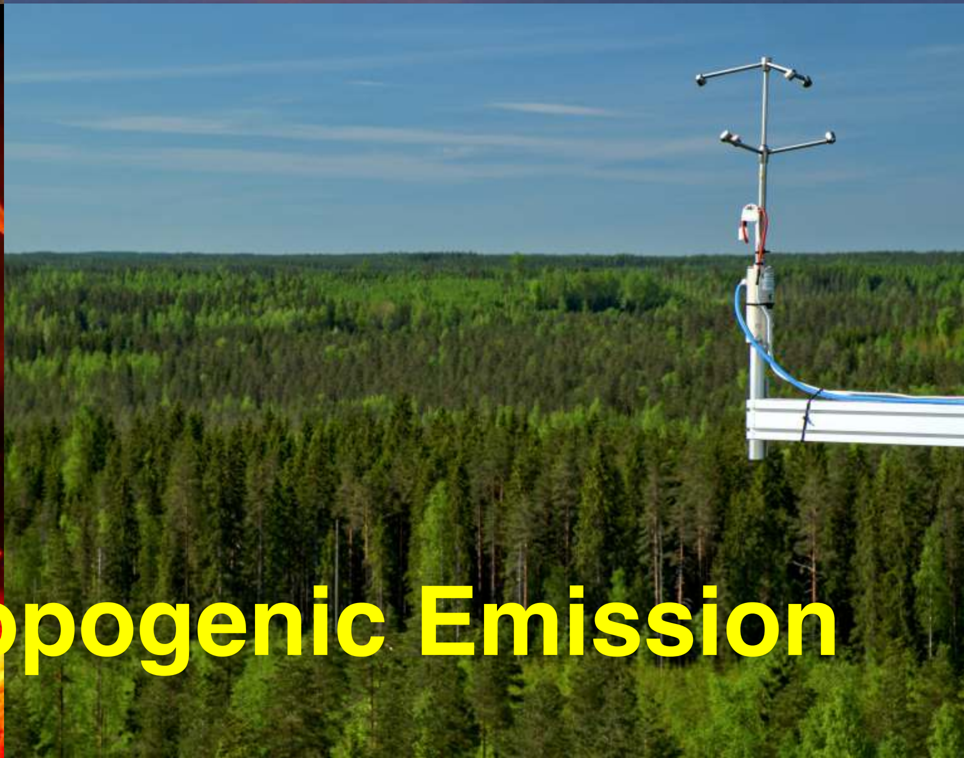


Natural and Anthropogenic Emission

Global emissions to the atmosphere (Tg a^{-1})

Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO_x (as N)	11	7	–	32	–	5	–	55
CO	80	460	20	610	–	–	–	1170
Methane	190	50	–	290	–	–	–	530
Isoprene	520	–	–	–	–	–	–	520
SO_2 (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_2 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_x (as N)	11	7	–	32	–	5	–	55
CO	80	460	20	610	–	–	–	1170
Methane	190	50	–	290	–	–	–	530
Isoprene	520	–	–	–	–	–	–	520
SO_2 (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.

Brasseur and Jacob, 2017

Global budget of methane (CH_4)

	Rate, Tg CH_4 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

D.J. Jacob

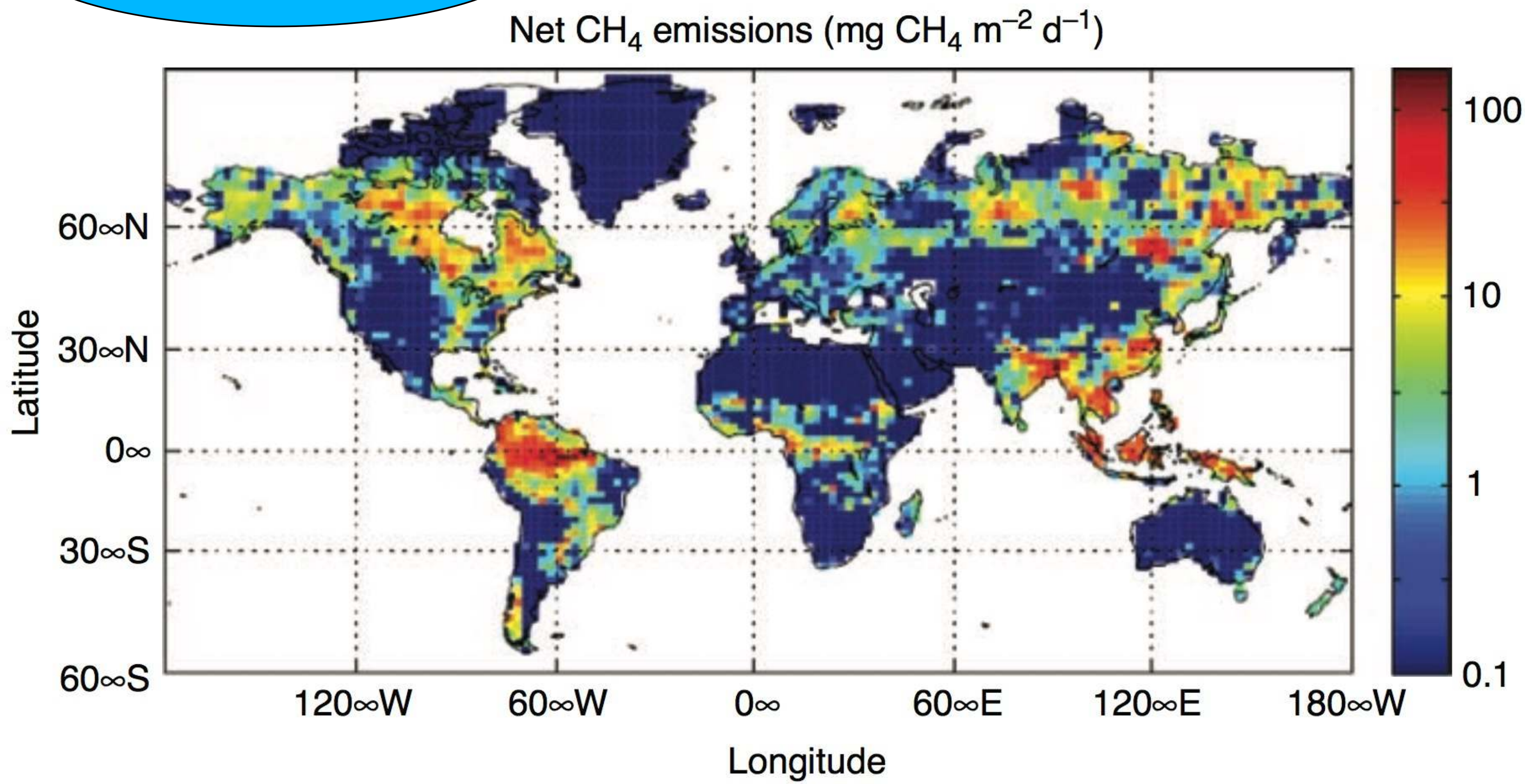
Terrestrial Biogenic Emissions
Methane

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

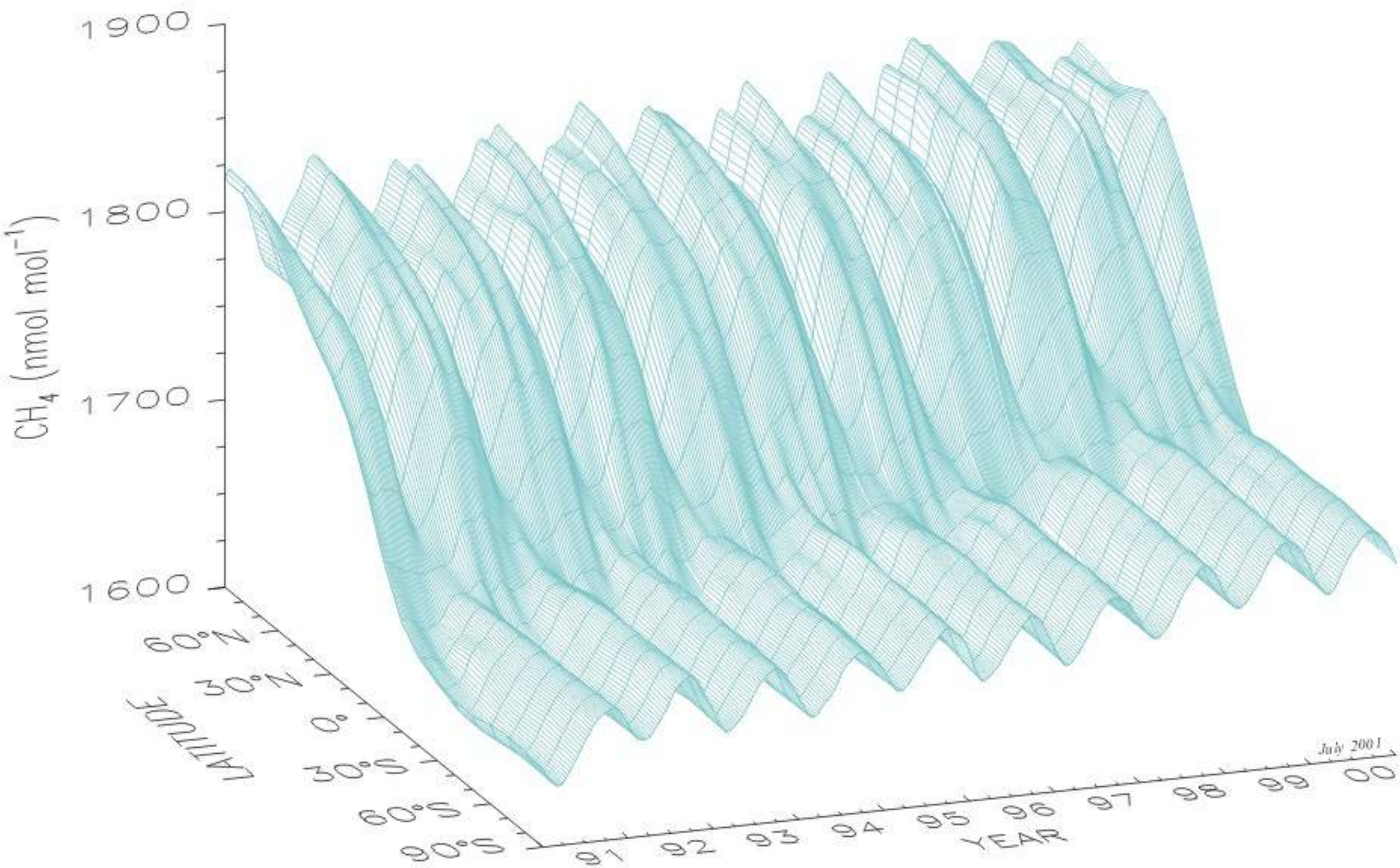
270 Tg CH_4 a^{-1}



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

Global distribution of methane

NOAA/CMDL surface air measurements



$[CH_4] \approx 1700$ ppbv commonly used

D.J. Jacob

Terrestrial Biogenic Emissions Nonemethane 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.

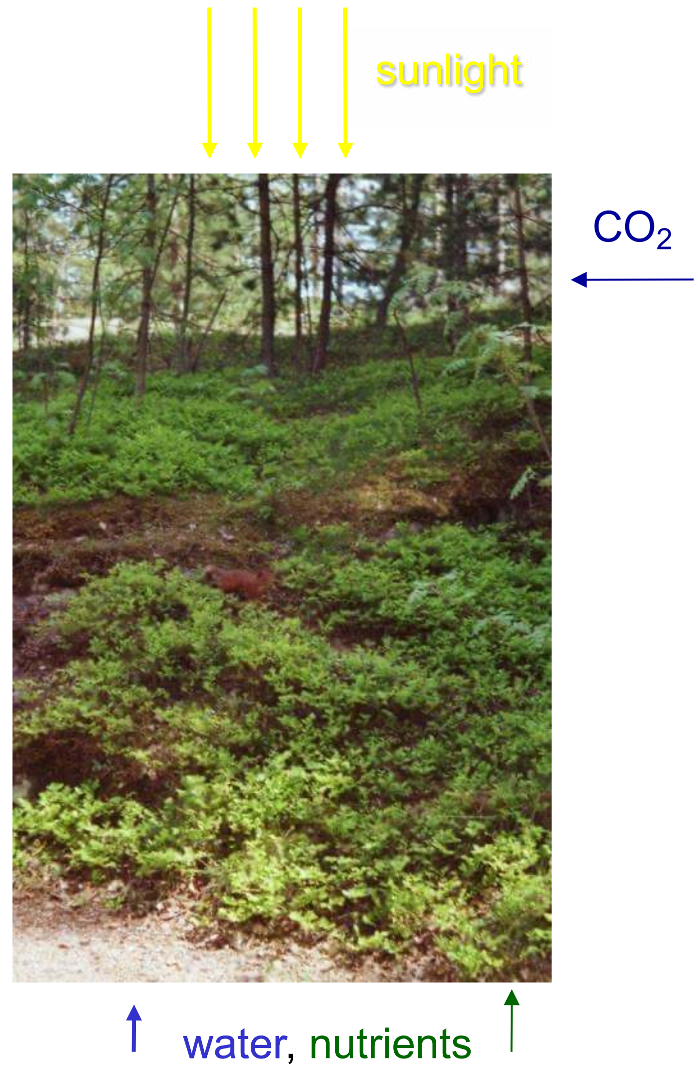
They may be emitted as by-products of photosynthesis, as responses to injury, and from metabolism and decay.

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_2, nutrients and solar radiation

1. Goal: uptake of sufficient CO_2 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_2 to O_2), 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

+hν

B) Oxidation

+OH

+Ozone

VOC

$+NO_3$

Transport

C) Cloud interactions (uptake, reactions)

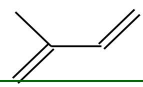
A) Emission

D) Aerosol formation

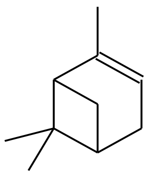
Biogenic volatile organic compounds (VOCs): Overview

- **Reactive VOCs**

Isoprene (C_5H_8)

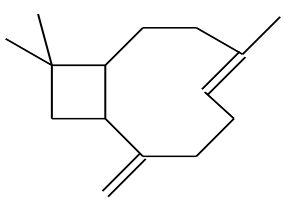


Monoterpenes ($C_{10}H_{16}$)



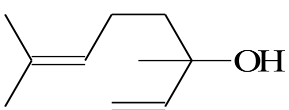
e.g. α-pinene

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



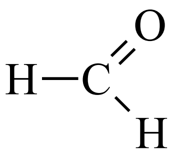
e.g. β-caryophyllene

Oxygenates

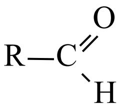


e.g. linalool

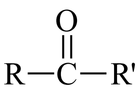
- Less reactive VOCs
  - Carbonyl compounds (e.g. formaldehyde HCHO)



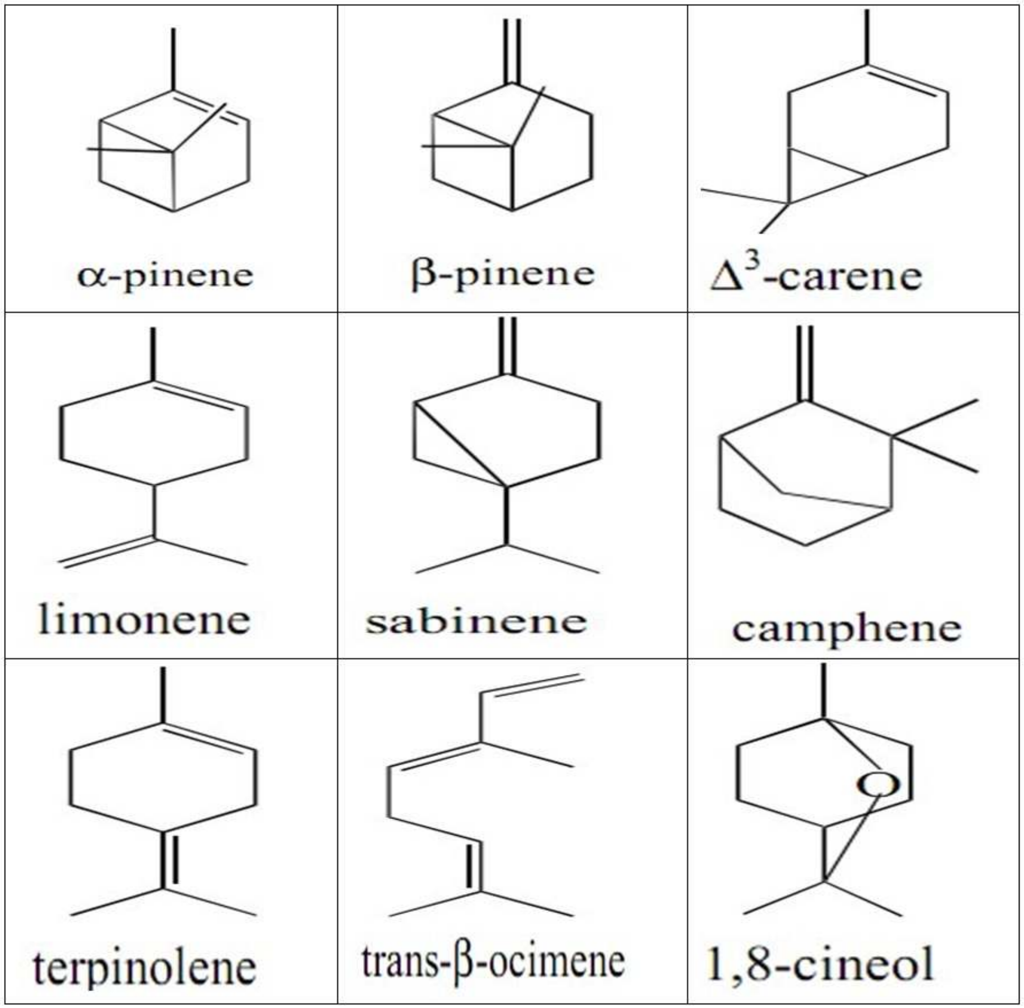
Aldehydes: R-CHO:



Ketones: RC(O)R':
(R and R' ≠ H)



Chemical structures of typical monoterpene in the emission of the biosphere



Important

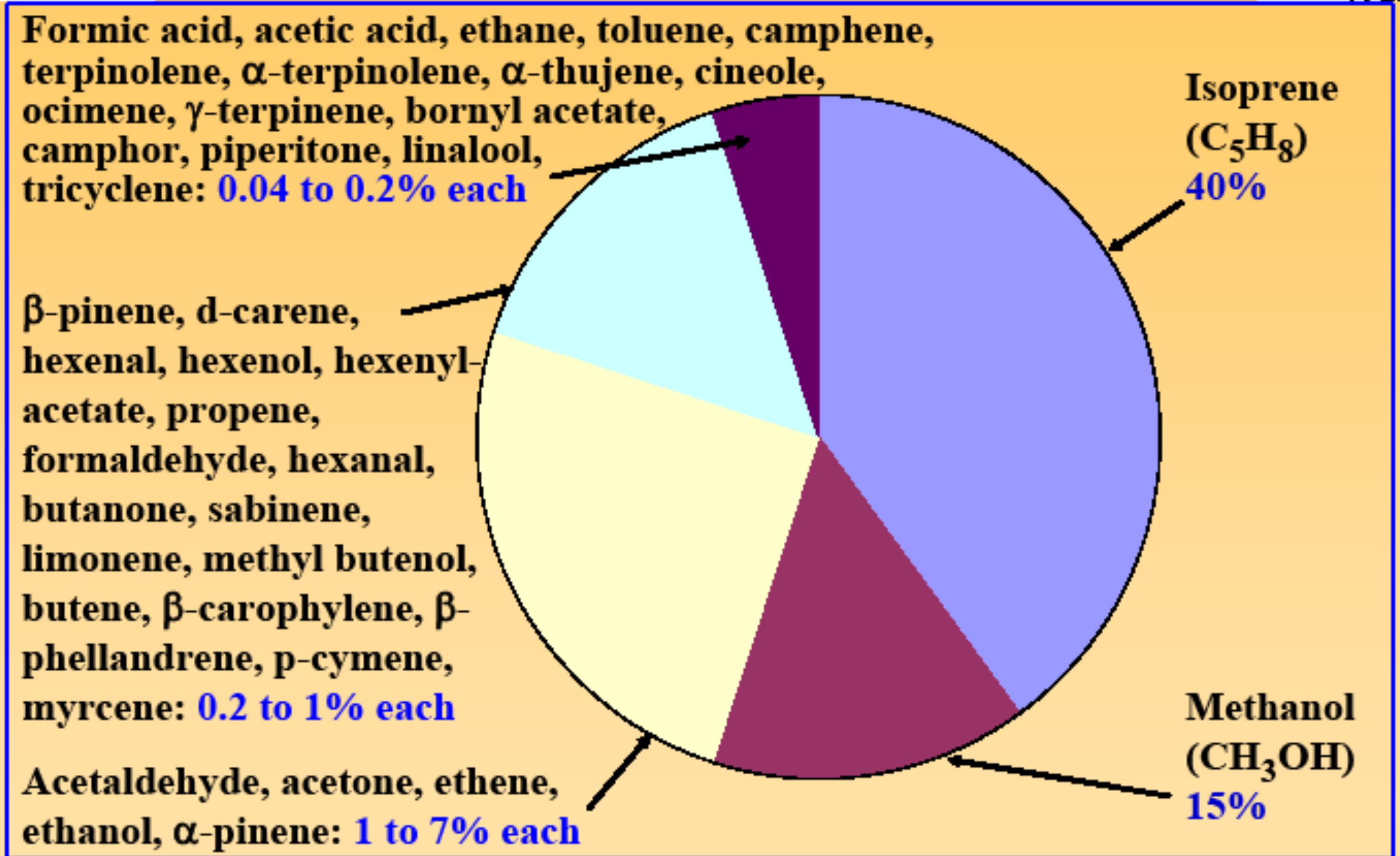
All have same molar mass

But different reaction rates with OH, O_3 and NO_3

Global biogenic VOCs

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

NCAR



Alex Guenther

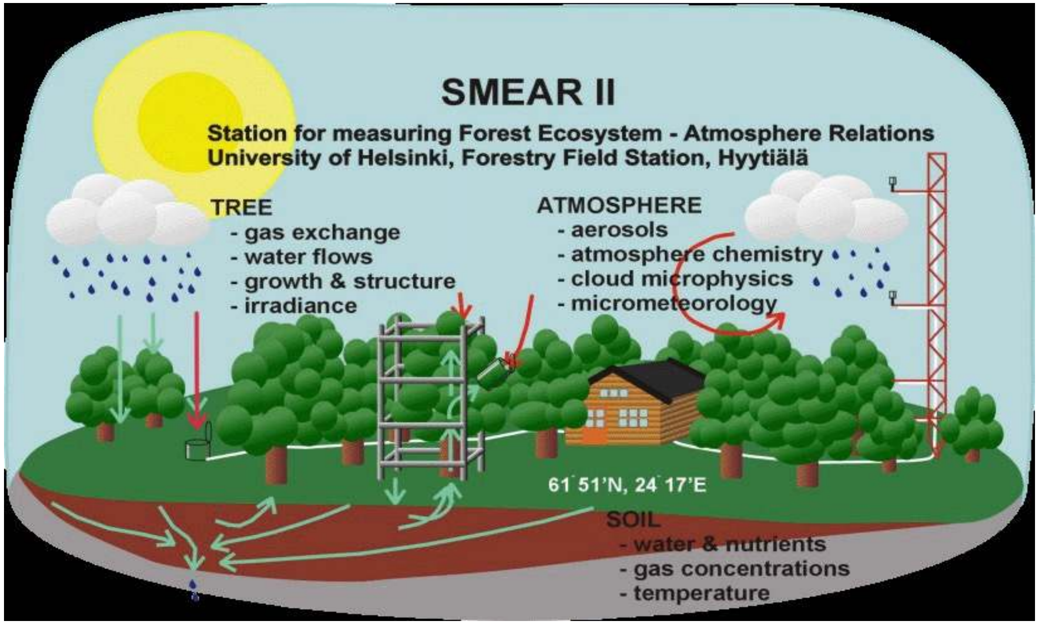
iLEAPS meeting- September 29, 2003

…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 emssion source**
- **B) indirect: Relaxed Eddy Accumulation (REA)-Systeme**



Hyytiälä,
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/SMEAR/index.php?option=com_content&task=view&id=22&Itemid=56

b) Indiret measurements

- Possible for large-scale areas of homogeneous vegetation

- Measurements of the individual compounds inside and above the forest

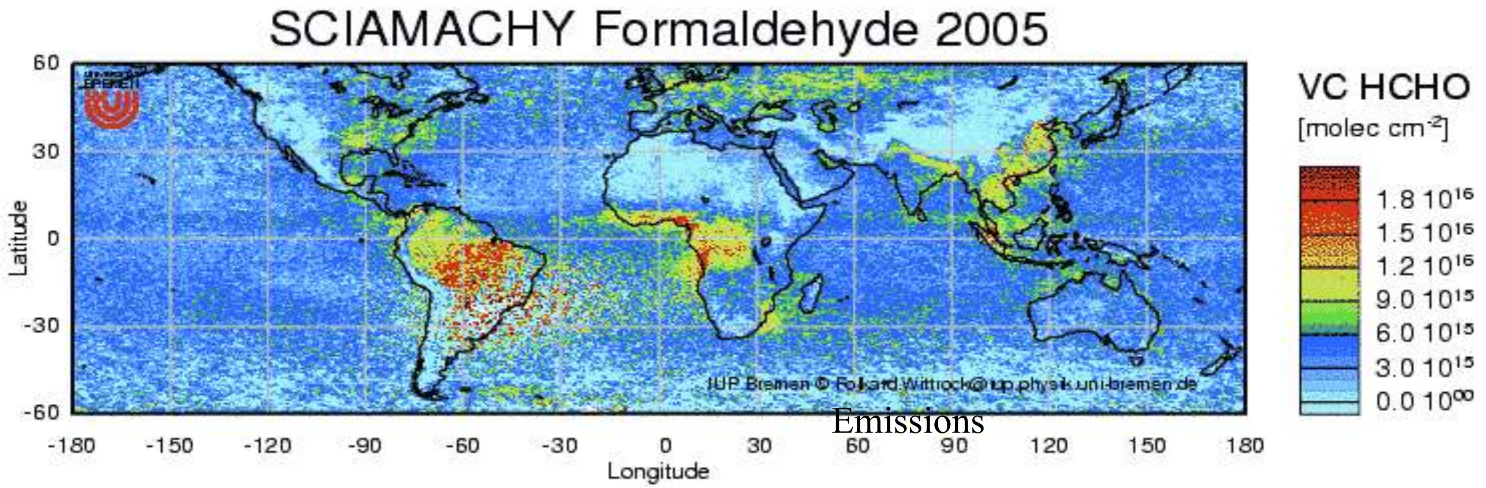
- Calculation of the exchange coefficients

➢ 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



IUP, Bremen

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 $F_{vegetation}$ from the vegetation [Guenther *et al.* (1995)]:

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

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

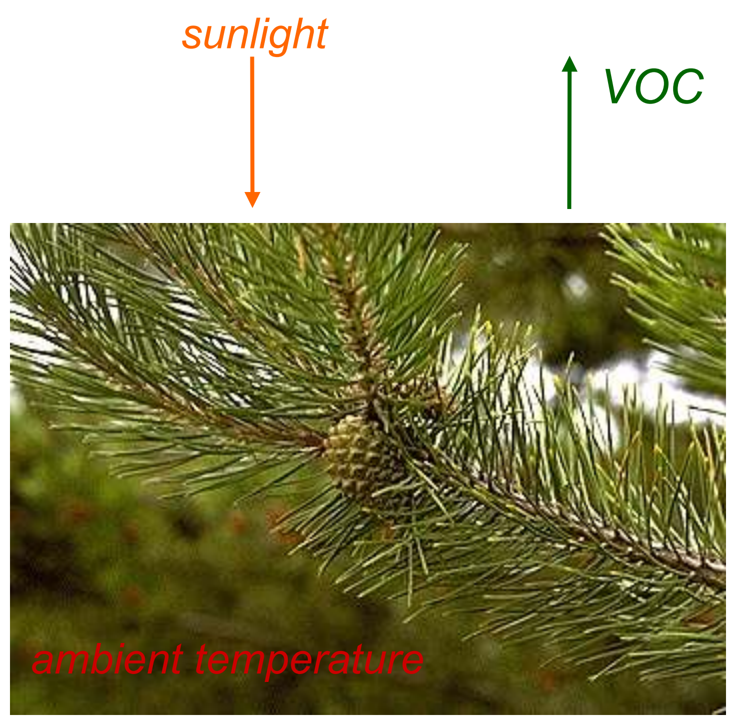
→ *e.g. amount of leaves/needles per surface area*

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

→ *amount of emission at standard conditions*

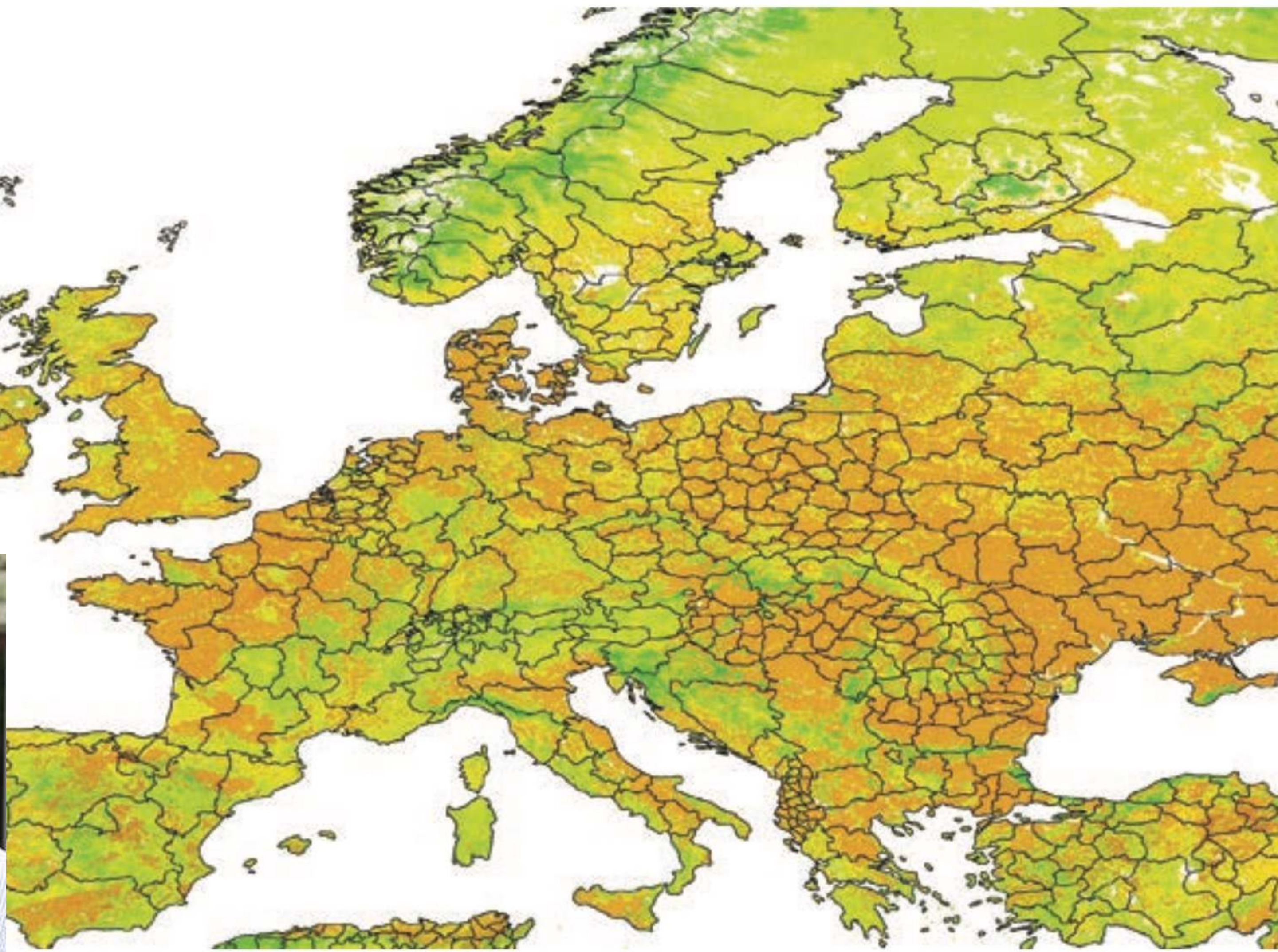
γ: adjustment factor for dependence on temperature and light – emission activity

δ: emission activity factor for long term controls



pine branch

Ecosystem dependent emission factors [µg m^{-2} h^{-1}] for isoprene (A. Guenther and C. Wiedenmeyer)



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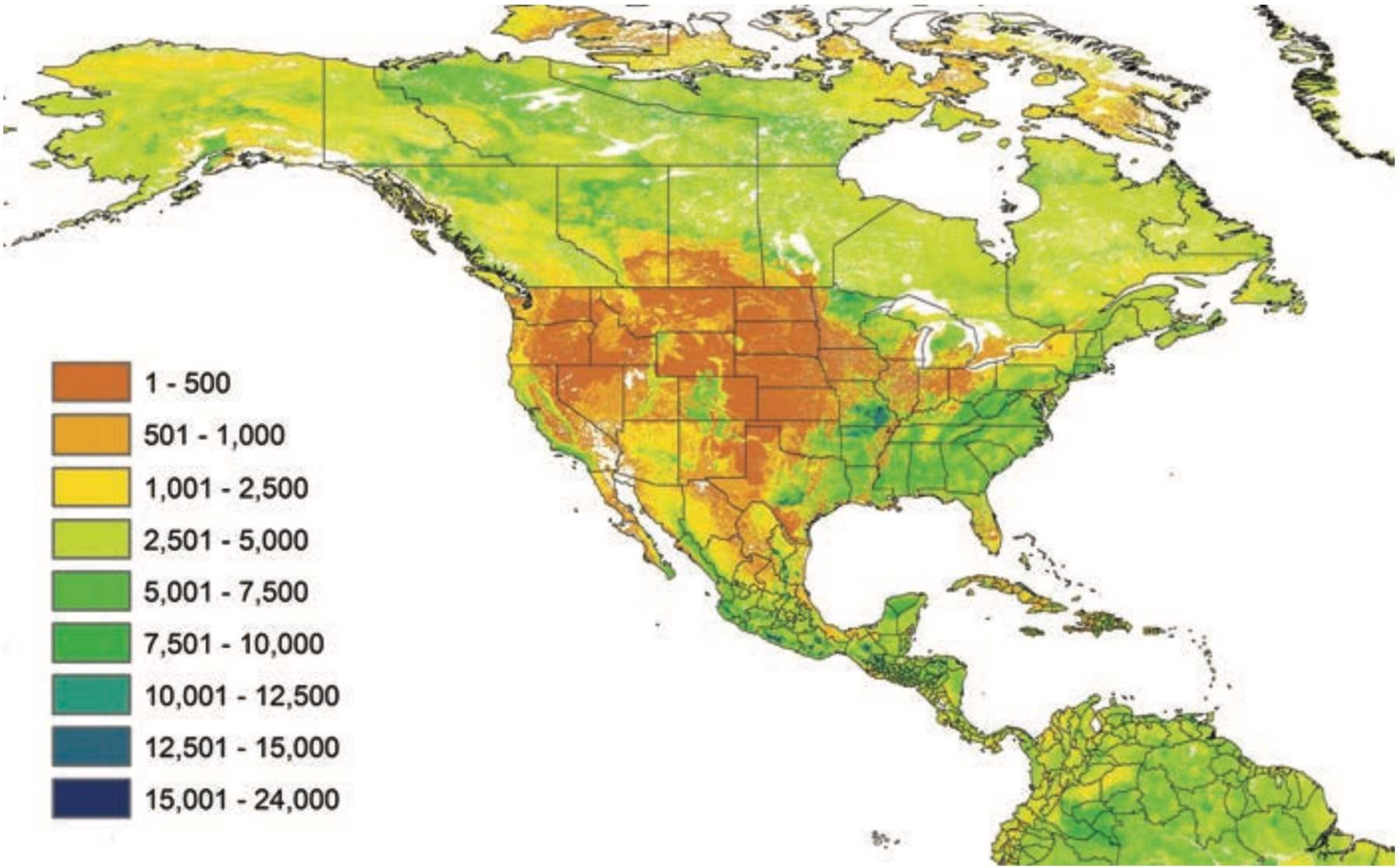
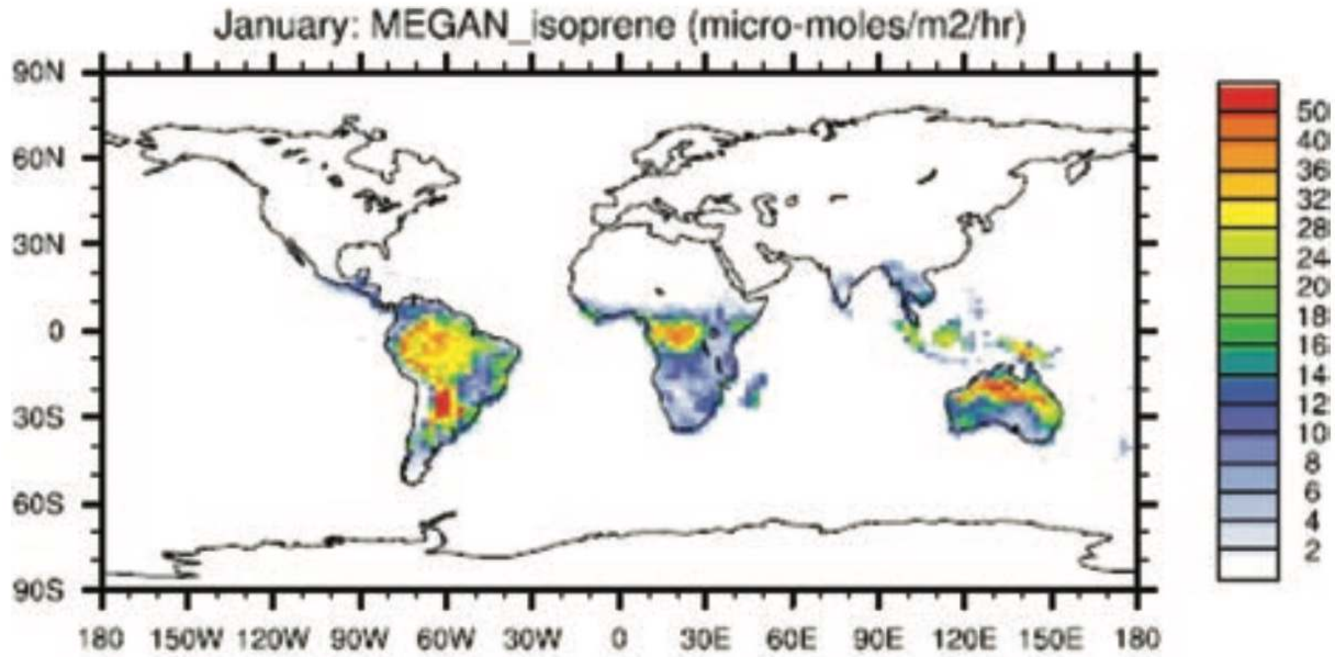


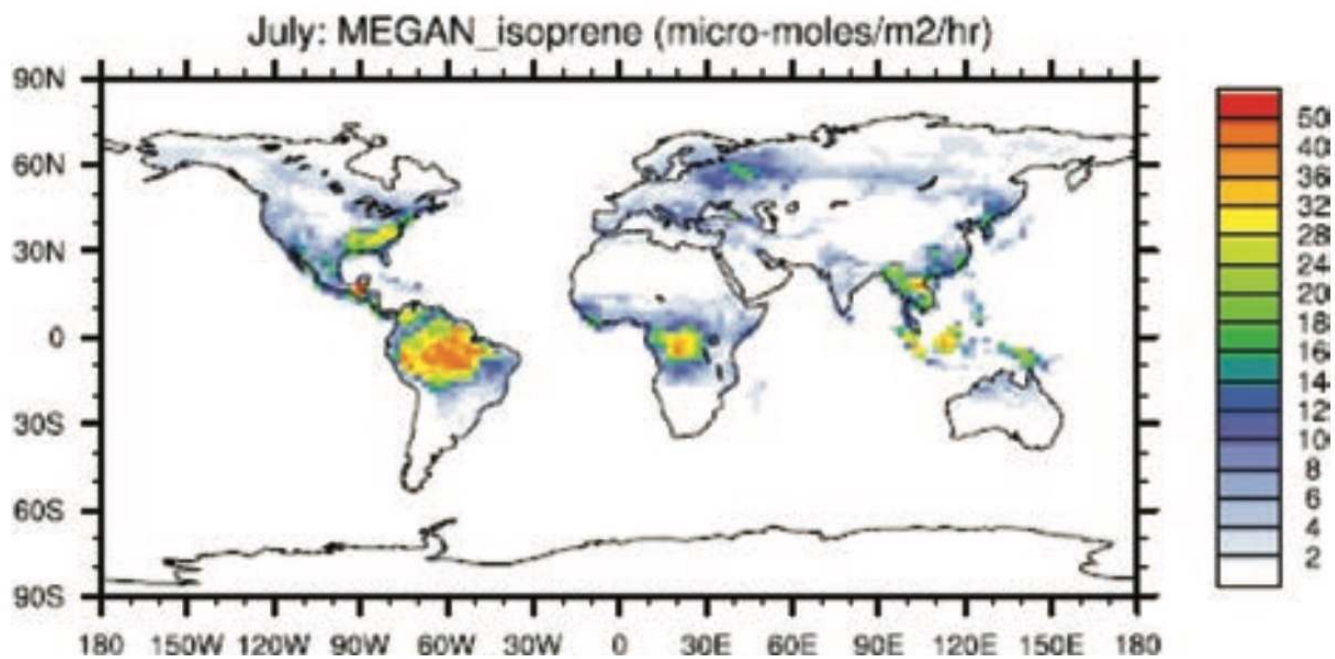
δ: emission activity factor for long term controls

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)



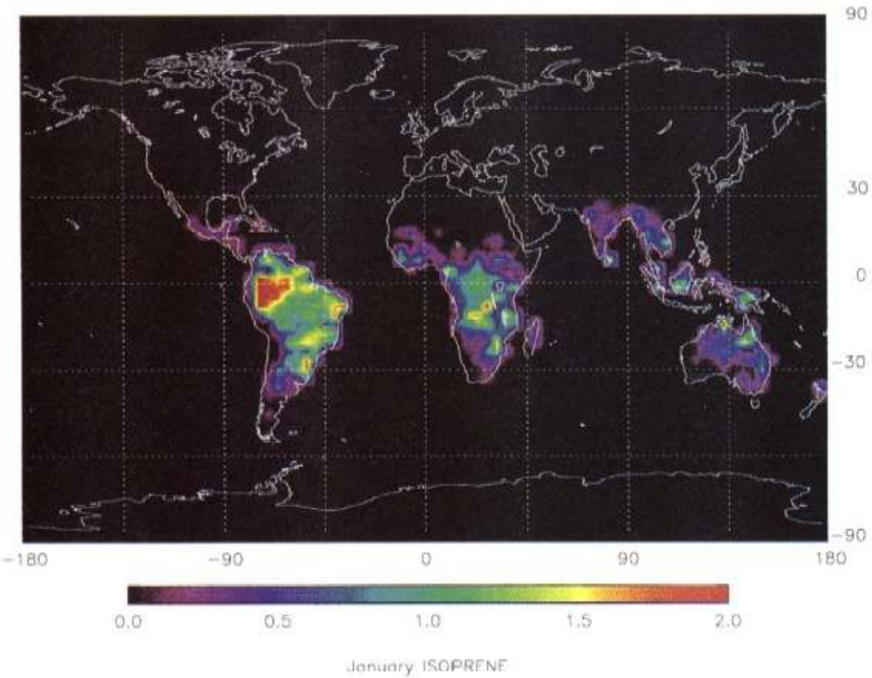


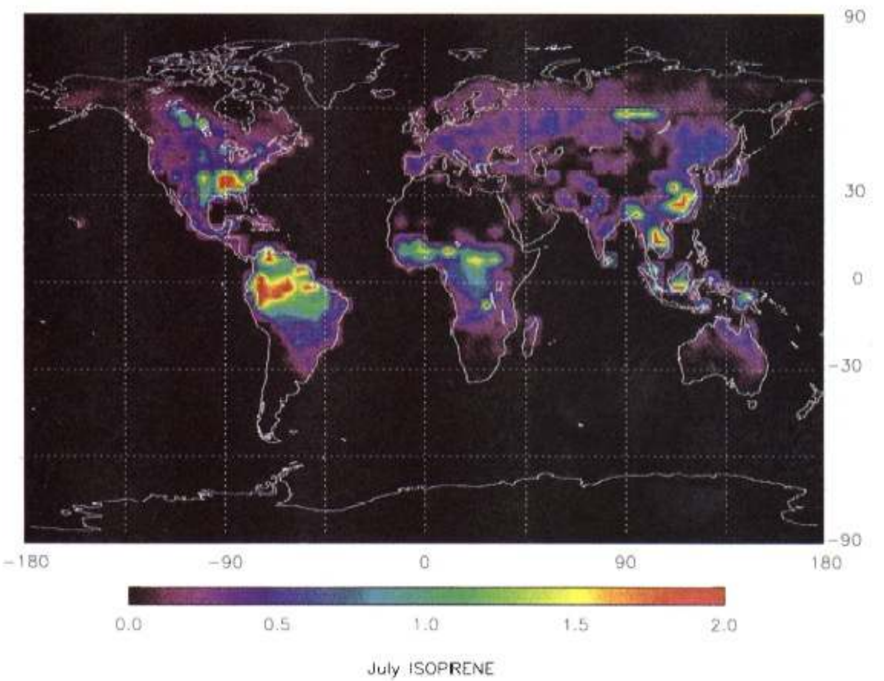
Isoprene (C_5H_8) emission

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 C m^{-2} $month^{-1}$ [Guenther *et al.*, 1995]

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

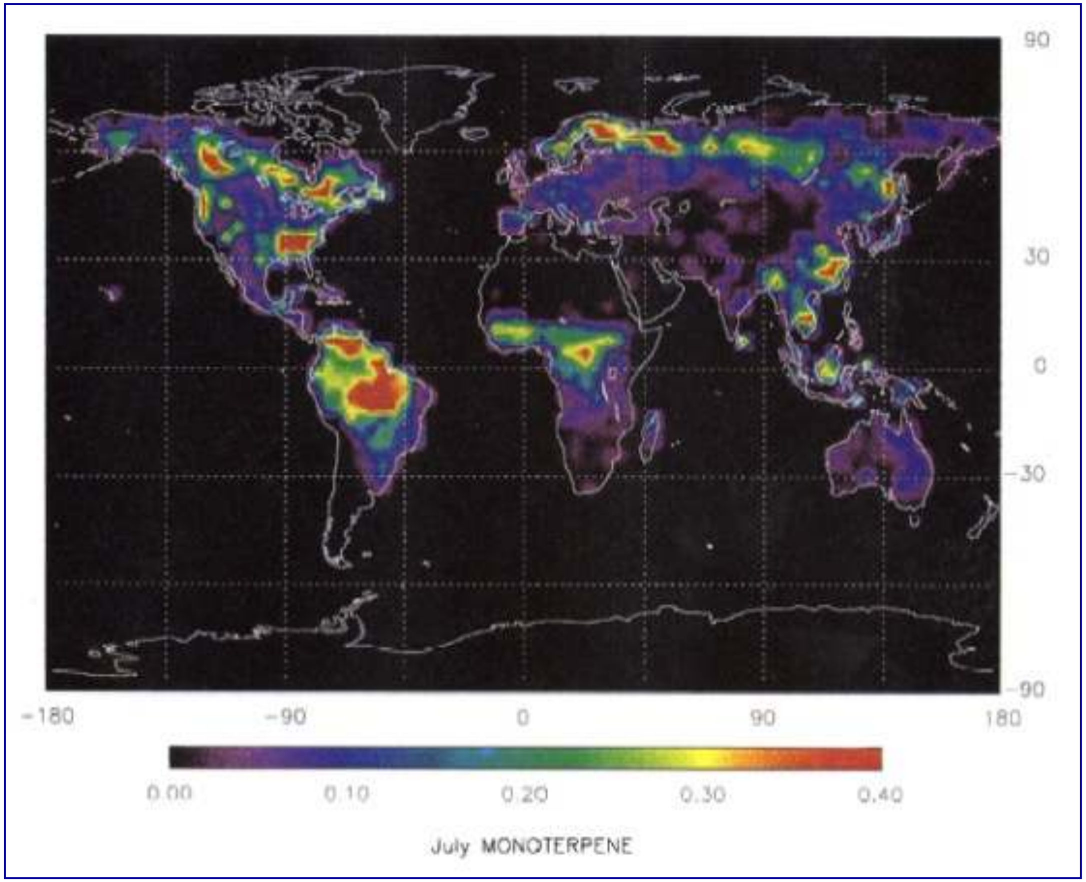
Estimated annual emission on the global scale:

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

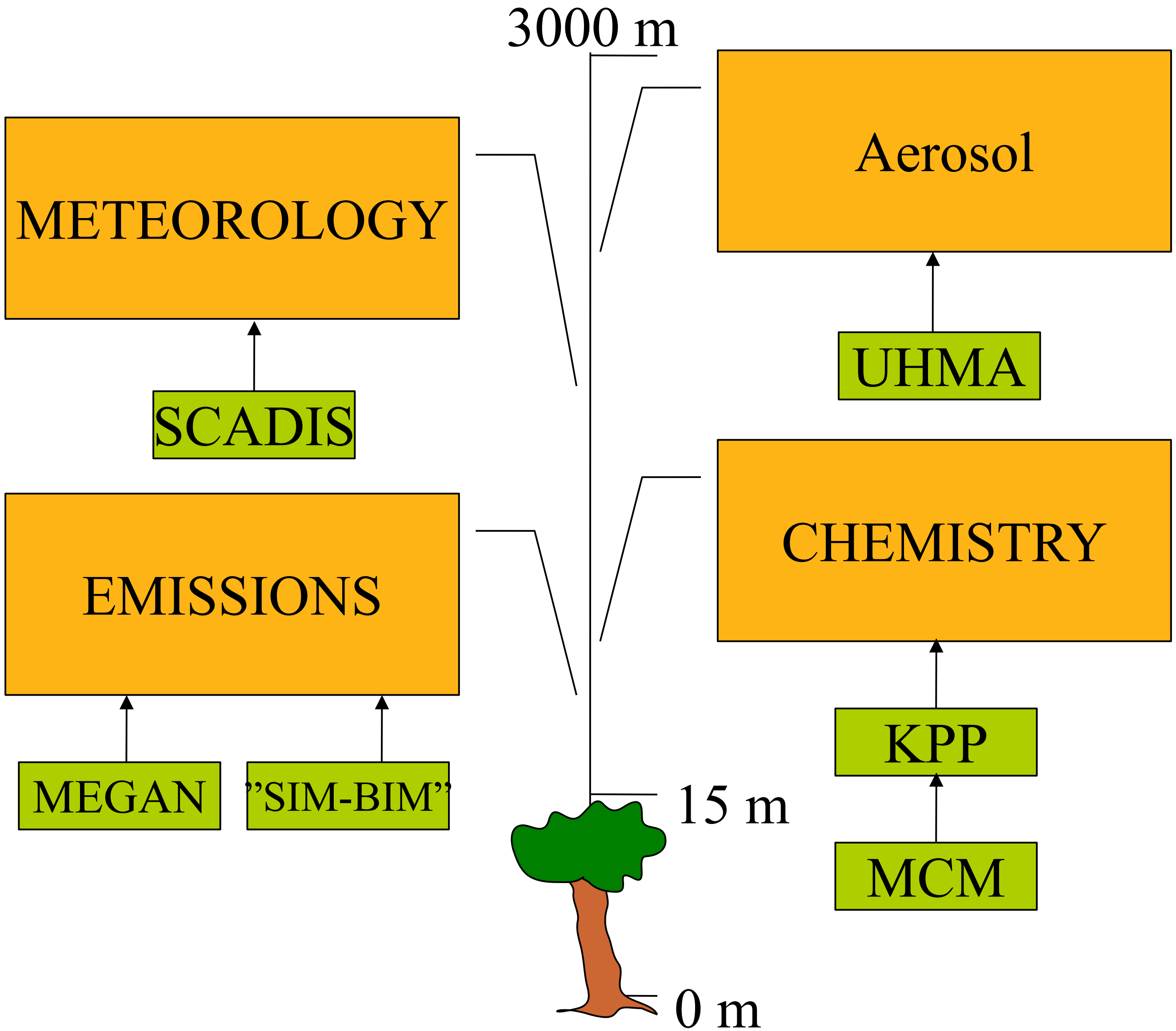
$$\gamma = \exp(\beta \cdot (T - T_s))$$

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

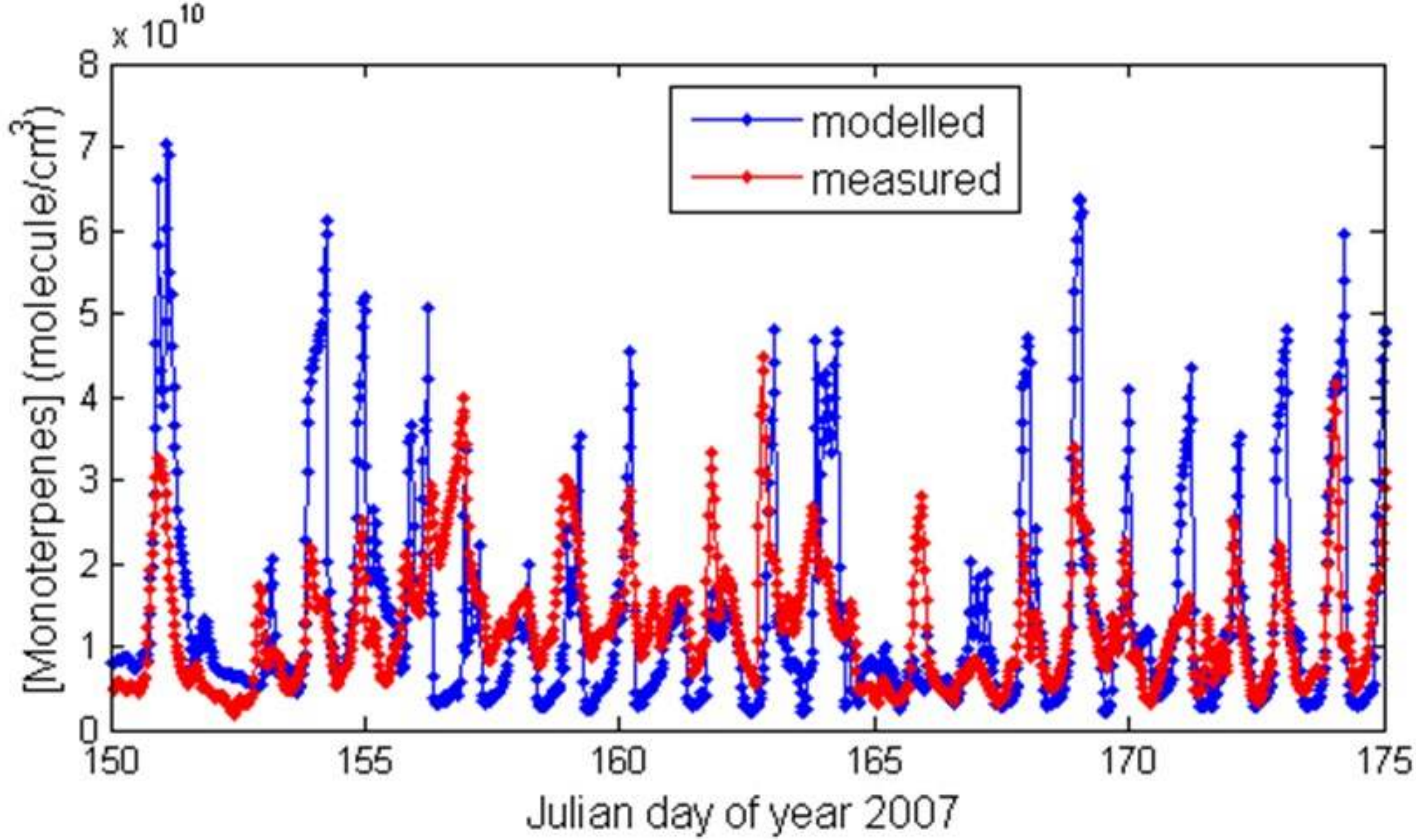


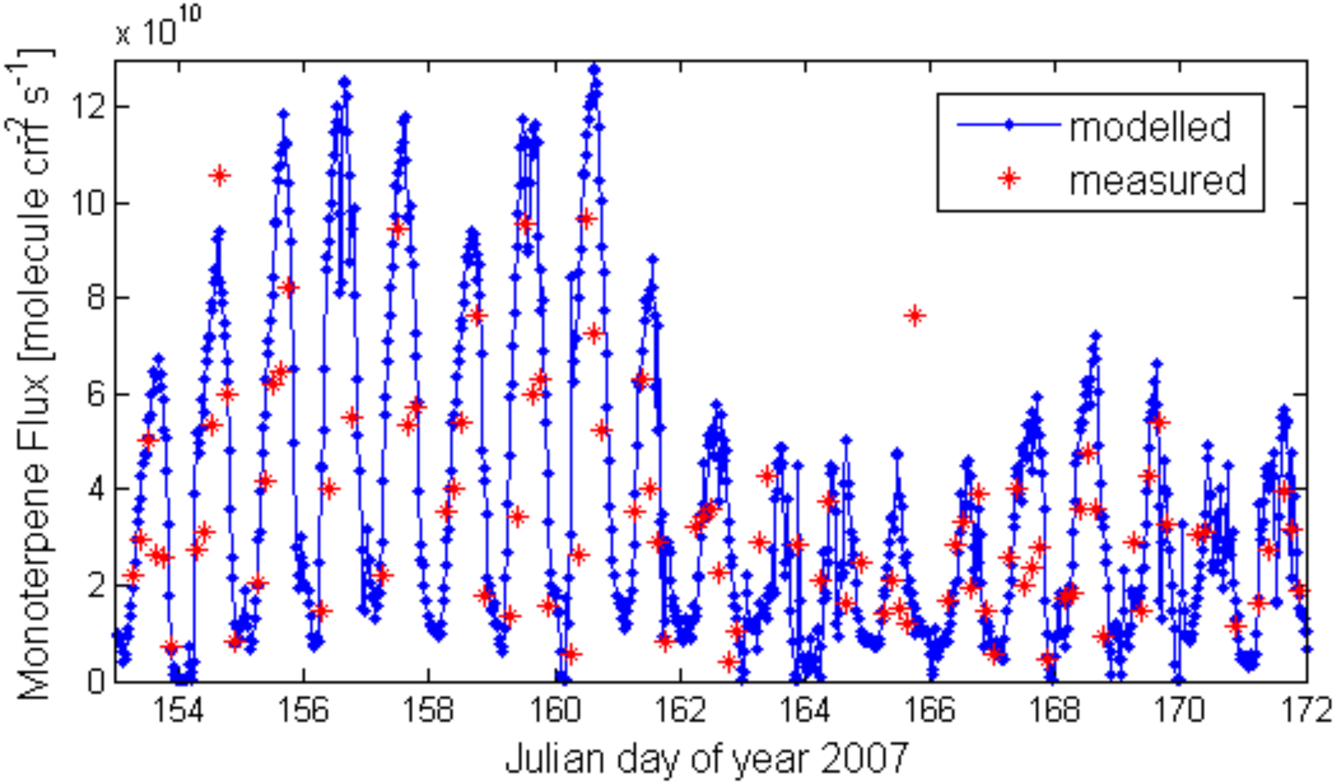
No emissions from the Guenther *et al.* approach during winter in the Northern hemisphere, but there are.

SOSAA is a combination of several models

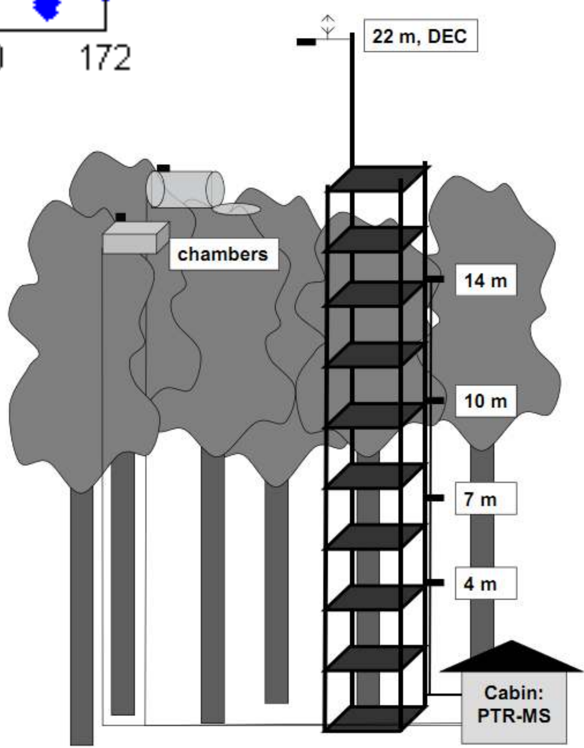


Modelled (MEGAN) and measured monoterpene concentrations at 4 m in June 2007 for SMEAR II

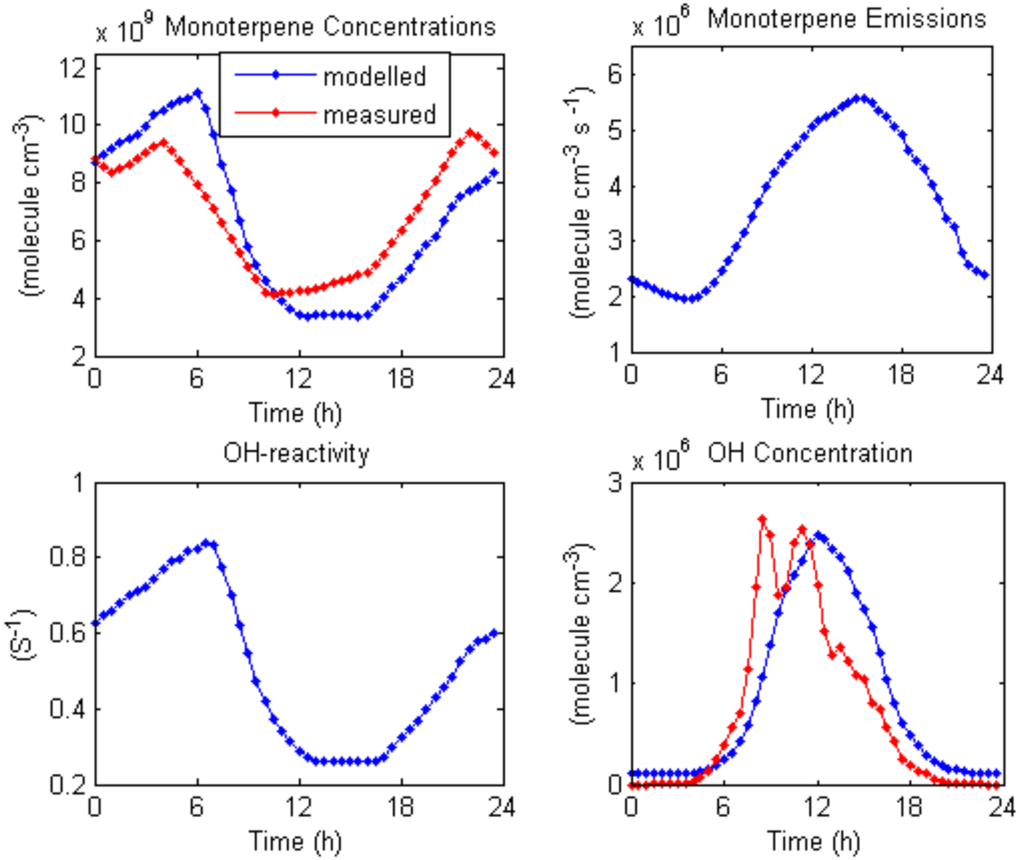


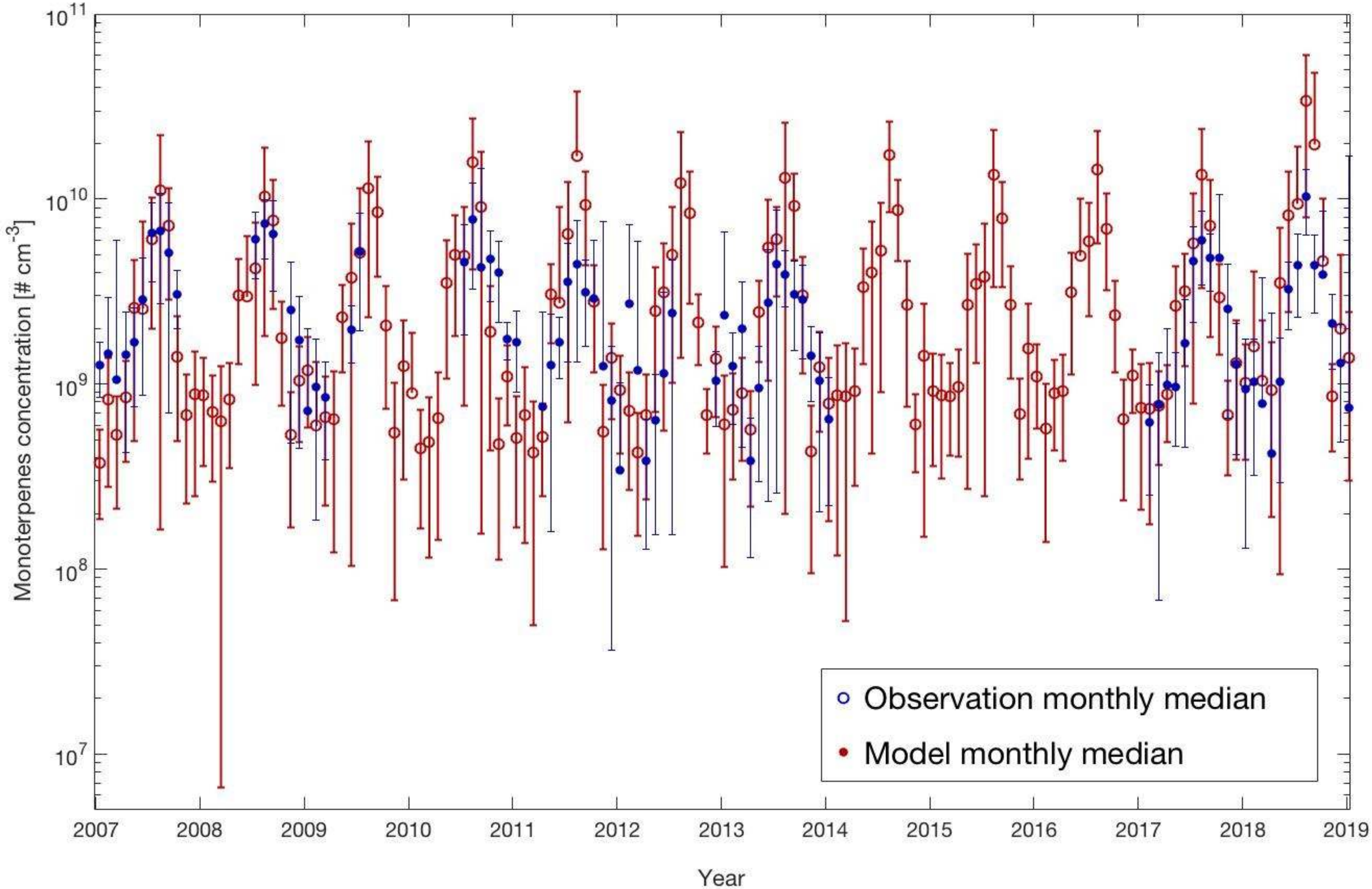


Modelled (MEGAN) and measured monoterpene fluxes at 22 m in June

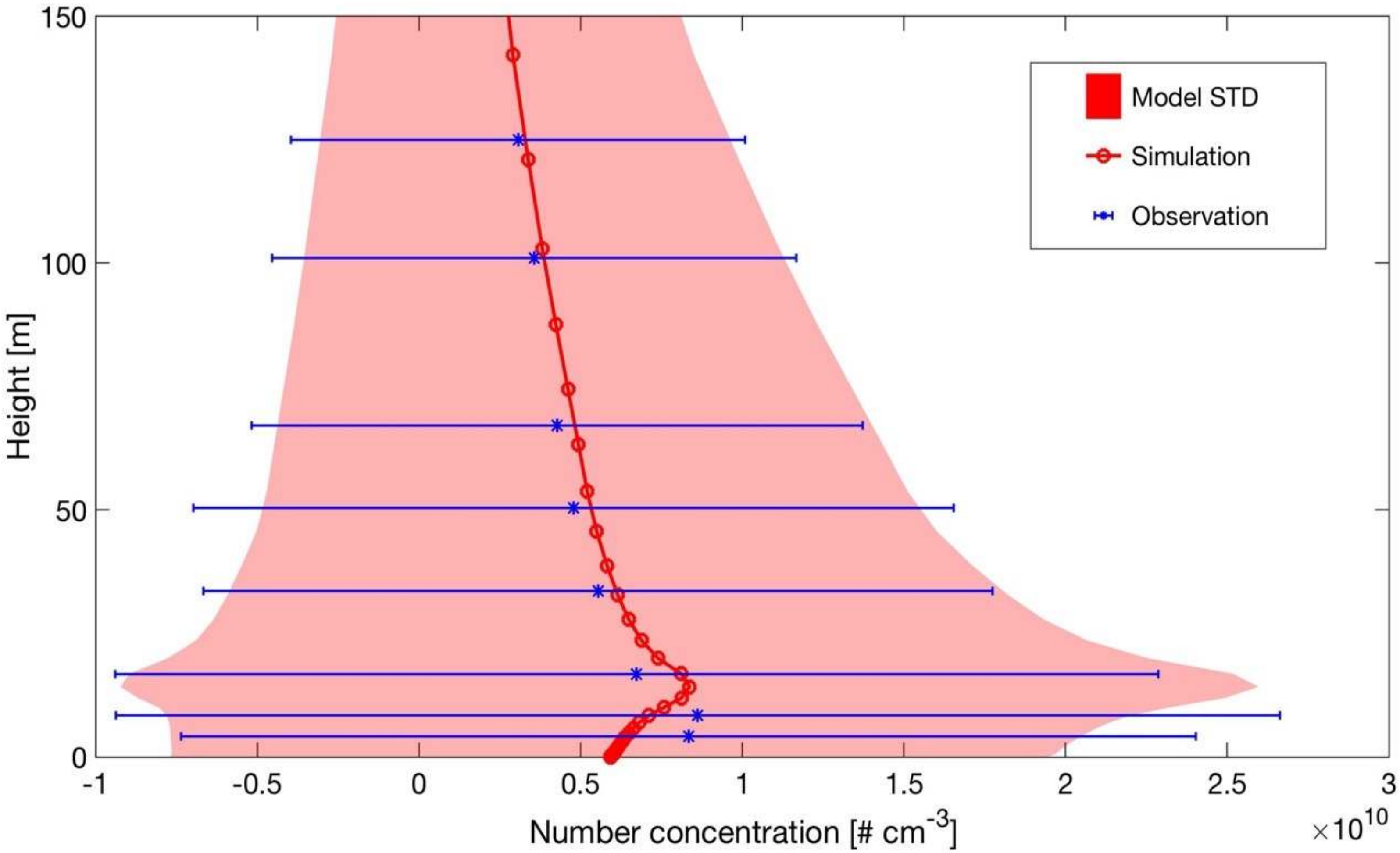


Modelled and measured diurnal variations at 14 m for the summer of year 2007



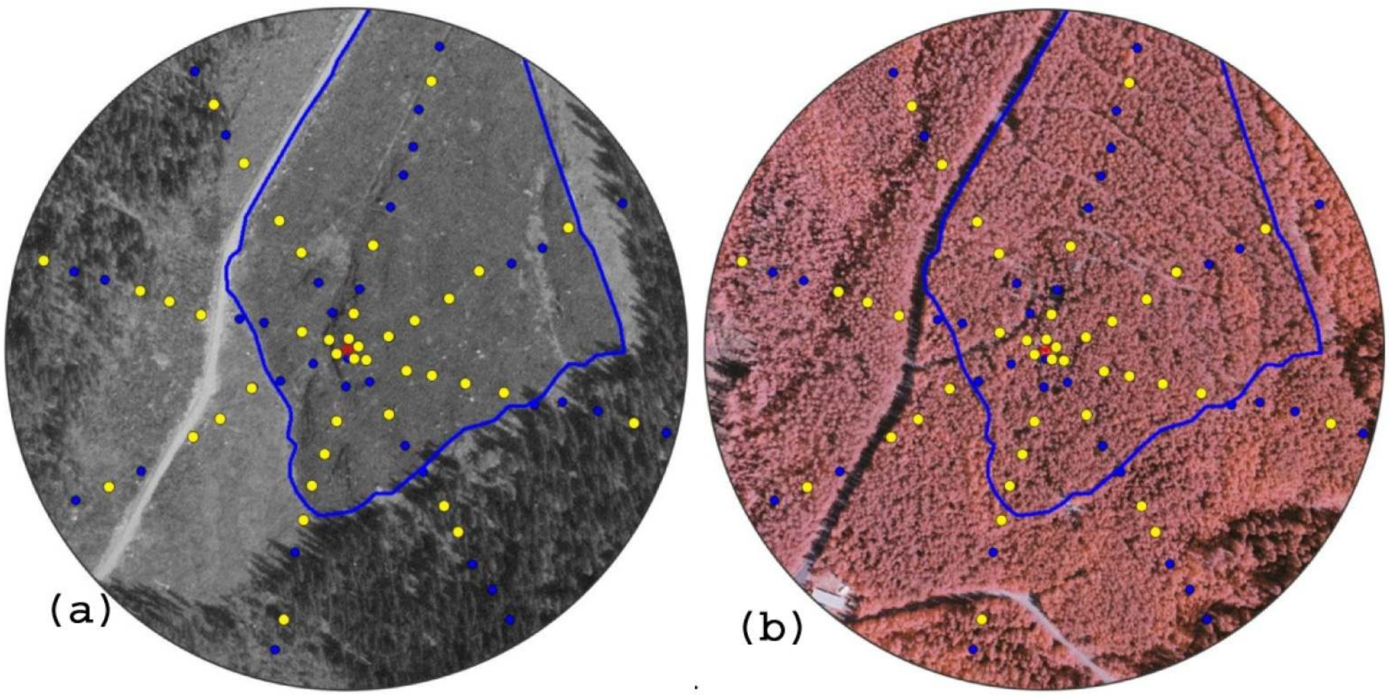


Measured and modelled monthly median values of monoterpene concentrations from 2007 to 2018 for the height interval 20m-40m. The ±1 standard deviation for both data sets are shown as vertical bars.



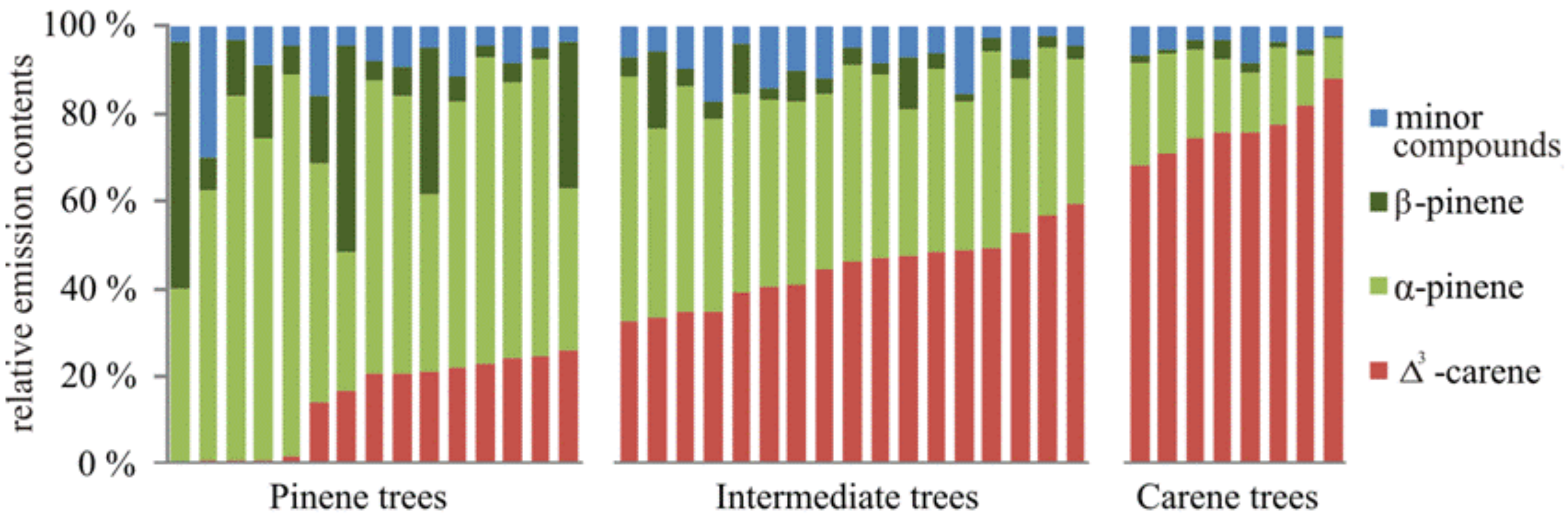
Vertical profiles of measured and modelled monoterpene concentrations and ±1 standard deviations at SMEAR II, Finland averaged for the years 2007-2014 and 2017-2018.

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

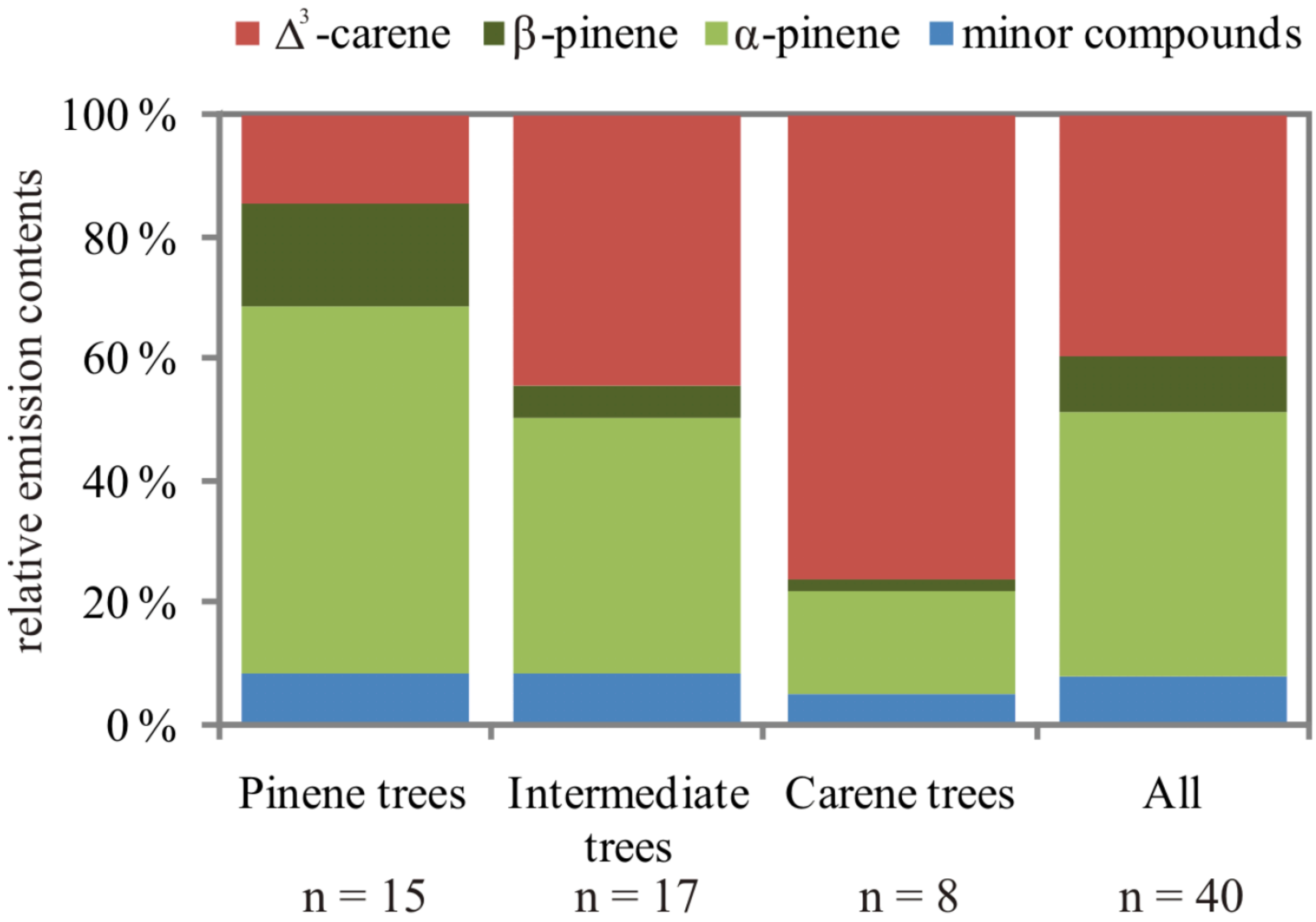


Aerial photographs of the sample area. Sampling grid is marked with blue (no sample) and yellow (sampled) circles. **(a) SMEAR II** stand (marked with blue line) and neighbouring stands in 1962; **(b) Same stands in 1997. Red dot = mast; diameter of circle 400 m.**

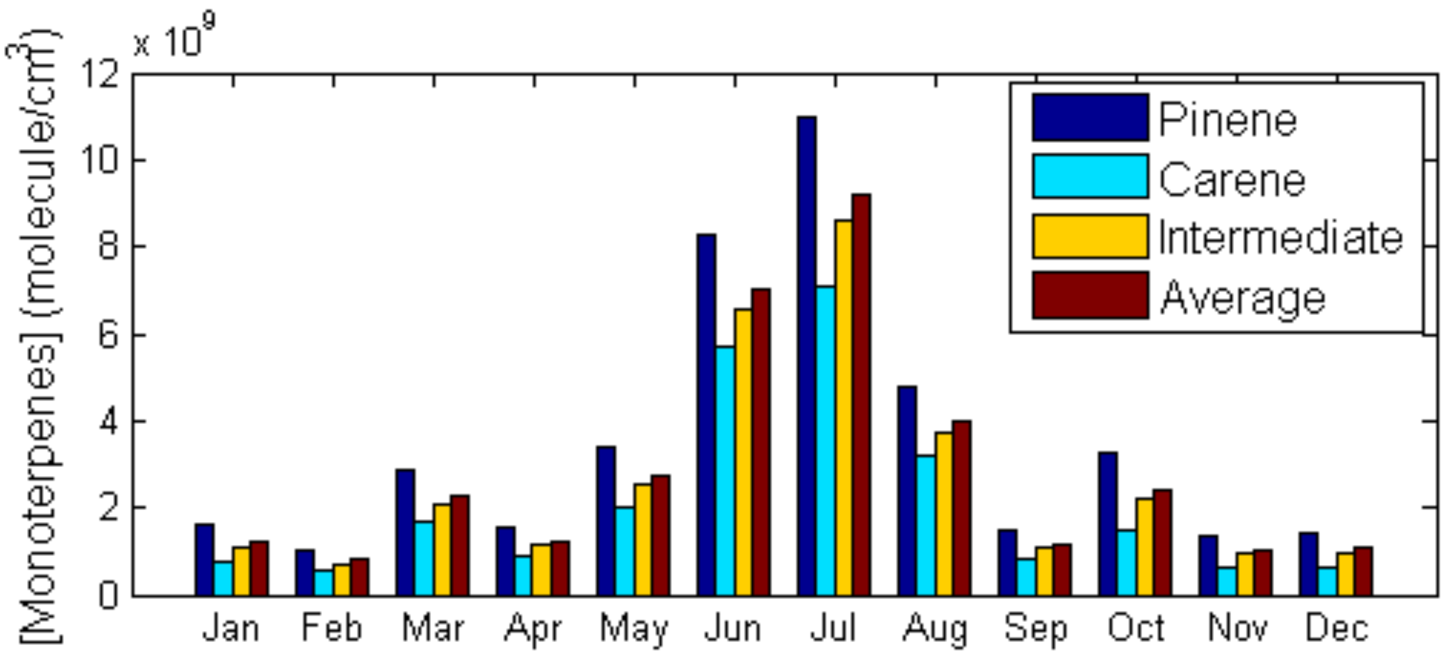
Emission content of the 40 selected trees (Bäck et al., Biogensiences, 2012)

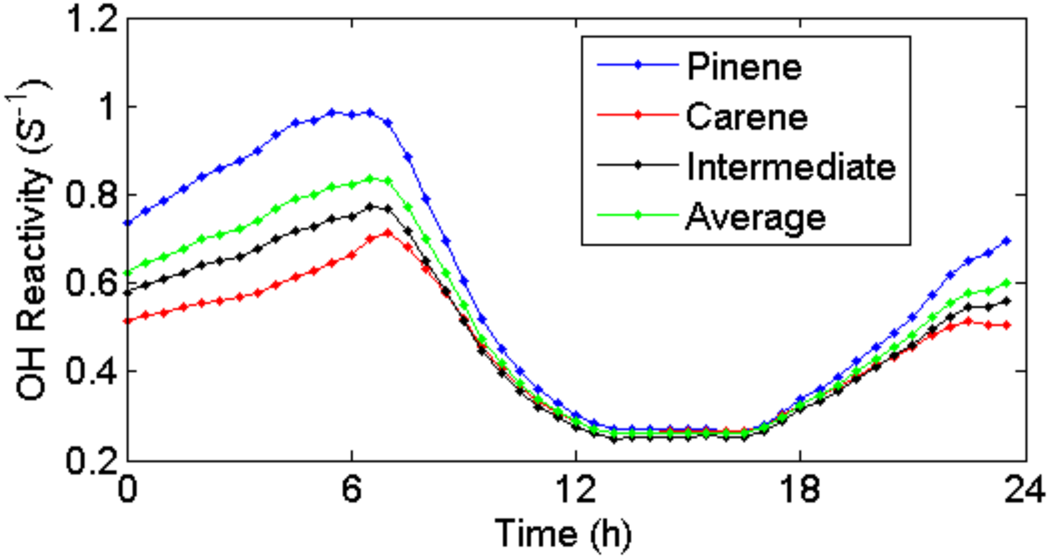


Average relative emission contents of three clusters. Clustering conducted with the major emitted compounds



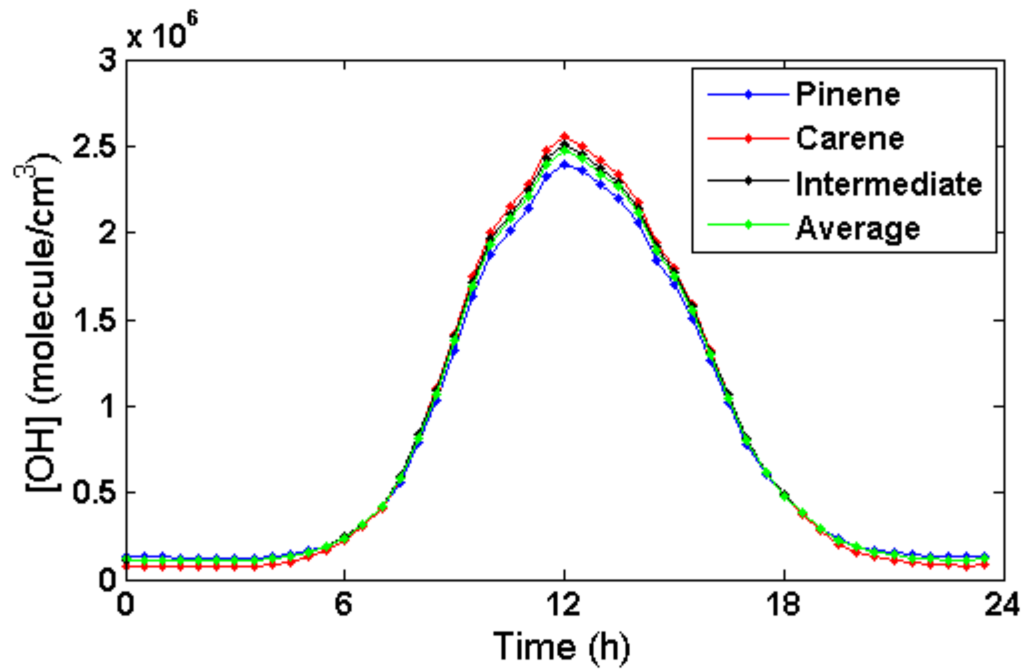
Modeled monthly mean monoterpene concentrations at 14 m for the year 2007





Modeled diurnal profiles of OH reactivity at 14 m for the summer of year 2007

Modeled diurnal profiles of OH concentrations at 14 m for the summer of year 2007



Chemical reactions

Isoprene and terpenes react with OH, ozone and NO_3

Compound	Chem. lifetime	Class
Isoprene	2.5 h	Isoprene
α-pinene	*2.3 h*	Monoterpene
Limonene	*50 min*	Monoterpene
β-caryophyllene	1-2 min	Sesquiterpene

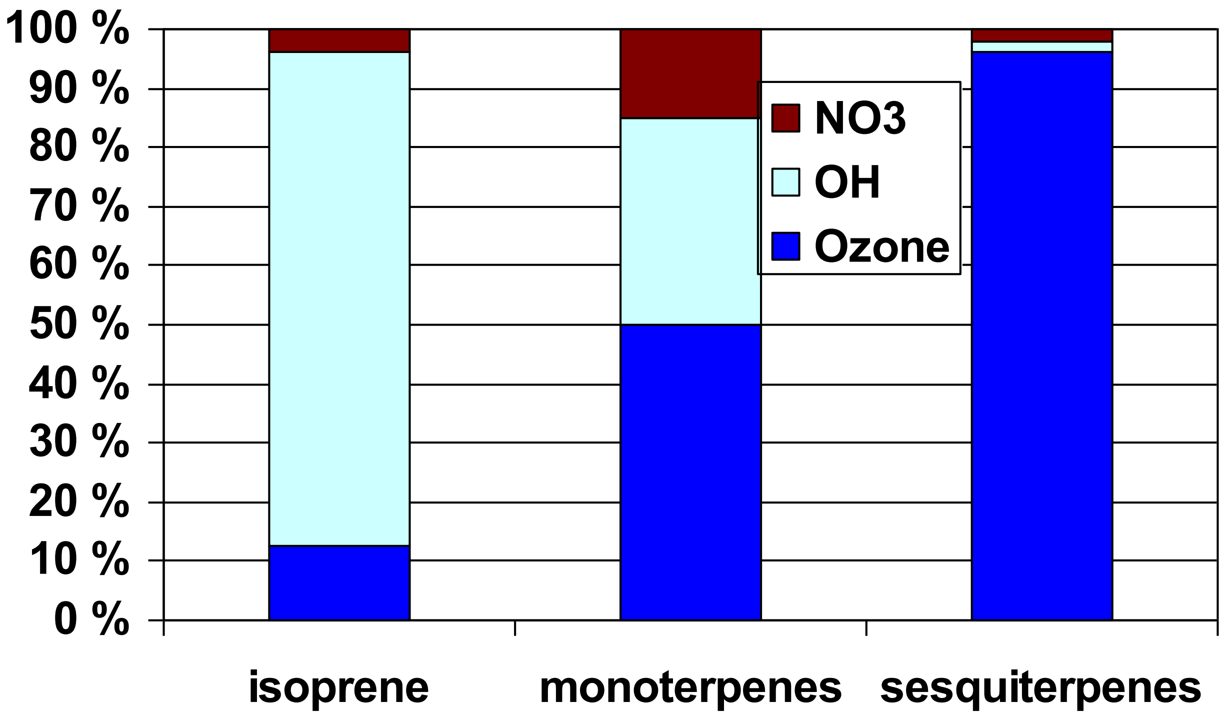
Consequences:

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 NO_3 displayed as fractions



Terrestrial Biogenic Emissions
Nitrogen oxides

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Methane	190	50	–	290	–	–	–	530
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SO_2 (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.

Brasseur and Jacob, 2017

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.

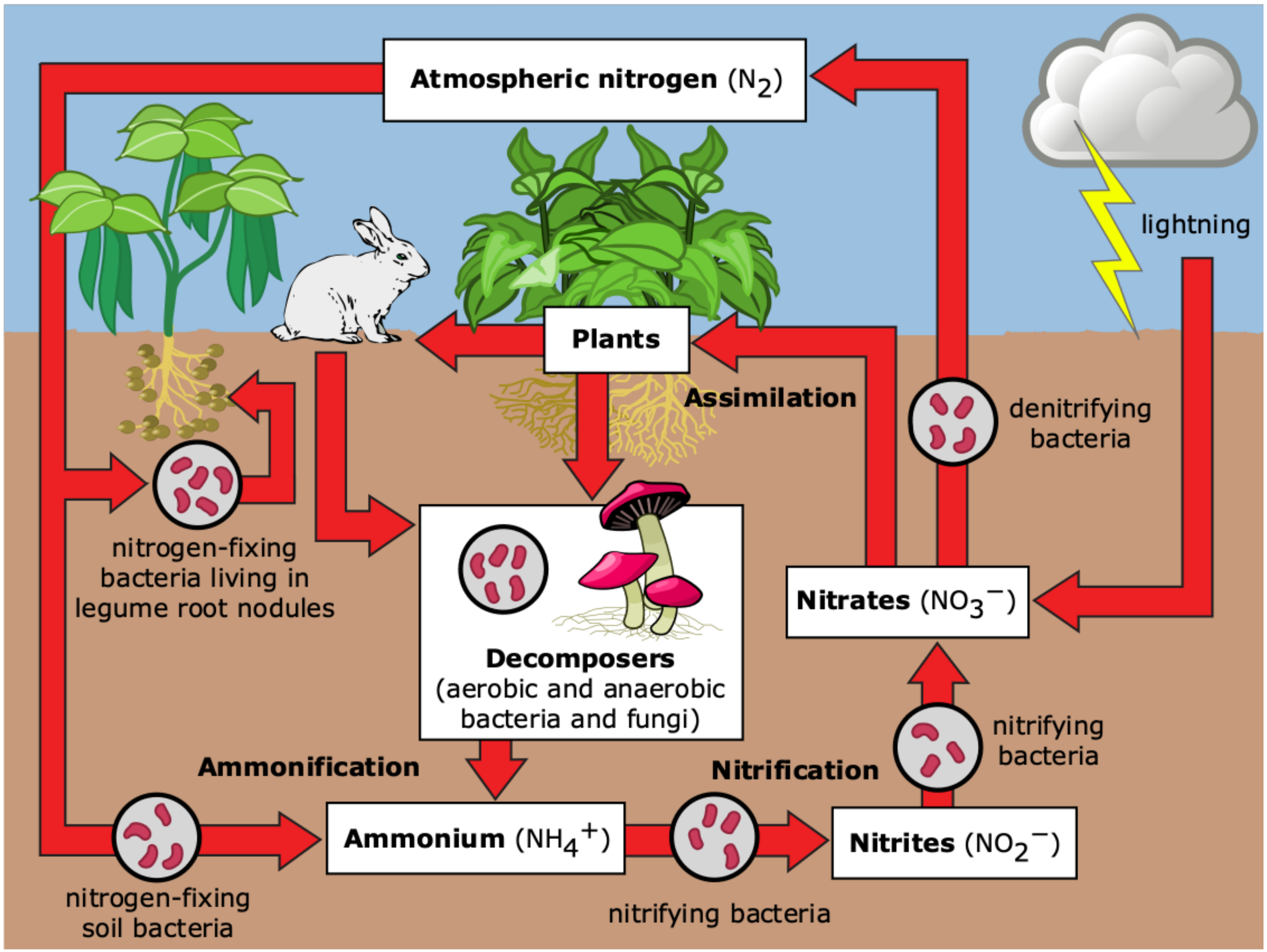
Fixed nitrogen can also be directly delivered to the ecosystem by fertilizer application or by deposition of atmospheric ammonia and nitrate.

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.

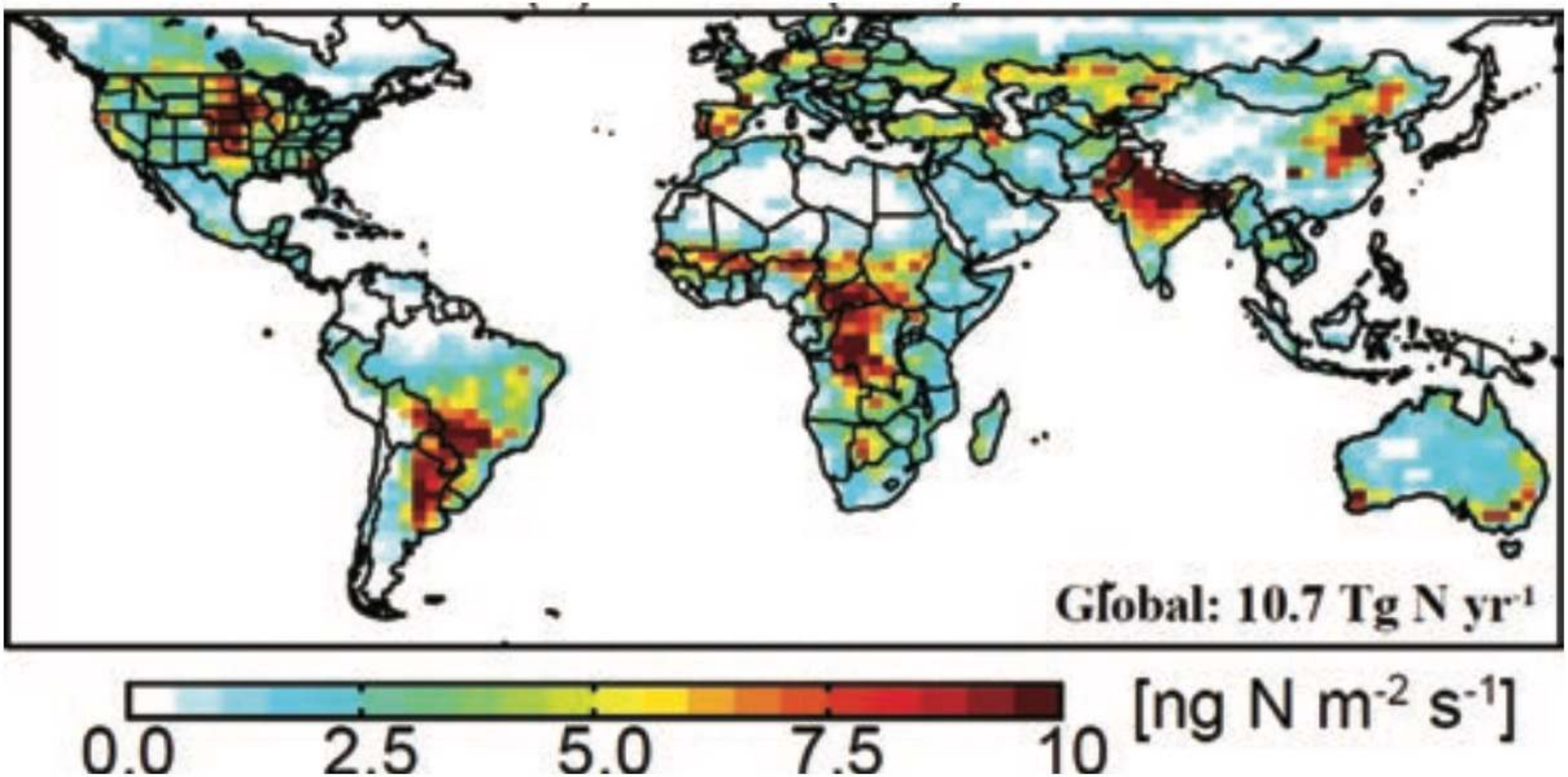
Terrestrial Biogenic Emissions
Nitrogen oxides



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.