

# Natural and Anthropogenic Emission

# Global emissions to the atmosphere (Tg a<sup>-1</sup>)

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	—	32	—	5	—	55
CO	80	460	20	610	—	—	—	1170
Methane	190	50	—	290	—	—	—	530
Isoprene	520	—	—	—	—	—	—	520
SO <sub>2</sub> (as S)	—	1	—	57	10	—	—	68
Ammonia	3	6	8	45	—	—	—	62
Black carbon (as C)	—	11	—	7	—	—	—	18
Dust	—	—	—	—	—	—	1500	1500
Sea salt	—	—	—	—	—	—	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.

Missing: nonmethane  
VOCs beside isoprene

Brasseur and Jacob, 2017

# Terrestrial Biogenic Emissions

Biological organisms emit a wide range of volatile compounds through growth, metabolism, and decay.

Photosynthesis and respiration are dominant processes.

Photosynthesis converts CO<sub>2</sub> to molecular oxygen and releases volatile organic by-products (VOCs).

# Terrestrial Biogenic Emissions

## Methane

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	—	32	—	5	—	55
CO	80	460	20	610	—	—	—	1170
<b>Methane</b>	<b>190</b>	<b>50</b>	<b>—</b>	<b>290</b>	<b>—</b>	<b>—</b>	<b>—</b>	<b>530</b>
Isoprene	520	—	—	—	—	—	—	520
SO <sub>2</sub> (as S)	—	1	—	57	10	—	—	68
Ammonia	3	6	8	45	—	—	—	62
Black carbon (as C)	—	11	—	7	—	—	—	18
Dust	—	—	—	—	—	—	1500	1500
Sea salt	—	—	—	—	—	—	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.

# Global budget of methane ( $\text{CH}_4$ )



*Rate,  $\text{Tg CH}_4 \text{ yr}^{-1}$ ;  
best estimate and range of  
uncertainty*



Sources, natural	160 (75–290)
Wetlands	115 (55–150)
Termites	20 (10–50)
Other	25 (10–90)
Sources, anthropogenic	375 (210–550)
Natural gas	40 (25–50)
Livestock (ruminants)	85 (65–100)
Rice paddies	60 (20–100)
Other	190 (100–300)
Sinks	515 (430–600)
Tropospheric oxidation by OH	445 (360–530)
Stratosphere	40 (30–50)
Soils	30 (15–45)
Accumulation in atmosphere	37 (35–40)



**Lifetime: 8-10 years**

# Terrestrial Biogenic Emissions

## Methane

The main natural source of methane is wetlands, where bacteria reduce organic carbon to methane under anaerobic conditions.

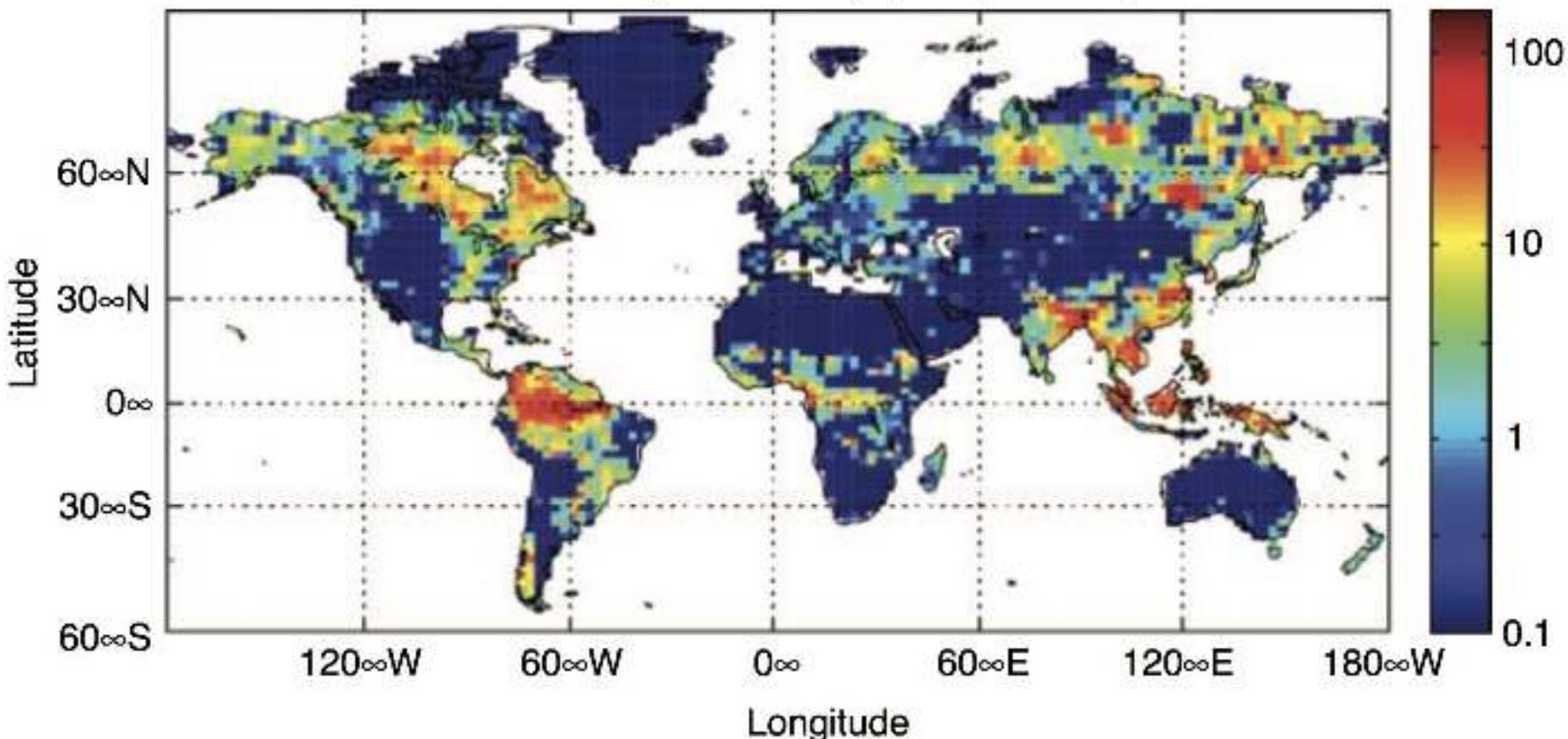
Some of that methane is oxidized as it rises to the surface and encounters aerobic waters, while the rest escapes to the atmosphere.

# Terrestrial Biogenic Emissions

## Methane

270 Tg CH<sub>4</sub> a<sup>-1</sup>

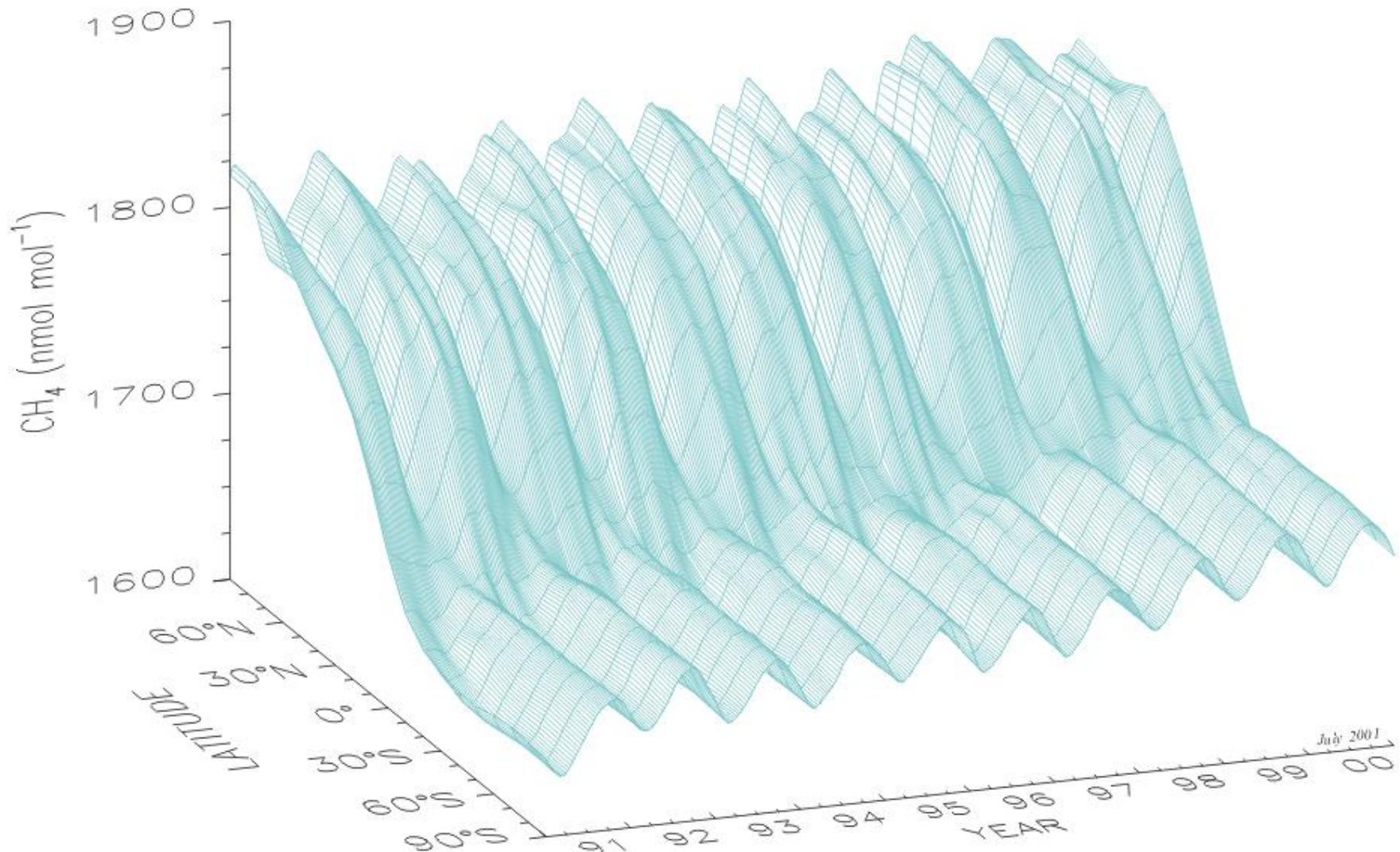
Net CH<sub>4</sub> emissions (mg CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>)



Annual emission of methane from wetlands (Riley et al., 2011)

# Global distribution of methane

NOAA/CMDL surface air measurements



$[\text{CH}_4] \approx 1700 \text{ ppbv}$  commonly used

# **Terrestrial Biogenic Emissions**

## **Nonmethane volatile organic compounds**

### **(BVOC)**

Terrestrial plants are the largest global source of NMVOCs.

Major species emitted by plants include isoprene, terpenes, sesquiterpenes, alkenes, carbonyls, and alcohols.

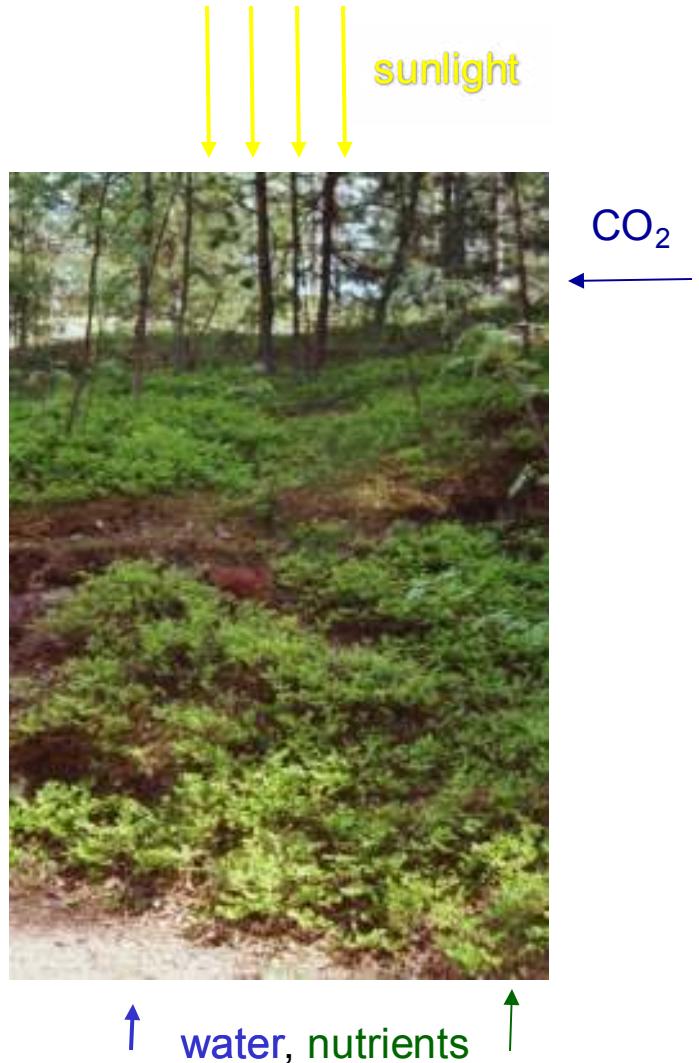
They may be emitted as by-products of photosynthesis, as responses to injury, and from metabolism and decay.

Emission fluxes depend on plant type, life stage (phenology), and foliage density; on radiative and meteorological variables within the canopy; and on external perturbations such as cutting, air pollution, and insect infestation.

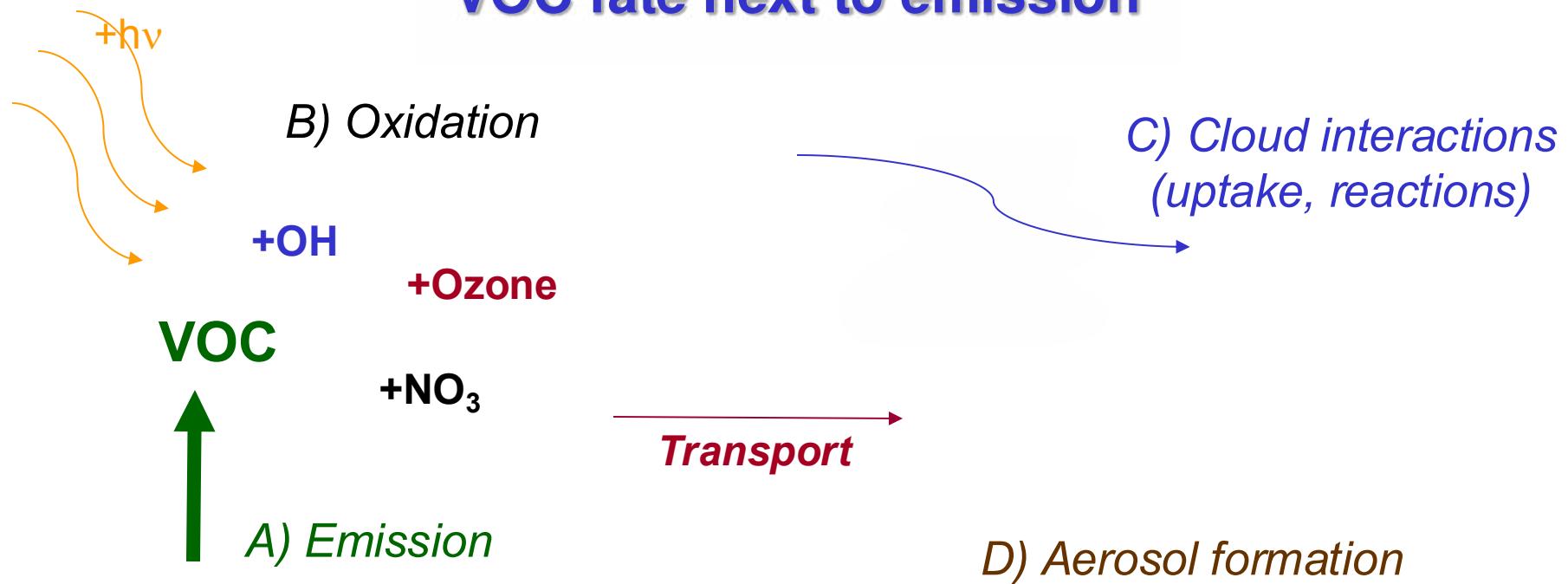
# Plants uptake and emission behaviour

To survive a plant requires water, CO<sub>2</sub>, nutrients and solar radiation

1. Goal: uptake of sufficient CO<sub>2</sub> diluted in ambient air
2. Goal: gain of sufficient water minimizing the loss at the needles/leaves
3. Goal: uptake of sufficient sunlight to get energy for all processes (growth, conversion of CO<sub>2</sub> to O<sub>2</sub>), but minimizing energy loss at the surfaces and preventing overheating.
4. Goal: uptake of nutrients from the soil level mainly for growth.
5. Goal: preventing damages caused by insects, herbivores, draught and hazardous chemicals (stress factors)



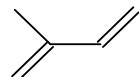
## VOC fate next to emission



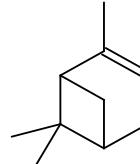
# Biogenic volatile organic compounds (VOCs): Overview

- **Reactive VOCs**

Isoprene ( $C_5H_8$ )

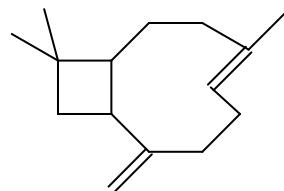


Monoterpenes ( $C_{10}H_{16}$ )



e.g.  $\alpha$ -pinene

Sesquiterpenes ( $C_{15}H_{24}$ )



e.g.  $\beta$ -caryophyllene

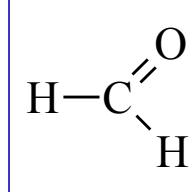
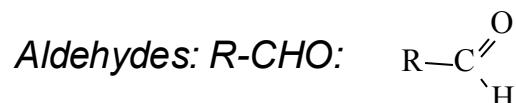
Oxygenates



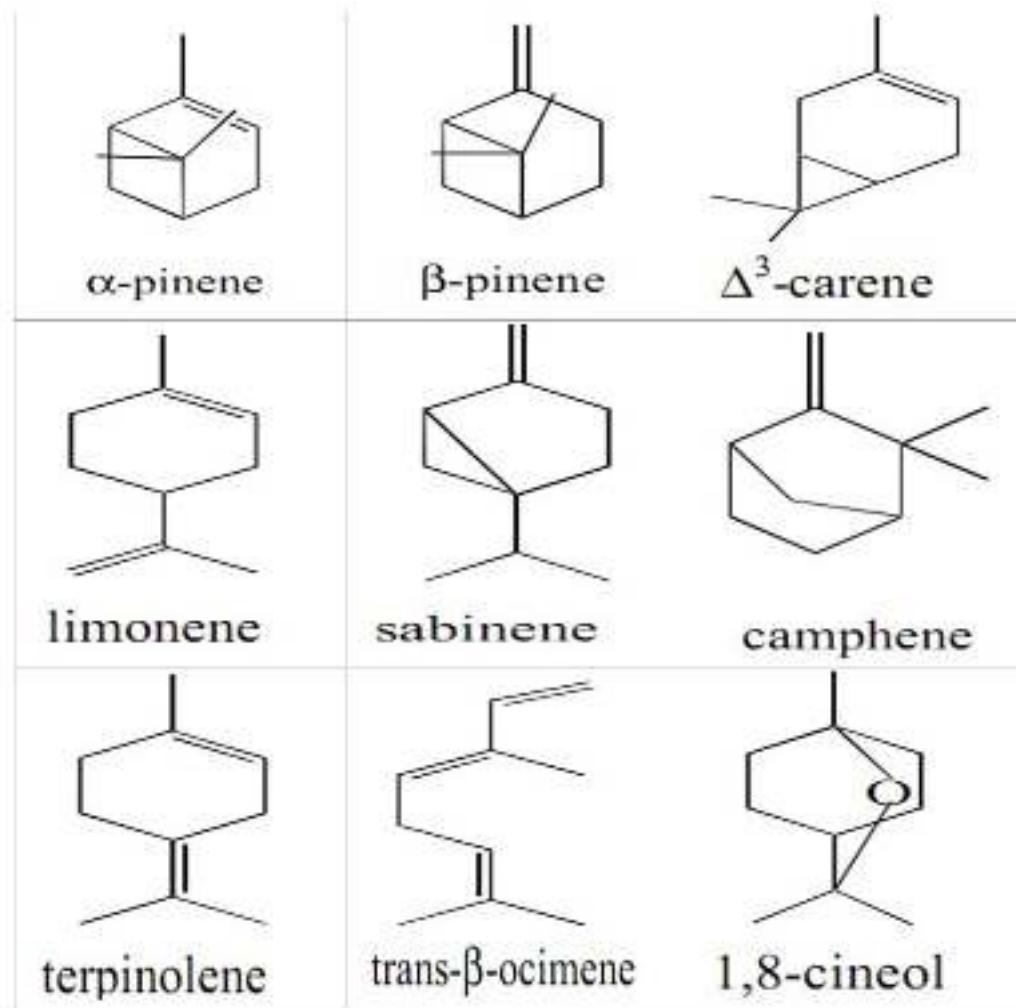
e.g. linalool

- **Less reactive VOCs**

- Carbonyl compounds (e.g. formaldehyde HCHO)



# Chemical structures of typical monoterpene in the emission of the biosphere



Important

All have same molar mass

But different reaction rates with OH, O<sub>3</sub> and NO<sub>3</sub>

# Global biogenic VOCs



## Biogenic Volatile Organic Compounds: Annual Global Total Emission > 1.5 Gt



NCAR

Formic acid, acetic acid, ethane, toluene, camphene, terpinolene,  $\alpha$ -terpinolene,  $\alpha$ -thujene, cineole, ocimene,  $\gamma$ -terpinene, bornyl acetate, camphor, piperitone, linalool, tricyclene: 0.04 to 0.2% each

$\beta$ -pinene, d-carene, hexenal, hexenol, hexenyl-acetate, propene, formaldehyde, hexanal, butanone, sabinene, limonene, methyl butenol, butene,  $\beta$ -carophylene,  $\beta$ -phellandrene, p-cymene, myrcene: 0.2 to 1% each

Acetaldehyde, acetone, ethene, ethanol,  $\alpha$ -pinene: 1 to 7% each

Isoprene  
(C<sub>5</sub>H<sub>8</sub>)  
40%

Methanol  
(CH<sub>3</sub>OH)  
15%

Alex Guenther

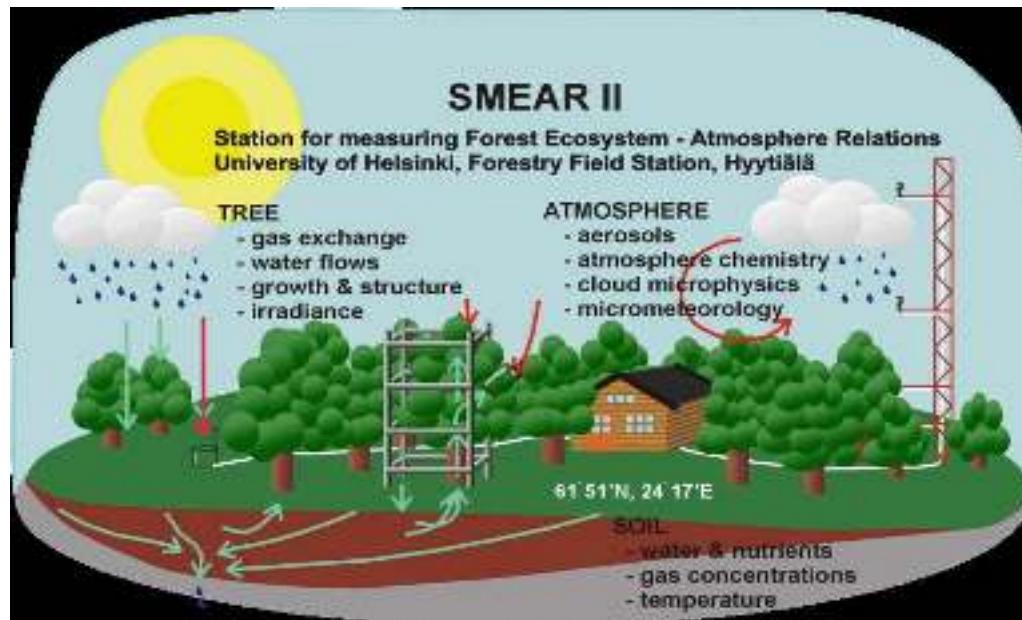
iLEAPS meeting- September 29, 2003

*...but take care, the most reactive VOCs (e.g. sesquiterpenes) are not included really!*

# Emission inventory

## Emission measurements (campaign or monitoring)

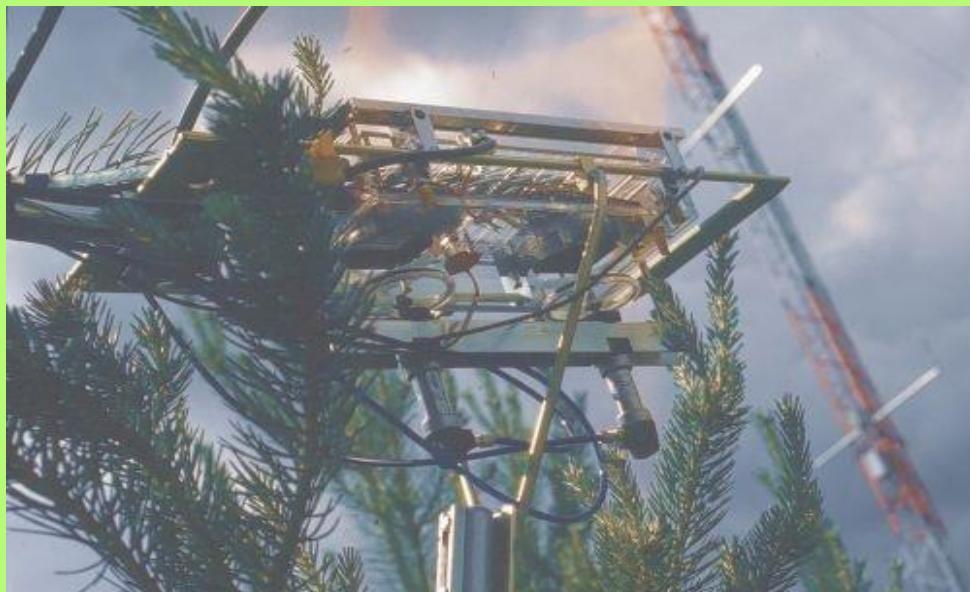
- A) direct: Measurement at the emission source
- B) indirect: Relaxed Eddy Accumulation (REA)-Systeme



Hytälä,  
Universität Helsinki

## a) Direct measurements

- **Emission measurements in the canopy**
  - **Enclosure of a certain part from the tree in a cuvette or teflon bag**
  - **Sampling over a certain time period on tenax tubes**
  - **Or online measurement with instruments of high temporal and high sensitivity**



[http://www.atm.helsinki.fi/S  
MEAR/index.php?option=co  
m\\_content&task=view&id=2  
2&Itemid=56](http://www.atm.helsinki.fi/SMEAR/index.php?option=com_content&task=view&id=22&Itemid=56)

## b) Indirect measurements

- Possible for large-scale areas of homogeneous vegetation
- Measurements of the individual compounds inside and above the forest
- Calculation of the exchange coefficients

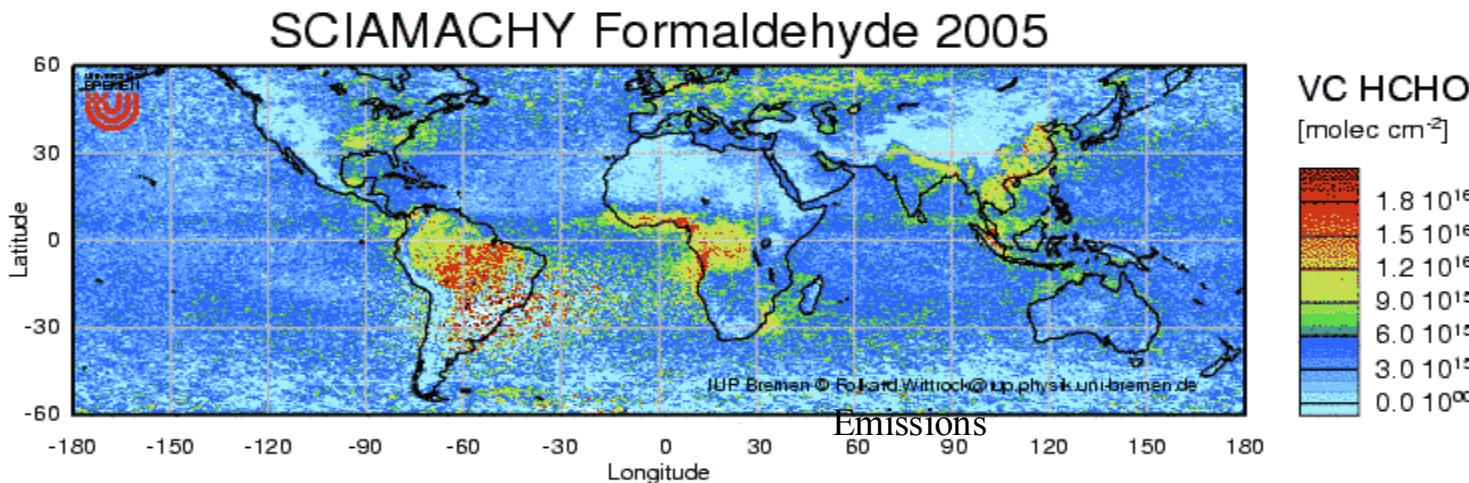
➤ **Relaxed Eddy Accumulation Systeme:**

- Vegetation considered as a box
- Up and down-ward transport will be calculated based on the vertical wind gradients



# Emission inventory: Satellites

- Advantages:
  - Global coverage with a quite high temporal and spatial resolution as input or evaluation for the global models
  - No man power needed for the measurements
- Problems:
  - Clouds disable the use of the measurements
  - Vertical distribution very difficult at the moment – but maybe better in future with the next generation of the satellites



# Description of global VOC emissions (isoprene, terpenes)

From database tables (EMEP or GEIA) obtained from measurements or by dynamic description.

## Dynamic description

Surface emission flux  $F_{\text{vegetation}}$  from the vegetation [Guenther *et al.* (1995)]:

$$F_{\text{vegetation}} = D_m \cdot \varepsilon \cdot \gamma \cdot \delta$$

$D_m$ : foliar density (kg dry matter  $\text{m}^{-2}$ )

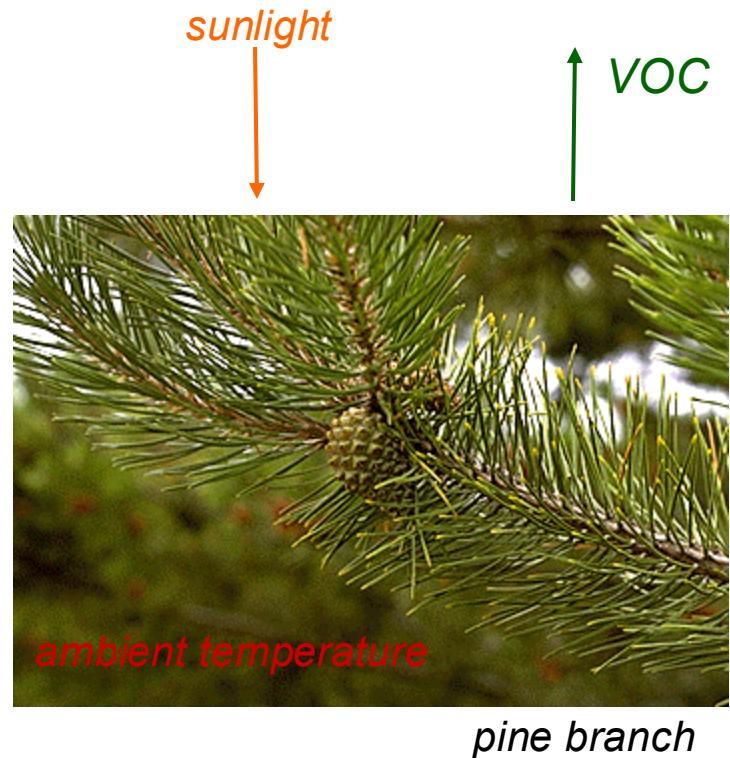
→ *e.g. amount of leaves/needles per surface area*

$\varepsilon$ : ecosystem dependent emission factor at  $T = 30 \text{ }^{\circ}\text{C}$  and  $\text{PAR} = 1000 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$   
( $\mu\text{g C m}^{-2} \text{ h}^{-1}$ )

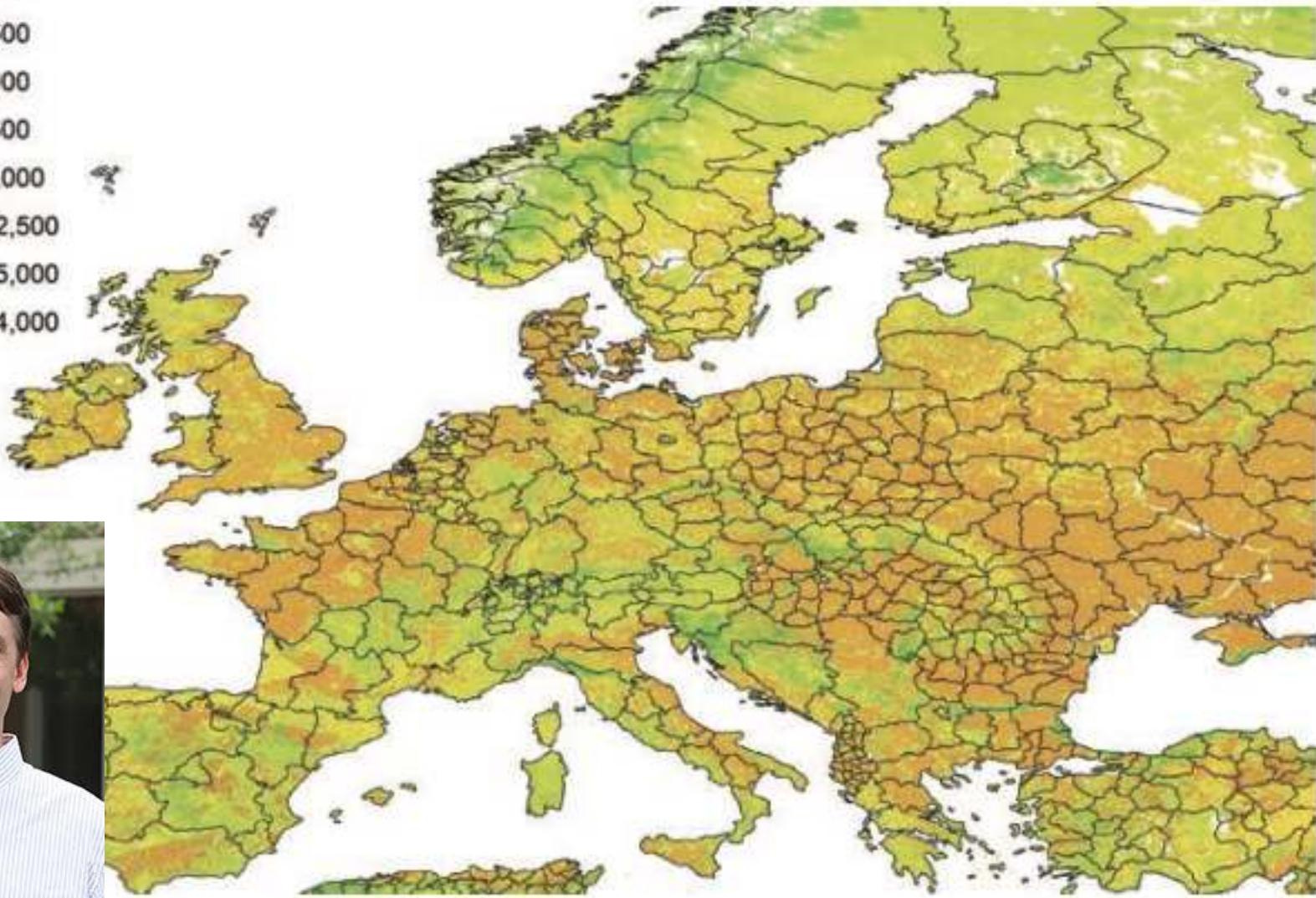
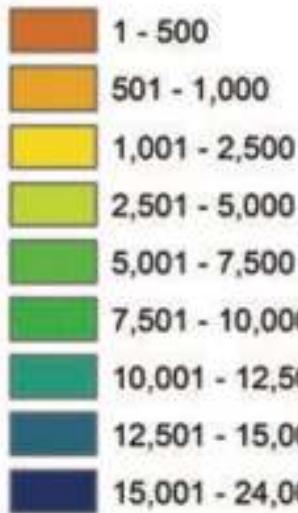
→ *amount of emission at standard conditions*

$\gamma$ : adjustment factor for dependence on temperature and light – emission activity

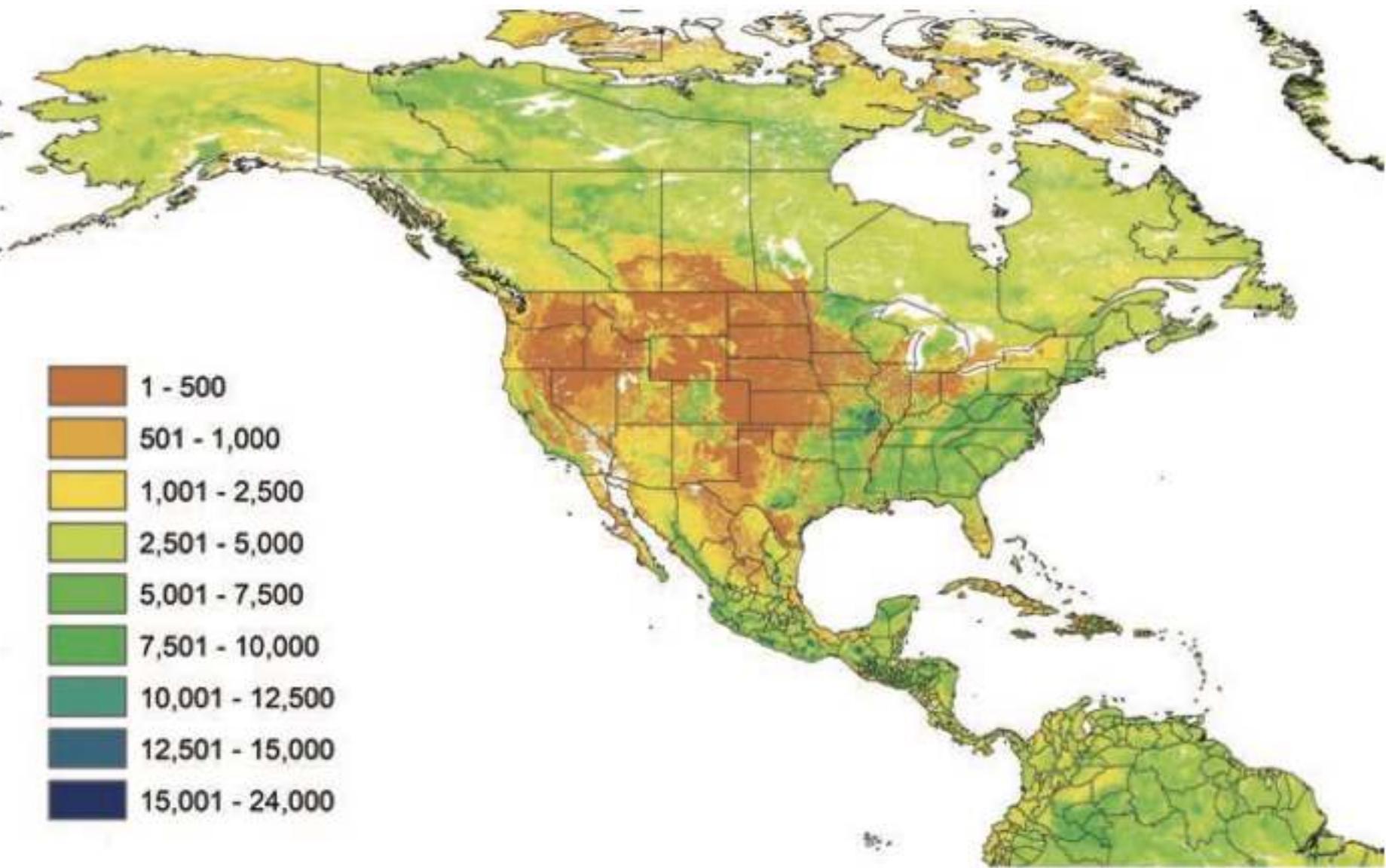
$\delta$ : emission activity factor for long term controls



# Ecosystem dependent emission factors [ $\mu\text{g C m}^{-2} \text{ h}^{-1}$ ] for isoprene (A. Guenther and C. Wiedenmeyer)



# Ecosystem dependent emission factors [ $\mu\text{g C m}^{-2} \text{ h}^{-1}$ ] for isoprene (A. Guenther and C. Wiedenmeyer)

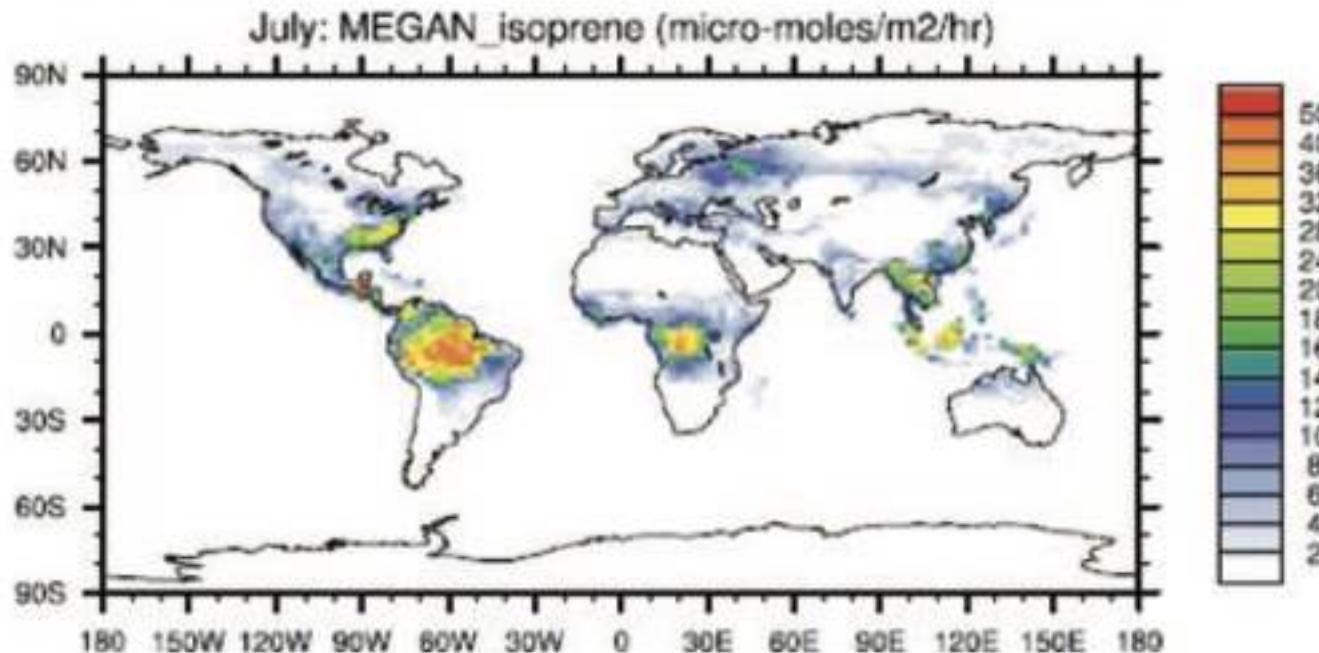
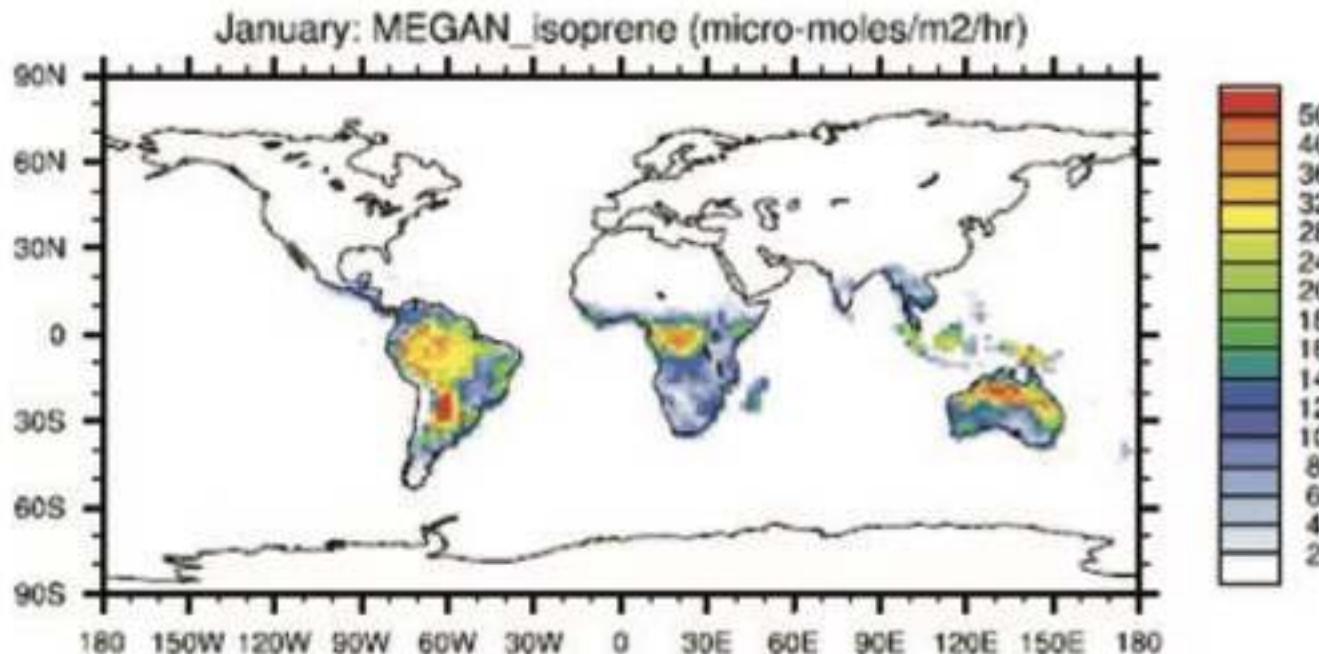


## **δ: emission activity factor for long term controls**

**Correction factor for:**

- **Soil moisture**
- **Leaf age**
- **Temperature and PAR averaged over the day and last 10 days**

Global  
distribution  
of isoprene  
emission in  
January  
and July  
(Guenther  
et al. 2012)

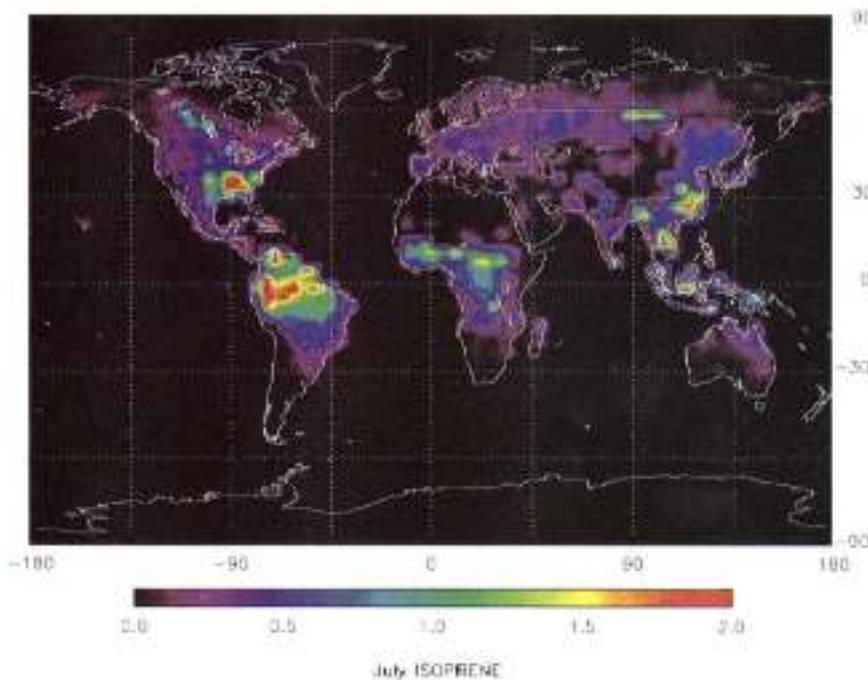
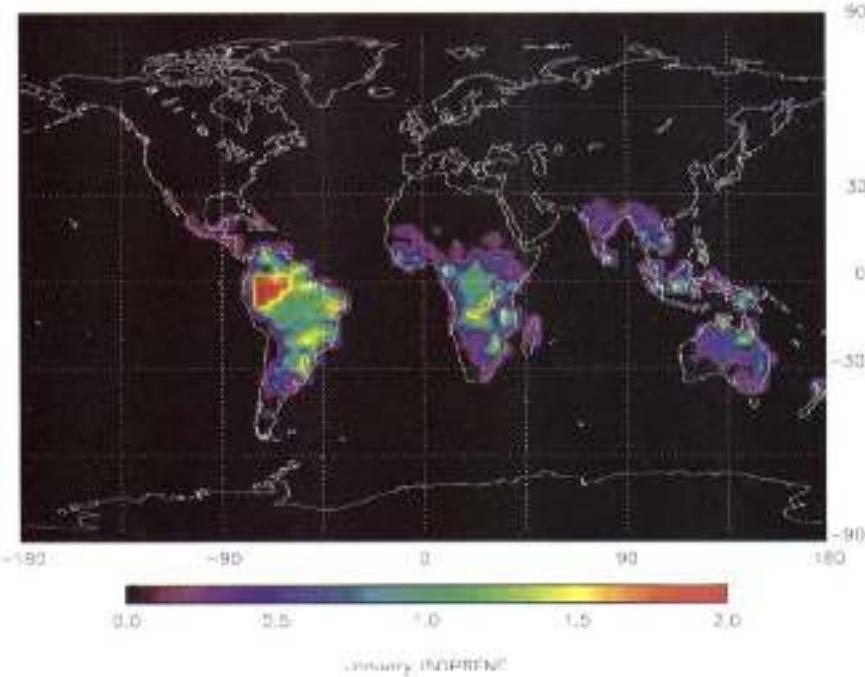


# Isoprene ( $C_5H_8$ ) emission

Estimated annual emission on the global scale:

506 Tg C [Guenther *et al.*, 1995]

Isoprene emissions depend on both, **sunlight** and **temperature**:



Emission in  $g\text{ C m}^{-2}\text{ month}^{-1}$  [Guenther *et al.*, 1995]

# Monoterpene ( $C_{10}H_{16}$ ) emissions

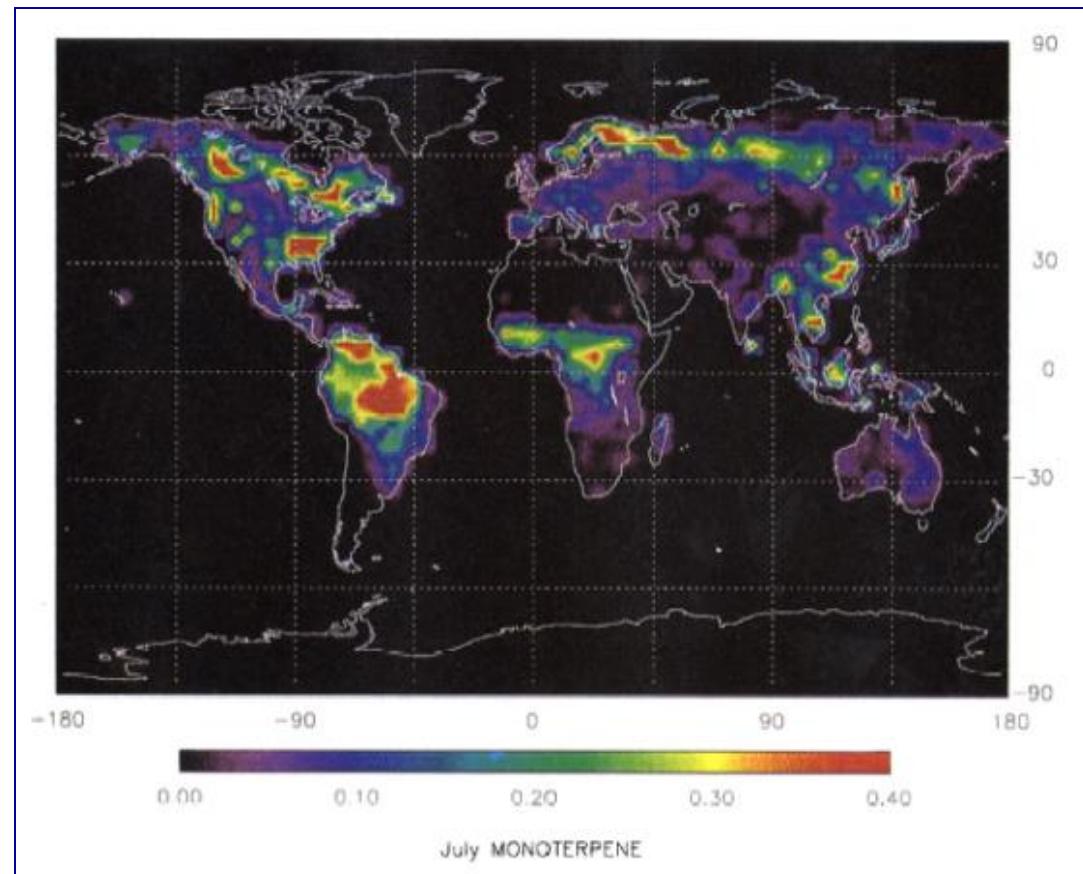
Estimated annual emission on the global scale:

127 Tg C [Guenther *et al.*, 1995]

Monoterpene emissions were believed to depend on **temperature** only, but we know nowadays this is not correct for all monoterpenes and plants

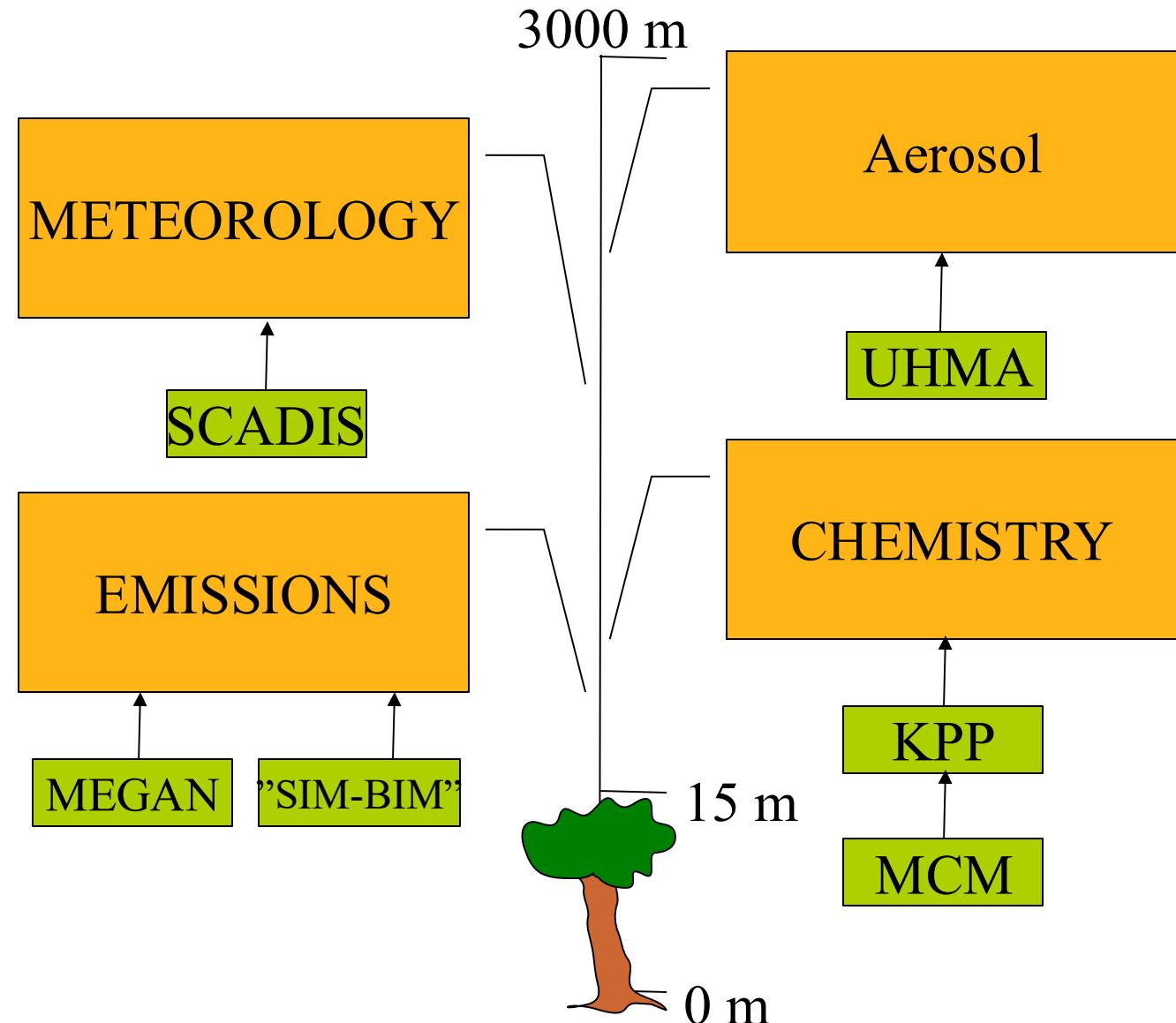
$$\gamma = \exp(\beta \cdot (T - T_s))$$

$$\beta = 0.09 \text{ } K^{-1}, T_s = 303.15 \text{ } K$$

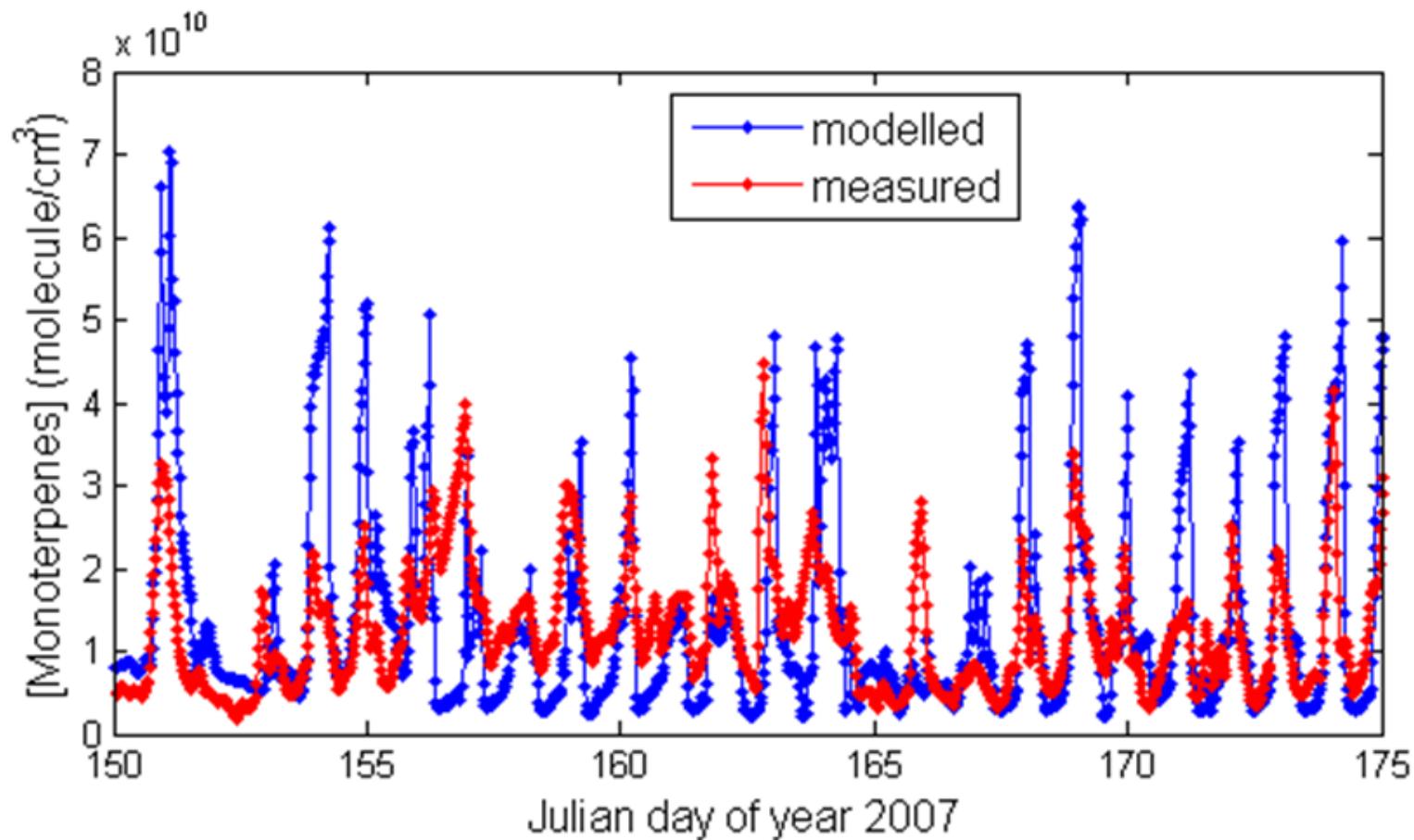


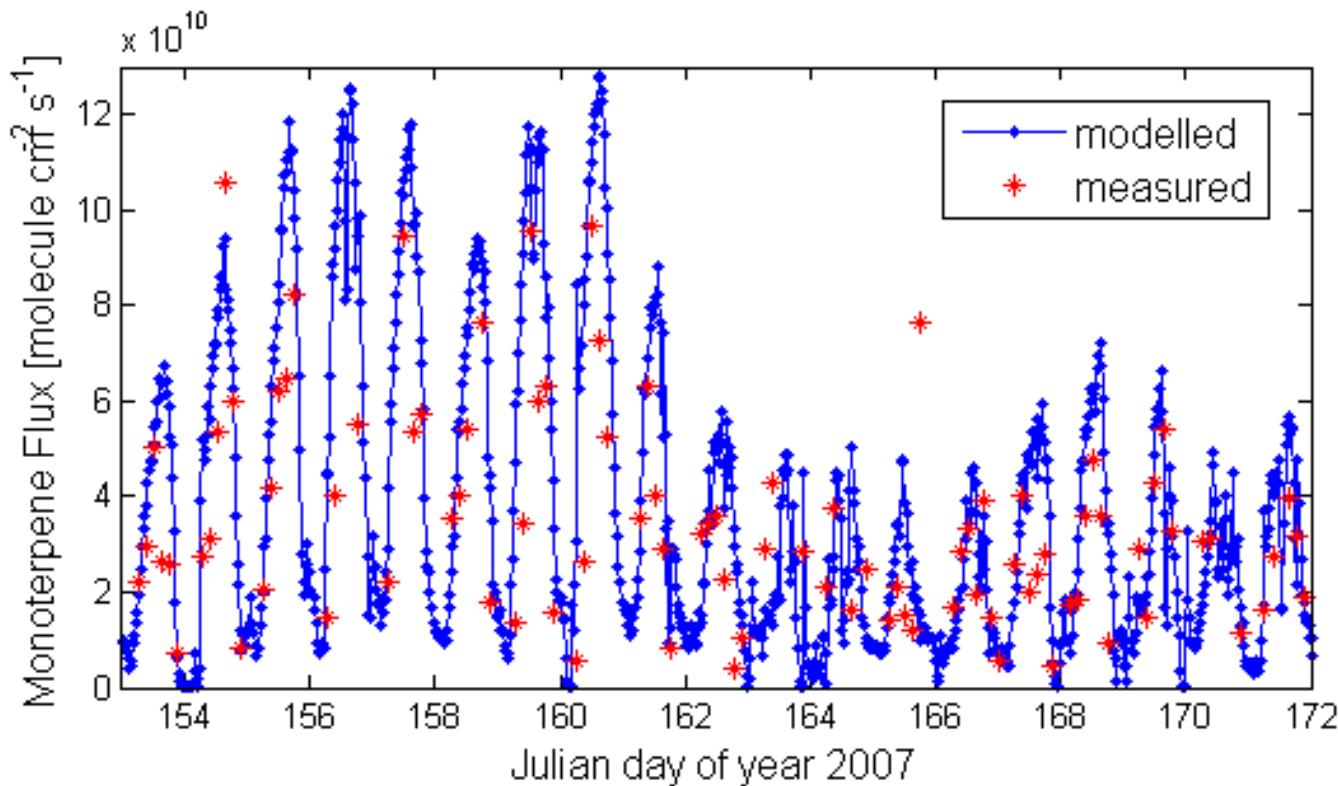
No emissions from the Guenther *et al.* approach during winter in the Northern hemisphere, but there are.

# SOSAA is a combination of several models

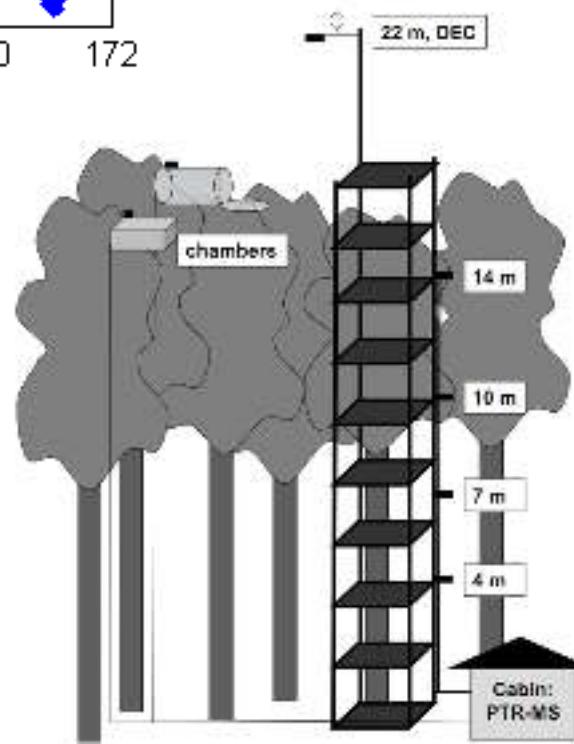


# Modelled (MEGAN) and measured monoterpene concentrations at 4 m in June 2007 for SMEAR II

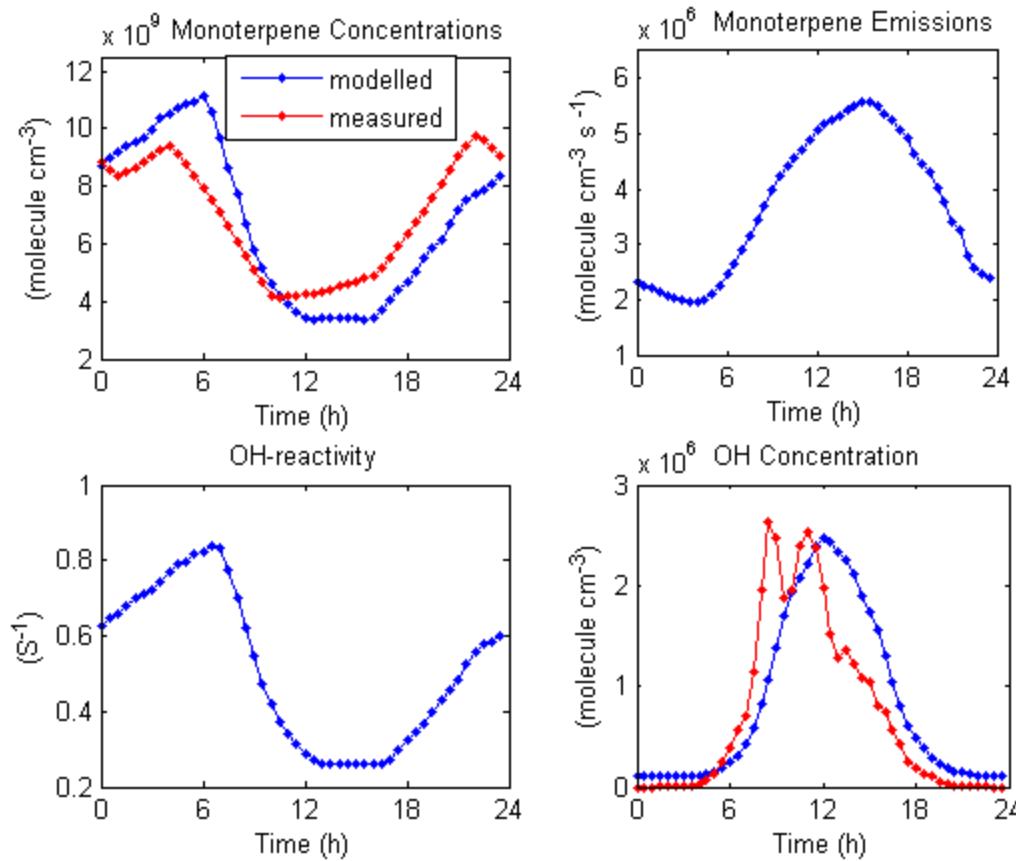


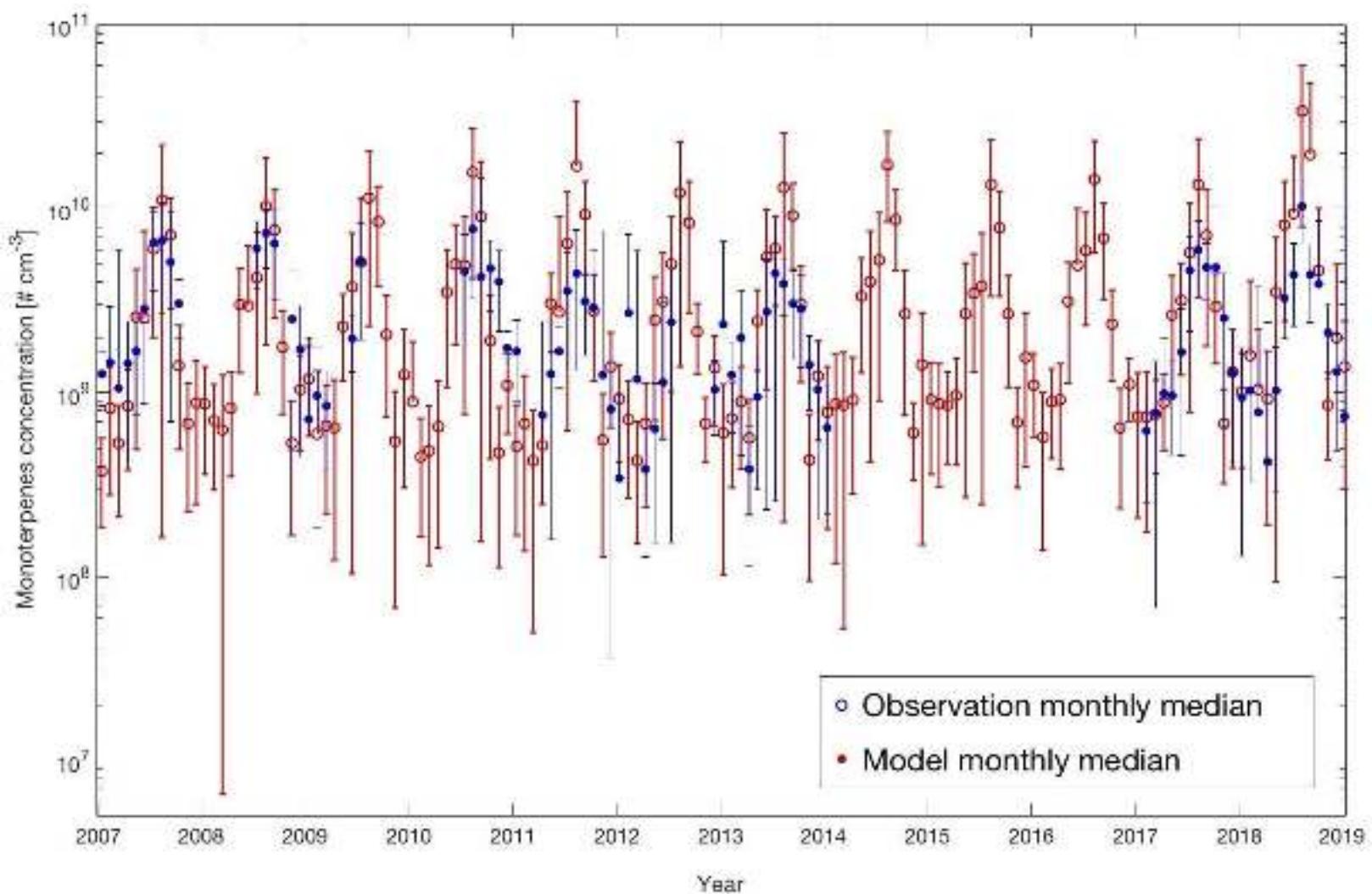


**Modelled (MEGAN) and  
measured monoterpene fluxes at  
22 m in June**

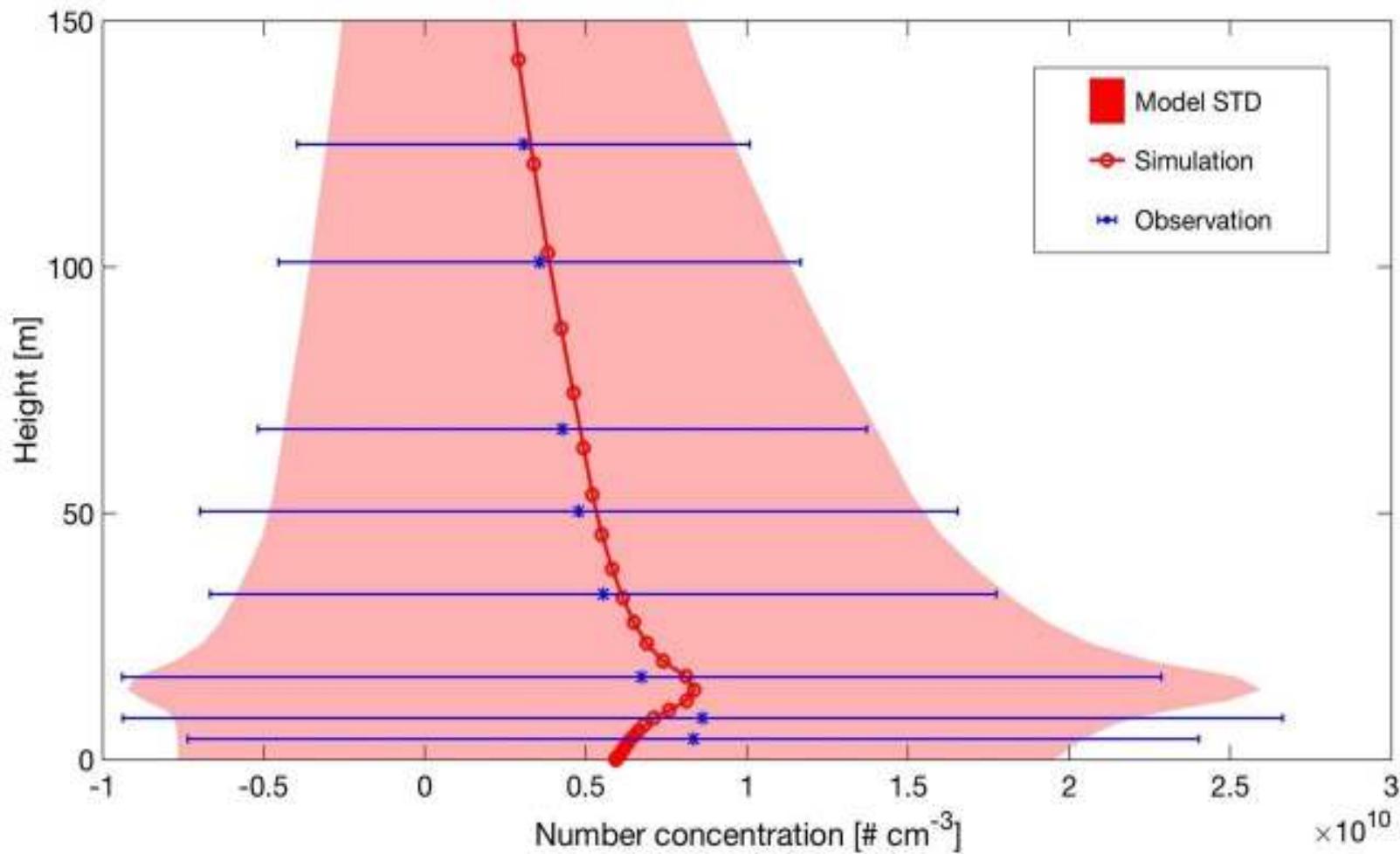


# Modelled and measured diurnal variations at 14 m for the summer of year 2007



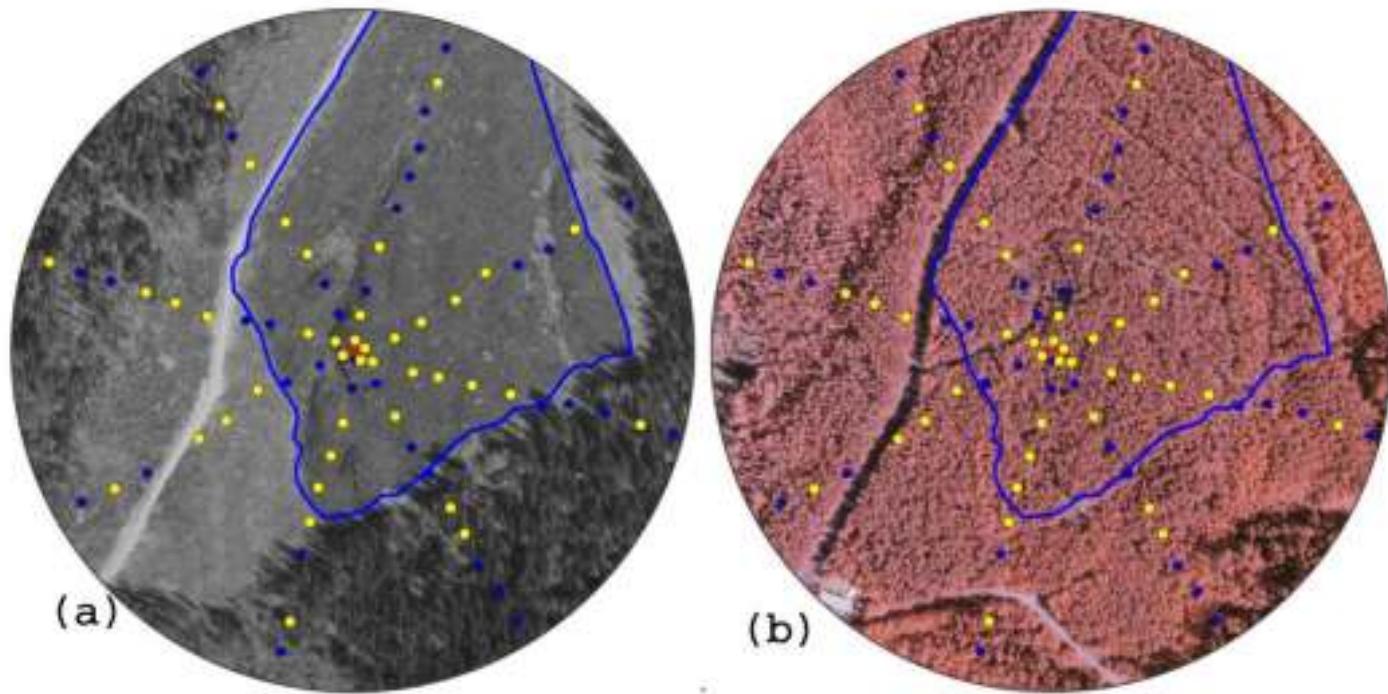


*Measured and modelled monthly median values of monterpene concentrations from 2007 to 2018 for the height interval 20m-40m. The  $\pm 1$  standard deviation for both data sets are shown as vertical bars.*



*Vertical profiles of measured and modelled monoterpenene concentrations and  $\pm 1$  standard deviations at SMEAR II, Finland averaged for the years 2007-2014 and 2017-2018.*

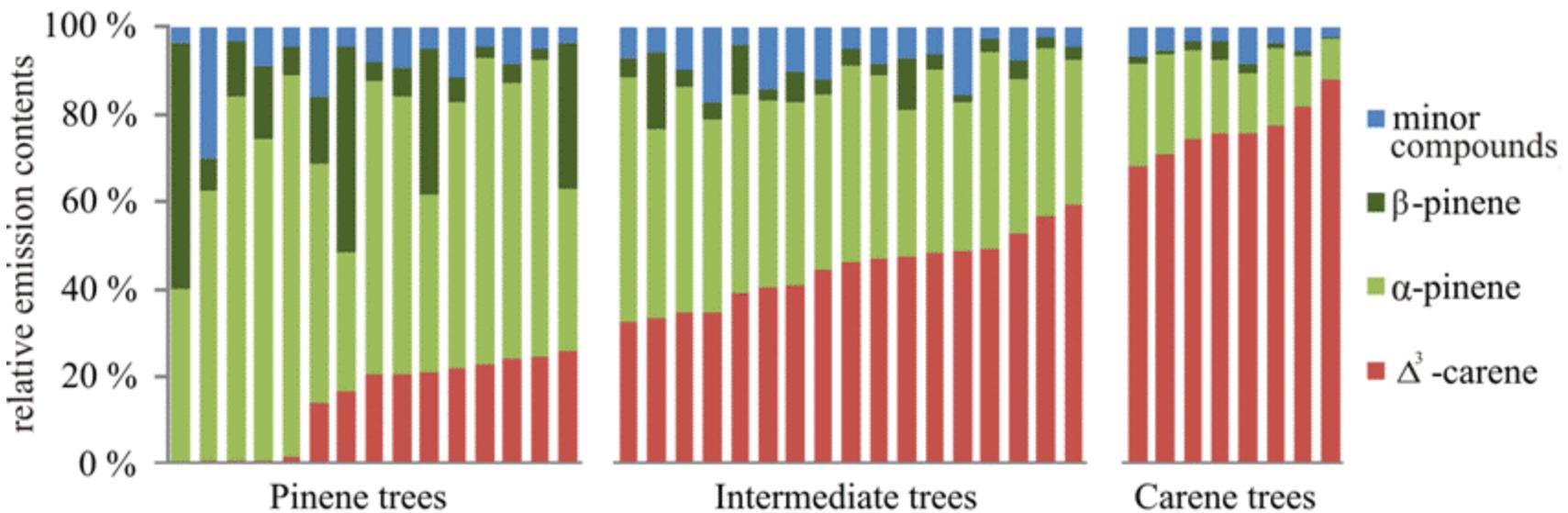
# Chemodiversity of a Scots pine stand and implications for terpene air concentrations (Bäck et al., 2012)



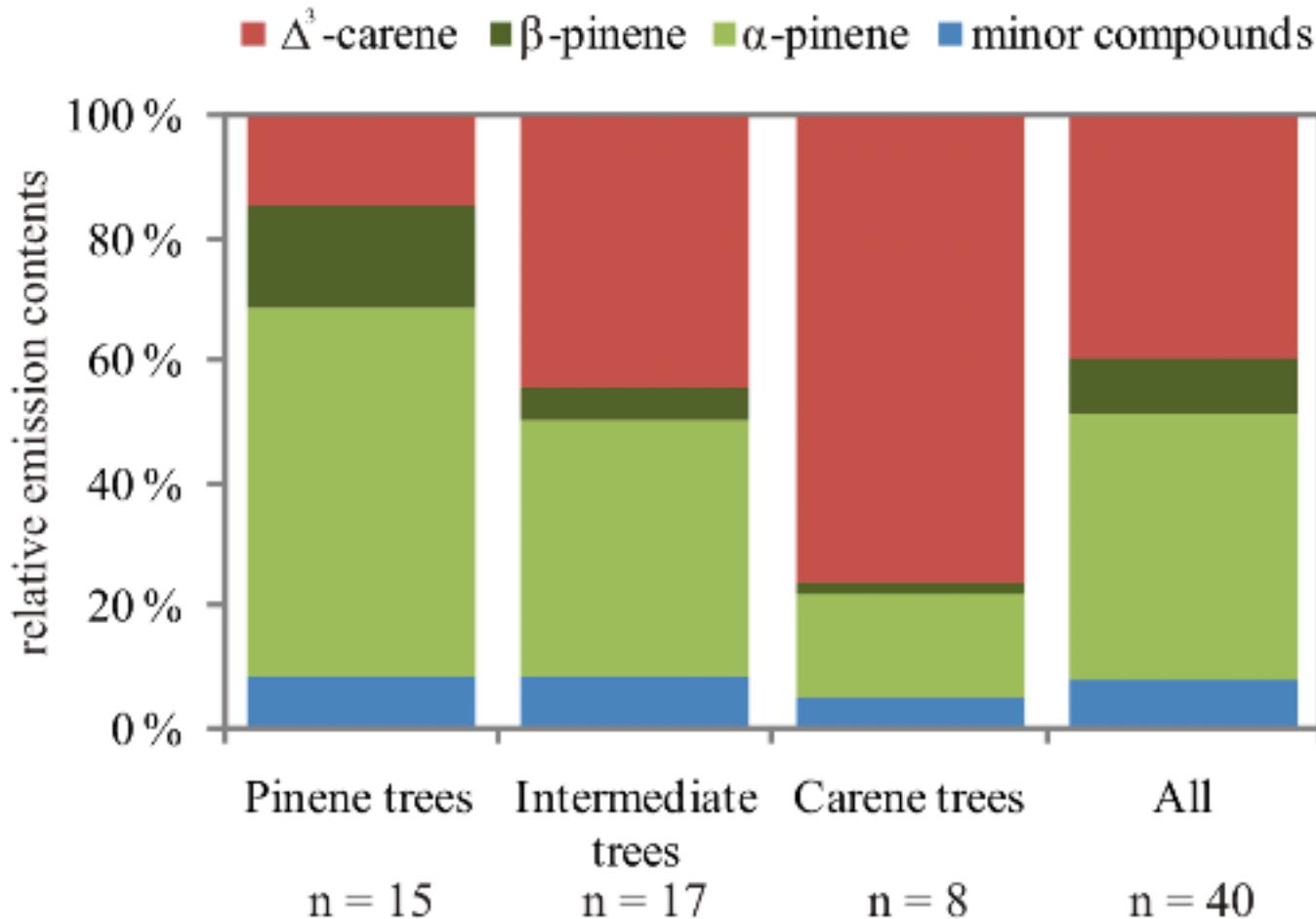
Aerial photographs of the sample area. Sampling grid is marked with blue (no sample) and yellow (sampled) circles. (a) SMEAR II stand (marked with blue line) and neighbouring stands in 1962; (b) Same stands in 1997. Red dot = mast; diameter of circle 400 m.

# Emission content of the 40 selected trees

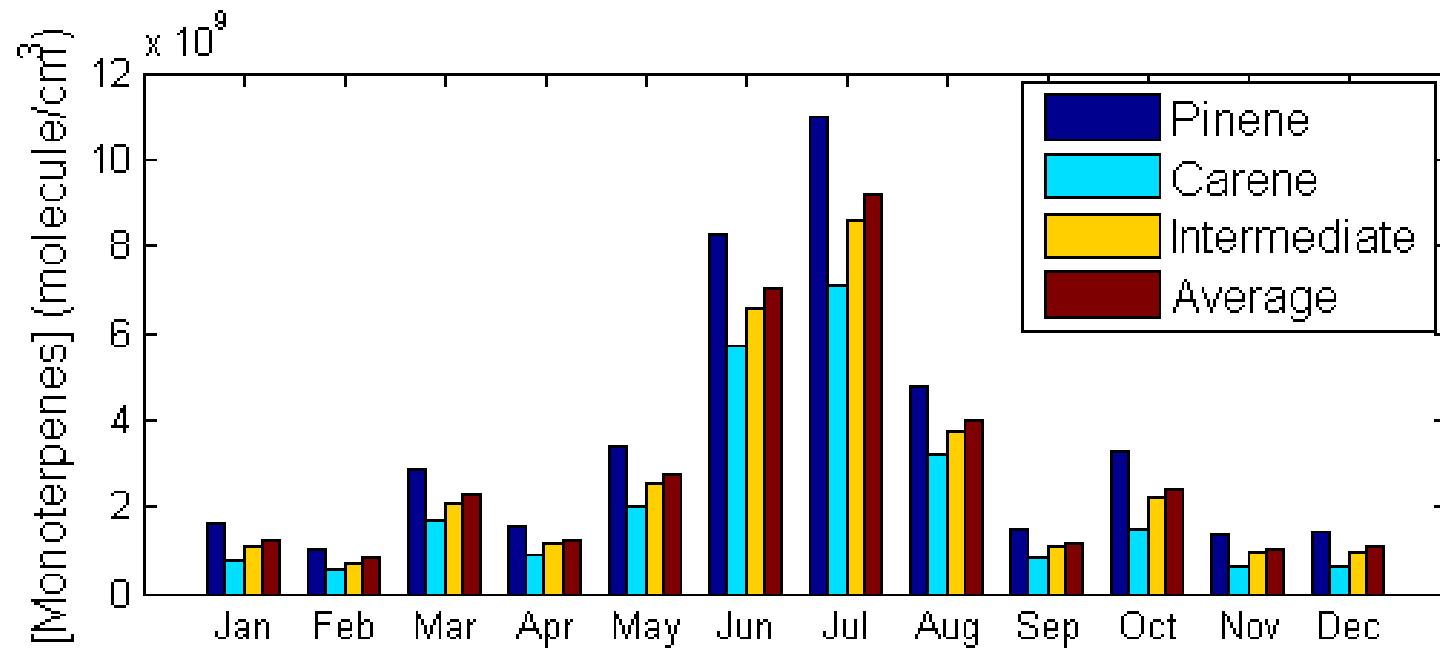
## (Bäck et al., Biogemsiences, 2012)



## Average relative emission contents of three clusters. Clustering conducted with the major emitted compounds



# Modeled monthly mean monoterpenes concentrations at 14 m for the year 2007



# Chemical reactions

Isoprene and terpenes react with OH, ozone and  $\text{NO}_3$

Compound	Chem. lifetime	Class
Isoprene	2.5 h	Isoprene
$\alpha$ -pinene	2.3 h	Monoterpene
Limonene	50 min	Monoterpene
$\beta$ -caryophyllene	1-2 min	Sesquiterpene

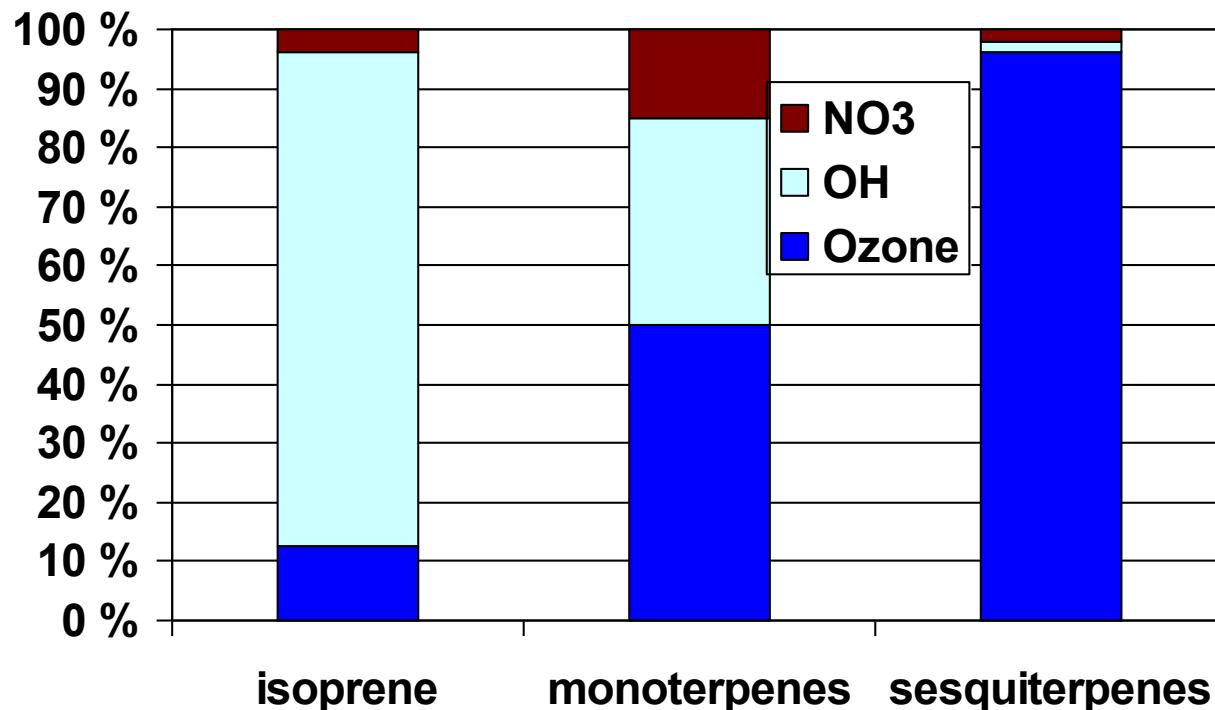
## Consequences:

Isoprene and monoterpenes are transported at least partially to the free troposphere, in convective cells at the equator up to the tropopause.

Sesquiterpenes are not. They even stay in the vicinity of the emission site.

All contribute to secondary organic aerosol formation.

# Atmospheric oxidation by ozone, OH and $\text{NO}_3$ displayed as fractions



# Terrestrial Biogenic Emissions

## Nitrogen oxides

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	–	32	–	5	–	55
CO	80	460	20	610	–	–	–	1170
Methane	190	50	–	290	–	–	–	530
Isoprene	520	–	–	–	–	–	–	520
SO <sub>2</sub> (as S)	–	1	–	57	10	–	–	68
Ammonia	3	6	8	45	–	–	–	62
Black carbon (as C)	–	11	–	7	–	–	–	18
Dust	–	–	–	–	–	–	1500	1500
Sea salt	–	–	–	–	–	–	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.

# Terrestrial Biogenic Emissions

## Nitrogen oxides

Nitrogen is essential to life and has an active biogeochemical cycle in terrestrial ecosystems.

Specialized bacteria present in all ecosystems convert atmospheric nitrogen ( $N_2$ ) to ammonia, a process called biofixation, and the resulting fixed nitrogen then cycles through the ecosystem.

Fixed nitrogen can also be directly delivered to the ecosystem by fertilizer application or by deposition of atmospheric ammonia and nitrate.

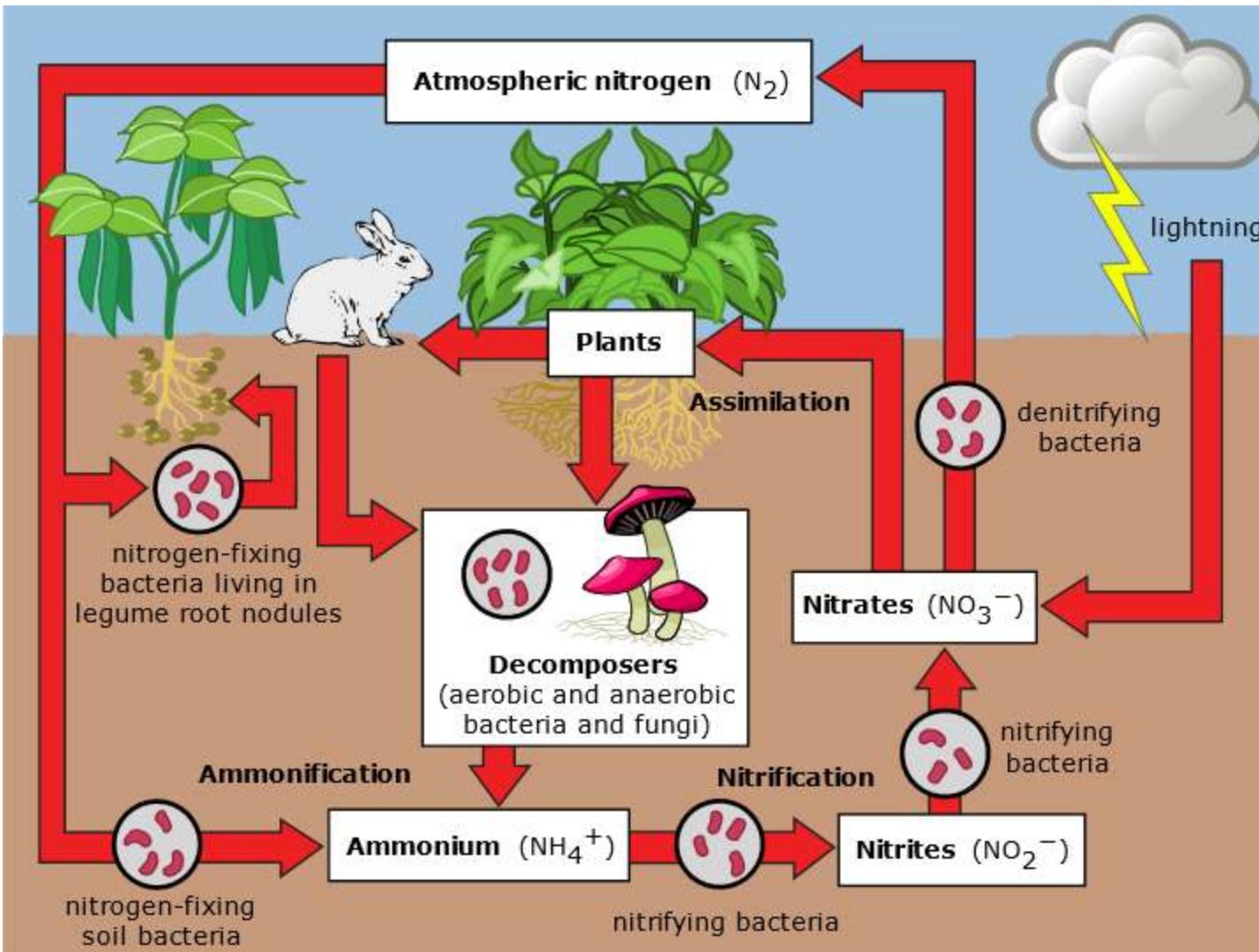
Biological processes cycle nitrogen within the ecosystem:

- Assimilation (conversion of inorganic nitrogen to biological material)
- Mineralization (conversion of organic nitrogen to inorganic forms)
- Nitrification (aerobic microbial oxidation of ammonium to nitrite ( $NO_2^-$ ) and on to nitrate ( $NO_3^-$ ))
- Denitrification (anaerobic microbial reduction of nitrate to  $N_2$ )

Volatile  $N_2O$  and  $NO$  are generated as by-products of nitrification and denitrification.

# Terrestrial Biogenic Emissions

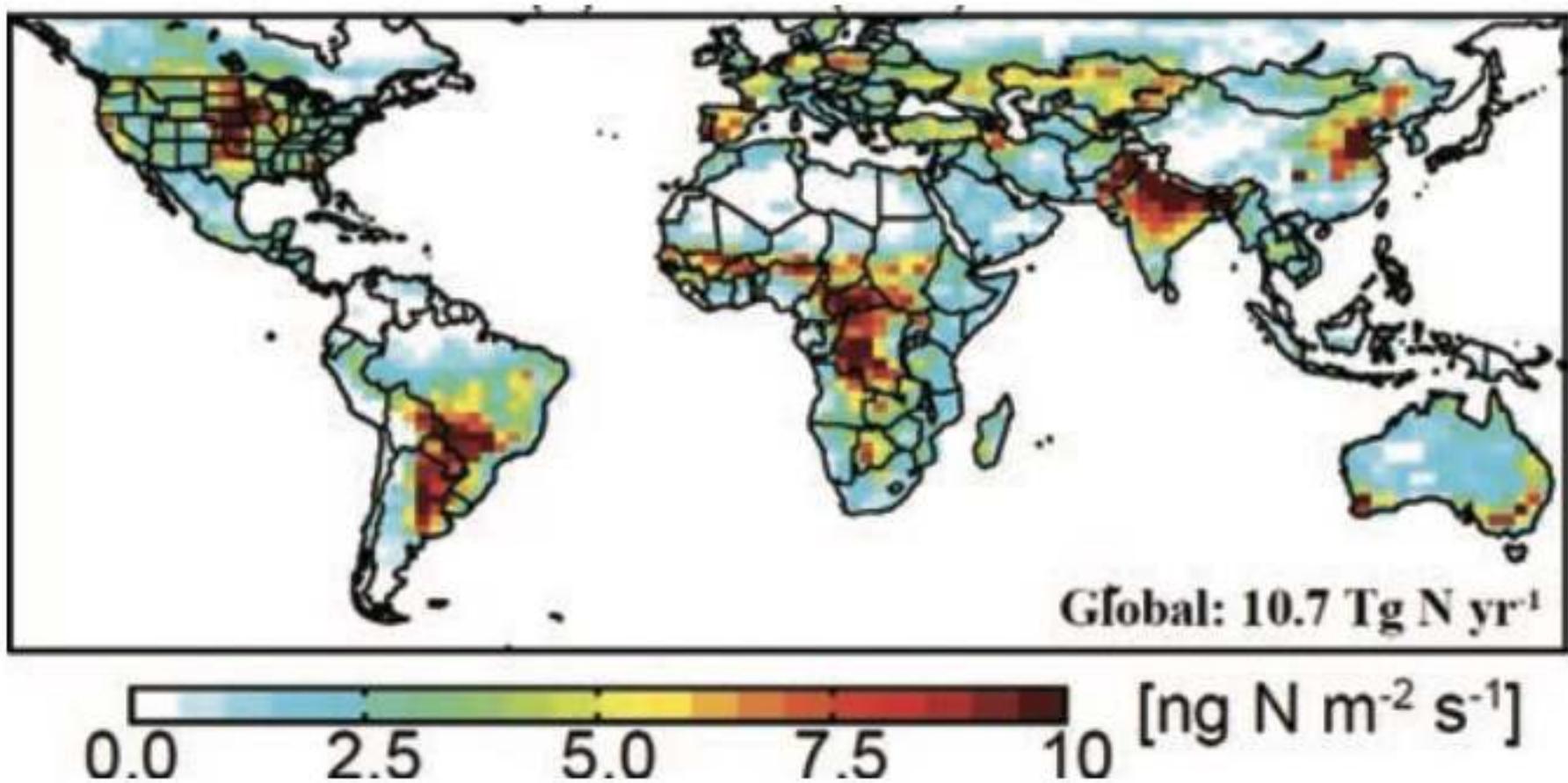
## Nitrogen oxides



Schematic representation of the flow of nitrogen through the ecosystem.

The importance of bacteria in the cycle is immediately recognized as being a key element in the cycle, providing different forms of nitrogen compounds able to be assimilated by higher organisms.

## Annual emission of NO from soils (Hudman et al. 2012)



Emissions are high in agricultural areas of northern mid-latitudes, reflecting the heavy use of fertilizer. Dry grasslands in South America and Africa also have high emissions, largely driven by the pulsing at the end of the dry season.

# Open fires

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	—	32	—	5	—	55
CO	80	460	20	610	—	—	—	1170
Methane	190	50	—	290	—	—	—	530
Isoprene	520	—	—	—	—	—	—	520
SO <sub>2</sub> (as S)	—	1	—	57	10	—	—	68
Ammonia	3	6	8	45	—	—	—	62
Black carbon (as C)	—	11	—	7	—	—	—	18
Dust	—	—	—	—	—	—	1500	1500
Sea salt	—	—	—	—	—	—	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.

# Open fires

Open fire emissions include contributions from:

- Wildfires
- Prescribed fires
- Land clearing
- Agricultural management

These emissions are often labelled in the literature as biomass burning, but that leaves ambiguity as to whether biofuels are included.

Most fires are set by humans, although some wildfires are triggered by lightning.

Even when set by humans, fires are not generally classified as “anthropogenic” in emission inventories because they may have happened anyway even without human intervention.

Fires emit mostly CO<sub>2</sub>, CO, and H<sub>2</sub>O, but also many other trace species. Emissions depend on the type of vegetation, the vegetation density, and the fire intensity.

# Open fires

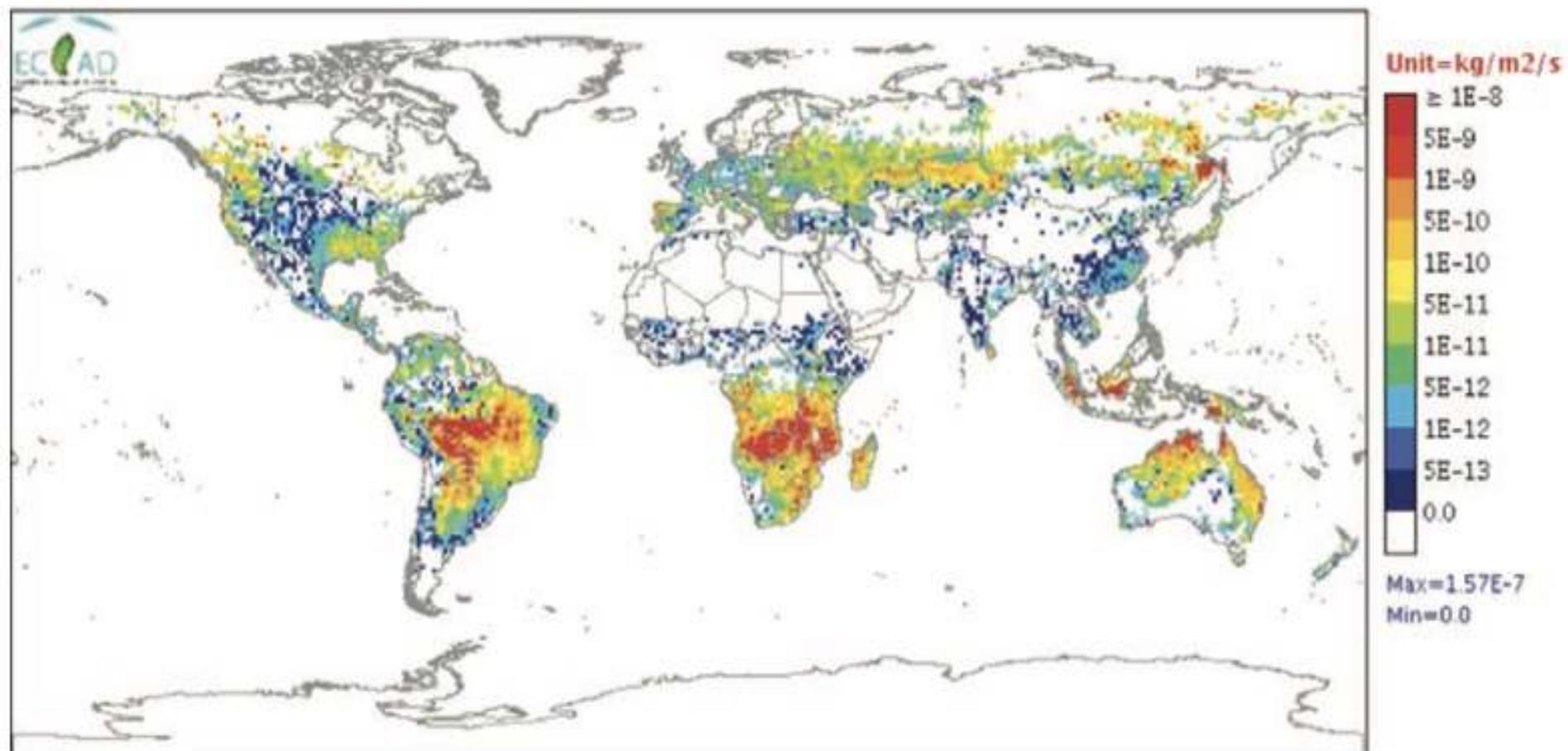
## Emission factors for open fires

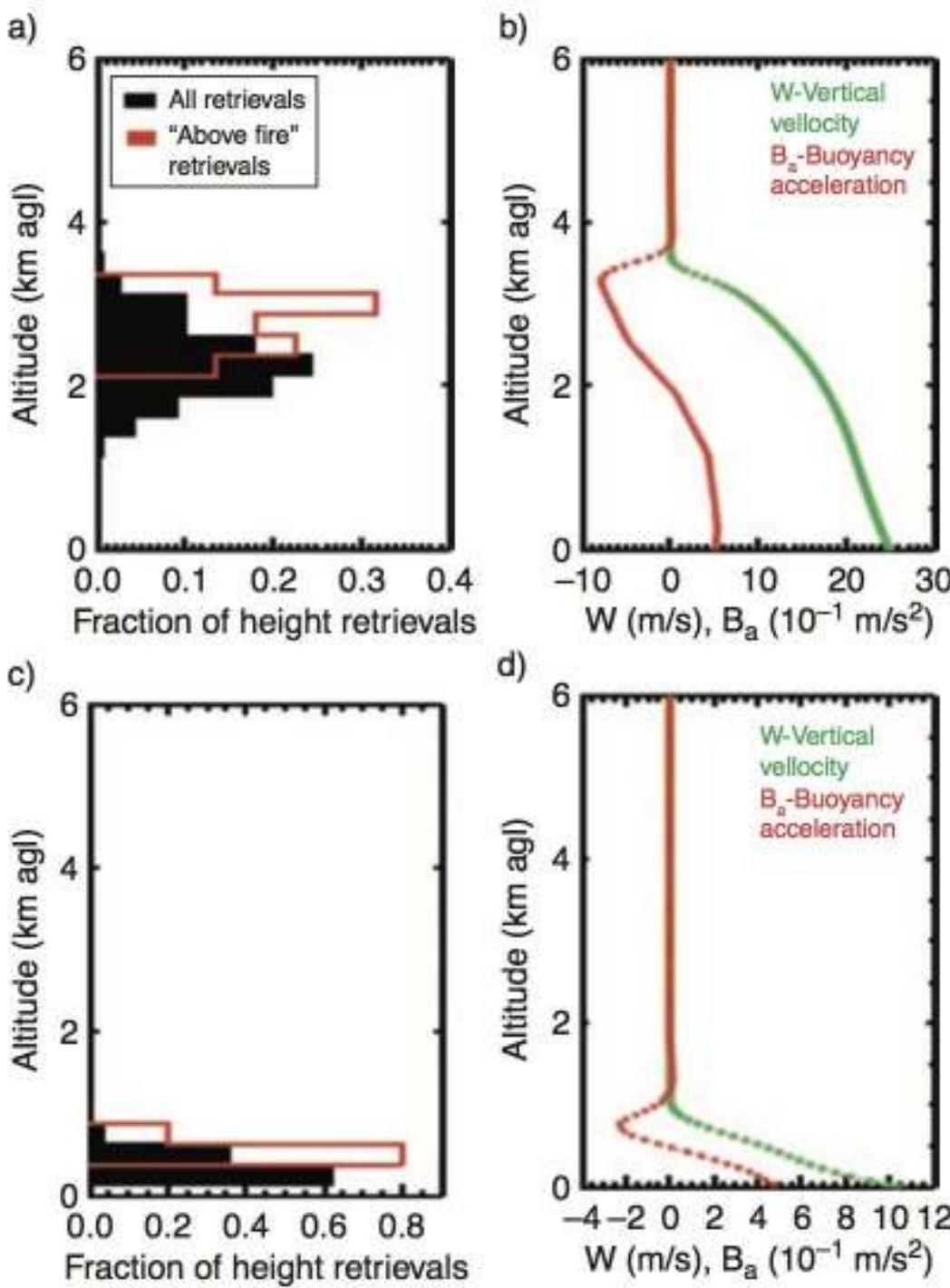
Chemical species	Savanna and grassland	Tropical forest	Extra-tropical forest	Crop residue	Pasture maintenance
CO <sub>2</sub>	1686	1643	1509	1585	1548
CO	63	93	122	102	135
CH <sub>4</sub>	1.9	5.1	5.68	5.82	8.71
NMVOCs	12.4	26	27	25.7	44.8
H <sub>2</sub>	1.7	3.36	2.03	2.59	—
NO <sub>x</sub>	3.9	2.55	1.12	3.11	0.75
N <sub>2</sub> O	—	—	0.38	—	—
Organic aerosol	2.62	4.71	9.1	2.3	9.64
Black carbon	0.37	0.52	0.56	0.75	0.91

Emission factors [g kg<sup>-1</sup>] for species emitted from combustion of different types of biomass. NO<sub>x</sub> is given as NO. From the review of Akagi *et al.* (2011).

# Open fires

Emission of CO from open fires in September 2000  
(Granier et al., 2011; Lamarque et al., 2010)





Plume rise from a large boreal forest fire in Canada (a and b) and from a small grassland fire in Texas (c and d).

The left panels show the plume rise inferred from aerosol retrievals by the MISR satellite instrument.

The right panels show results from the 1-D plume rise model of Freitas et al. (2007).

(Points of zero vertical velocity marks the top of the plume.)

# Volcanoes

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	—	32	—	5	—	55
CO	80	460	20	610	—	—	—	1170
Methane	190	50	—	290	—	—	—	530
Isoprene	520	—	—	—	—	—	—	520
SO <sub>2</sub> (as S)	—	1	—	57	10	—	—	68
Ammonia	3	6	8	45	—	—	—	62
Black carbon (as C)	—	11	—	7	—	—	—	18
Dust	—	—	—	—	—	—	1500	1500
Sea salt	—	—	—	—	—	—	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.

# Volcanoes

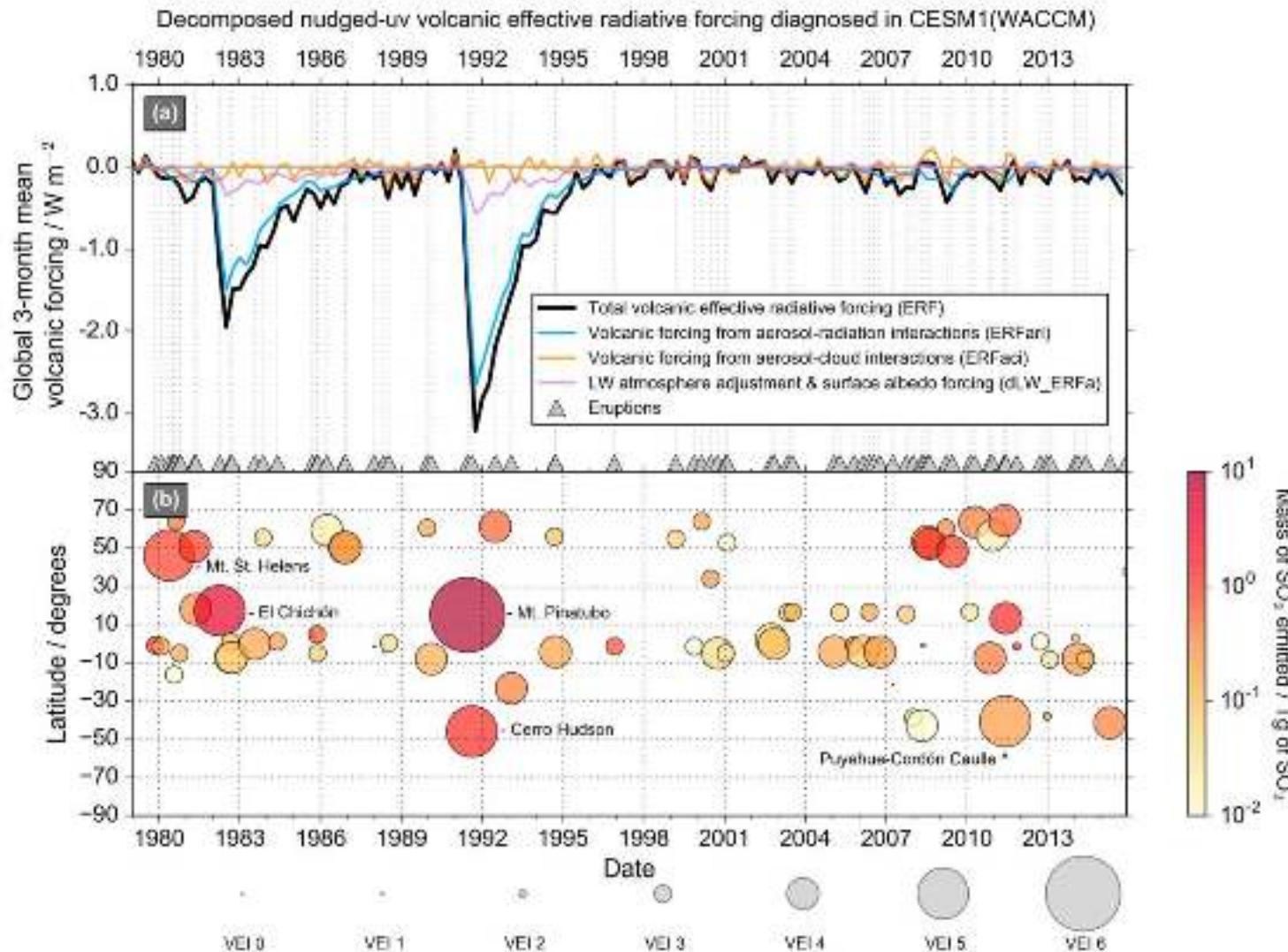
Volcanoes play a fundamental role in the cycling of elements on geologic timescales by transferring material from the lithosphere to the atmosphere.

On the shorter perspective of atmospheric sources and sinks, volcanoes are of most interest as sources of ash and sulphur gases (mainly  $\text{SO}_2$  and  $\text{H}_2\text{S}$ ).

Volcanoes often release material in the free troposphere. Large volcanic eruptions inject material into the lower stratosphere, and the resulting long-lived sulphate aerosol has important implications for climate and for stratospheric ozone.

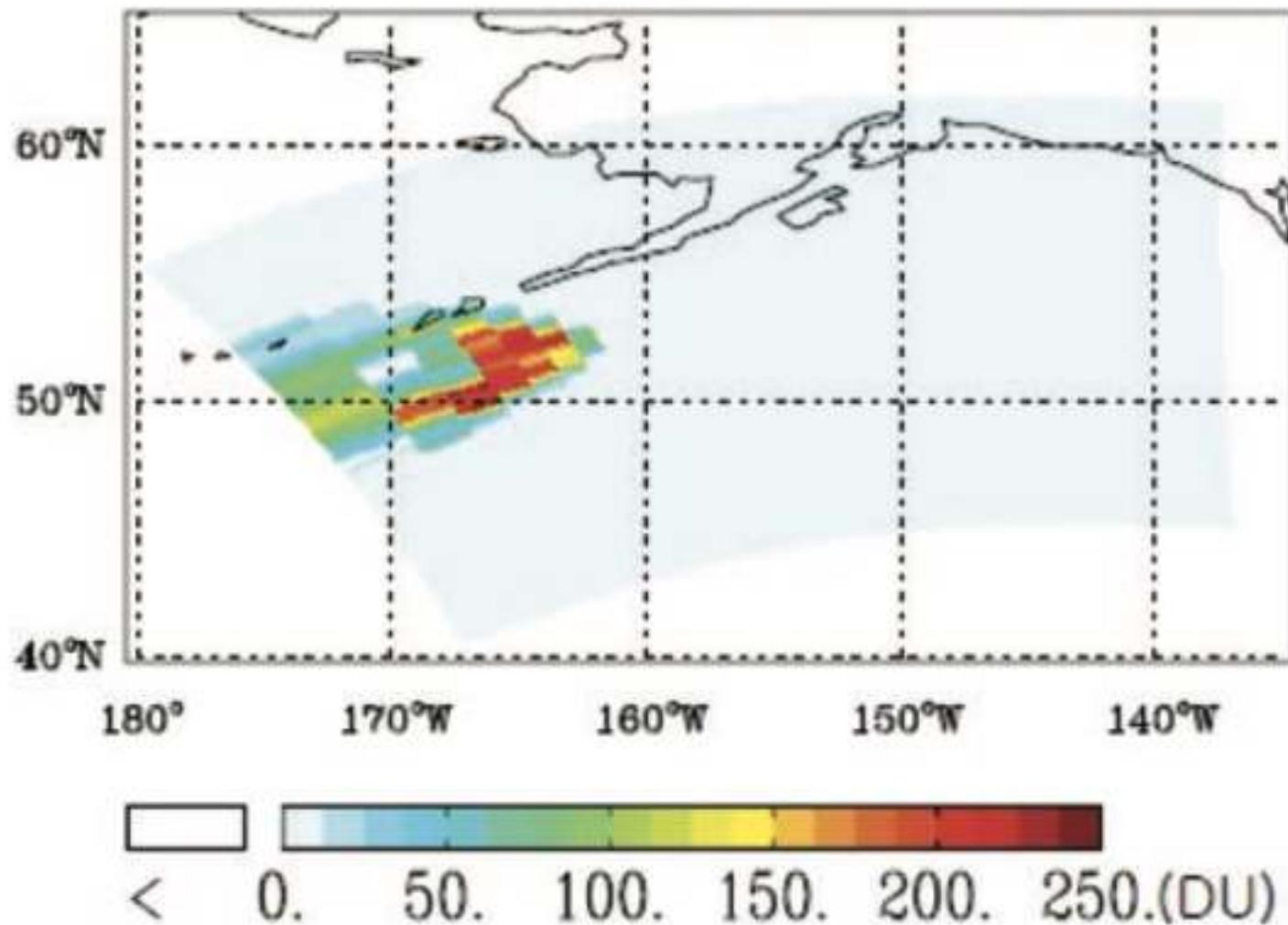
Volcanic emissions can be non-eruptive or eruptive. Non-eruptive emissions are released at the volcano mouth while eruptive emissions are injected to higher altitude.

Worldwide databases of volcanic eruptions are available with eruption dates and strengths measured by the logarithmic volcanic explosivity index.



Time series of (a) global 3-month mean nudged-uv total volcanic effective radiative forcing (ERF, in  $\text{W/m}^2$ , black line) diagnosed in CESM1-WACCM as the difference between simulations with and without volcanic emissions. The volcanic ERF is further decomposed into the forcings from aerosol-radiation interactions (ERFari, blue line) and aerosol-cloud interactions (ERFaci, orange line), and a longwave atmosphere adjustment and surface albedo term (dLW\_ERFa, purple line; see section 2). (b) A time series of volcanic sulfur dioxide ( $\text{SO}_2$ ) emissions (in  $\text{Tg of SO}_2$ , shown by the color) used in our simulations as a function of latitude, with the eruption size (indicated by seven distinct sizes of grey circles) using the Volcanic Explosivity Index (Schmidt et al., 2018).

# Volcanoes

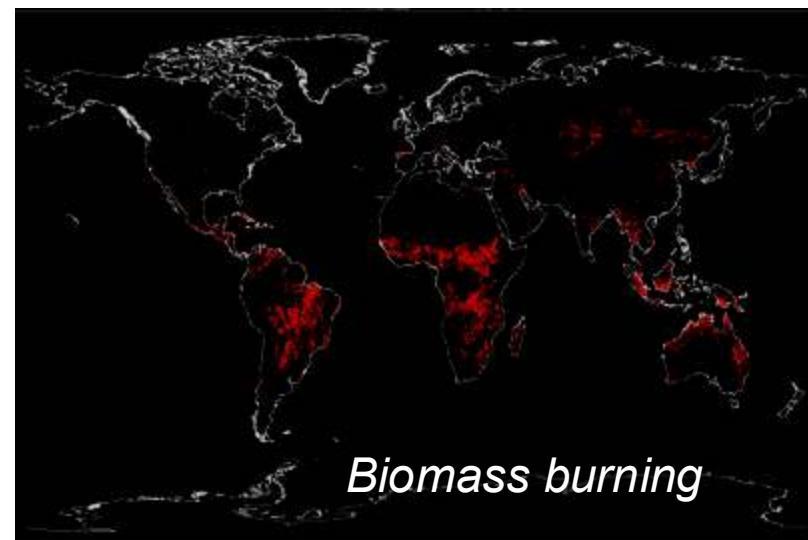


$\text{SO}_2$  plume from the Kasatochi volcanic eruption in the Aleutians observed by the OMI satellite instrument on August 8, 2008 (Wang et al. 2013).

# Anthropogenic Emissions

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	—	32	—	5	—	55
CO	80	460	20	610	—	—	—	1170
Methane	190	50	—	290	—	—	—	530
Isoprene	520	—	—	—	—	—	—	520
SO <sub>2</sub> (as S)	—	1	—	57	10	—	—	68
Ammonia	3	6	8	45	—	—	—	62
Black carbon (as C)	—	11	—	7	—	—	—	18
Dust	—	—	—	—	—	—	1500	1500
Sea salt	—	—	—	—	—	—	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.



# Anthropogenic Emissions

Anthropogenic emissions span a wide range of processes (most important):

- Combustion
- Industry
- Agricultural

The “anthropogenic” label in the literature can be ambiguous and inconsistent:

- e.g. anthropogenic inventories include prescribed and agricultural fires while others do not.
- e.g. anthropogenic inventories typically include emissions of ammonia from agricultural fertilizer, but may not include emissions of  $\text{NO}_x$  from the same process.
- e.g. regional inventories may include emissions from aircraft in airports but not in the air.
- e.g. they may include ship emissions in ports but not at sea.

Because of definitional problems such as these, care is needed when using anthropogenic emission inventories. It is important to ascertain which sources are included.

# Anthropogenic Emissions

Anthropogenic emissions are usually better quantified than other emissions because activity rates are available as economic data and emission factors are documented for air quality management purposes.

Emission inventories commonly distinguish between area sources and point sources.

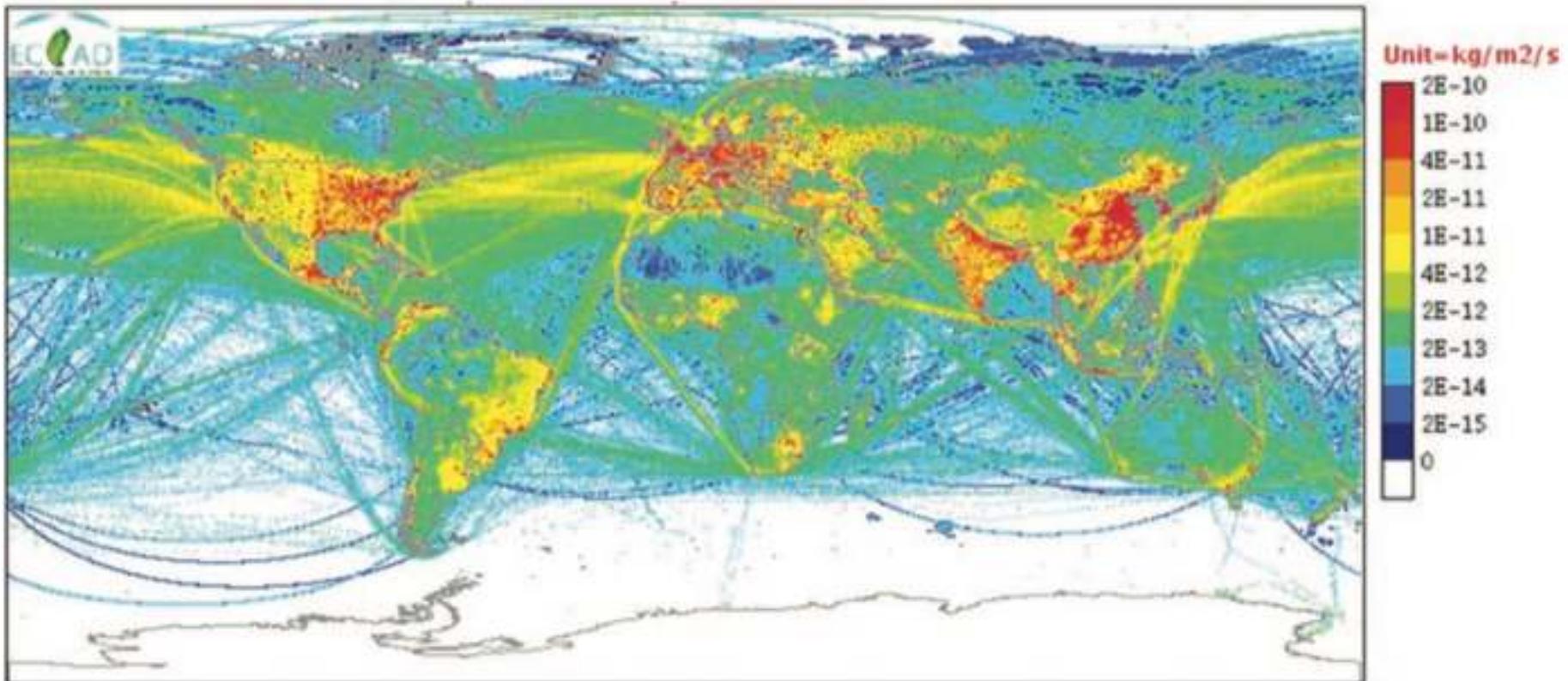
Area sources include vehicles and other individually small sources for which emissions are distributed over the activity area with best estimates of emission factors.

Point sources are concentrated discharges from localized sources such as power plants.

Anthropogenic emission inventories are produced by various groups and agencies to serve air quality management and climate modelling needs.

# Anthropogenic Emissions

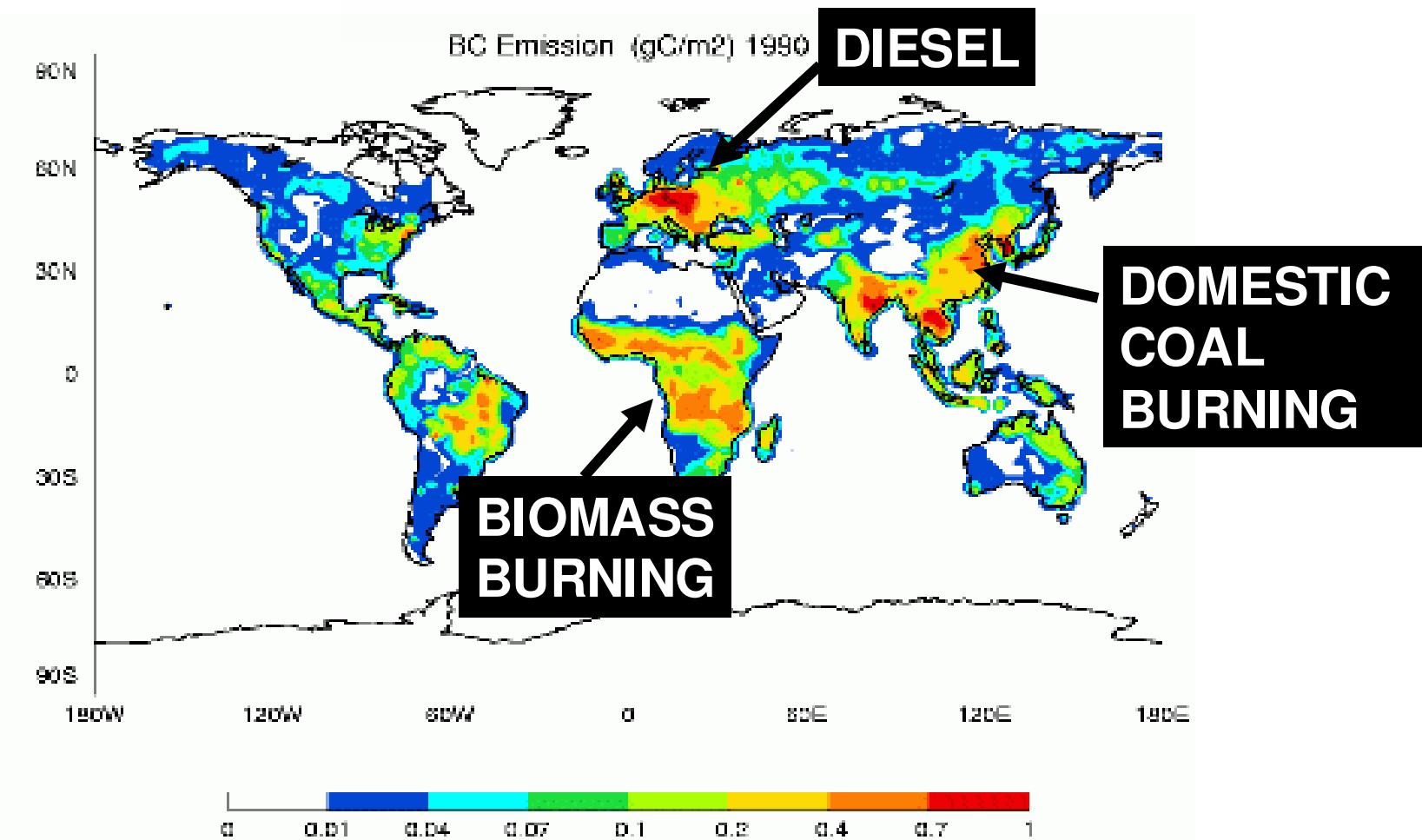
## $\text{NO}_x$



Anthropogenic  $\text{NO}_x$  emissions from the MACCity inventory at  $0.5 \times 0.5$  resolution for the year 2008 (C. Granier, Centre National de la Recherche Scientifique, CNRS).

# Anthropogenic Emissions

## Black carbon



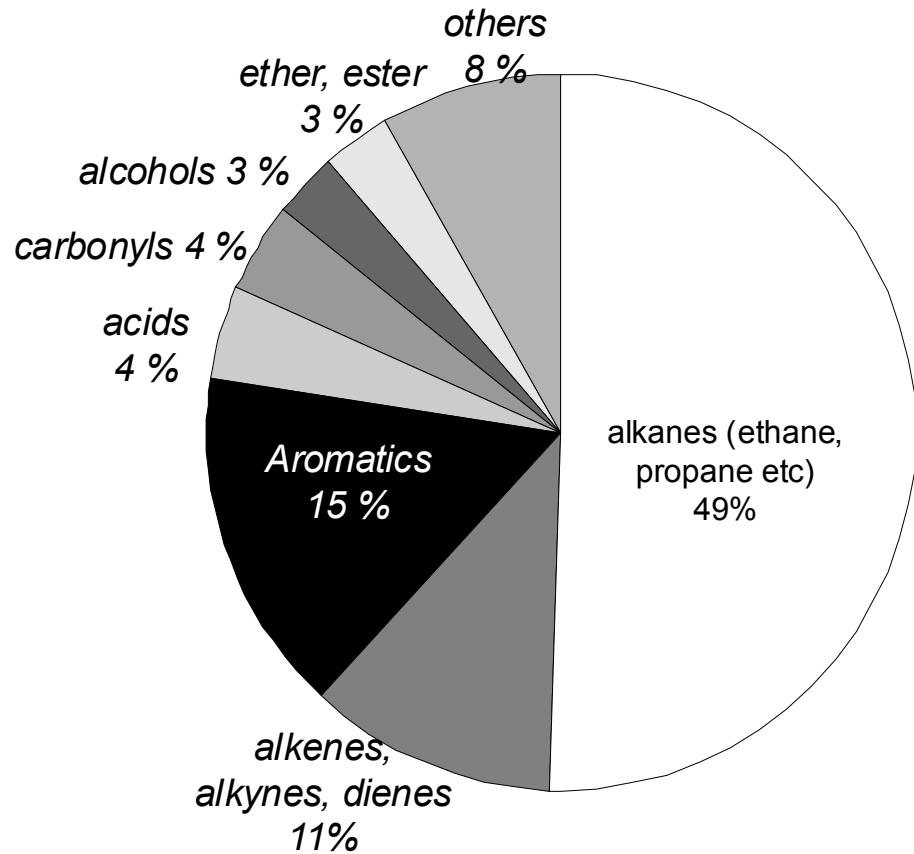
Chin et al. [2000]

# Anthropogenic Emissions

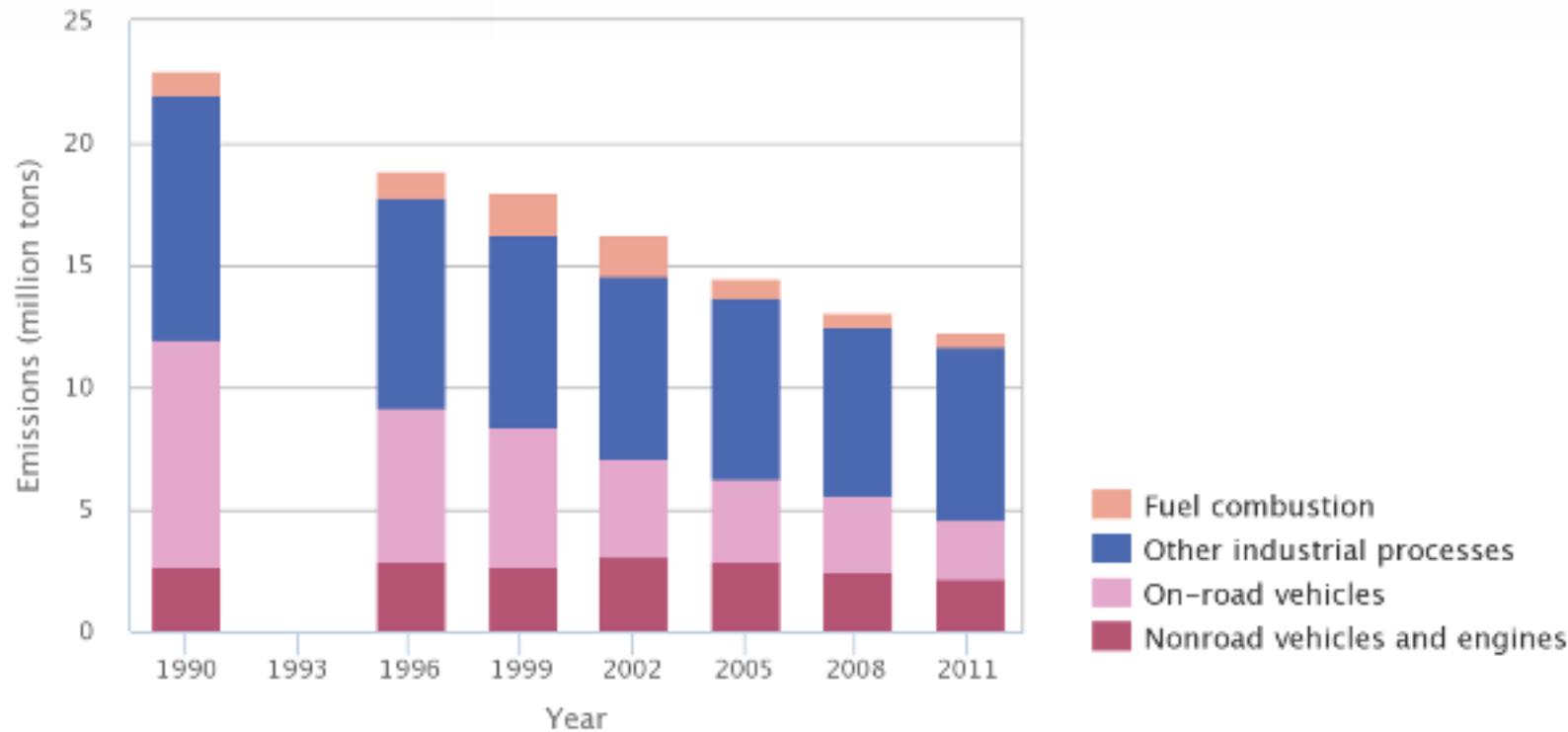
## Anthropogenic VOC

$\Sigma(\text{aromatics}) \approx 20 \text{ Tg carbon/year}$   
 $\Sigma \approx 100-200 \text{ Tg/yr. (mainly NH)}$

- Major fraction are alkanes (49 %)
- Substantial fraction of reactive ones: aromatics and alkenes (26 %)
  - Notable fraction of water-soluble ones: acids, alcohols and ethers/esters (10 %)



# AVOC emission in the U.S. by source categories 1990-2011 (EPA – report on the Environment 2014)



**Fuel combustion:** Emissions from coal-, gas-, and oil-fired power plants and industrial, commercial, and institutional sources, as well as residential heaters and boilers

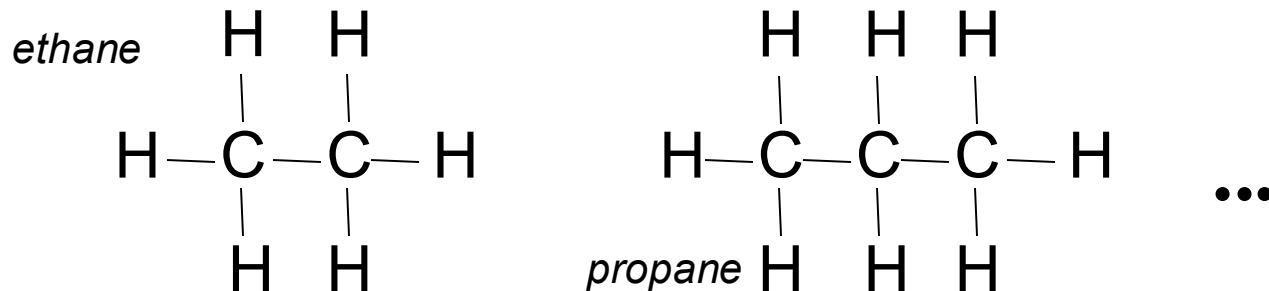
**Other industrial processes:** Chemical production, petroleum refining, metals production, and processes other than fuel combustion

**On-road vehicles:** Cars, trucks, buses, and motorcycles

**Nonroad vehicles and engines:** Such as farm and construction equipment, lawnmowers, chainsaws, boats, ships, snowmobiles, and aircraft.

## Anthropogenic alkanes (49 % = 50-100 Tg C/y)

*Saturated hydrocarbons ( $C_xH_y$ ) excluding methane, emitted from all sources*



### Atmospheric characteristics:

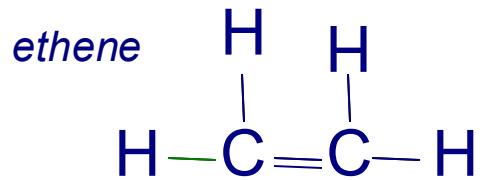
- react only with  $OH$ , but slow (Ethane:  $k_{OH}^{298K} = 2.55e-13 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , Propane:  $k_{OH}^{298K} = 1.12e-12 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )

- long lived (days – months)

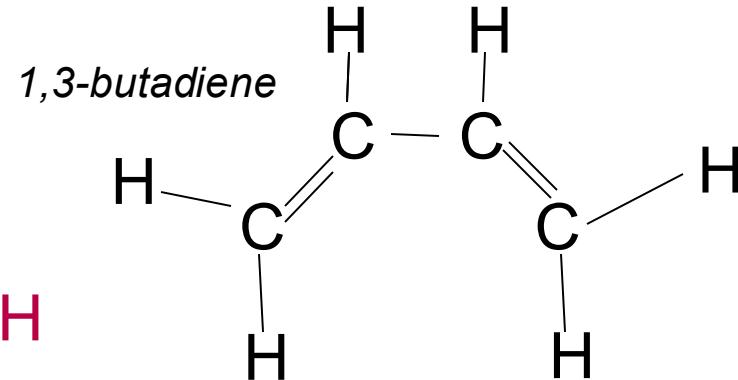
ethane:  $C_2H_6 = 2.7 \text{ months}$ , propane:  $C_3H_8 = 28 \text{ days}$

- long range transport

# Anthropogenic reactive hydrocarbons: Alkenes, alkynes, dienes



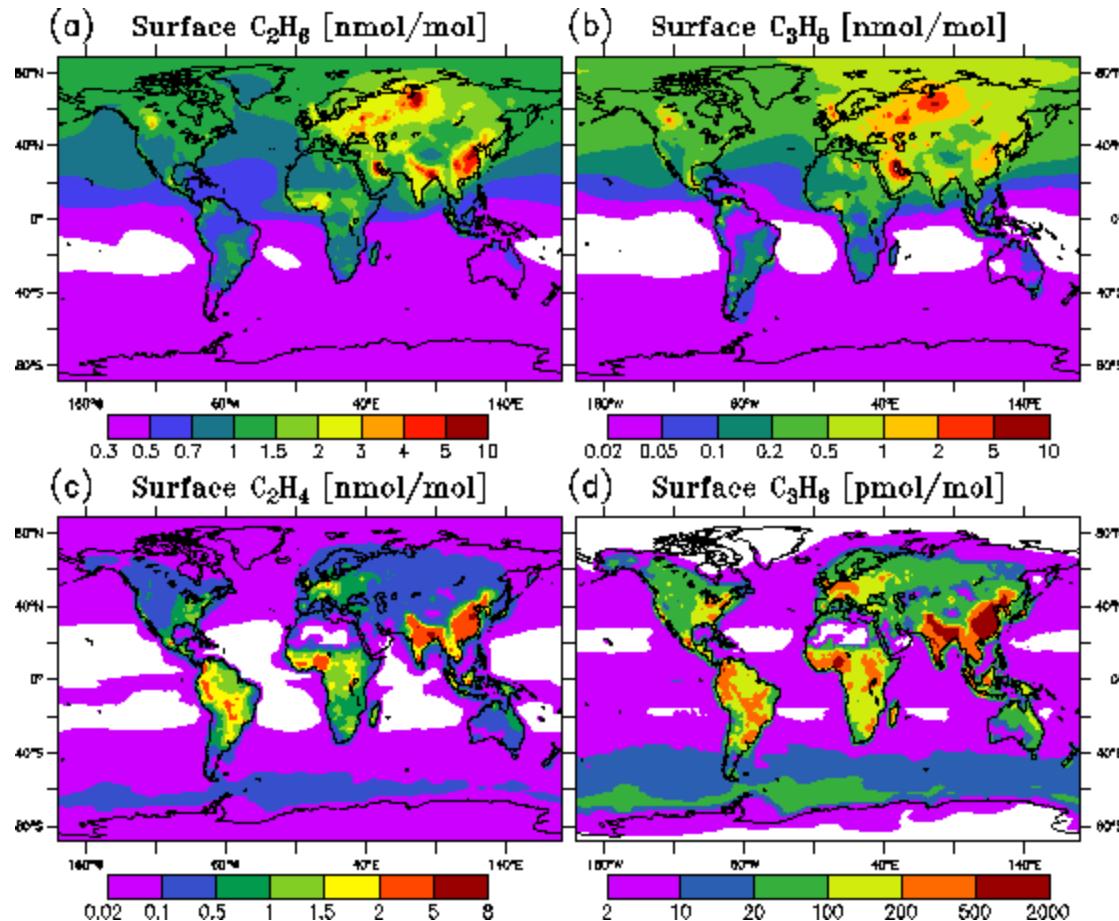
*ethyne*



## Atmospheric characteristics:

- Alkenes/dienes: reaction with OH, radicals and ozone, short lifetime (propene: C<sub>3</sub>H<sub>6</sub> = 20 h, butadiene: C<sub>4</sub>H<sub>6</sub> = 3-4 h), larger ones: aerosol mass formation
- Alkynes: reaction only with OH (ethyne: C<sub>2</sub>H<sub>2</sub> = 12.9 d)
- Alkenes and dienes: stay in the local emission area, but formation of products with much longer lifetimes such as carbonyls, acids, alcohols; affect ozone formation.
- Alkynes: long distance transport possible

# Distribution of surface ethane and propane top and ethene and propene lower plots



von Kuhlmann, 2002

¶ The simulation clearly shows the hot spots at metropolitan areas, industries, harbours, oil refineries and the transpotation pattern of the long lived gases

# Anthropogenic VOCs: Aromatics

*The gases you inhale in cities behind a vehicle.*

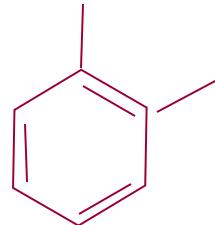
*Emitted by fossil fuel combustion and biomass burning*



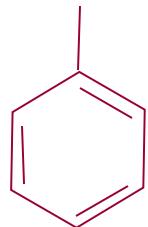
Benzene



Xylene



Toluene



- shorter live times (1h-2d)
- local air pollution
- aerosol formation



# **How are Emissions Inventories Developed?**

**Continuous monitoring of emissions from a source;**

**Short-term emission measurements that are extrapolated to a longer time period, and use of emissions factors.**

**An emissions factor is a representative value that attempts to relate the quantity of a pollutant emitted with an activity level associated with the emission of that pollutant**

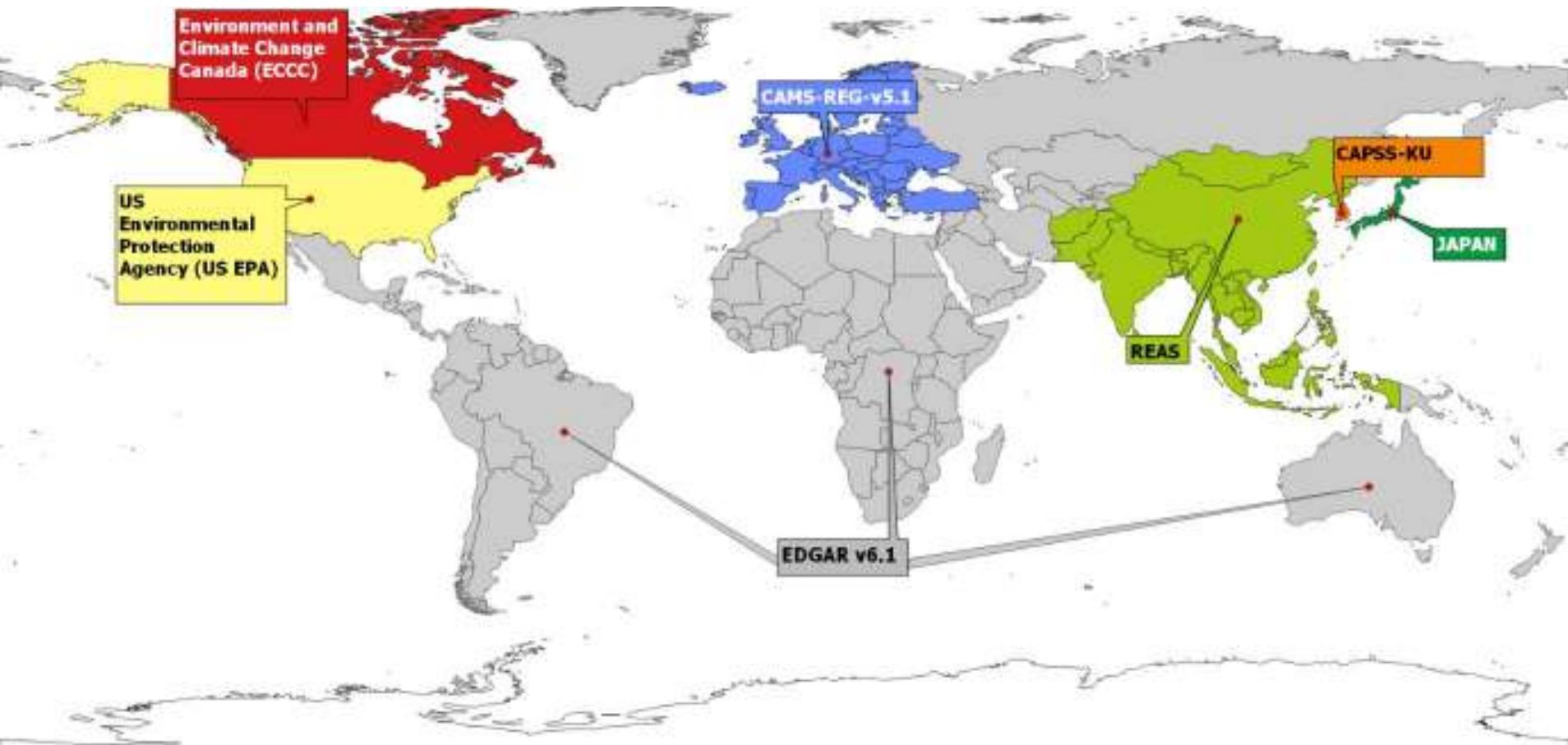
**Emissions factors in the published literature typically are averages of available data of acceptable quality, and are assumed to represent long-term averages for similar facilities.**

# **How Does an Emissions Inventory Contribute to the Air Quality Management Process?**

**Governments use emission inventories to help determine significant sources of air pollutants and to target regulatory actions.**

**Emissions inventories are an essential input to mathematical models that estimate air quality.**

**The effect on air quality of potential regulatory actions can be predicted by applying estimated emissions reductions to emissions inventory data in air quality models.**





Inventories Species Sectors Versions Temporal Geographical

Q Search

**CAMS**

CAMS-RE9-ANT •  
 CAMS-GLOB-TERM •  
 CAMS-GLOB-CH4 •  
 CAMS-GLOB-EDG •  
 CAMS-GLOB-AR4 •  
 CAMS-GLOB-TEMPO •  
 CAMS-RFG-TEMPO •  
 CAMS-GLOB-ANT •

**EDGAR**

HTAP2 •  
 EDGARv6 monthly •  
 EDGARv6 12 •  
 EDGARv6 12 •  
 EDGARv7 •  
 EDGARv7 •

**CEDS**

CEDS •

**ECLIPSE**

ECLIPSE-95 •

ECLIPSE-GLOB-TERM •

**GEIA**

GEIA-Windermere •  
 GEIA-GLOB-CH4 •  
 GEIA-Subs •  
 GEIA-BC •  
 GEIA-PC (General Model) •

**Future Scenarios**

RCP-2.6 •  
 RCP-4.5 •  
 RCP-6.0 •  
 RCP-8.5 •

**Inverse Modelling**

ISCL •  
 F2R4GOL •  
 J2R2 •  
 Model •  
 E-MIP-CH4 •  
 P2R4-CH4 •

GEIA-Subs •  
 WRF-TD4Cv1-HDF •  
 EDGARv6-Toronto •  
 VTPR-FireKML •  
 IC3D7 •

**GLOBAL, more datasets**

CLIMAP •  
 FNL •  
 FOET •  
 FDPF •  
 JJA-1000 •  
 MILC4N2 •  
 RETRO •  
 MOCUP •  
 MOCUP-Subs •  
 S41-FDS •  
 UM-CH4 •

CLIMAP •  
 Andrus-CH4-2010 •  
 Global CH4 •  
 GPPV •  
 IM3-12 •  
 UHarp2 •  
 VEGAN-CH4 •  
 AMIBRS •  
 UNCDP-Subs •  
 CO2 •  
 VADOC-Subs-CH4 •

**REGIONAL datasets**

LMIP •  
 GPCWMA •  
 DACOMA •  
 WRF-AMF •  
 E-HARVE •  
 ECO-CH4C •  
 PAP-LA •  
 T42-CH4C •

WHDRC •  
 REASv2 •  
 MVE2 •  
 SAWW-AMF •  
 DACOMA •  
 DACOMA-Subs •  
 CHE-34-SEAS •  
 REAS2 •

# EDGAR - Emissions Database for Global Atmospheric Research

EDGAR is a multipurpose, independent, global database of anthropogenic emissions of greenhouse gases and air pollution on Earth. EDGAR provides independent emission estimates compared to what reported by European Member States or by Parties under the United Nations Framework Convention on Climate Change (UNFCCC), using international statistics and a consistent IPCC methodology.

EDGAR provides both emissions as national totals and gridmaps at  $0.1 \times 0.1$  degree resolution at global level, with yearly, monthly and up to hourly data.

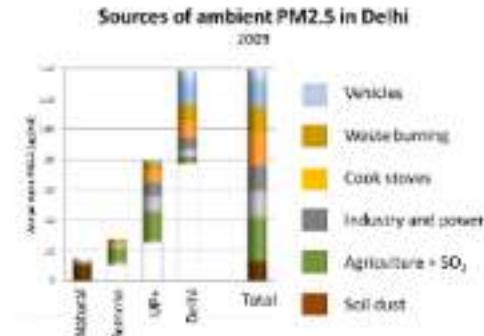
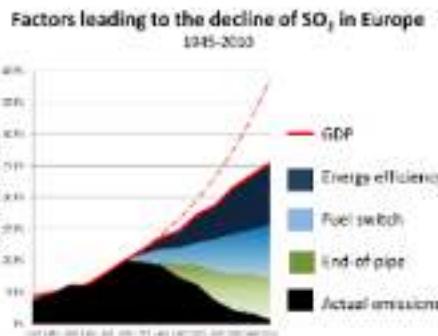




# GAINS Online

Greenhouse Gas - Air Pollution Interactions and Synergies

Reveal win-win policy interventions with GAINS-online



Many traditional air pollutants and greenhouse gases have common sources. Their emissions interact in the atmosphere, and—jointly and individually—cause a variety of harmful environmental effects at the local, regional, and global scales.

The GAINS model explores cost-effective emission control strategies that simultaneously tackle local air quality and greenhouse gases so as to maximize benefits at all scales.

## EMEP

[Home](#)  
[Overview](#)  
[Publications](#)  
[Grid](#)  
[Logo](#)

## CLRTAP resources

## Collaborating organizations

[Google search](#) >

Technical comments:  
[emep.mscw@met.no](mailto:emep.mscw@met.no)

Last updated:  
5 March 2021

## EMEP

*The co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (inofficially 'European Monitoring and Evaluation Programme' = EMEP) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems.*

Five EMEP Centers and four Task Forces undertake efforts in support of the EMEP work plan. We refer to the respective websites for in-depth information:

### CEIP

Centre on  
Emission Inventories and Projections

Direct link to  
emission data

### CCC

Chemical Coordinating Centre

Direct link to  
measurement data

### MSC-W

Meteorological Synthesizing Centre  
- West

Direct link to  
model results  
(sulphur, nitrogen,  
ozone, and PM)

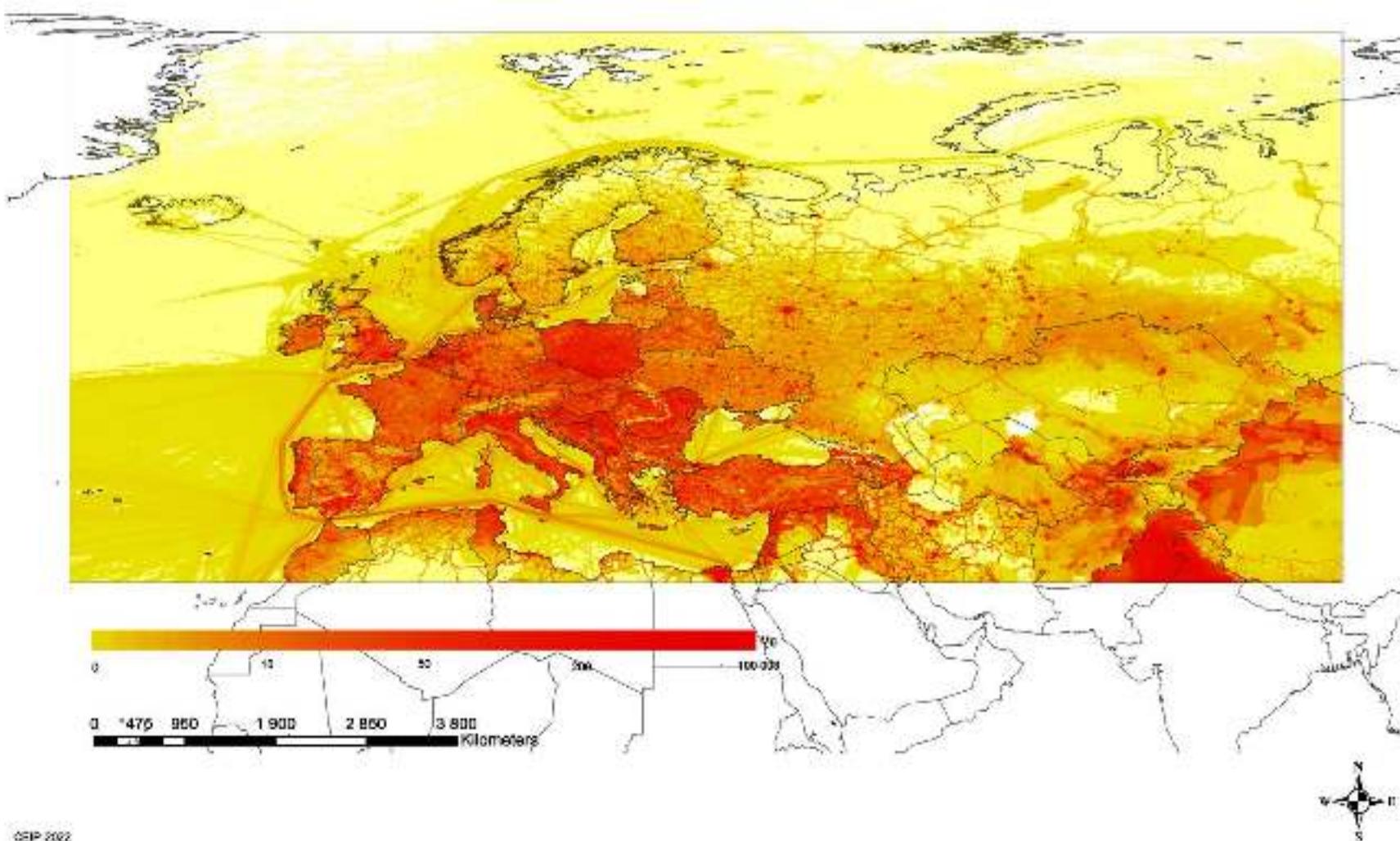
GNFR_Category	GNFR_Category_Name	Link to SNAP
A	A_PublicPower	SNAP 1, only power and heat plants
B	B_Industry	SNAP 1 (non-power and heat plants) + SNAP 34 (or SNAP 3+4)
C	C_OtherStationaryComb	SNAP 2
D	D_Fugitives	SNAP 5
E	E_Solvents	SNAP 6
F	F_RoadTransport	SNAP 7
G	G_Shipping	SNAP 8, only shipping (all types)
H	H_Aviation	SNAP 8, only aviation
I	I_OffRoad	SNAP 8, non-shipping and non-aviation
J	J_Waste	SNAP 9
K	K_AgriLivestock	SNAP 10, livestock only
L	L_AgriOther	SNAP 10, non-livestock only
F1	F_RoadTransport_exhaust_gasoline	SNAP 71
F2	F_RoadTransport_exhaust_diesel	SNAP 72
F3	F_RoadTransport_exhaust_LPG_gas	SNAP 73
F4	F_RoadTransport_non-exhaust	SNAP 74 + SNAP 75 Note that SNAP 74 has only NMVOC and SNAP 75 has only PM emissions

Table 2.1: GNFR Sector explanation and link to SNAP nomenclature previously used in TNO-MACC-III and CAMS-REG version 1.

Name	Real name	ENE	RCO	TRO	TNR	FEF	SLV	AGR	SHP	SWD
voc1	Alcohols	X	X	X	X	X	X		X	X
voc2	Ethane	X	X	X	X	X	X	X	X	X
voc3	Propane	X	X	X	X	X	X	X	X	X
voc4	Butanes	X	X	X		X	X	X		X
voc5	Pentanes	X	X	X	X	X	X	X	X	X
voc6	Hexanes	X	X	X	X	X	X	X	X	X
voc7	Ethene	X	X	X	X	X	X	X	X	X
voc8	Propene	X	X	X	X	X	X	X	X	X
voc9	Ethyne	X	X	X	X	X	X	X	X	X
voc10	Isoprenes	X	X	X	X	X	X	X	X	X
voc11	Monoterpenes	X	X	X	X		X	X	X	X
voc12	Other alkad.	X	X	X	X	X	X	X	X	X
voc13	Benzene	X	X	X	X	X	X	X	X	X
voc14	Methylbenzene	X	X	X	X	X	X	X	X	X
voc15	Dimethylbenzenes	X	X	X	X	X	X	X	X	X
voc16	Trimethylbenzenes	X	X	X	X	X	X	X	X	
voc17	Other aromatics	X	X	X	X	X	X	X	X	X
voc18	Esters	X	X	X	X	X	X		X	X
voc19	Ethers	X	X	X	X	X	X	X	X	X
voc20	Chlorinated	X	X	X	X	X	X		X	
voc21	Methanal	X	X	X	X	X	X	X	X	X
voc22	Other alkanals	X	X	X	X	X	X	X	X	X
voc23	Alkanones	X	X	X	X	X	X	X	X	
voc24	Acids	X	X	X	X		X		X	X
voc25	Others	X	X	X	X	X	X	X	X	X

Table 3: List of VOCs considered in the inventory and corresponding sectors

PM2.5 - National Total - 2020



# Mechanical emissions: sea salt and dust

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO <sub>x</sub> (as N)	11	7	—	32	—	5	—	55
CO	80	460	20	610	—	—	—	1170
Methane	190	50	—	290	—	—	—	530
Isoprene	520	—	—	—	—	—	—	520
SO <sub>2</sub> (as S)	—	1	—	57	10	—	—	68
Ammonia	3	6	8	45	—	—	—	62
Black carbon (as C)	—	11	—	7	—	—	—	18
Dust	—	—	—	—	—	—	1500	1500
Sea salt	—	—	—	—	—	—	5000	5000

Typical estimates for circa 2015. Dash indicates a zero or negligible source.

# Mechanical emissions: sea salt and dust

Wind stress on the Earth's surface causes mechanical emission of aerosol particles including sea salt, mineral dust, pollen, and plant debris.

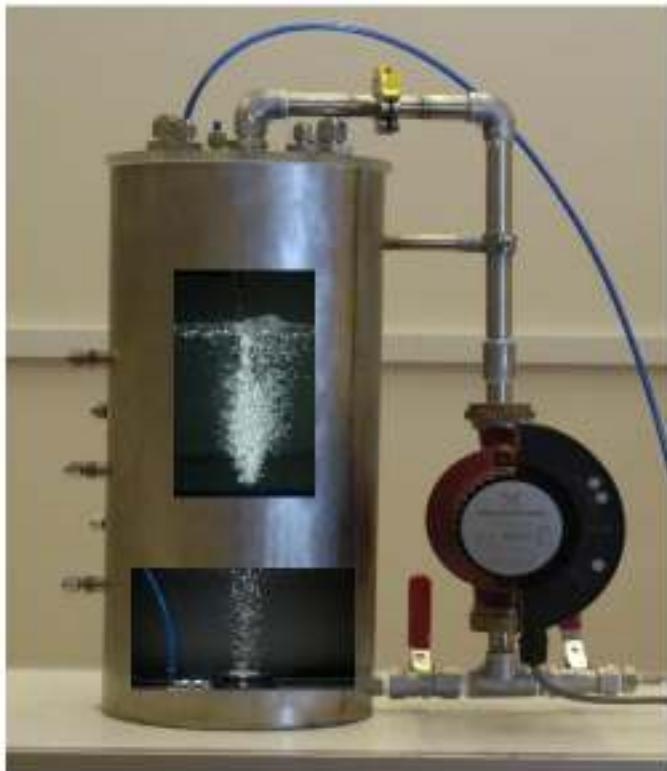
Sea salt and dust are dominant components of the coarse-mode (supermicron) aerosol over ocean and land, respectively, and generally make important contributions to total aerosol mass concentrations and optical depth.

Pollen and plant debris have more localized influences.

Emission of sea salt particles is mostly driven by the entrainment of air into seawater by wave-breaking. The resulting air bubbles rise and burst at the sea surface injecting particles into the air.

The emission flux is a strong function of wind speed.

# Mechanical emissions: sea salt

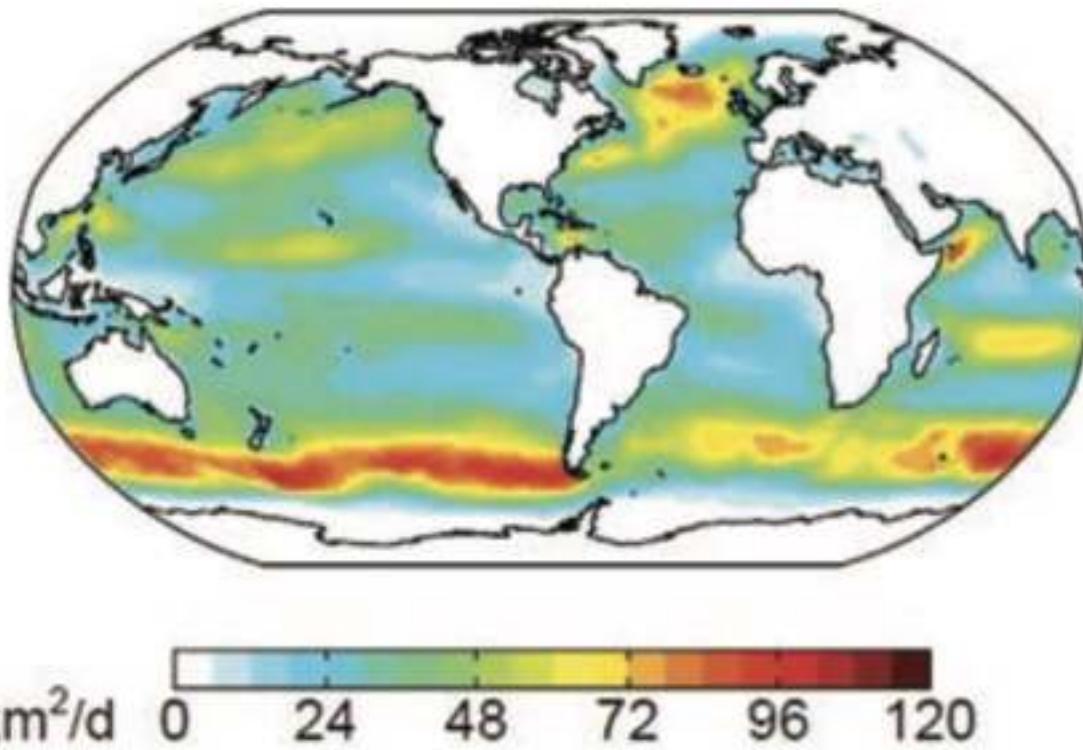


During CRAICC (Boy et al., 2019) significant effort was devoted to improving the understanding of sea spray aerosol.

One important development was the design, construction, and use of new temperature-controlled sea spray aerosol simulation tanks (King et al., 2012; Salter et al., 2014).

In these tanks air is entrained in real or artificial seawater via frits, diffusers, or plunging jets. The entrained air breaks up into bubbles, which rise to the surface where aerosols are generated by bubble-bursting processes.

# Mechanical emissions: sea salt



Annual mean mass emission flux of sea salt aerosol (Jaeglé et al. (2011))

# Mechanical emissions: dust

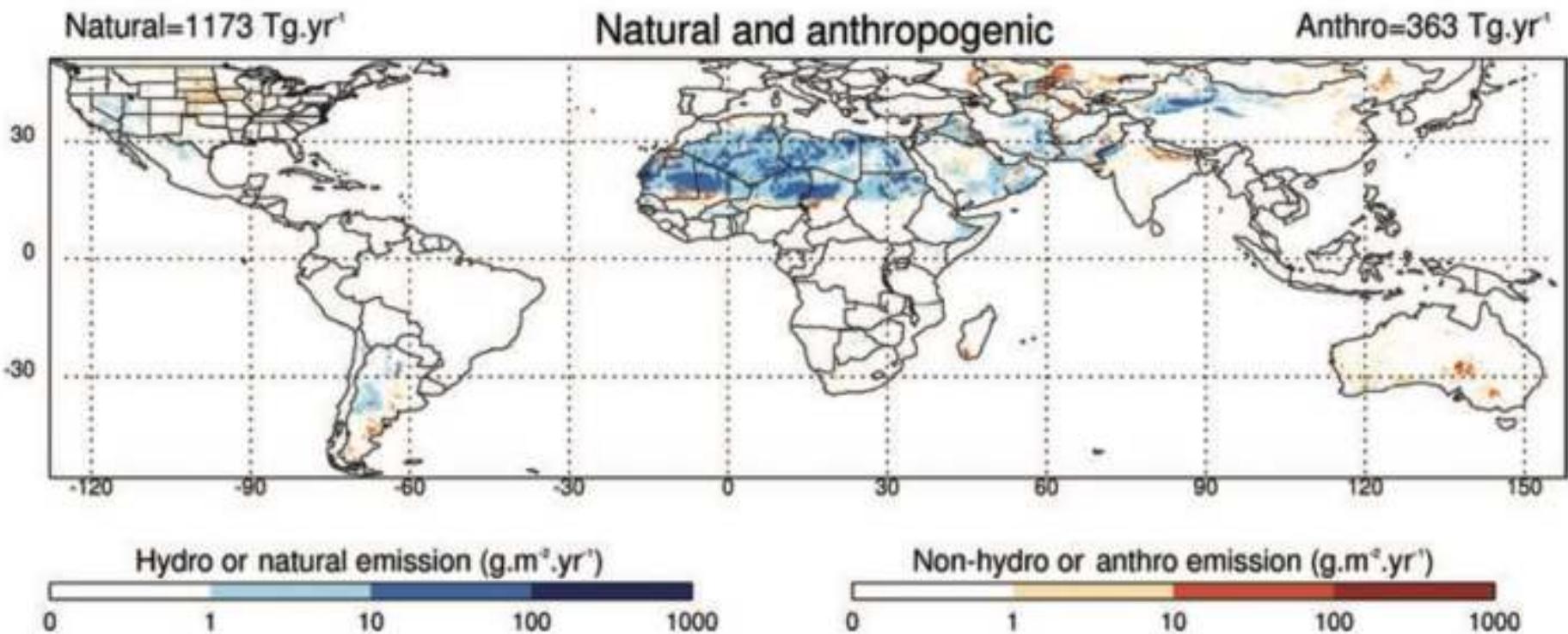
Mineral dust is emitted by sandblasting of soils, a process called saltation.

Wind lifts large sand particles (diameter  $D_s > 50 \mu\text{m}$ ) that travel over only short horizontal distances before falling back to the surface by gravity.

As the sand particles fall, they eject dust particles of diameter  $D_d$  small enough to be transported over long distances in the atmosphere. These fine particles are classified as

- Clay ( $D_d < 2 \mu\text{m}$ )
- Silt ( $2 < D_d < 50 \mu\text{m}$ )

# Mechanical emissions: dust



Annual mean dust emission from natural and anthropogenic sources (Ginoux et al. 2012)

# How we implement the emission of isoprene and one selected monoterpenes in your 1-D model!

Surface emission flux  $F_{\text{vegetation}}$  from the vegetation [Guenther *et al.* (1995)]:

$$F_{\text{vegetation}} = D_m \cdot \varepsilon \cdot \gamma \cdot \delta$$

$D_m$ : foliar density (kg dry matter  $\text{m}^{-2}$ )

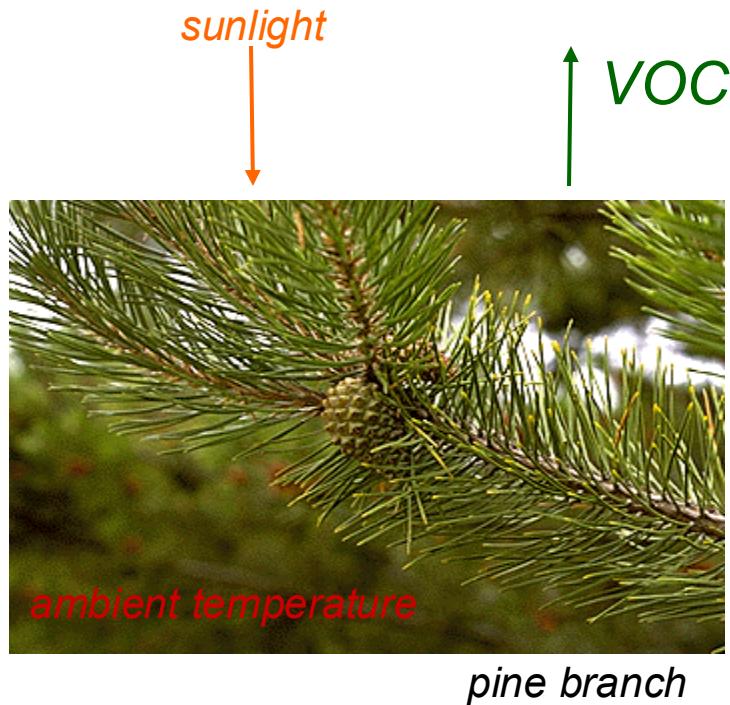
→ *e.g. amount of leaves/needles per surface area*

$\varepsilon$ : ecosystem dependent emission factor at  $T = 30 \text{ }^{\circ}\text{C}$  and  $\text{PAR} = 1000 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$   
( $\mu\text{g C m}^{-2} \text{ h}^{-1}$ )

→ *amount of emission at standard conditions*

$\gamma$ : adjustment factor for dependence on temperature and light – emission activity

$\delta$ : emission activity factor for long term controls



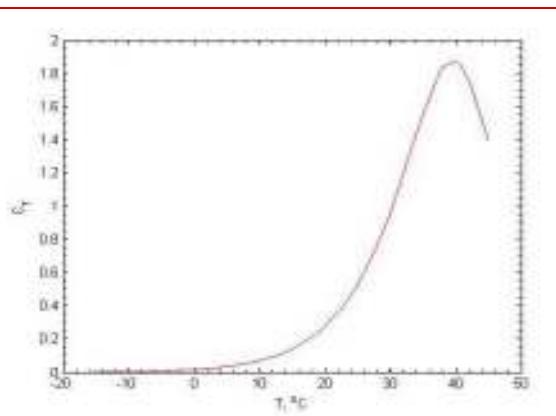
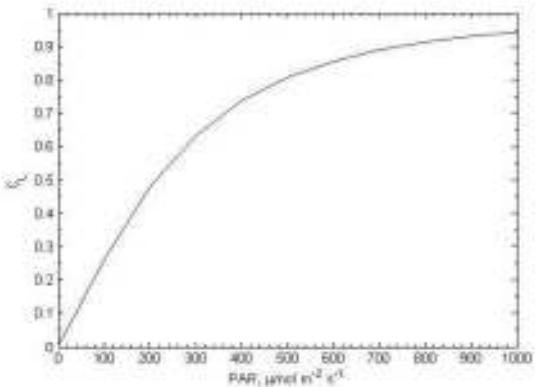
# Isoprene: dependence on temperature and PAR

$$\gamma = C_L C_T$$

Light (PAR denoted as Q):

$$C_L = \frac{\alpha c_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}}$$

$$\alpha = 0.0027, c_{L1} = 1.006$$



$$c_{T1} = 95 \text{ kJ mol}^{-1}, c_{T2} = 230 \text{ kJ mol}^{-1},$$

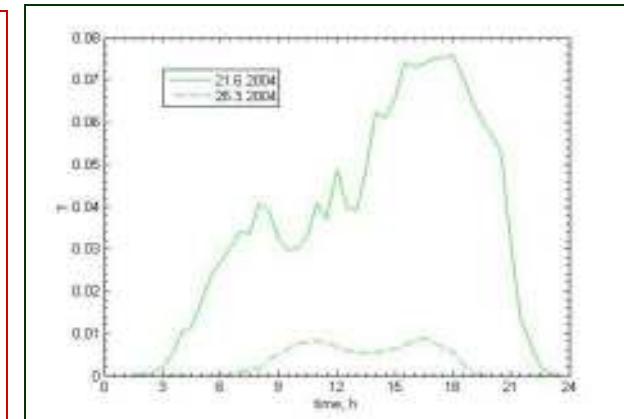
$$T_s = 303.15 \text{ K}; T_M = 314 \text{ K}$$

Temperature T (leaf):

$$C_T = \frac{\exp\left(\frac{c_{T1}(T - T_s)}{RTT_s}\right)}{1 + \exp\left(\frac{c_{T2}(T - T_M)}{RTT_s}\right)}$$

*Note! Take needle or leaf temperature not the ambient one.*

*Spring and summer time in Hyytiälä*



# Isoprene: dependence on temperature and PAR

$$\gamma = C_L C_T$$

Light (PAR denoted as Q):

$$C_L = \frac{\alpha c_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}}$$

$$a = 0.0027$$

$$c_{L1} = 1.006$$

$$C_T = \frac{\exp\left(\frac{c_{T1}(T - T_s)}{RTT_s}\right)}{1 + \exp\left(\frac{c_{T2}(T - T_M)}{RTT_s}\right)}$$

Temperature T (leaf):

*Note! Take needle or leaf temperature not the ambient one.*

$$c_{T1} = 95 \text{ kJ mol}^{-1}$$

$$c_{T2} = 230 \text{ kJ mol}^{-1}$$

$$T_s = 303.15 \text{ K}$$

$$T_M = 314 \text{ K}$$

# Monoterpene ( $C_{10}H_{16}$ ) emissions

Estimated annual emission on the global scale:

127 Tg C [Guenther *et al.*, 1995]

**Monoterpene** emissions are believed to depend on **temperature** only:

$$\gamma = \exp(\beta \cdot (T - T_s))$$

$$\beta = 0.09 \text{ } K^{-1}, T_s = 303.15 \text{ } K$$

$D_m$ : foliar density (kg dry matter  $m^{-2}$ ):

Standing leaf biomass:

0.0538 [g/cm<sup>2</sup>]

Vertical distribution in the canopy:

the emissions should be between level 1 and 2

$\epsilon$ : ecosystem dependent emission factor at  $T = 30$  °C and  $PAR = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$  [ $\mu\text{g C m}^{-2} \text{h}^{-1}$ ]

Standard emission potentials:

100 [ng / g (needle-dry-weight) / h]

$\delta$ : emission activity factor for long term controls:

1 (not taken into account)

PAR = 1000 \* exp\_coszen

Temperature from level 2 (so emissions between 5-15 m)

Remember that the emission rates have to be in the units of [ $\# \text{ cm}^{-3} \text{ s}^{-1}$ ] when you move it over to the chemistry part. So, you have to divide by your height interval which is 10 m!!!

