
Biogenic / natural / anthropogenic emissions

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

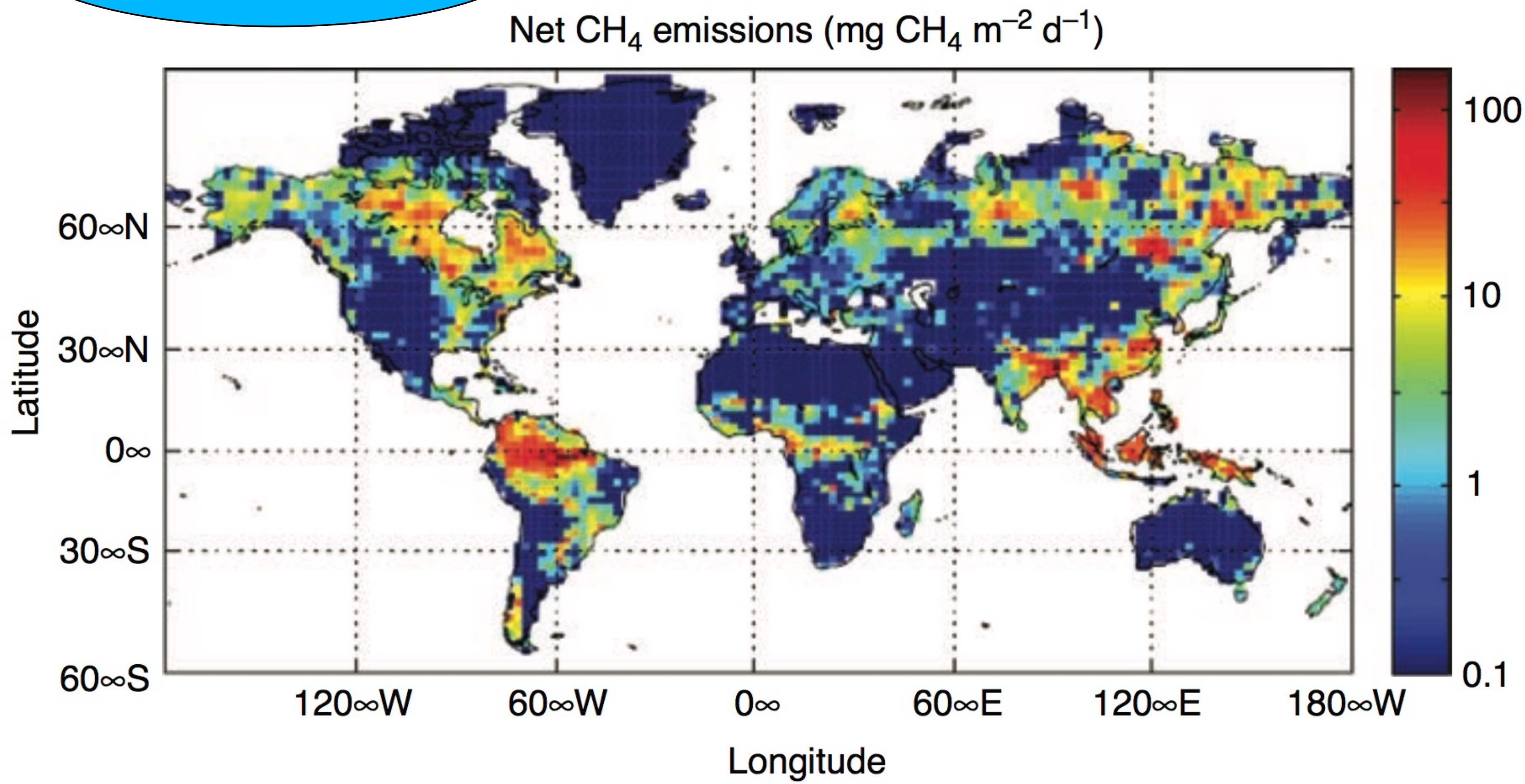
Terrestrial Biogenic Emissions
Methane

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

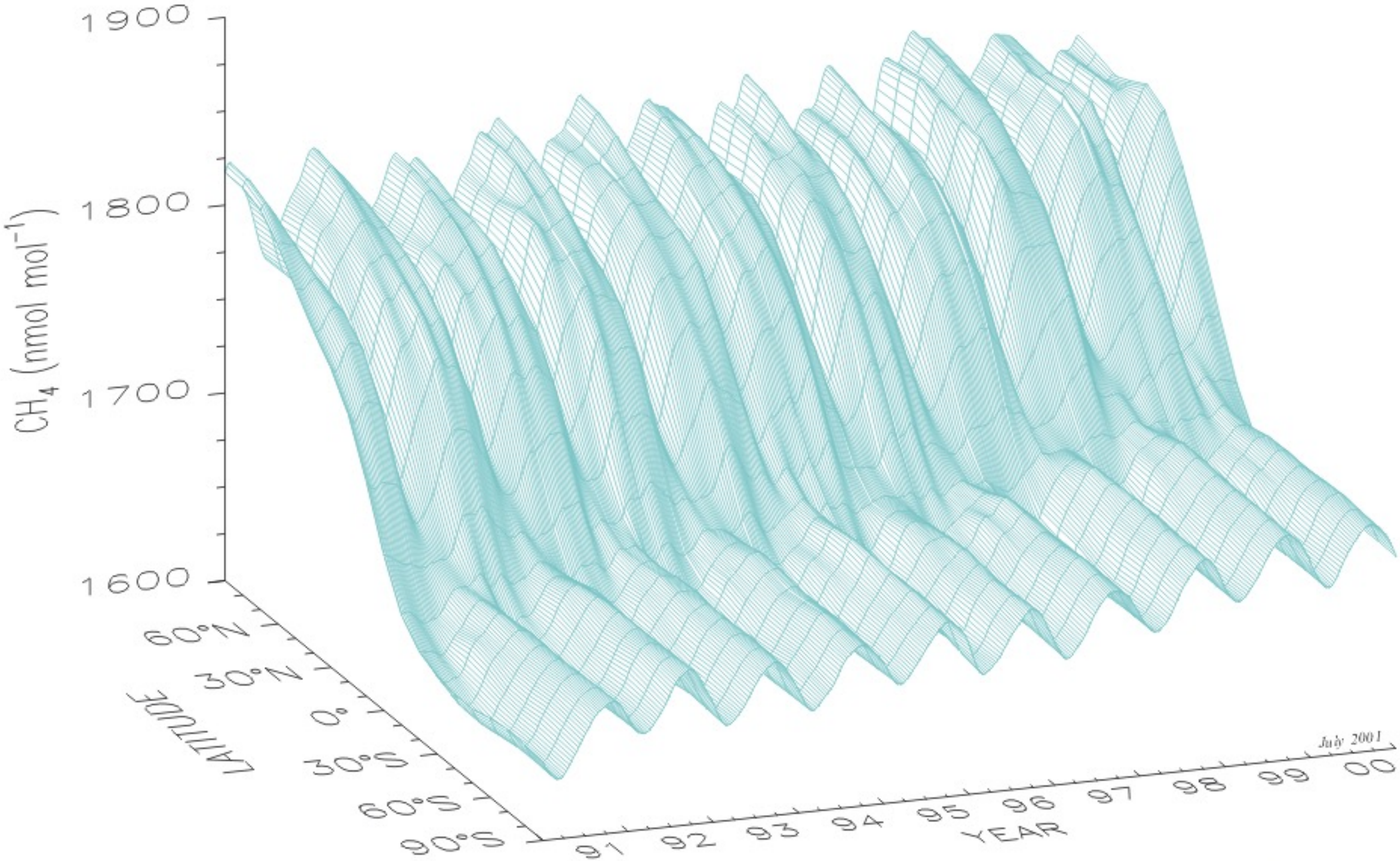
270 Tg CH_4 a^{-1}



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

Global distribution of methane

NOAA/CMDL surface air measurements



D.J. Jacob

[CH_4] ≈ 1700 ppbv commonly used

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.

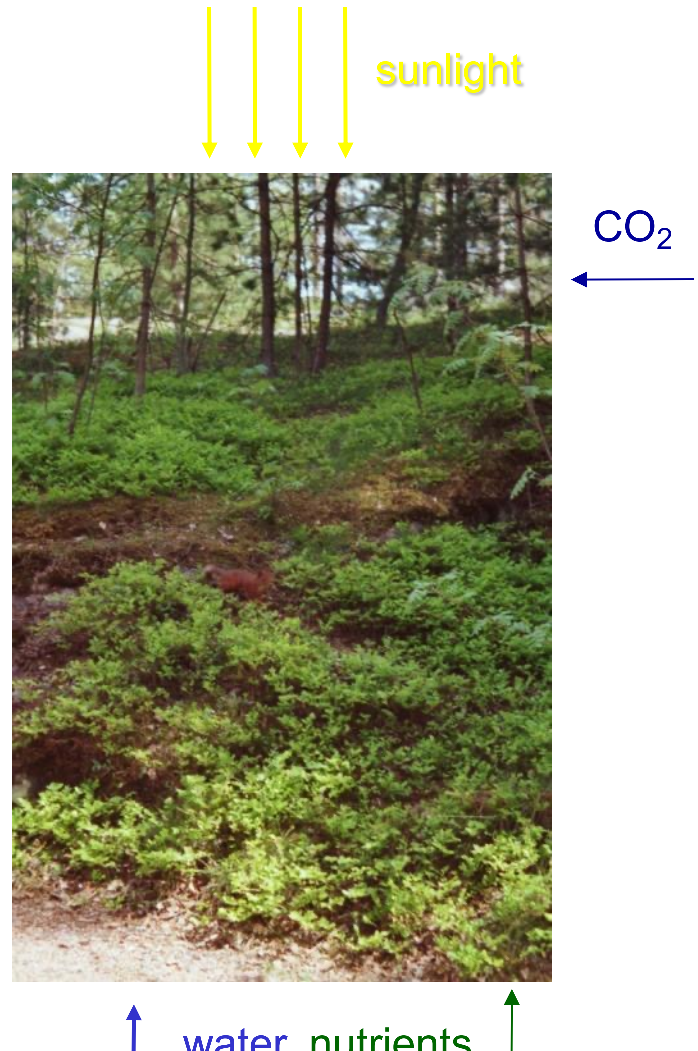
They may be emitted as by-products of photosynthesis, as responses to injury, and from metabolism and decay.

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

C) Cloud interactions (uptake, reactions)

+OH

+Ozone

VOC

+NO_3

Transport

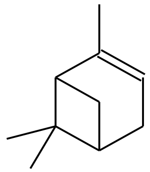
A) Emission

D) Aerosol formation

Biogenic volatile organic compounds (VOCs): Overview

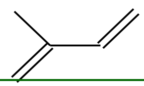
- **Reactive VOCs**

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

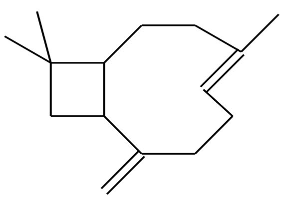


e.g. α-pinene

Isoprene (C_5H_8)

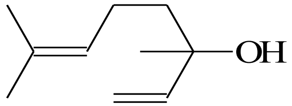


Sesquiterpenes ($C_{15}H_{24}$)



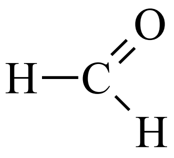
e.g. β-caryophyllene

Oxygenates

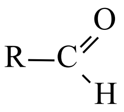


e.g. linalool

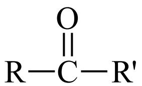
- Less reactive VOCs
  - Carbonyl compounds (e.g. formaldehyde HCHO)



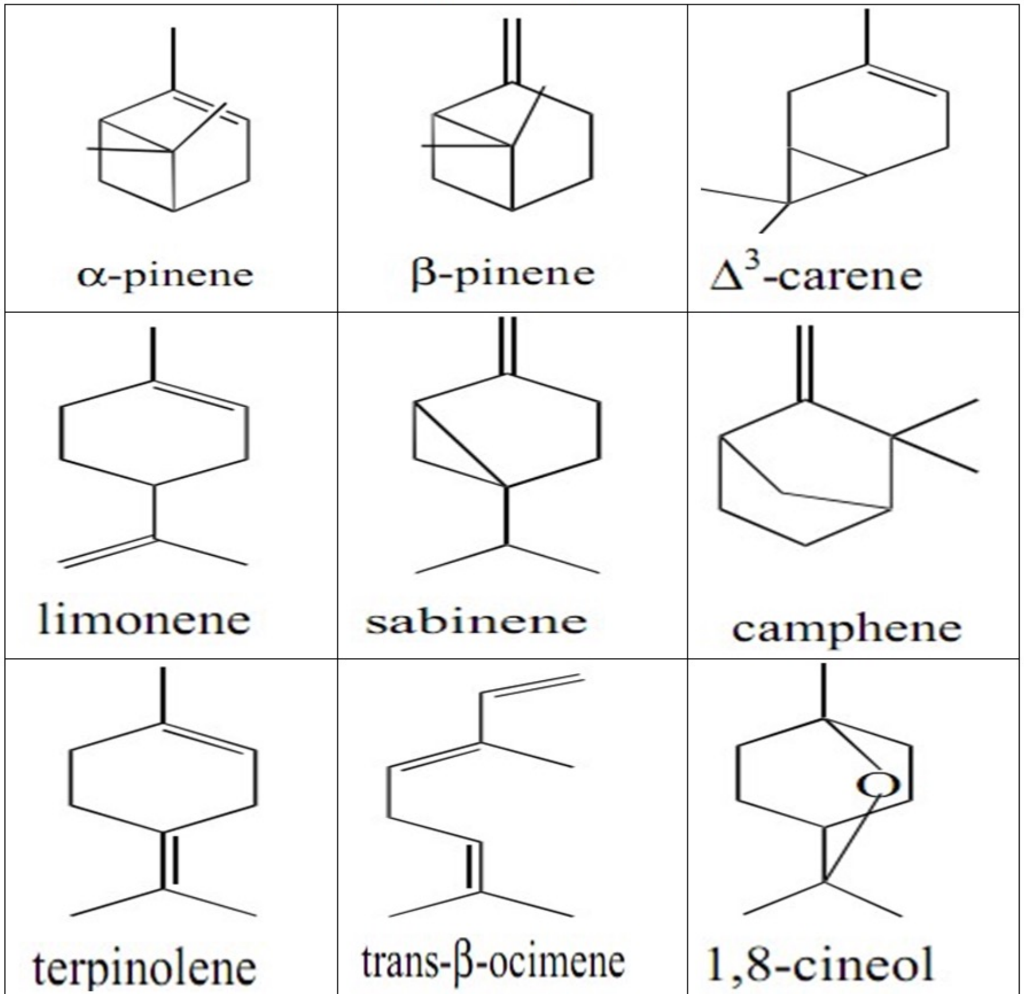
Aldehydes: R-CHO:



Ketones: RC(O)R':
(R and R' ≠ H)



Chemical structures of typical monoterpene in the emission of the biosphere

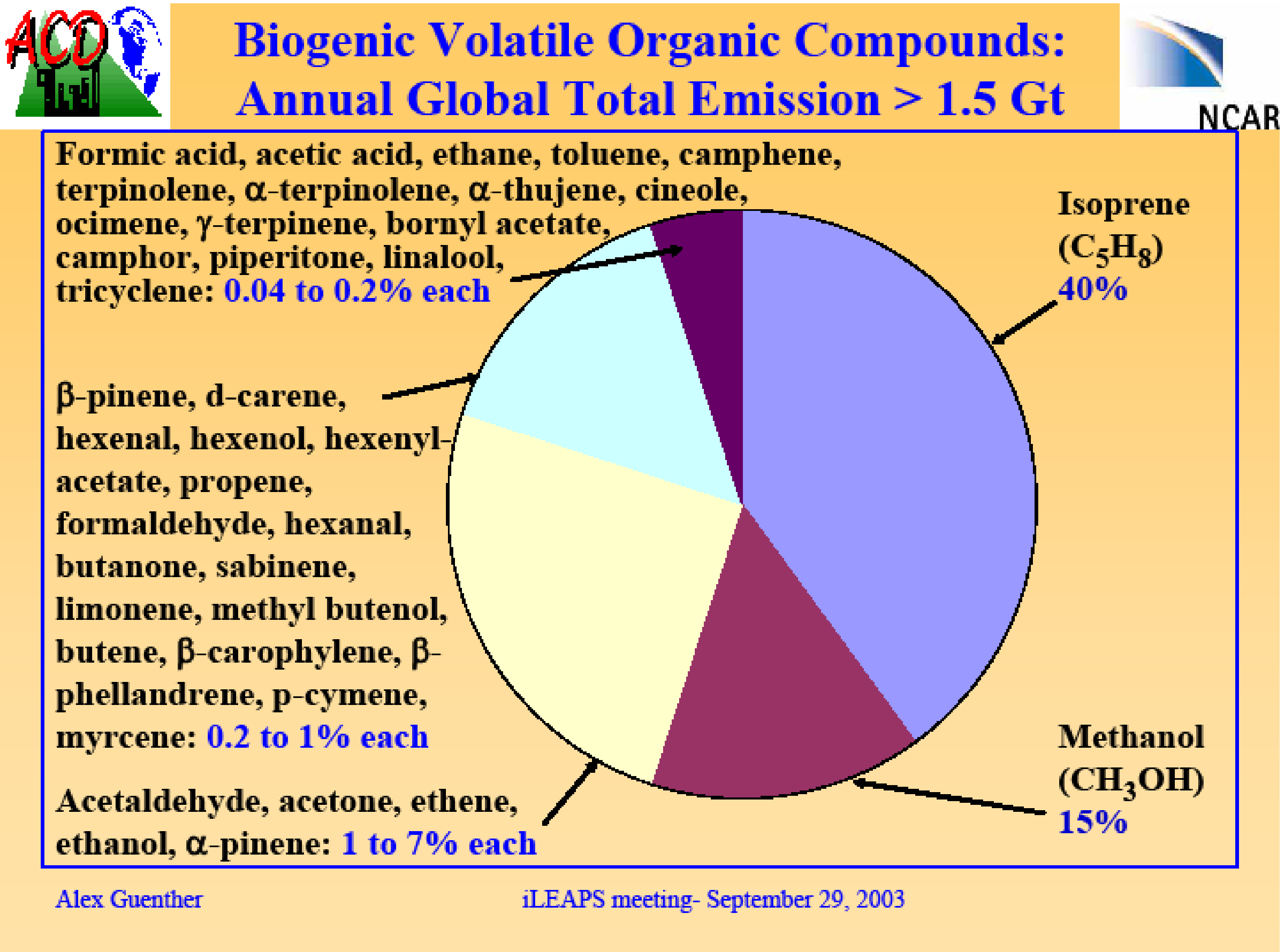


Important

All have same molar mass

But different reaction rates with OH, O_3 and NO_3

Global biogenic VOCs

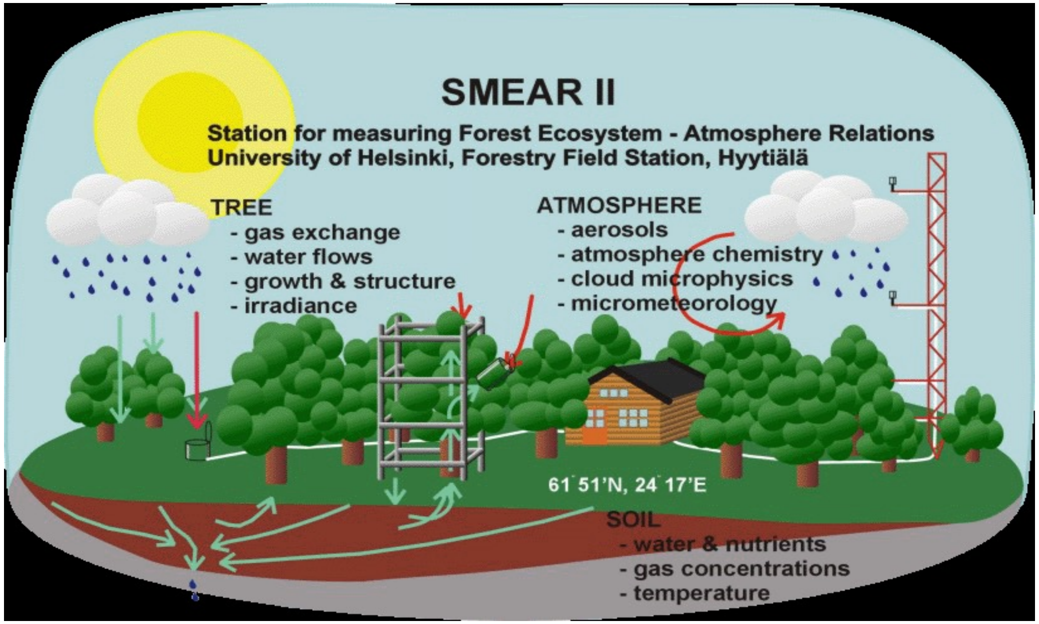


…but take care, the most reactive VOCs (e.g. sesquiterpenes) are not included really!

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

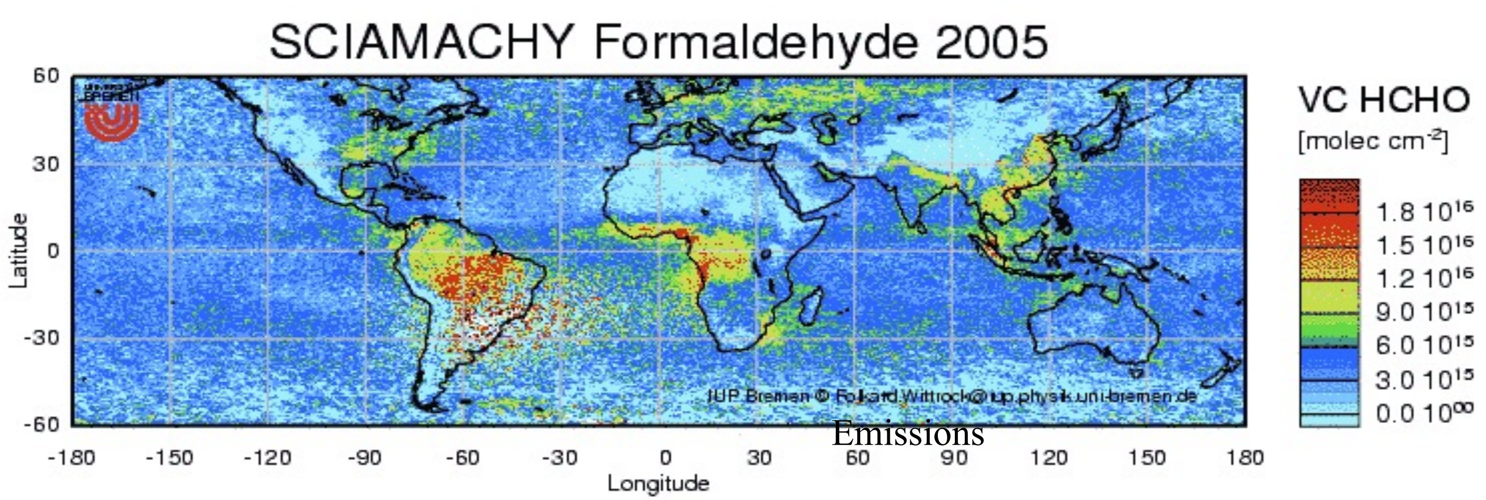
- Calculation of the exchange coefficients

➢ **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)]:

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

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

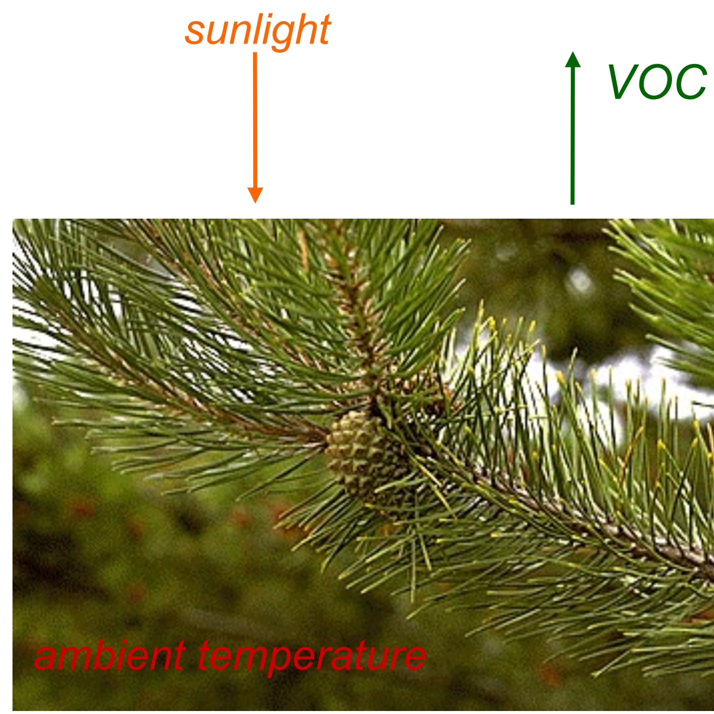
→ *e.g. amount of leaves/needles per surface area*

ε: ecosystem dependent emission factor at T = 30 °C and PAR = 1000 μmol m^{-2} s^{-1} (μg 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



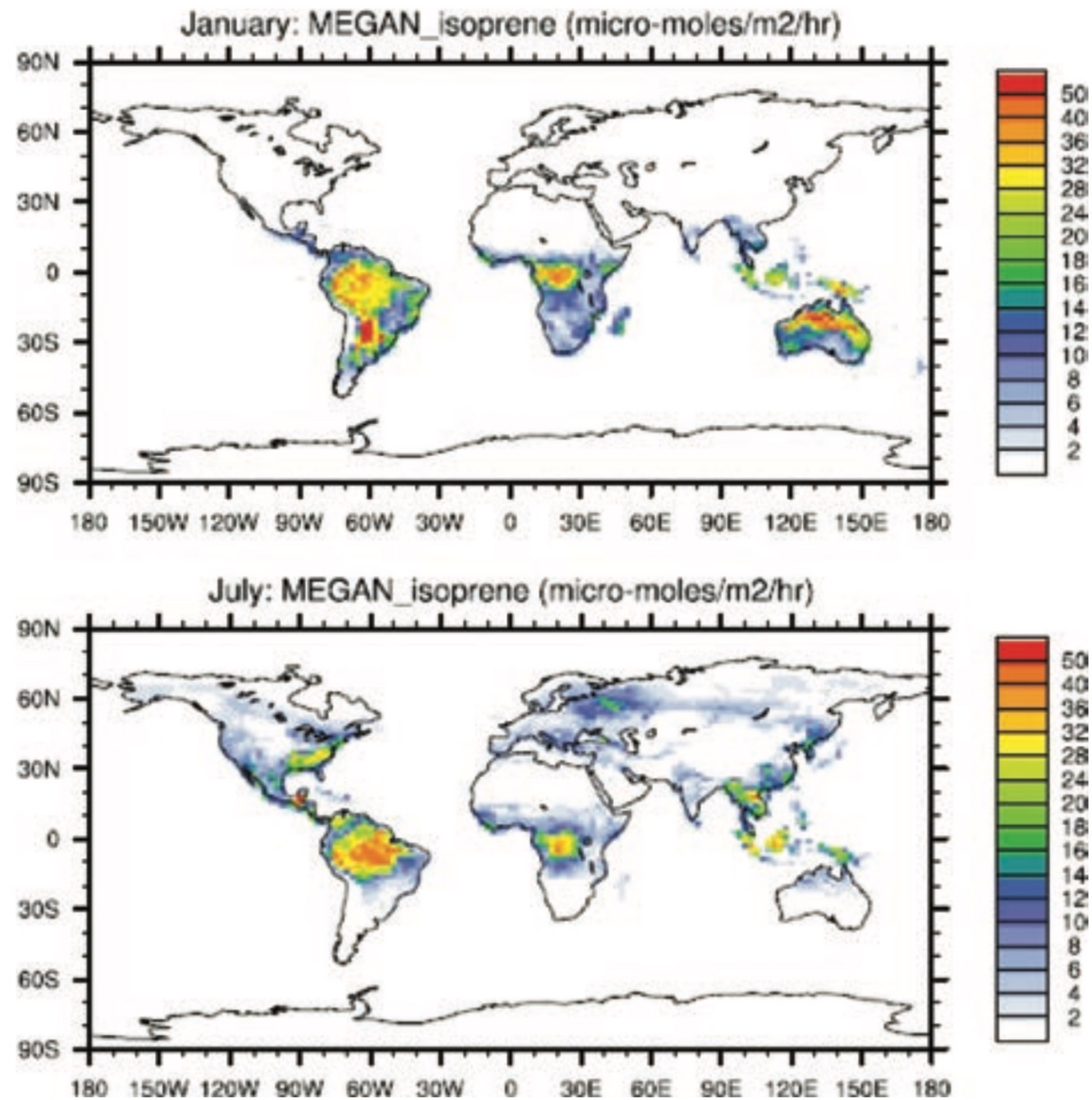
pine branch

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)



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

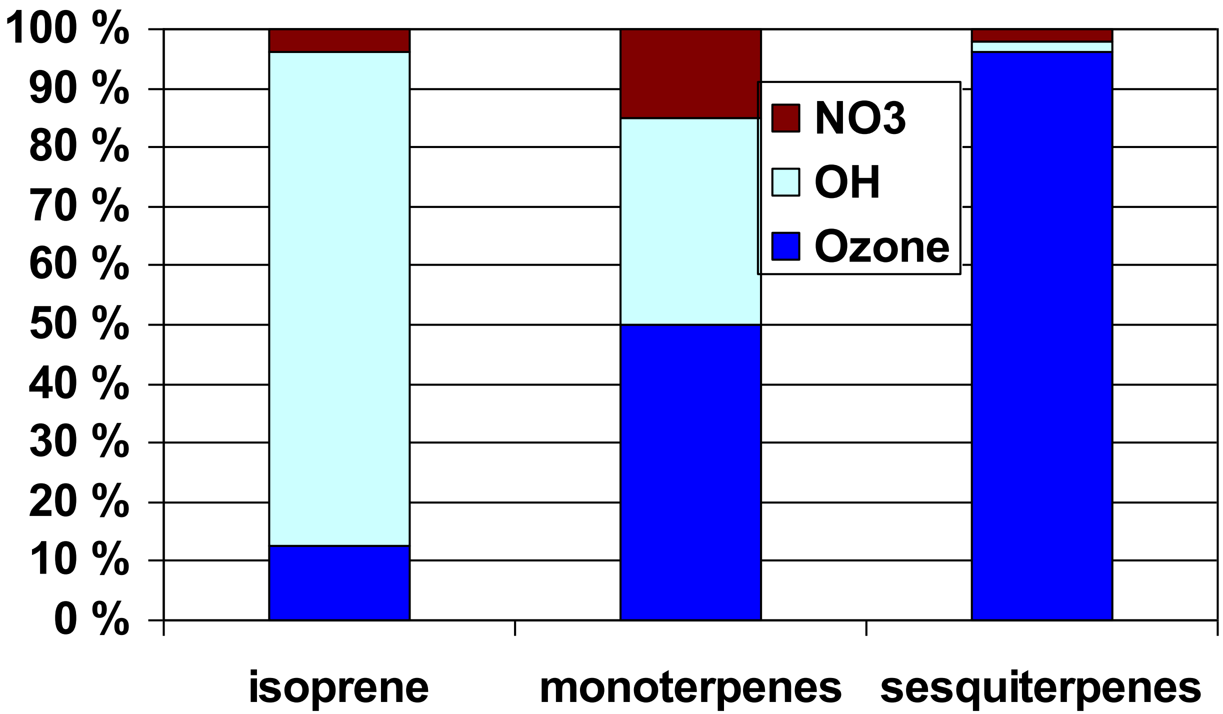
Consequences:

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

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

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.

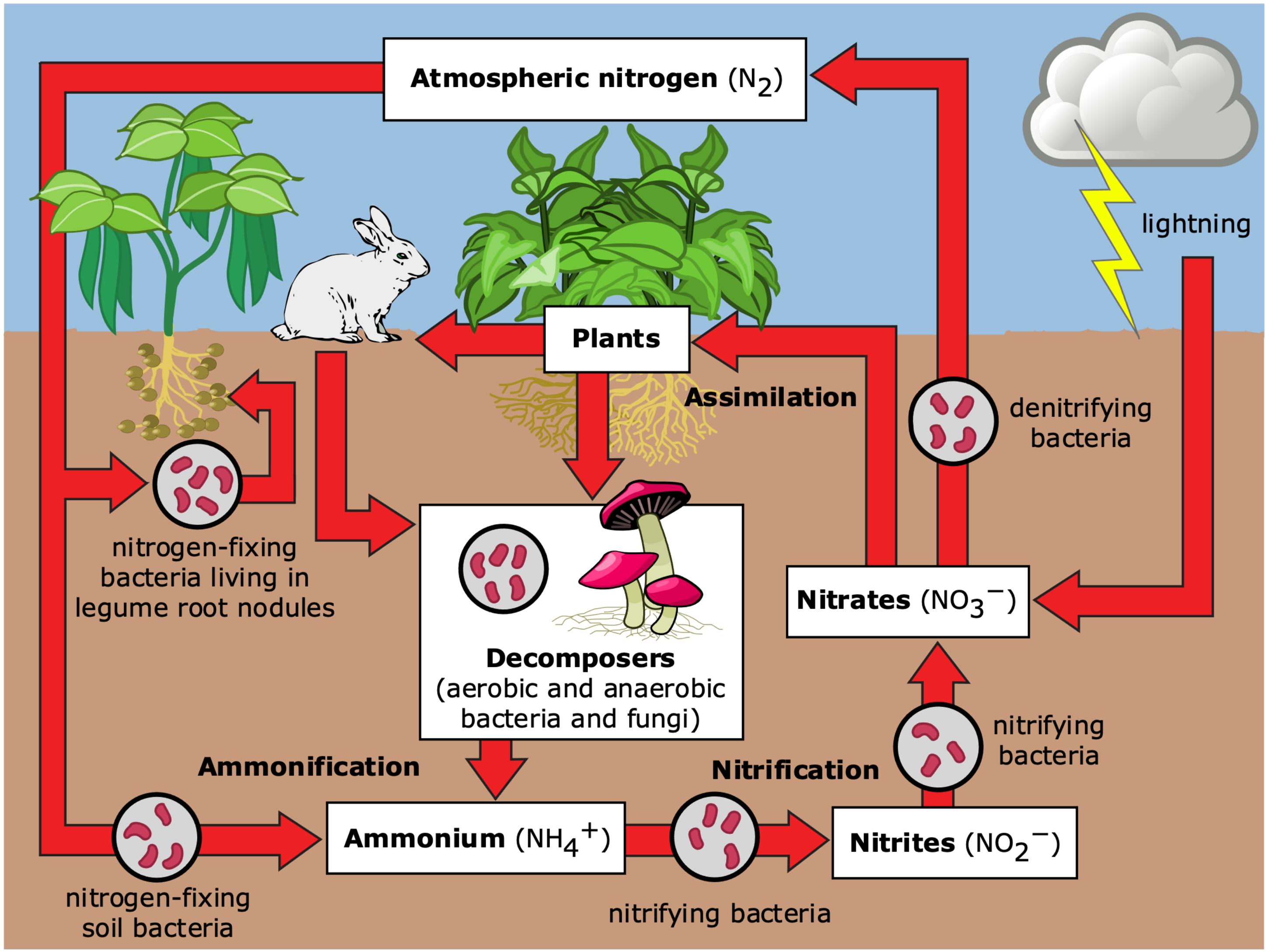
Fixed nitrogen can also be directly delivered to the ecosystem by fertilizer application or by deposition of atmospheric ammonia and nitrate.

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.

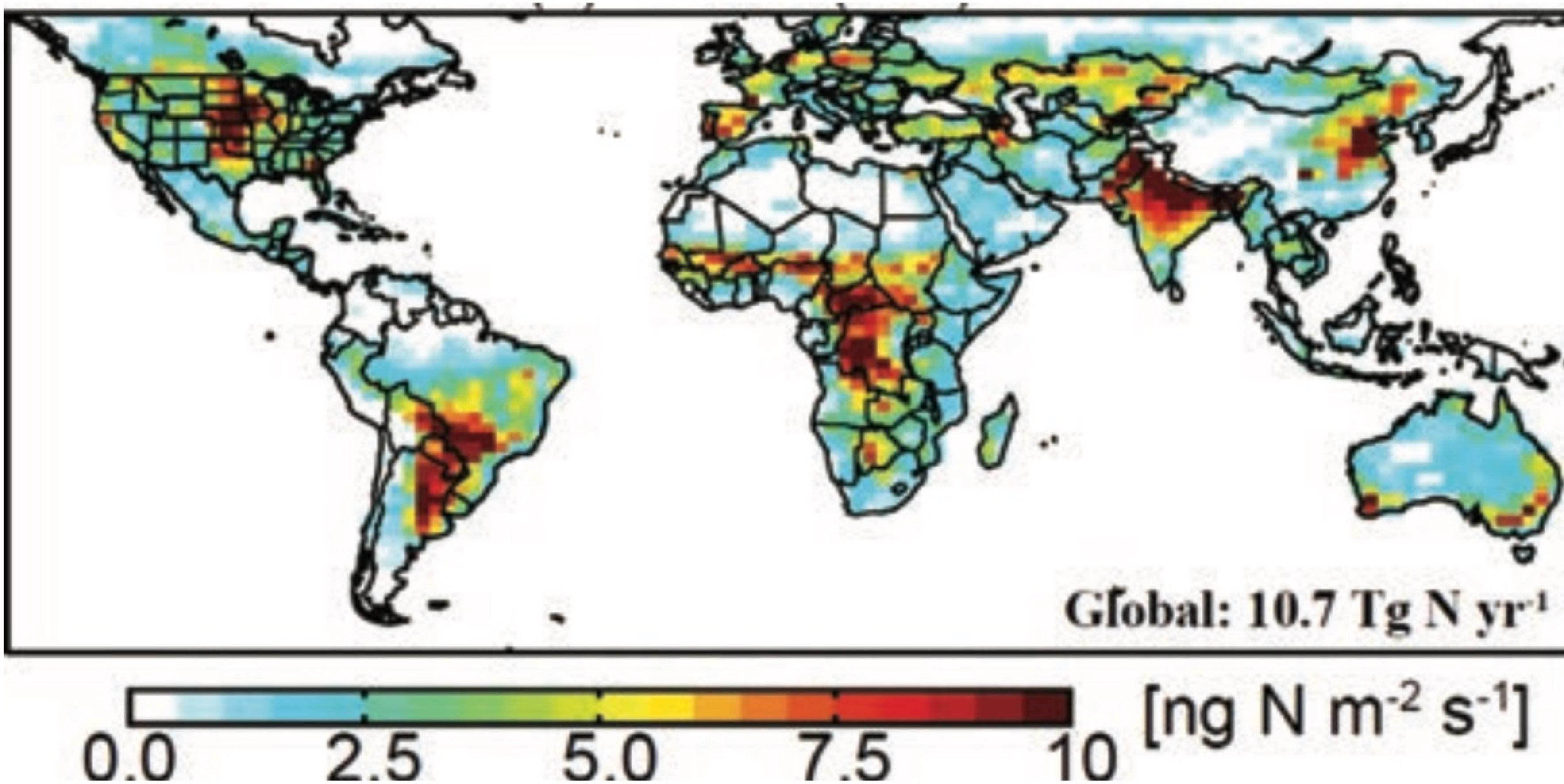
Terrestrial Biogenic Emissions
Nitrogen oxides



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_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

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_2, CO, and H_2O, but also many other trace species. Emissions depend on the type of vegetation, the vegetation density, and the fire intensity.

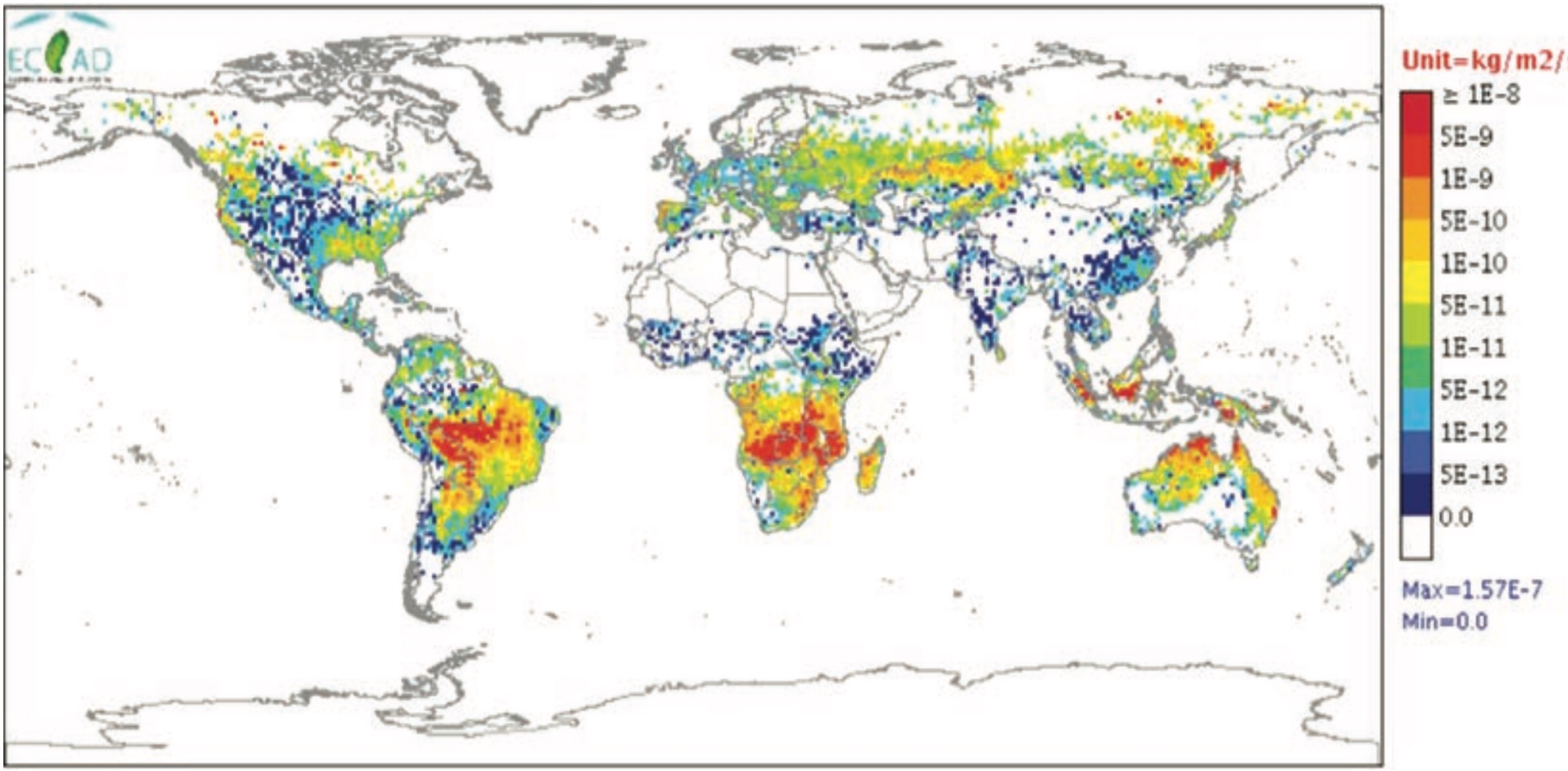
Open fires
Emission factors for open fires

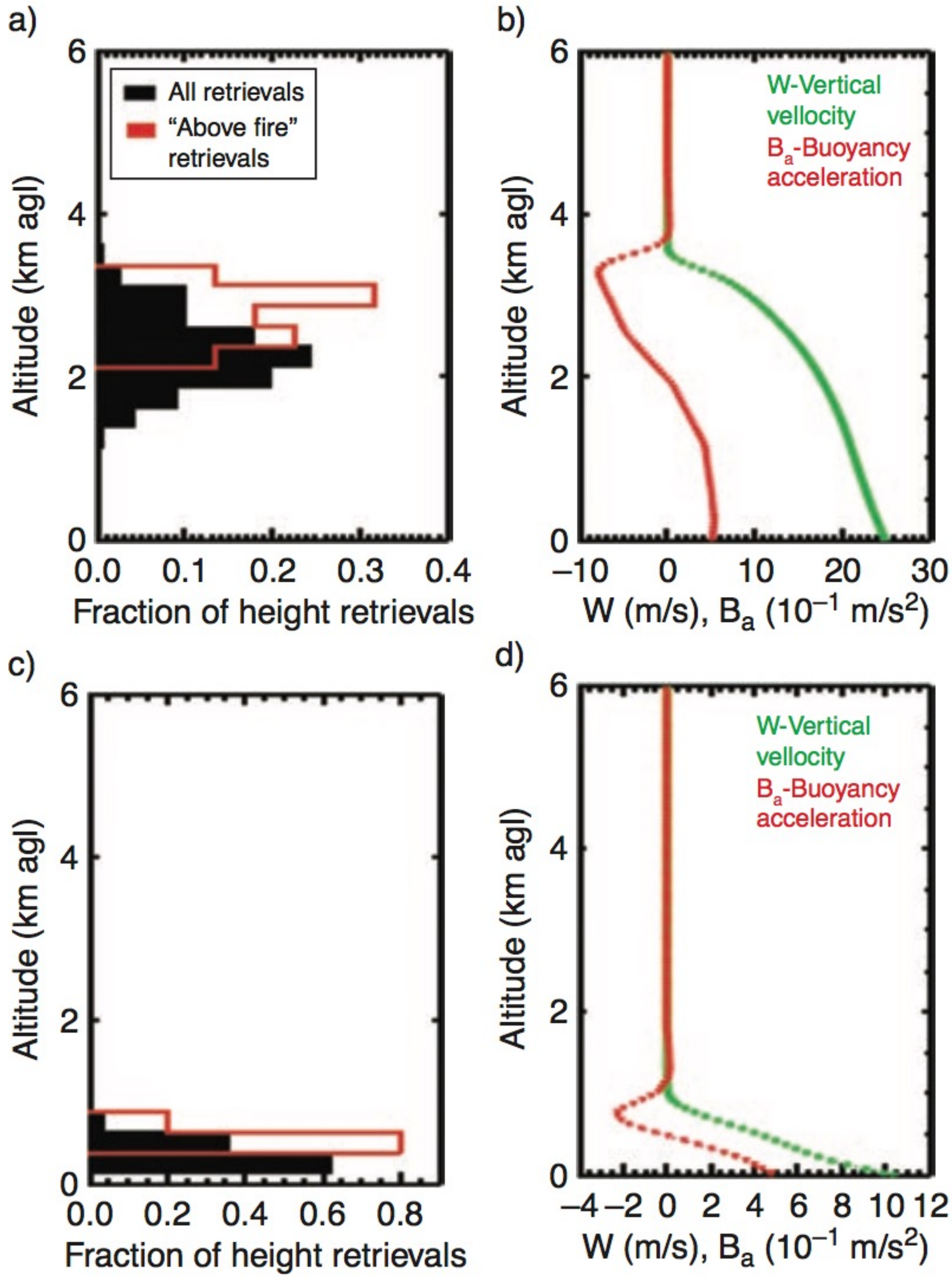
Chemical species	Savanna and grassland	Tropical forest	Extra-tropical forest	Crop residue	Pasture maintenance
CO_2	1686	1643	1509	1585	1548
CO	63	93	122	102	135
CH_4	1.9	5.1	5.68	5.82	8.71
NMVOCs	12.4	26	27	25.7	44.8
H_2	1.7	3.36	2.03	2.59	–
NO_x	3.9	2.55	1.12	3.11	0.75
N_2O	–	–	0.38	–	–
Organic aerosol	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^{-1}] for species emitted from combustion of different types of biomass. NO_x 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_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

Volcanoes

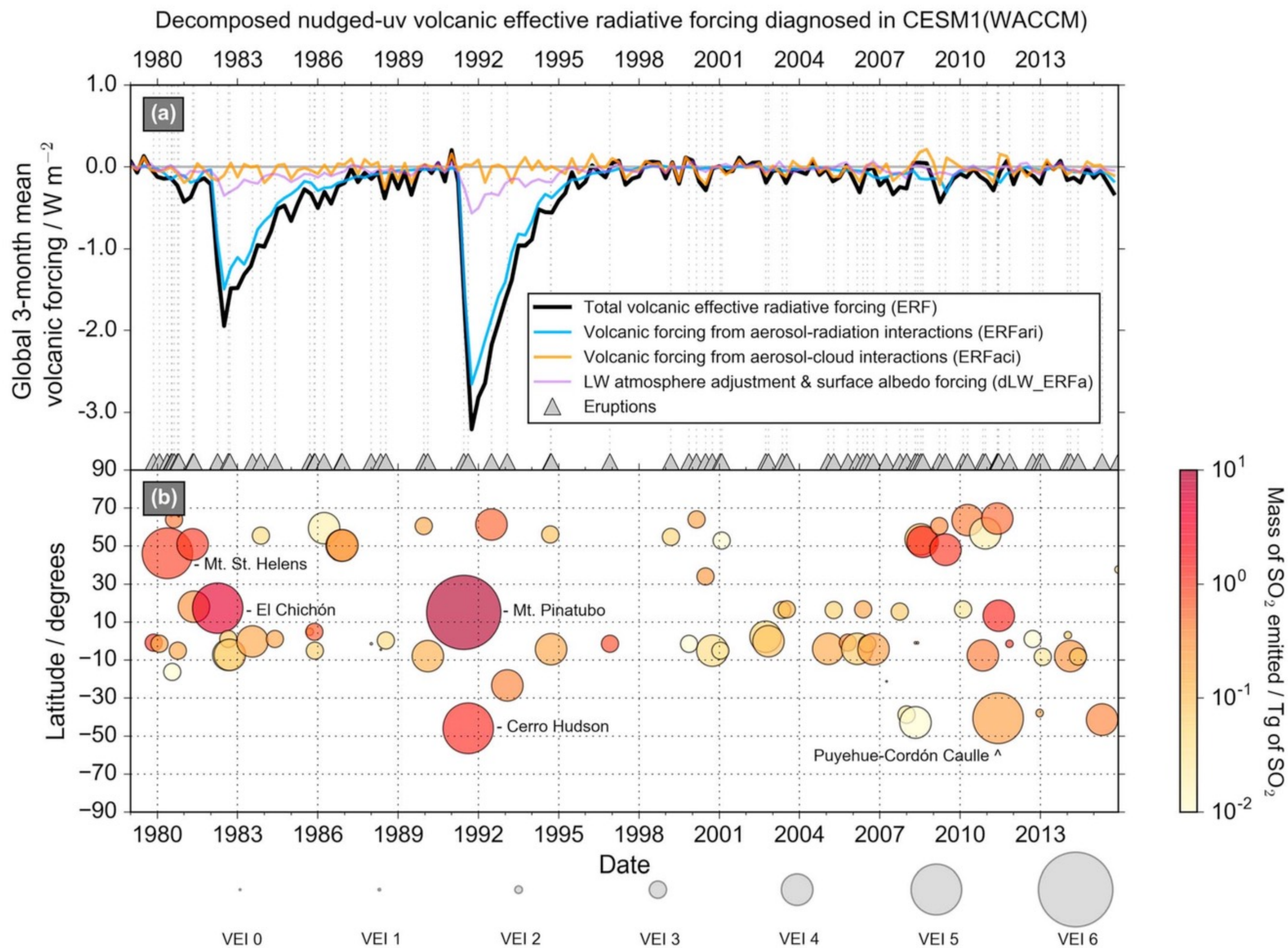
Volcanoes play a fundamental role in the cycling of elements on geologic timescales by transferring material from the lithosphere to the atmosphere.

On the shorter perspective of atmospheric sources and sinks, volcanoes are of most interest as sources of ash and sulphur gases (mainly SO_2 and H_2S).

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.



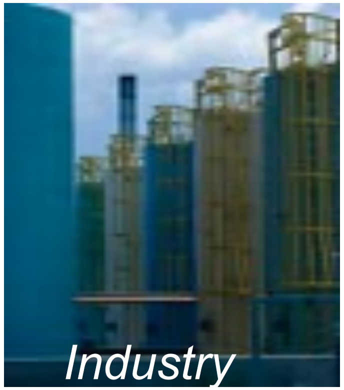
Time series of (a) global 3-month mean nudged-uv total volcanic effective radiative forcing (ERF, in W/m2, black line) diagnosed in CESM1-WACCM as the difference between simulations with and without volcanic emissions. The volcanic ERF is further decomposed into the forcings from aerosol-radiation interactions (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 (SO2) emissions (in Tg of SO2, 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).

Anthropogenic Emissions

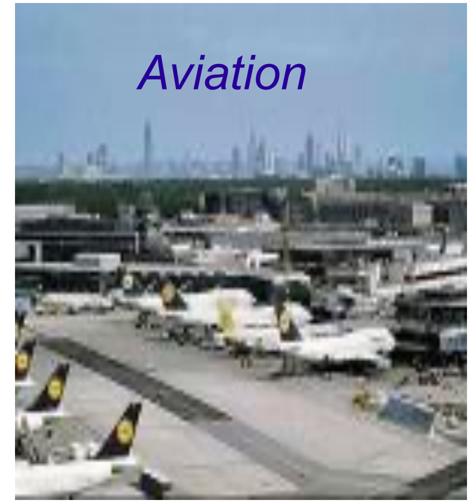
Species	Terrestrial biogenic	Open fires	Ocean biogenic	Anthropogenic	Volcanic	Lightning	Mechanical	Total
NO_x (as N)	11	7	–	32	–	5	–	55
CO	80	460	20	610	–	–	–	1170
Methane	190	50	–	290	–	–	–	530
Isoprene	520	–	–	–	–	–	–	520
SO_2 (as S)	–	1	–	57	10	–	–	68
Ammonia	3	6	8	45	–	–	–	62
Black carbon (as C)	–	11	–	7	–	–	–	18
Dust	–	–	–	–	–	–	1500	1500
Sea salt	–	–	–	–	–	–	5000	5000

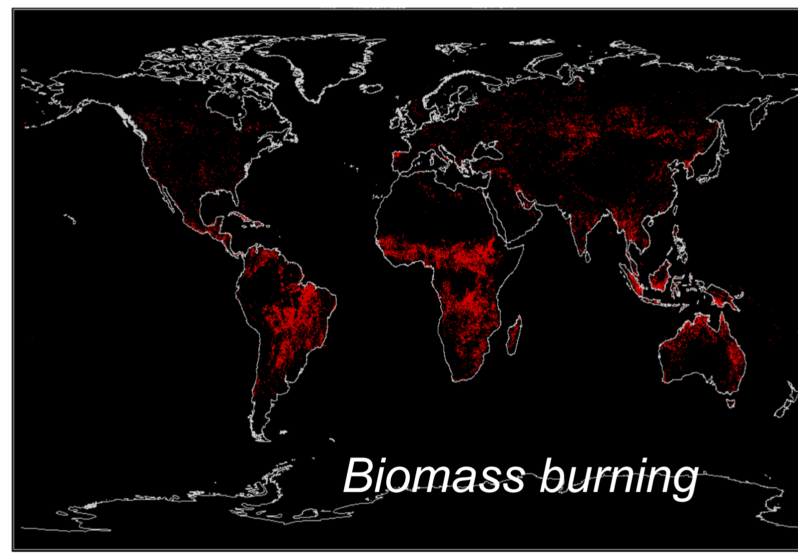
Typical estimates for circa 2015. Dash indicates a zero or negligible source.

Brasseur and Jacob, 2017



Anthropogenic Emission





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 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.

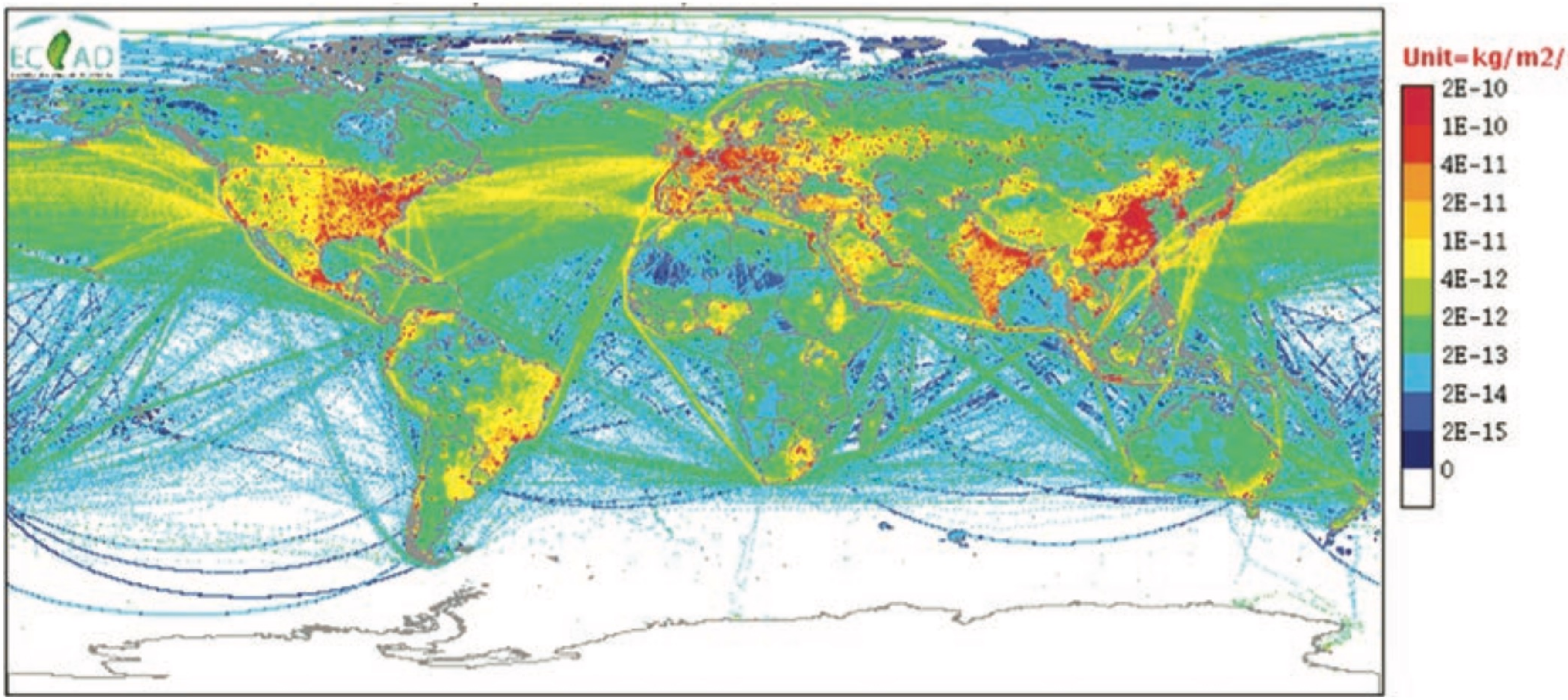
Emission inventories commonly distinguish between area sources and point sources.

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
NO_x

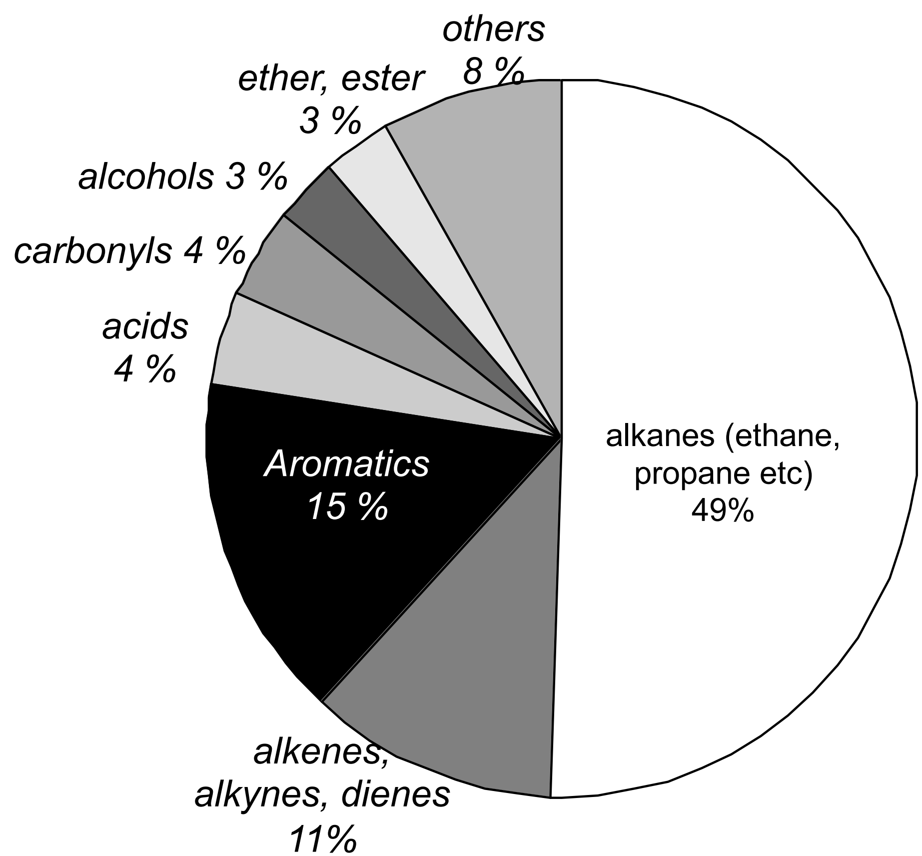


Anthropogenic NO_x emissions from the MACCity inventory at 0.5 x 0.5 resolution for the year 2008 (C. Granier, Centre National de la Recherche Scientifique, CNRS).

Anthropogenic Emissions
Anthropogenic VOC

$\sum$(aromatics) ≈ 20 Tg carbon/year
$\sum$ ≈100-200 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 %)



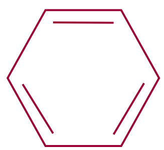
IPCC (2001)

Anthropogenic VOCs: Aromatics

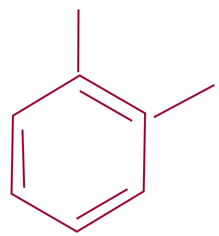
The gases you inhale in cities behind a vehicle.

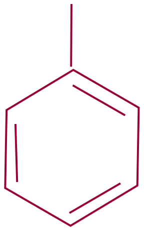
Emitted by fossil fuel combustion and biomass burning

Benzene



Xylene





Toluene

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

Anthropogenic VOCs – how to get this data

E.g.: EDGAR
A set of global emission inventories of greenhouse gases and ozone-depleting substances for all anthropogenic and most natural sources on a per country basis and on 1 degree x 1

Another source is EMEP - The European Monitoring and Evaluation Programme

ECCAD: Emissions of atmospheric Compounds and Compilation of Ancillary Data

Making data accessible and providing tools for data analysis

Mechanical emissions: sea salt and dust

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

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.

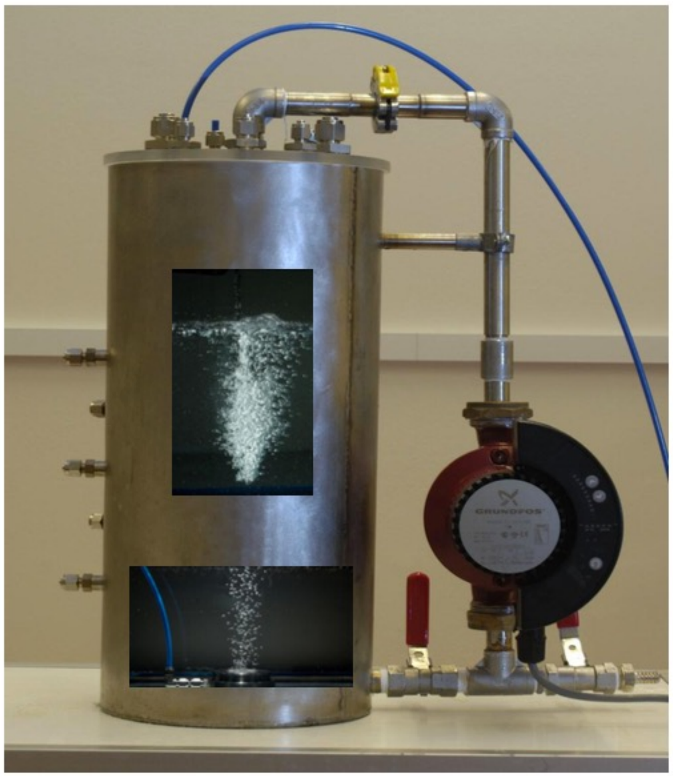
Sea salt and dust are dominant components of the coarse-mode (supermicron) aerosol over ocean and land, respectively, and generally make important contributions to total aerosol mass concentrations and optical depth.

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

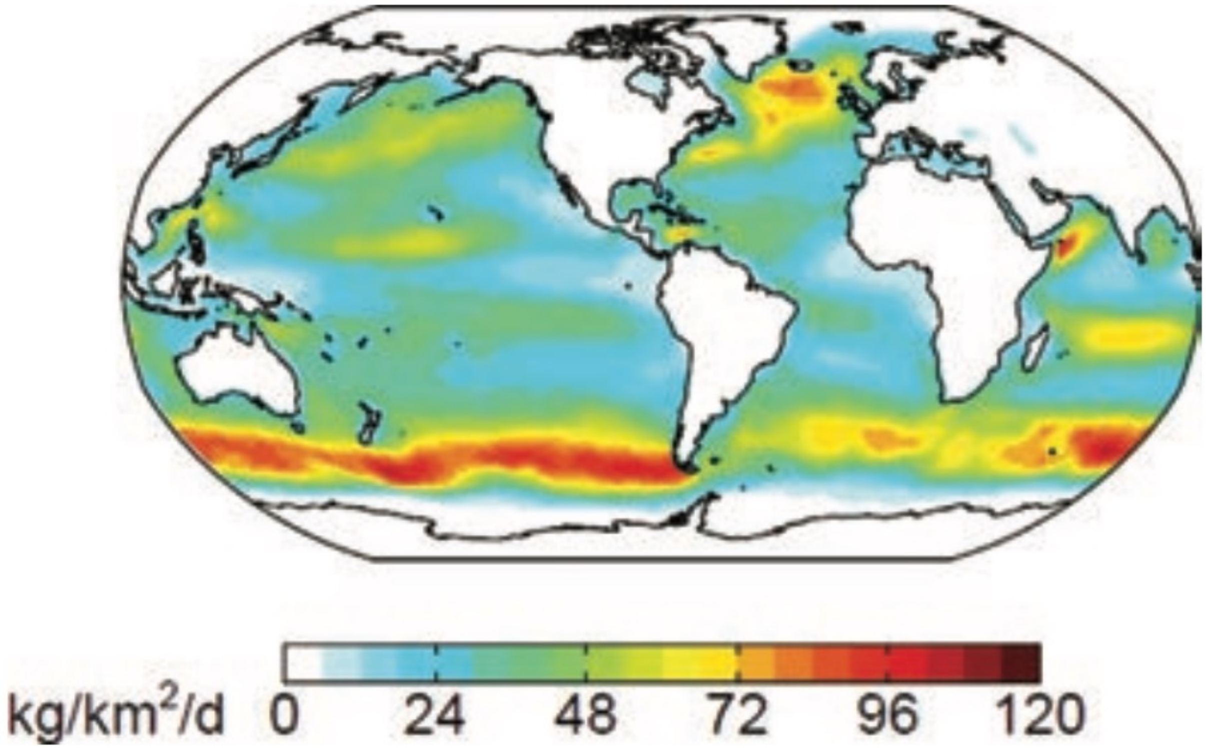


During CRAICC (Boy et al., 2019) significant effort was devoted to improving the understanding of sea spray aerosol.

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 a. (2011)

Mechanical emissions: dust

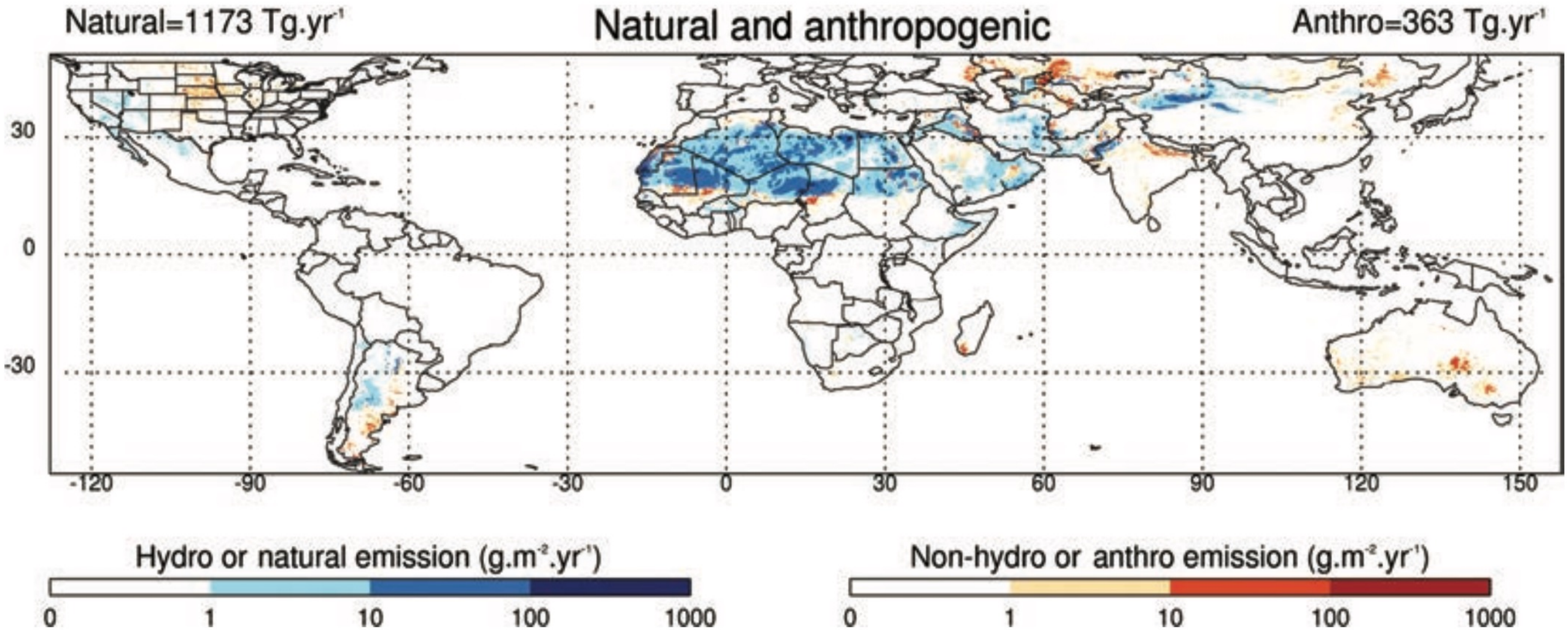
Mineral dust is emitted by sandblasting of soils, a process called saltation.

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

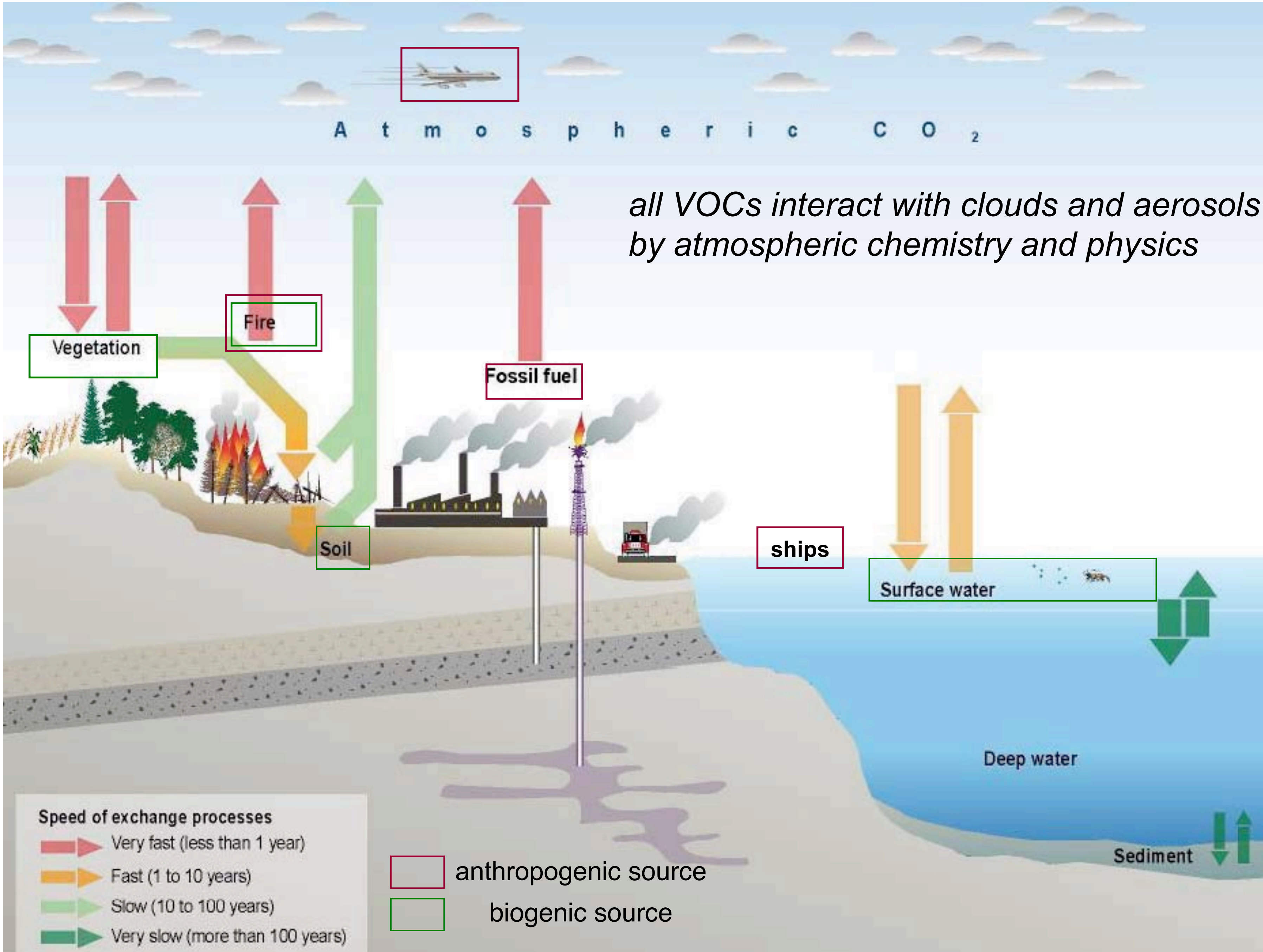
As the sand particles fall, they eject dust particles of diameter D_d small enough to be transported over long distances in the atmosphere. These fine particles are classified as

- Clay ($D_d < 2$ µm)
- Silt ($2 < D_d < 50$µm)

Mechanical emissions: dust



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



Source: modified **http://www.defra.gov.uk/environment/airquality/publications/airqual-climatechange/pdf/chapter02.pdf**