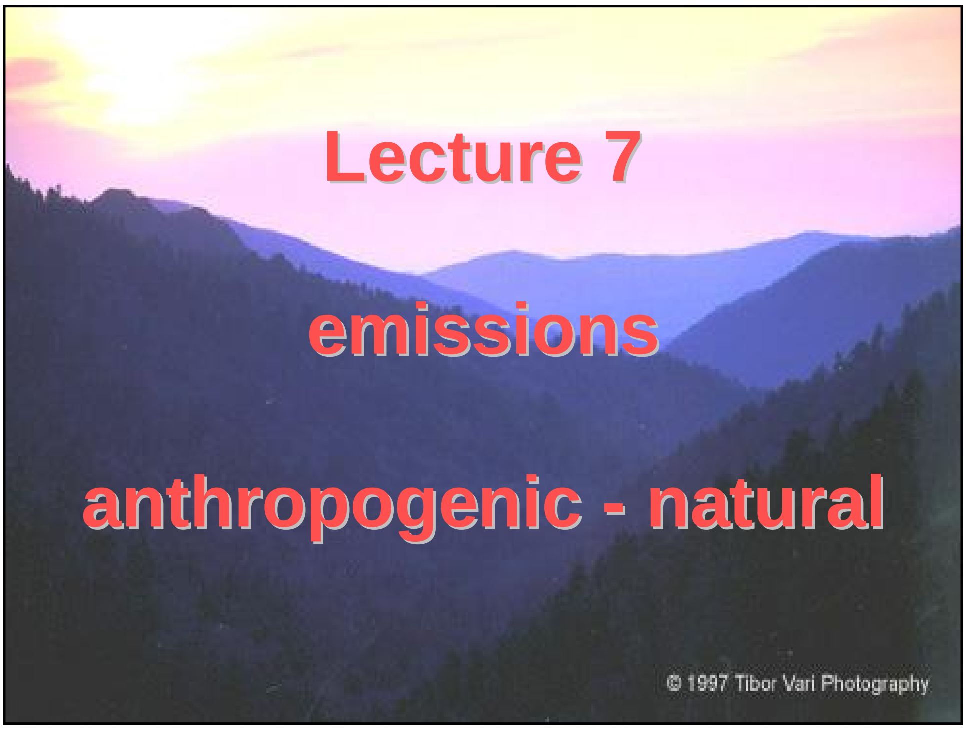
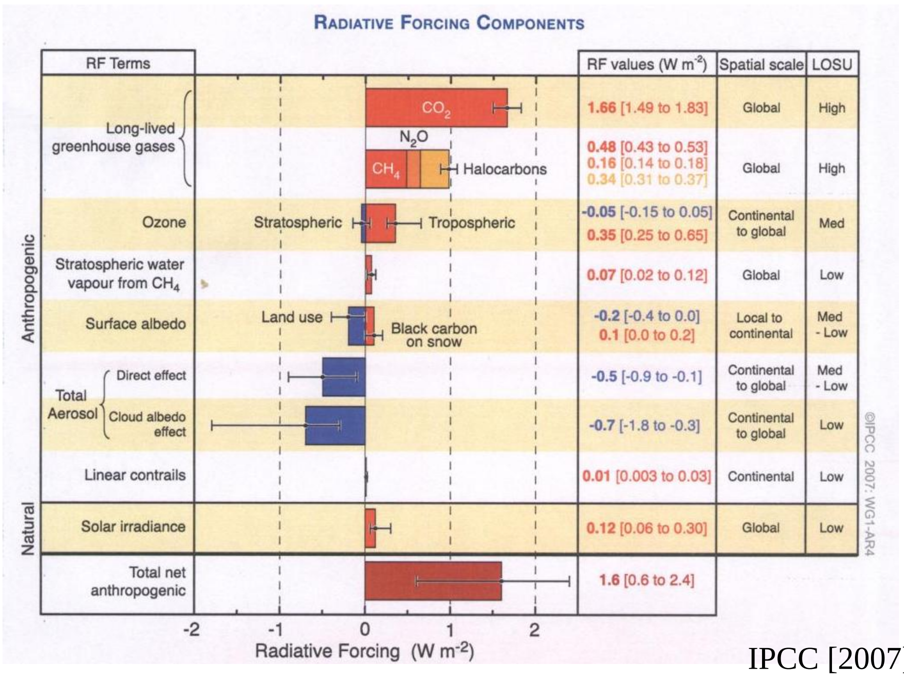
Lecture 7

emissions

anthropogenic - natural



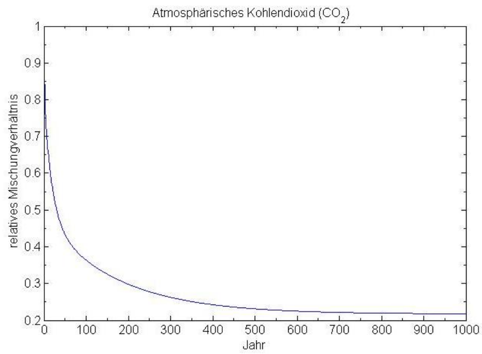


IPCC [2007]

Atmospheric lifetime

Lifetime τ = time necessary that the concentration decrease to 1/e concerning the start value:

$$[X](t) = [X](t=0) \cdot \exp\left(-\frac{t}{\tau}\right)$$



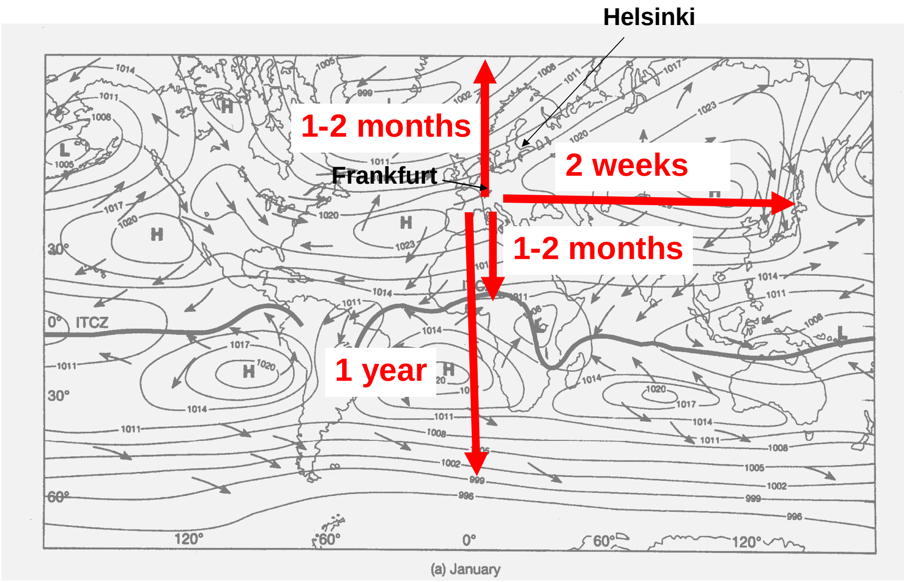
Chemical Lifetimes of atmospheric compounds (average for total atmosphere)

Compound	*Chemical lifetime*
Tropospheric O_3	3-18 days **
Carbon monoxide (CO)	57 days*
Methane (CH_4)	8.4 years **
SF_6	3200 years **
Toluene (traffic, anthropog.)	2 days*
monoterpenes (α-pinene)	1.6 hours*
CFCs (sprays, cooling, anthropog.)	45-1700 years **

* [OH] = 1.0×10^6 molecules cm^{-3} at room temperature assumed

** IPCC, 2001

Time scales for horizontal transport (troposphere)



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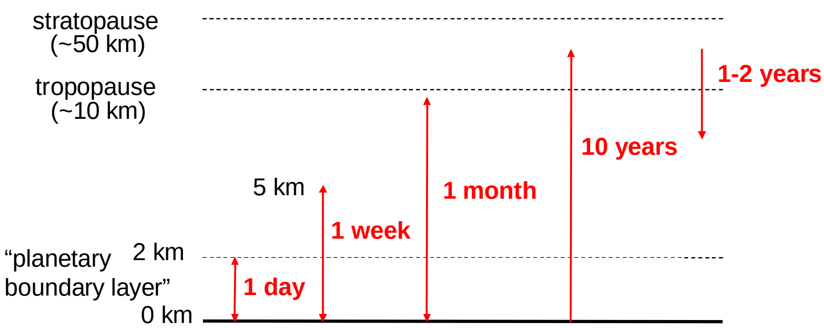
Typical time scales for vertical mixing

- Estimate time Δt to travel Δz by turbulent diffusion:

$$\Delta t = \frac{(\Delta z)^2}{2K_{turb}} \quad with \quad K_{turb} = 10^5 \quad cm^2 s^{-1}$$



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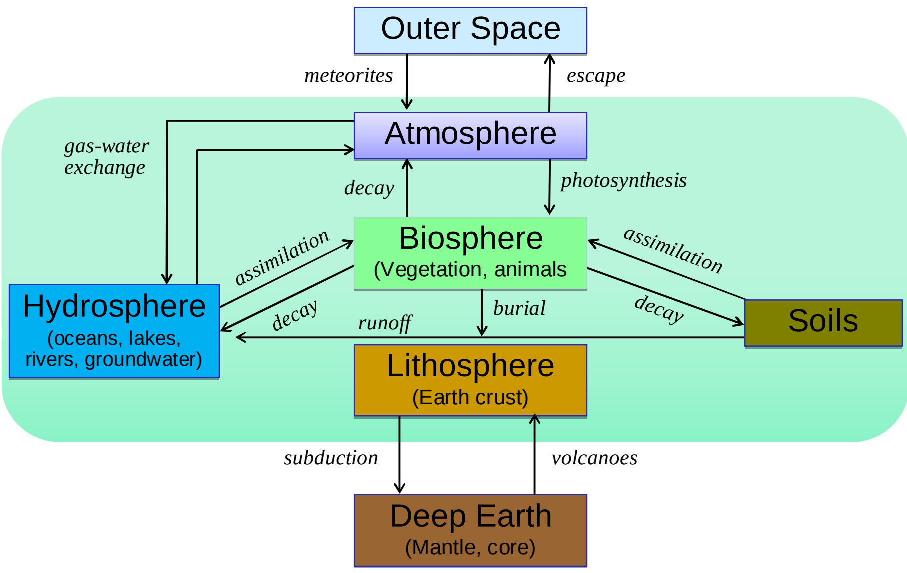
Reservoir of the Earth system and examples of processes exchanging elements between resrevoirs



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: 9 years

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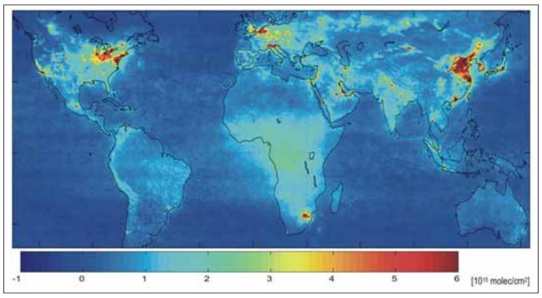
Estimated present-day sources of tropospheric NO_x

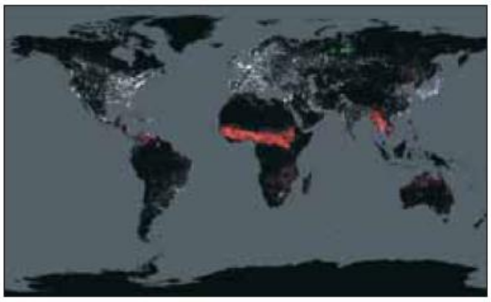
	Source, Tg N yr^{-1}
Fossil fuel combustion	21
Biomass burning	12
Soils	6
Lightning	3
NH_3 oxidation	3
Aircraft	0.5
Transport from stratosphere	0.1

Mapping of tropospheric NO_2 from the GOME satellite instrument



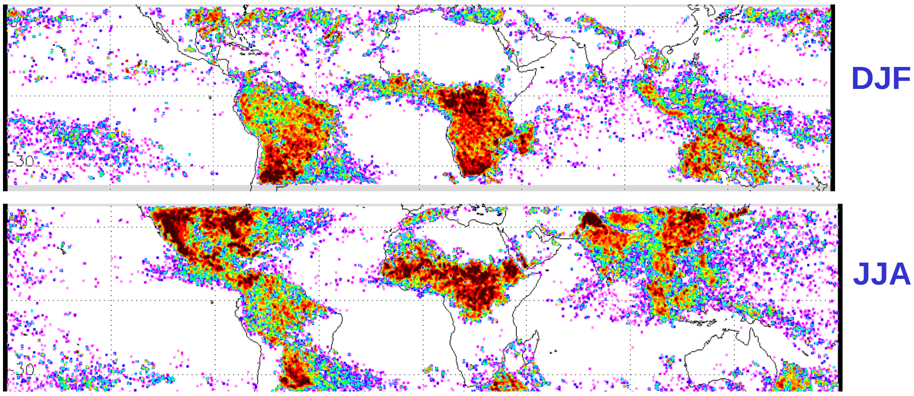
Can you observe an effect of mankind?

Lights at night from space



AFO2000, 2004

Lightning observed from space (2000)



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Present day global budget of atmospheric N_2O (1994)

Source:IPCC [2001]

Sources (Tg N yr^{-1})	17.7 (6.7 – 36.6)	
Oceans	3 (1 - 5)	Natural:
Atmosphere (NH_3 oxidation)	0.6 (0.3 - 1.2)	9.6 (4.6 – 15.9)
Tropical soils (forest, savannah)	4 (2.7 – 5.7)	
Temperate soils (forest, grassland)	2 (0.6 – 4)	
Agricultural soils	4.2 (0.6 – 14.8)	Anthropogenic:
Livestock (cattle, feedlots)	2.1 (0.6 – 3.1)	8.1 (2.1 – 20.6)
Biomass burning	0.5 (0.2 – 1.0)	
Industrial	1.3 (0.7 – 1.8)	
Sink (Tg N yr^{-1}) (stratosphere) Photolysis and oxidation	12.3 (9 – 16)	
Accumulation/ trend (Tg N yr^{-1})	3.9 (3.1 – 4.7)	

Although a closed budget can be constructed, uncertainties in sources are large!

Global budget of CO

	Range of estimates (Tg CO yr^{-1})
Sources	1800–2700
Fossil fuel combustion/industry	300–550
Biomass burning	300–700
Vegetation	60–160
Oceans	20–200
Oxidation of methane	400–1000
Oxidation of other hydrocarbons	200–600
Sinks	2100–3000
Tropospheric oxidation by OH	1400–2600
Stratosphere	~ 100
Soil uptake	250–640

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Sink and source terms for ozone

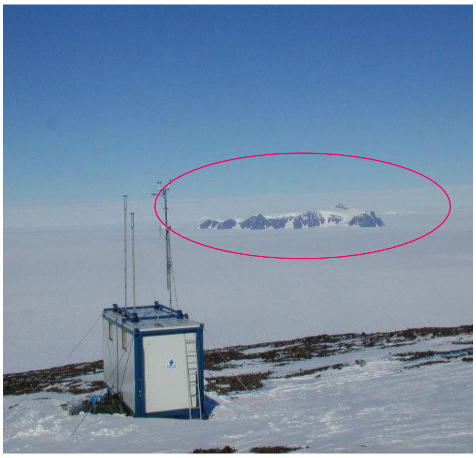
	Tg O_3 yr^{-1}
SOURCES	3400-5700
Chemical production	3000-4600
HO_2 + NO	(70 %)
CH_3O_2 + NO	(20 %)
RO_2 + NO	(10 %)
Transport from Stratosphere	400-1100
SINKS	3400-5700
Chemical loss	3000-4200
$O(^1D)$ + H_2O	(40 %)
HO_2 + O_3	(40 %)
OH + O_3	(10 %)
others	(10 %)
Dry deposition	500-1500

Dust storm

Microscopic picture

Why we have to know something about aerosols in the atmosphere ???

- health (respiration)
- visibility
- radiative balance
- cloud formation
- heterogeneous reactions
- delivery of nutrients
- disease carier
- …..



Antarctica: > 100

New Delhi: < 1.5 km

Pictures by: Ismo K. Koponen ja Petteri Mönkkönen

Atmospheric aerosols – basic characteristics

Definition:
solid or liquid particles suspended in air
('aero' (greek) = air + 'sol' (greek) = solid),
but no single molecules or water droplets!

Sizes:
between 1 nm (molecule clusters) and about 100 μm,
therefore covering about 5 orders of magnitude in size.

Atmospheric lifetimes:
a few minutes up to 10 days depending on size, altitude and water solubility

Types of atmospheric aerosols

Primary aerosols:

released preformed from the Earths surface *e.g. mineral dust, sea salt, pollen, black soot from fire exhaust*

Secondary aerosols:

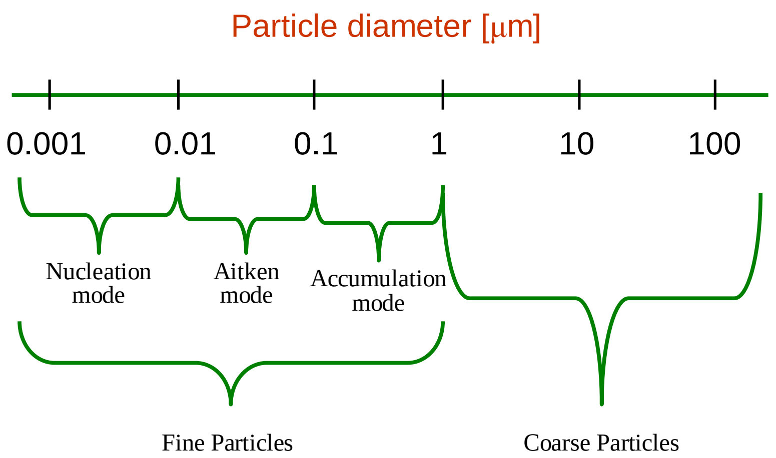
formed from low-volatile chemical or reactive compounds in the atmosphere (gas-phase) *e.g. sulphuric acid, organics, nitric acid*

Cloud-phase induced aerosols:

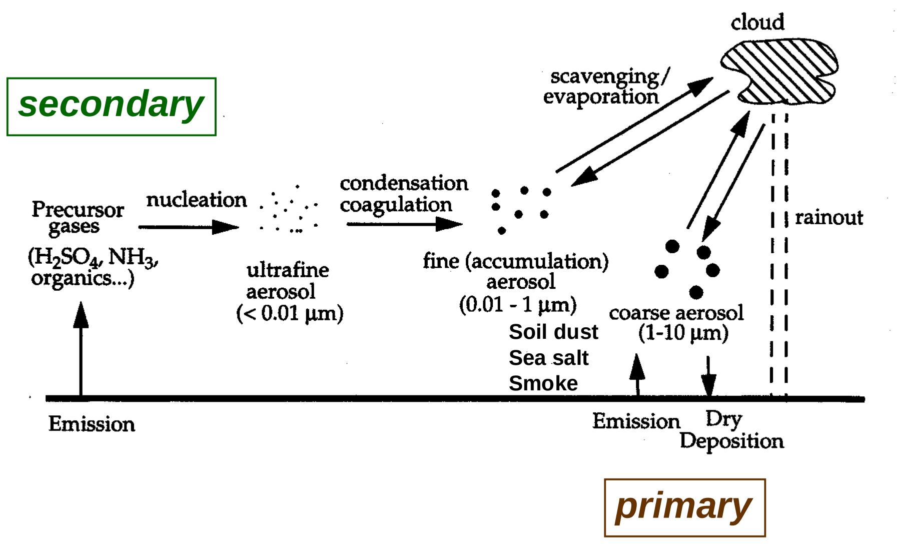
formation of low-volatile chemical compounds in the water droplet, which is evaporating, releasing the new particle e.g. sulphuric acid, organics, nitric acids (similar to sec. particles)

But the longer their residence time in the atmosphere, the more these types interact and get mixed!

Size characteristics for aerosols



Origin of the atmospheric aerosol



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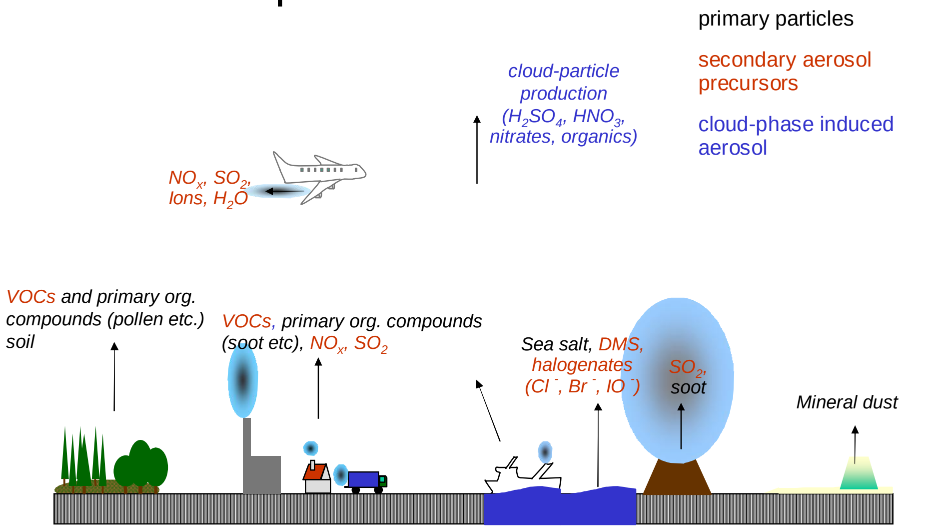
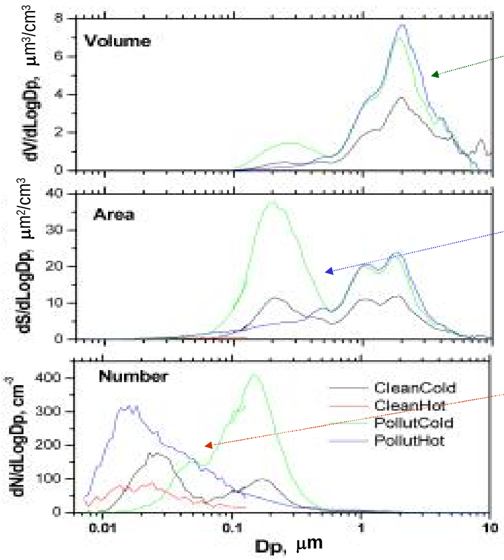
Atmospheric chemistry and atmospheric aerosols



Ambient aerosol size distributions



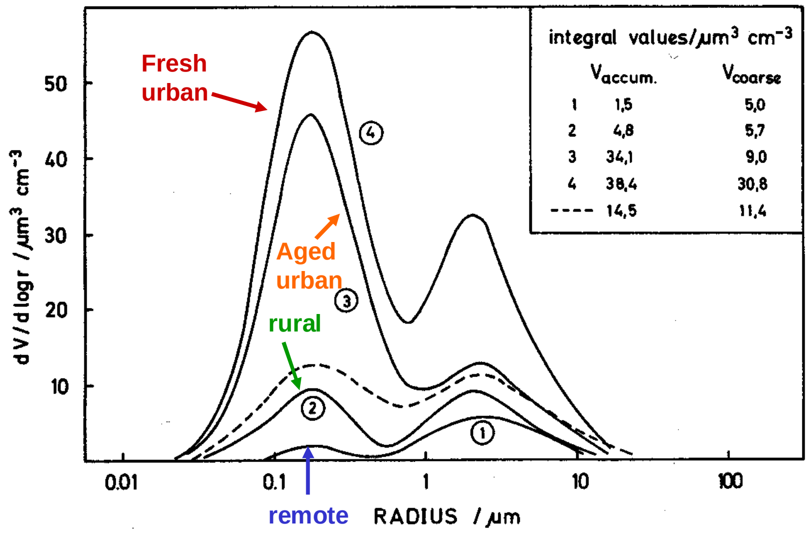
Volume highest at largest sizes

Surface area highest at medium sizes

Number highest at smaller sizes

SEAS experiment, 2000

Typical aerosol volume size distributions



Warneck [1999]

Note: Concentrations especially of larger particles decrease rapidly with height.

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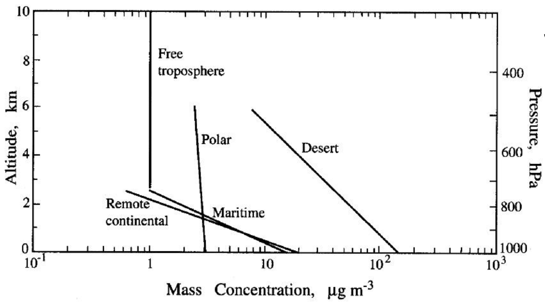
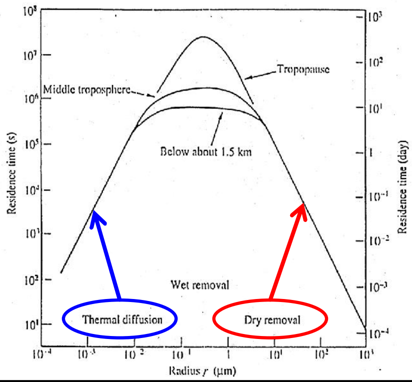
Vertical distribution and lifetime



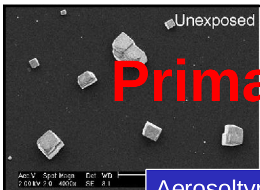
Jaenicke, 1993

Jaenicke, 1978



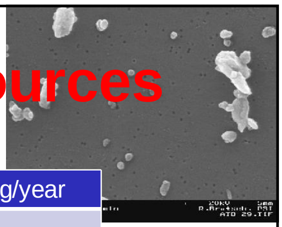
Aerosols with sizes around between 100 nm and 1 μm have the longest lifetime

Primary aerosols: sources

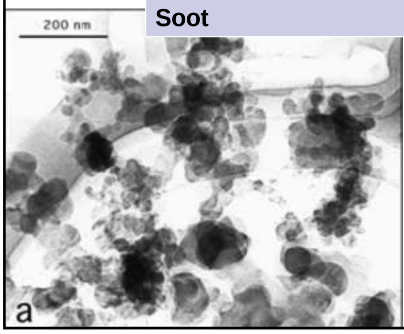


Sea salt
Gaspar, 2004

Aerosoltyp	Yearly production Tg/year
Mineral dust	**2980**
Sea salt	**10100**
Vulcano dust	**30**
Primary biological particles	**50**
Soot	**200**



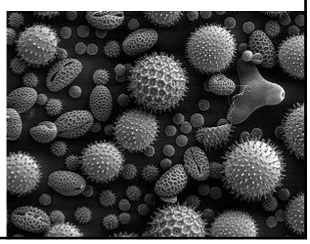
Mineral dust
Vlasenko, PSI, CH



Primary particles are larger and observed normally above 1 μm

Soot

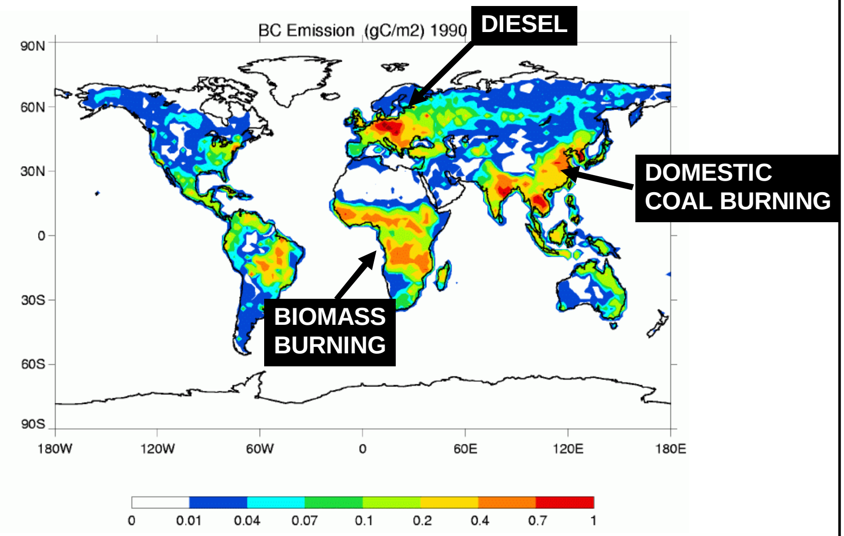
Pollen
www.wikipedia.org



Secondary aerosol sources:
Oxidation products by gas phase chemistry

Precursors	Yearly production in Tg/year
Dimethylsulfid (DMS) from algae	**12.4**
SO_2 from volcanos	**20**
Biogenic VOCs	**11-270 (could be higher up to 1000)**
SO_2 (antropogenic) from fossil fuels	**ca. 50**
NO_x (antropogenic) from fossil fuels	**22**
Antropogenic VOCs	**ca. 2**

Black carbon emissions



Chin et al. [2000]

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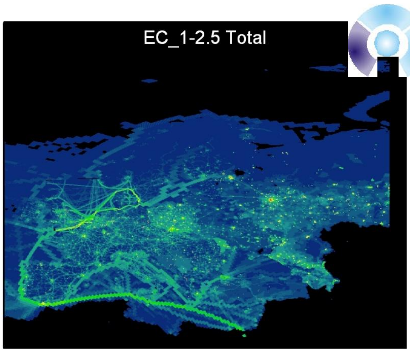
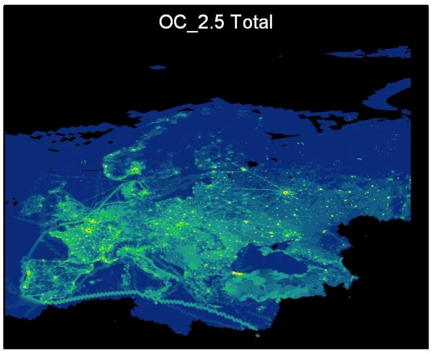
Primary emissions



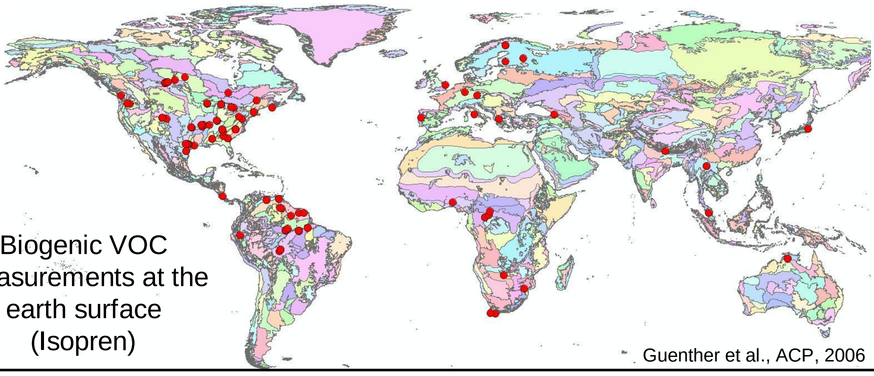


New European emission inventories for 2005

(EC and OC emission inventory of PM1, PM2.5 and PM10)

Emission inventory

- **Measurements of emissions normally only on selected places**
  - *Important:*
    - It most be representative for a certain area
    - Measurements under different atmospheric relevant conditions (temperature, humidity, stress, ...)
    - If possible measurements with different techniques (‚cross check‘)

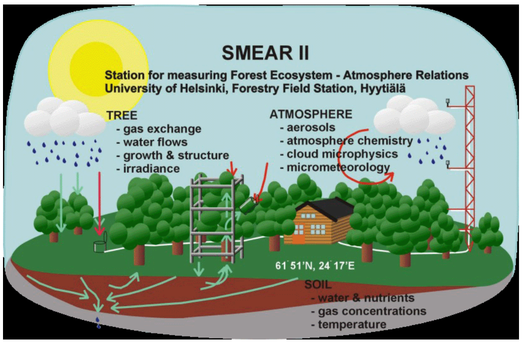


Biogenic VOC measurements at the earth surface (Isopren)

Guenther et al., ACP, 2006

Emission inventory

- **Emission measurements (campaign or monitoring)**
  - A) direct: Measurement down-wind of an emission source (e.g. at the exhaust pipe of a car or at the chimney of a factory)
  - B) indirect: Relaxed Eddy Accumulation (REA)-Systeme



Hyytiälä,
Universität Helsinki

a) Direct measurements

- Measurements direct in the exhaust gas flow of a chimney or exhaust pipe
  - Sensor will be mounted direct at the exhaust pipe or the exhaust gas will be measured in a chamber
  - Adsorption on sampling material or online measurement
  - Variation in the way you run the engine (motor speed)

Yu et al., 2008

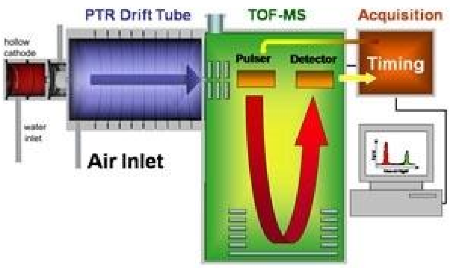
- Emission measurements in the canopy
  - Enclousure of a certain part from the tree in a cuvette or teflon bag
  - Sampling over a certain time period on tenax tubes
  - Or online measurment with insturments of high temporal and high sensitive sensitivity

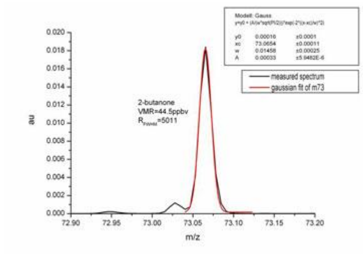
http://www.atm.helsinki.fi/SMEAR/index.php?option=com_content&task=view&id=22&Itemid=56

Direct analyses: PTR-MS(-TOF)

- Proton-Transfer-Reaction Mass Spectroscopie (PTR-MS)
- Important: the concentration has to be hgher than the detection limit (about 20-50 ppt depending on compound) and the proton affinity has to be stronger than the one for water

$$H_3O^+ + X \rightarrow H_2O + XH^+$$





Ionicon, 2007

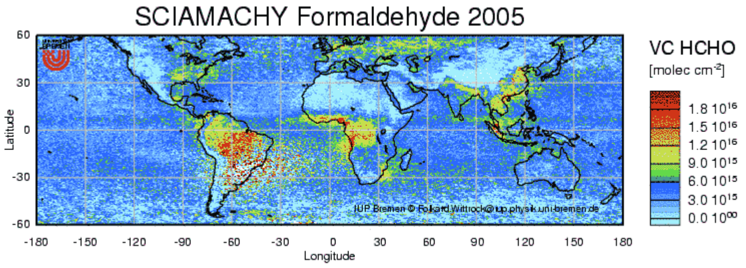
b) Indiret measurements

- Possible for large-scale areas of homogeneous vegetation or street canyons
- Measurements of the individual compounds inside and above the forest
- Calcualtion 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 moels
  - 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



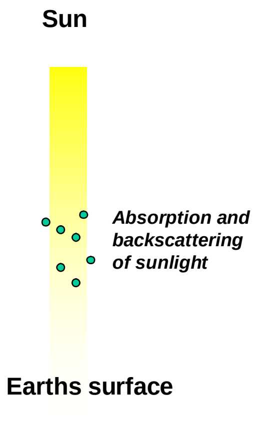
IUP, Bremen

Aerosol optical depth

The *aerosol optical depth* $\delta_{aerosol}$ is a dimensionless measure of the solar radiation ($F_{radiation}$) absorption and scattering by aerosol particles, when crossing the atmosphere:

$$F_{radiation,surface} = F_{radiation,top\ of\ the\ atmosphere} \cdot \exp(-\delta_{aerosol})$$

$$\delta_{aerosol} = \int_{top\ of\ the\ atmosphere}^{surface} b_{aerosol}(z) \cdot dz$$

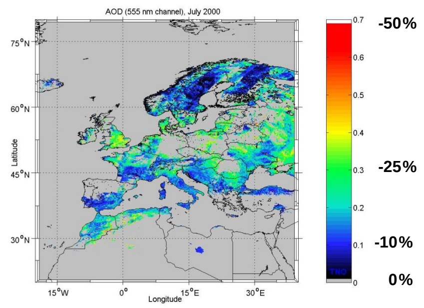


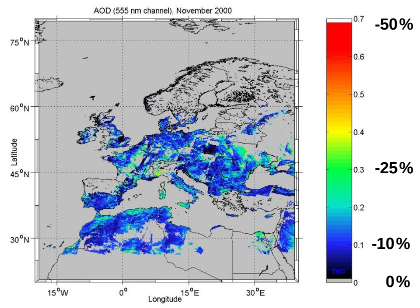
$b_{aerosol}$ is the extinction coefficient of the present aerosol mixture (including all processes removing the incoming radiation from the linear further path)

Aerosol optical depth from satellite measurements (ATSR-2)

July 2000 | November 2000

at 555 nm

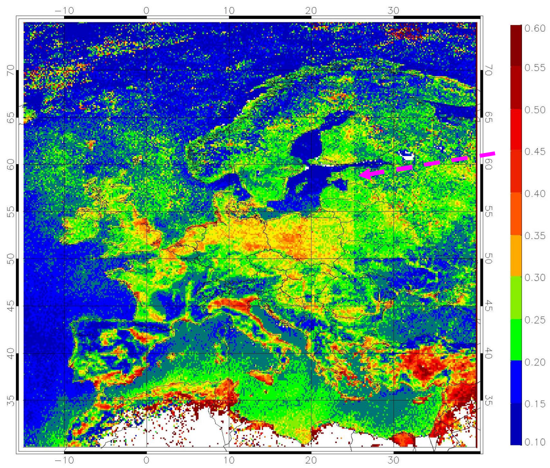




courtesy of *ESA* (TEMIS)

Aerosol optical depth (AOD) in Europe, 2003

PARMA project final report, Jan. 2007



Highest light absorption:

- large cities (e.g. London)
- industrialized areas (e.g. Benelux)
- at strong sources but prevented mixing (e.g. Po Valley)
- at traffic ways and oil platforms (e.g. North Sea)
- close to deserts because of mineral dust (e.g. Marocco, Lybia)

Figure 6.1 Yearly average aerosol optical thickness over Europe (at 0.55 μm) measured by MODIS in 2003. White: missing data.

PARMA project final report, …, 2007

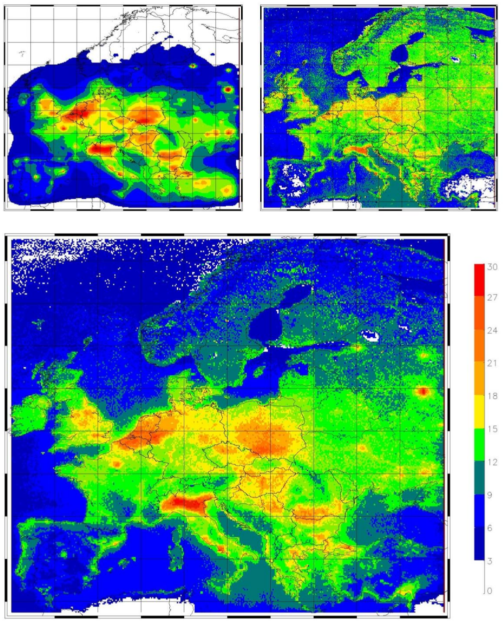


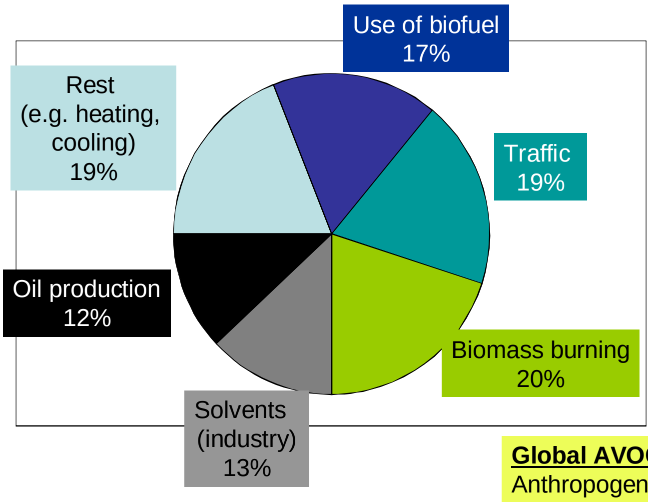
Figure 6.7 Fitted fields for $PM_{2.5}$ using only LOTOS/EUROS as explanatory variable (top left), using only the AOT_F filed as explanatory variable (top right), using both explanatory fields (bottom, large). For these map, the fits were forced through (0,0). All maps have the same colour scale.

PM 2.5 concentrations in Europe 2003
(fit of PM2.5 data to AOD from MODIS satellite)

Fit relies on known aerosol composition and size distribution!

Emission of anthropogenic volatile organice compounds (AVOCs)

Anthropogenic (man made) VOC sources



Global AVOC Emissions
Anthropogenic: 100 Tg/year
Biomass burning : 50 Tg/year

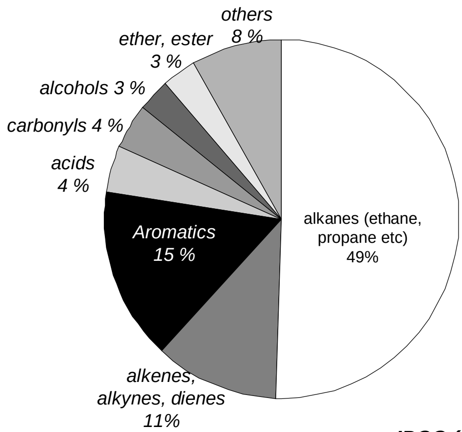
Total: 140-160 Tg/year
1990 tendency increasing

GEIA, 1995;
Seinfeld and Pandis, 1998

Anthropogenic VOCs: global source estimation

$\sum$(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 %)

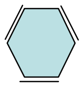


IPCC (2001)

What single compounds are emitted?

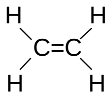
Energy production

Aromatics: e.g. benzene, toluene
Alkene: e.g. ethene, propene, butene
Alkane: e.g. ethane, propane, butane



Benzene

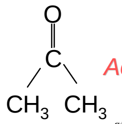
Industrial production



Ethene

Oxidised hydrocarbons
Aldehydes: e.g. formaldehyde (HCHO)
Ketones: e.g. acetone (CH_3COCH_3)
Alcoholes: e.g. ethanol (C_2H_5OH)
Acids: e.g. formic acid (HCOOH)

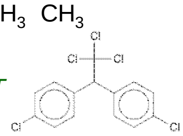
Agriculture



Acetone

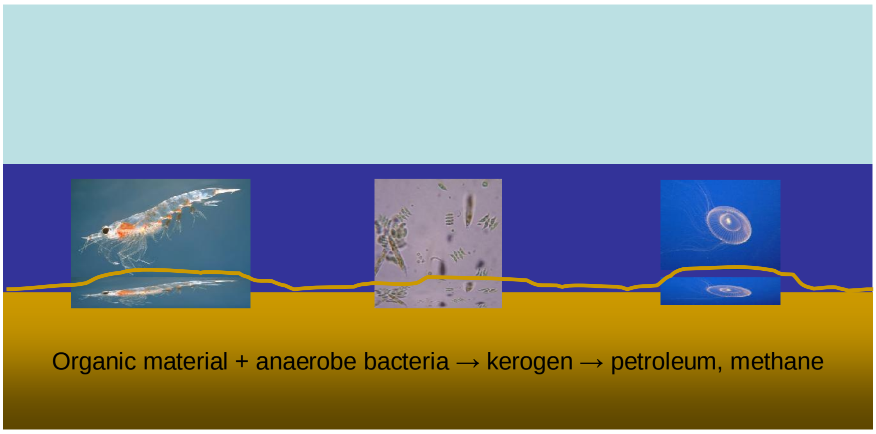
Nitrate, Sulfate etc.: e.g. PAN
Peroxides: e.g. Methylhydroperoxide

DDT



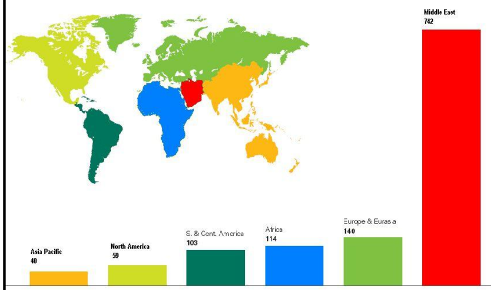
Organic compound = hydrocarbon (C_xH_y)+ other molecules: nitrogen (N), oxygen (O), sulphur (S) …).

Energy production - petroleum:



necessary: temperature and pressure are high without oxygen

Petroleum resources and consumption

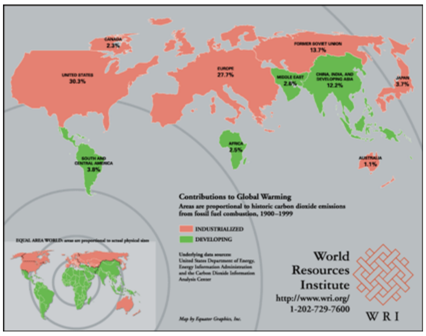


Proved oil reserves in billion barrel in 2005

http://de.wikipedia.org/wiki/Erd%C3%B6l#Weltreserven_und_Bevorratung

Contribution to Global Warming

Areas are proportional to historic carbon dioxide emissions from fossil fuel combustion, 1900-1999



Energy production - fuel: composition

Diesel:

about 75% paraffines, kerosine
about 25% aromatics + Octane

Regular gasoline:

43% aromatics (e.g. benzene)
29% alkanes (e.g. octane)
18% alkenes (e.g. propene)

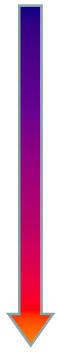
Super gasoline:

43% aromatics (e.g. benzene)
26% alkanes (e.g. octane)
21% alkenes (e.g. propene)

The more reactive the substance, the more energetic it is in the combustion

Nomenclature

ENERGIE-CONTENT



- Alk-**ane** – relative unreactive gases with long atmospheric lifetimes (months and more)
- Alk-**ene** – more reactive gases or liquide with shorter lifetimes (hours up to days)
- Alk-**ine** – high reactive liquide with short lifetime (minutes up to hours)

Combustion Processes

Hydrocarbon (C_nH_m) will be burned in the precense of oxygen (O_2).

$$C_nH_m + \frac{3}{2} n \cdot O_2 \rightarrow n \cdot CO_2 + n \cdot H_2O$$

Which amount of CO_2 will be produced per liter of benzene (C_6H_6)?

Example:

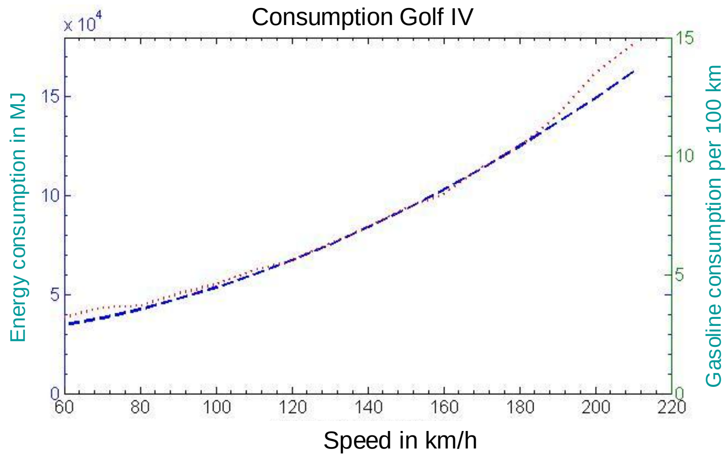
Benzene: $2(C_6H_6) + 15\ O_2 \rightarrow 12\ CO_2 + 6\ H_2O$

1 L Benzene = 876,5 g → 2966,6 g CO_2

***Problem:* The fuel will not be burned up to 100%**

A certain fraction (about 3%) will volatilize

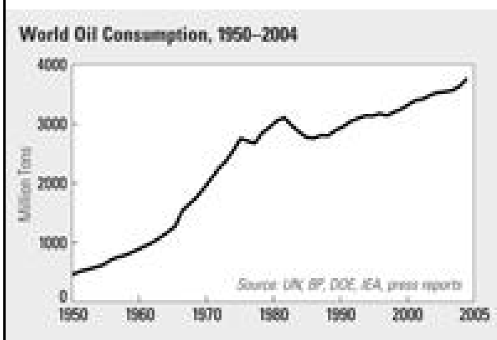
Consumption of a normal car



http://home.foni.net/~michaelbosch/auto/economic/calconsu.htm

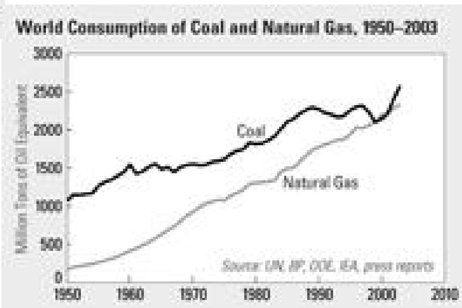
Civil passanger plane: aim = 3.8 L / 100 km / passanger

Global Emission of fuel



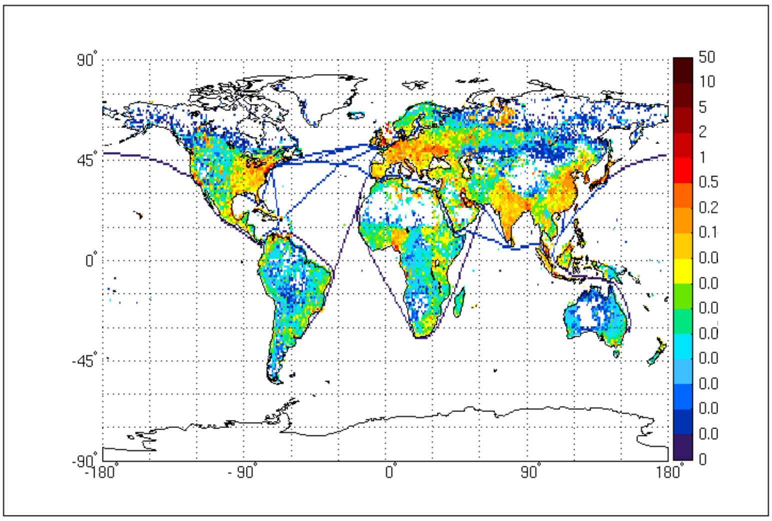
Fossil fuel emissions (unburnt):
ca. 16 Tg/year
(2000)

http://www.worldwatch.org/



Global Emission of fuels

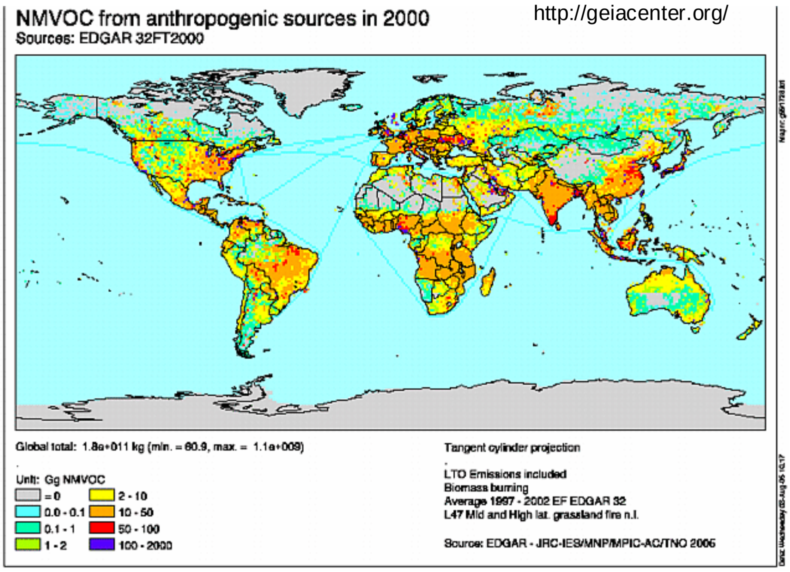
EDGAR - Total anthrop. nmv emission flux - year 2000, month 1



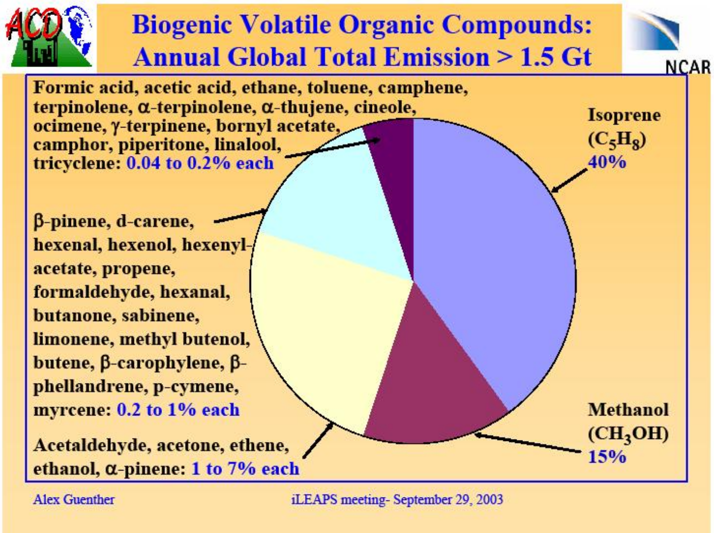
http://www.geiacenter.org/ (GEIA = Global Emissions Inventory Activity)

Total global emissions of anthropogenic VOCs

EDGAR database 2007
http://geiacenter.org/



Global biogenic VOCs



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

VOC fate next to emission

+hν

B) Oxidation

C) Cloud interactions (uptake, reactions)

+OH

+Ozone

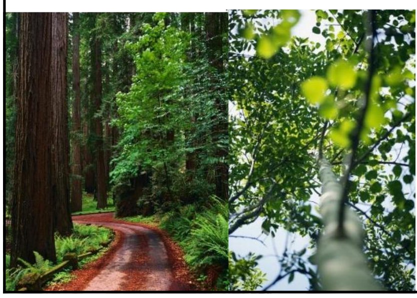
VOC

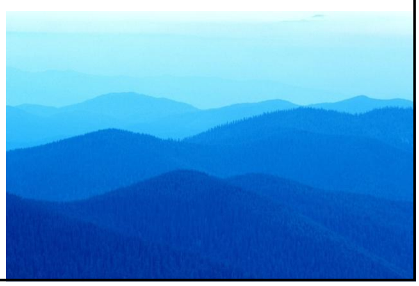
+NO_3

Transport

A) Emission

D) Aerosol formation

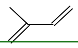




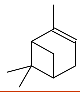
Biogenic volatile organic compounds (VOCs): Overview

- Reactive VOCs

Isoprene (C_5H_8)

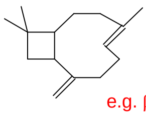


Monoterpenes ($C_{10}H_{16}$)



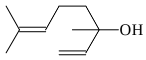
e.g. α-pinene

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



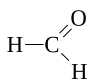
e.g. β-caryophyllene

Oxygenates

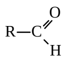


e.g. linalool

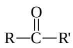
- Less reactive VOCs
  - Carbonyl compounds (e.g. formaldehyde HCHO)



Aldehydes: R-CHO:



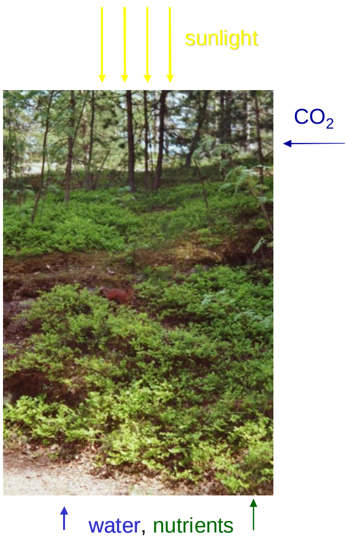
Ketones: RC(O)R':
(R and R' ≠ H)



Plants uptake and emission behaviour

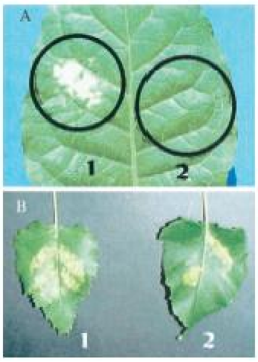
To survive a plant requires water, CO_2, nutrients and solar radiation

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)



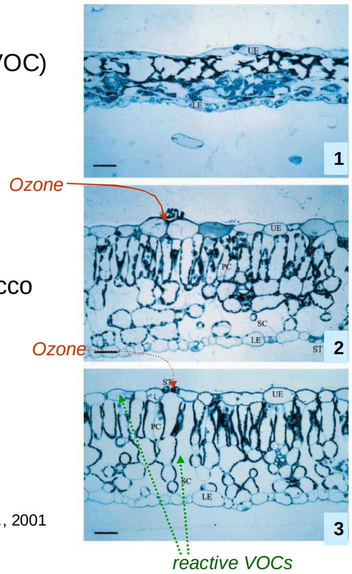
Stress factors:
Effect of hazardous chemicals (NO, O_3, acids):
Ozone impacts on vegetation

1 – ozone fumigation
2 – ozone and isoprene (VOC)
3 – before treatment



A - tobacco

B - birch



Loreto *et al.*, 2001

Description of VOC emissions

From database tables (EMEP or GEIA), obtained from measurements, by process-based or empirical 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})

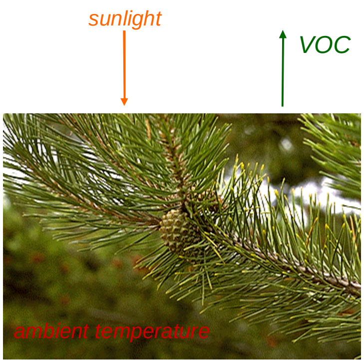
→ *e.g. amount of leaves/needles per surface area*

ε: ecosystem dependent emission factor at T = 30 °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

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

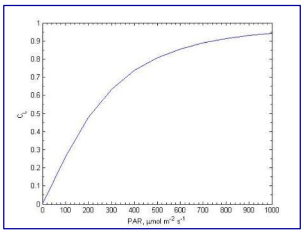
Temperature T (leaf):

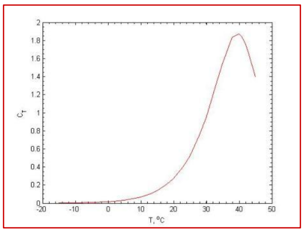
Note! Take needle or leaf temperature not the ambient one.

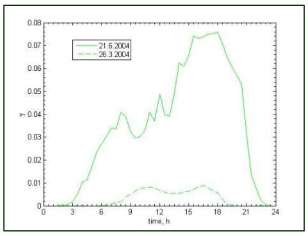
$$C_T = \frac{\exp\left(\frac{c_{T1}(T-T_s)}{RTT_s}\right)}{1+\exp\left(\frac{c_{T2}(T-T_M)}{RTT_s}\right)}$$

c_{T1} = 95kJ mol^{-1}, c_{T2} =230 kJ mol^{-1}, T_s = 303.15 K; T_M = 314 K

Spring and summer time in Hyytiälä





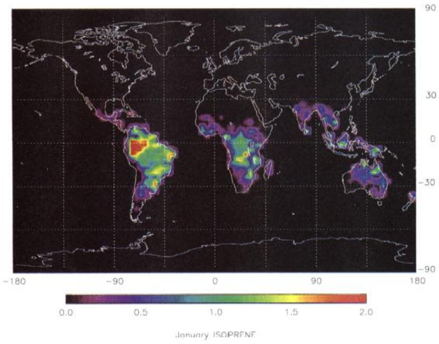


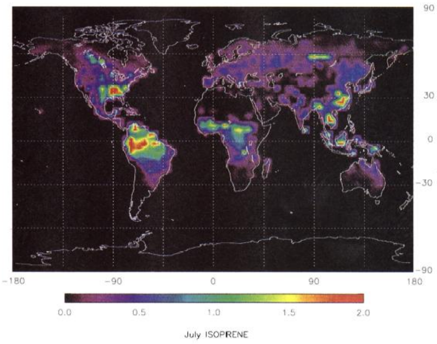
Isoprene (C_5H_8) emission

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

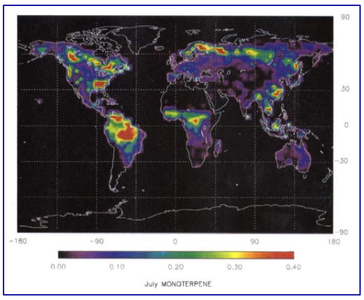
Estimated annual emission on the global scale:

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

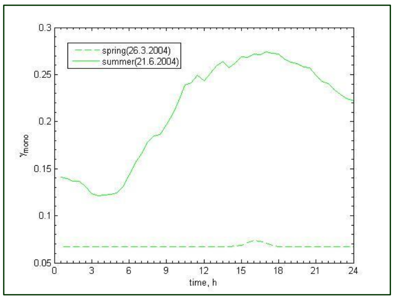
Monoterpene emissions are believed to depend on **temperature** only:

$$\gamma = \exp(\beta \cdot (T - T_s)) \qquad \beta = 0.09\ K^{-1},\ T_s = 303.15\ K$$

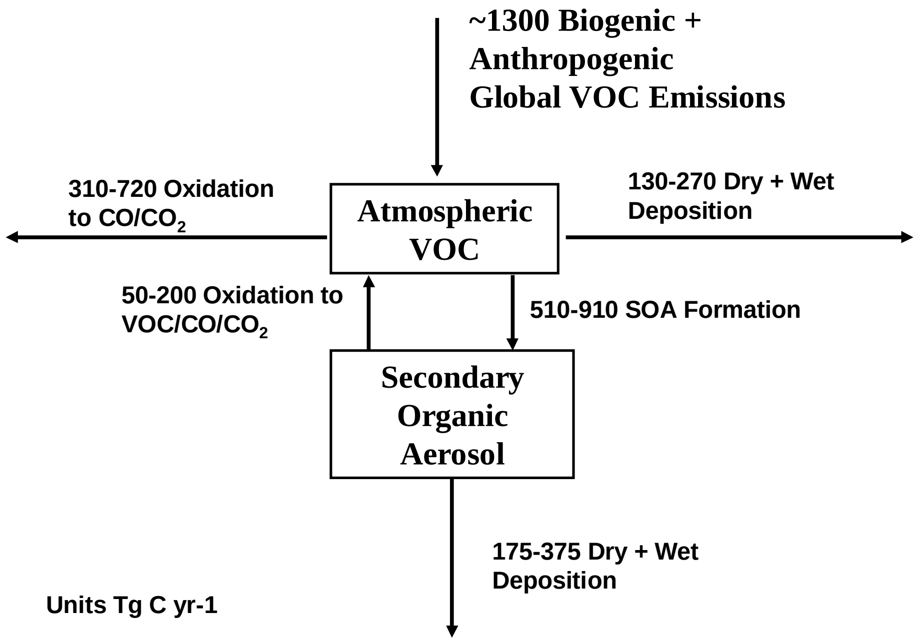
global



Hyytiälä



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



Goldstein und Galbally, 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