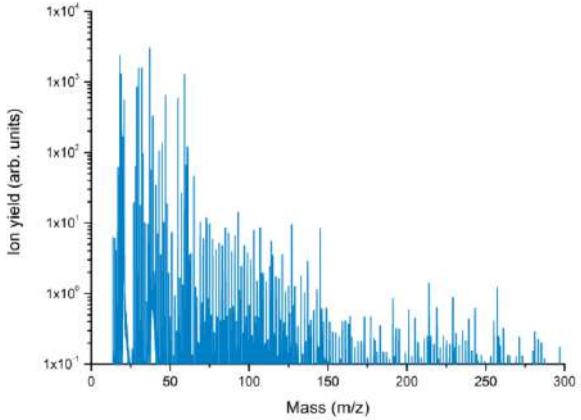
✓ More information

– Low time resolution

VS

Mass Spectrometry
Ionization with protons





✓ Less information

– High time resolution

The Cyprus Atmospheric Observatory (CAO)

Cyprus Atmospheric Observatory

EMME-CARE
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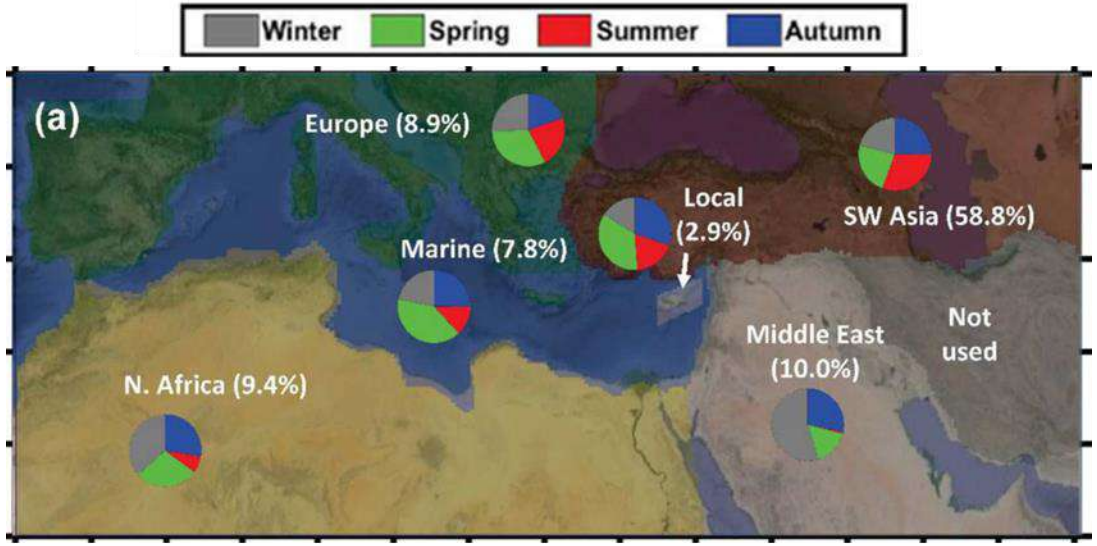
CAO-AMX
Regional (rural) background

CAO-NIC
Urban background

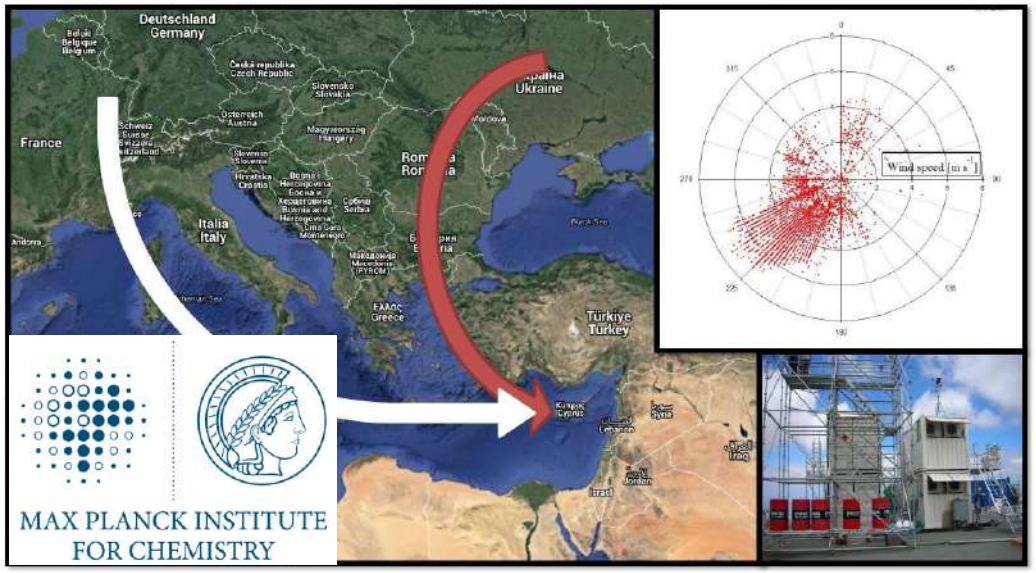
CAO-TRO
Free troposphere (1820m alt.)

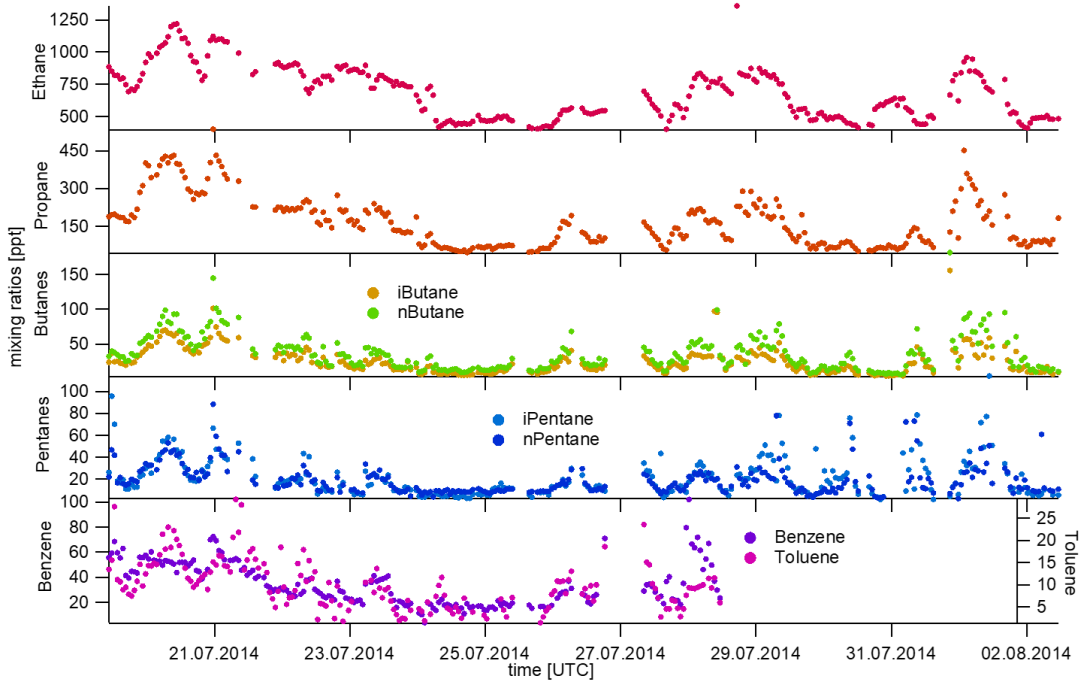
CAO-INEIA
Regional bg. (ICOS)

The CAO-Ineia station (Data from CYPHEX 2014)



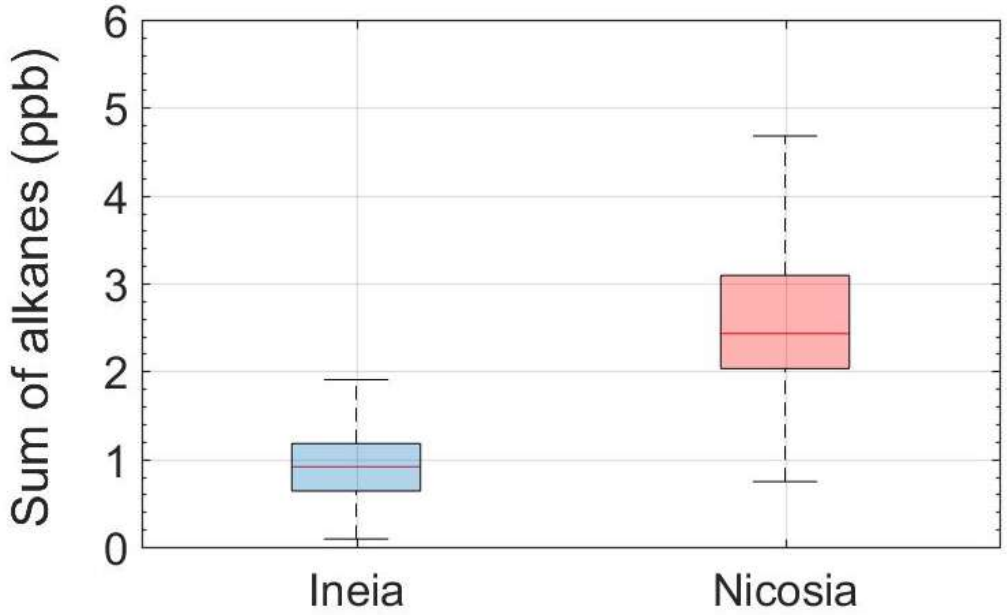
Pikridas et al., 2018

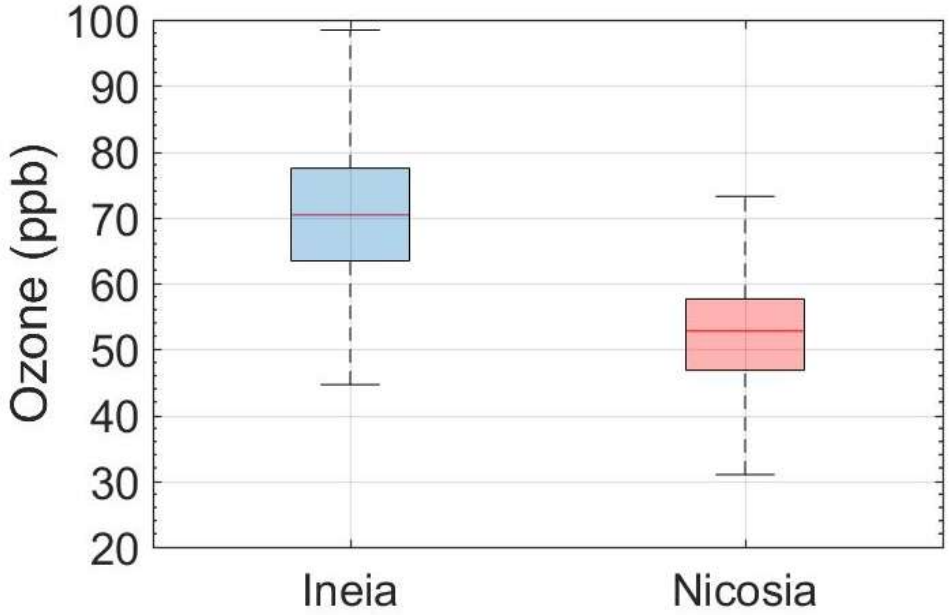




Credit: C. Sauvage

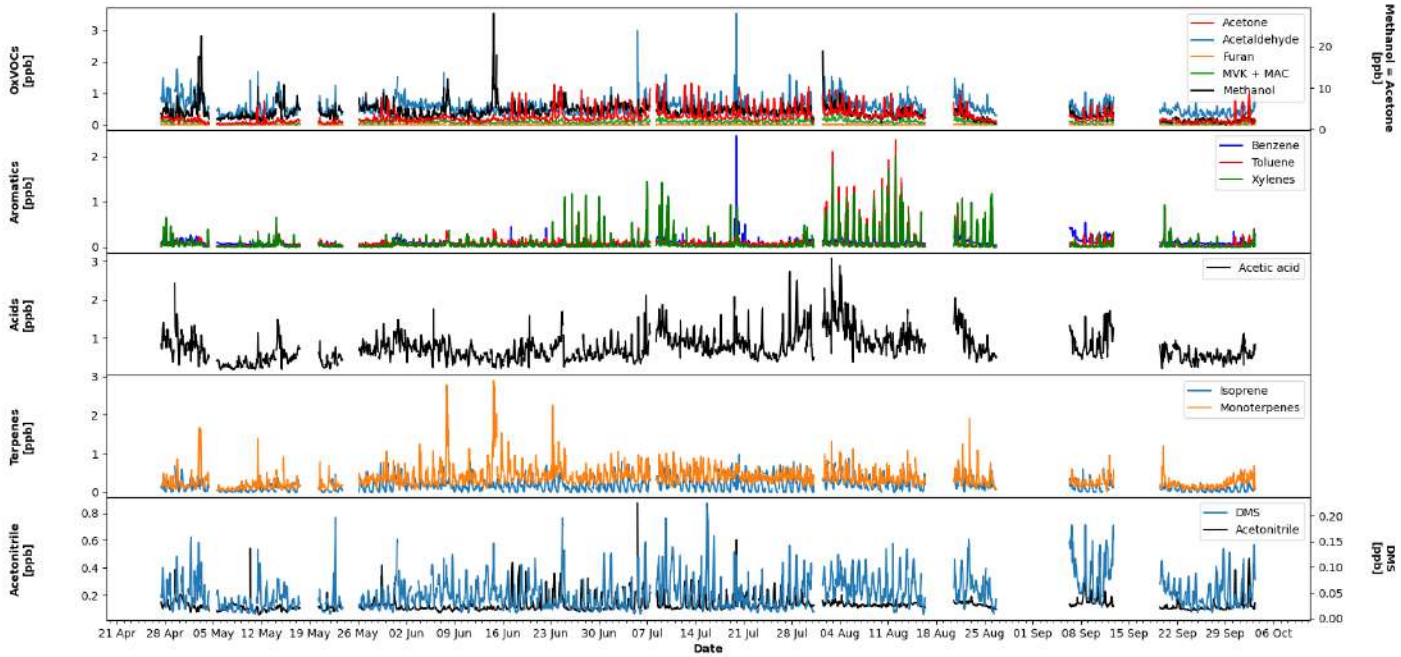
Summertime observations at Ineia vs Nicosia

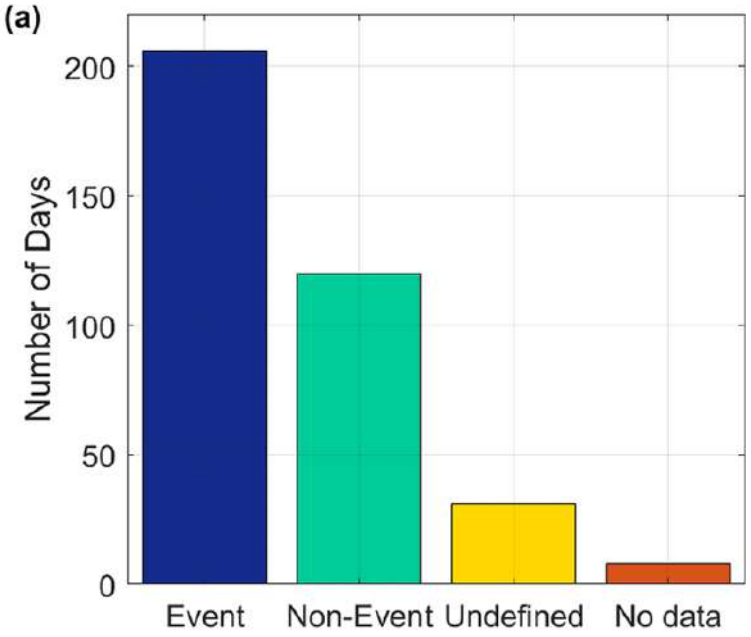




Credit: E. Germain-Piaulenne, S. Agathokleous, C. Sauvage

Long-term observations at CAO-AMX

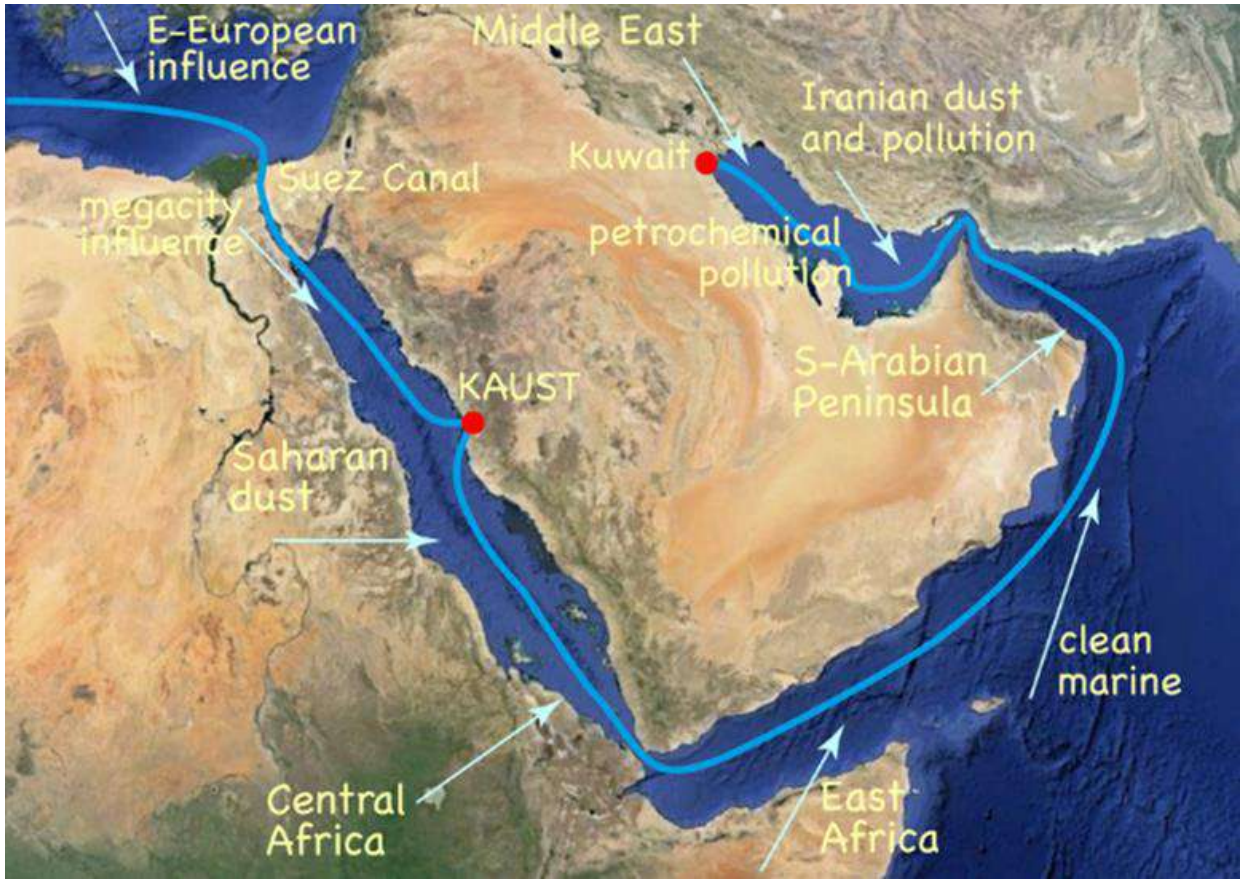




Credit: M. Desservettaz

Baalbaki et. al., 2021

Exemplary approach (NMHCs): The AQABA ship campaign

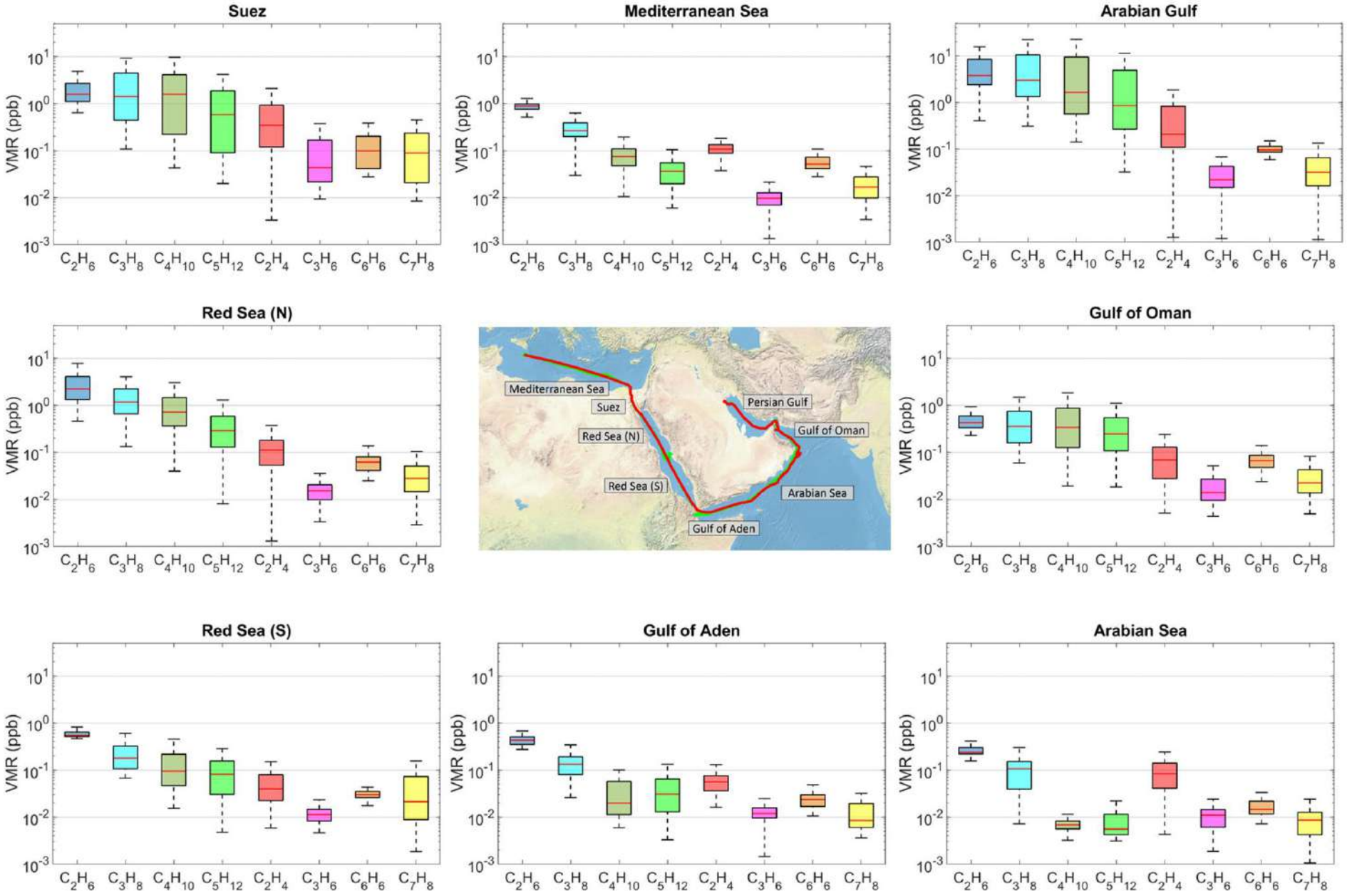


	Alkanes		Alkenes		Aromatics
1	Ethane	1	Ethene	1	Benzene
2	Ethene	2	Propene	2	Toluene
3	Propane	3	trans-2-butene	3	m,p-xylenes
4	Propene	4	1-Butene		
5	i-Butane	5	1-Pentene		
6	n-Butane	6	Isoprene		
7	i-Pentane				
8	2-Methylpentane				
9	2,2,4-Trimethylpentane				
10	n-Hexane				
11	n-Heptane				
12	Octane				

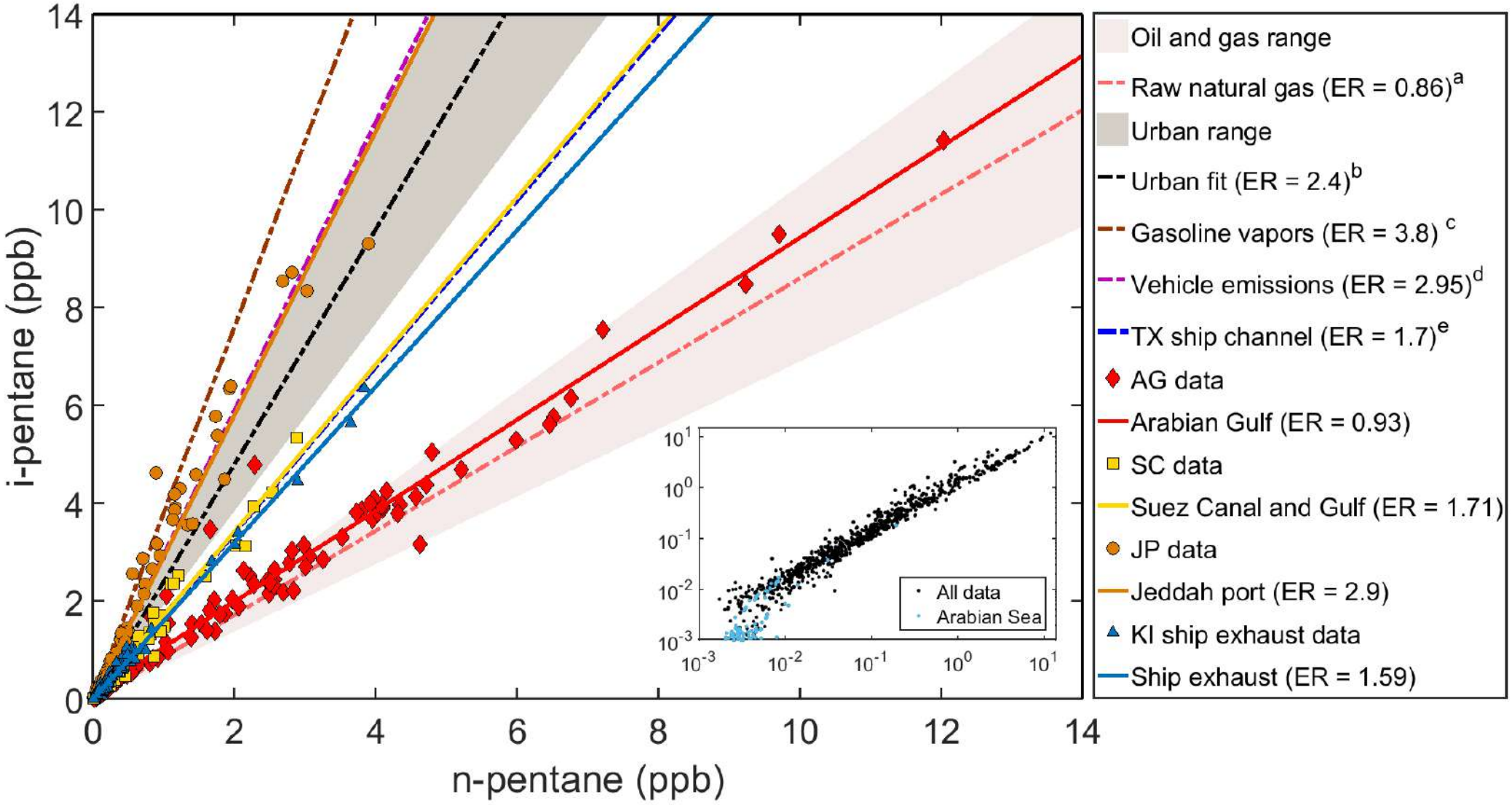
Compounds measured during the AQABA ship campaign

Photo by S. Dörner

Exemplary approach (NMHCs): The AQABA ship campaign

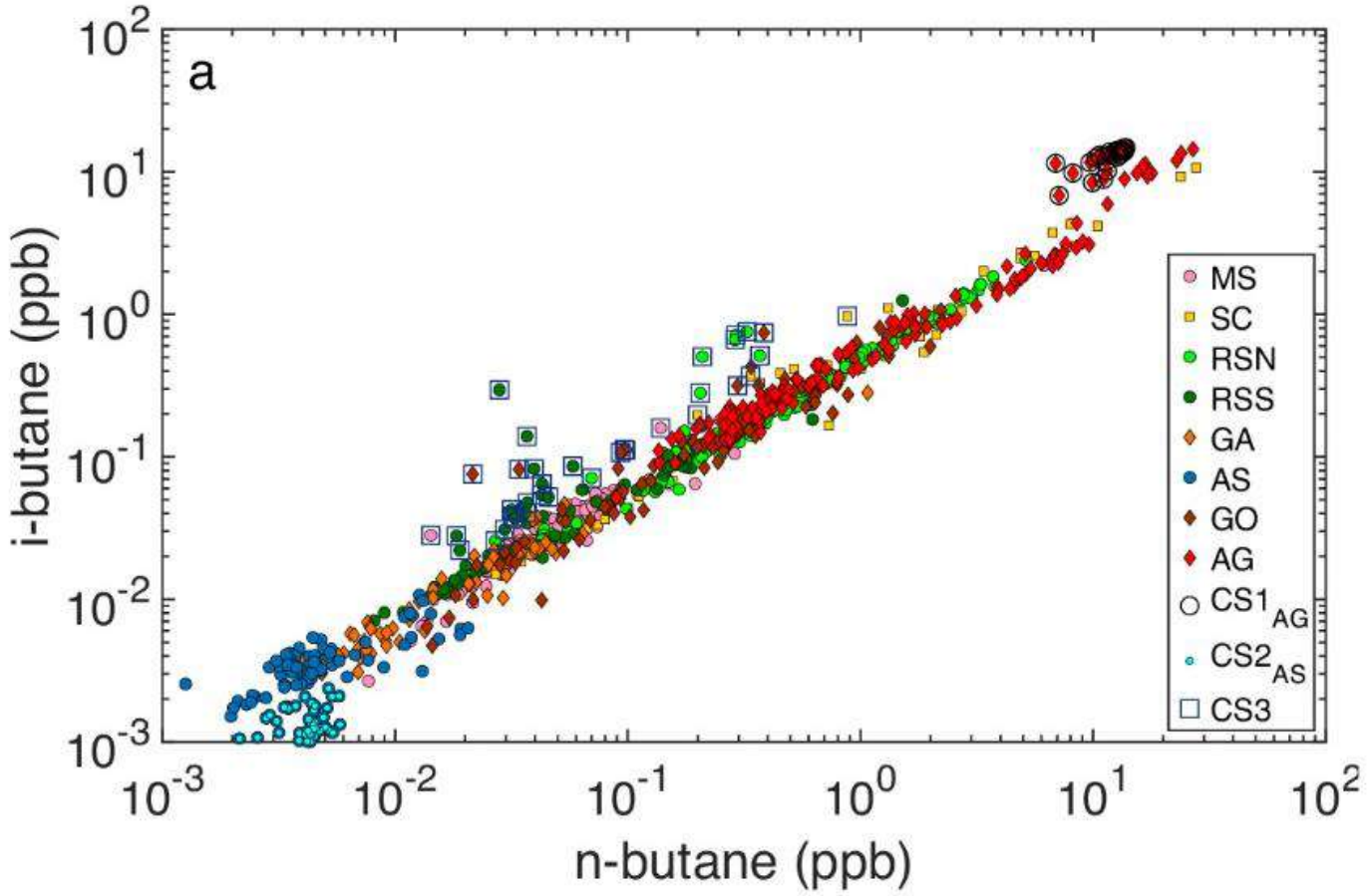


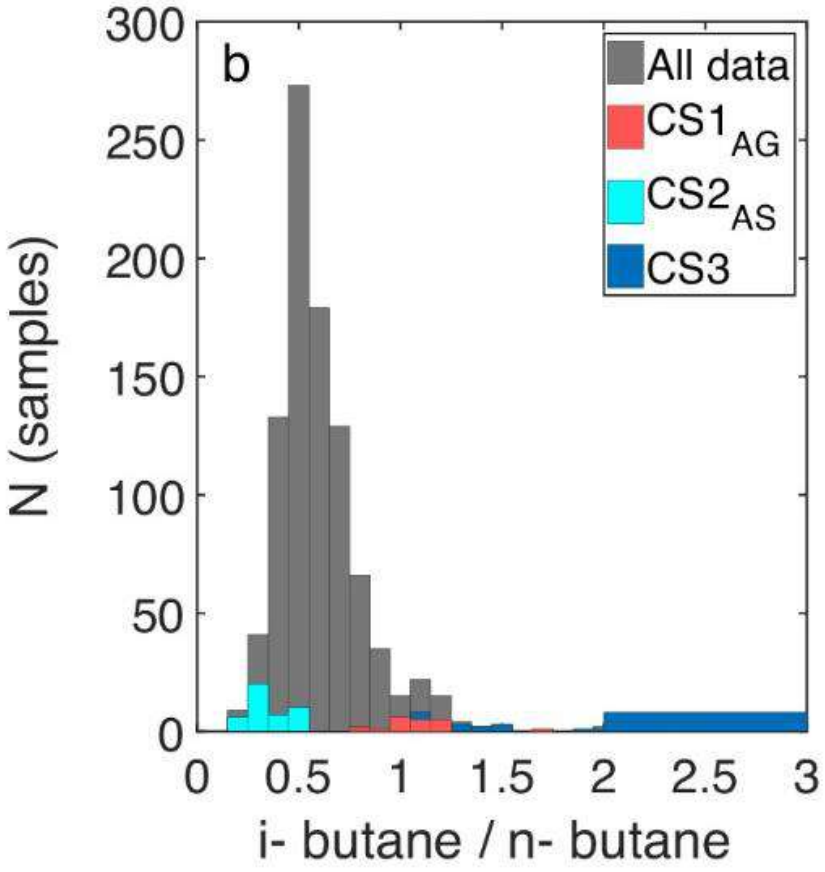
Pentane concentrations as source identification tool



Bourtsoukidis et al. ACP, 2019

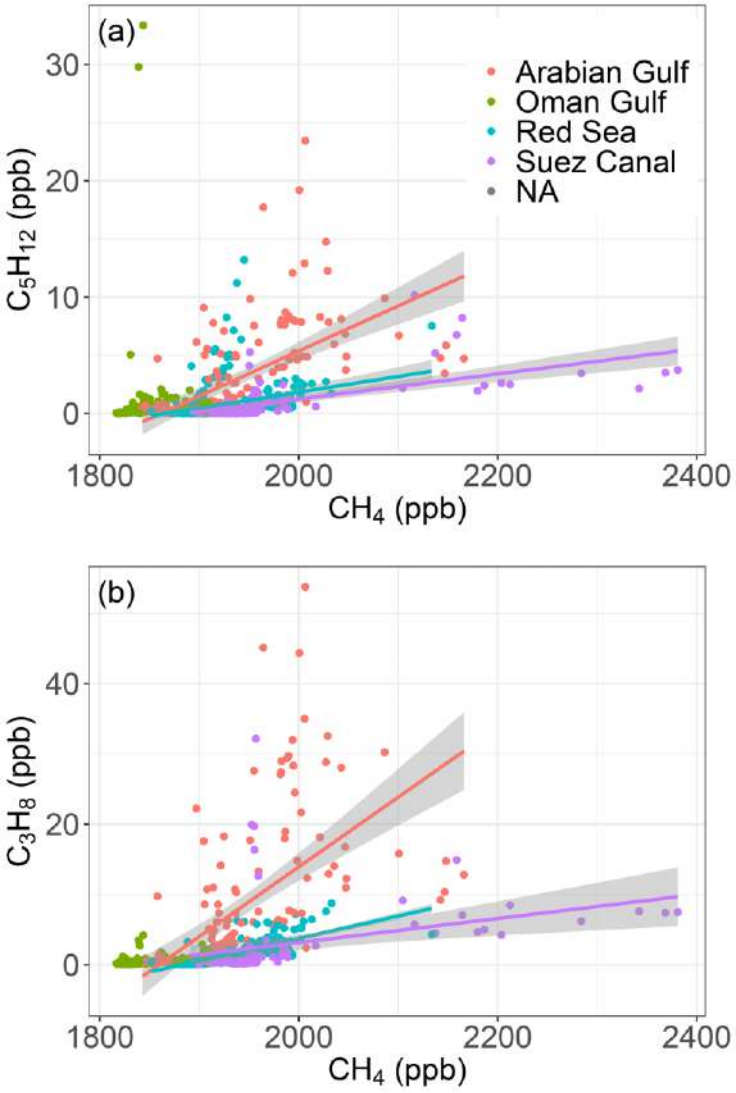
The butane isomers





Bourtsoukidis et al. ACP, 2019

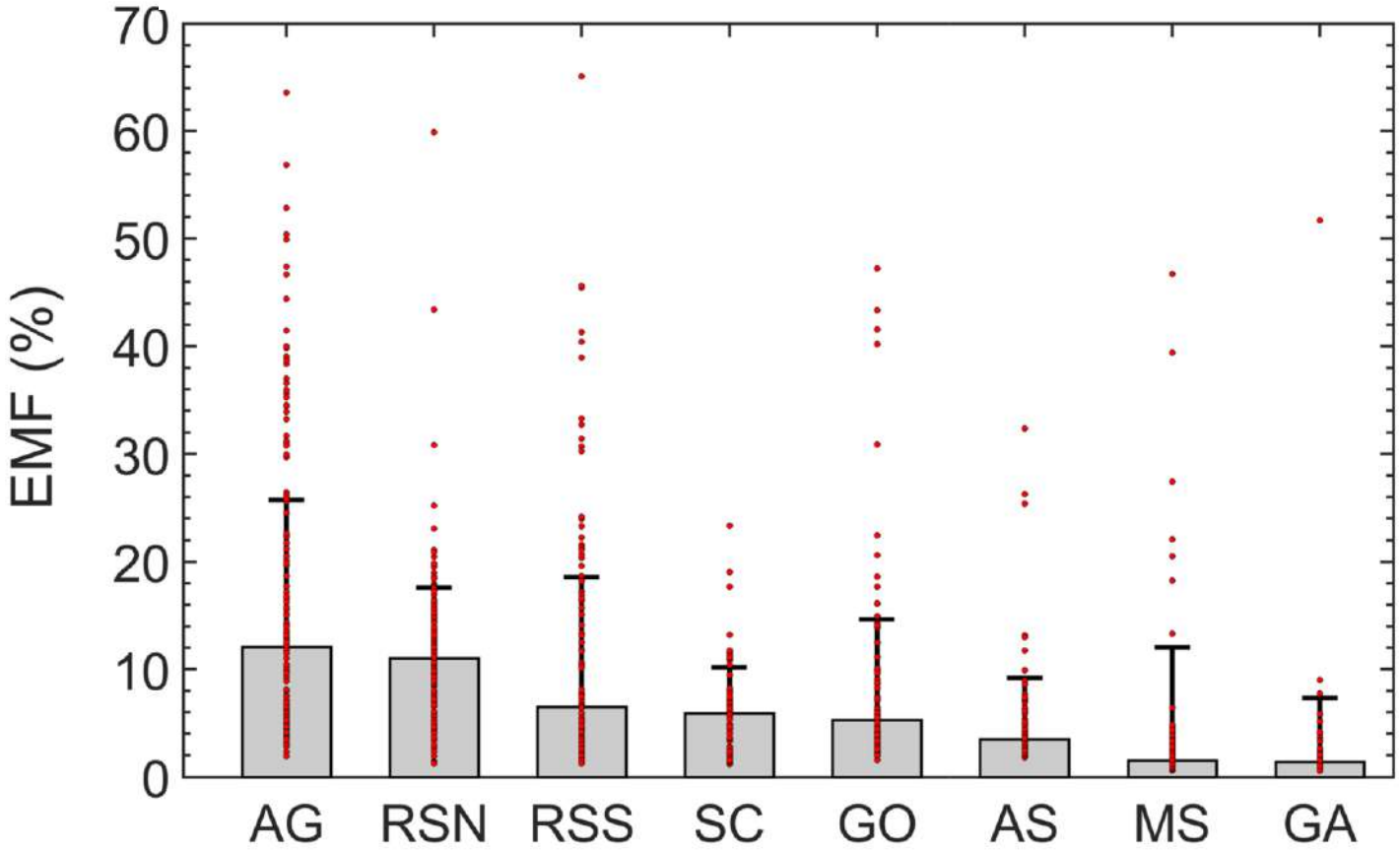
The excess NMHC mole fraction (EMF)



Paris et al. ACP, 2021

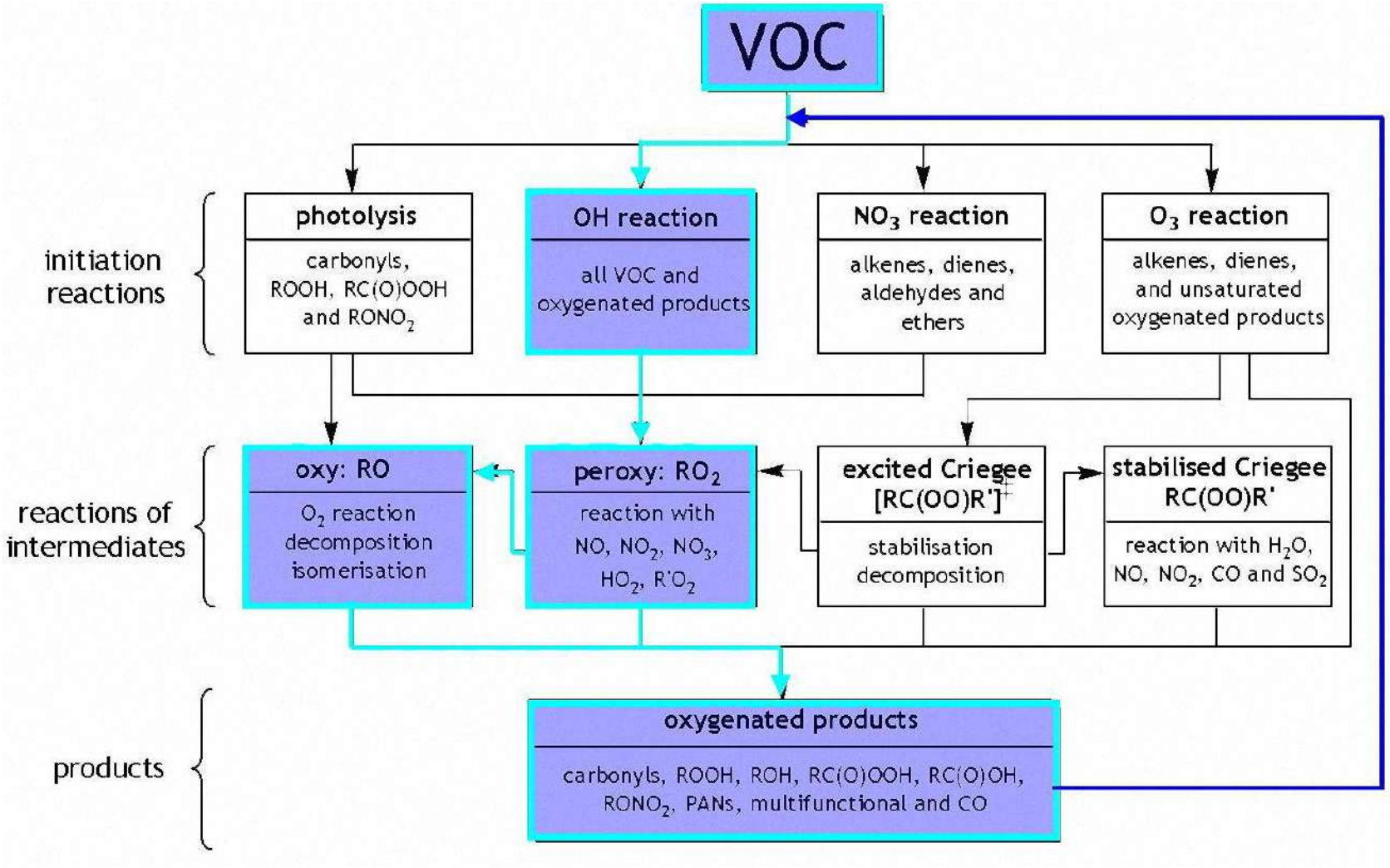
Excess NMHC mole fraction (EMF)

$$= \frac{\sum(\mathrm{NMHC} - \mathrm{NMHC_{BG}})}{([\mathrm{CH_4}] - [\mathrm{CH_4}]_{\mathrm{BG}}) + \sum(\mathrm{NMHC} - \mathrm{NMHC_{BG}})} \times 100\ \%.$$



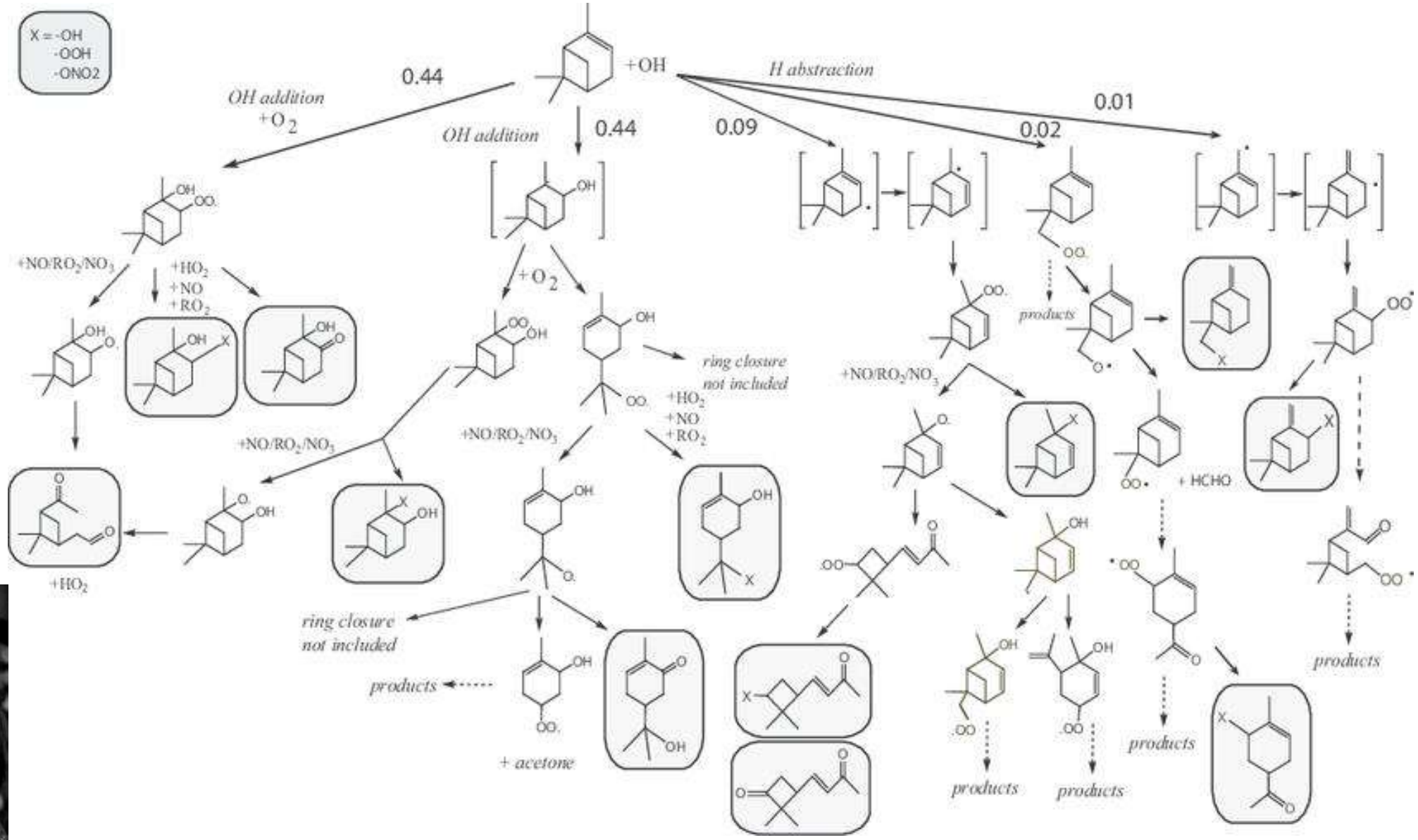
Bourtsoukidis et al. ACP, 2019

VOC sinks



Master Chemical Mechanism, Leeds Univ.

VOC sinks : a-pinene oxidation by OH



Chemical lifetimes

Greenhouse gas	Chemical symbol	Lifetime (years)
Carbon dioxide	$C0_2$	5-200
Methane	CH_4	12
Nitrous oxide	N_20	114
Sulphur hexafluoride	SF_6	3 200
CFC-12	CCl_2F_2	102
HCFC-22	$CHClF_2$	12
Perflouromethane	CF_4	50 000

Ibtisam and Karim, 2016

Compound	Atmospheric lifetime (approx.)	Characteristic sources
Ethane	1.5 months	Natural gas, biomass burning
Acetylene	15 days	Vehicle emissions, biomass burning
Methanol	12 days	Plants, VOC oxidation
Propane	11 days	Liquefied petroleum gas, natural gas
Benzene	10 days	Industrial emissions, vehicle emissions, biomass burning
iso/n-Butane	5 days	Vehicle emissions, liquefied petroleum gas
Ethanol	4 days	Plants, biofuel
iso/n-Pentane	3 days	Vehicle emissions, gasoline evaporation
Toluene	2 days	Solvents, vehicle emissions
Ethene	1 day	Vehicle emissions
Formaldehyde	1 day	VOC oxidation, biomass burning
Isoprene	3 hours	Plants

WHO, 2016

Superheroes of atmospheric chemistry

Biogenic VOCs			Biogenic VOC oxidation products		
Isoprene	τ_{OH}	τ_{O3}		τ_{OH}	τ_{O3}
	1.4 h	1.3 d	Methacrolein	4.1 h	15 d
			Methyl vinyl ketone	6.8 h	3.6 d
			3-Methyl furan	1.5 h	19 h
Monoterpenes	τ_{OH}	τ_{O3}		τ_{OH}	τ_{O3}
Limonene	49 min	2 h	Limononaldehyde	1.26 h	2 d
Terpinolene	37 min	13 min	4-Methyl-3-cyclohexenone	1.5 h	n.r.
α-Pinene	2.6 h	4.6 h	Pinonaldehyde	2.9 h	>2.4 year
β-Pinene	1.8 h	1.1 d	Nopinone	12 h	>4.5 year
Δ^3-Carene	1.6 h	11 h	Caroaldehyde	2.9 h	>2.3 year
Sabinene	1.2 h	4.6 h	Sabinaketone	18.8 d	>0.9 year
Camphene	2.6 h	18 d	Camphenilone	2.3 d	>4.5 year
Sesquiterpenes	τ_{OH}	τ_{O3}			
β-Caryophyllene	42 min	2 min			
α-Humulene	28 min	2 min			
α-Cedrene	2.1 h	14 h			
α-Copaene	1.5 h	2.5 h			
Alcohols	τ_{OH}	τ_{O3}		τ_{OH}	τ_{O3}
2-Methyl-3-buten-2-ol	2.4 h	1.7 d	5-Methyl-5-vinyltetrahydrofuran-2-ol	1.56 d	8.7 d
cis-3-Hexen-1-ol	1.3 h	6.2 h			
Linalool	52 min	55 min			
1,8-Cineole	1.0 d	>110 d			
Methanol	12 d	>4.5 year			

Ciccioli et al., 2014

Photochemical clocks: Lifetime-variability relationship

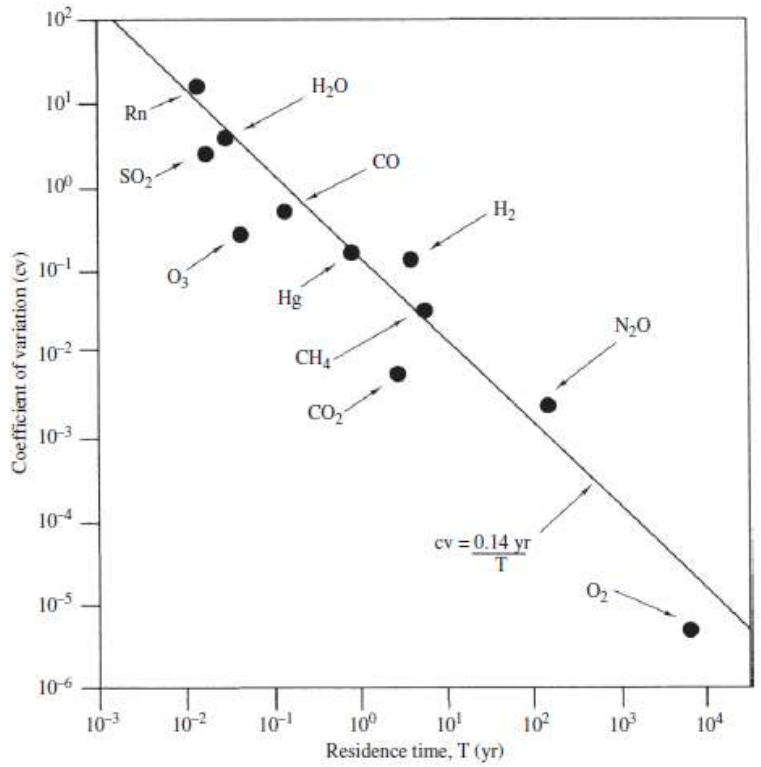
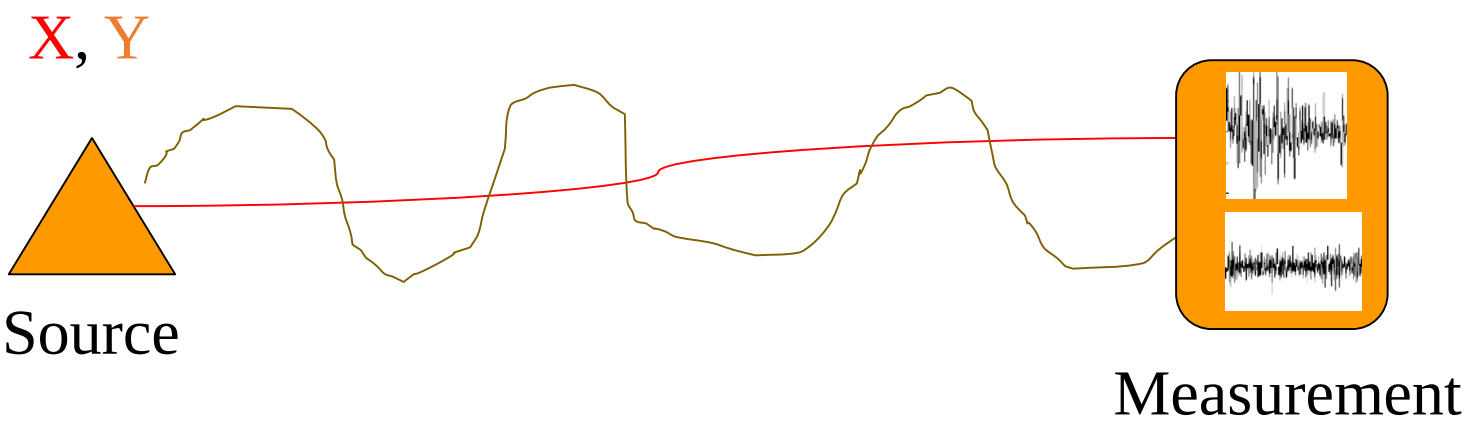
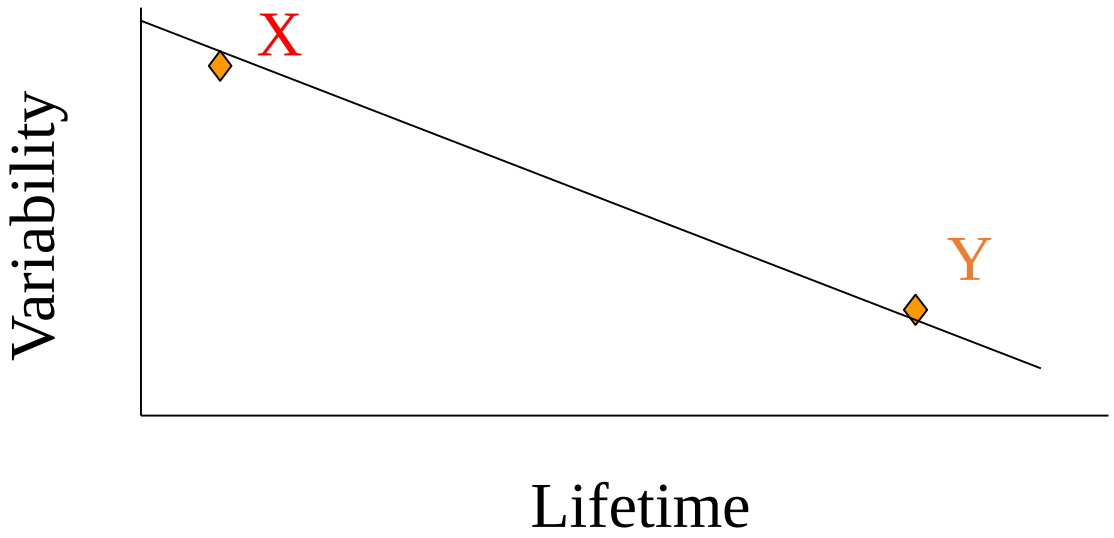


FIG. 3.5 Variability in the concentration of atmospheric gases, expressed as the coefficient of variation among measurements, as a function of their estimated mean residence times in the atmosphere. *Modified from Junge (1974), as updated by Slinn (1988).*

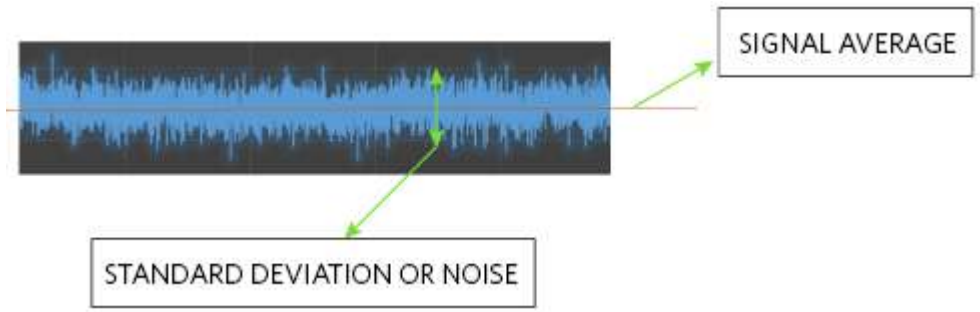


X = short lifetime, Y = long lifetime



Lifetime-variability on VOCs

$$S(\ln(X)) = A \cdot \tau^{-b}$$



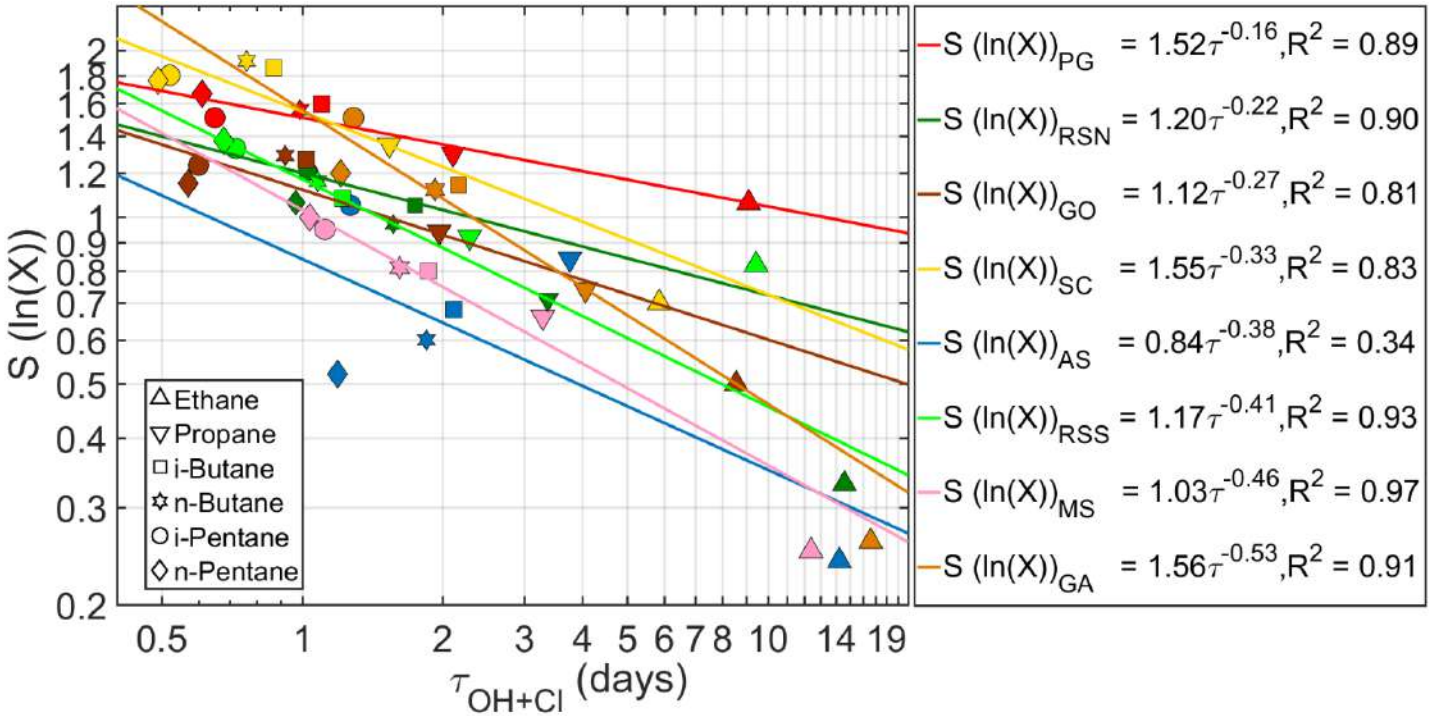
S : StDev of vmr

X : selected NMHC

A, b : regression derived parameters

$$\tau = \frac{1}{k_{OH,X}[OH] + k_{Cl,X}[Cl]}$$

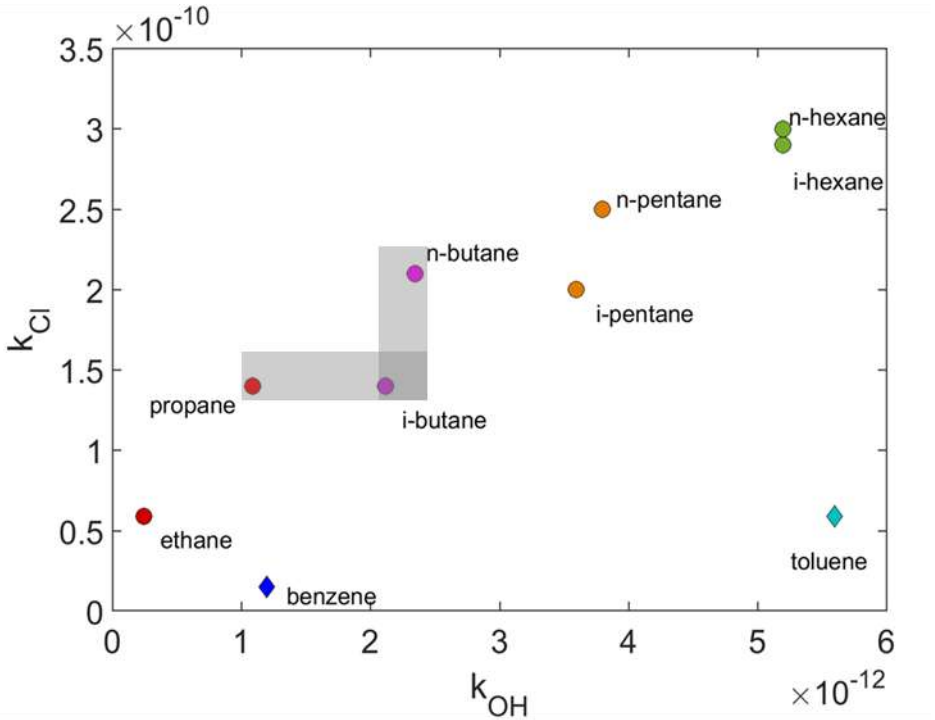
Determine the proximity of the source

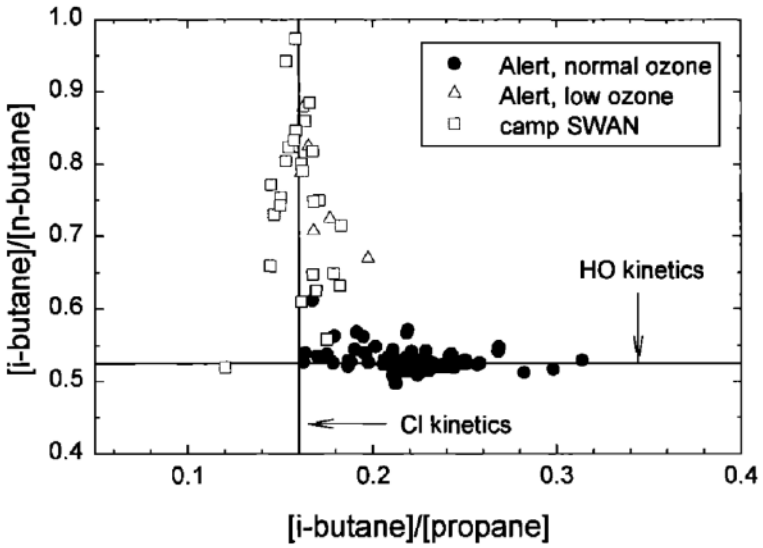


Bourtsoukidis et al., 2019

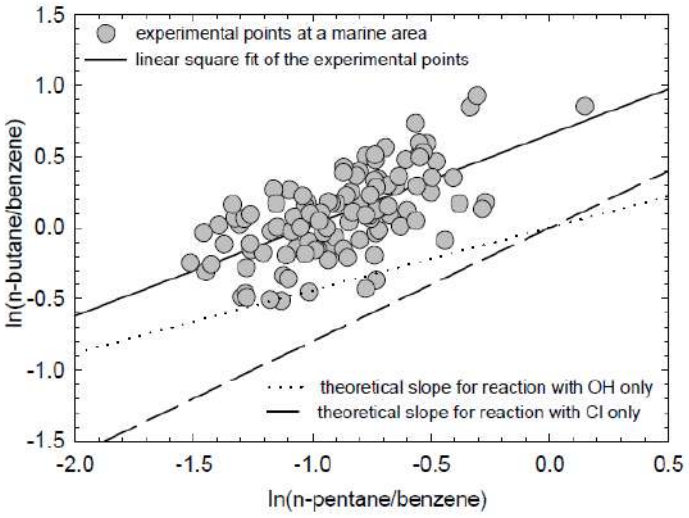
Identifying radical chemistry

Oxidative triangles

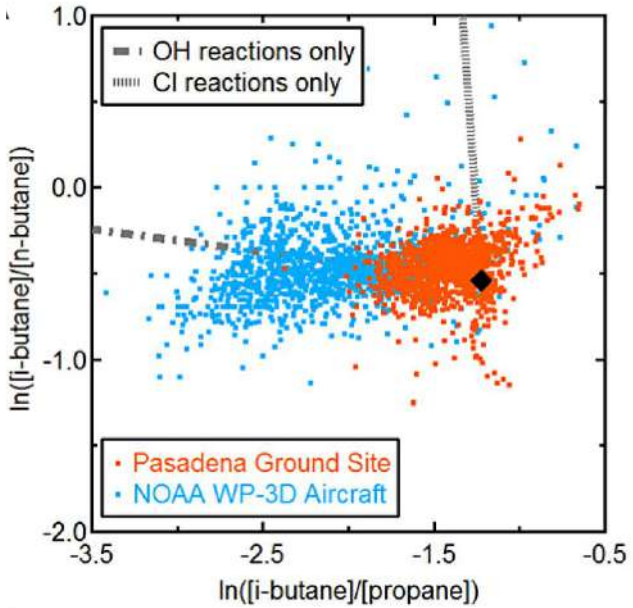


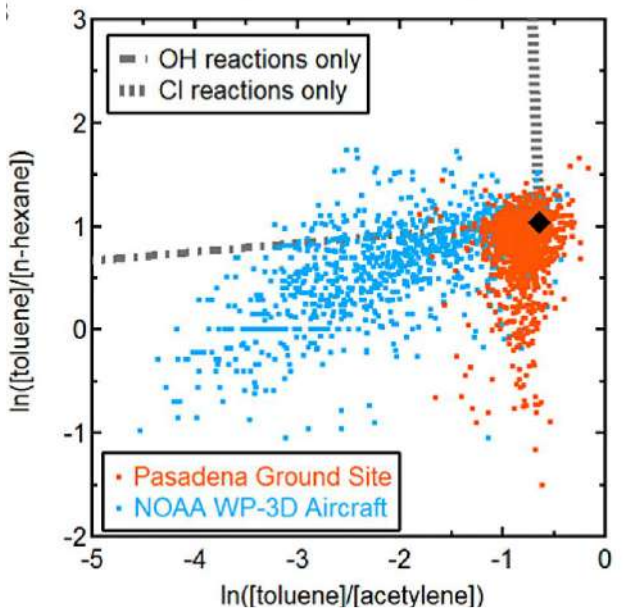


Jobson et al., 1994



Arsene et al., 2007

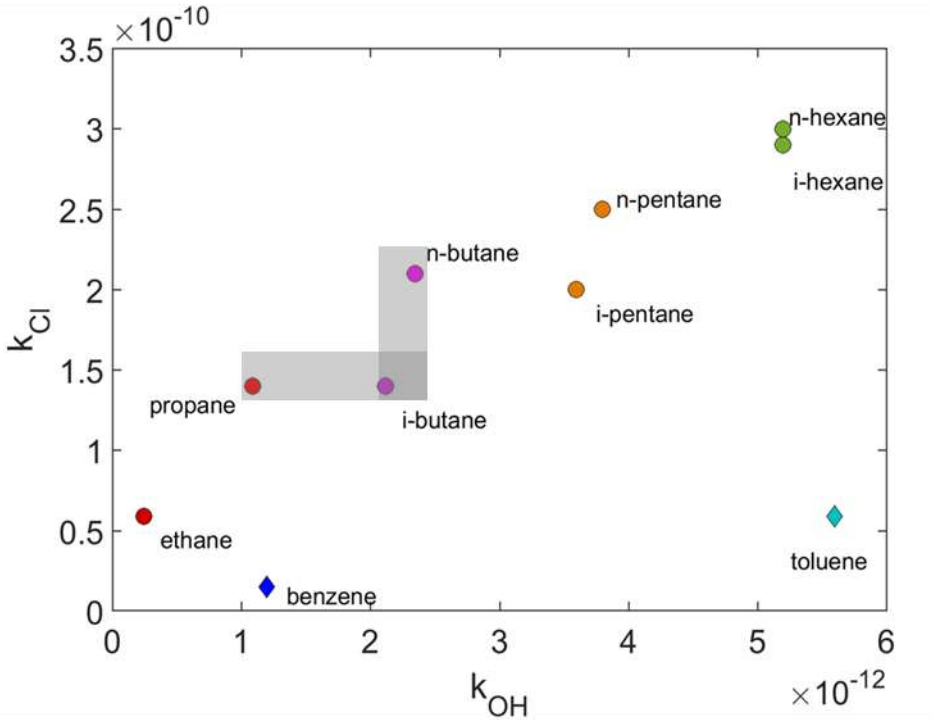


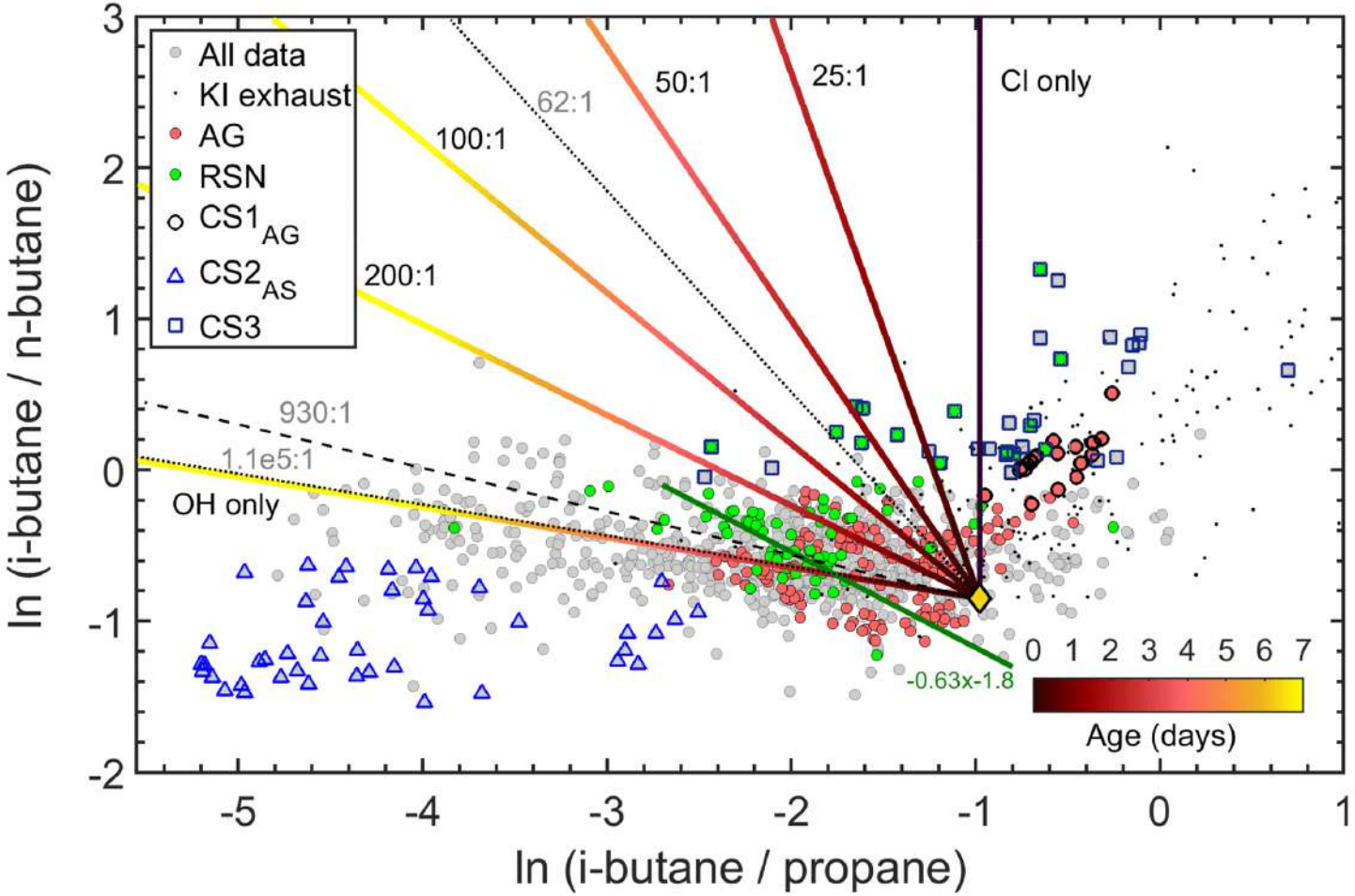


Young et al., 2014

Identifying radical chemistry

Oxidative triangles





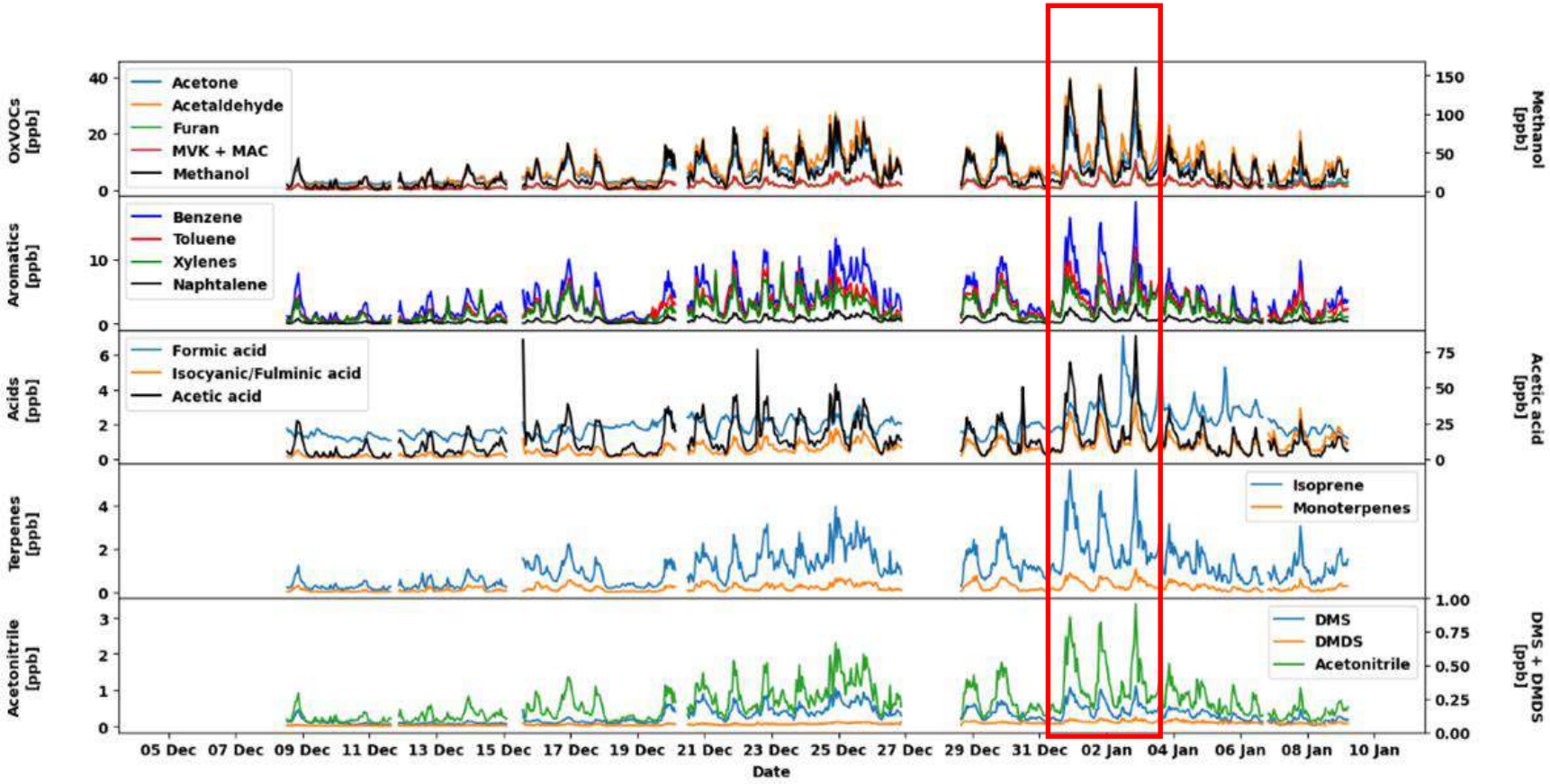
Bourtsoukidis et al., 2019

$$\frac{OH}{Cl} = \frac{-80}{\sigma + 0.2}$$

e.g. σ = -0.63 → OH/Cl = 186:1

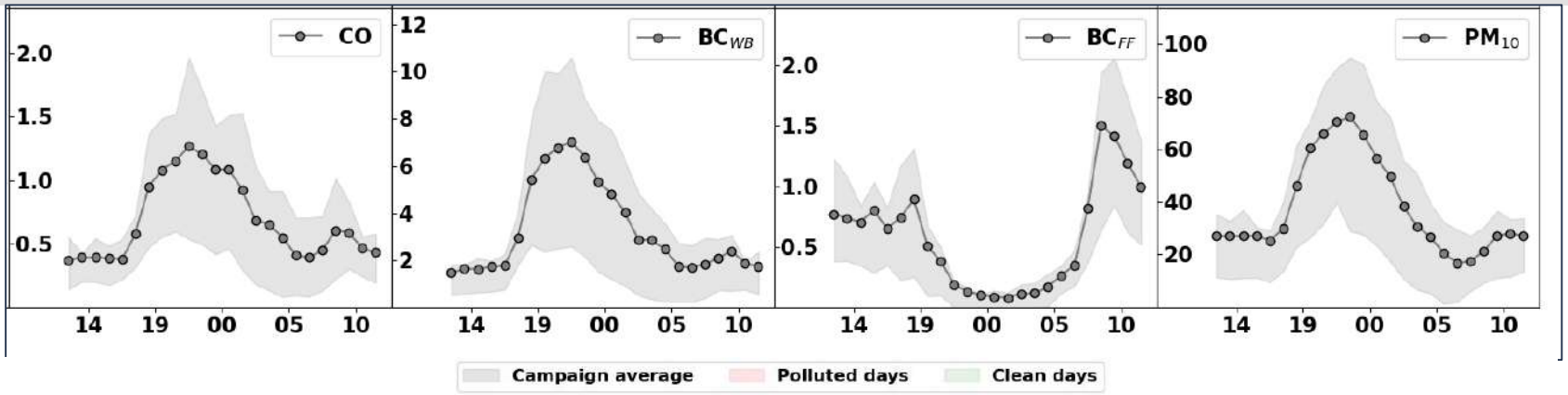
Ioannina, Greece : Residential combustion

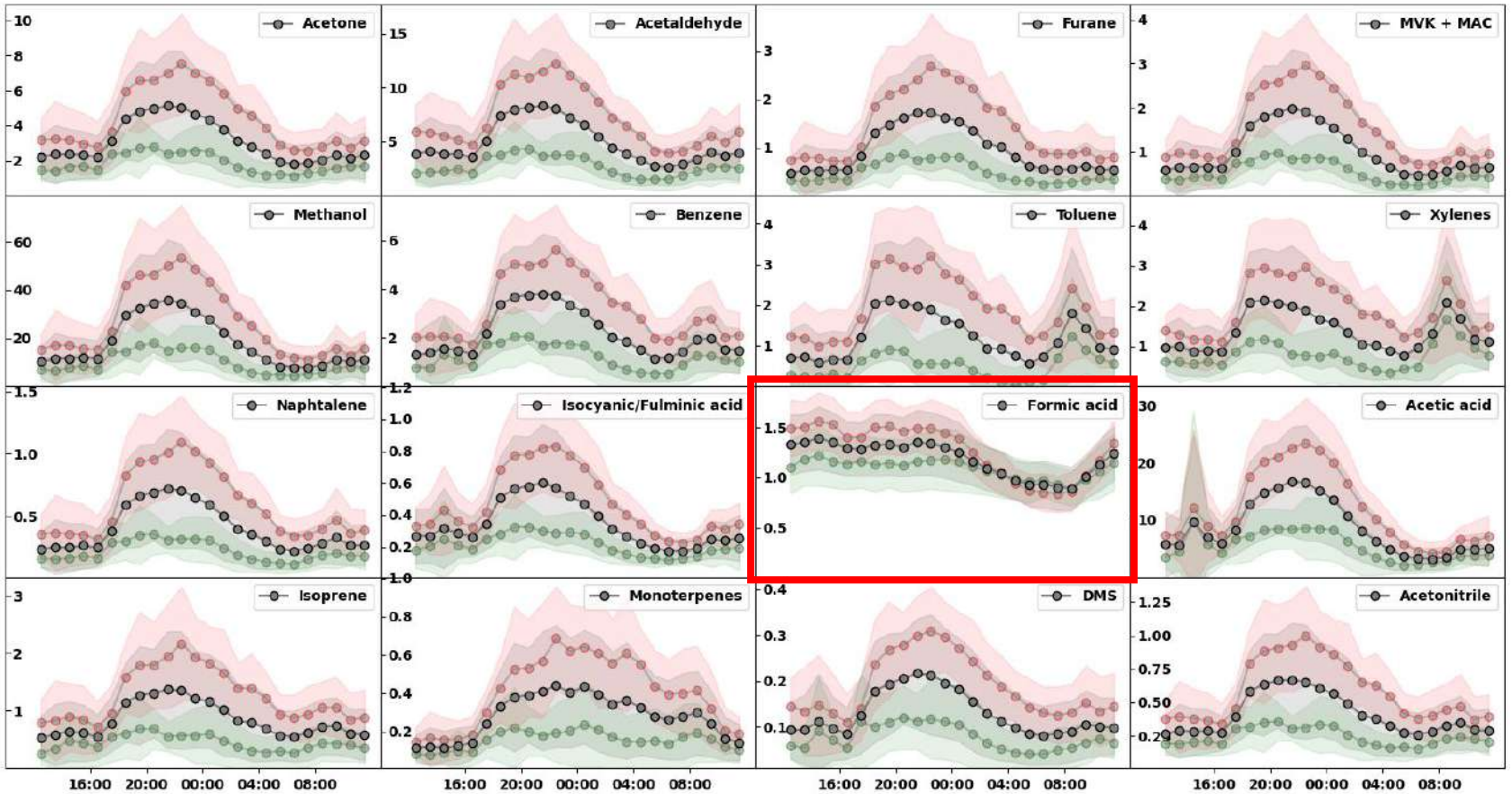
Higher than what was measured in polluted megacities (Delhi, Tokyo, London, Beijing etc)

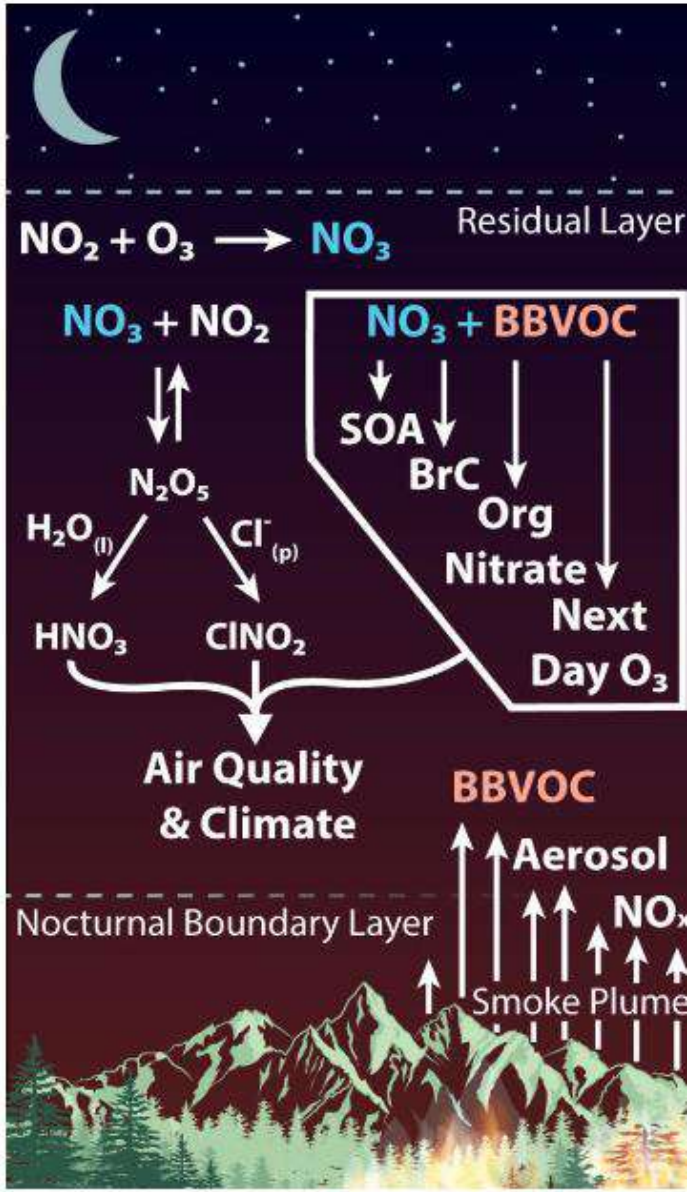


Credit: M. Desservetaz

Diurnal cycles

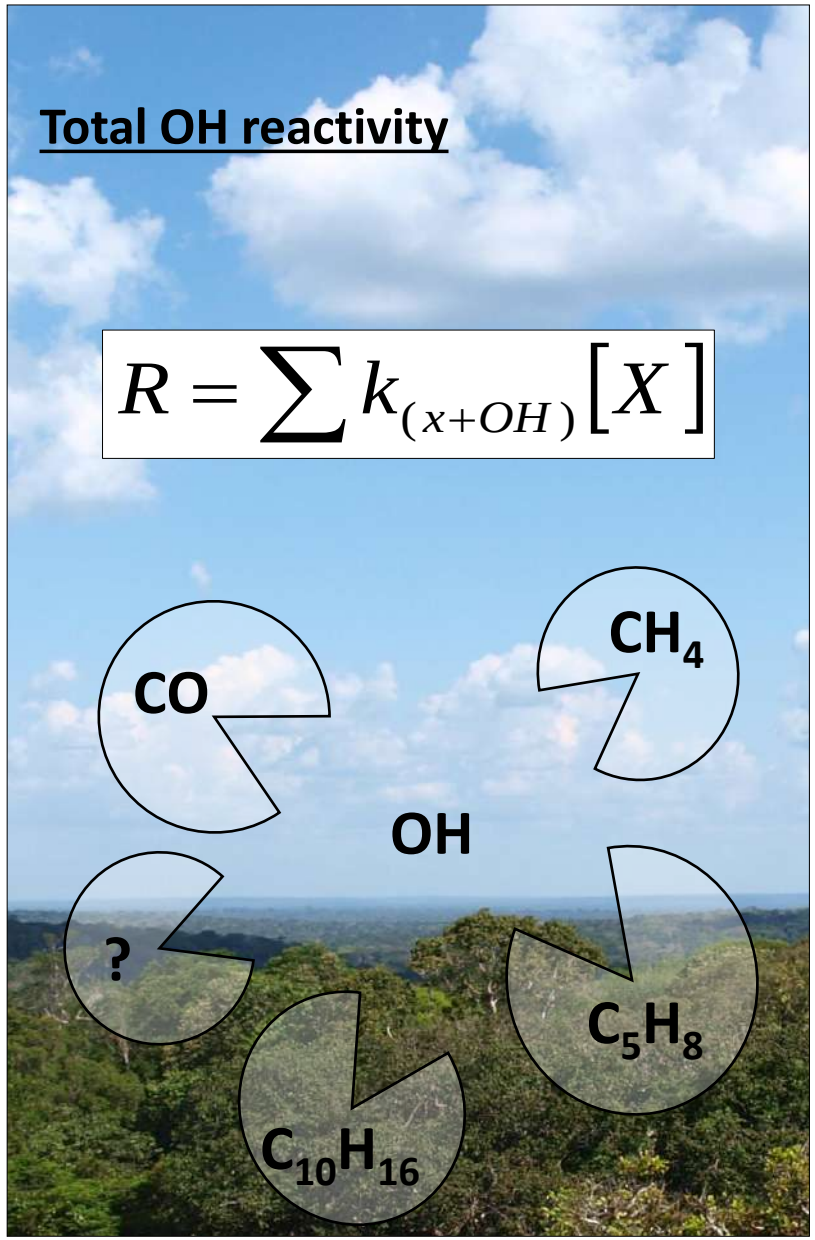






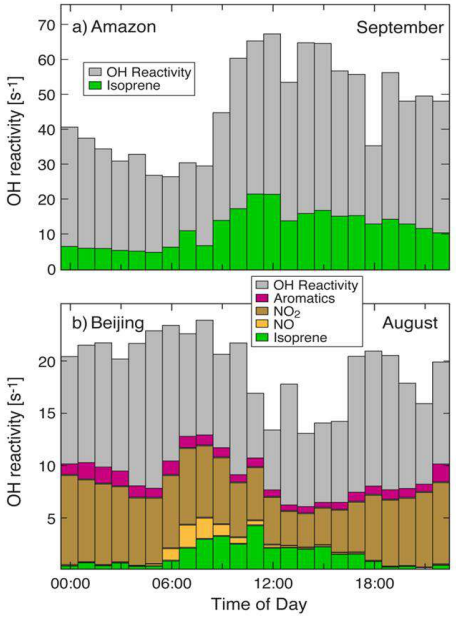
Decker et al., 2019

The OH reactivity



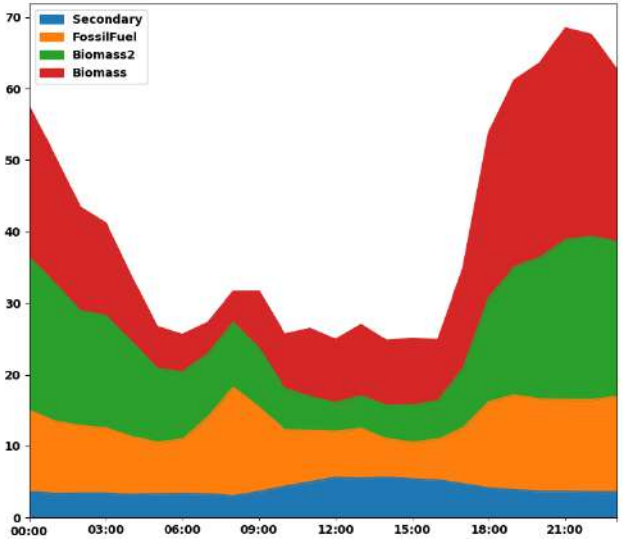
Credit: A. Noelscher

Total OH reactivity is defined as **the total loss rate of reaction of the hydroxyl radical OH with atmospheric chemical compounds**. It represents the inverse of the OH radical lifetime. Since OH is the main atmospheric oxidant during daytime, measuring the total OH reactivity represents an estimate of the total loading of reactive molecules in the atmosphere.



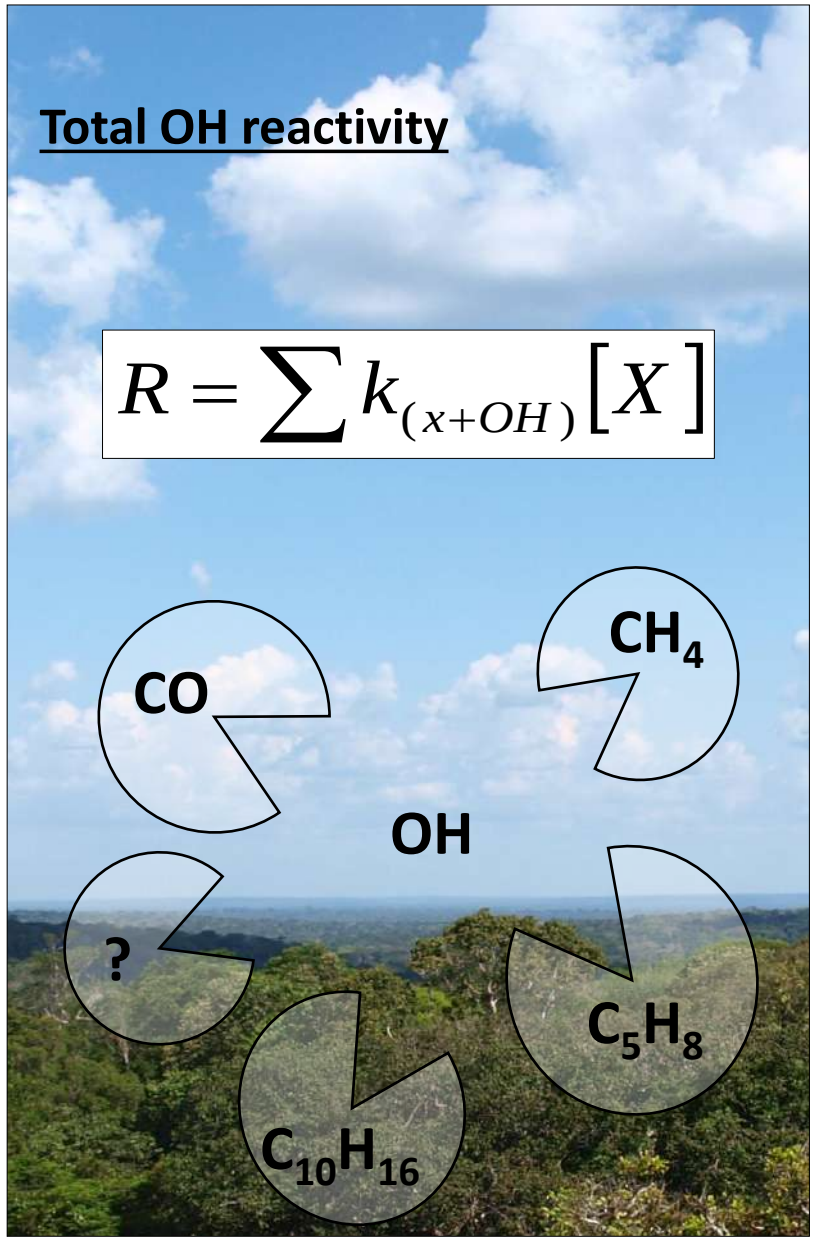
Williams et al., 2016

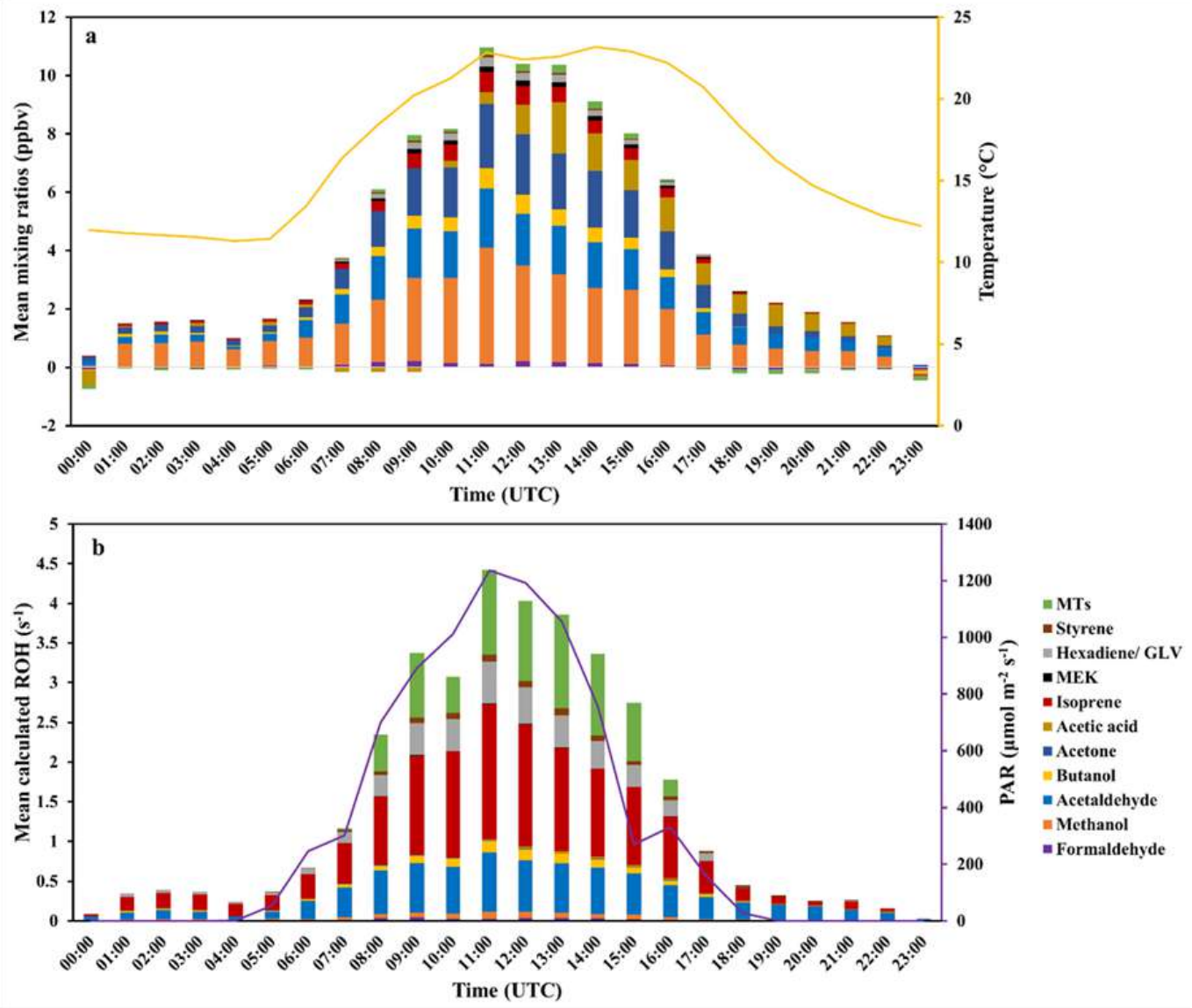
Ioannina 2021/2022



Credit: M. Desservetaz

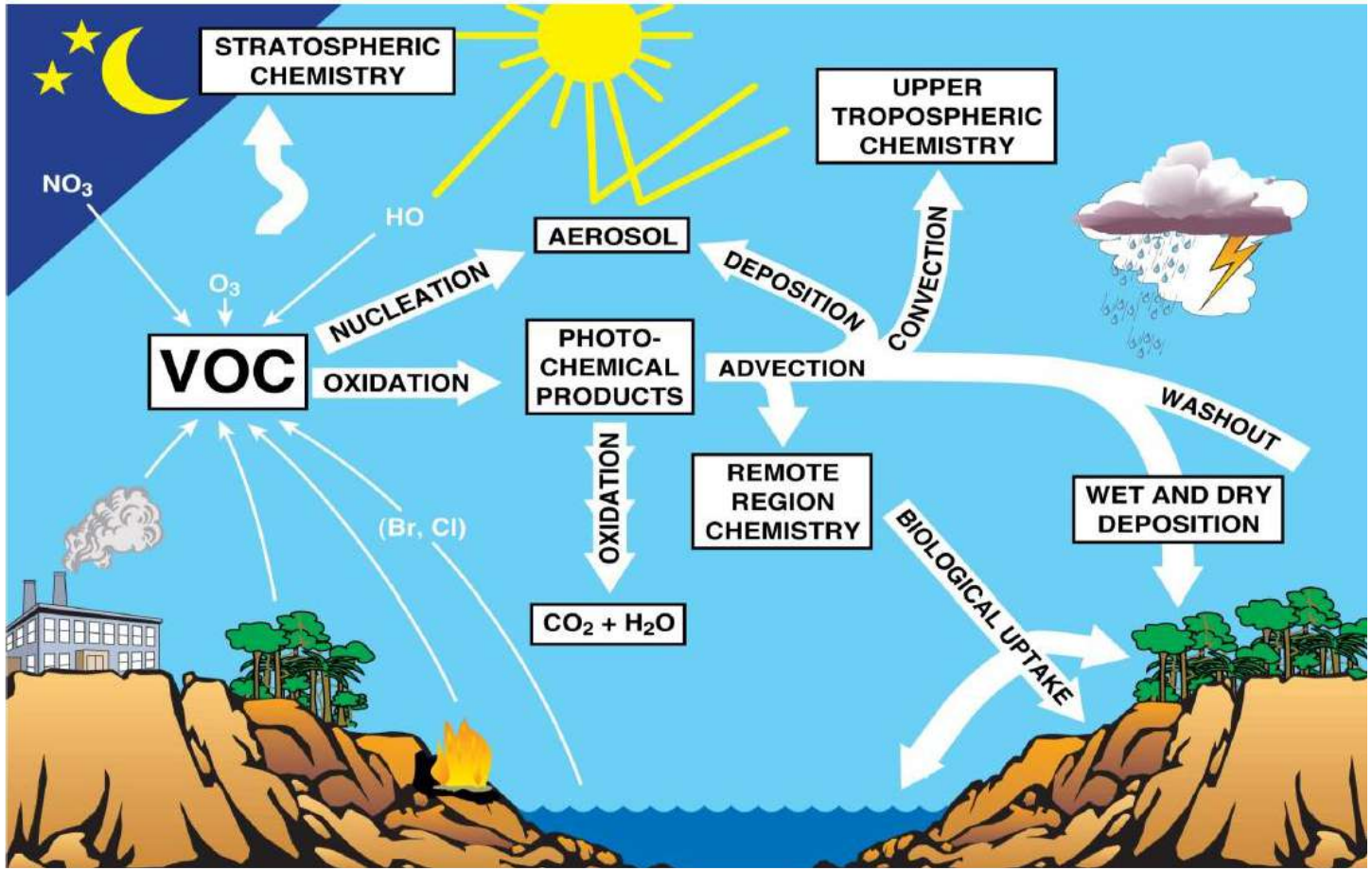
The OH reactivity





Bsaibes et al., 2020

Summary



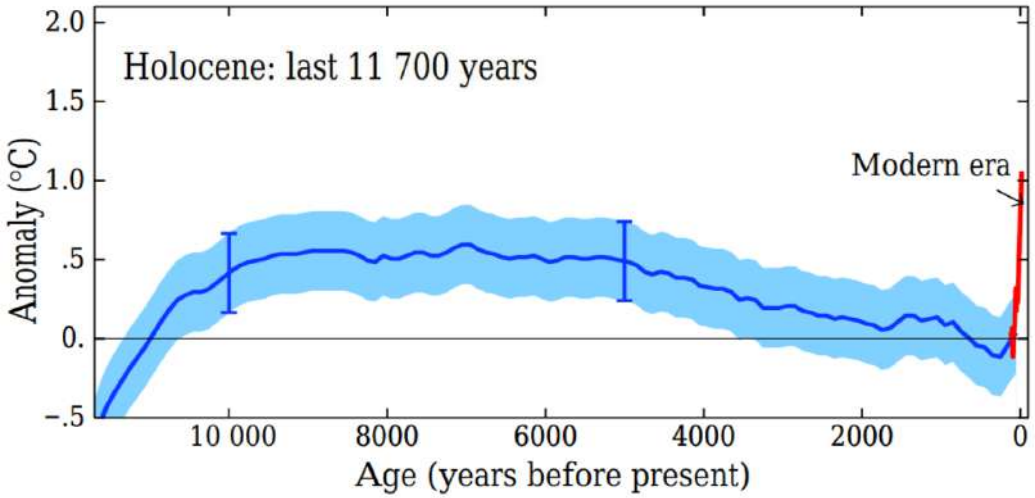
nature

POLICY & ETHICS

Anthropocene Now: Influential Panel Votes to Recognize Earth's New Epoch

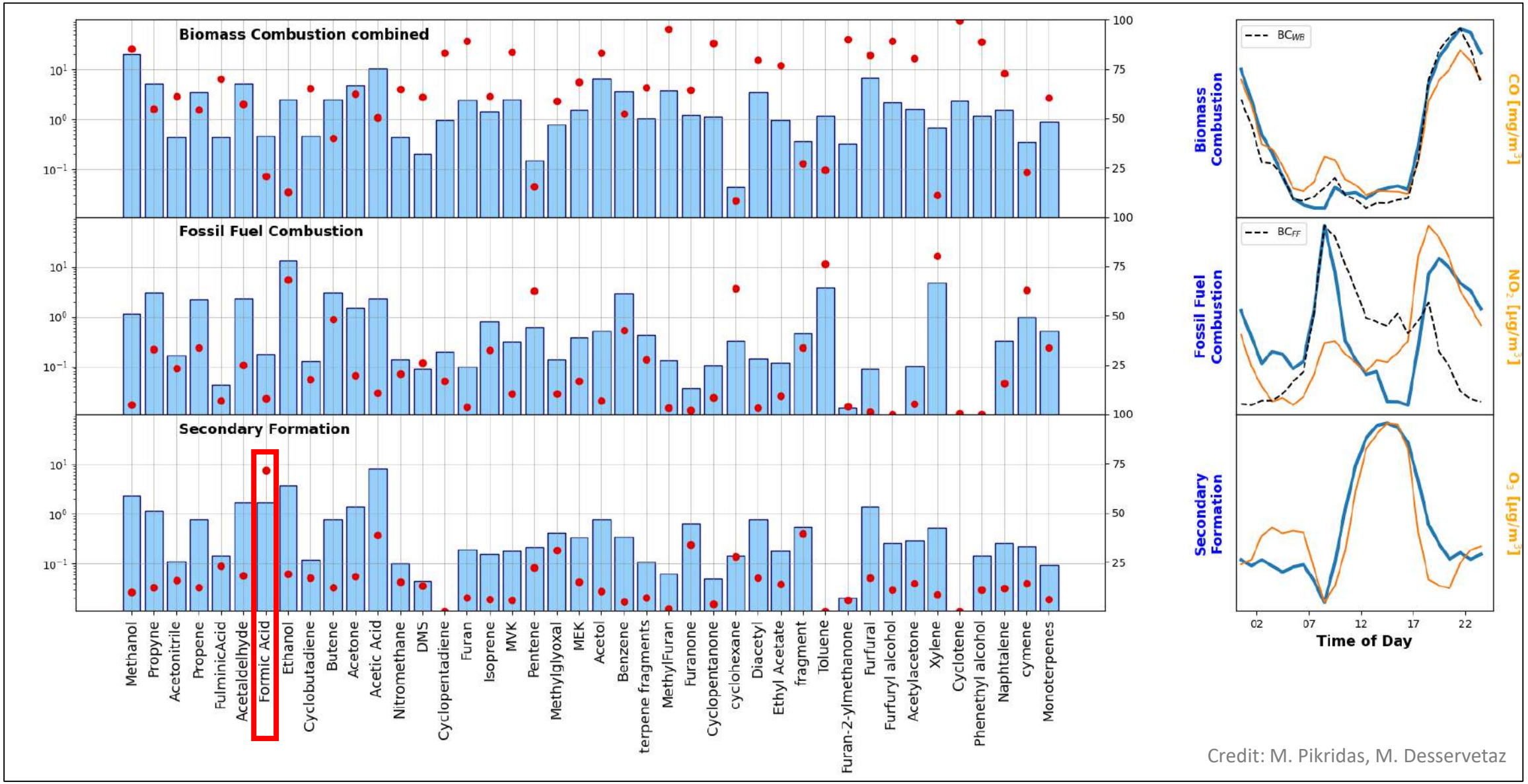
The atomic age would mark the start of the current geologic time unit, if proposal receives final approval

By Meera Subramanian, Nature magazine on May 22, 2019



Hansen et al., Earth Sys. Dynam.,2017

Positive Factorization Matrix (PMF)



Credit: M. Pikridas, M. Desservetaz