Swiss Legal Air Pollution Limits

https://www.ekl.admin.ch/inhalte/dateien/pdf/EKL-231120_de_orig.pdf

Pollutant	Averaging time	WHO AQG 2021	Current OAPC ambient limit value	FCAH recommen-dation 2023
Sulphur dioxide (SO_2), µg/m³ (see Chapter 8)	Annual average and new mean value over winter half-year	–	30[a]	20[b]
	95 % of ½ h mean value for a year	–	100	remove
	24h mean value	40[c]	100[d]	40[c]
Nitrogen dioxide (NO_2), µg/m³ (see Chapter 7)	Annual average	10	30	10
	95 % of ½ h mean value for a year	–	100	remove
	24h mean value	25[c]	80[d]	25[c]
Carbon monoxide (CO), mg/m³ (see Chapter 9)	24h mean value	4[c]	8[d]	4[c]
Ozone (O_3), µg/m³ (see Chapter 6)	Summer season[e]	60	–	60
	98 % of ½ h mean value for a month	–	100	100
	8h mean value	100[c]	–	–
	1h mean value	–	120[d]	120[d]
Suspended particulates / particulate matter (PM10), µg/m³ (see Chapter 4)	Annual average	15	20	15
	24h mean value	45[c]	50[c]	45[c]
Suspended particulates / particulate matter (PM2.5), µg/m³ (see Chapter 5)	Annual average	5	10	5
	24h mean value	15[c]	–	15[c]

[a] Ambient air quality standard, which also includes the protection of animals and plants, their biological communities and habitats according to Article 1 paragraph 1 EPA, and corresponds to the state of knowledge when the Air Pollution Control Ordinance was adopted in 1985.
[b] Value stipulated in the 2000 WHO AQGs (WHO, 2000) for the protection of forests and other seminatural ecosystems. Valid as an annual average as well as for the winter half-year. (October–March).
[c] 99th percentile (i.e. limit value may be exceeded three times per year).
[d] May only be exceeded once per year.
[e] Average of the maximum daily 8h mean value ozone concentrations in the six consecutive months with the highest six-month average for ozone concentration. For Switzerland, this corresponds to April to September.

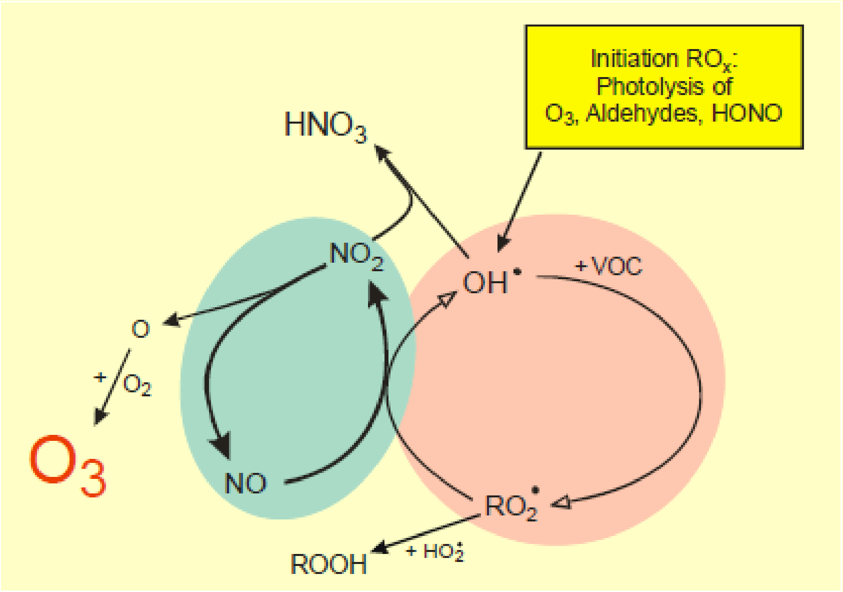
Why is NO_2 an air pollutant?

Direct health effect:

- Lung irritation ($NO_2 + H_2O \Rightarrow HNO_3$)

Indirect health/environment effect:

1. Formation of O_3
    - Plant damage
    - Greenhouse effect
2. Formation of HNO_3 (nitric acid)
    - Aerosol precursor
    - Deposition
        - Forest decline
        - Acidification of lakes and soils
        - Feritilising natural ecosystems
        - Production of N_2O (nitrous oxide) in soils (greenhouse effect)



Fluxes of NO_x in the atmosphere

Sources NO_x (as N):

Anthropogenic (34 Tg N/y)	
fossil fuel/industrial combustion:	26 Tg/y
Biomass/biofuel burning:	6 Tg/y
Agriculture:	1.5 Tg/y
Natural (12 Tg N/y)	
Natural soils:	7 Tg/y
Lightning:	5 Tg/y
Total	**46 Tg/y**

Sinks:

1. **Wet deposition (as NO_3^-)**
2. **Dry deposition (as NO_x)**

Source IPCC 4AR

History of ozone (O_3) in the atmosphere

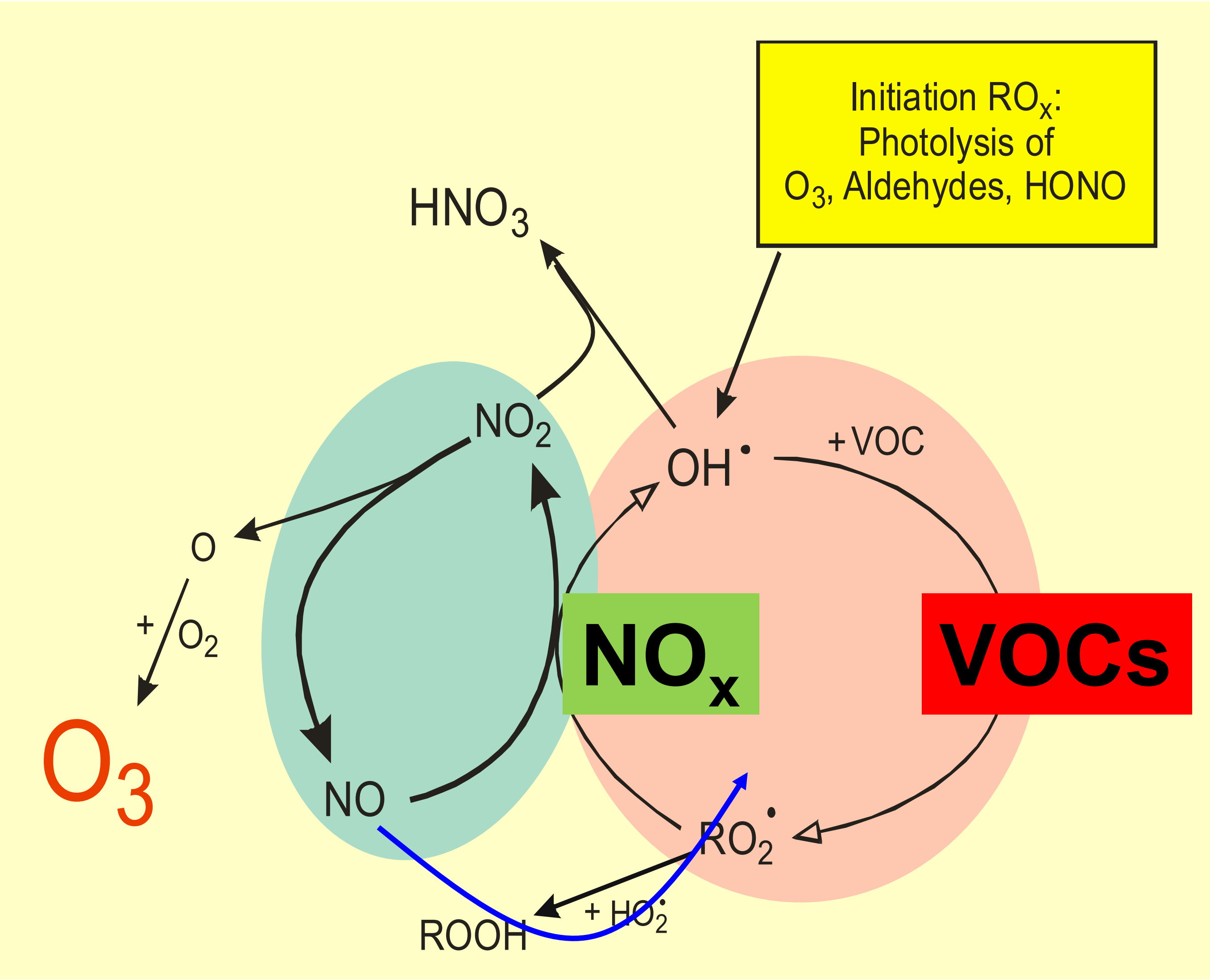
Christian Friedrich Schönbein, 1799-1868

1839 — O_3 is detected by C.F. Schönbein in Basel
1845 — Schönbein detects O_3 in the atmosphere
-1950 — O_3 in troposphere is from stratosphere
1950- — Link of O_3 with photosmog (Los Angeles)

Basel, Münsterplatz

Los Angeles, smog

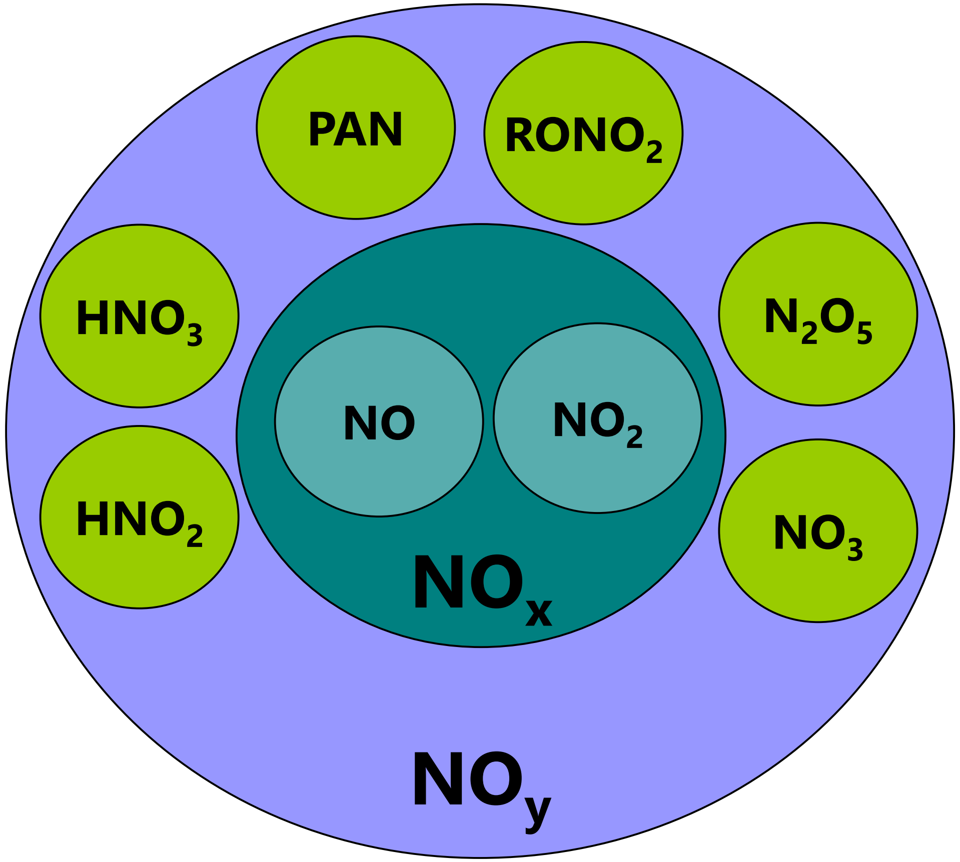
Photochemical smog (NOx + VOCs ➔ Ozone)



Two coupled radical reactions:
No$_x$ (green):NO,NO_2
RO$_x$ (red): VOCs, OH·, HO_2·, RO·, RO_2·

from Staehelin, ETHZ

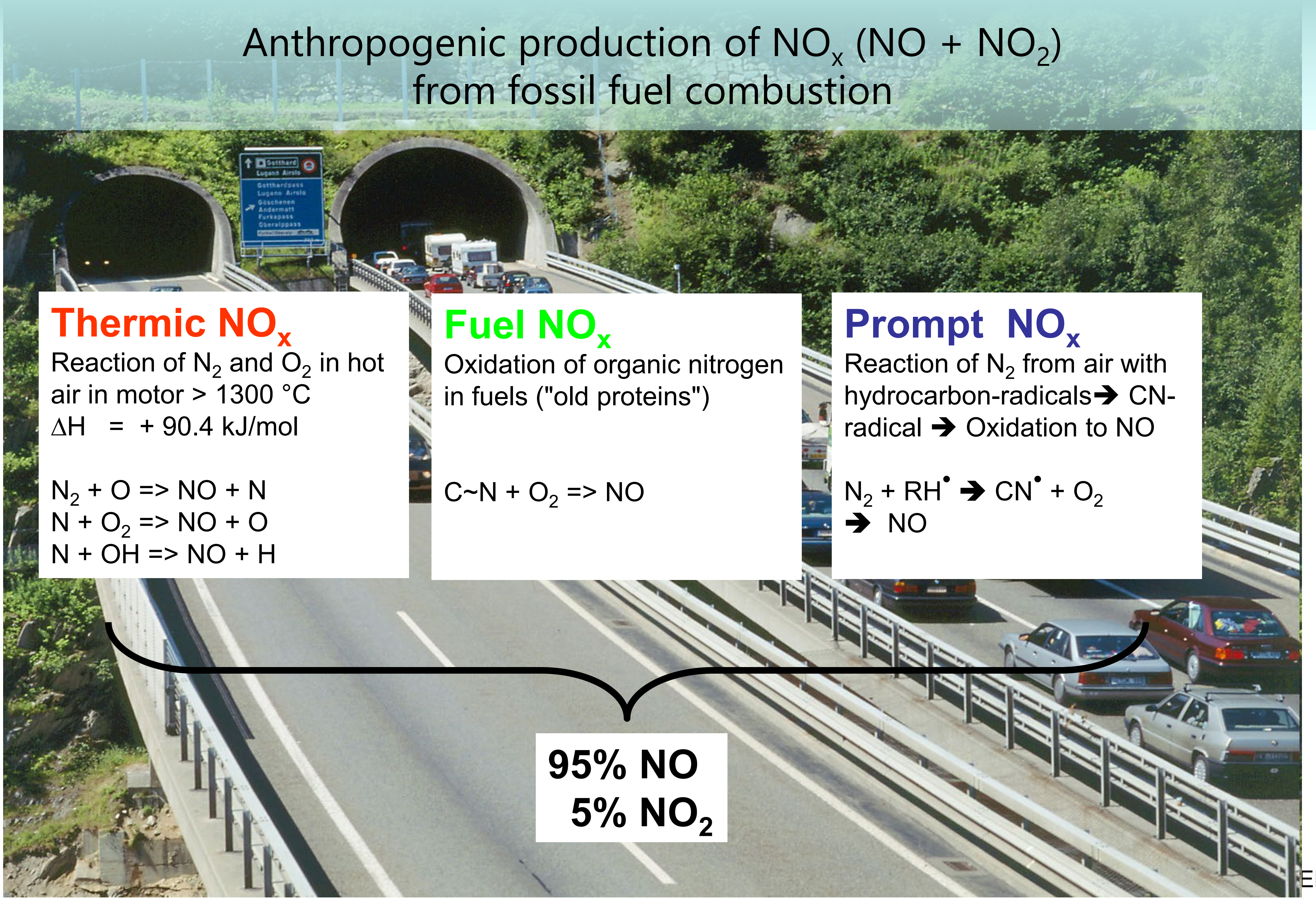
Definition of NO_x/NO_y



NO_x: NO + NO_2

NO_y: total reactive nitrogen, odd nitrogen

Anthropogenic production of NO_x ($NO + NO_2$) from fossil fuel combustion



Thermic NO_x

Reaction of N_2 and O_2 in hot air in motor > 1300 °C
$\Delta H = + 90.4$ kJ/mol

$N_2 + O \Rightarrow NO + N$
$N + O_2 \Rightarrow NO + O$
$N + OH \Rightarrow NO + H$

Fuel NO_x

Oxidation of organic nitrogen in fuels ("old proteins")

$C{\sim}N + O_2 \Rightarrow NO$

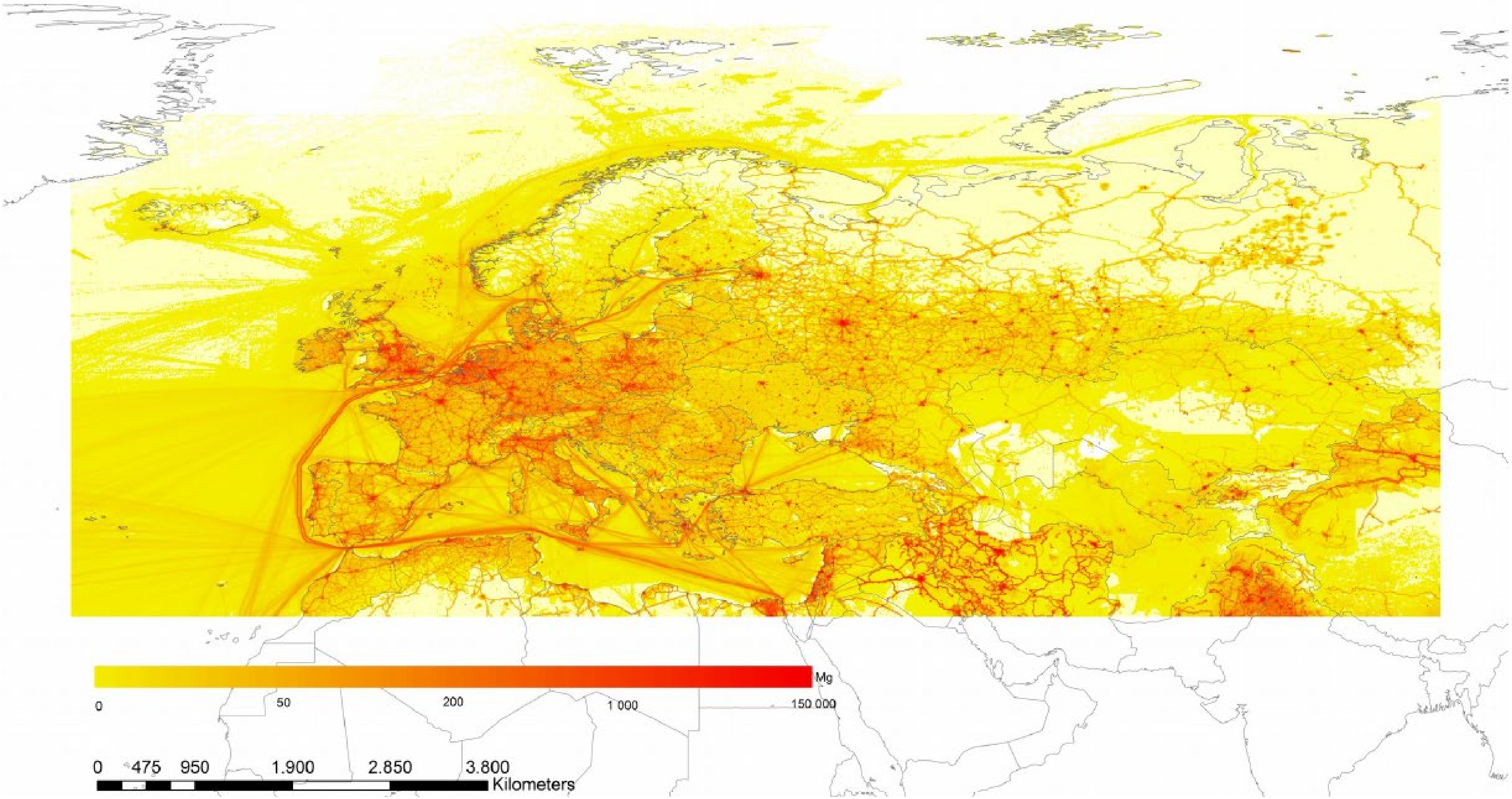
Prompt NO_x

Reaction of N_2 from air with hydrocarbon-radicals ➔ CN-radical ➔ Oxidation to NO

$N_2 + RH^{\bullet} \rightarrow CN^{\bullet} + O_2$
$\rightarrow NO$

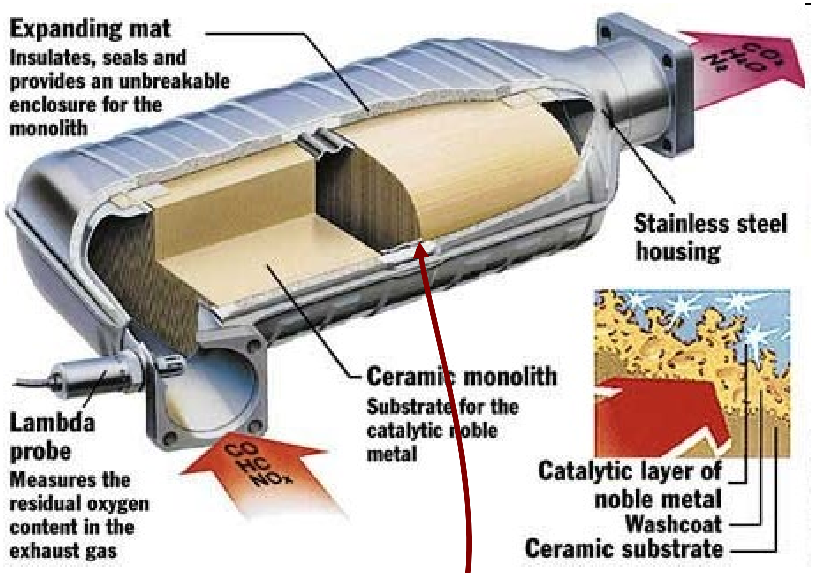
95% NO
5% NO_2

NO_x emissions in Europe



EMEP Status report 2018

NO_x Reduction using 3-way catalysts
Principle: reduction of reaction energy on catalytic surface



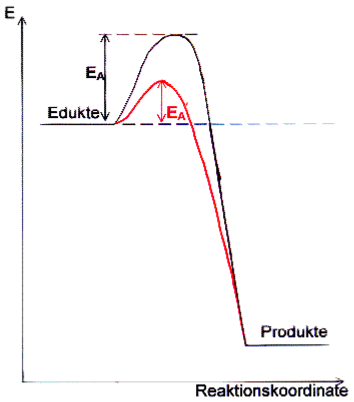
Reaction:

Reduction (using Rhodium):
A) 2 NO => N_2 + O_2 or 2 NO_2 => N_2 + 2 O_2

Oxidation (using Platin/Palladium)
B) 2 CO + O_2 => 2 CO_2

C) VOCs (unburnt gasoline) + O_2 => CO_2 + H_2O

parts:
Lambda-Sonde for regulation of oxygen (O_2)
Palladium/Platin/Rhodium auf ceramic



Reduction of activation energy (in red)

Ceramic

Lambda λ:
the magic sign of exhaust science

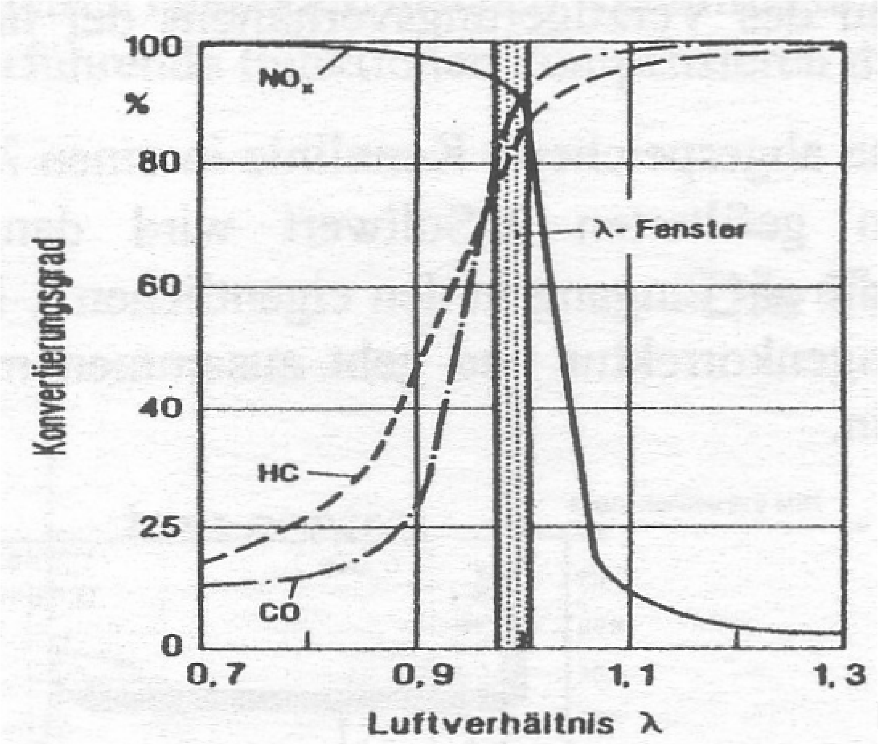
Air which is needed for a complete conversion of fuel into CO_2:

$$L_{min} = \frac{14.7\ kg\ air}{1\ kg\ petrol} \qquad \lambda = \frac{L}{L_{min}}$$

λ =1: best reduction efficiency (Lambda-window)

λ >1 (too much air): less reduction of NO/NO_2

λ <1 (too much fuel): less reduction of CO/unburnt fuel

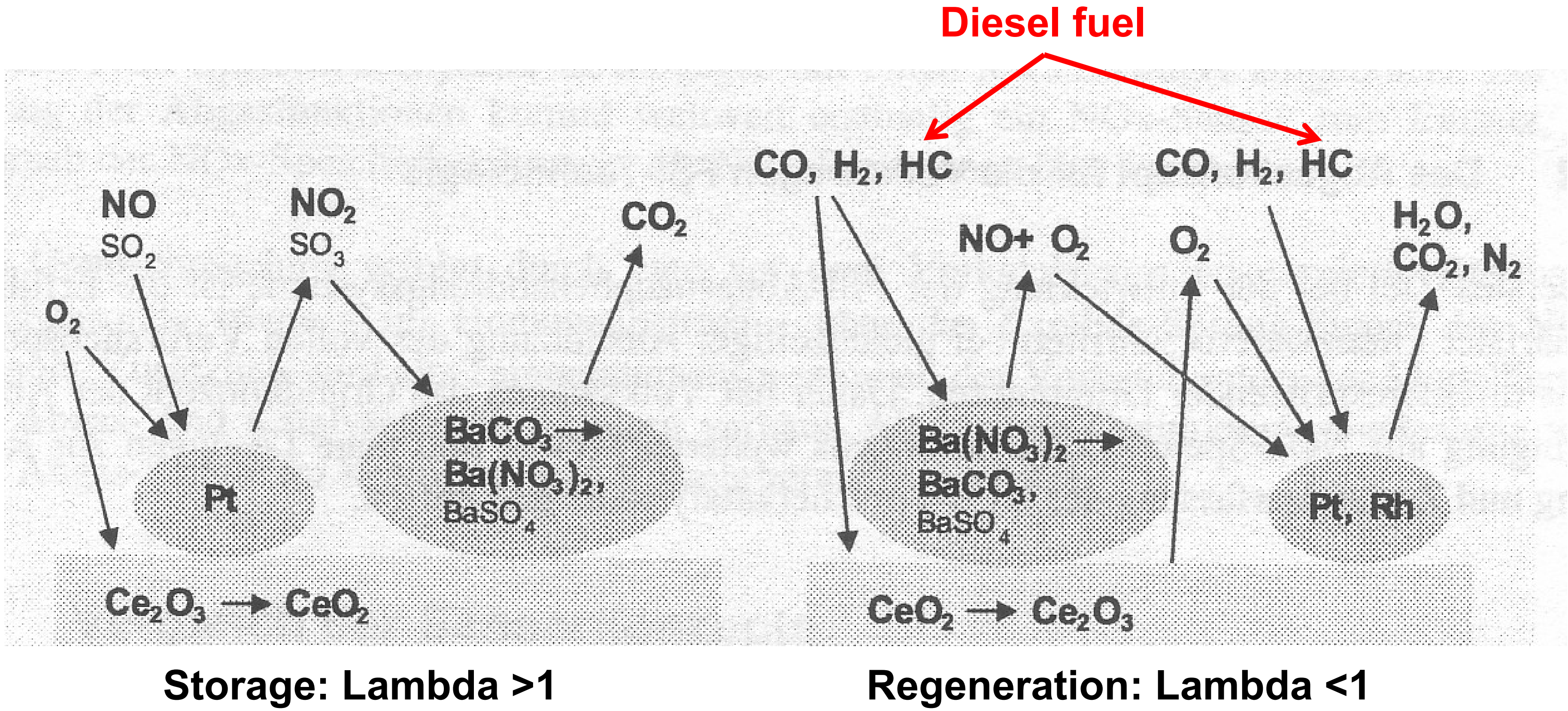


Diesel NO_x reduction strategies

in Diesel: no 3-way catalyst as there is Lambda > 1 (too much air)

1st strategy, mostly used in cheaper cars:

Lean NO_x traps (LNT) in principle a 3-way catalyst but NO is stored actively

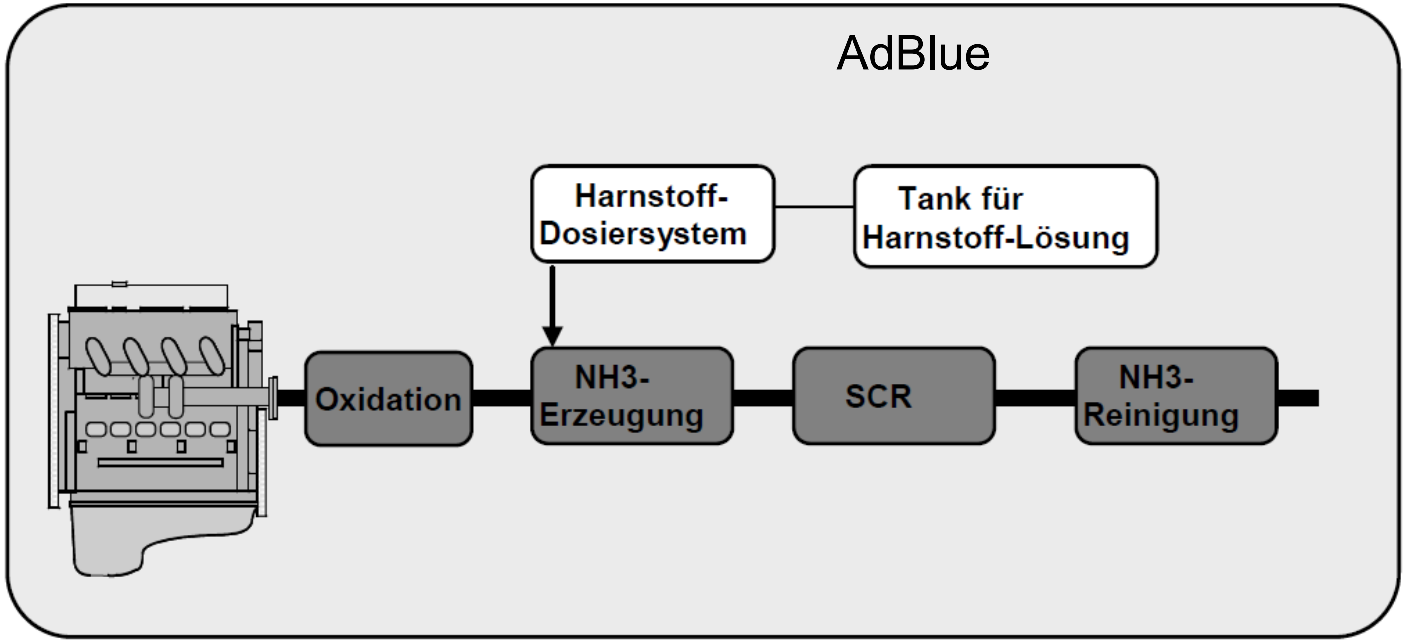


Diesel NO_x reduction strategies

in Diesel: no 3-way catalyst as there is Lambda > 1 (too much air)

2nd strategy, mostly used in more expensive cars :

Selective Catalytic Reduction (SCR): urea is actively injected



$$NO + NO_2 + 2\,NH_3 + O_2 \rightarrow 2\,N_2 + 3\,H_2O + O_2$$

The Volkswagen scandal, September 2015

Tests found that the levels of NO_x emitted by a Volkswagen Jetta (using LNT) were 15–35 times greater than dictated by the US standard (31 milligrams per kilometre), depending on road and driving conditions.

Those for a Volkswagen Passat (using SCR) were 5–20 times greater.

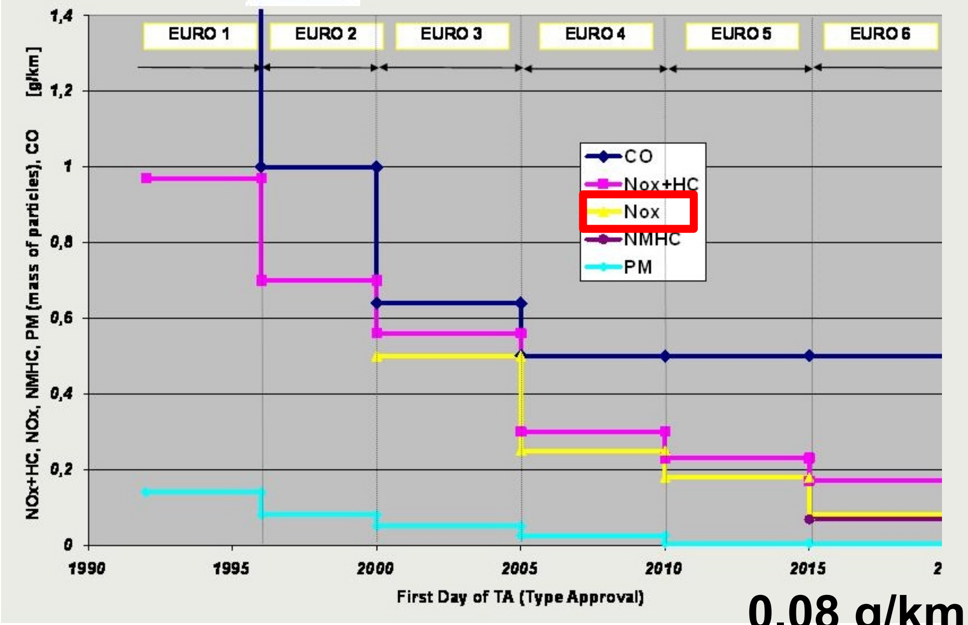
The findings prompted the US Environmental Protection Agency (EPA) to launch investigations into Volkswagen tests in the United States. The EPA also threatened to withdraw its approval for all Volkswagen diesel vehicles approved for sale there; Volkswagen responded by admitting that it had tricked emissions tests by using software that senses when the car is being tested, and switches on full emissions control.

Comment in Nature, 2015

Emission limits EU and US

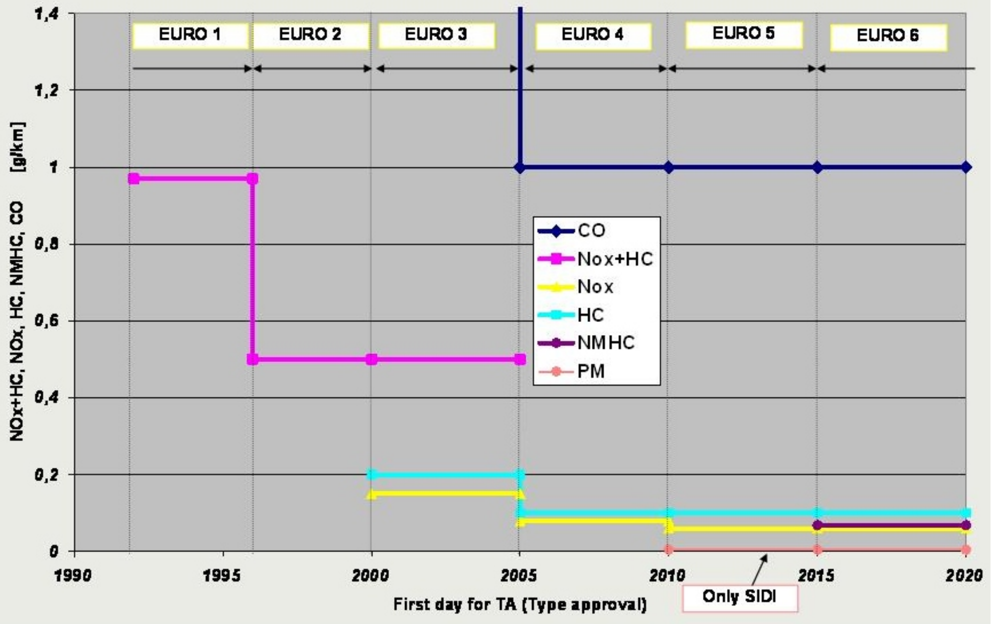
https://de.wikipedia.org/wiki/Abgasnorm

EU: Diesel



0.08 g/km

EU: Gasoline



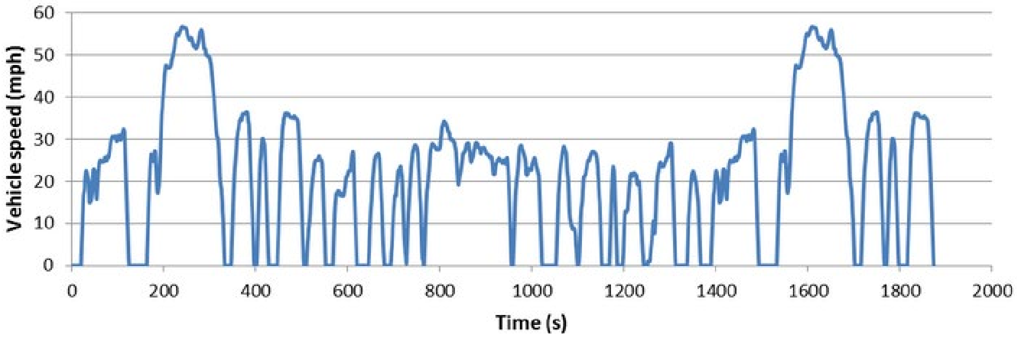
US: Diesel

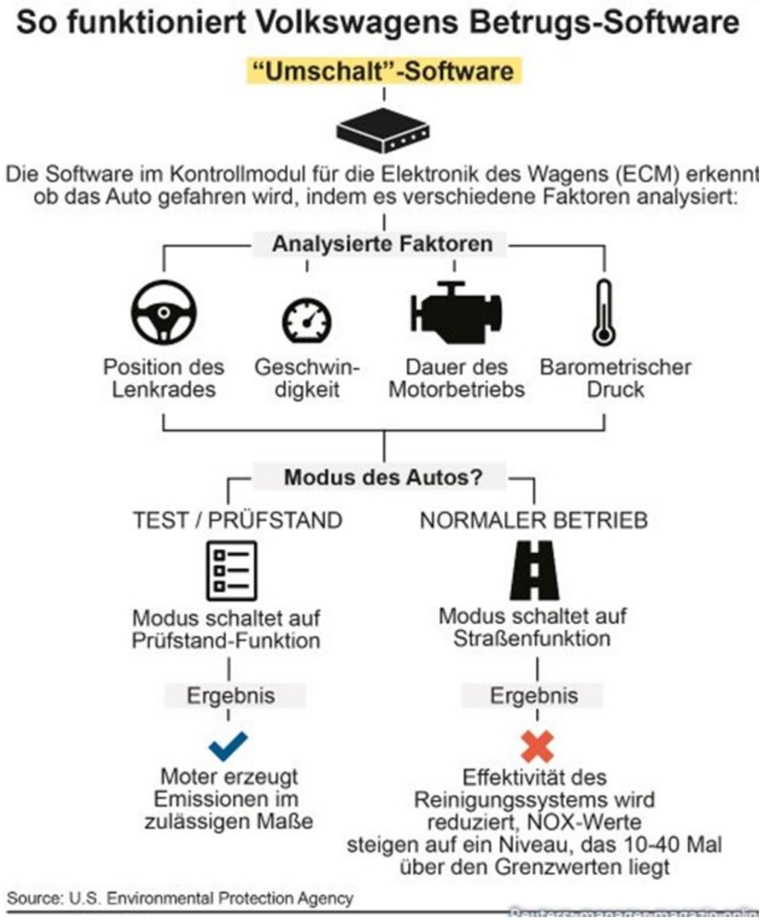
	Standard	Emission Limits at 50,000 miles					Emission Limits at Full Useful Life (120,000 miles)[2]				
		NOx (g/mi)	NMOG (g/mi)	CO (g/mi)	PM (g/mi)	HCHO (g/mi)	NOx (g/mi)	NMOG (g/mi)	CO (g/mi)	PM (g/mi)	HCHO (g/mi)
Federal	Bin 1	–	–	–	–	–	0	0	0	0	0
	Bin 2	–	–	–	–	–	0.02	0.01	2.1	0.01	0.004
	Bin 3	–	–	–	–	–	0.03	0.055	2.1	0.01	0.011
	Bin 4	–	–	–	–	–	0.04	0.07	2.1	0.01	0.011
	Bin 5	0.05	0.075	3.4	–	0.015	0.07	0.09	4.2	0.01	0.018
	Bin 6	0.08	0.075	3.4	–	0.015	0.1	0.09	4.2	0.01	0.018
	Bin 7	0.11	0.075	3.4	–	0.015	0.15	0.09	4.2	0.02	0.018
	Bin 8	0.14	0.100 / 0.125[c]	3.4	–	0.015	0.2	0.125 / 0.156	4.2	0.02	0.018
	Bin 9[b]	0.2	0.075 / 0.140	3.4	–	0.015	0.3	0.090 / 0.180	4.2	0.06	0.018
	Bin 10[b]	0.4	0.125 / 0.160	3.4 / 4.4	–	0.015 / 0.018	0.6	0.156 / 0.230	4.2 / 6.4	0.08	0.018 / 0.027
	Bin 11[b]	0.6	0.195	5	–	0.022	0.9	0.28	7.3	0.12	0.032

The Volkswagen scandal, September 2015

test stand at Empa

Test stand driving cycle
FTP-75 cycle, old, unrealistic





software blocks effective action of the lean nitrogen oxide (NOx) trap (LNT) in 11 million Volkswagen Group cars (including VW, Audi, Skoda, Seat)

Results: real world vs. test stand
ICCT, May 2014

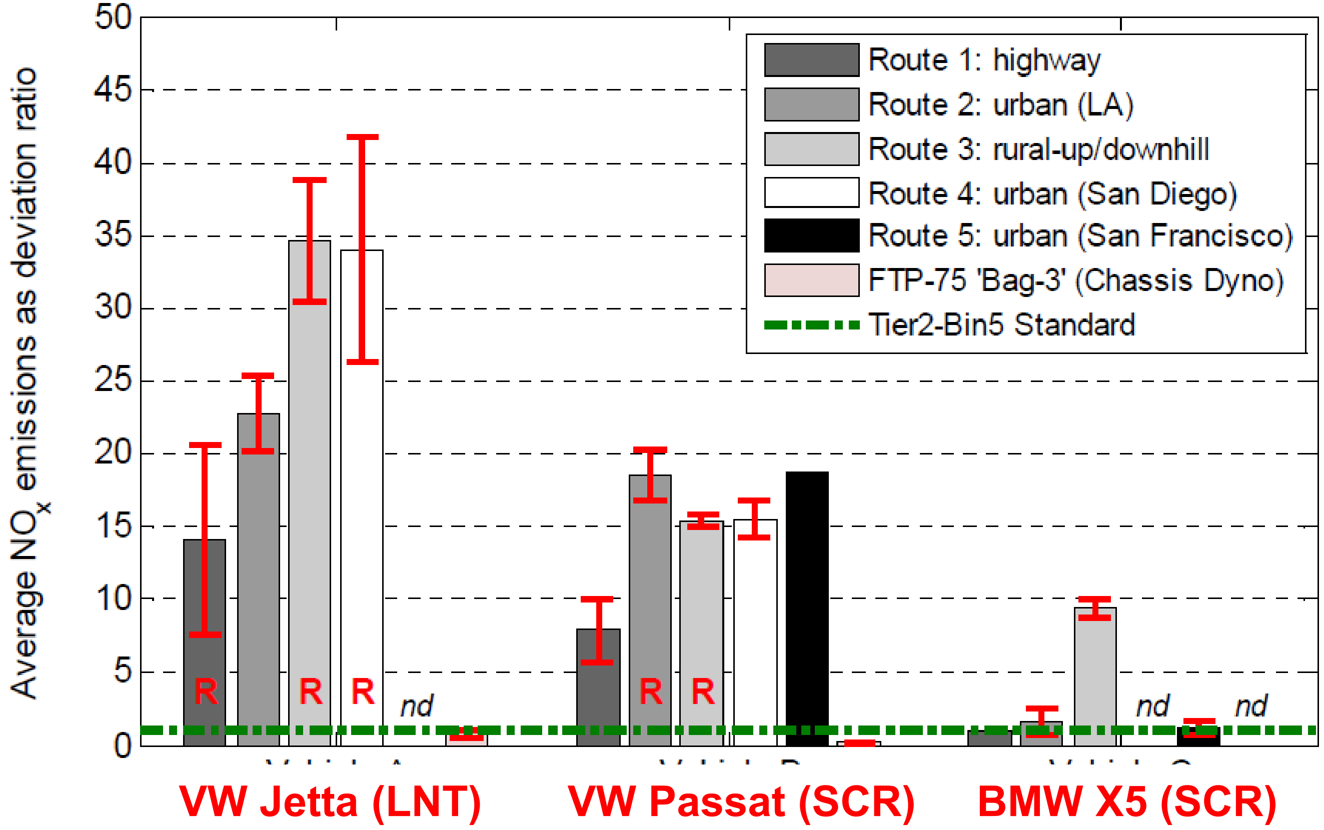


Figure 4.4: Average NO_x emissions of test vehicles over the five test routes expressed as deviation ratio; repeat test variation intervals are presented as $\pm 1\sigma$, '*R*' designates routes including a test with DPF regeneration event, '*nd*' - no data available

Update 2018-2021

NZZ, 12.09.18

Absprache-Verdacht deutscher Autobauer zu Adblue-Tanks erhärtet sich

Der Mitte 2017 erstmals aufgetauchte Vorwurf, die grössten deutschen Autokonzerne hätten sich auf zu kleine Tanks für die Abgasnachbehandlung geeinigt, scheint sich nach «Handelsblatt»-Informationen zu bestätigen.

Tanks for Adblue were too small: 1.0 Liter instead of 1.2 Liter!

Customer would have to refill the tank before the service cycle (~10'000 km).

So producers talked together and switched the Adblue off.

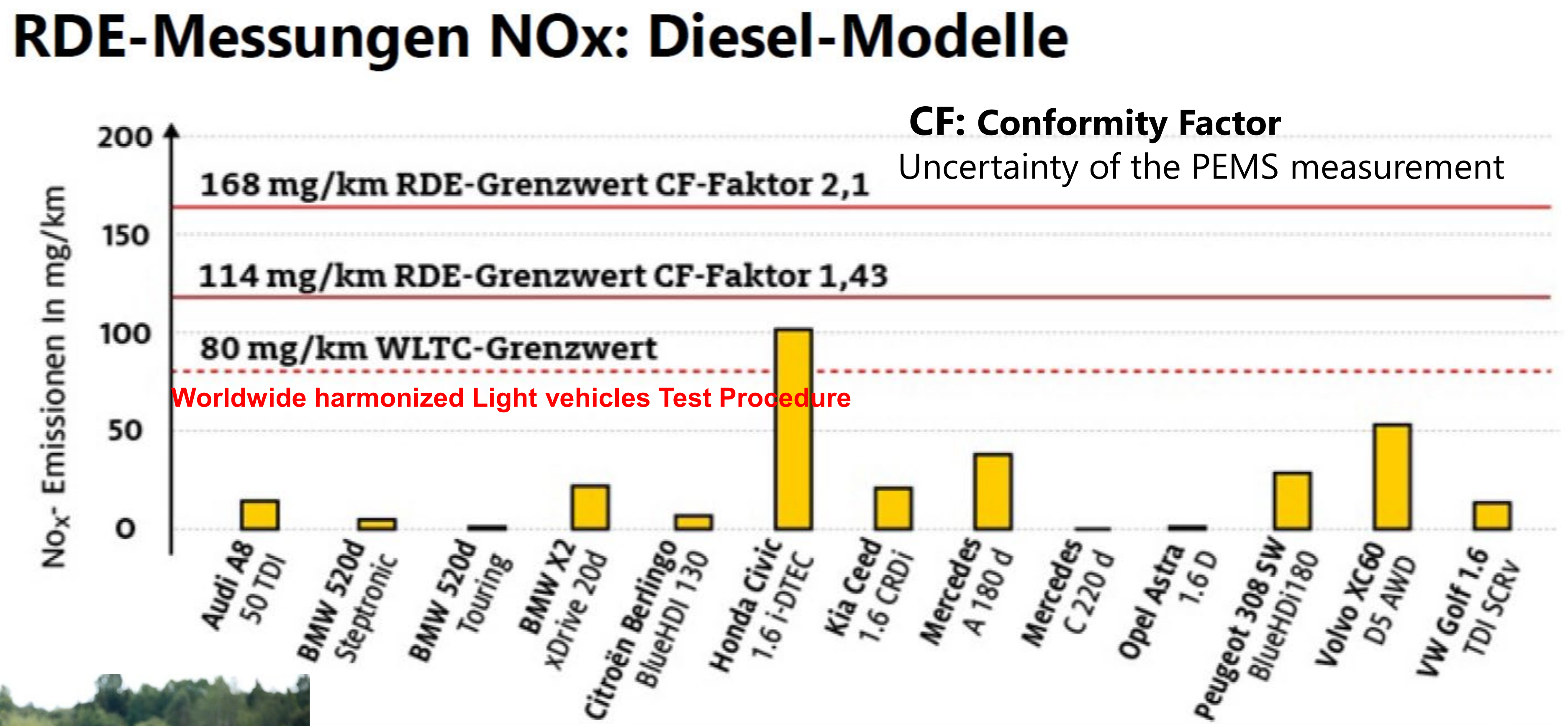
2020: law case
Zitat in email: «Ohne Bescheissen werden wir es nicht schaffen, Alle Kunden in das 1 Liter Fenster zu bekommen.»

July 2021

EU verhängt Millionenstrafe gegen VW und BMW

(dpa) · Die deutschen Autobauer Volkswagen und BMW müssen im seit Jahren laufenden EU-Kartellverfahren tief in die Tasche greifen. Wegen rechtswidriger Absprachen zu Adblue-Tanks für eine bessere Abgasreinigung soll BMW knapp 373 Mio. € zahlen, Volkswagen gut 502 Mio. €, wie die Kommission am Donnerstag in Brüssel mitteilte. Daimler kommt wegen der Kronzeugenregelung ohne Busse davon. «Alle Unternehmen haben ihre Kartellbeteiligung eingeräumt und einem Vergleich zugestimmt», hiess es von der Brüsseler Behörde. Sie wirft den Autobauern vor, sich in unzulässiger Weise über die Grösse der Adblue-Tanks abgesprochen zu haben. Die Tanks gehören zur Abgasreinigung in Dieselautos. Sie nehmen eine spezielle Harnstoff-Lösung auf, mit denen in neueren Katalysator-Generationen giftige Stickoxid-Emissionen gesenkt werden sollen.

Real test on streets
RDE: Real **D**riving **E**missions



CF: Conformity Factor
Uncertainty of the PEMS measurement

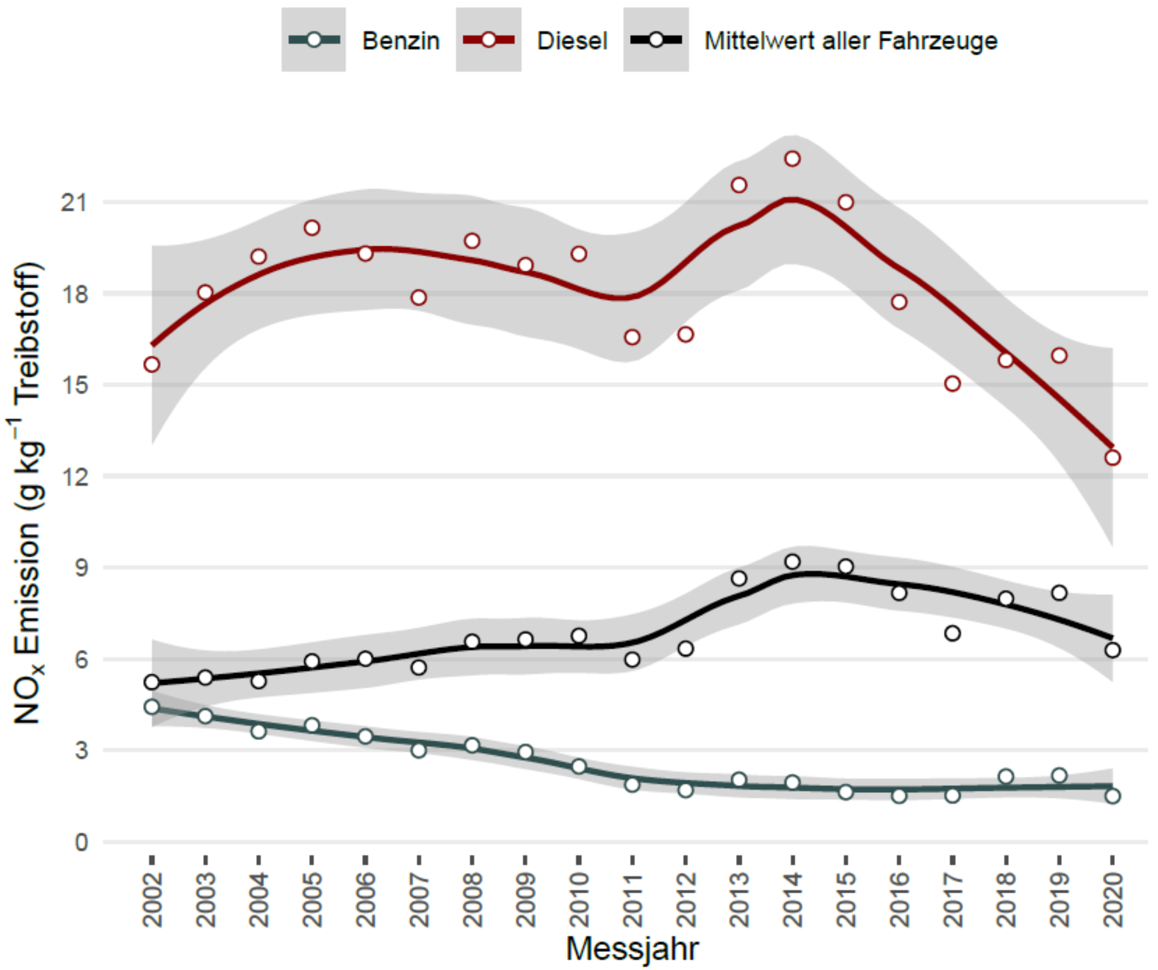
Worldwide harmonized Light vehicles Test Procedure

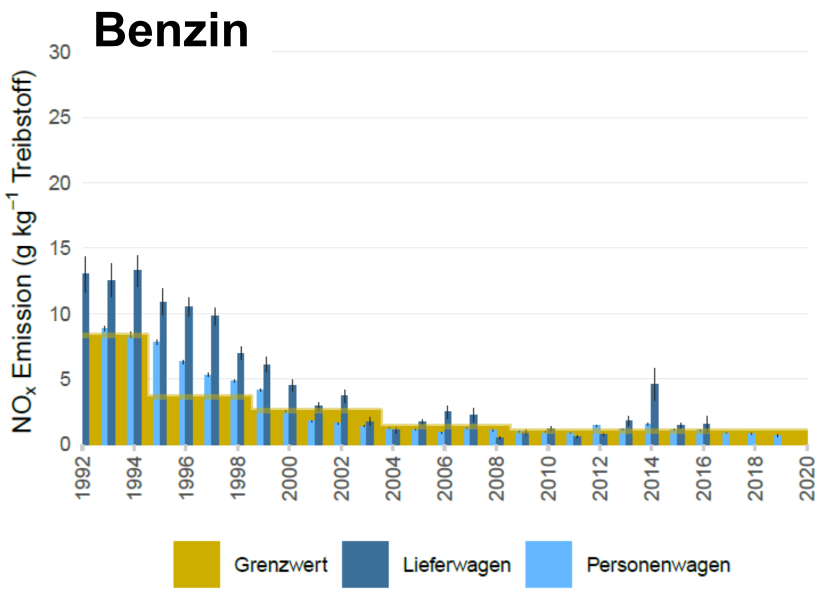
Euro 6d Diesel

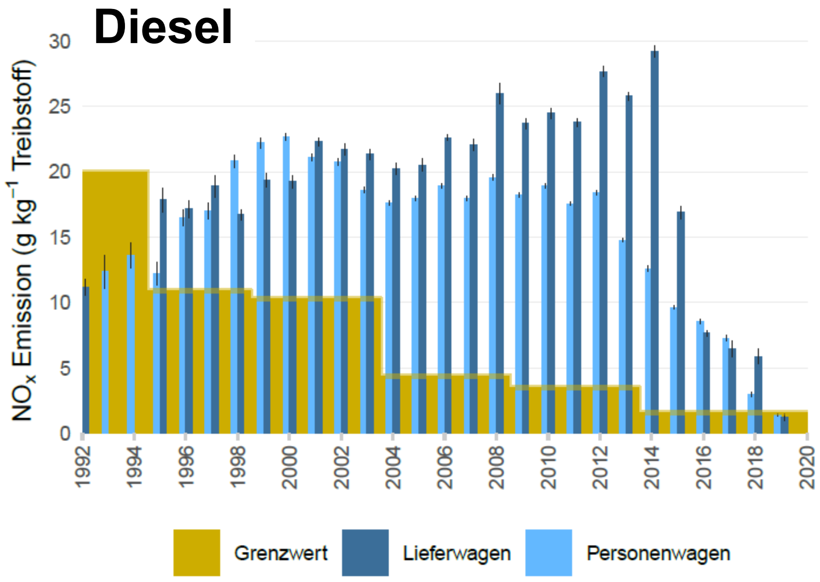
ADAC Bericht 2019
https://www.adac.de/rund-ums-fahrzeug/abgas-diesel-fahrverbote/abgasnorm/rde-messungen-cf-faktor/

PEMS (Portable Emission Monitoring System)

NO_x measurements Canton Zürich







Langjährige Abgasmessungen im realen Fahrbetrieb mittels Remote Sensing, Kt. Zürich, 2020

Overview of measurement-techniques for tropospheric trace compounds

	Compound	Monitor	GC – (MS)	Laser	Satellite
air pollutants in OPair	SO_2	XX			X
air pollutants in OPair	**NO_x**	**XX**			**X**
air pollutants in OPair	CO	XX	X	X	X
air pollutants in OPair	O_3 (Troposph.)	XX			(X)
air pollutants in OPair	Particles	X			(X)
	VOCs	(X)	X		
greenhouse gases in Kyoto Protocol	CO_2	XX	X	XX	(X)
greenhouse gases in Kyoto Protocol	CH_4	X	XX	XX	X
greenhouse gases in Kyoto Protocol	N_2O		XX	X	(X)
greenhouse gases in Kyoto Protocol	Halocarbons*		X		(X)

XX: best available method
X: good method
(X): possible

* also causing ozone depletion

Official Method:
NO_2 Measurement after conversion to NO, using a metal catalyst

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

prEN 14211

May 2003

ICS

English version

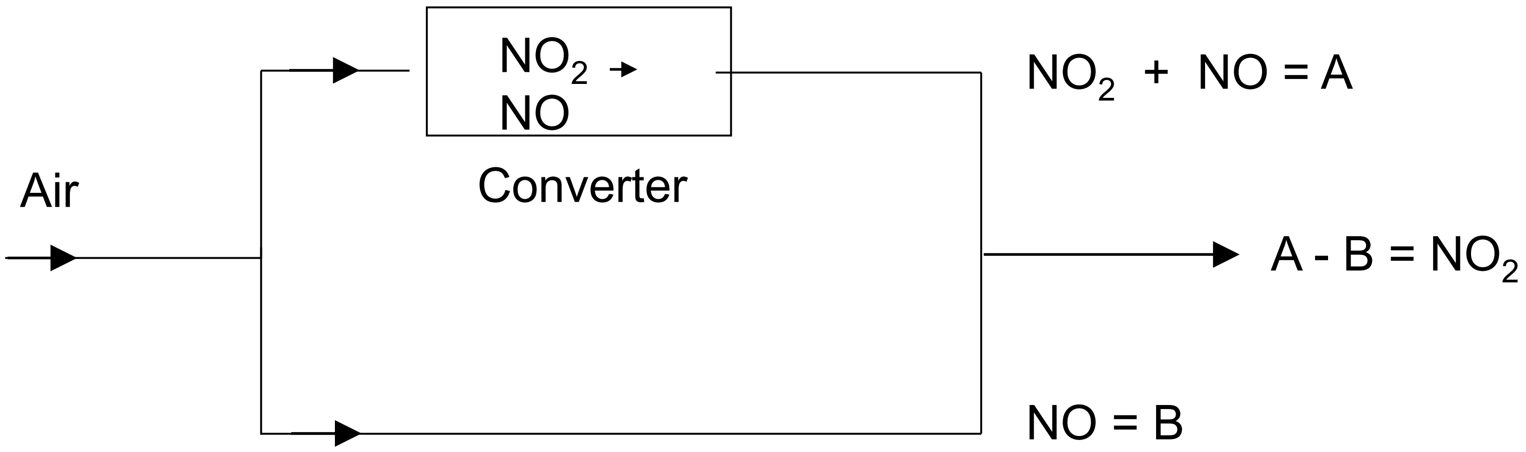
Ambient air quality - Measurement method for the determination of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence

7.2 Converter

The converter converts the amount of nitrogen dioxide in the sampled air to nitrogen monoxide.

The converter shall consist of a heated furnace maintained at a constant temperature and is made of material such as stainless steel, copper, molybdenum, tungsten or spectroscopically pure carbon. It shall be capable of converting at least 95 % of the nitrogen dioxide to nitrogen monoxide. The conversion efficiency has to be checked according to 8.4.14. A mathematical correction for the NO_2 concentration shall be made when the converter efficiency is between 95 % and 100 %.

Converter for NO_x measurements



Converter efficiency $E_{ff} < 1$:

$NO_2 = "NO_2" \cdot (1/E_{ff})$

Nitrogen Oxides NO_x with different converters metal catalyst and photolysis

"NO_2" = $\mathbf{NO_2}$ + *a* PAN + *b* HNO_3 + *c* HNO_2 + *d* NO_3 + *e* 2 N_2O_5 + *f* org. Nitrate + *g* NH_3 + ...

Selectivity of converter for various N-Compounds

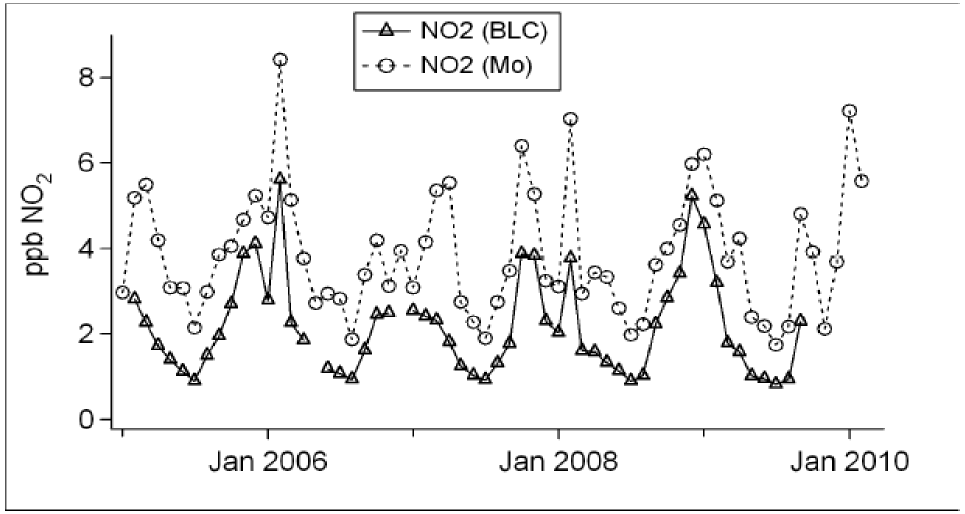
	Converter	NH_3	HNO_2	HNO_3	PAN
Monitor Labs 8841	molybdenum	0 – 10 %	100 %	0 %	100 %
Monitor Labs 9841A	molybdenum	1 – 10 %	_[b)]	_[b)]	_[b)]
Horiba APNA 350E	Oxid	1 %	80 %	0 %	100 %
ECO Physics CLD 700	molybdenum	0 – 10 %	_[b)]	_[b)]	_[b)]
ECO Physics CLD 770 (CRANOX)	photolysis	< 0.1 %	< 20 %	< 0.1 %	<1 – 5 % [a)]

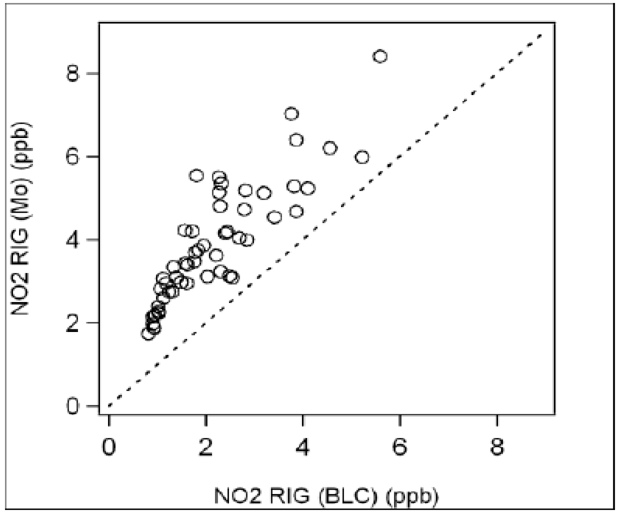
a) Depending on Temperature (according to Manual)
b) No Information from the Manifacturer

Photolysis: state-of-the art

Overestimation of NO_2 by molybdenum converters example Rigi: photolysis (BLC vs. molybdenum)

NO_2 (molybdenum converter) >> NO_2 (photolysis converter)





Reasons:

- In summer, PAN and HNO_2 are most likely the dominating interfering species.
- In winter, particulate nitrate sampled at the inlet filter and subsequently evaporated might also contribute significantly.

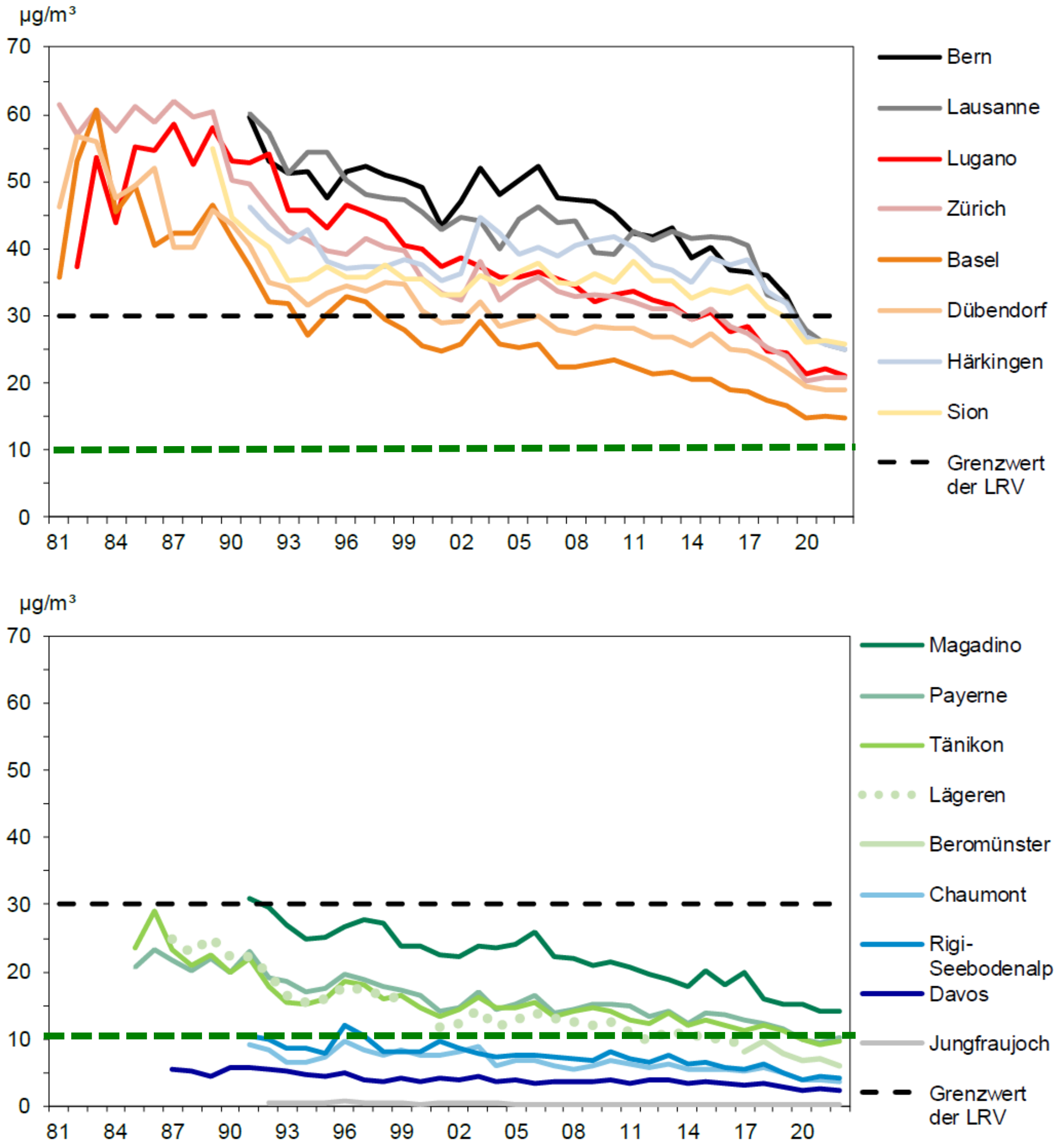
Remedy:

- multiple linear model approach by comparing with concurrent measurements at a similar site.

NO_2 concentration Switzerland (1981-2022) yearly average

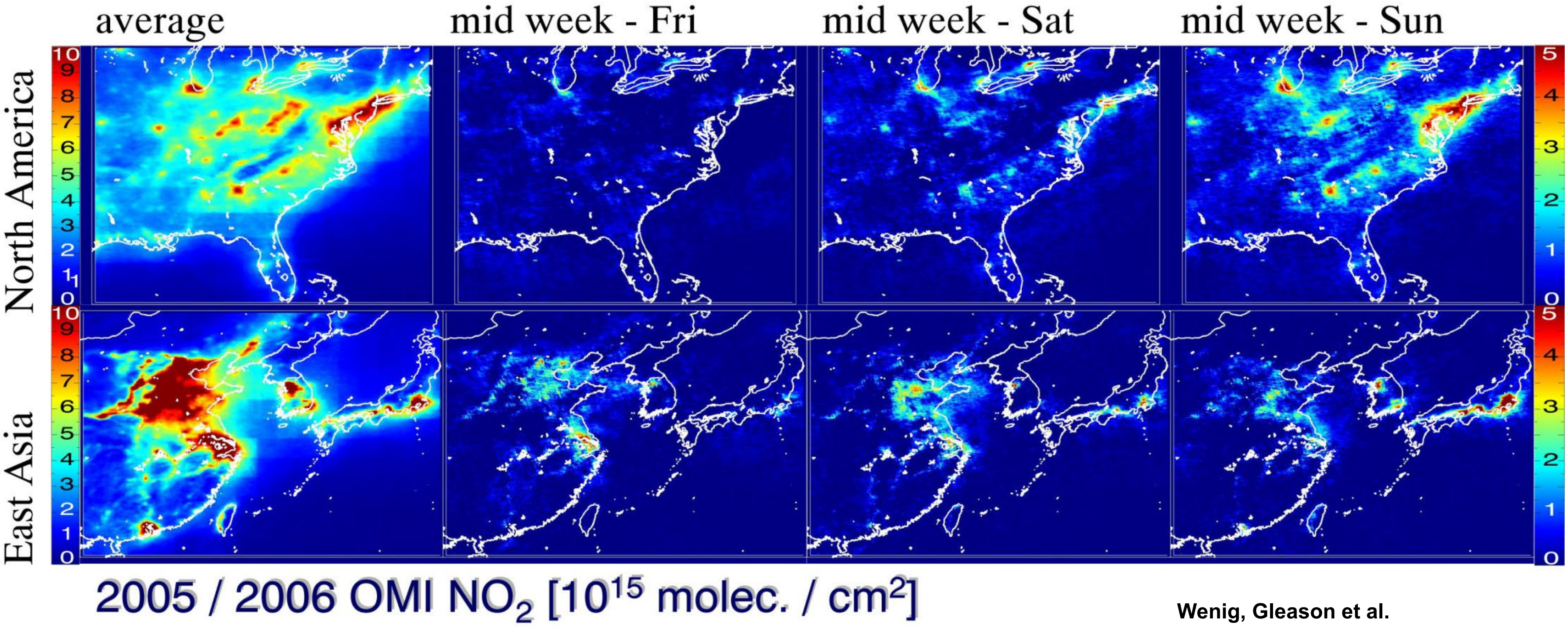
Annual limit CH

NEW



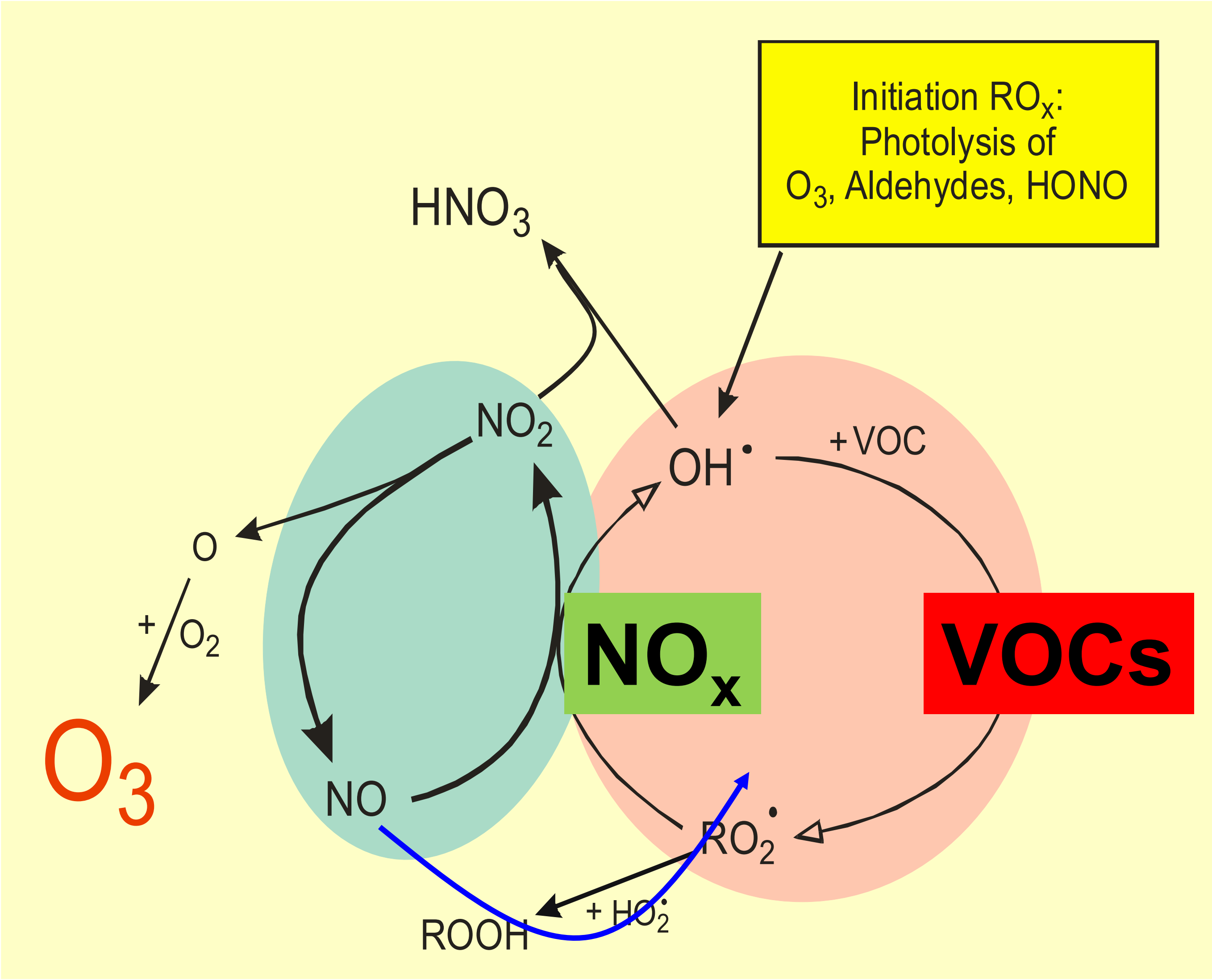
EPFL 2024

NO_2 by satellites: weekend/weekday in USA and China



Wenig, Gleason et al.

Photochemical smog (NOx + VOCs ➔ Ozone)



Two coupled radical reactions:
No$_x$ (green):NO,NO_2
RO$_x$ (red): VOCs, OH·, HO_2·, RO·, RO_2·

from Staehelin, ETHZ

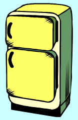
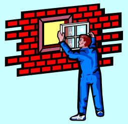
Sources of atmospheric VOCs

Anthropogenic (~200 TgC/y)

fossil fuel
- combustion
- evaporation


biofuel
- heating
- cooking

consumer products
- solvents
- refrigerants
- foams

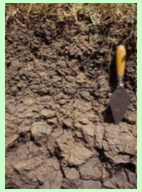



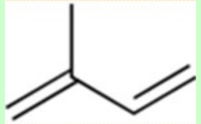

biomass burning

Biogenic (~400-1200 TgC/y)

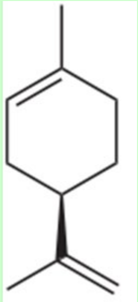
major: vegetation

minor: soil/ocean



Isopren



Limonen

The oxidising atmosphere of the earth

Oxidation and deposition are the removing processes of trace gases from the atmosphere

Oxidation is mostly initiated by OH radicals (OH = the detergent of the atmosphere) reacts with most trace gases (VOCs, CO, CH_4, NO_x) and controls their atmospheric lifetime

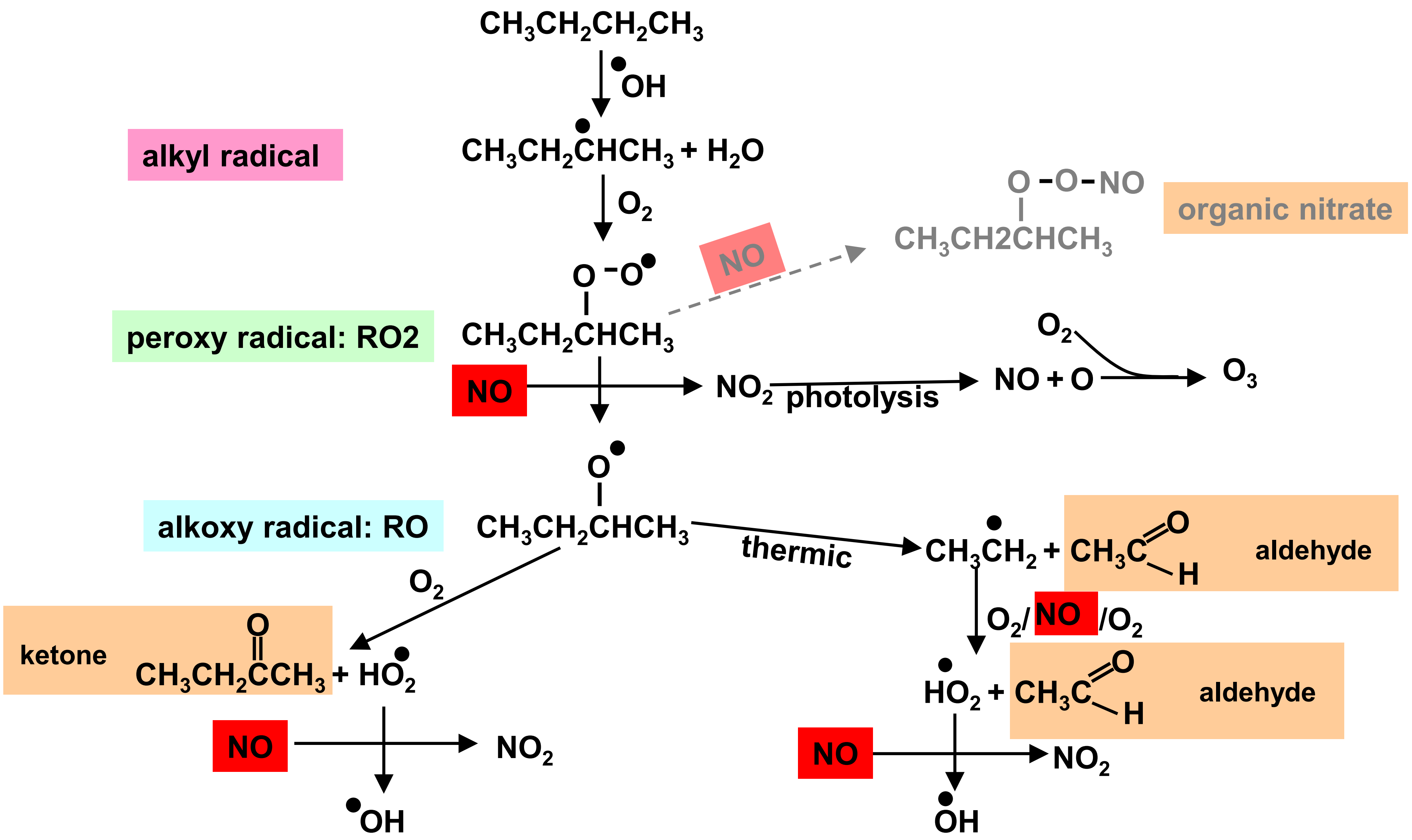
[OH]= 1.1 x 10^6 molecules/cm^3 (~0.04 ppt)

- **average life-time is about 1 second**
- **mixing ratio is highest in summer during day hours and, conversely, lowest in winter and during the night**

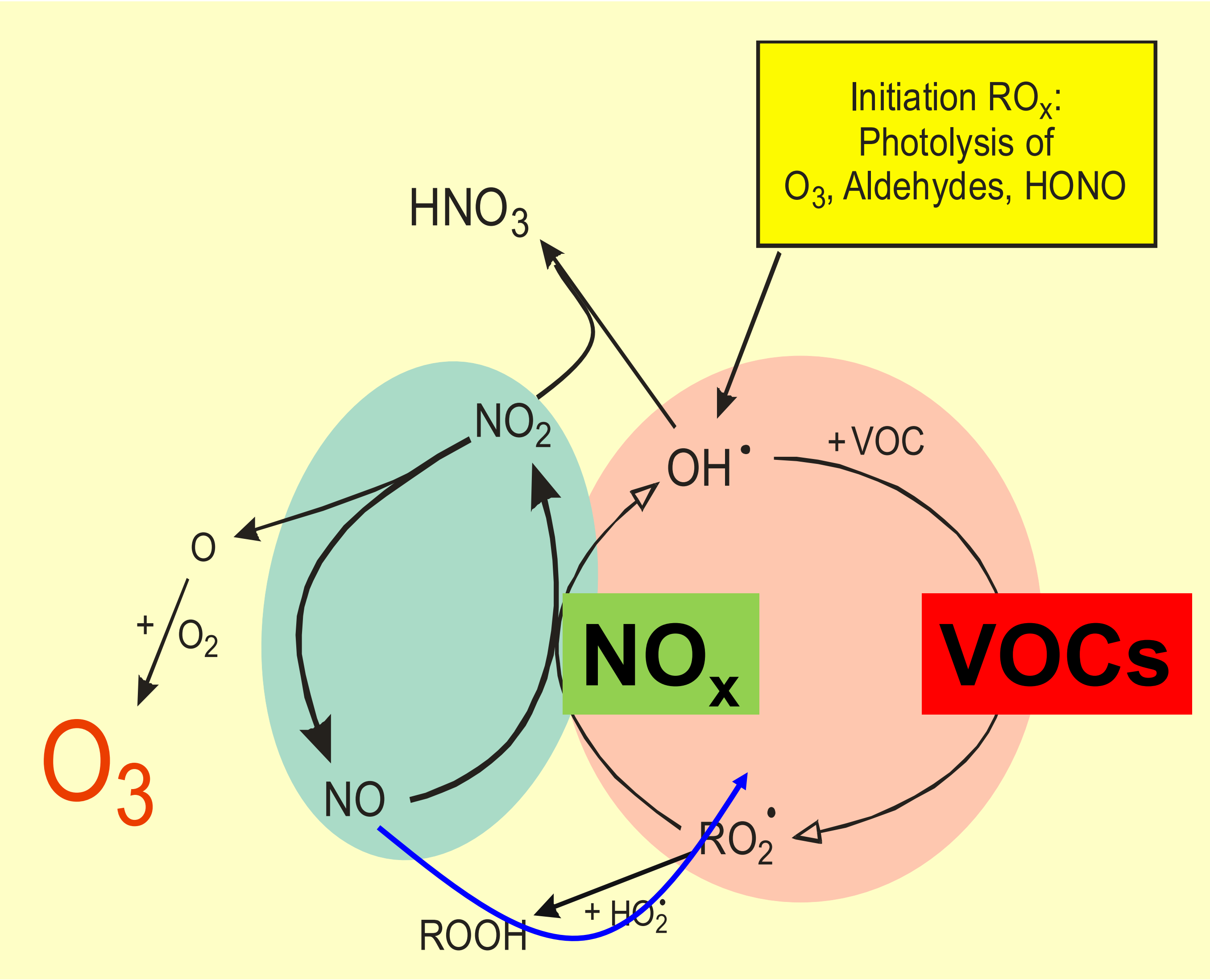
Oxidation of **Alkanes** CH_3-$(CH_2)_x$-CH_3 (e.g. n-butane) in polluted air (with NO)

NO

blackboard



Photochemical smog (NOx + VOCs ➔ Ozone)



Two coupled radical reactions:
No$_x$ (green):NO,NO_2
RO$_x$ (red): VOCs, OH·, HO_2·, RO·, RO_2·

from Staehelin, ETHZ

Overview of measurement-techniques for tropospheric trace compounds

Group	Compound	Monitor	GC – (MS)	Laser	Satellite
air pollutants in OPair	SO_2	XX			X
	NO_x	XX			X
	CO	XX	X	X	X
	O_3 (Troposph.)	XX			(X)
	Particles	X			(X)
	VOCs	**(X)**	**X**		
greenhouse gases in Kyoto Protocol	CO_2	XX	X	XX	(X)
	CH_4	X	XX	XX	X
	N_2O		XX	X	(X)
	Halocarbons*		X		(X)

XX: best available method
X: good method
(X): possible

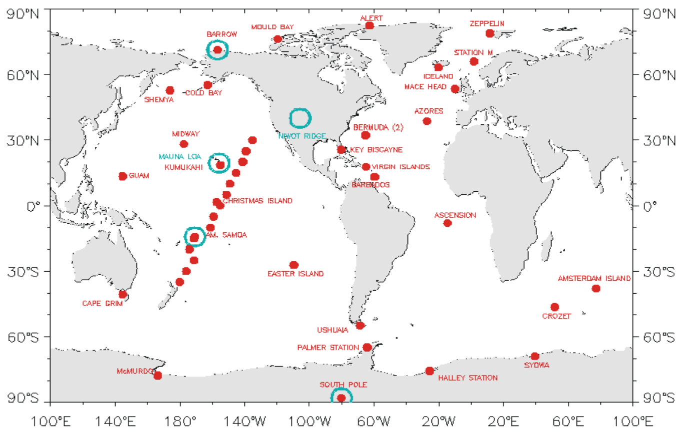
* also causing ozone depletion

Online measurement methods for VOCs

- Technique based on gas chromatography (GC)
  - Pre-concentration
  - Separation (gas chromatography)
  - Analysis
    - flame ionization detection (FID)
    - mass spectrometry (MS)

Canister based VOC measurements

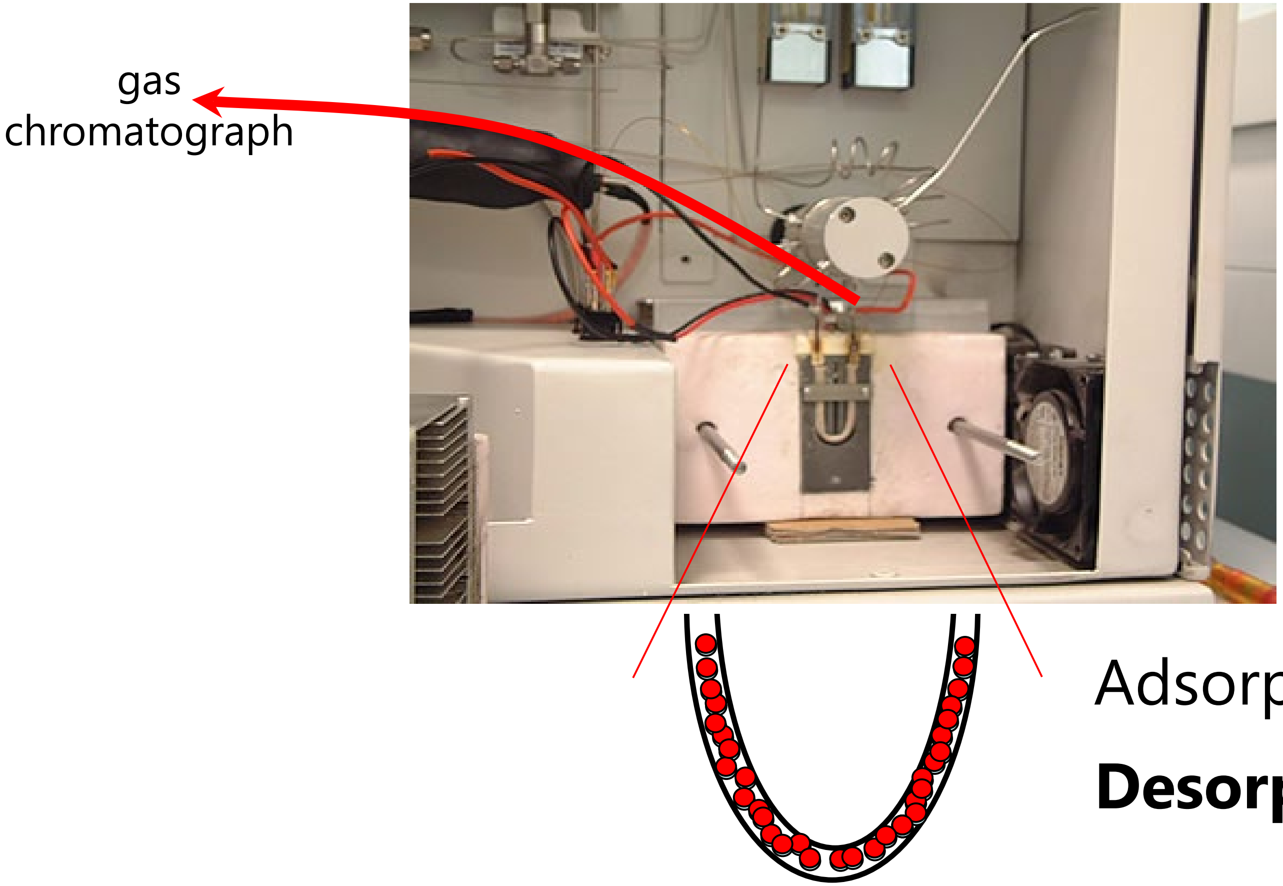
- ”whole air”-samples taken in suitable canisters taken daily or weekly at the sites or on campaigns
- ability to serve different measurement sites with one instrument
- very few measurements of hydrocarbons on a global scale and over longer periodes of time



NOAA world-wide network

The preconcentration of VOCs from the atmosphere

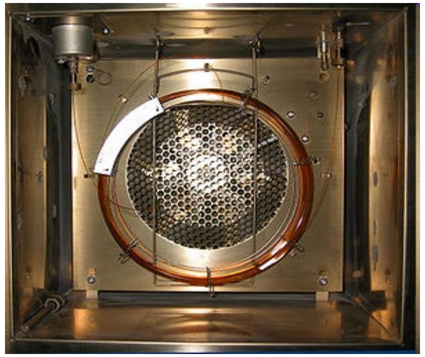
preconcentration of VOCs from 400 ml of air



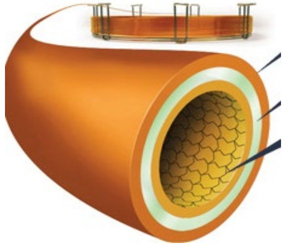
Adsorption: - 44 °C

Desorption: 245 °C

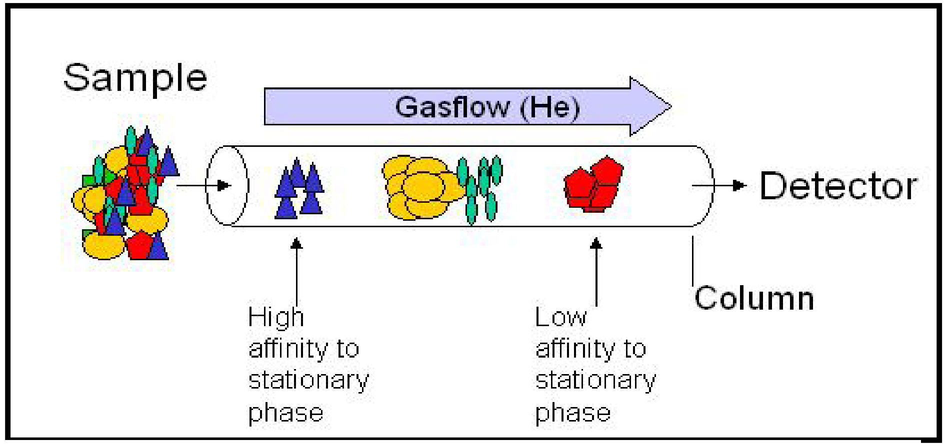
gas chromatography for analysis of VOC

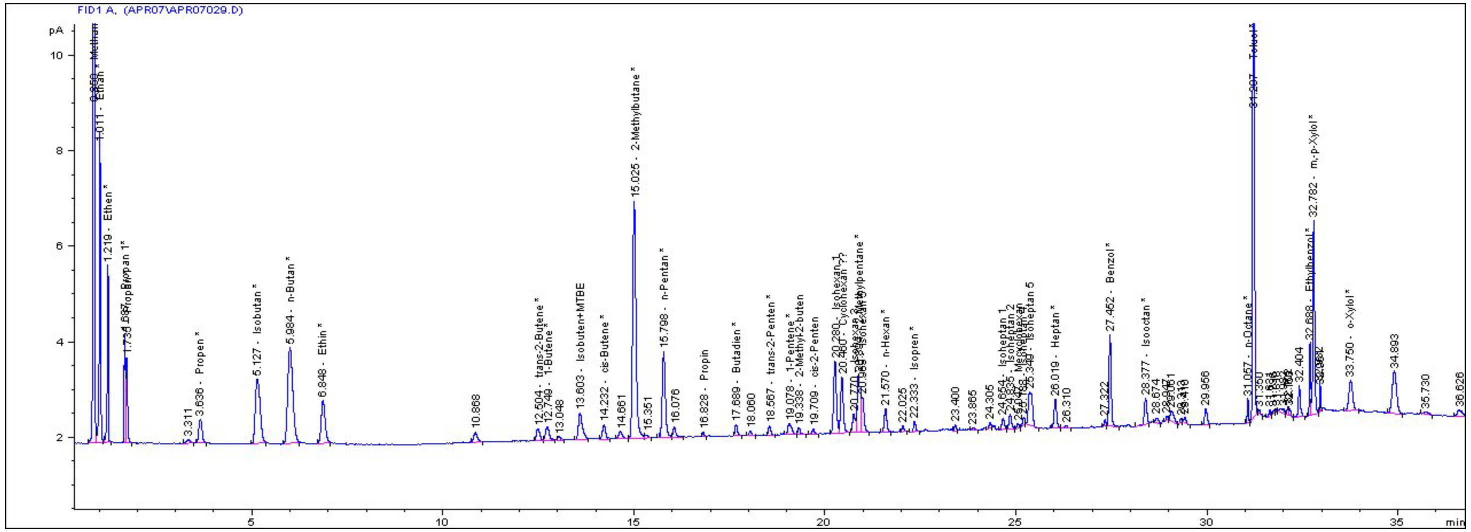


GC-oven



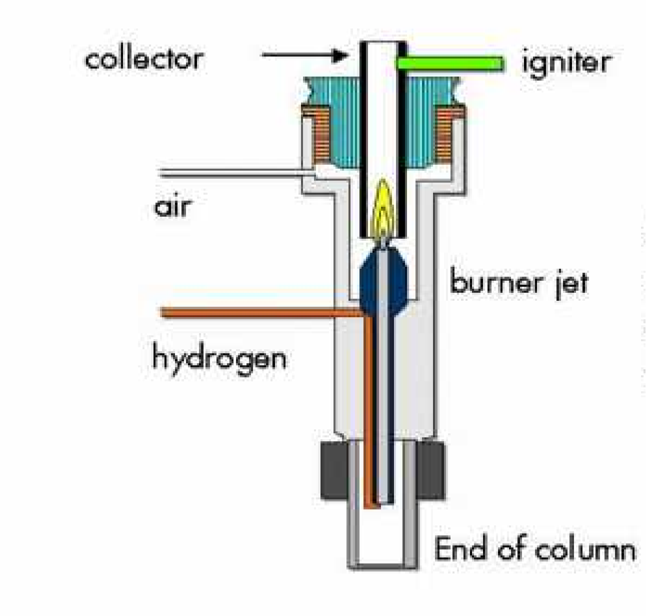
GC-column



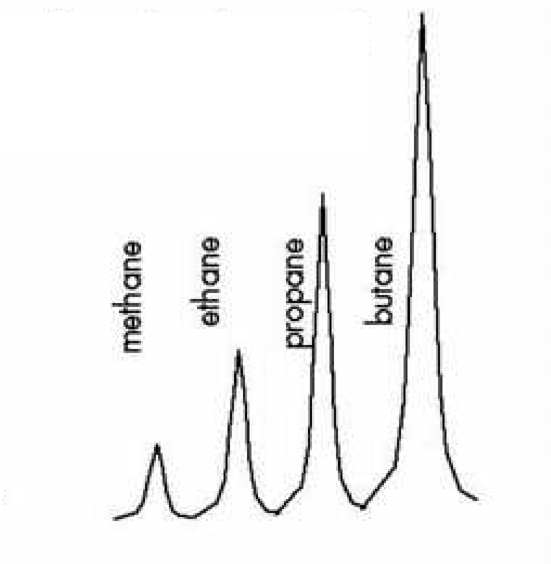


GC-chromatogram with VOCs

1. Flame ionization detection (FID)



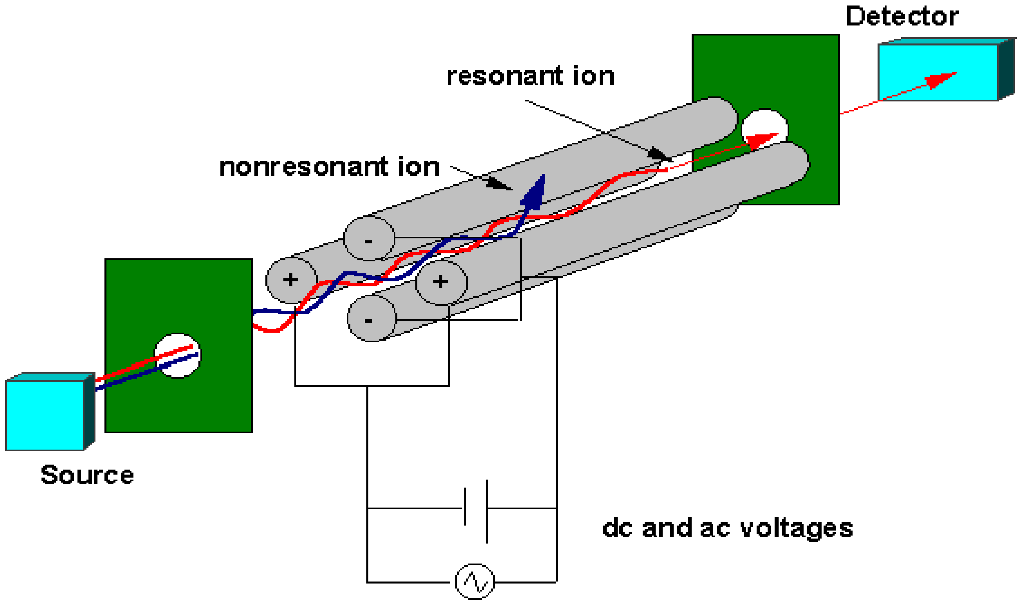
sensitivity dependent on number of C-atoms



application:
VOCs, (OVOCs)

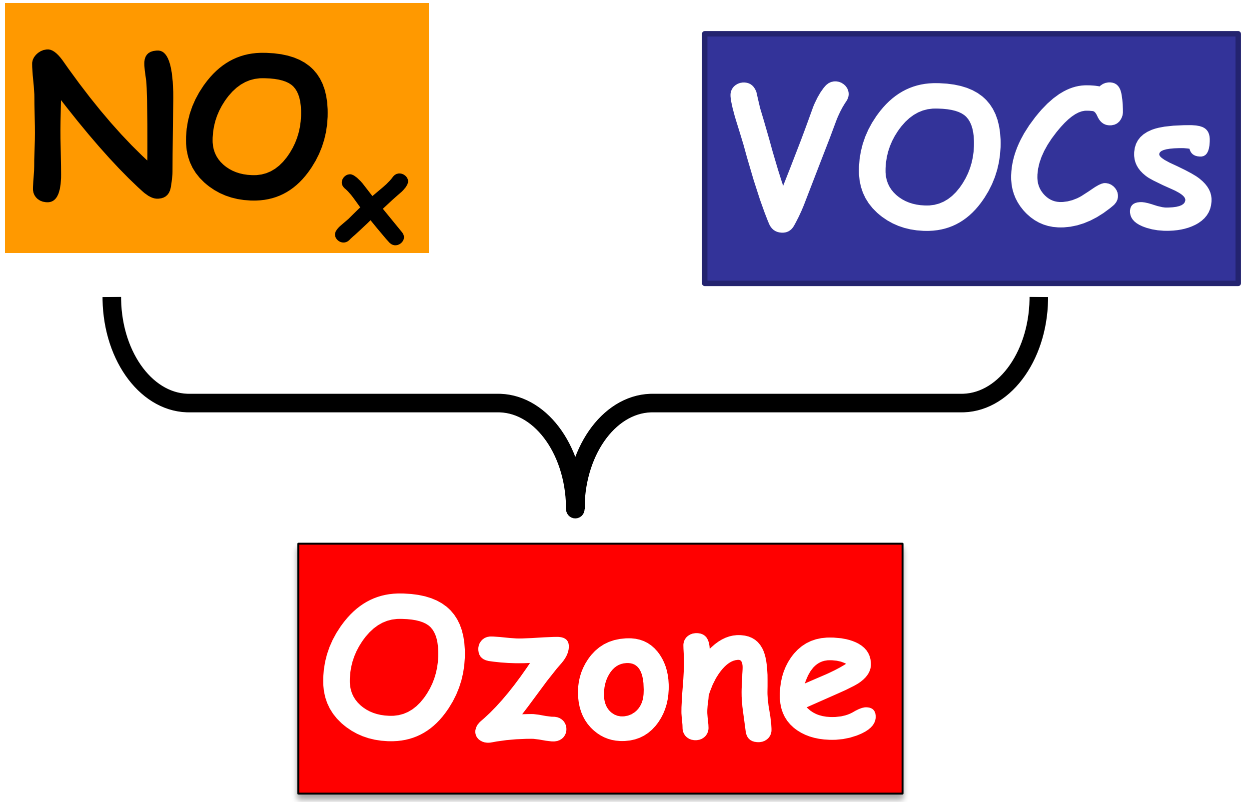
instruments: Agilent, Varian, SIS, Airmotec usw.

2. mass spectrometer (MS)



application:
VOCs, OVOCs, halocarbons

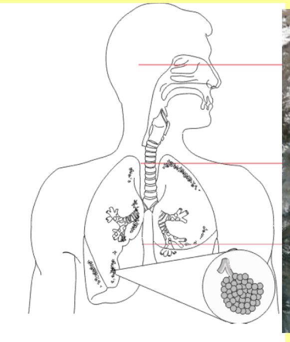
instruments: Agilent, Varian

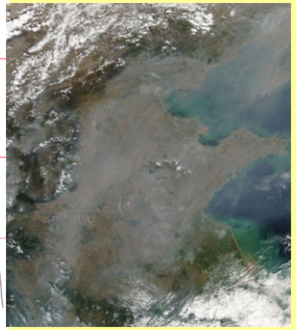

NO_x
VOCs
Ozone

O_3-rationale for legislation

Effects on human health

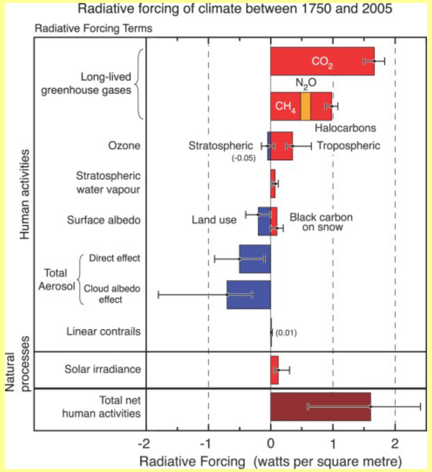
- Lung irritation
- Indirect effect
- O_3 oxidation of terpenes leads to aerosols





Effects on the environment

- phytotoxic
- greenhouse effect



O_3-damages on tree leaves
http://www.ozone.wsl.ch/

birch, Birke

hornbeam, Hagebuche

evening primrose, Nachtkerze

clover, Klee

Overview of measurement-techniques for tropospheric trace compounds

	Compound	Monitor	GC – (MS)	Laser	Satellite
air pollutants in OPair	SO_2	XX			X
	NO_x	XX			X
	CO	XX	X	X	X
	O_3 (Troposph.)	XX			(X)
	Particles	X			(X)
	VOCs	(X)	X		
greenhouse gases in Kyoto Protocol	CO_2	XX	X	XX	(X)
	CH_4	X	XX	XX	X
	N_2O		XX	X	(X)
	Halocarbons*		X		(X)

XX: best available method
X: good method
(X): possible

* also causing ozone depletion

Swiss Legal Air Pollution Limits

https://www.ekl.admin.ch/inhalte/dateien/pdf/EKL-231120_de_orig.pdf

Pollutant	Averaging time	WHO AQG 2021	Current OAPC ambient limit value	FCAH recommendation 2023
Sulphur dioxide (SO_2), µg/m³ (see Chapter 8)	Annual average and new mean value over winter half-year	–	30[a]	20[b]
	95 % of ½ h mean value for a year	–	100	remove
	24h mean value	40[c]	100[d]	40[c]
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	95 % of ½ h mean value for a year	–	100	remove
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Carbon monoxide (CO), mg/m³ (see Chapter 9)	24h mean value	4[c]	8[d]	4[c]
Ozone (O_3), µg/m³ (see Chapter 6)	Summer season[e]	60	–	60
	98 % of ½ h mean value for a month	–	100	100
	8h mean value	100[c]	–	–
	1h mean value	–	120[d]	120[d]
Suspended particulates / particulate matter (PM10), µg/m³ (see Chapter 4)	Annual average	15	20	15
	24h mean value	45[c]	50[c]	45[c]
Suspended particulates / particulate matter (PM2.5), µg/m³ (see Chapter 5)	Annual average	5	10	5
	24h mean value	15[c]	–	15[c]

[a] Ambient air quality standard, which also includes the protection of animals and plants, their biological communities and habitats according to Article 1 paragraph 1 EPA, and corresponds to the state of knowledge when the Air Pollution Control Ordinance was adopted in 1985.
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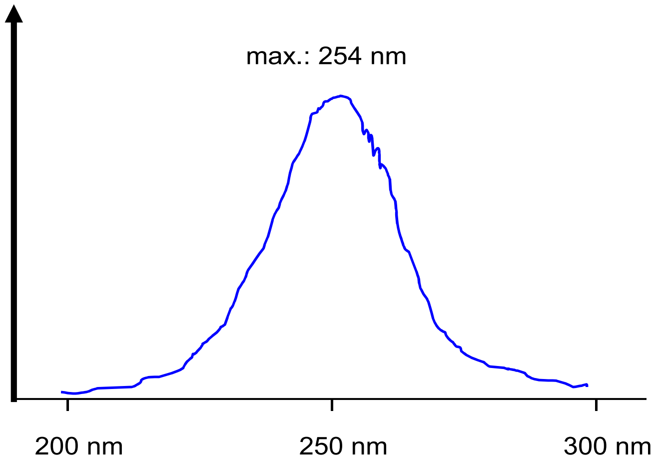
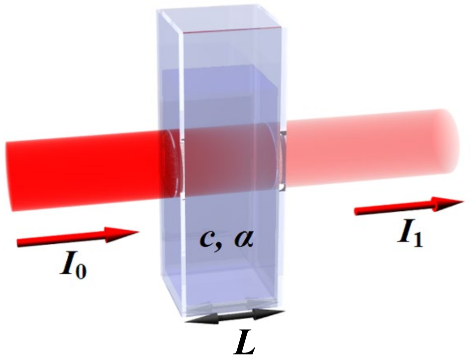
[e] Average of the maximum daily 8h mean value ozone concentrations in the six consecutive months with the highest six-month average for ozone concentration. For Switzerland, this corresponds to April to September.

Absorption spectra and measurement principle of ozone

Ozone UV-absorption spectrum





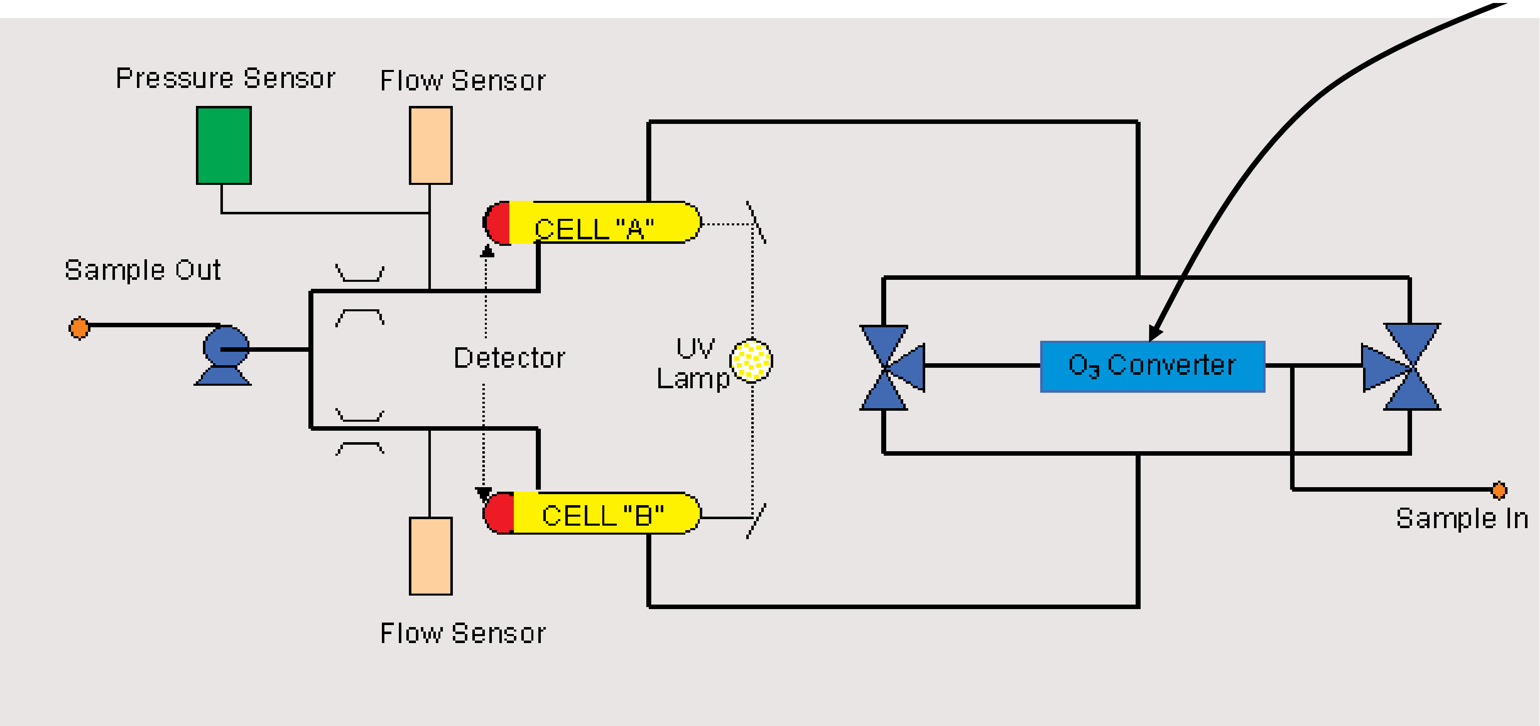
The Law of Lambert-Beer

$$c = \frac{1}{\alpha \bullet L} \bullet \frac{T}{T_0} \bullet \frac{p_0}{p} \bullet 10^9 \bullet \log \frac{I_0}{I_1}$$

c	=	ozone mixing ratio [ppb]
T	=	gas temperature in Kelvin
T_0	=	standard temperature: 273 K
P	=	pressure [mbar]
P_0	=	standard pressure: 1013 mbar
I_0	=	light intensity with zero air
I_1	=	light intensit y with ozone
α	=	absorption coefficient 134 atm^{-1} cm^{-1}
L	=	optical lenght [cm]

O_3 Detection Method: UV Absorption
Schematic of a O_3 monitor

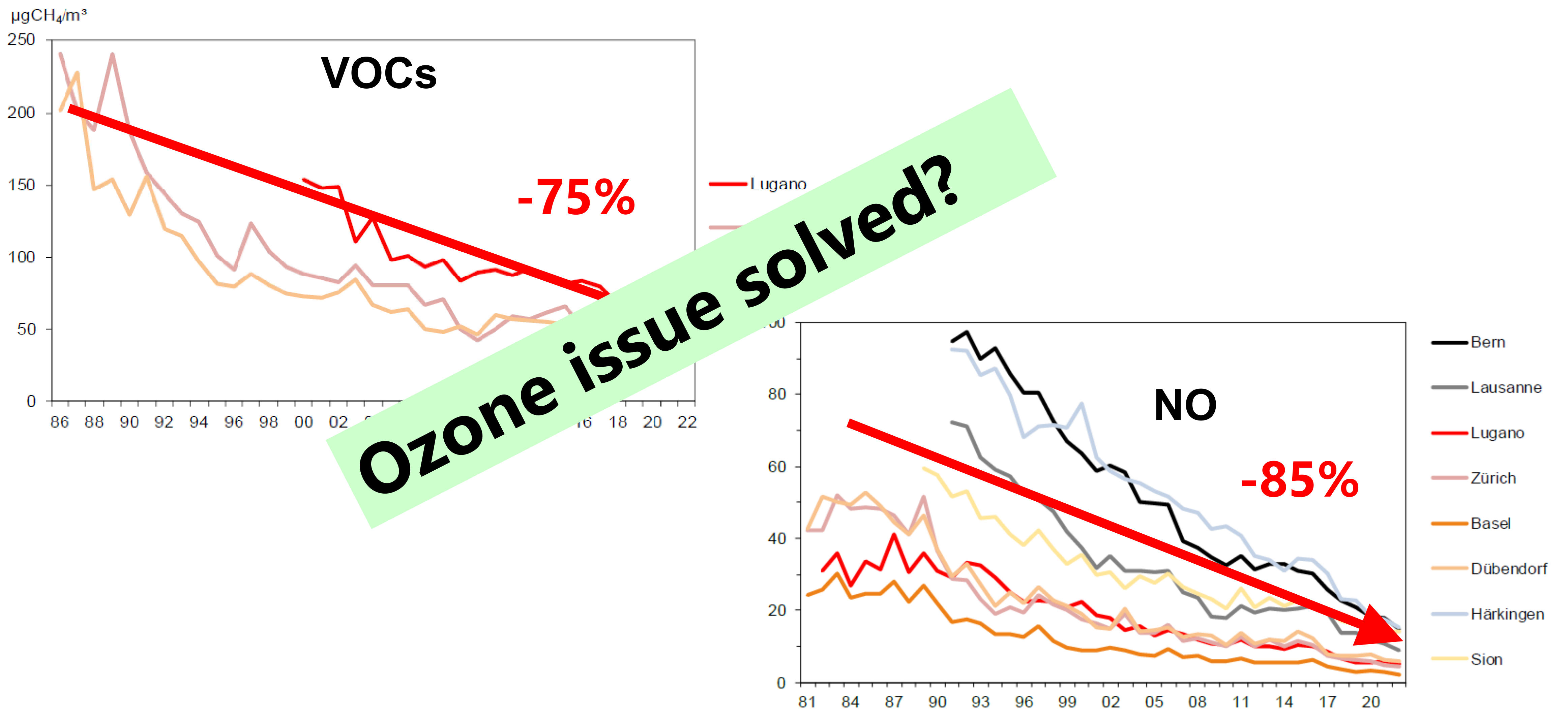
Removes the ozone



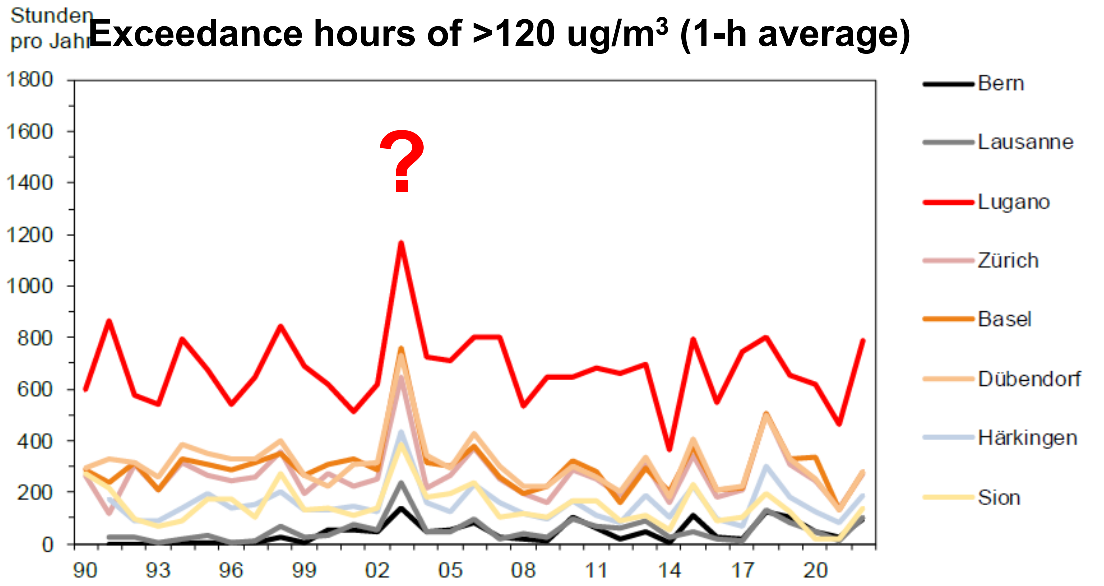
Example: Thermo, Model 49C O_3 Analyzer

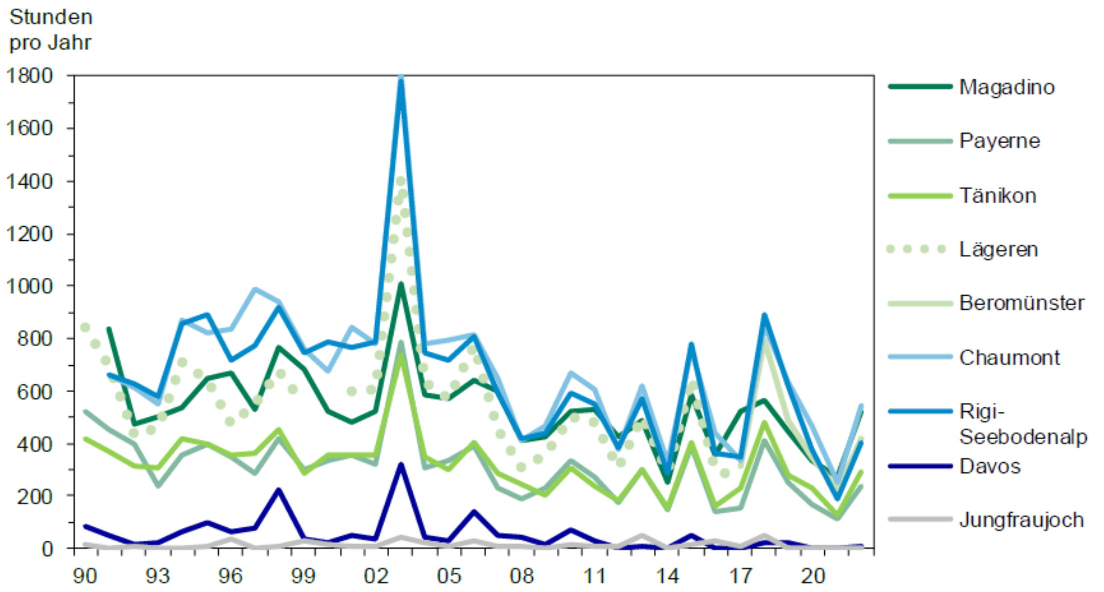
http://www.thermo.com/eThermo/CMA/PDFs/Product/productPDF_12775.pdf

O_3 precursors: VOCs and NO



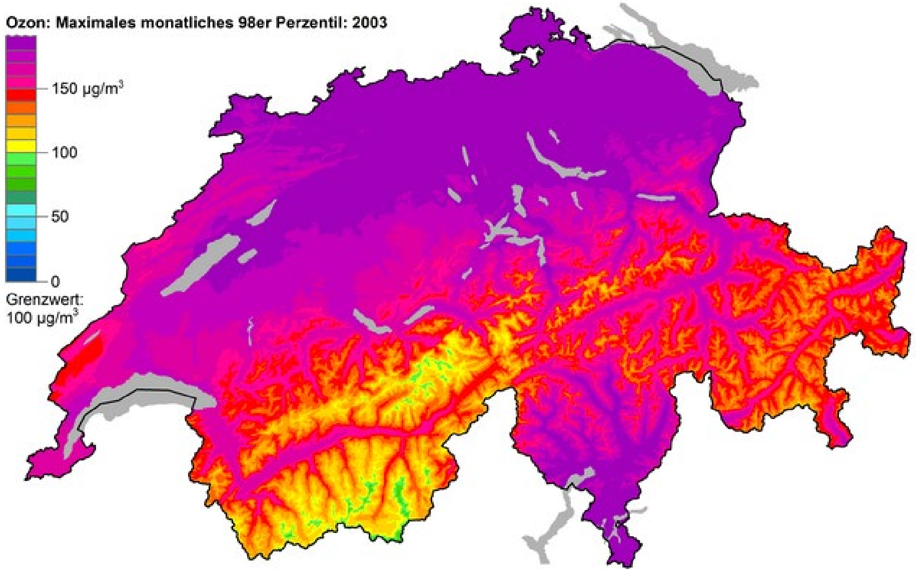
Swiss Legal Air Pollution Limits
Luftreinhalteverordnung



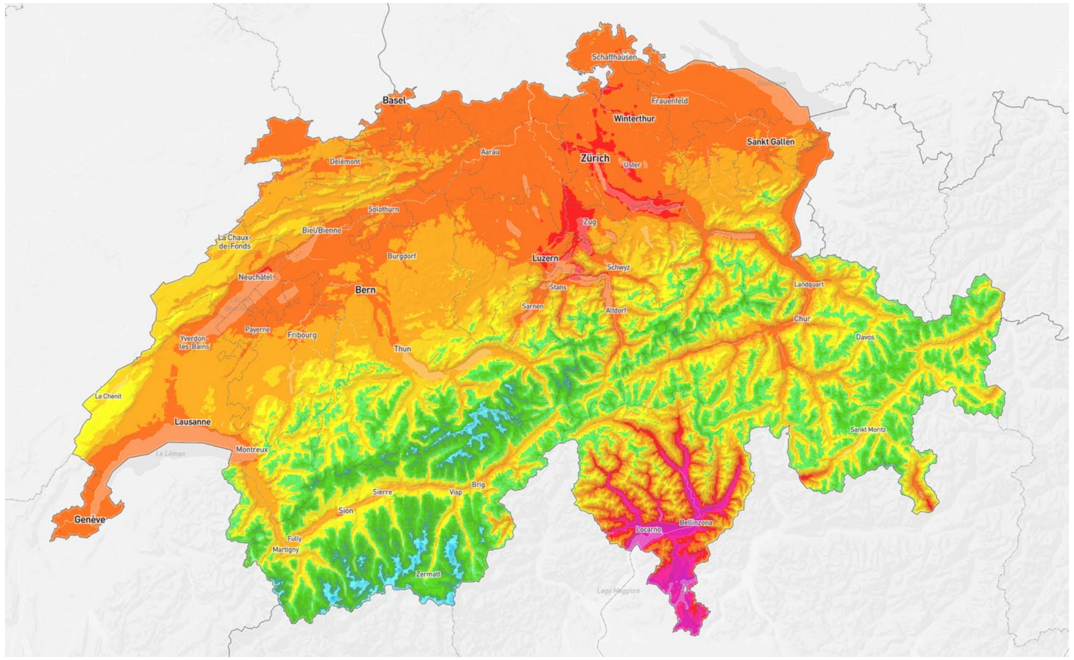


O_3 98% Percentiles (maximum monthly mean)

2003

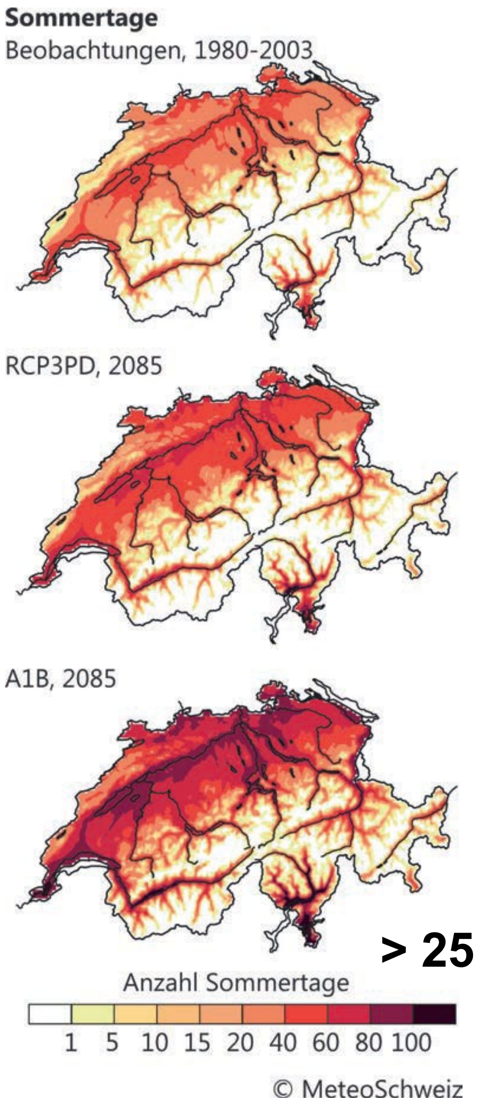


2020

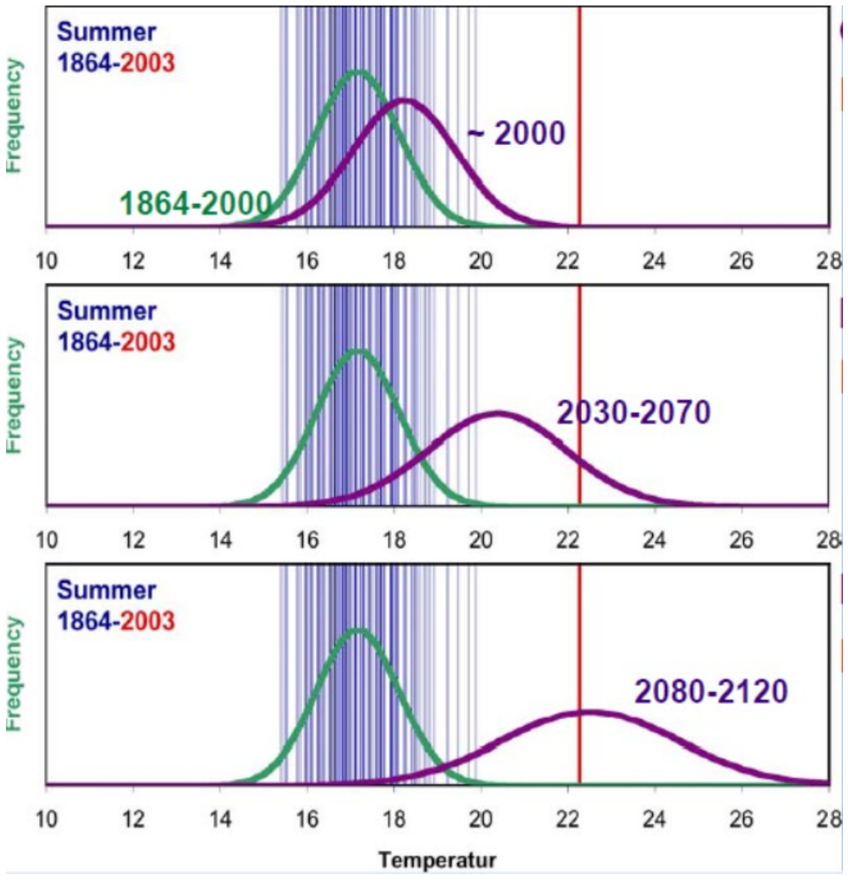


http://www.bafu.admin.ch/luft/luftbelastung/schadstoffkarten/

What happens if climate change happens?



> 25 °C



2000: ~ every 1000 yr

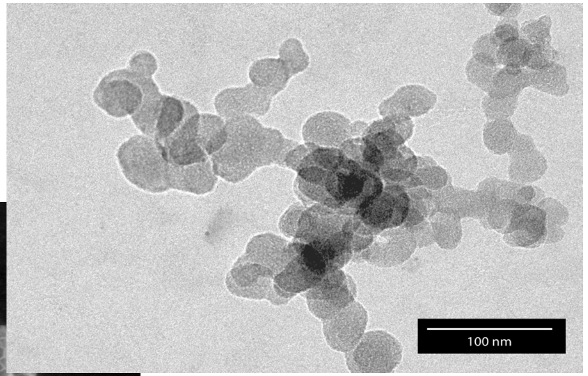
2050: ~ every 10 yr

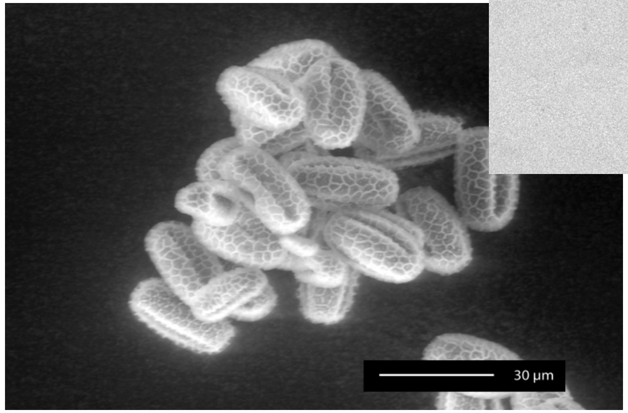
2100: ~ every 2 yr

SCNAT, 2016
Schär et al., Nature, 2004

Particles in the atmosphere

- Introduction
- Sources and sinks
- Particles in Switzerland
- Measurement techniques
- Effects
  - regional
  - global
  - health





historic development of particles

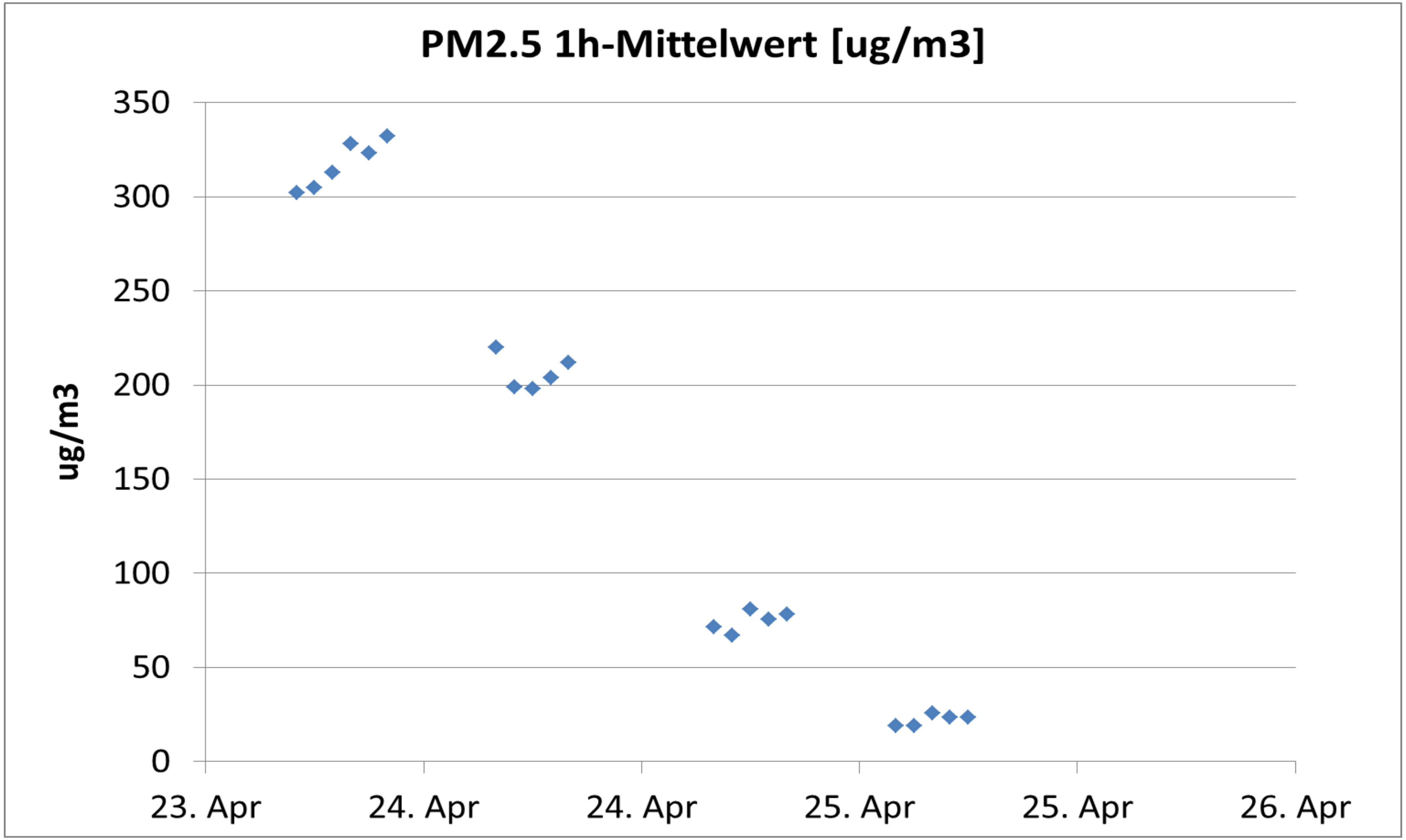
local

How do you want to be known: As the discoverer of fire or as the first man to pollute the atmosphere?

regional

global

Beijing Monday 23.04.12 –Wednesday 25.04.12

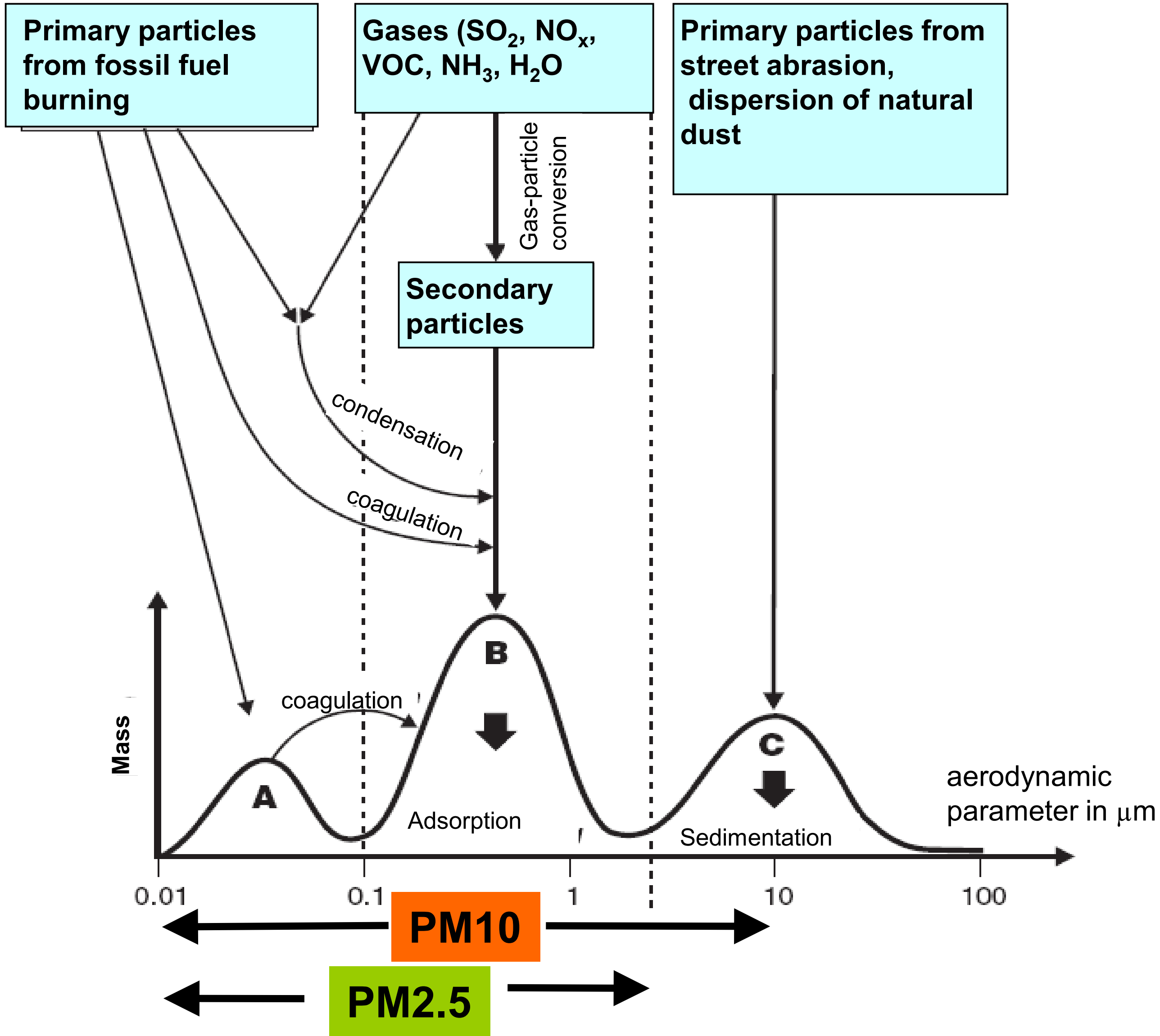


Beijing Monday 23.04.12 –Wednesday 25.04.12

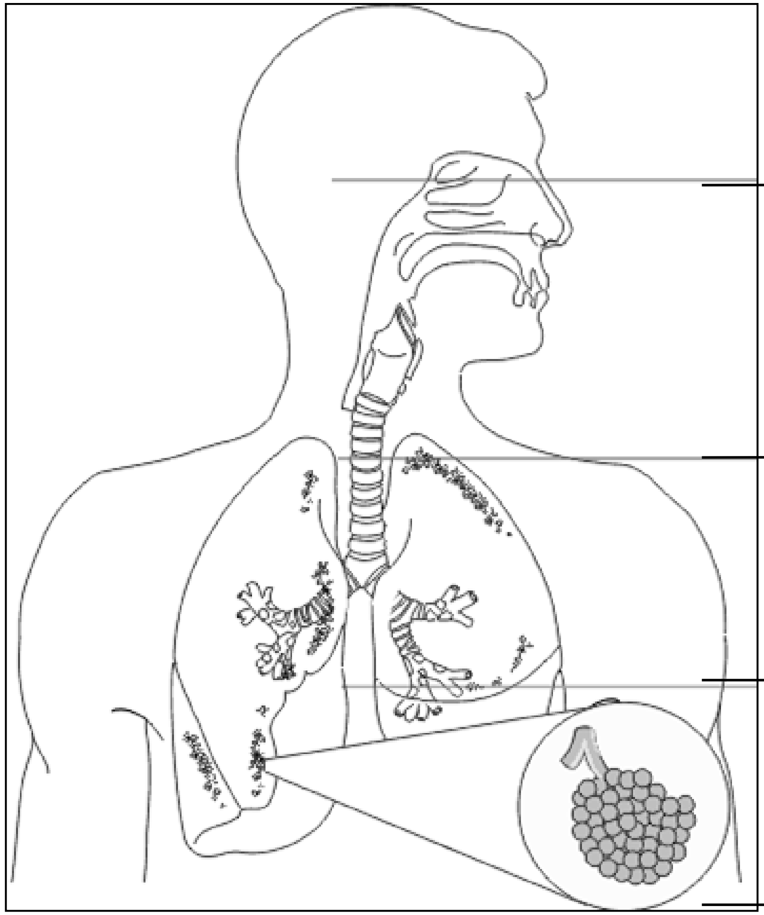
23.05.2012
300 µg/m^3 PM 2.5

25.05.2012
30 µg/m^3 PM 2.5

Fine Particles
Characterization of by size: PM10, PM1



Mechanistic pathways
Penetration depth of pollutants in the respiratory tract



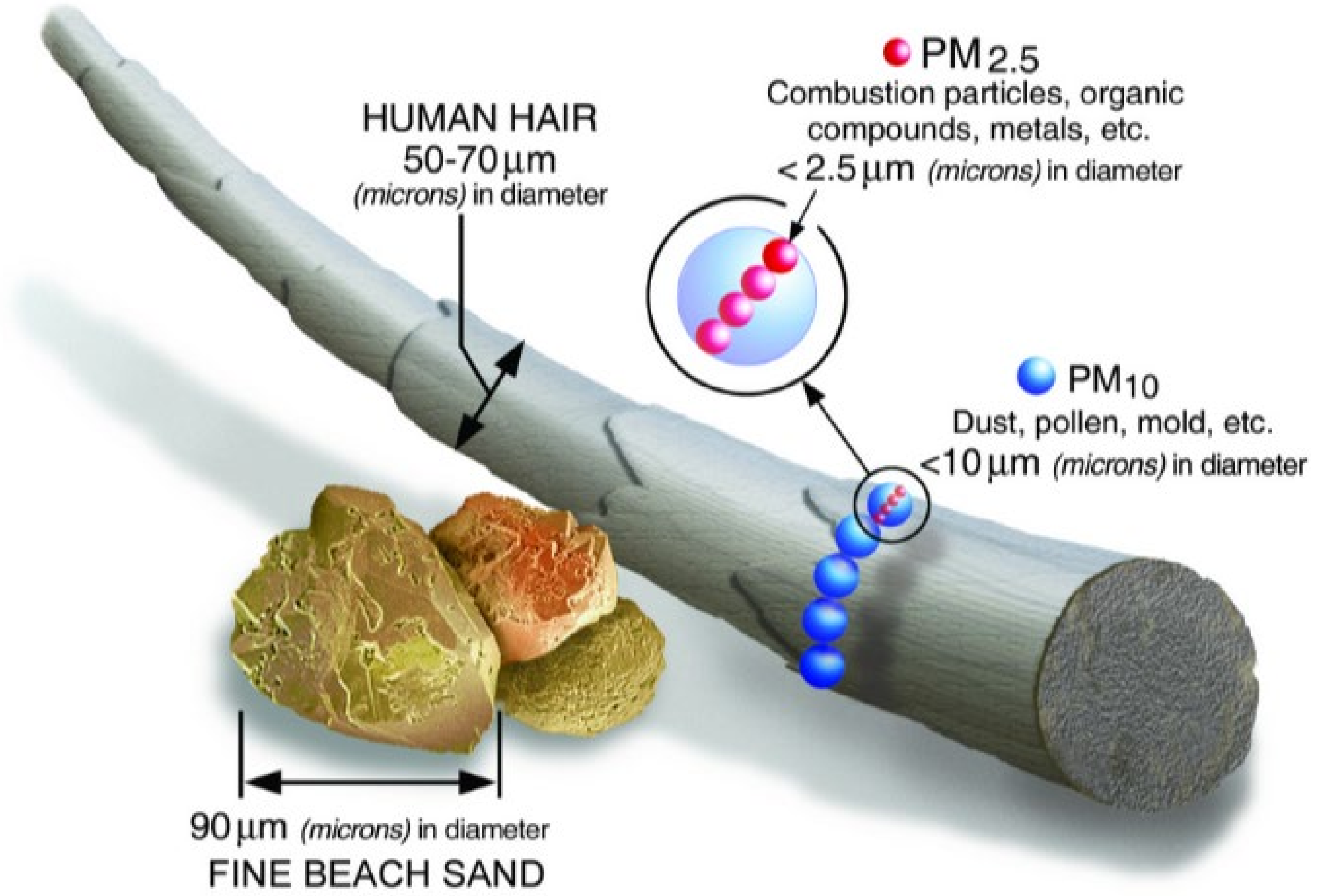
Nose, throat: **particles < 30 μm**

Trachea, bronchi, bronchioli: **particles < 10 μm, SO_2, NO_2, Ozone**

Pulmonary alveoli: **particles < 2-3 μm, NO_2, Ozone**

Pulmonary tissue, circulation: **Ultrafine particles < 0.1 μm**

The size of particles



Swiss Legal Air Pollution Limits

https://www.ekl.admin.ch/inhalte/dateien/pdf/EKL-231120_de_orig.pdf

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	1h mean value	–	120[d]	120[d]
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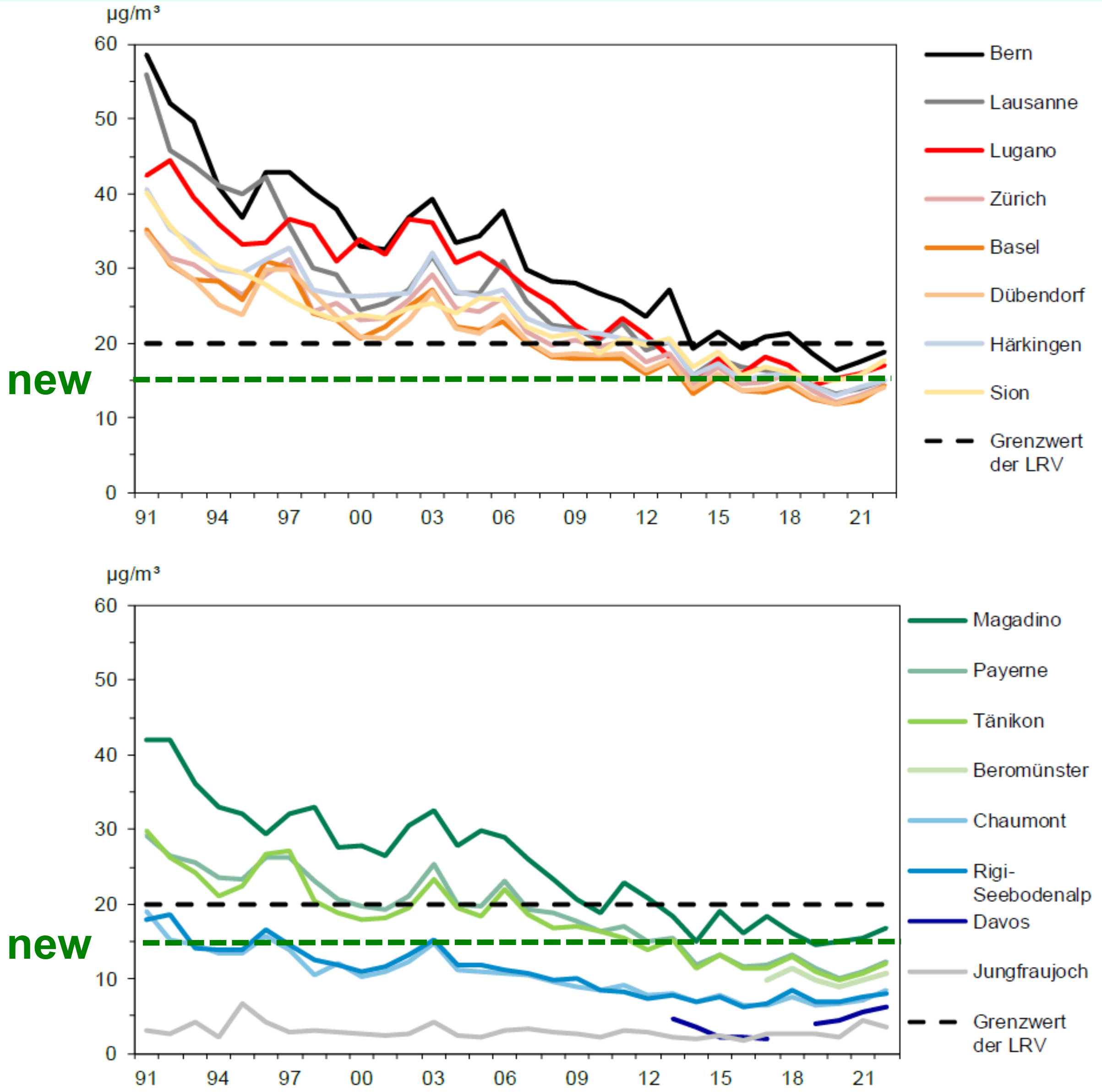
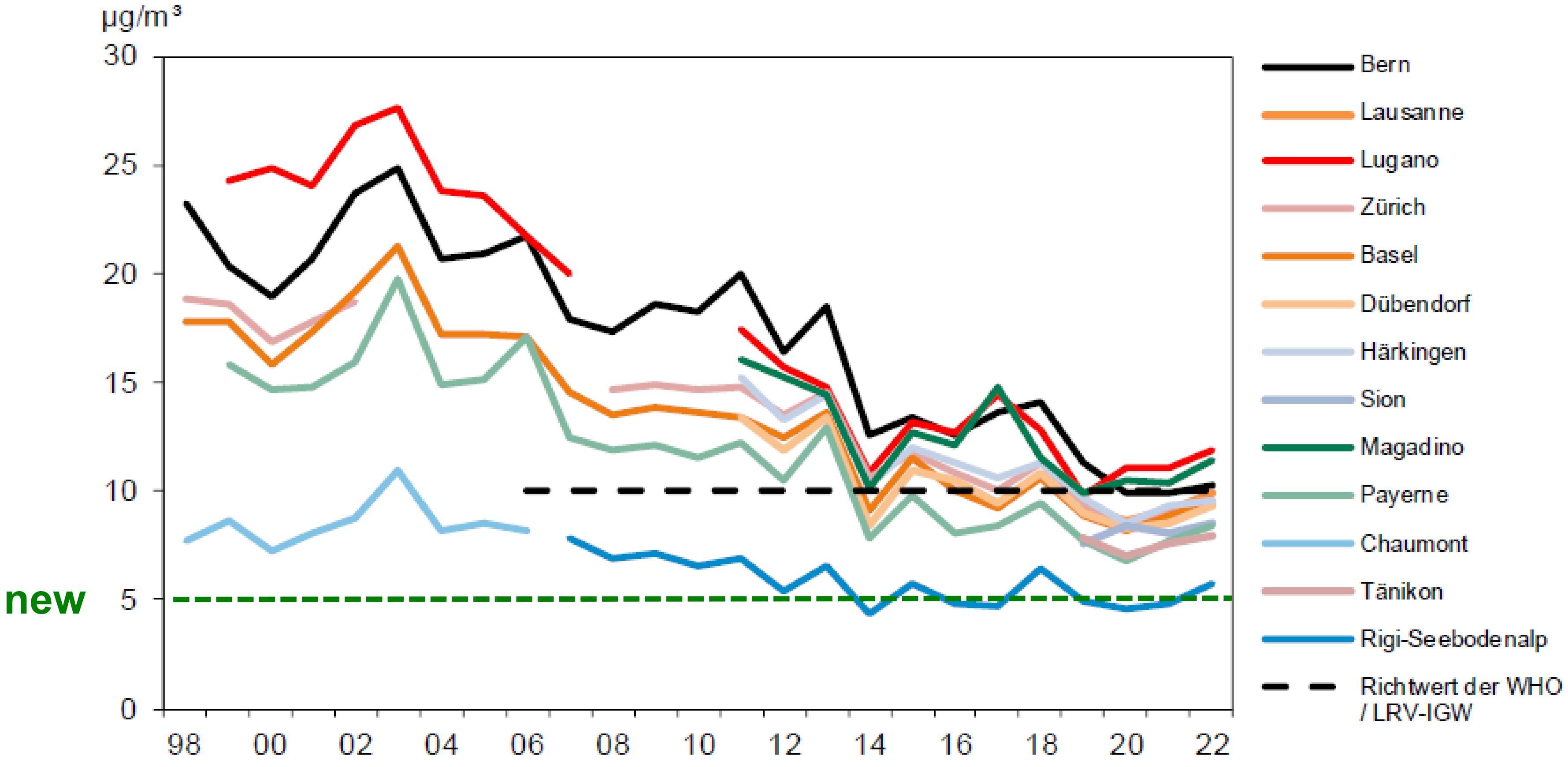
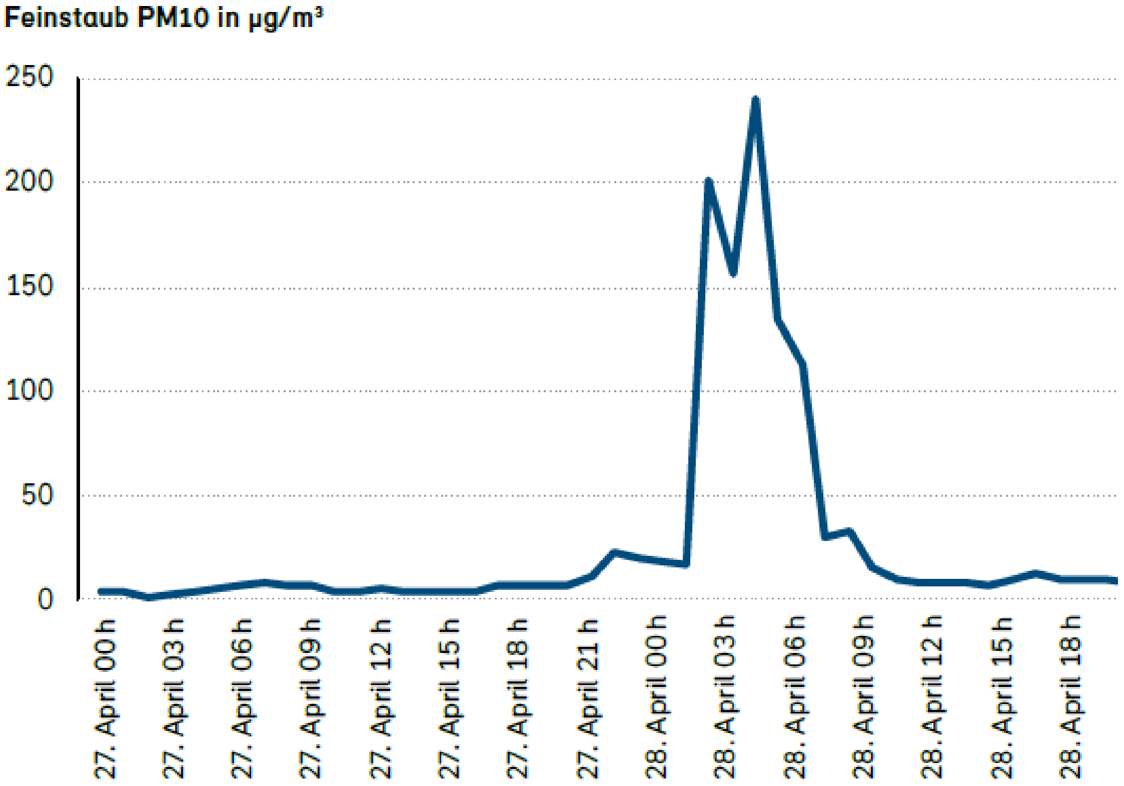
PM_{10} – annual means in Switzerland



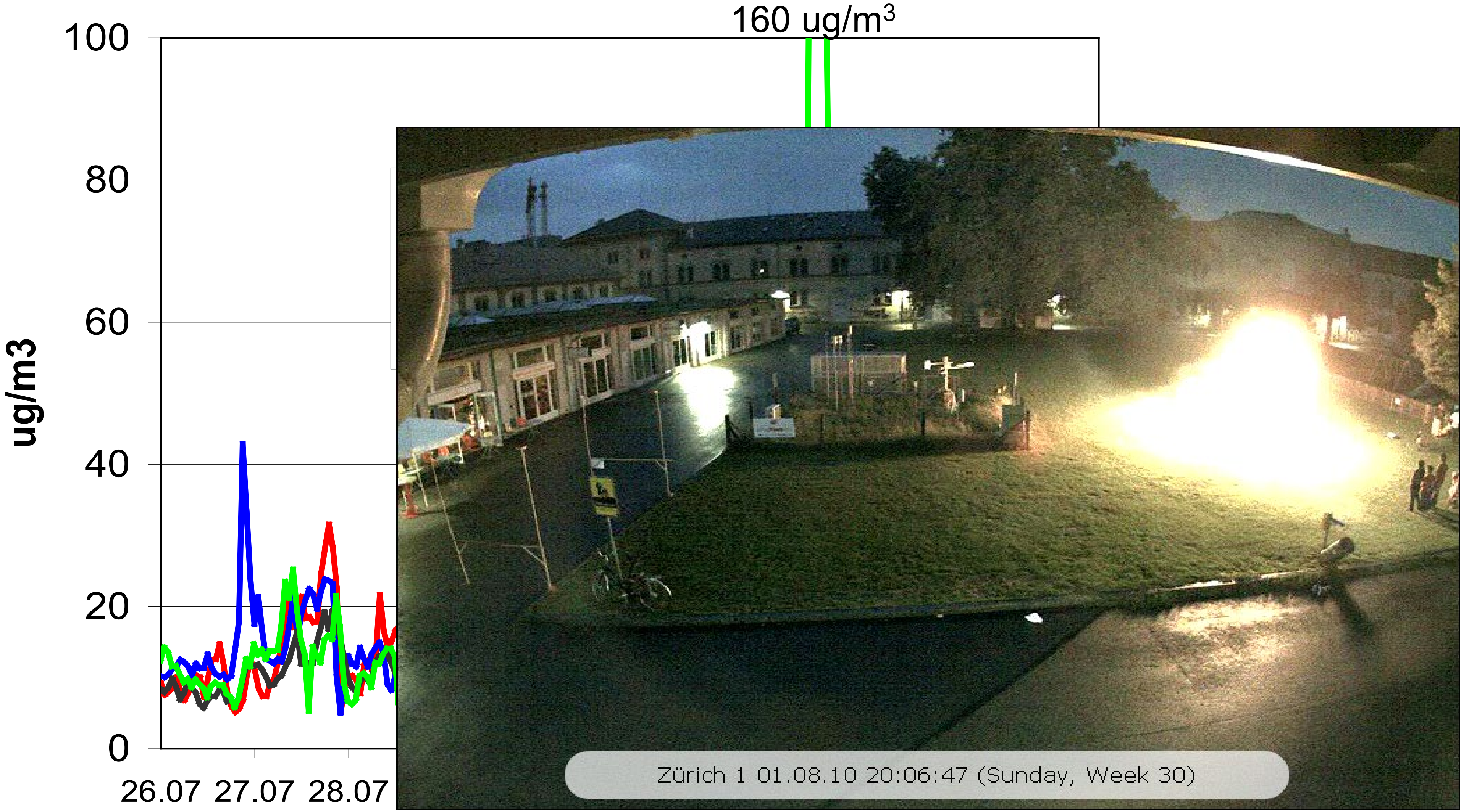
concentrations of particles (PM2.5) in Switzerland 1998-2020



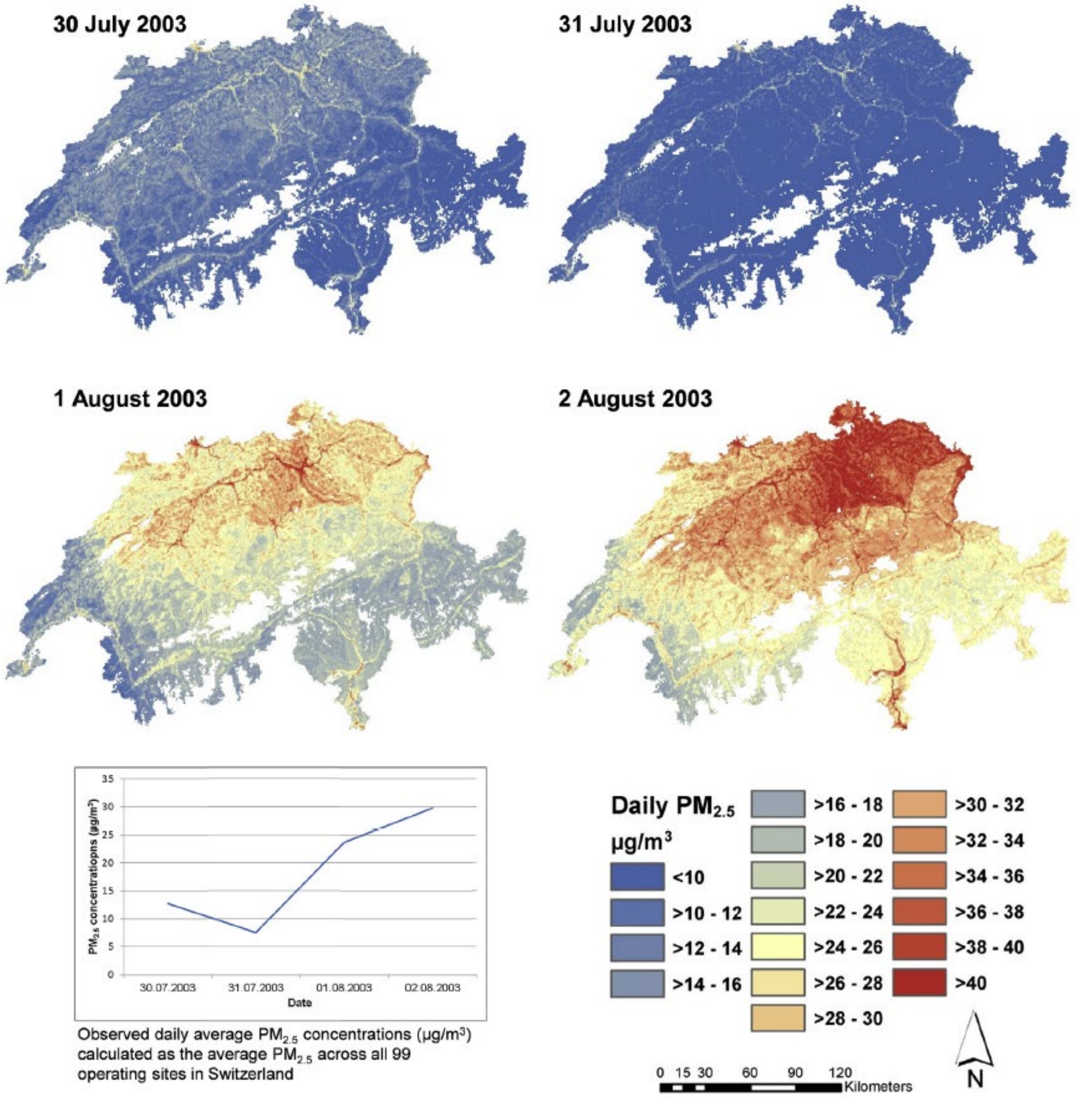
Frost candles and PM10 concentration
Wallis, April 2016



PM_{10} –in Lausanne/Payerne summer

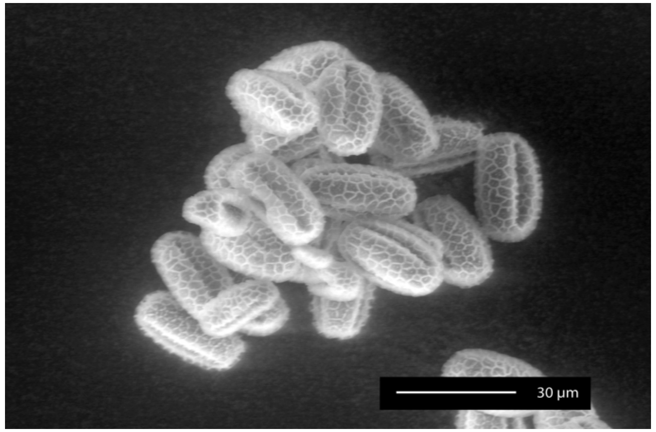


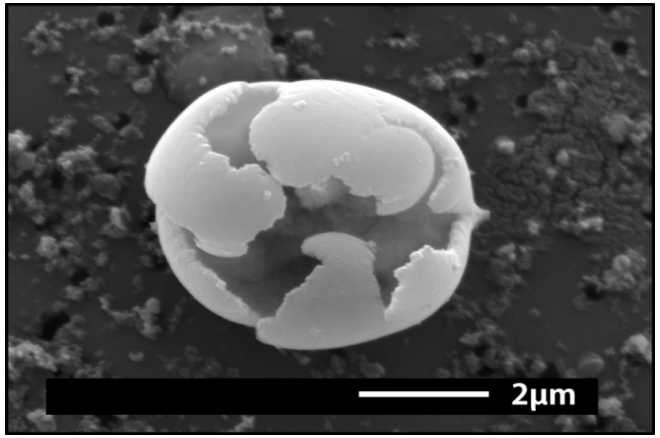
PM 2.5 around 1st August in Switzerland

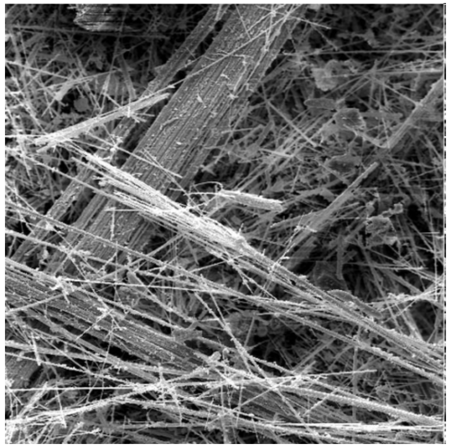


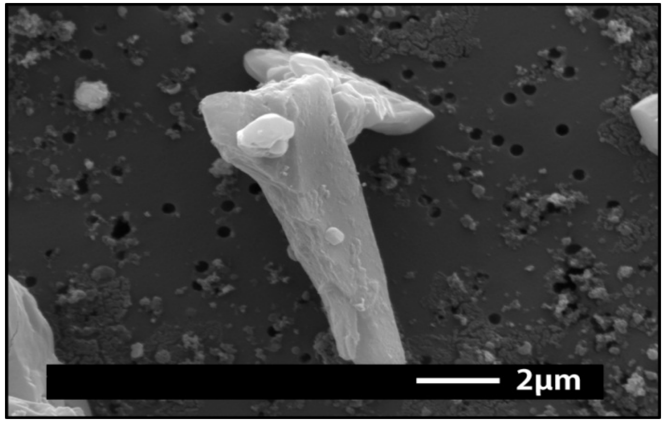
de Hoogh et al., Environ. Poll., 2017

Particles in the microscope
railway break, asbestos, pollen, diesel soot, Sahara dust, special guest

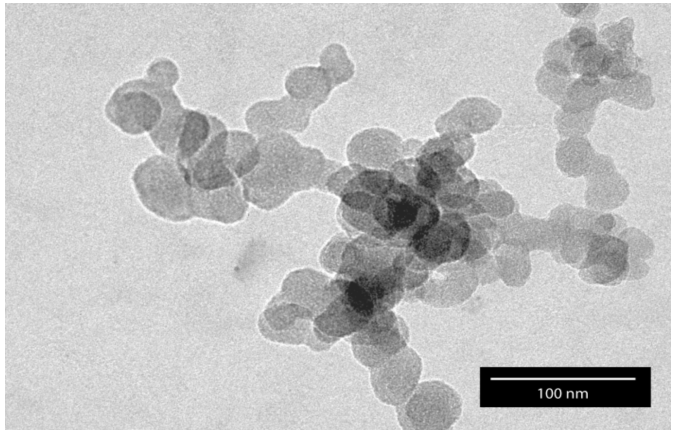


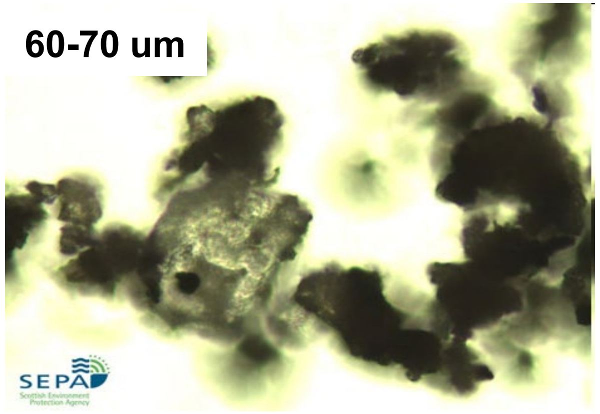






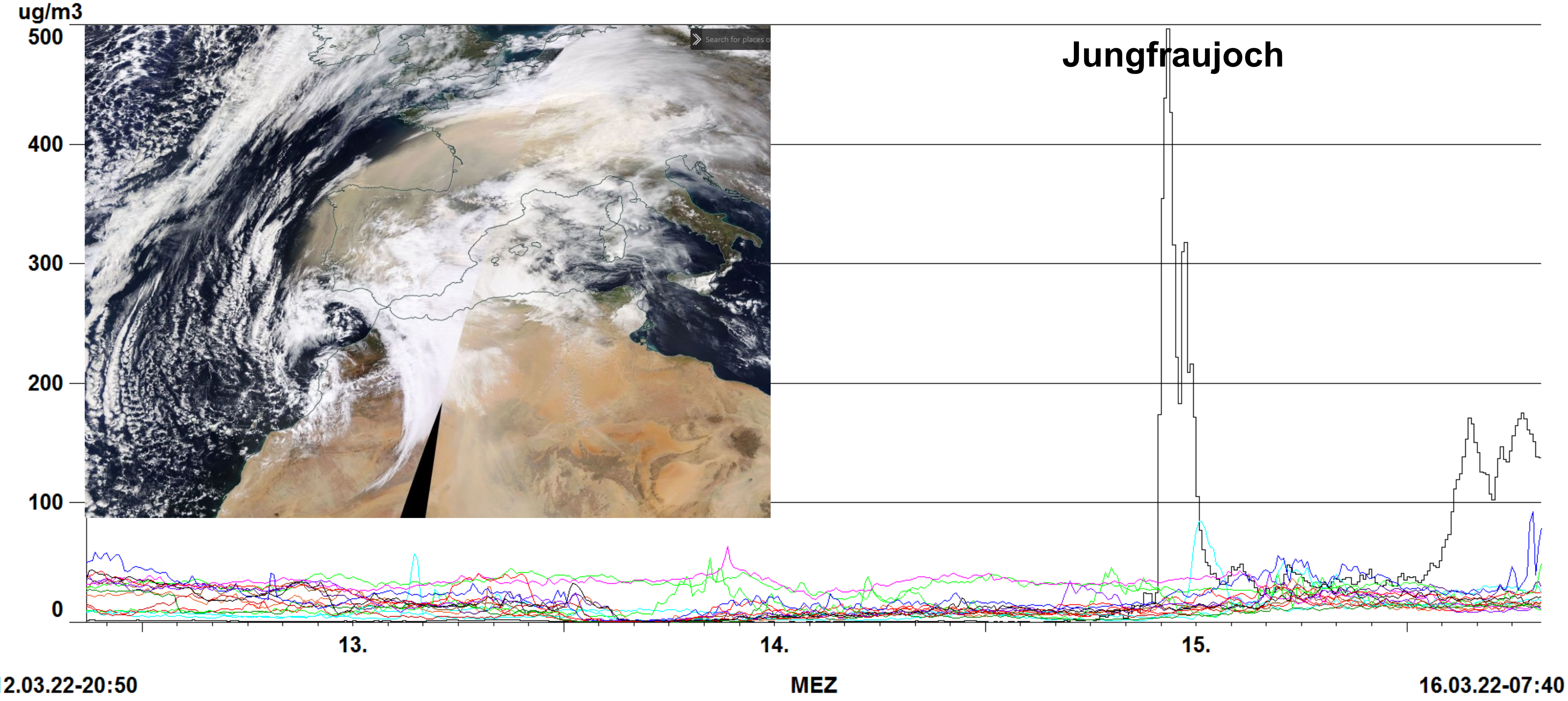
?





Saharan dust event Tuesday 15 Mar 2022

Station	DUE	BAS	BER	BRM	CHA	HAE	LUG	MAG	PAY	RIG	SIO	ZUE	LAU	TAE	JUN	DAV	ZZD
Messw	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_	PM10_
MW-Ty	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10	MM10
Muster																	



Saharan dust event Tuesday 15 Mar 2022

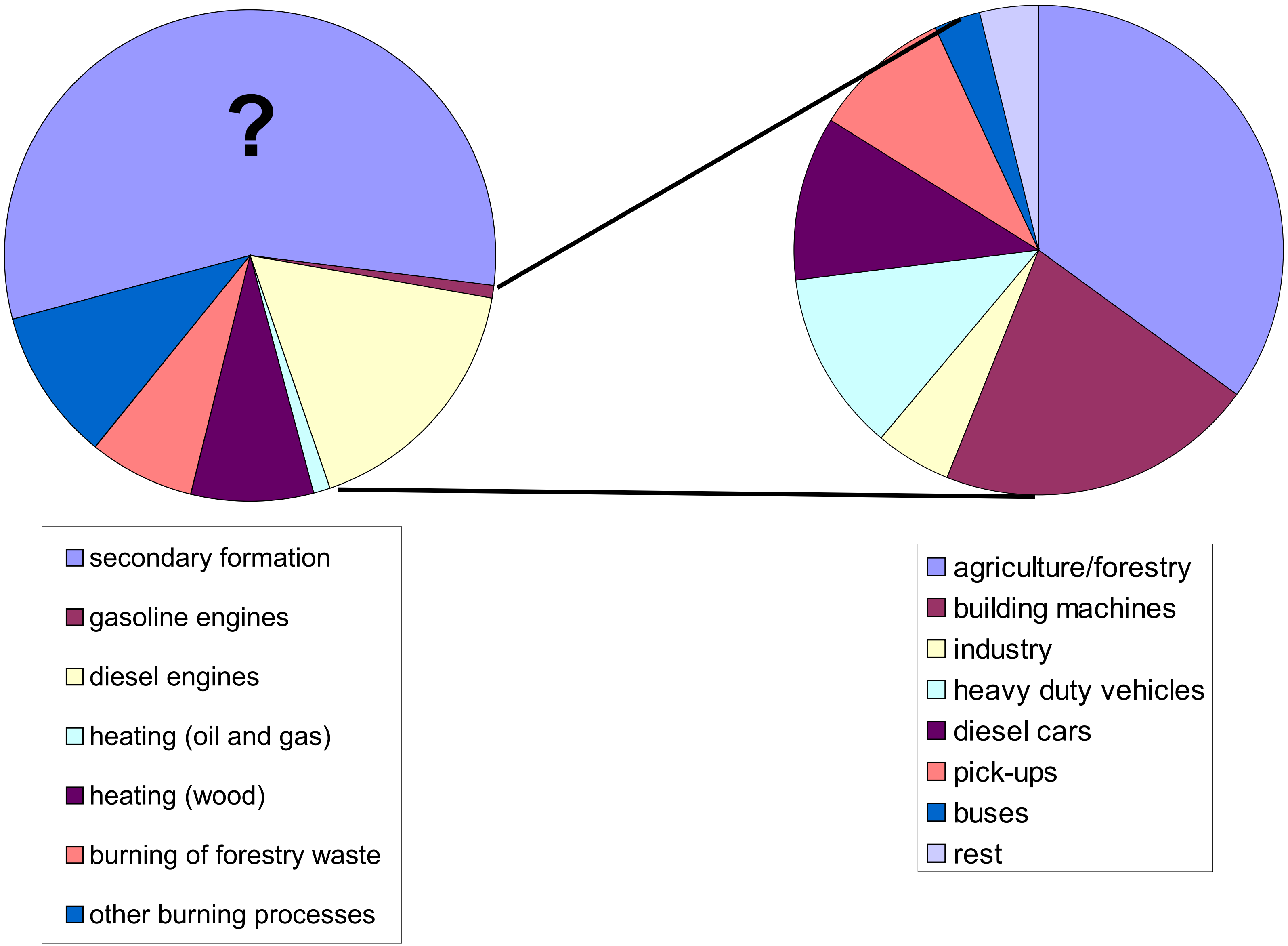
1 day before

09:00

09:50

500 ug/m3 ➔ estimated 1km height
0.5g/m² above Switzerland
➔ 21’000 t dust above Switzerland
➔ 1000 railway cars ➔ 10 km freight train

Sources of particles in Switzerland



Types of secondary aerosols

1. Sulphate aerosols

SO_2 (anthropogenic/volcanic) and DMS (dimethylsulfide, ocean) are oxidised to H_2SO_4 and build aerosols.
NH_3 (agriculture) + H_2SO_4 => Ammoniumsulphate aerosol

2. Nitrate aerosols

NH_3 + HNO_3 (fossil fuel burning) => Ammoniumnitrate aerosol

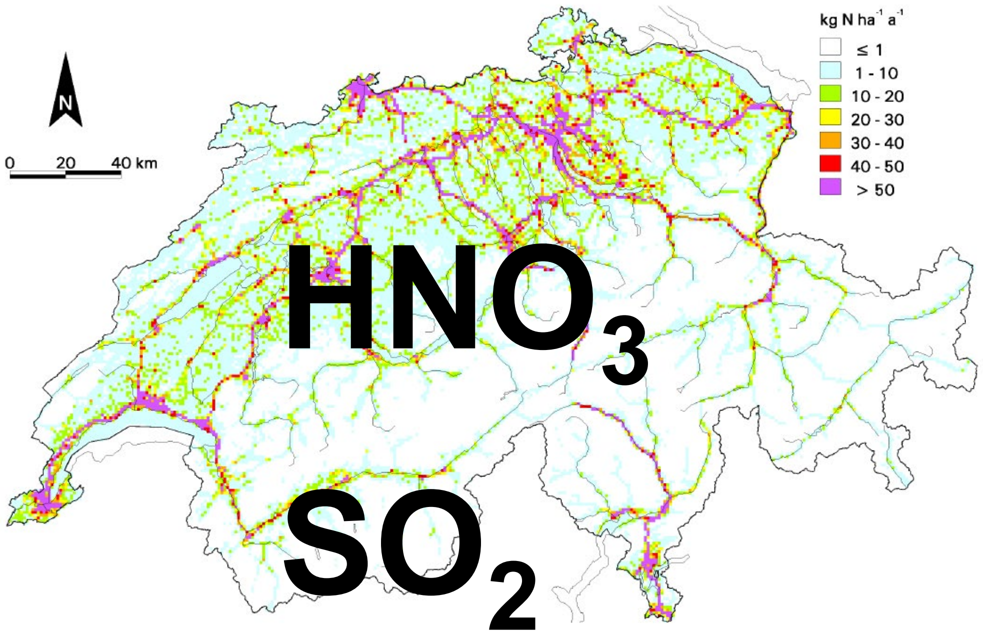
3. Organic aerosols (SOA)

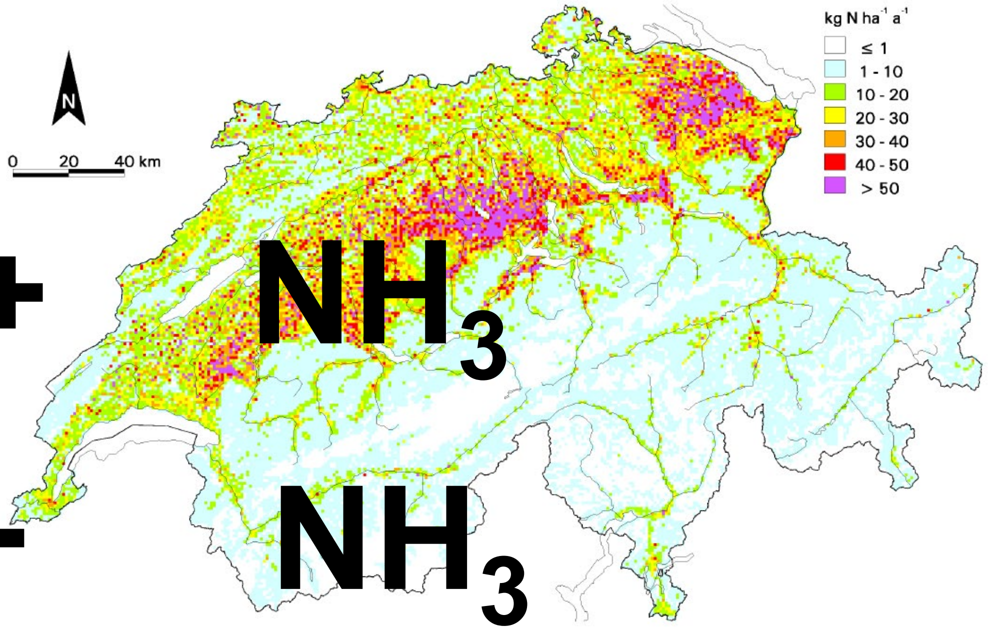
oxidation of volatile organic compounds (VOCs) leads to SOA. Global production from biogenic VOCs (mostly terpenes) is much higher than from anthropogenic VOCs (unburnt fossil fuel)

Nitrate and Sulfate Aerosols from NH_3 and NO/SO_2 as Precursors

Swiss NO emission inventory

Swiss NH_3 emission inventory

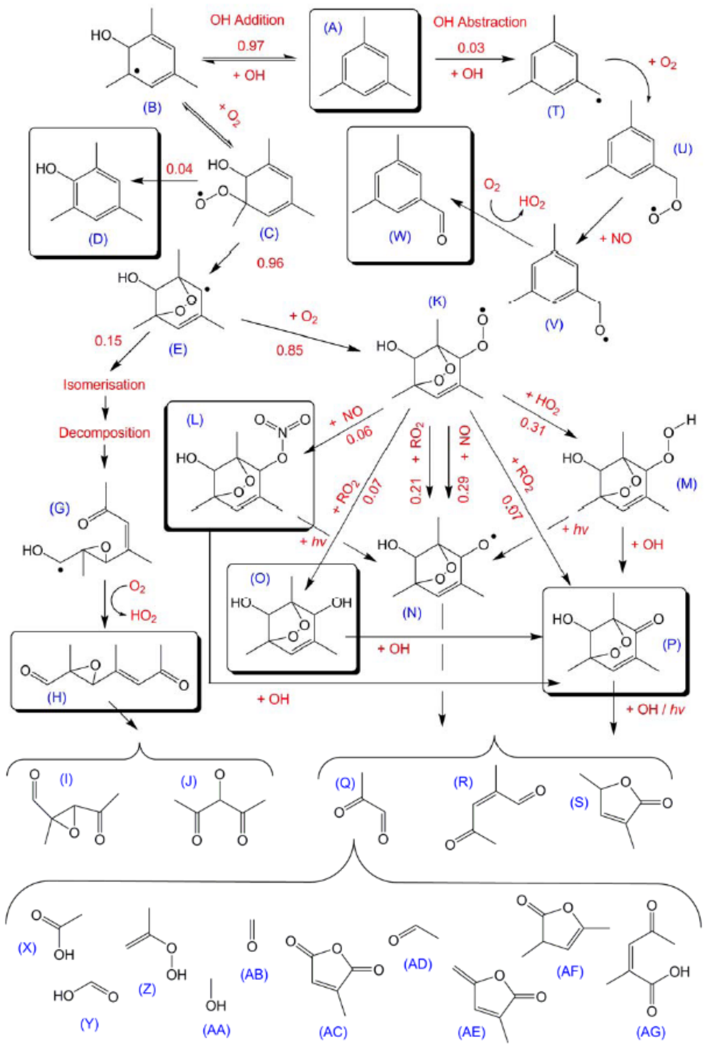




$$HNO_3 + NH_3$$

$$SO_2 + NH_3$$

3. secondary organic compounds (SOA)
Importance of oxidation of VOCs



Wyche, ACP, 2009

Oxidation of trimethyl benzene
leads to products which are
- less volatile
- more polar

⇒ particle formation/adsorption

Particles from volcanoes

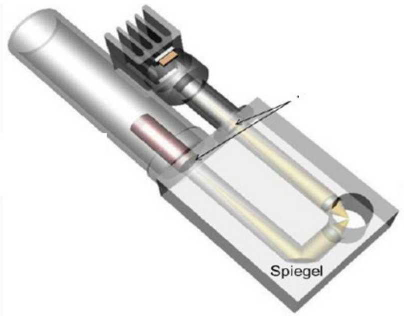
Methods for measurements of particles in the atmosphere

detection of mass

Gravimetry

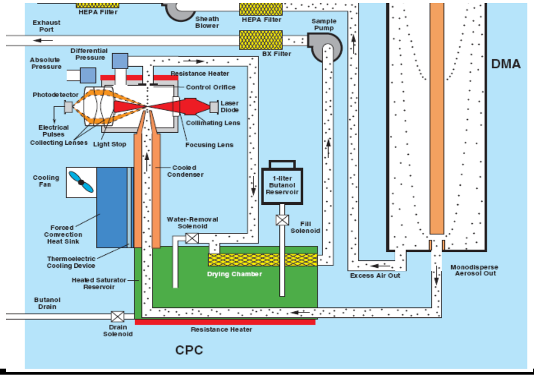
On-line method

FIDAS

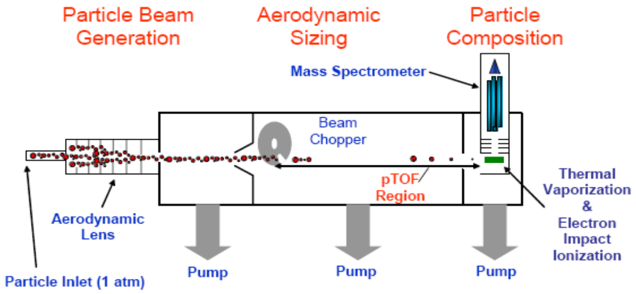


detection of properties

Scanning Mobility Particle Sizer (SMPS)



Aerosol Mass Spectrometer (AMS)



Gravimetric particle measurements = reference method

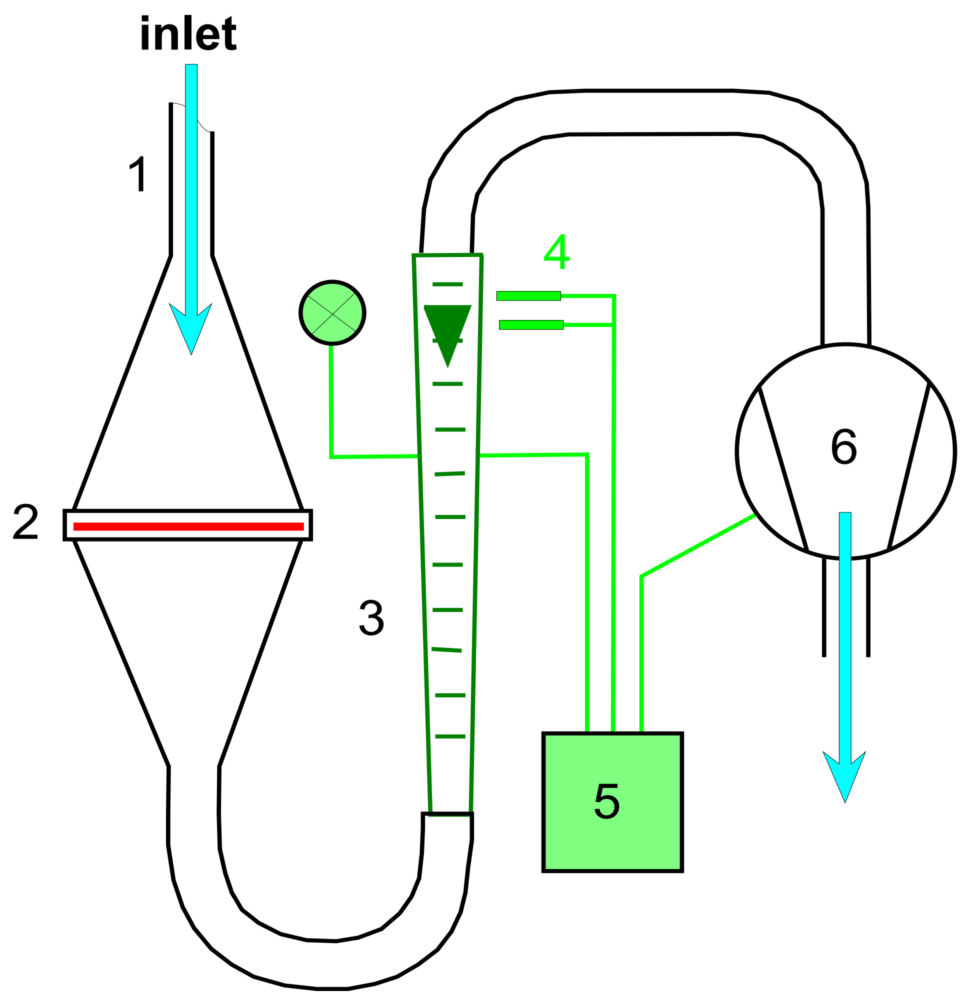
off-line analysis:
- conditioning of filter (air moisture)
- weighting of conditioned, clean filter
- one-day exposure (720 m^3 of air)
- re-weighting of exposed filter

Human breath volume/day? 0.5 L x 14 breath/min ~10 m^3

Advantage : high volume = high amount of particles (useful for further analyses)

Disadvantage: non-continuous analysis, laborious

Gravimetric particle measurements
the high volume sampler



1 sampling tube

2 filter

3 flow meter

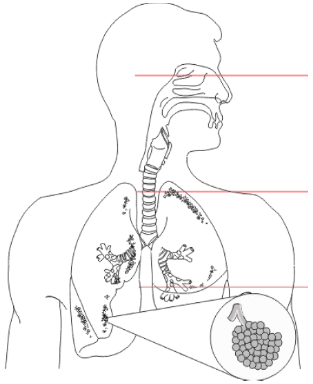
4 flow check

5 flow regulation

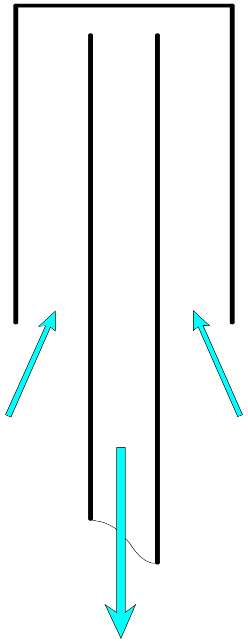
6 pump

Gravimetric particle measurements
the high volume sampler

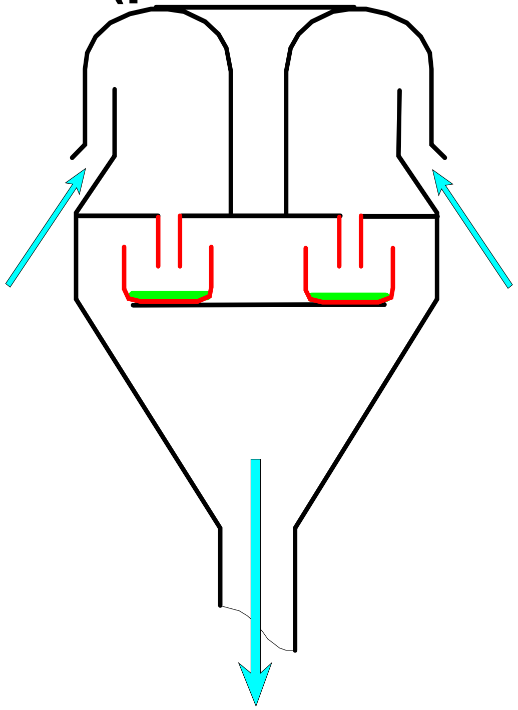
Inlets for
gravimetric measurement of particles



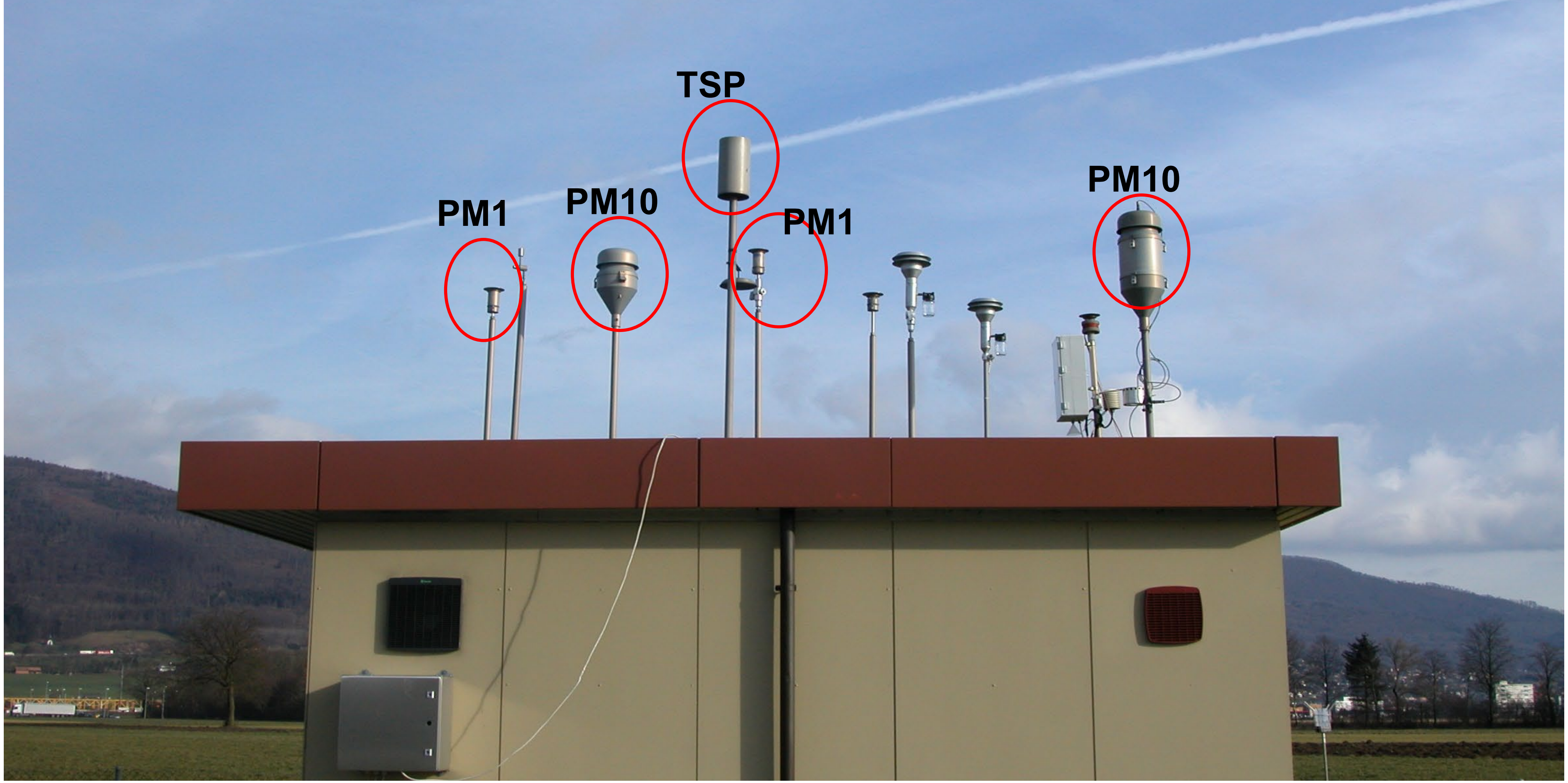
Total particles (TSP)



PM10 (particles < 10 µm)

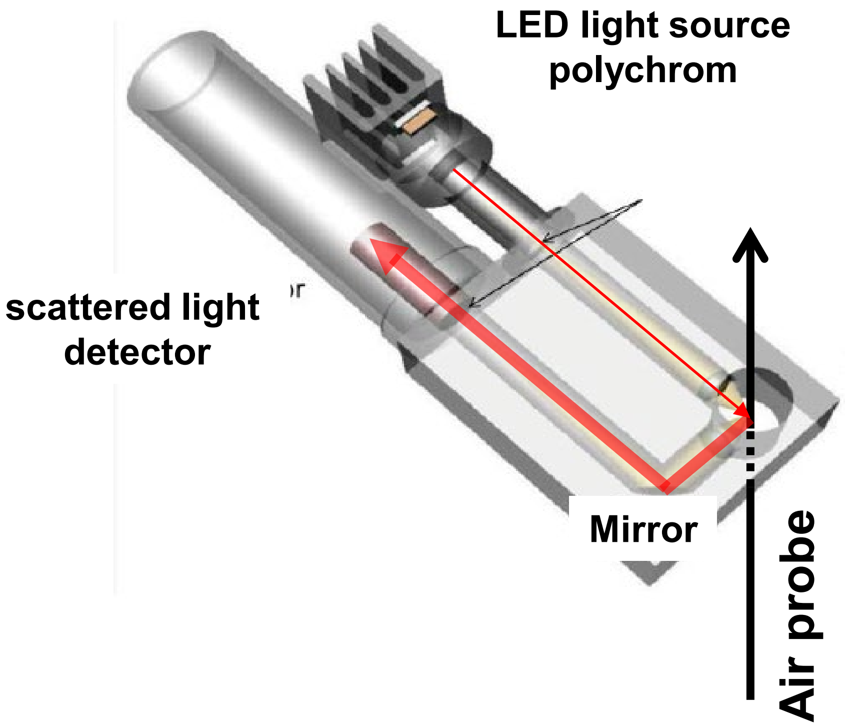


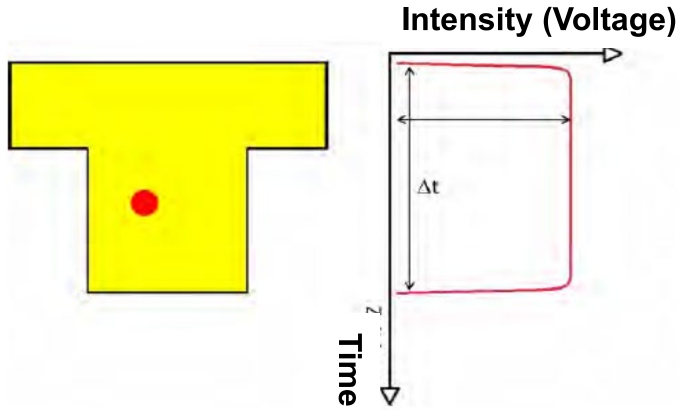
Inlets for gravimetric measurement of particles e.g. Haerkingen (near highway)



Impactor inlets for gravimetric measurement of particles
the theory

on-line measurements of particle mass
FIDAS



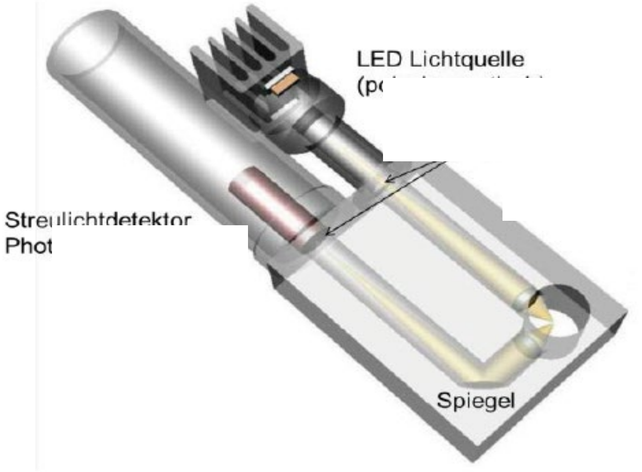


1. Particle Counter:
Each particle is detected by its scattered light beam

2. Gravimetry/size distribution
The intensity of the light beam is dependent on the size

comparison of on-line measurements of particle mass

FIDAS

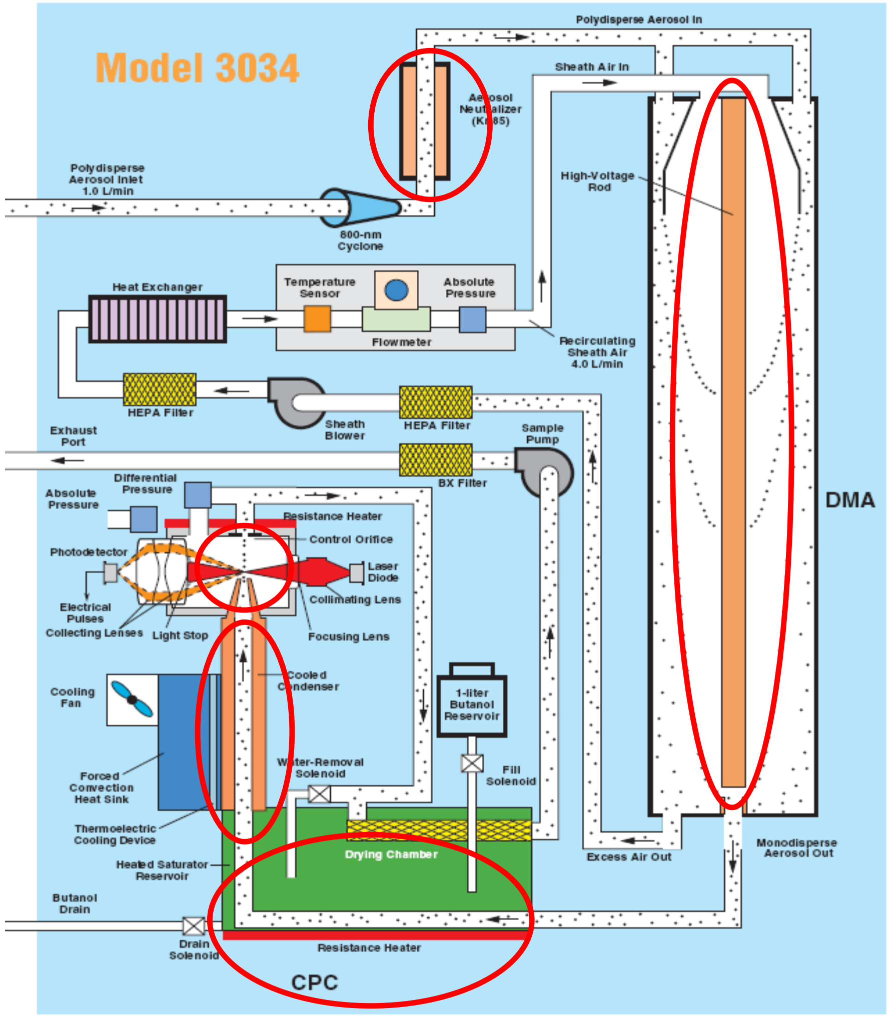


- on-line
- fast response
- high time-resolution

Gravimetry

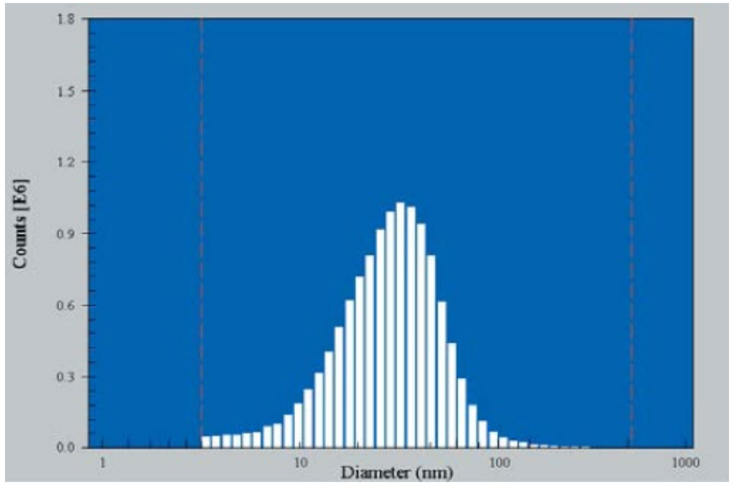
- less interference
- samples used for further analyses (e.g. carcinogens)

measurement of particle size and number
Scanning Mobility Particle Sizer (SMPS)



1.Differential Mobility Analyzer (DMA)
Particles are charged and are then separated depending on their size.
Changing the conditions leads to different sizes exiting the DMA.

2. Condensation Particle Counter (CPC)
Selected particles are immersed in a n-butanol flow.
Subsequent cooling leads to enlargement of particles.
Extinction measurement in a laser beam.

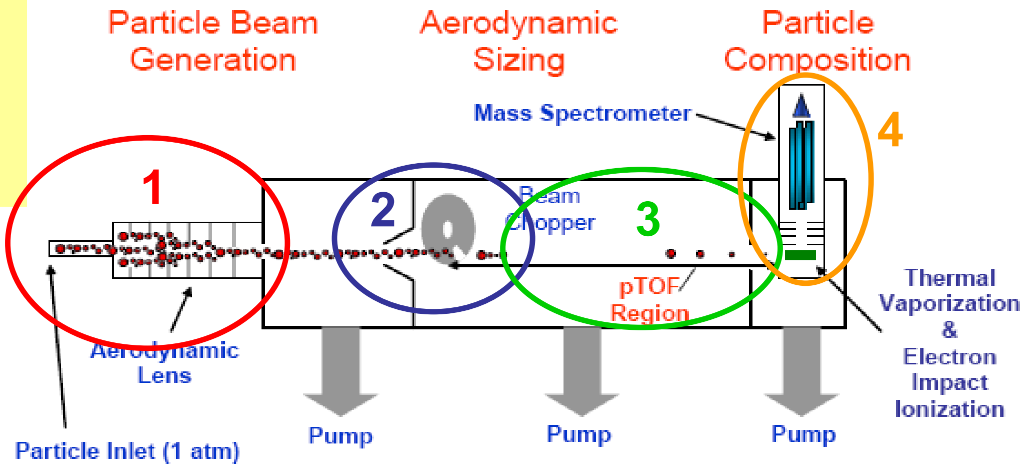


measurement of particle ingredients
Aerosol Mass Spectrometer (AMS)

on-line analysis of particulate composition

elements: C, H, O, N , Fe, Zn, Pb, Hg

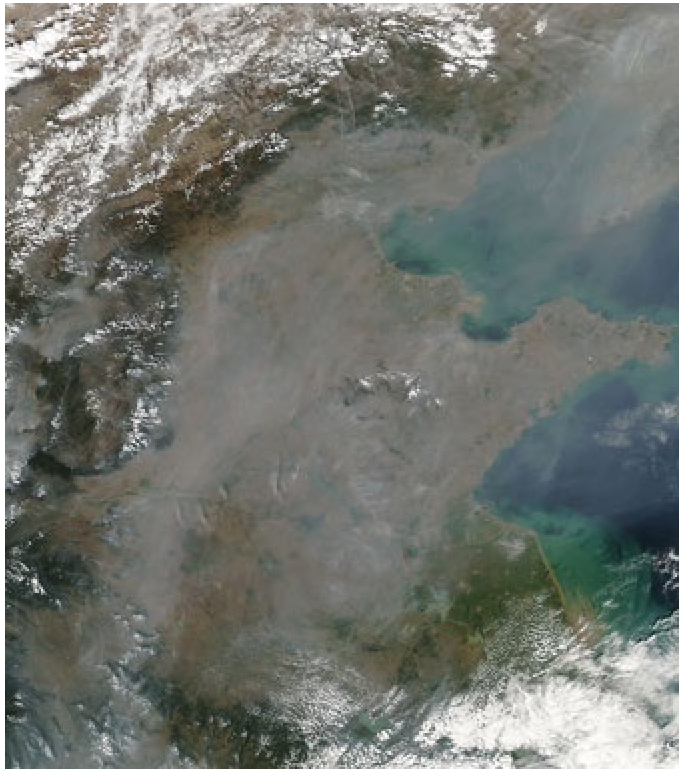
and PAHs



1. Aerosol particles (0.04-1μm) are sampled into a vacuum system and focused
2. A rotating beam chopper provides packages of particles
3. Size separation with the time-of-flight (TOF) technique
4. Detection of elements by quadrupole mass spectrometry

Aerodyne and TSI

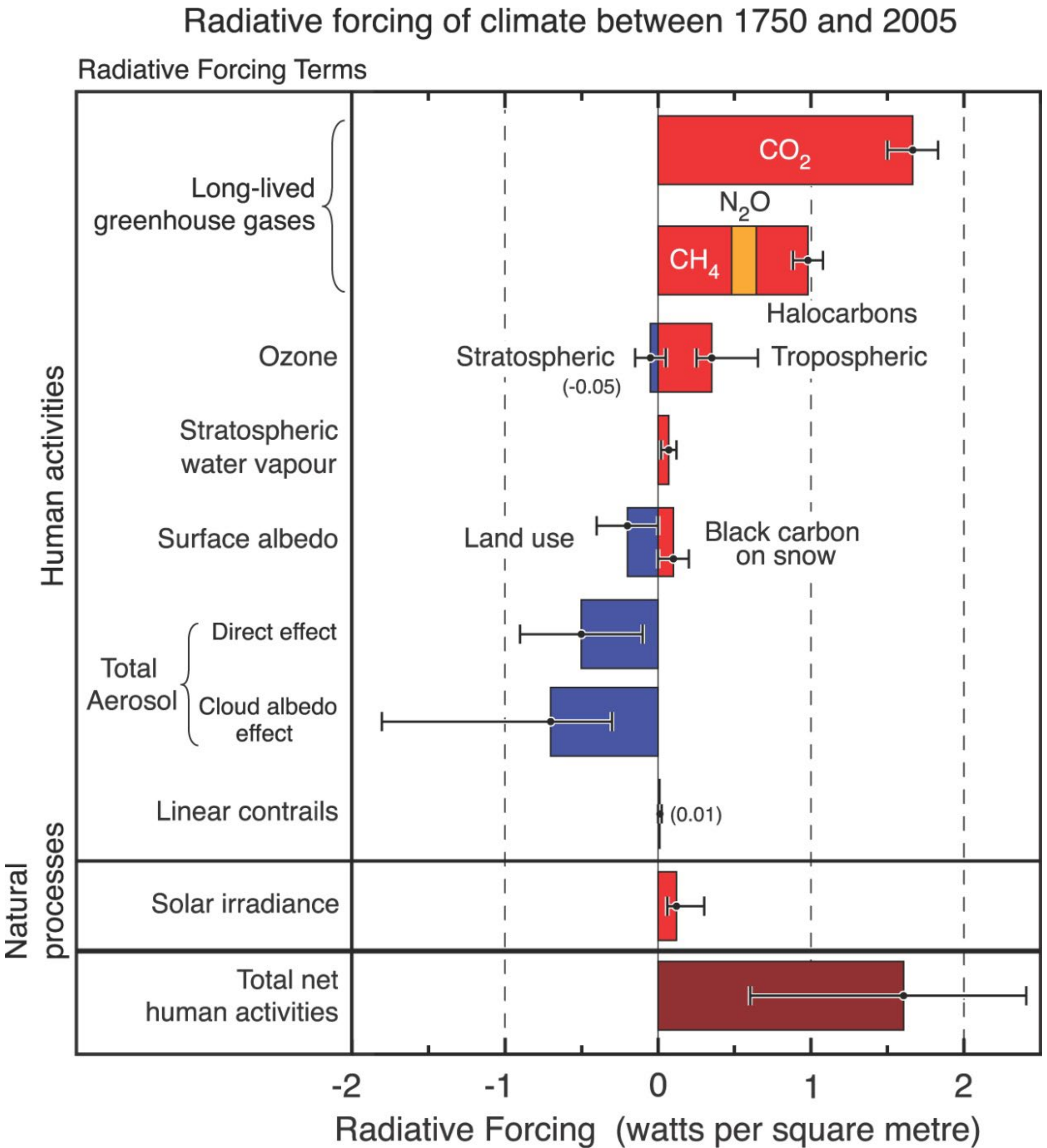
Determination of particles by Aerosol Optical Depth (AOD) from satellites and



Haze over China

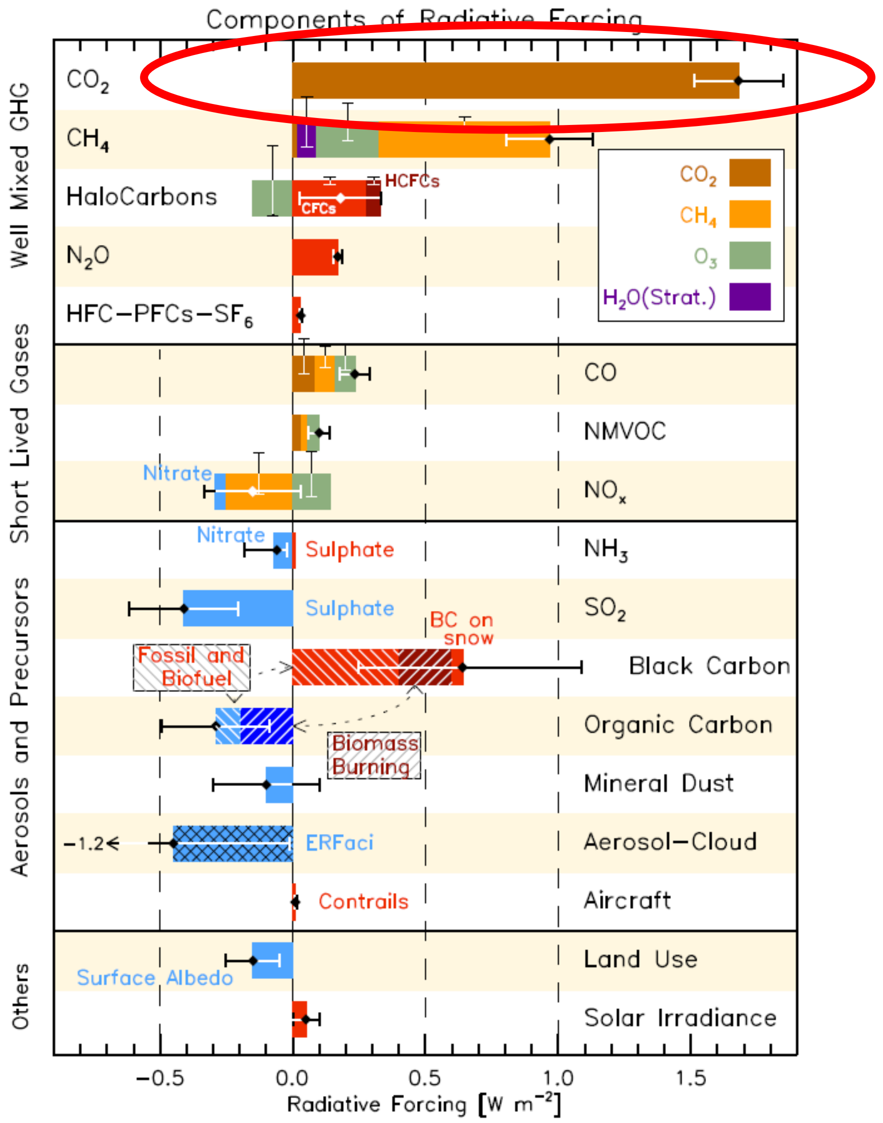
Biomass burning in Brazil, 2019

particles as a greenhouse drivers
(more in the greenhouse effect section)

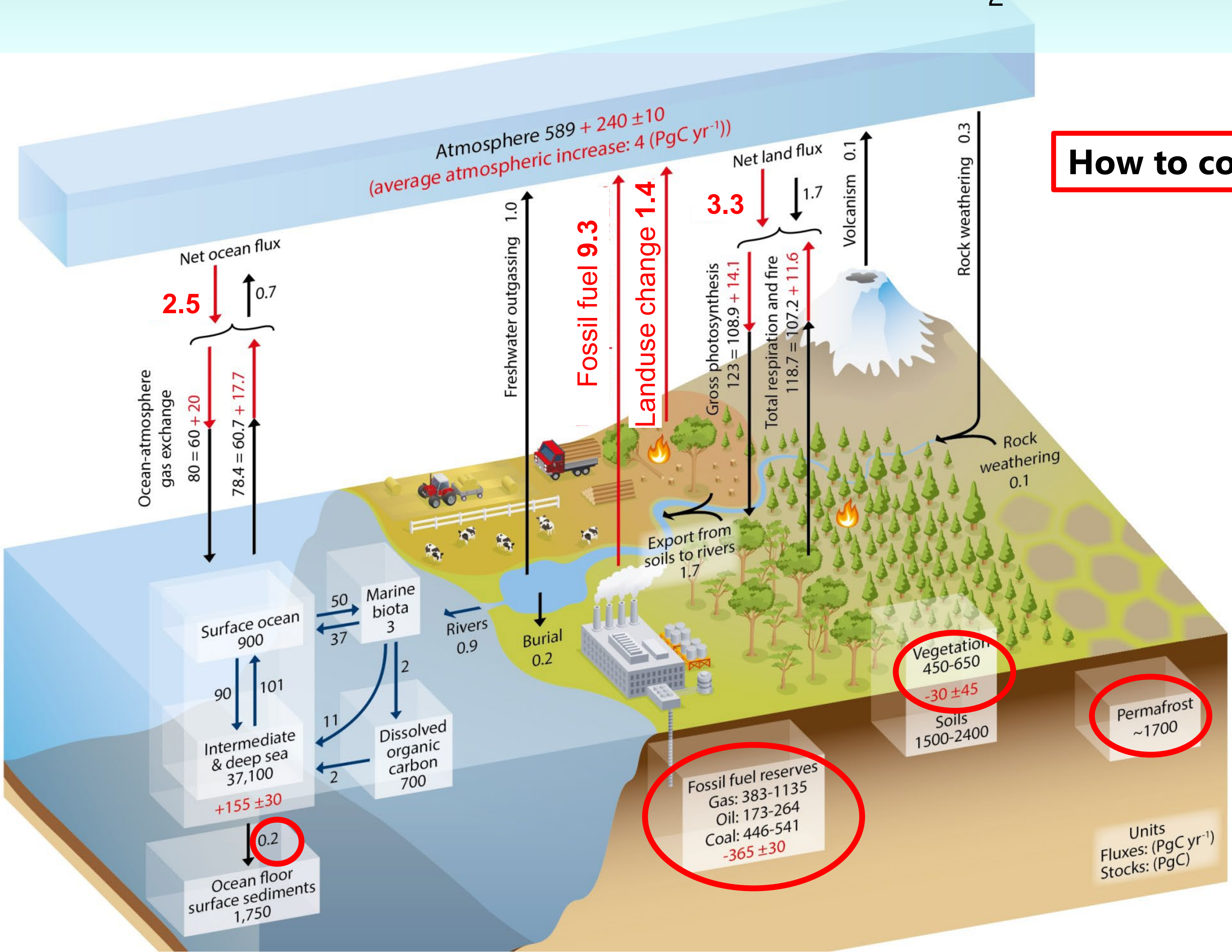


GREENHOUSE GASES
Anthropogenic Radiative Forcing in AR5

CO_2



IPCC AR5: Sources and sinks of CO_2



How to convert CO_2 in C?

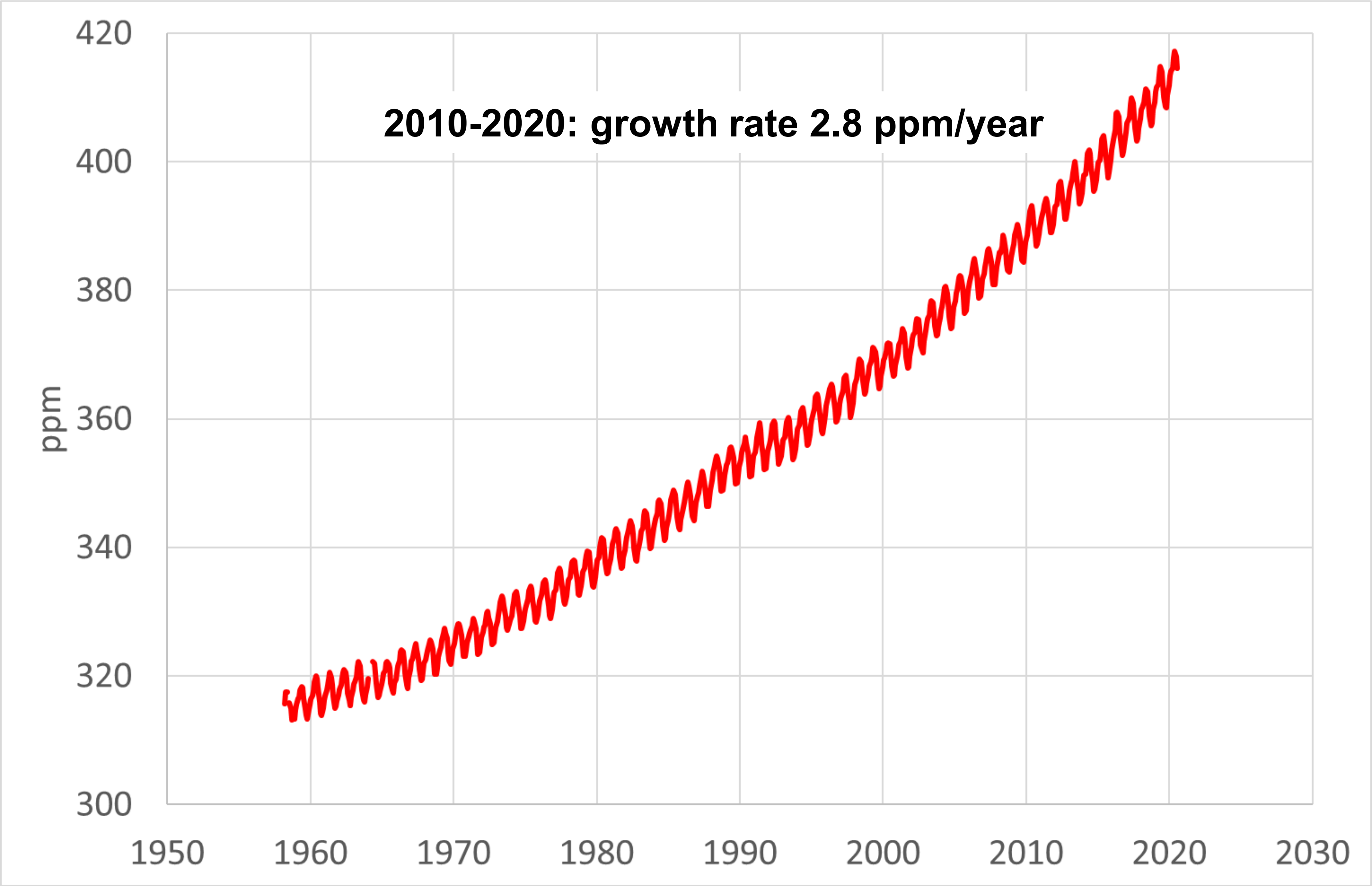
Overview of measurement-techniques for tropospheric trace compounds

	Compound	Monitor	GC – (MS)	Laser	Satellite
air pollutants in OPair	SO_2	XX			X
	NO_x	XX			X
	CO	XX		X	X
	O_3 (Troposph.)	XX			(X)
	Particles	X			(X)
	VOCs	(X)	X		
greenhouse gases in Kyoto Protocol	**CO_2**	**XX**	**X**	**XX**	**(X)**
	CH_4	X	XX	XX	X
	N_2O		XX	X	(X)
	Halocarbons*		X		(X)

XX: best available method
X: good method
(X): possible

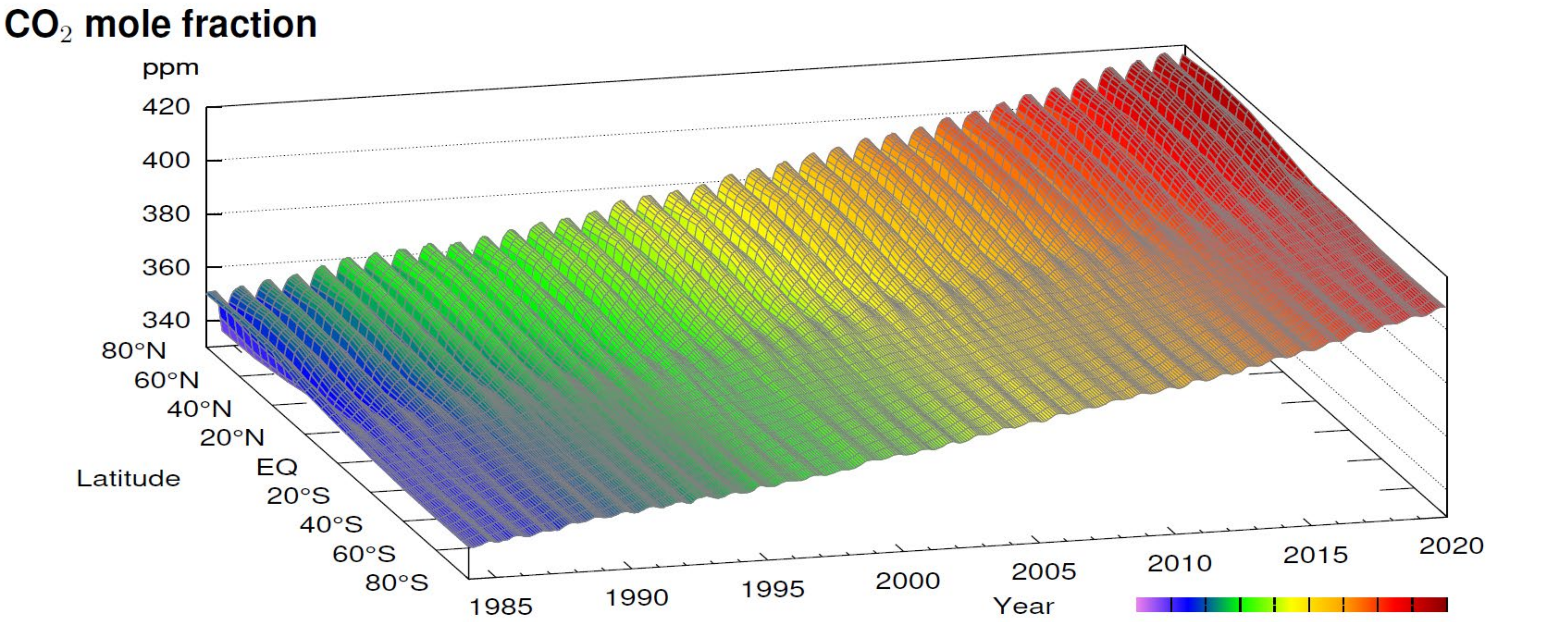
* also causing ozone depletion

CO_2 measured at Mauna Loa – a very important data set



http://scrippsco2.ucsd.edu/data/atmospheric_co2/primary_mlo_co2_record

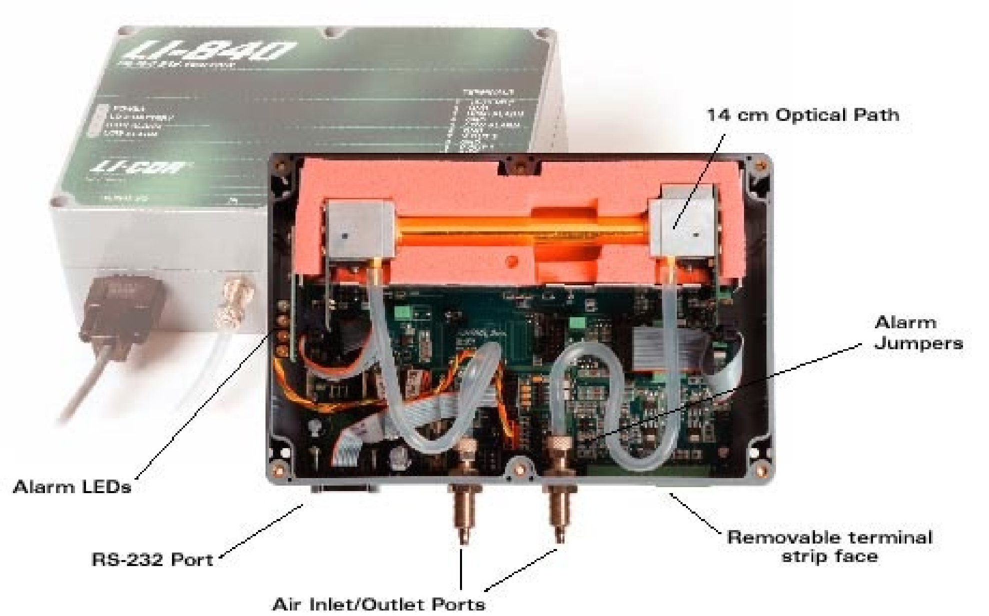
CO_2 measured world-wide



WDCGG, 2021

CO_2 measurement methods

non-dispersive, infrared (**NDIR**) gas analyzer



LI-COR

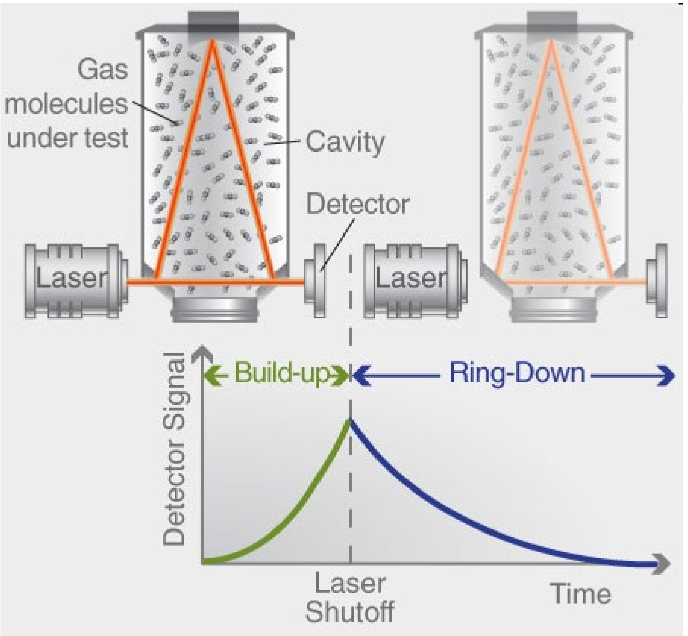
High stability with low zero and span drift

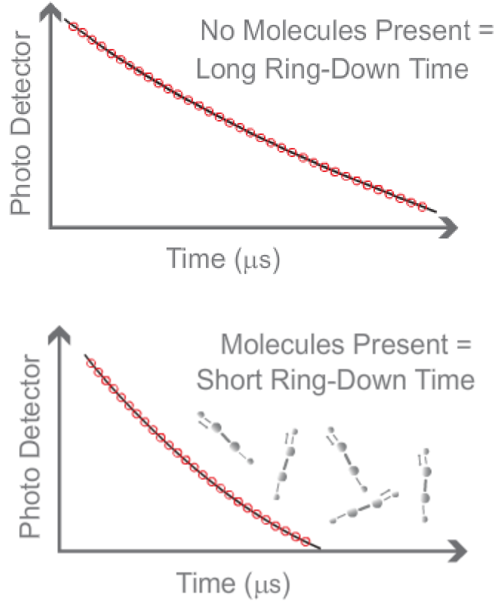
< 1 ppm signal noise at 390 ppm for CO_2

http://www.licor.com/env/Products/GasAnalyzers/li840/840.jsp

CRD Laser from Picarro (G2301)

CO_2, CH_4, H_2O





Precision (1 stand. dev.)
5 sec: **<** 0.070 ppm
300 sec: 0.025 ppm

CO_2 measurement methods
Satellites

http://www.jaxa.jp/projects/sat/gosat/index_e.html

http://oco.jpl.nasa.gov

Ibuki („vitality") on GOSAT Japan

Ibuki-1 launched in January 2009

Ibuki-2 launched in 2018

Orbiting Carbon Observatory (OCO, NASA)

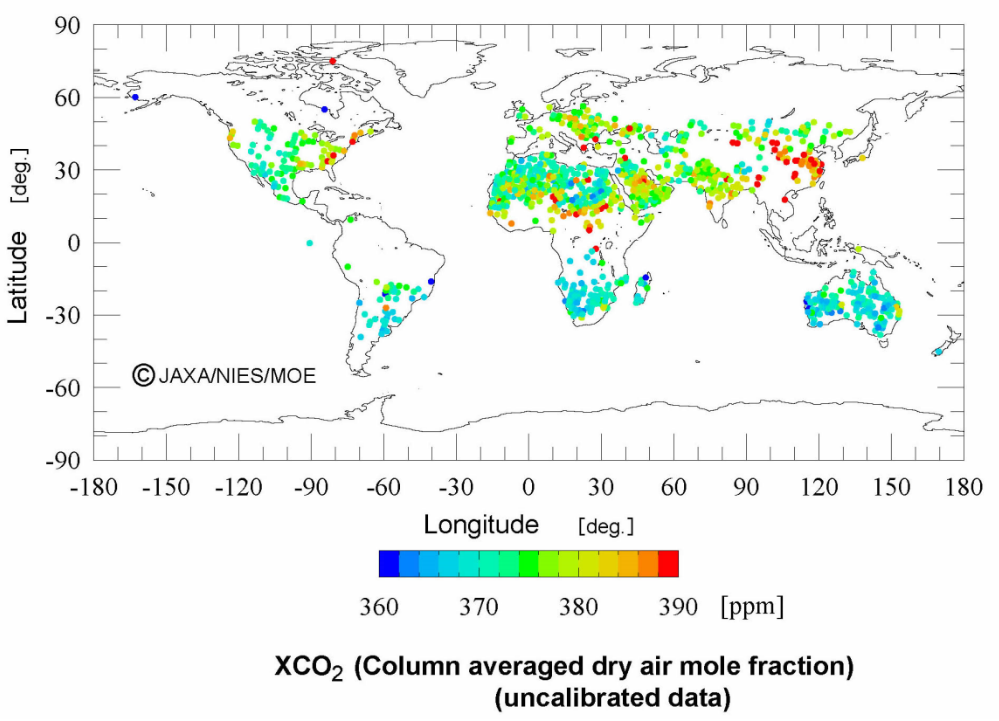
OCO-1 launched in February 2009, but destroyed

OCO-2 was launched in July 2014
Resolution ~1000 km^2

OCO-3 was launched in May 2019
Resolution 4 km^2

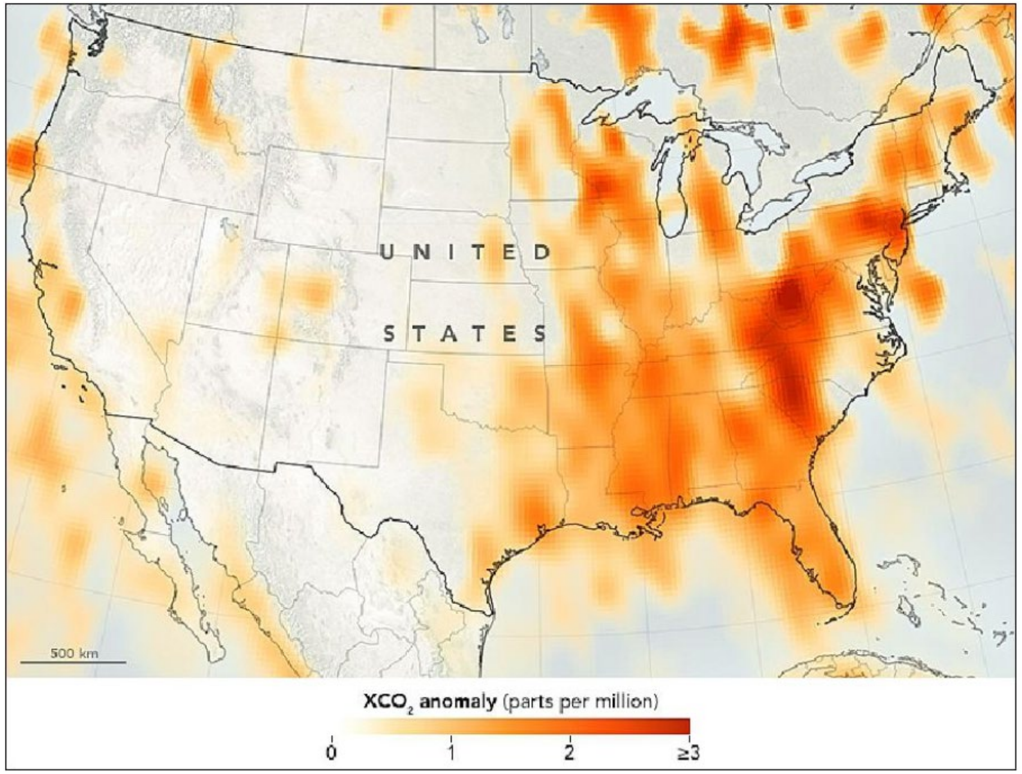
CO_2 measurement methods
Satellites

Ibuki („vitality“) on GOSAT Japan



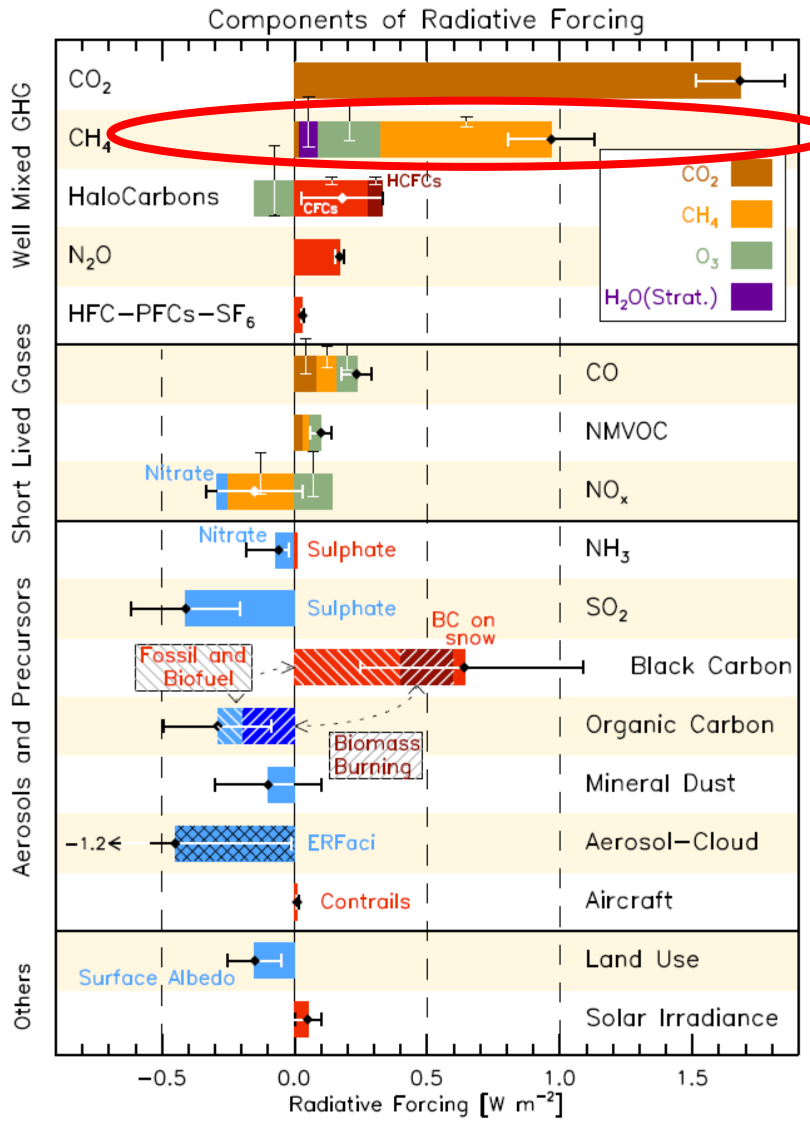
April 20-28 2009

OCO-2 (2016-1018)



GREENHOUSE GASES
Anthropogenic Radiative Forcing in AR5

CH_4



global budget of CH_4

IPCC AR5 (Chapter 6.3.3)

natural

Sources (678 Tg, 2000-09)

Fossil fuel	14%
Livestock, ruminants	13%
Rice paddies	5%
Landfill	11%
Biomass/biofuel burning	5%
Natural wetland	32%
Other natural	19%

Sinks

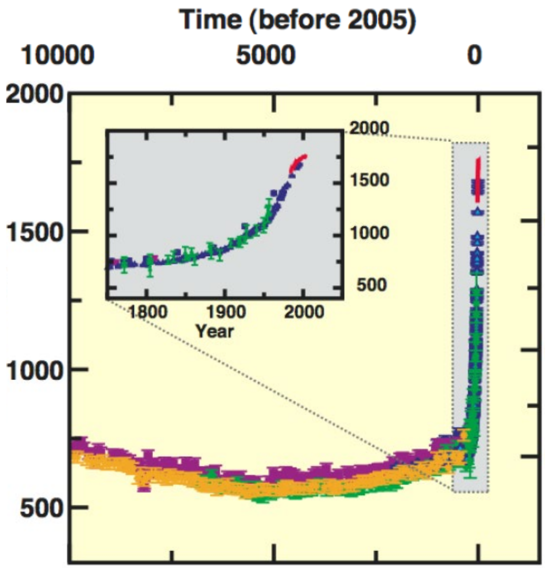
Oxidation by OH/Cl radicals	88%
Soil uptake	4%
Stratosphere	8%

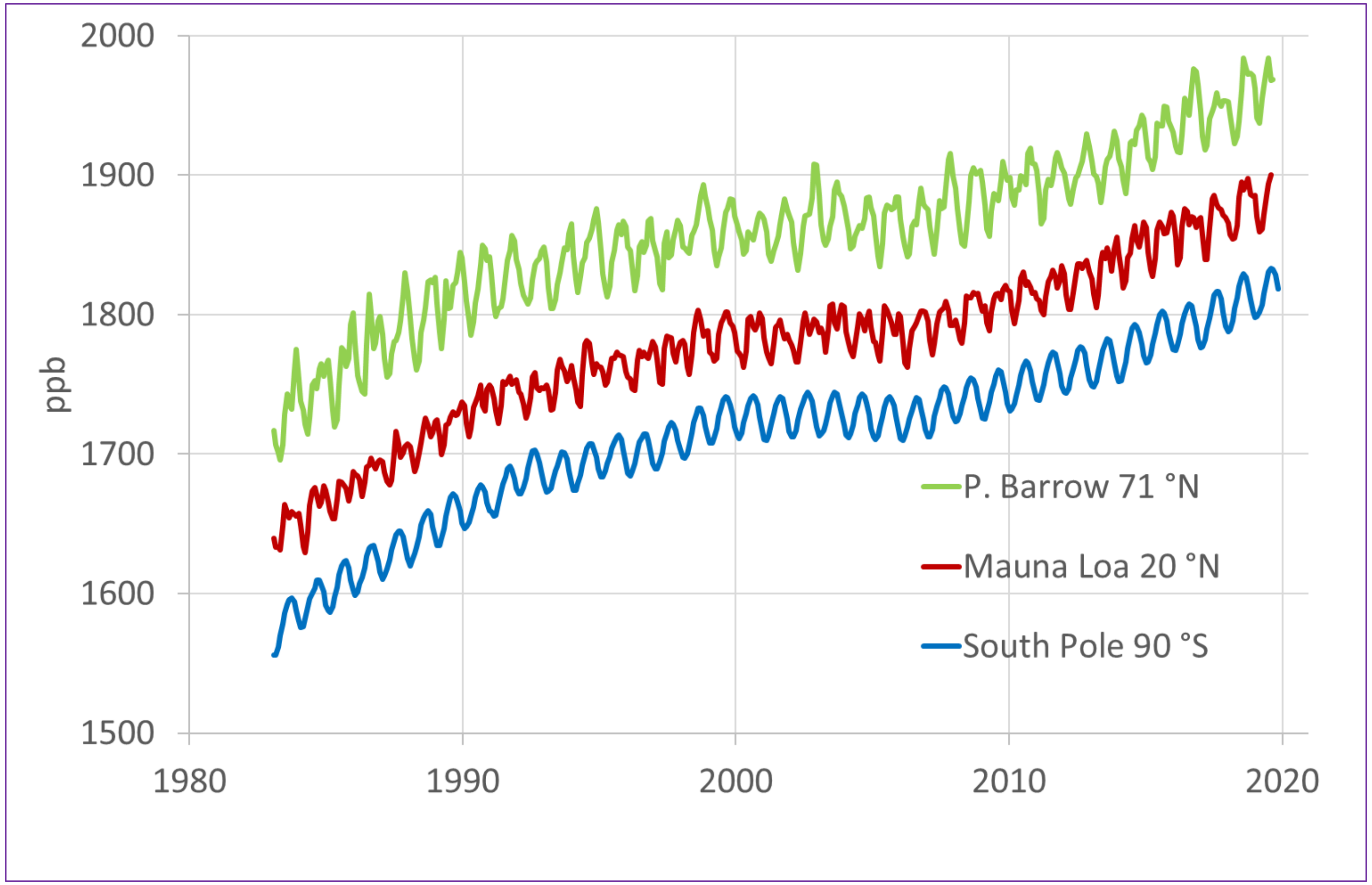
Lifetime: 12 years

GWP^{100}: 28

anthropogenic

global behaviour of CH_4





Possible reasons for reincrease
- **warmer and wetter tundra**
- thawing of Siberian permafrost soils?
- emissions from dissolving gas hydrates?

Overview of measurement-techniques for tropospheric trace compounds

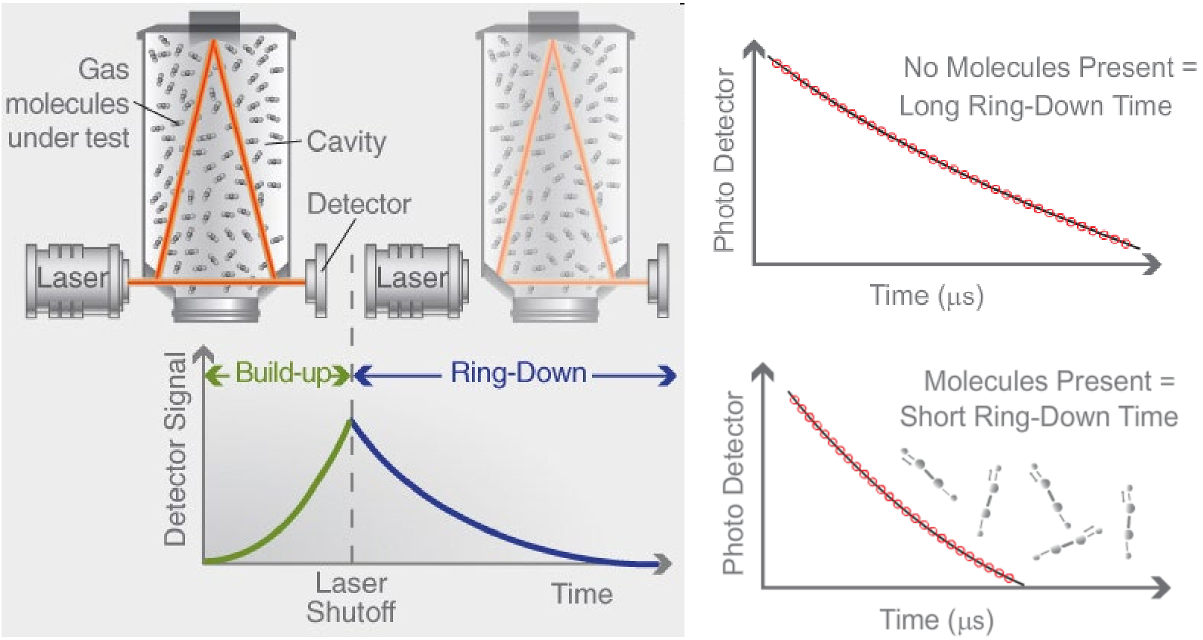
Group	Compound	Monitor	GC – (MS)	Laser	Satellite
air pollutants in OPair	SO_2	XX			X
	NO_x	XX			X
	CO	XX		X	X
	O_3 (Troposph.)	XX			(X)
	Particles	X			(X)
	VOCs	(X)	X		
greenhouse gases in Kyoto Protocol	CO_2	XX	X	XX	(X)
	CH_4	**X**	**XX**	**XX**	**X**
	N_2O		XX	X	(X)
	Halocarbons*		X		(X)

XX: best available method
X: good method
(X): possible

* also causing ozone depletion

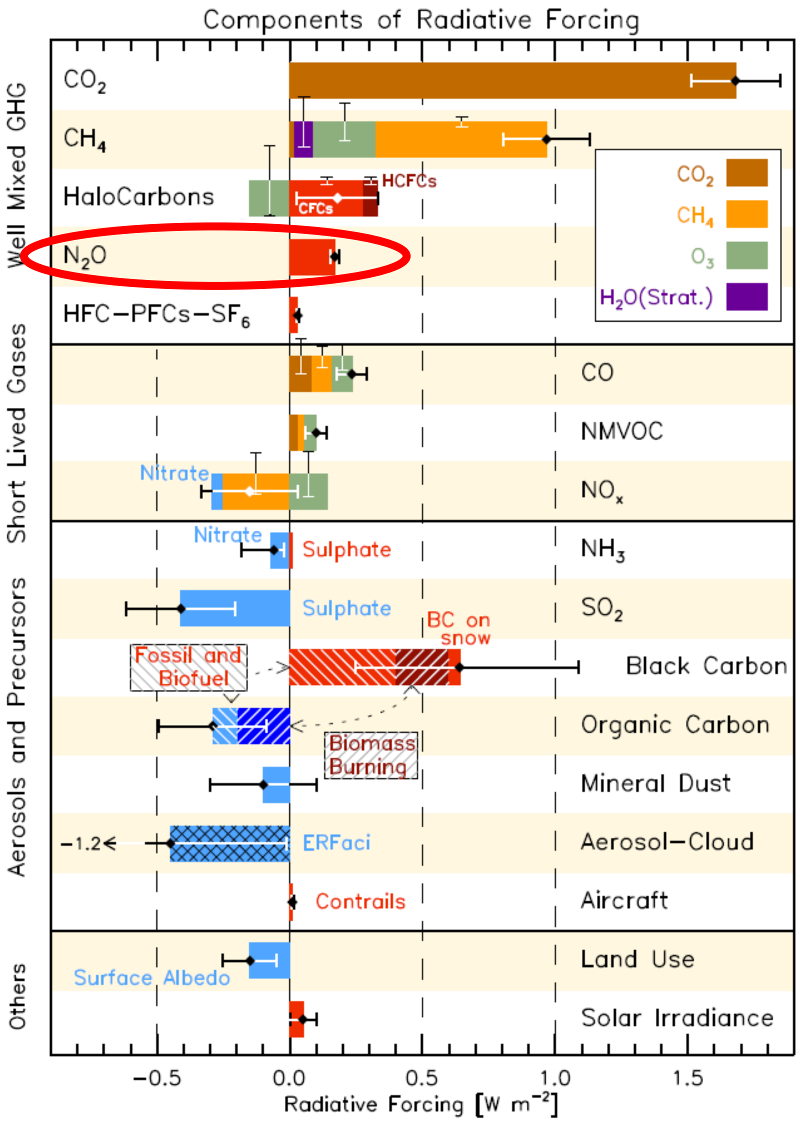
Measurement method for CH_4: CRD Laser from Picarro (G2301)

CO_2, CH_4, H_2O



GREENHOUSE GASES
Anthropogenic Radiative Forcing in AR5

N_2O



EPFL 2024

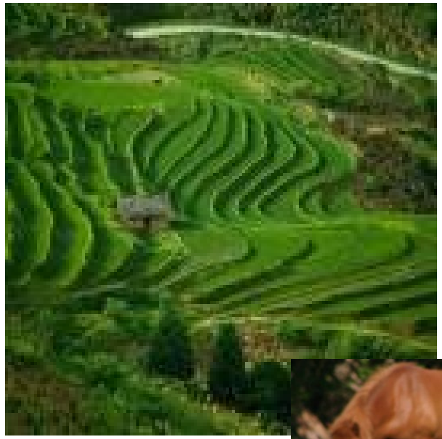
global sources/sinks of N_2O
IPCC 5AR

Sources 17.9 Tg (2006-11)	
natural (soils/oceans)	**61%**
Anthropogenic	**39%**
Agriculture soils/manure	23%
Industry/fossil fuel	4%
Biomass/biofuel burning	4%
Other anthropogenic	8%

Sinks

Stratosphere

Lifetime:	**GWP^{100}:**
123 years	265



Measurement methods for N_2O:

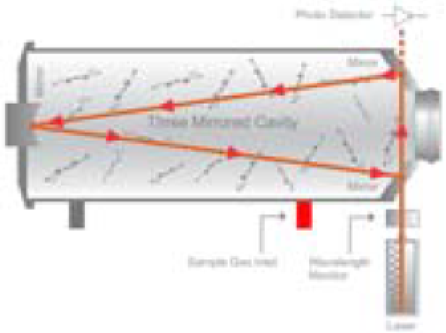
1. GC-ECD

slow, high accuracy

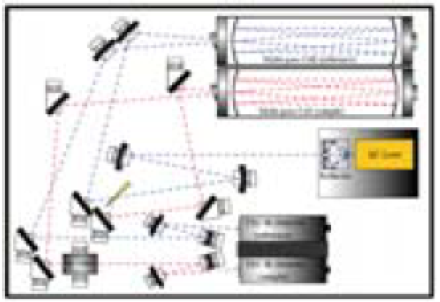
Non-linear

Detection limit
~ 0.2 ppb (10 min)

2a. CRD laser



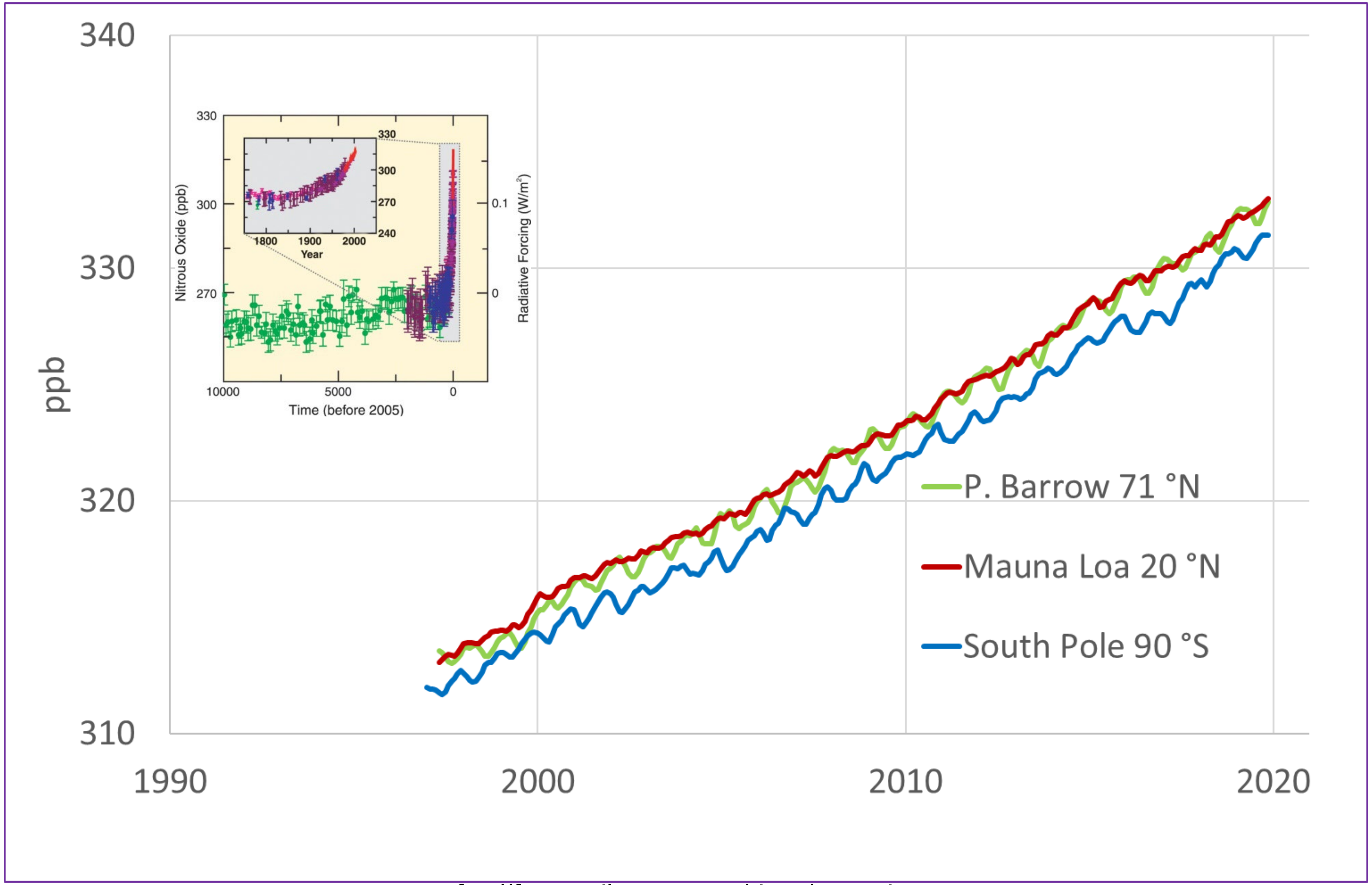
2b. QCL-laser



fast, high accuracy

	2a. CRD laser	2b. QCL-laser
	Linear	Linear
Detection limit	~ <0.2 ppb (30s)	0.1 ppb (100s)

N_2O measurement data



ftp://ftp.cmdl.noaa.gov/data/greenhouse_gases