Measurements of atmospheric trace gases

Stefan Reimann

stefan.reimann@empa.ch

Empa

Laboratoire fédéral d'essai des matériaux et de recherche

Empa

Materials Science and Technology

?

?

What is the heaviest thing in this room?

?

?

?

?

?

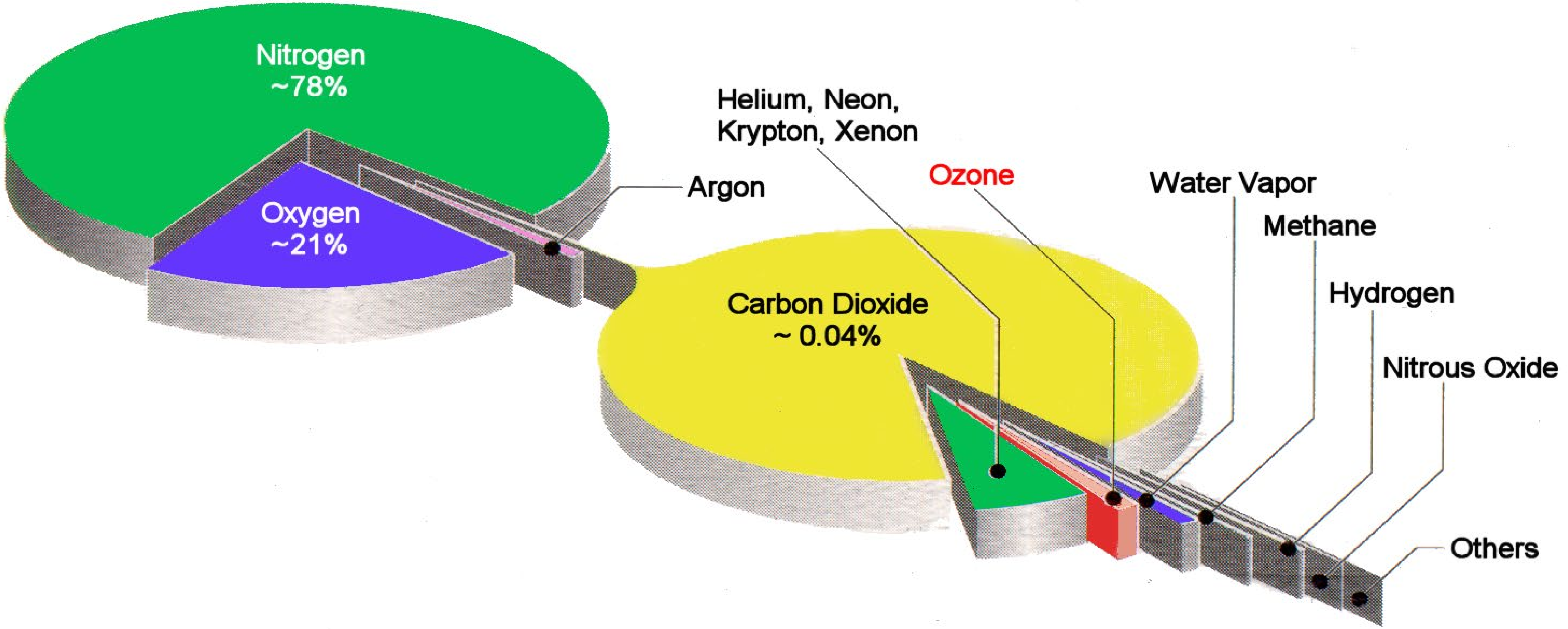
?

?

?

What is the heaviest thing in this room?

trace components in the atmosphere



400 ppm:
What is the volume of CO_2 in this room?
10 x 10 x 3 m

Aims of the course

- overview on atmospheric trace compounds
- understanding of how trace compounds are monitored
- measurement practice – good and bad
- using atmospheric measurements for interpretation

providing a good base for starting

Schedule of the lessons

08.03.23:

- introduction
- measurement strategiesdesign of a station
- measurements of trace compounds (1)
- exercise: measurement strategy

15.03.23:

- measurements of trace compounds (2)
- exercise: quality assurance
- instrument exhibition/exercise: contamination

historic development of air pollution

local

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

regional

global

Measurement strategies and quality assurance

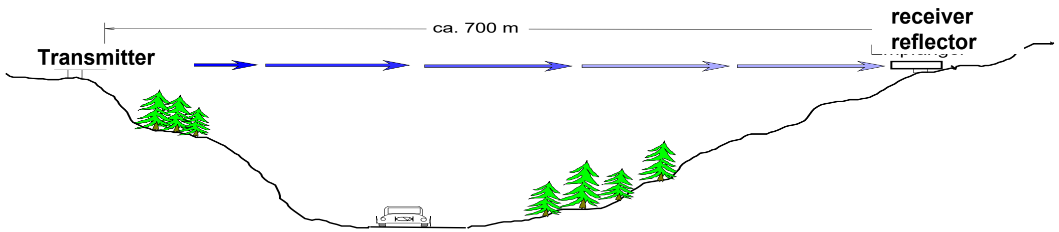
Measurement strategies

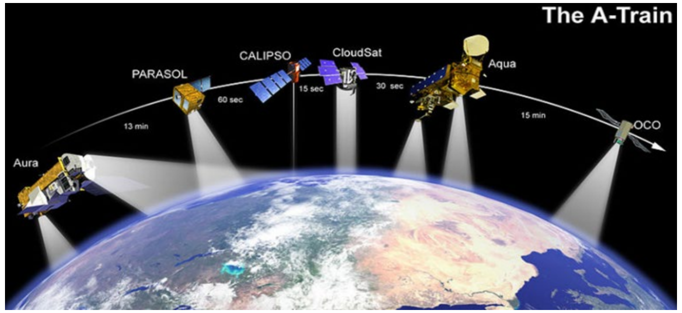
- *why are ambient air measurements performed?*
  legislation (limit values), research
- *which compounds should be measured?*
  gases, particles
- *time resolution of the measurements?*
  continuous (<second, minute,hour,day)? non-continuous?
  limit values: hourly/annual means?
- *location of the measurements?*
  stack emissions (chimney), urban air, background air, personal samplers (exposition) , fluxes (ecosystems)
  is the sampled air representative?
  are there undesirable sources nearby?)

two principal measurement strategies

- **with sampling (in-situ)**
  - online, automatic analysis at site (monitor)
  - quasi online (automated GC)
  - offline, sampling at site, analysis in laboratory
    (passive samplers)

- **without sampling** (**remote sensing**, ground-based/satellites)
  - DOAS (Differential Optical Absorption Spectroscopy)
  - FTIR (Fourier Transformation Infrared Spectroscopy)
  - LIDAR (Light Detection and Ranging
  - TDLS (Tuneable Diode Laser Spectroscopy)





Introduction to measurements of trace gases in the atmosphere

1. Regional/National networks (mostly for legislation)
- e.g. NABEL network, Switzerland

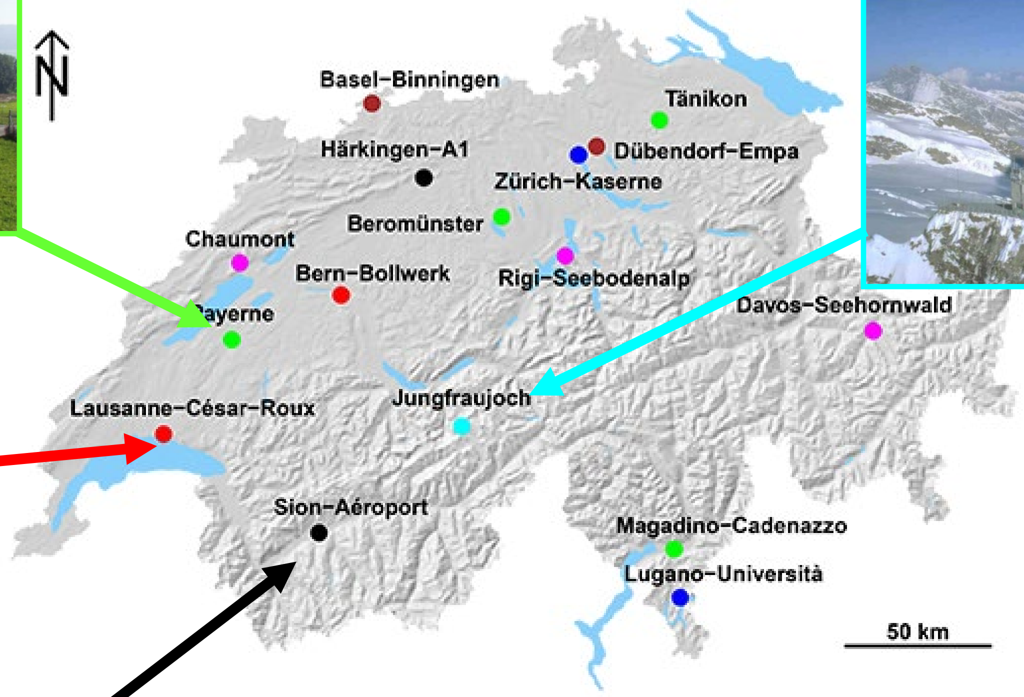
2. Global networks (for detection of trends/source regions)
- in-situ (NOAA/AGAGE)
- airplanes (e.g. CARIBIC)
- Remote sensing (ground-based, e.g. FTIR, NDAAC)
- Remote sensing (satellites)

3. Emission measurements
- stack emissions/tail-pipe emissions (in-situ/remote sensing)
- tunnel measurements/street canyon/highway
- flux measurements (ecosystems)

4. Exposition measurements
- Personal samplers, models including human behaviour (indoor vs. outdoor)

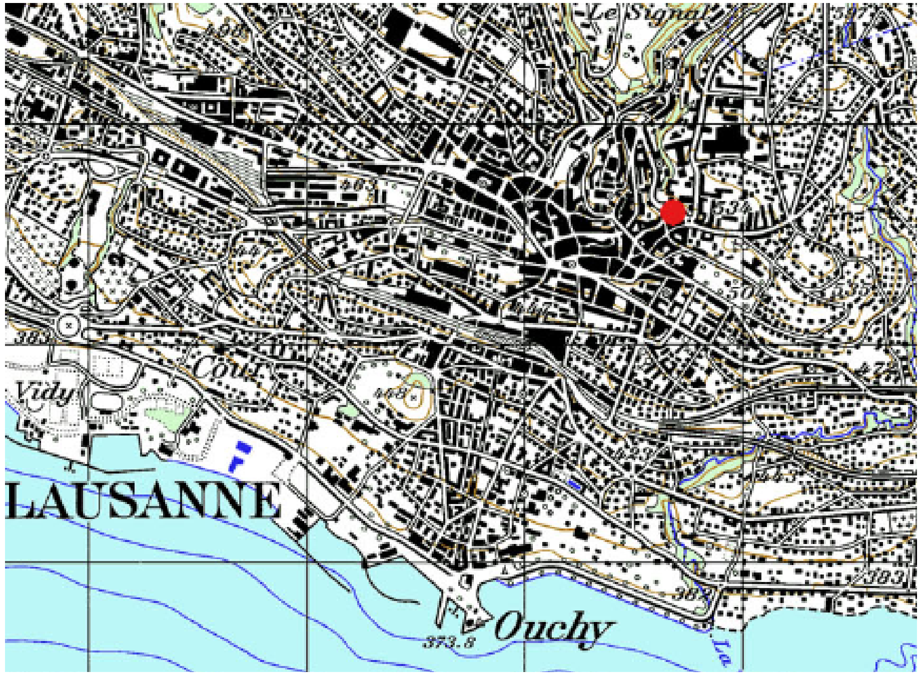
5. Scientific campaigns (various aims)

1. Swiss Network for Air Pollution Monitoring NABEL

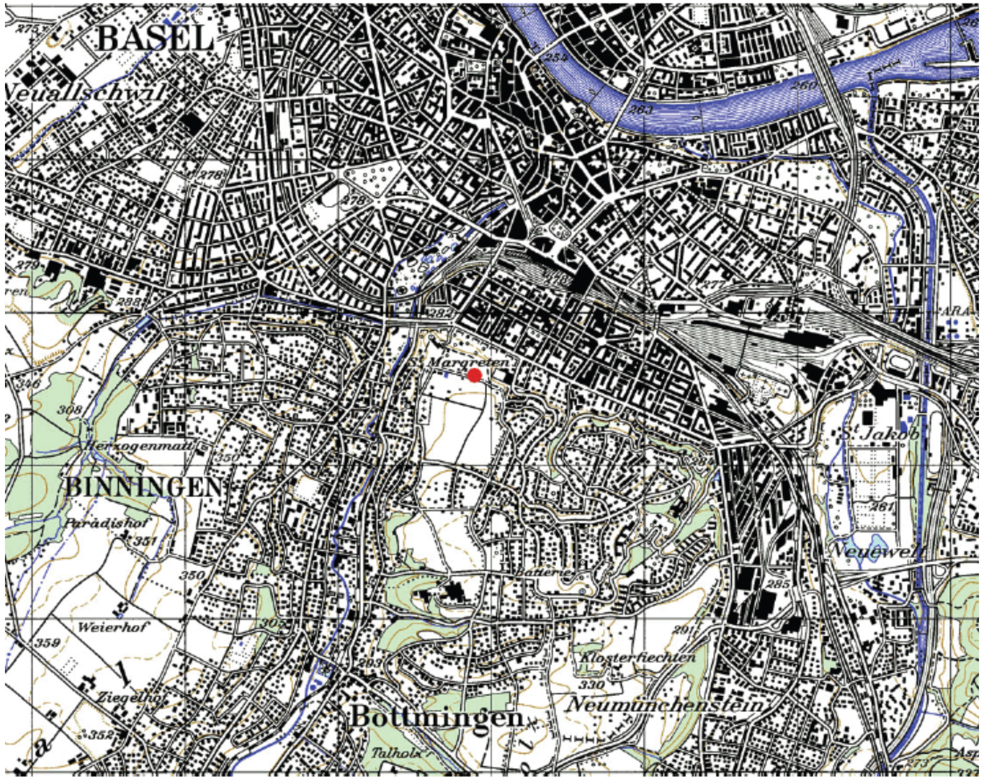


- City center, street
- City center, park
- Rural, highway
- rural, below 1000 m
- rural, above 1000 m
- agglomeration
- high-Alpine

NABEL
Station Lausanne



NABEL
Station Basel-Binningen

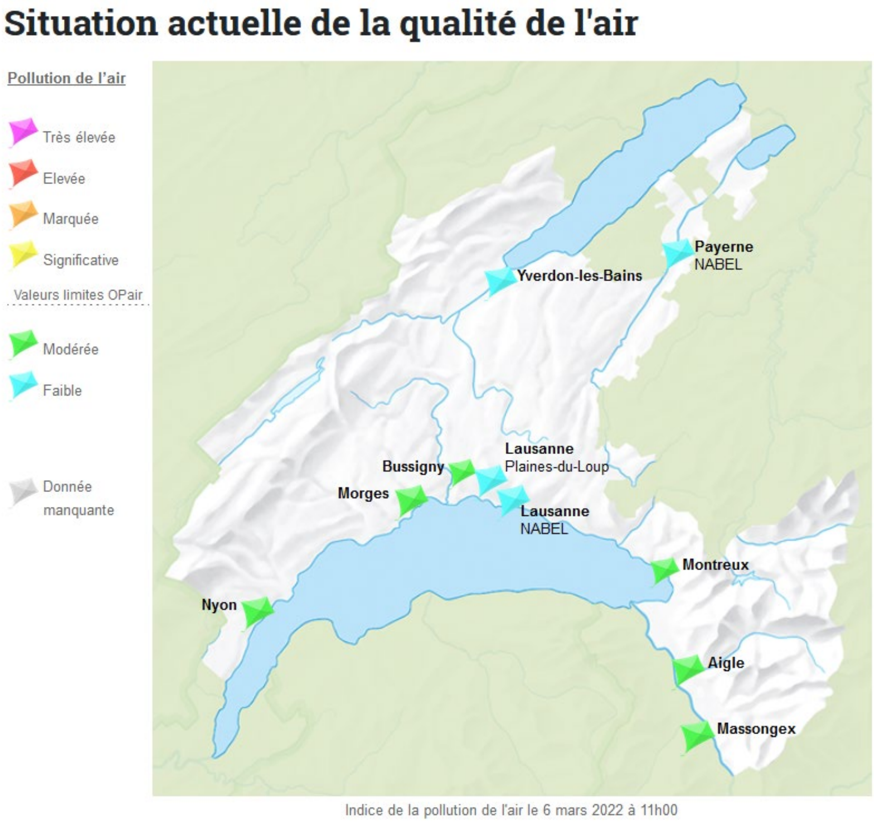


Canton Vaud

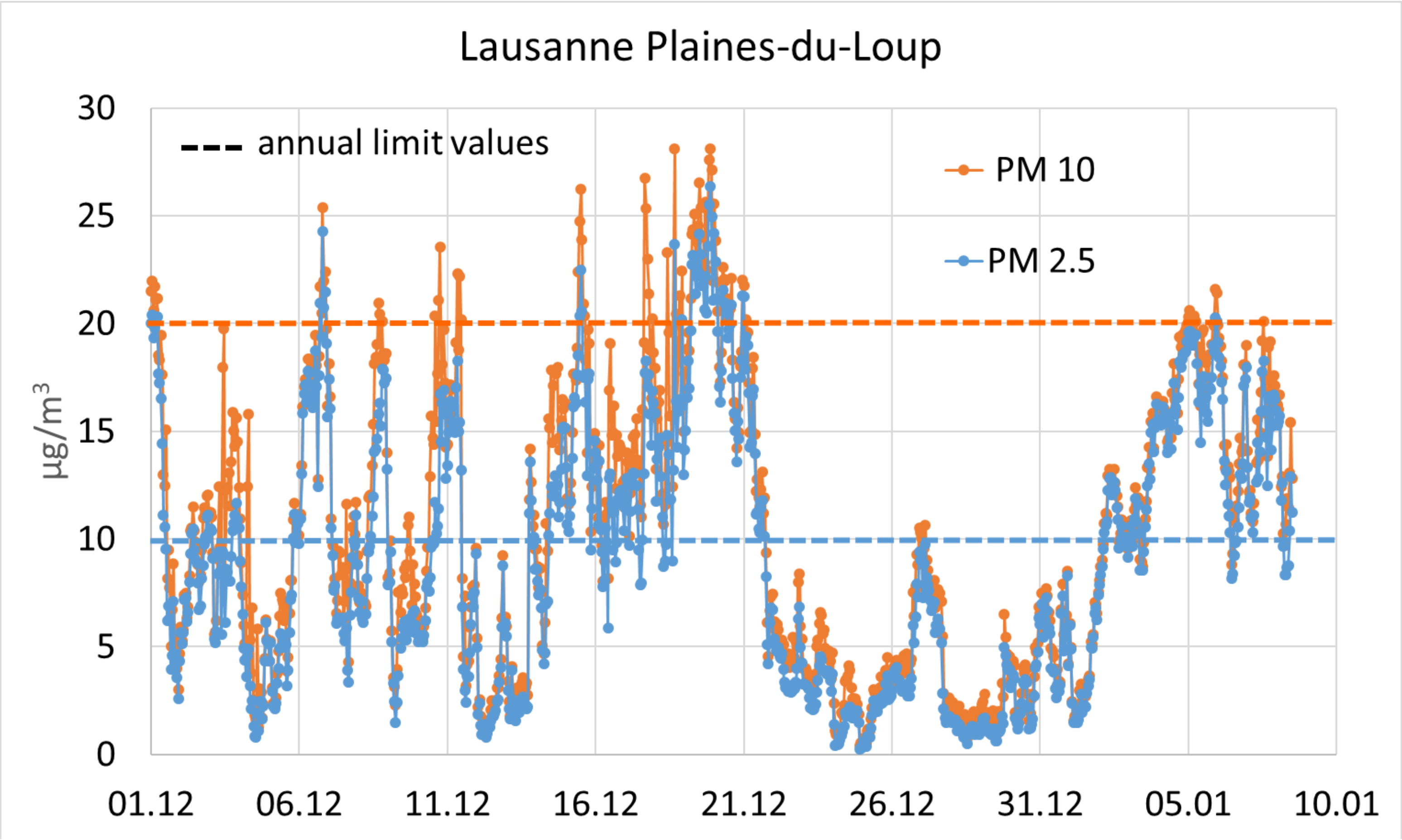
https://www.vd.ch/themes/environnement/air/qualite-de-lair/

App: airCHeck

Sunday, 06.03.22

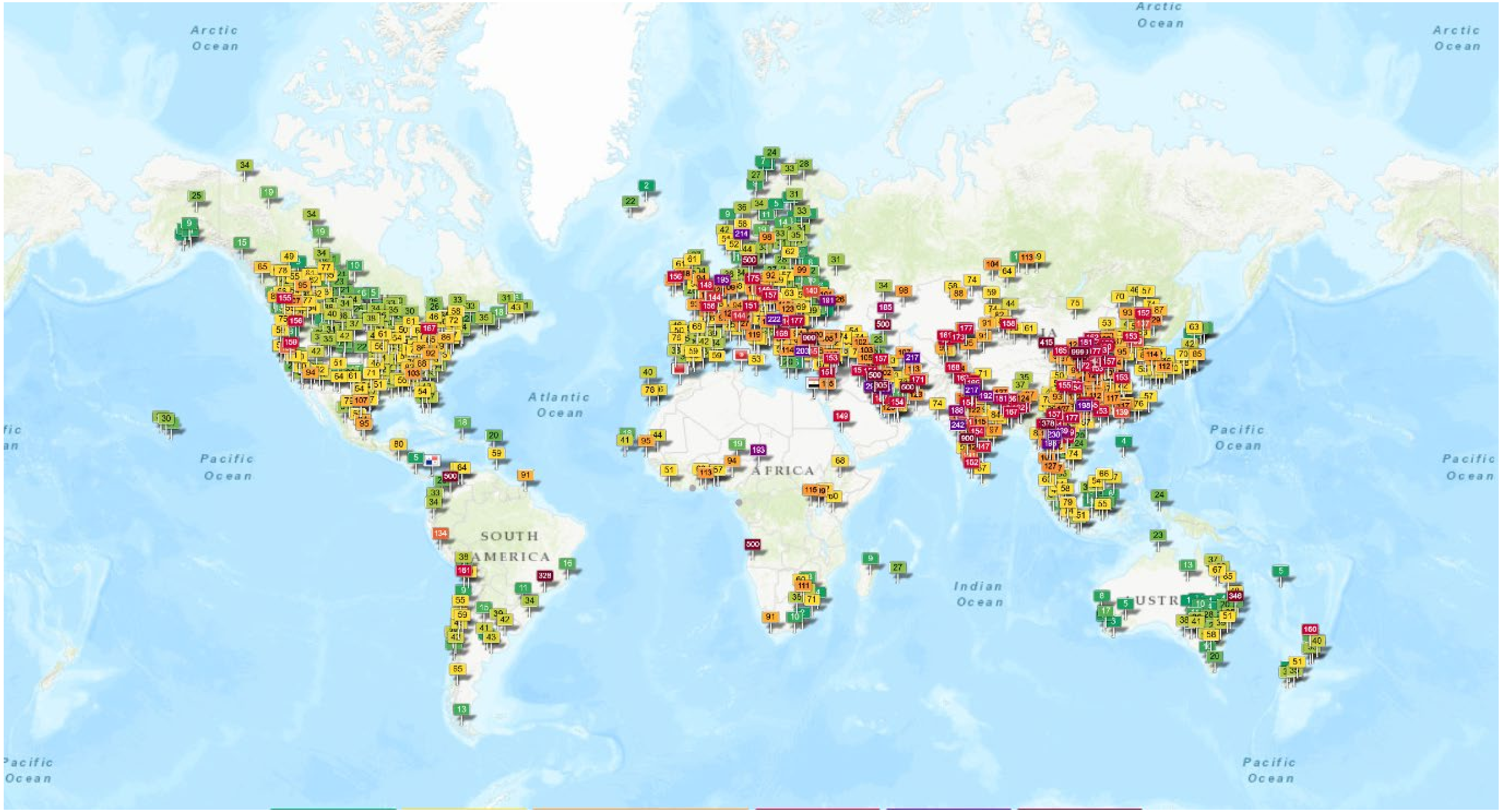


December 2021



lobal air pollution ressource
http://aqicn.org/map/world

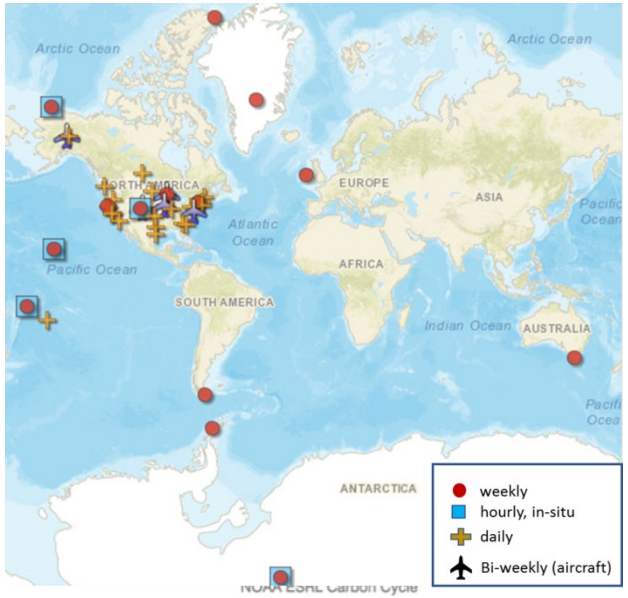
Air Quality Indices



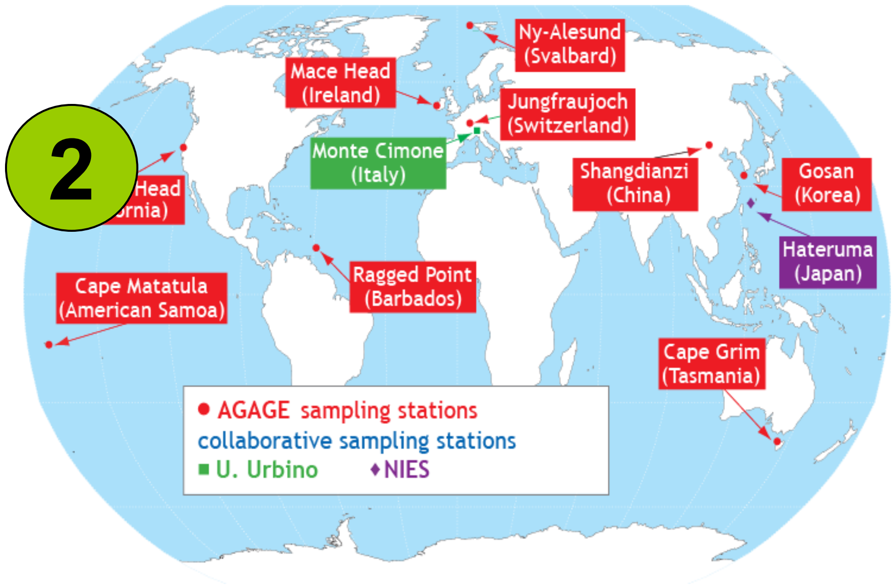
Global networks (ground-based, continuous)

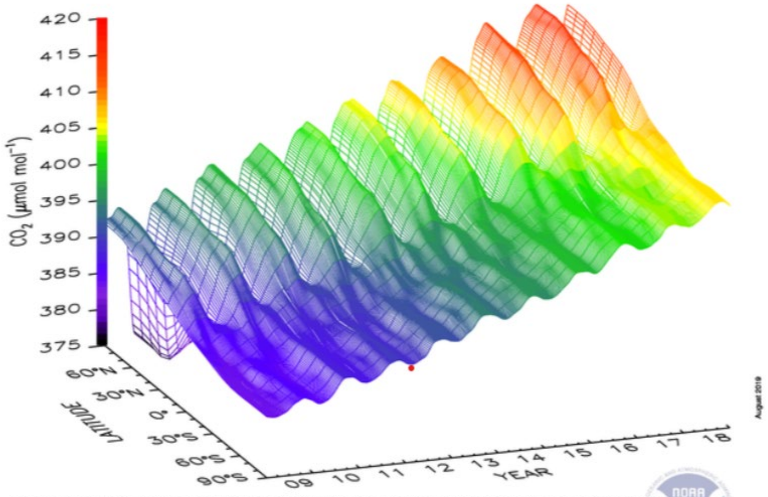
1. NOAA flask measurement programme for CO_2/CH_4/N_2O/halocarbons
2. AGAGE network for halocarbons/CH_4/N_2O

1

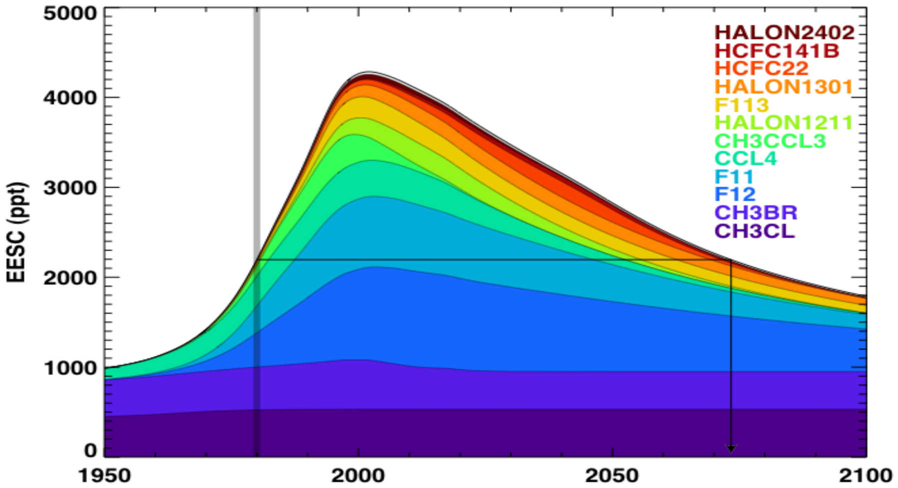


2



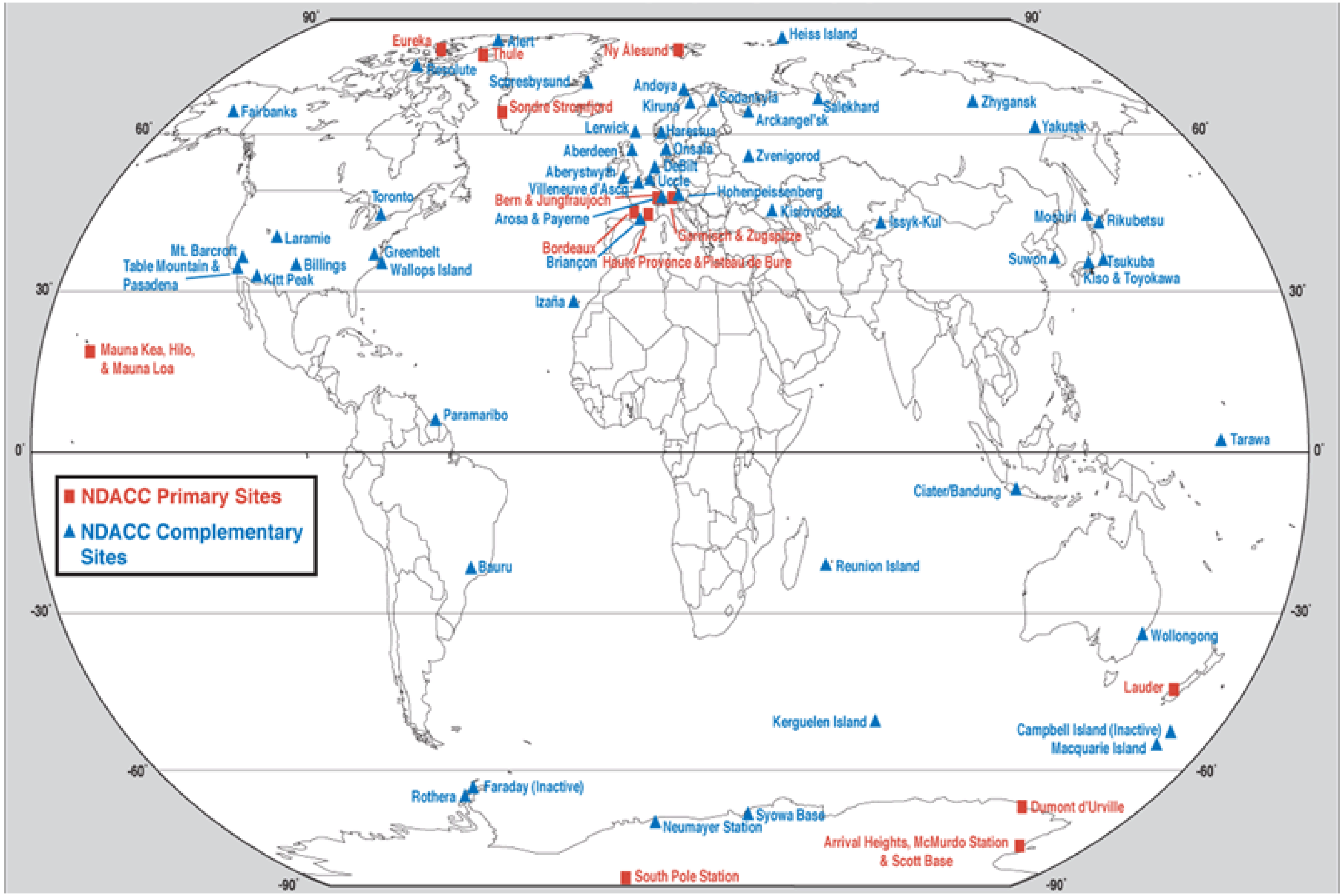


Three-dimensional representation of the latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer. Data from the Carbon Cycle cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Contact: Dr. Pieter Tans and Dr. Ed Dlugokencky, NOAA ESRL Carbon Cycle, Boulder, Colorado, (303) 497-6678, pieter.tans@noaa.gov, http://www.esrl.noaa.gov/gmd/ccgg/.



2. Global networks

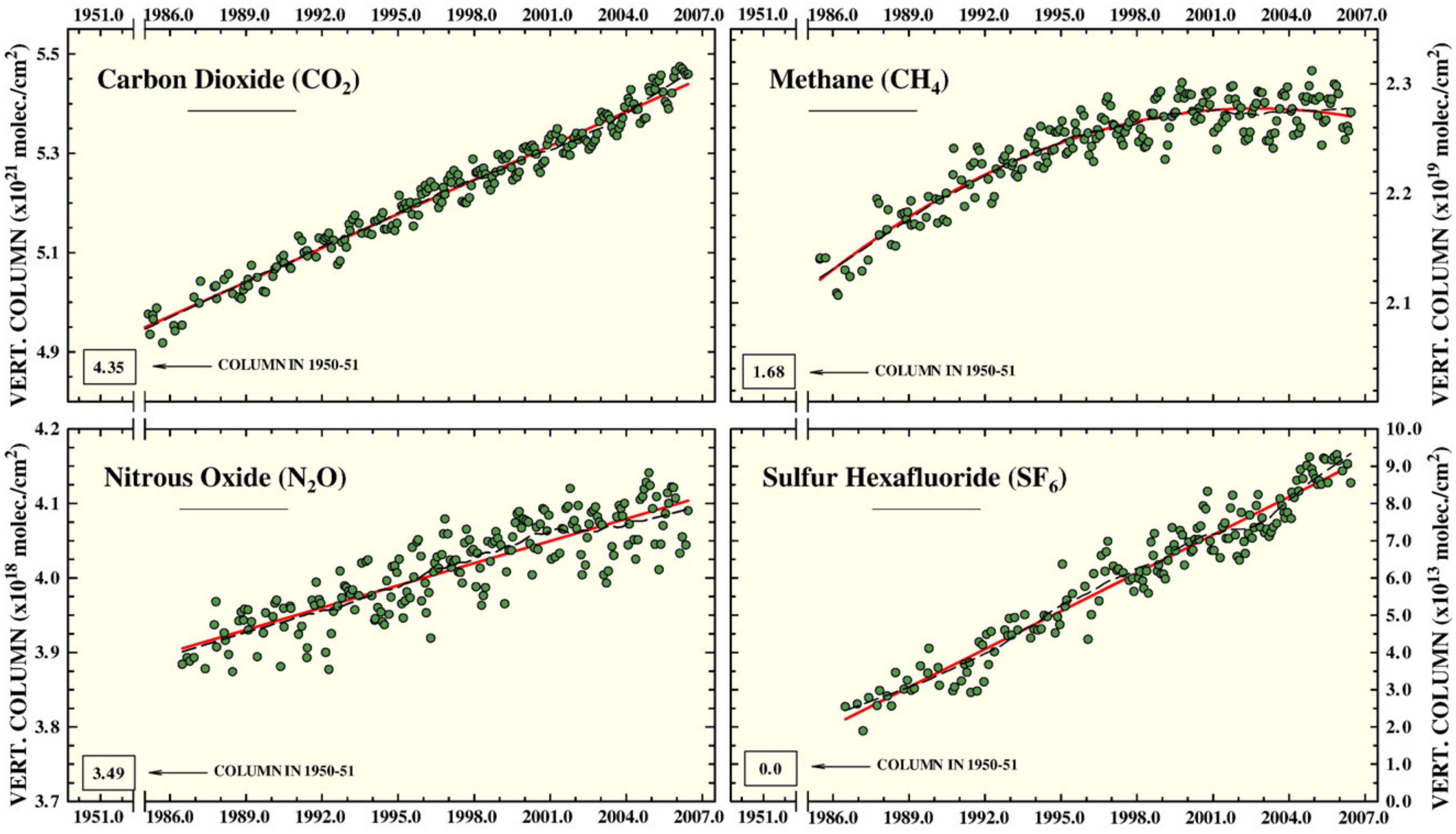
NDACC (Network for Detection of Atmospheric Composition Change)



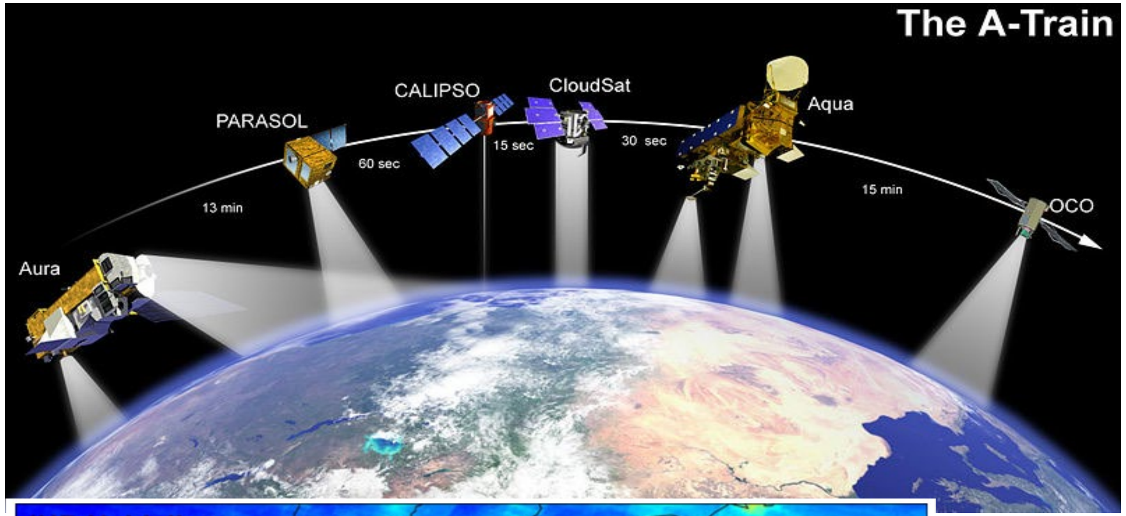
2. Global networks

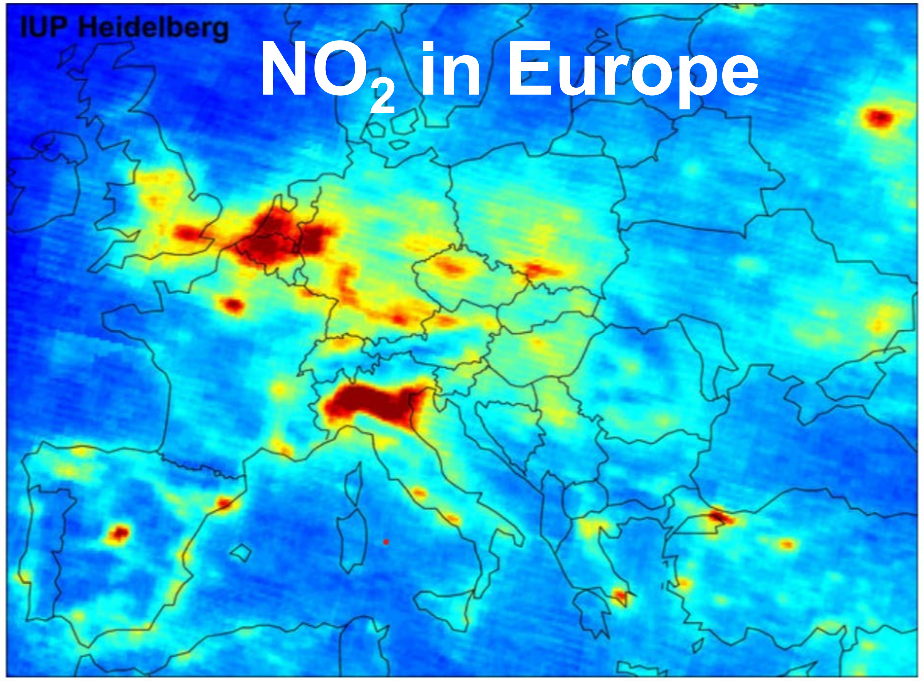
NDACC

FTIR measurements at Jungfraujoch



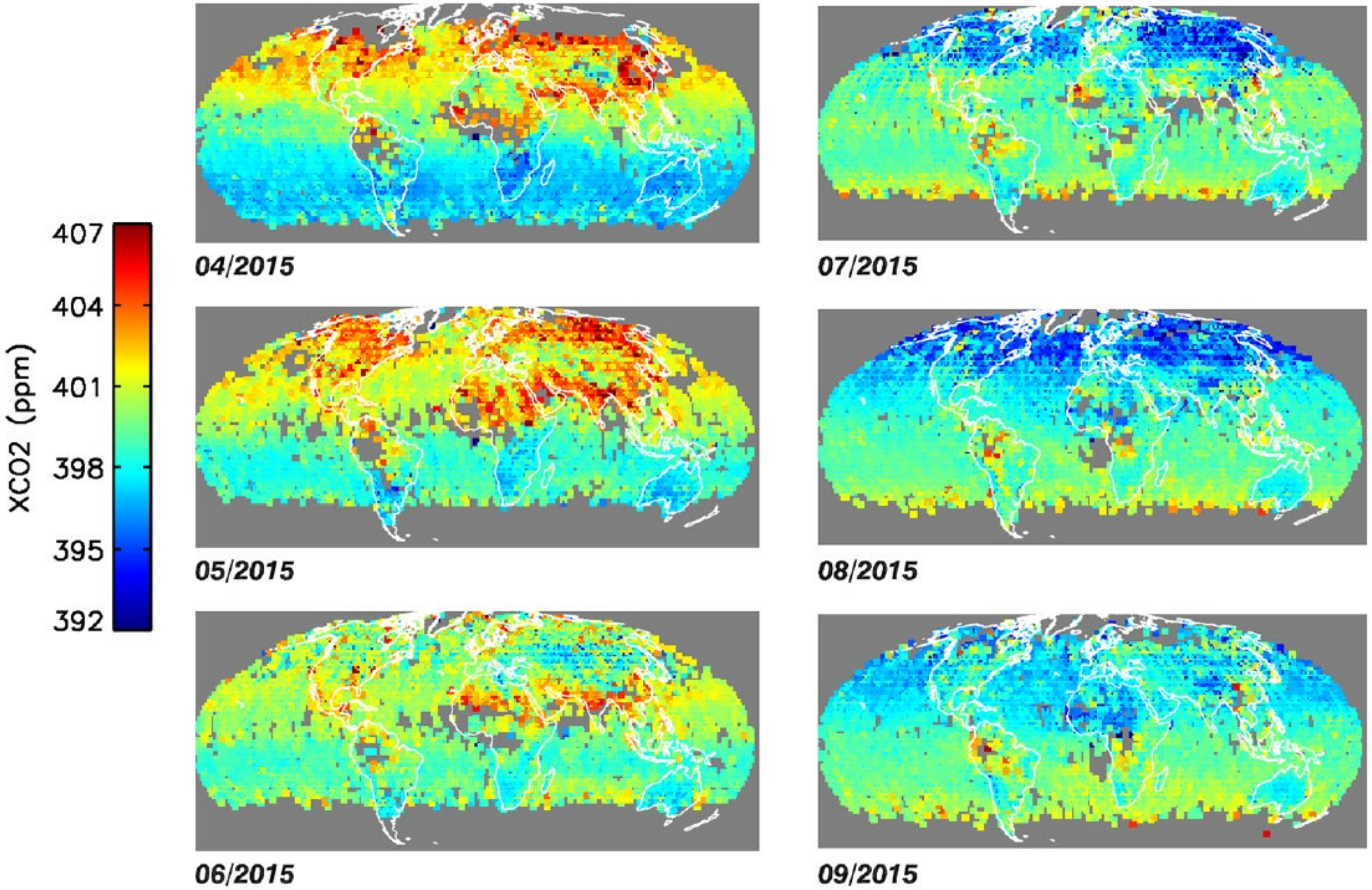
Remote sensing: Global networks
satellites



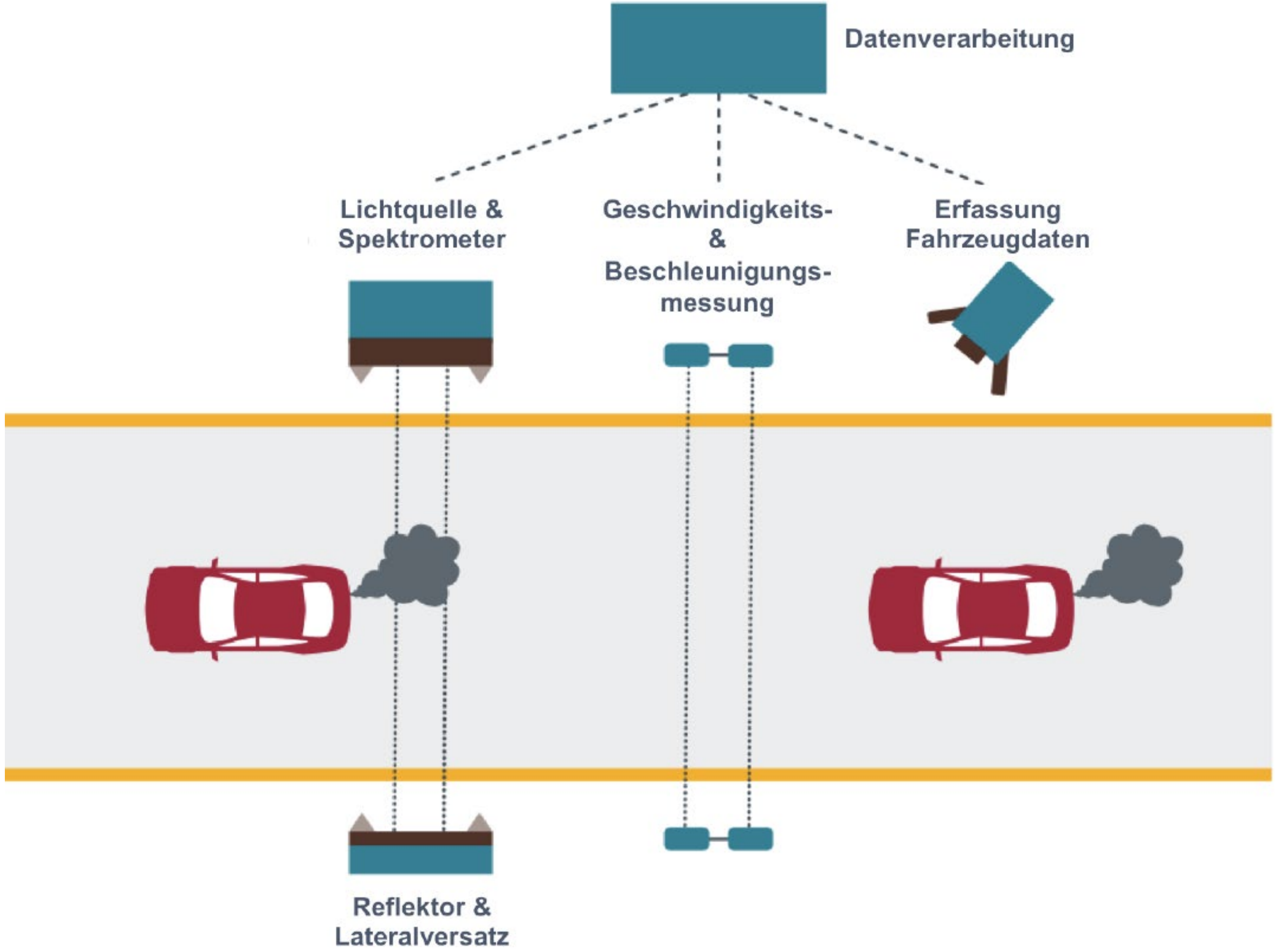


http://www.esa.int/Our_Activities/Observing_the_Earth/Envisat/

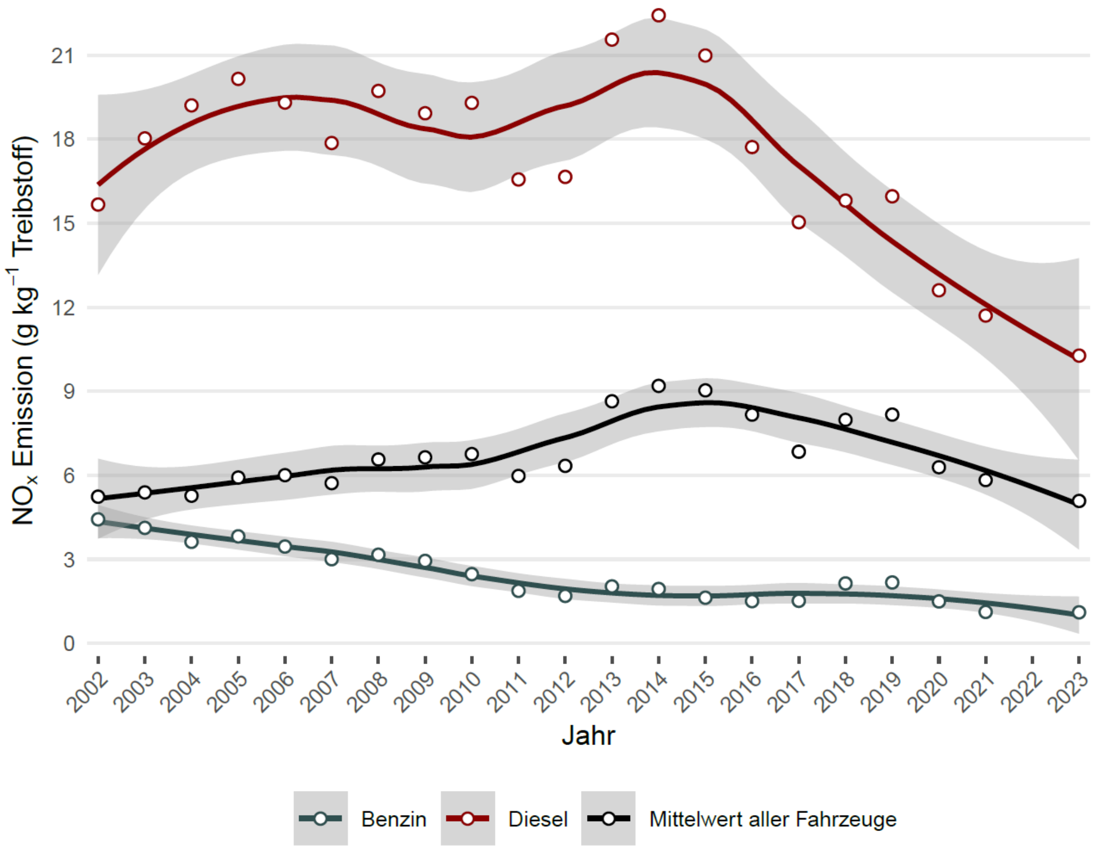
CO_2 from OCO-2
Eldering et al., 2016

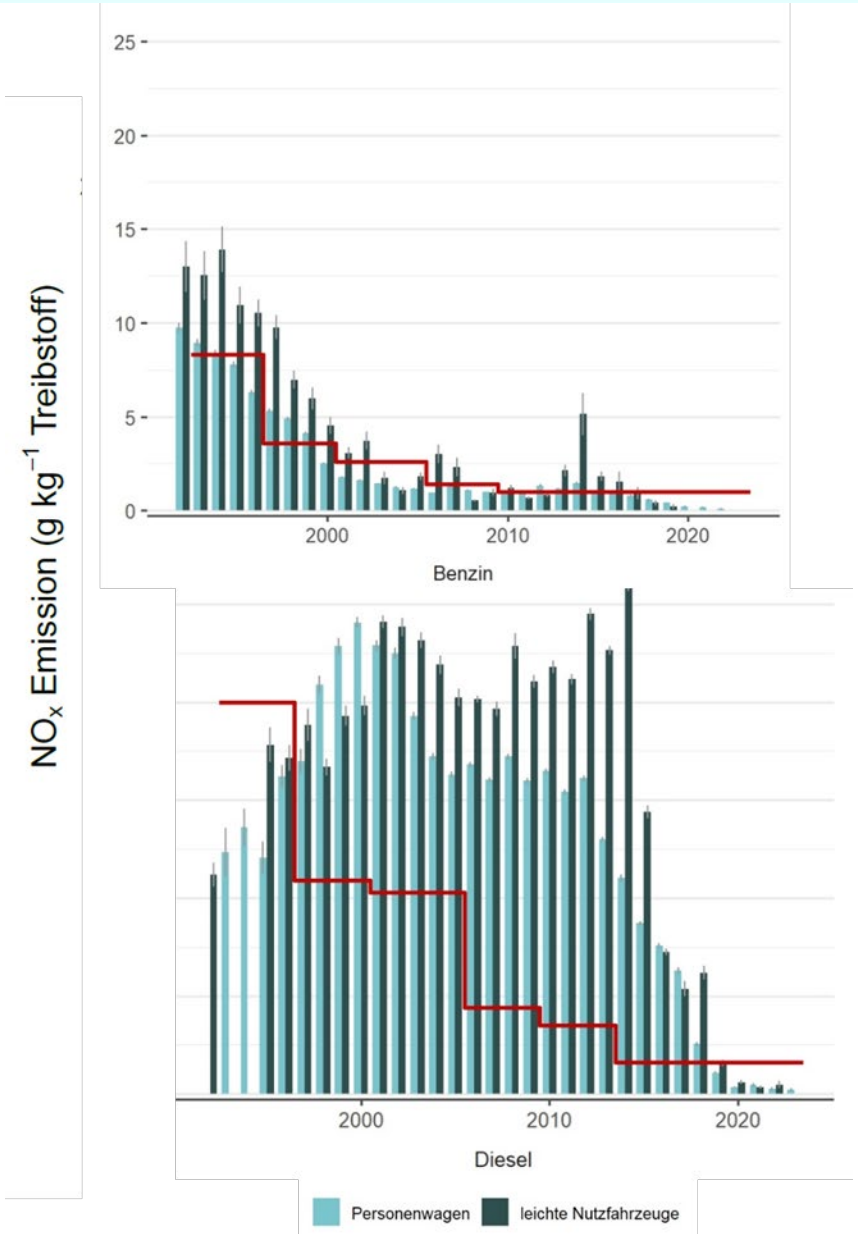


3. Emission in-situ: Remote Sensing: NO_x Messungen Kanton Zürich



NO_x measurements Canton Zürich



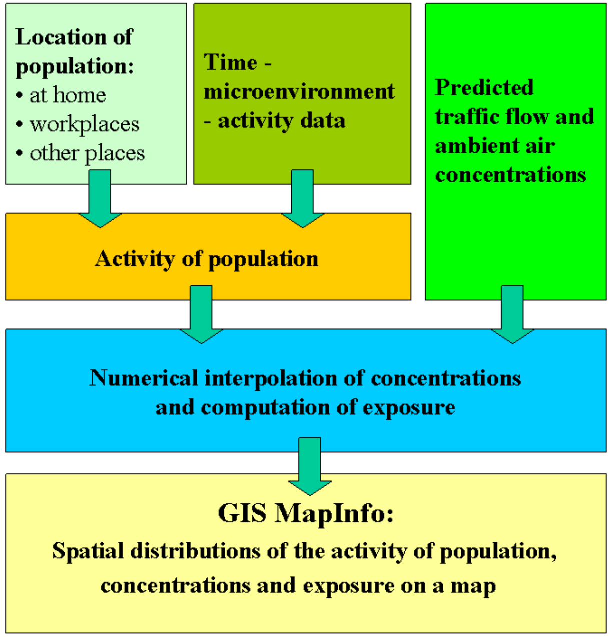


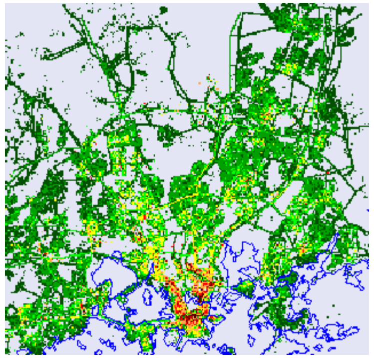
Langjährige Abgasmessungen im realen Fahrbetrieb mittels Remote Sensing, Kt. Zürich, 2024

Mobile in-situ measurements for NO_2, particles, CO and CO_2
PEMS (Portable Emission Monitoring System)

4. Exposure measurements personal samplers

Personal passive samplers





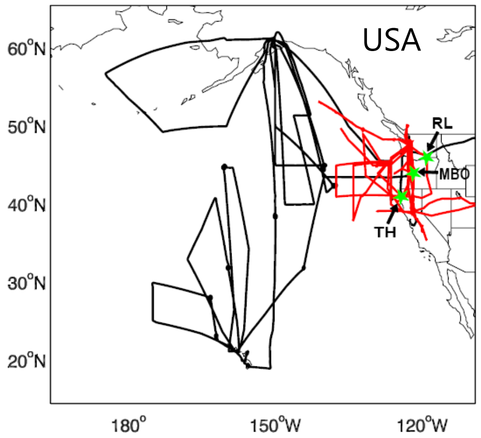
The predicted exposure of population to NO_2 in the afternoon (3 - 6 p.m.), in March 1996, ($\mu g/m^3$ *persons).

Ref. Kousa, A., et al., 2002.

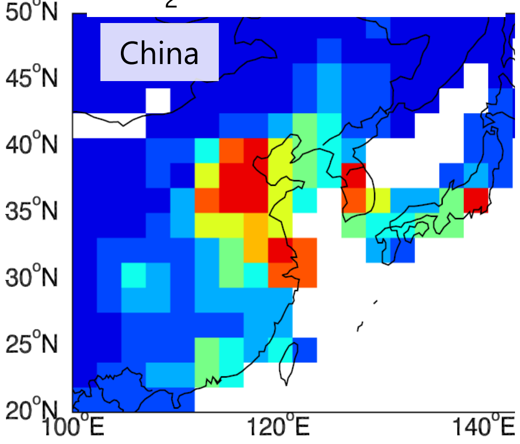
5.Scientific campaigns
(in-situ, air planes, satellites, modelling)

INTEX-B campaign (2006)

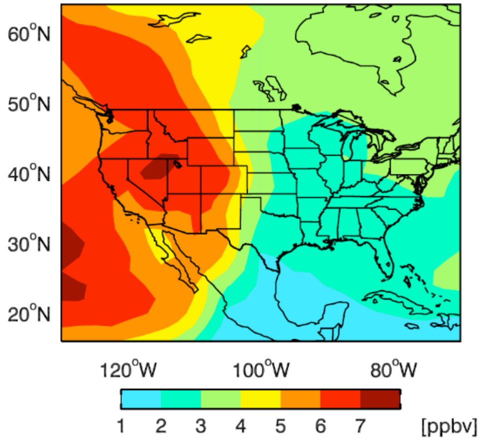
in-situ/air planes



NO_2 from OMI satellite



Chemical-Transport Model



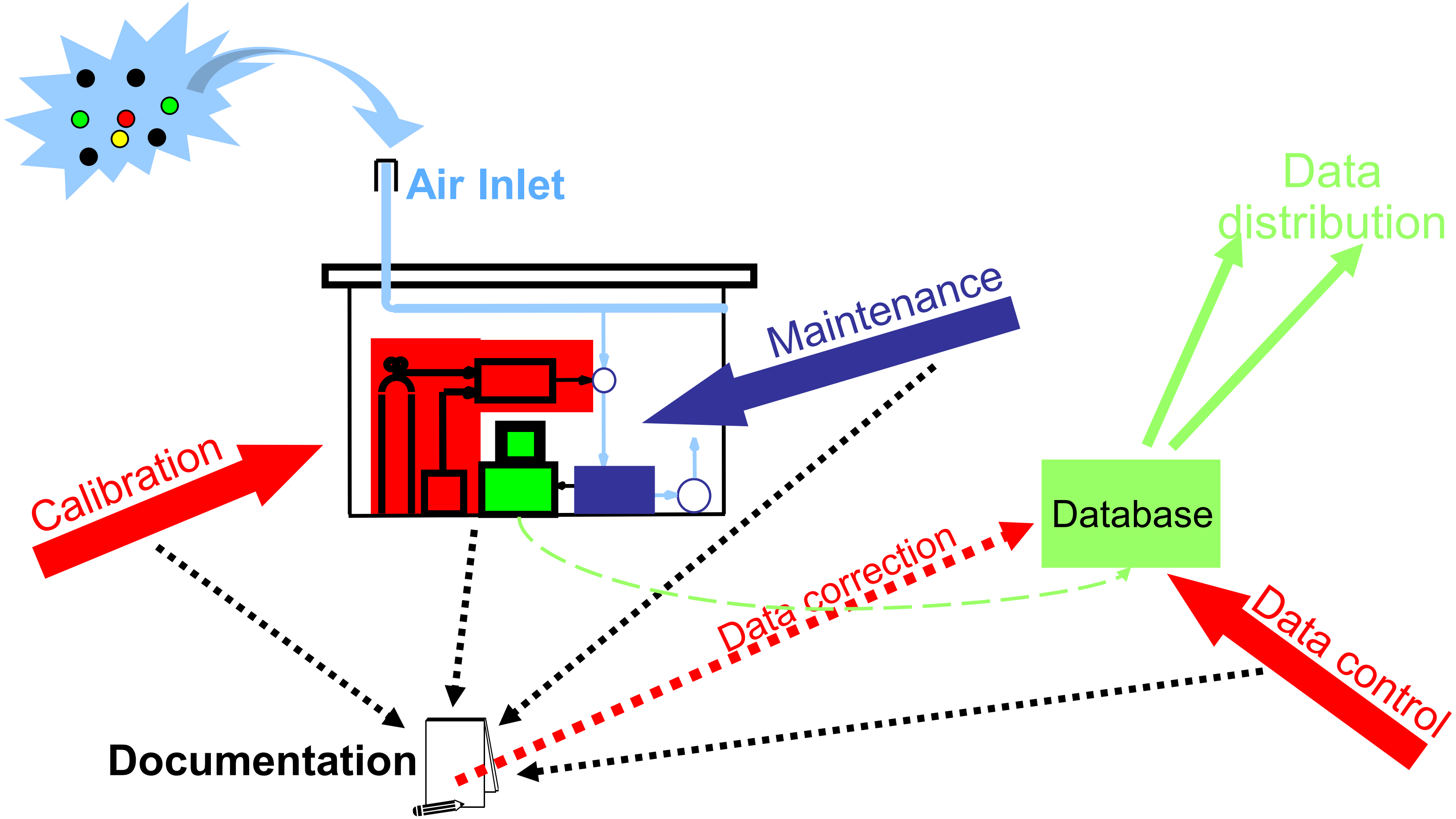
Asian O_3 enhancement

Zhang et al., ACP, 2008

quality assurance

example NABEL

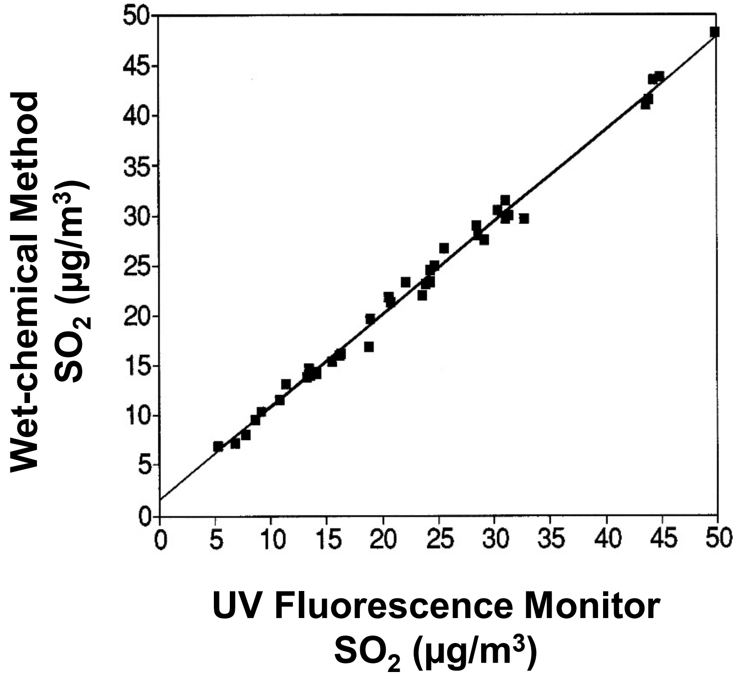
Swiss Network for Air Pollutant Monitoring

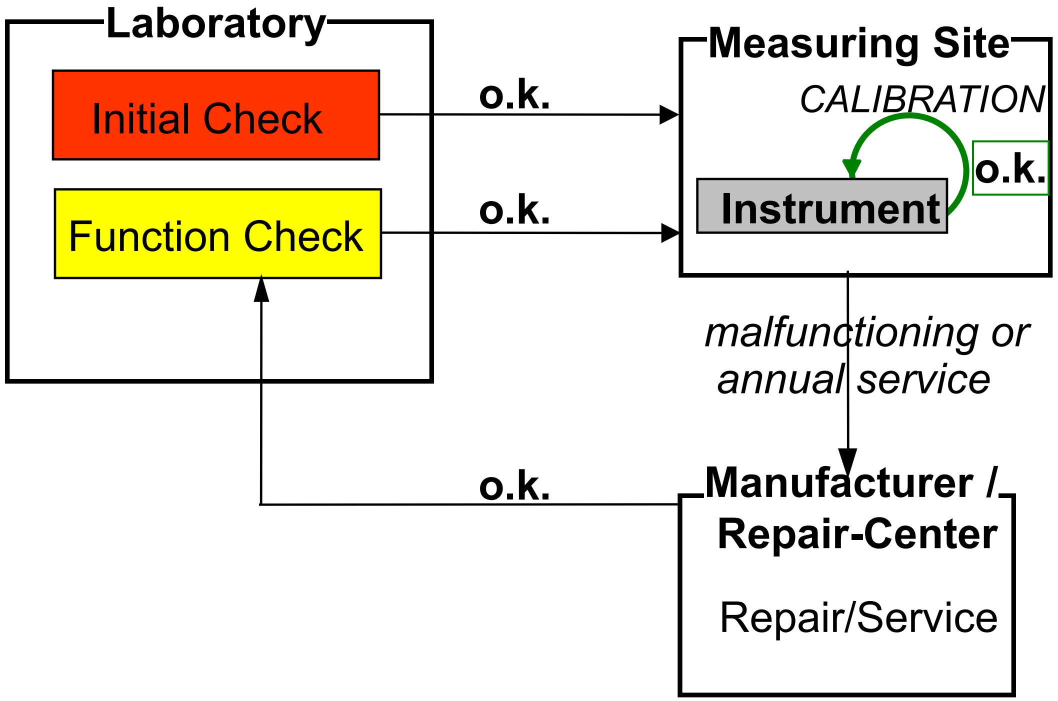


NABEL
Quality Assurance

- adequate measuring instrument
- air inlet/distribution device/pump
- data acquisition system
- traceability of calibration gases (to international references)
- calibration device/dilution unit
- calibration gases/zero air
- periodic maintenance
- manual data control/documentation
- meteorological data

NABEL
Equipment – Initial checks

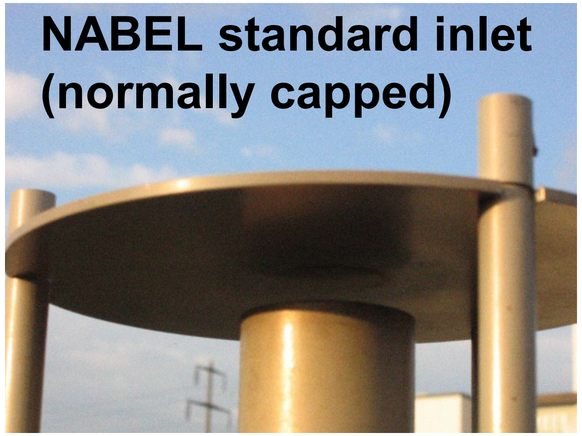




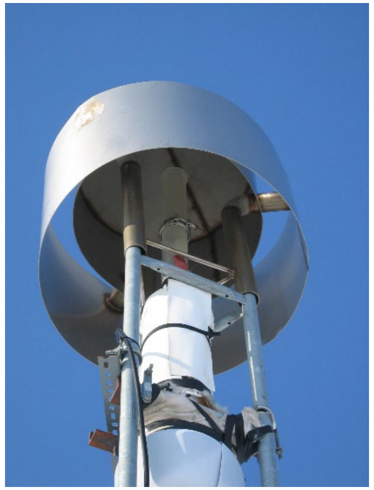
NABEL
Quality Assurance

- adequate measuring instrument
- air inlet/distribution device/pump
- data acquisition system
- traceability of calibration gases (to international references)
- calibration device/dilution unit
- calibration gases/zero air
- periodic maintenance
- manual data control/documentation
- meteorological data

NABEL
air inlet



other solutions



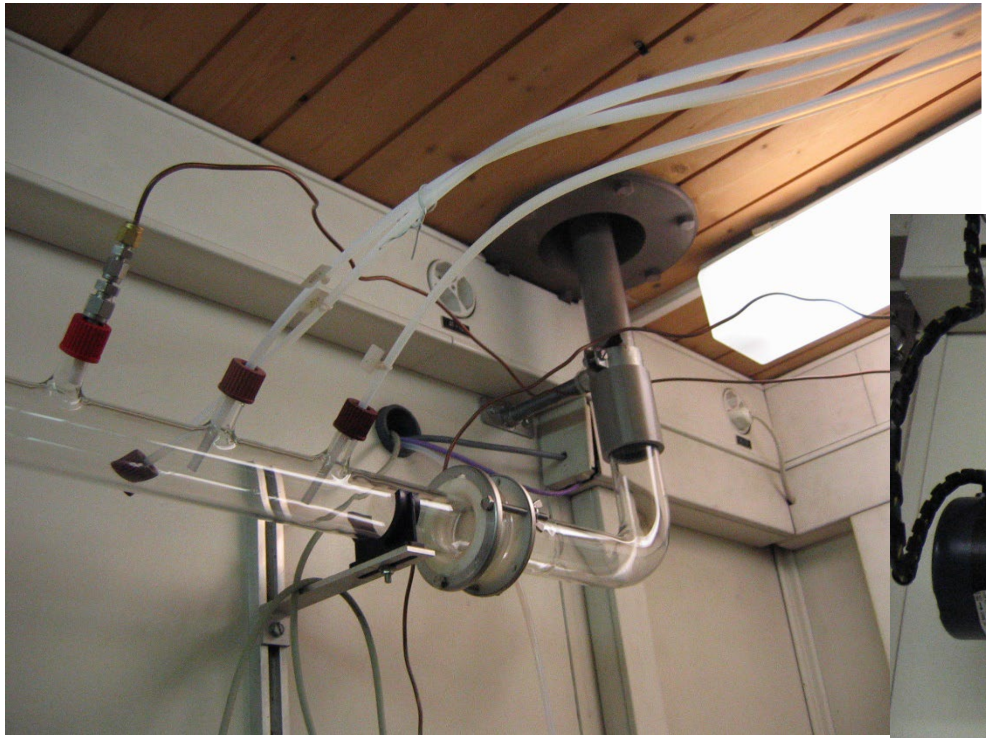
Alert, Canada

Mt. Kenia, Kenia

Ny-Alesund, Spitsbergen

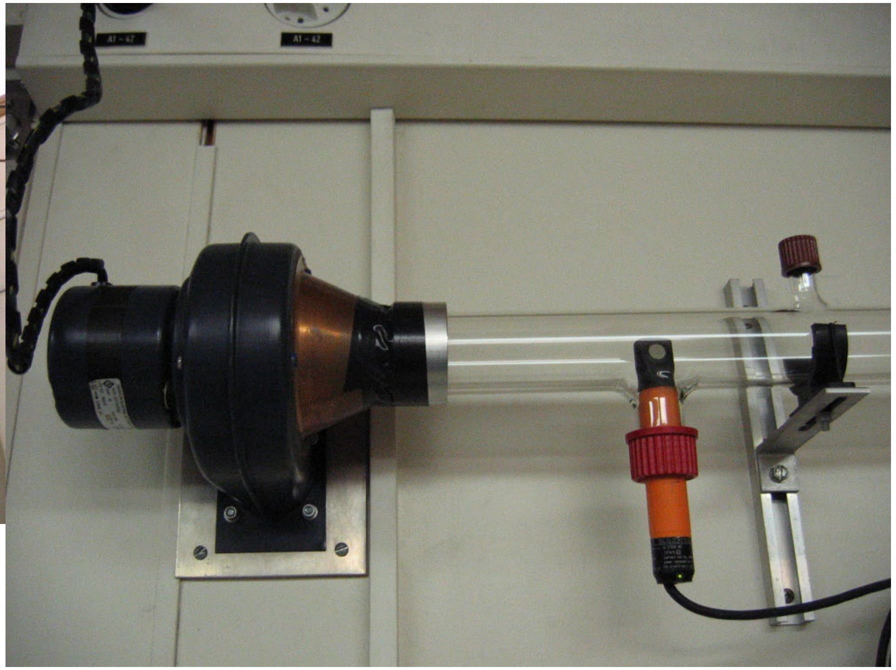
Mace Head, Ireland

NABEL
distribution device/pump



Glass manifold/tubing to instruments

Flow: 100 liter/min



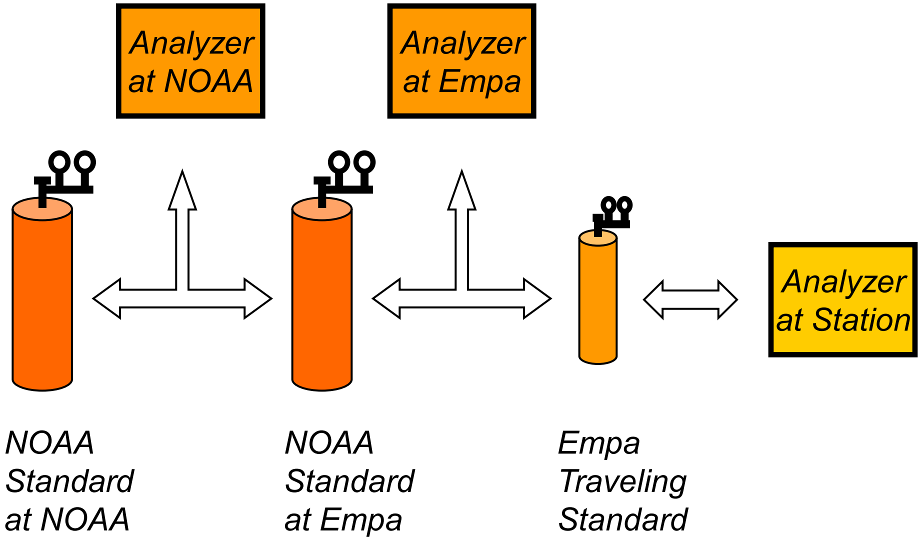
Pump/air flow meter

NABEL
Equipment – Quality Assurance

- adequate measuring instrument
- air inlet/distribution device/pump
- data acquisition system
- traceability of calibration gases (to international references)
- periodic maintenance
- calibration device/dilution unit
- calibration gases/zero air
- manual data control/documentation
- meteorological data

NABEL
international traceability

Stable gases
(CO, NO_2, CO, SO_2)



Inter-Comparison | *Inter-Comparison (and Calibration)* | *Inter-Comparison (and Calibration)*

Non-stable gases
O_3

NIST SRP#2 ⇔ **EMPA SRP#15** ⇔ ***EMPA TS*** ⇔ ***Station OM***

__S__tandard __R__eference __P__hotometer

__T__ransfer __S__tandard

__O__zone __M__onitor

NABEL traceability

stable gases

Empa-Lab

primary standards
NO, SO_2, O_3, CO

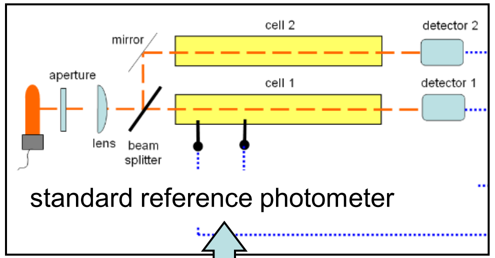
calibration

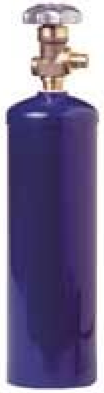
calibration instrument
Empa

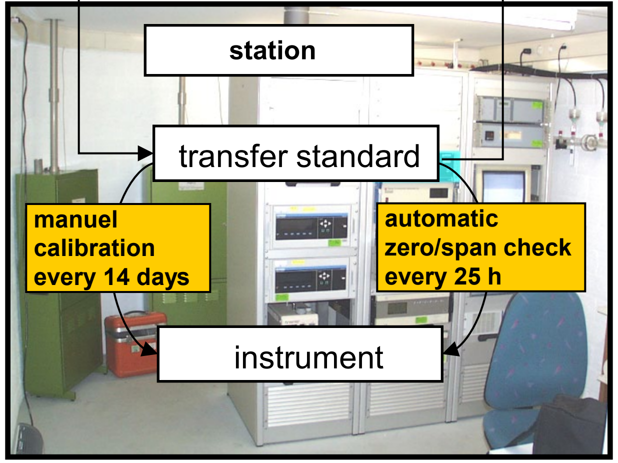
comparison

transfer standard

ozone







NABEL
Quality Assurance – periodic maintenance

- daily: check data availability/instrument status
  calibration zero / span checks

- 2-weekly: general preventive maintenance
  manual calibration
  check impact on data series

- annualy: final data check, submission to BAFU
  instrument check/replacement
  update standard operation procedures

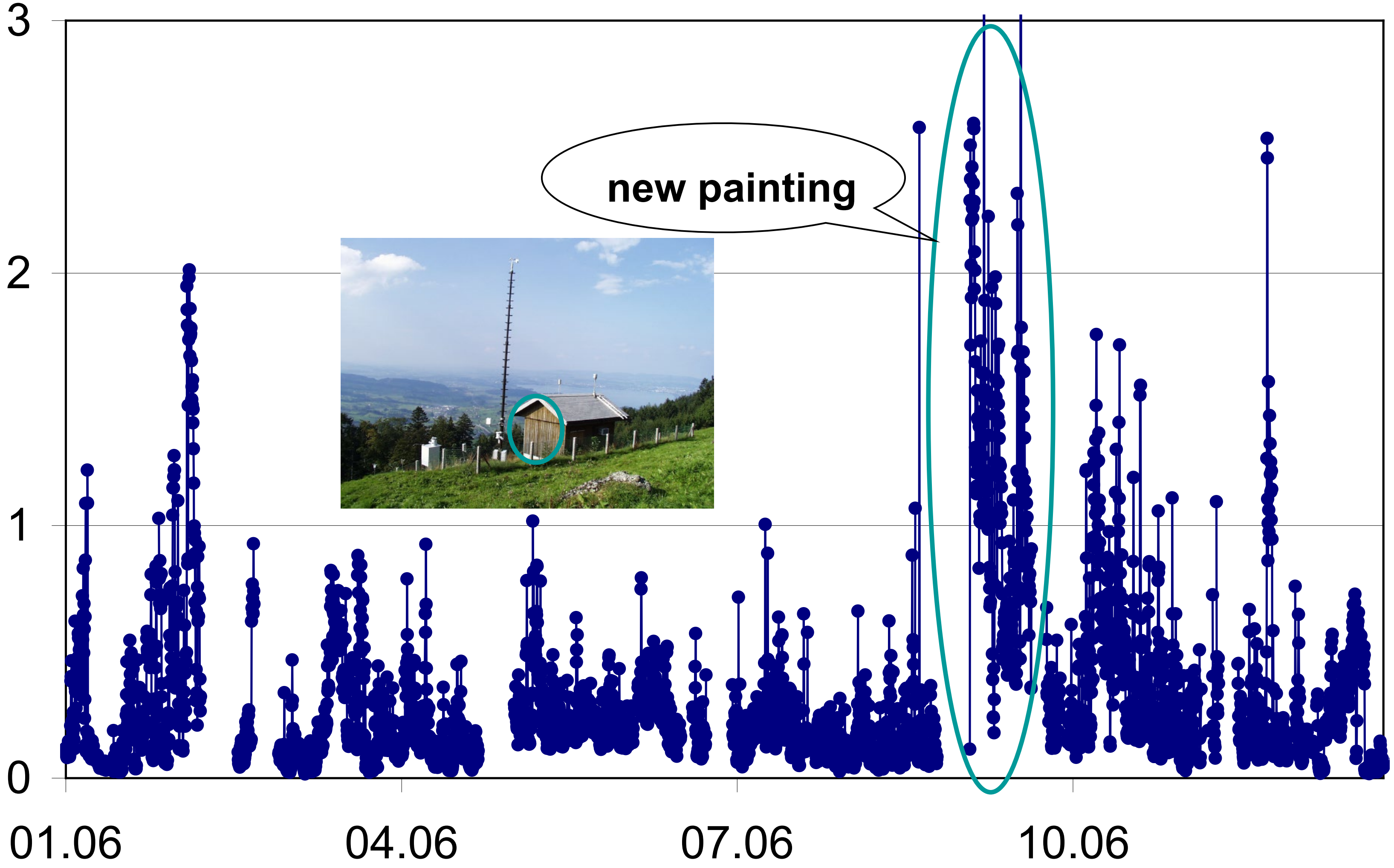
NABEL
Quality Assurance – Documentation

- instrument conditions (log book)
- maintenance procedures (SOP)
- calibration procedures (SOP)
- calibration data (zero/span)
- data control procedures
- data correction functions

NABEL
Quality Assurance – Data control

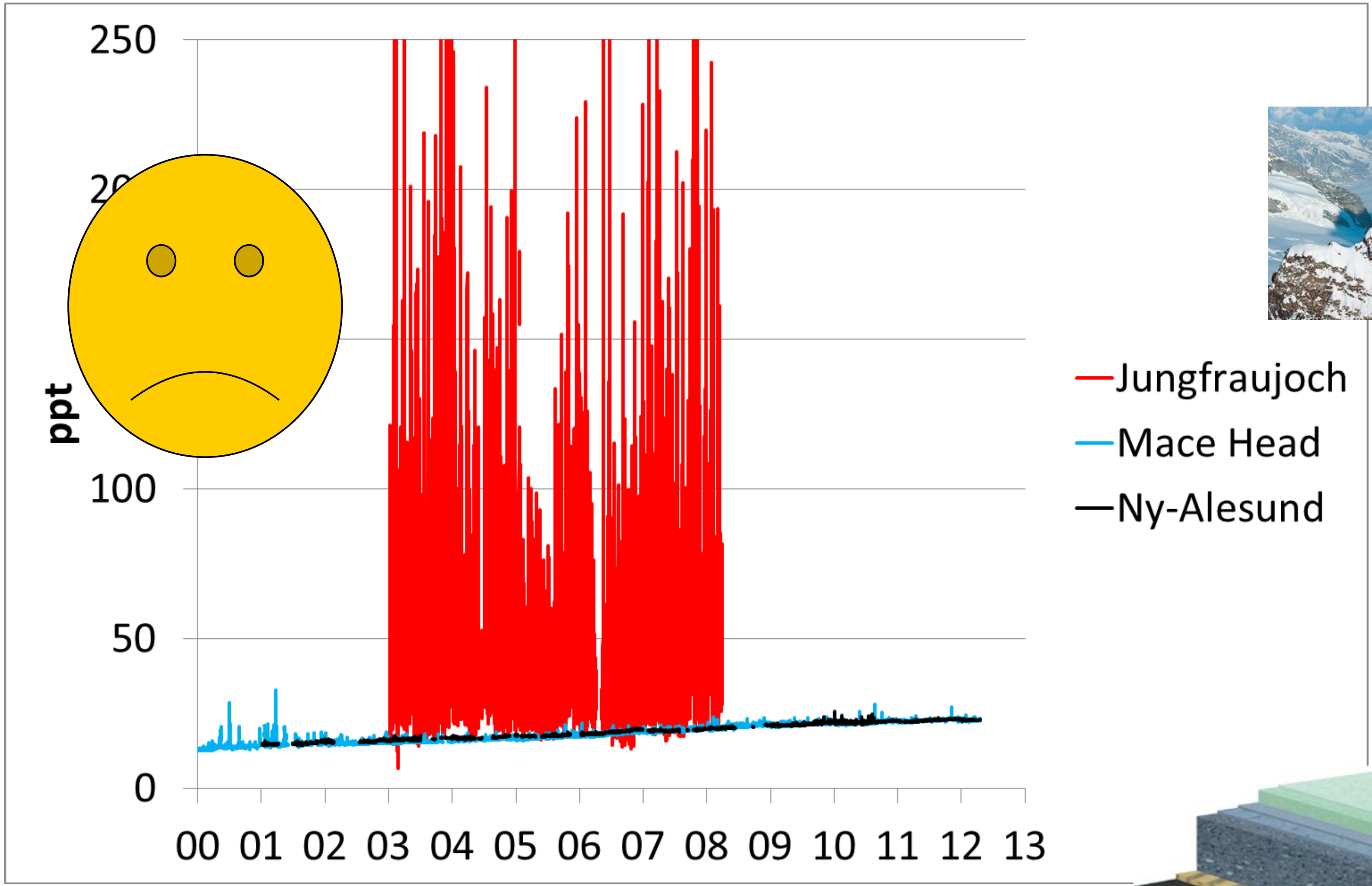
- apply calibration function
- include consequences of log book remarks
- internal data control procedure:
  - *check with plausibility limits/meteorology*
  - *look at daily and annual behaviour*
  - *check variability*
  - *compare with other compound*
  - *compare similar stations*
  - *check data before and after gap*
- possible external data control
- final data release

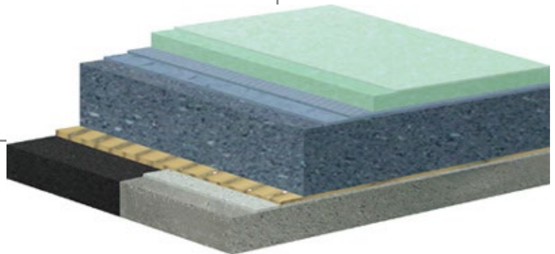
Data quality checks
contaminations
Example 1: toluene at Rigi (NABEL)



Quality Assurance – Data control

Example 2:
HCFC-142b at Jungfraujoch, Switzerland





Quality Assurance – Data control

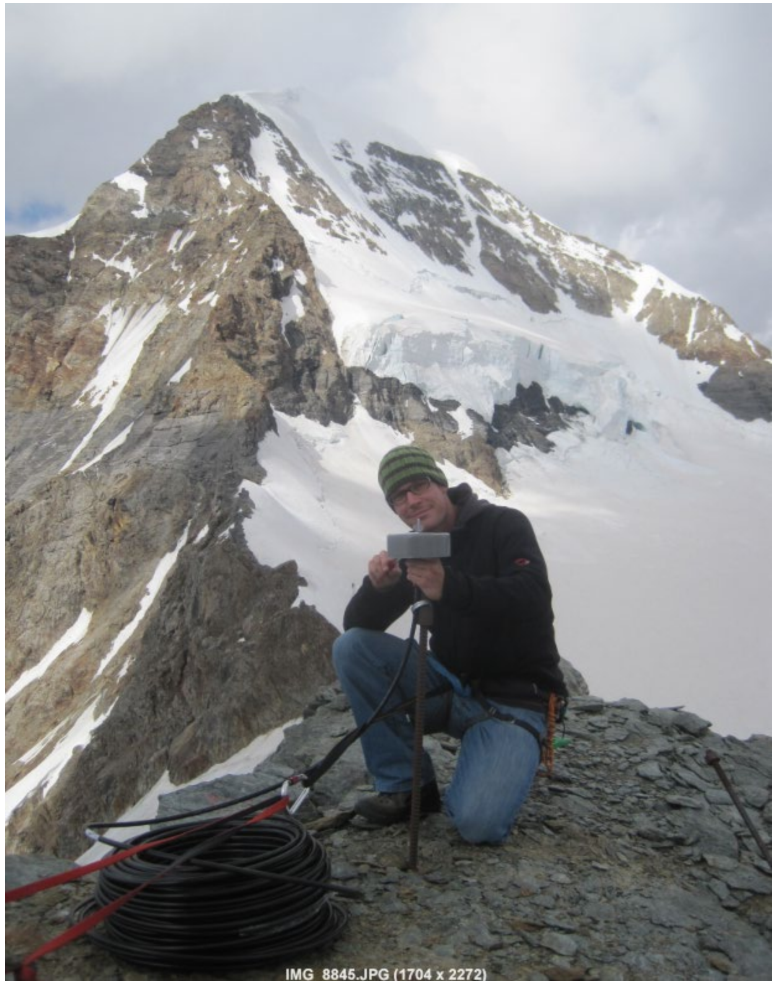
Example 2:
HCFC-142b at Jungfraujoch, Switzerland

relocation of the inlet: August 2012

Quality Assurance – Data control

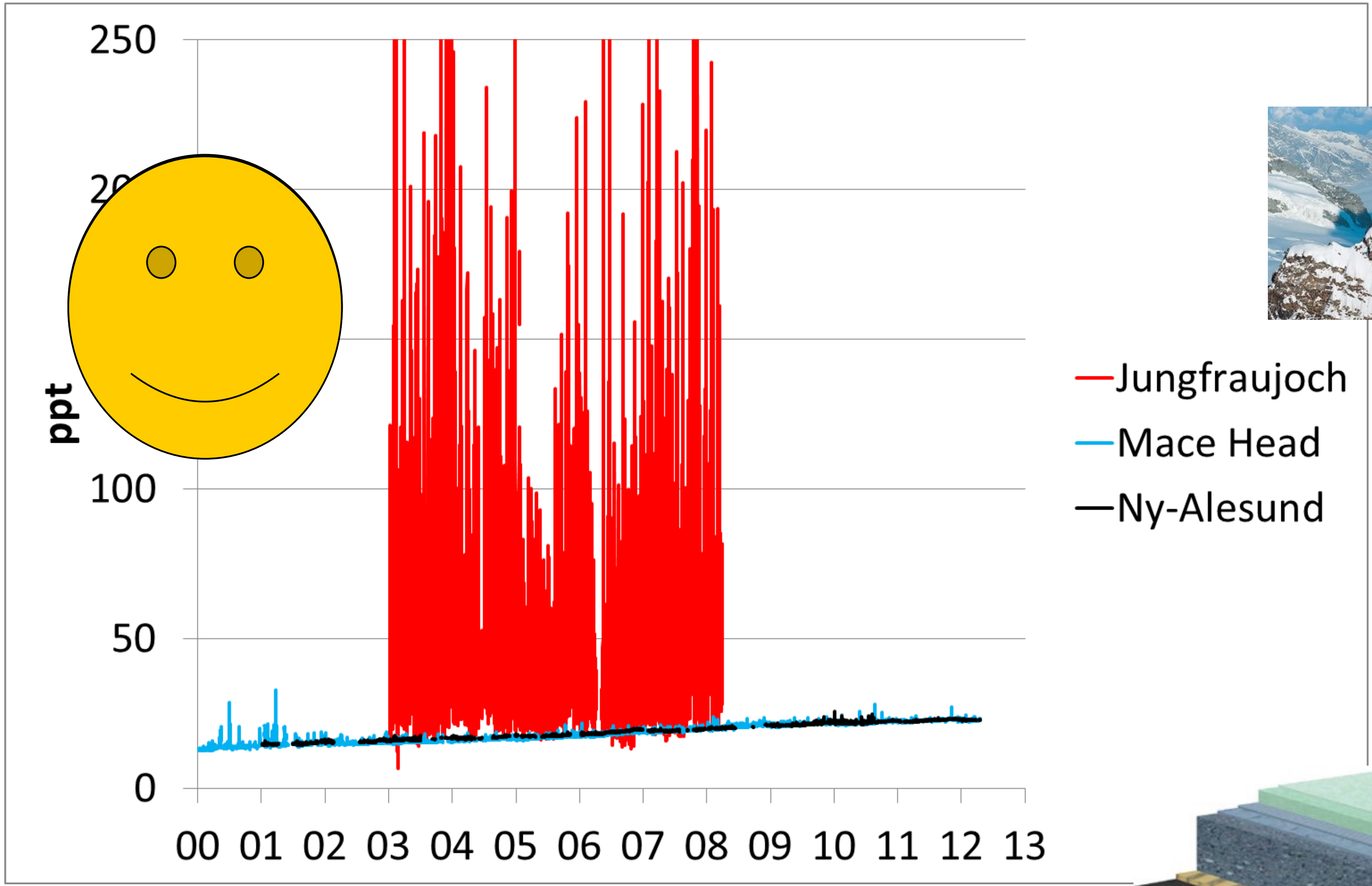
Example 2:
HCFC-142b at Jungfraujoch, Switzerland

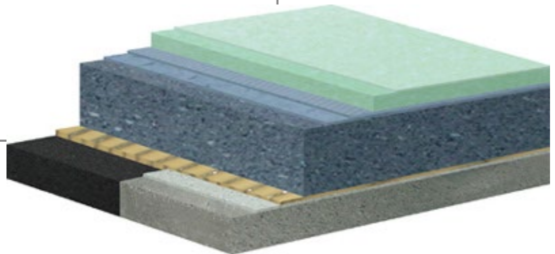
relocation of the inlet: August 2012



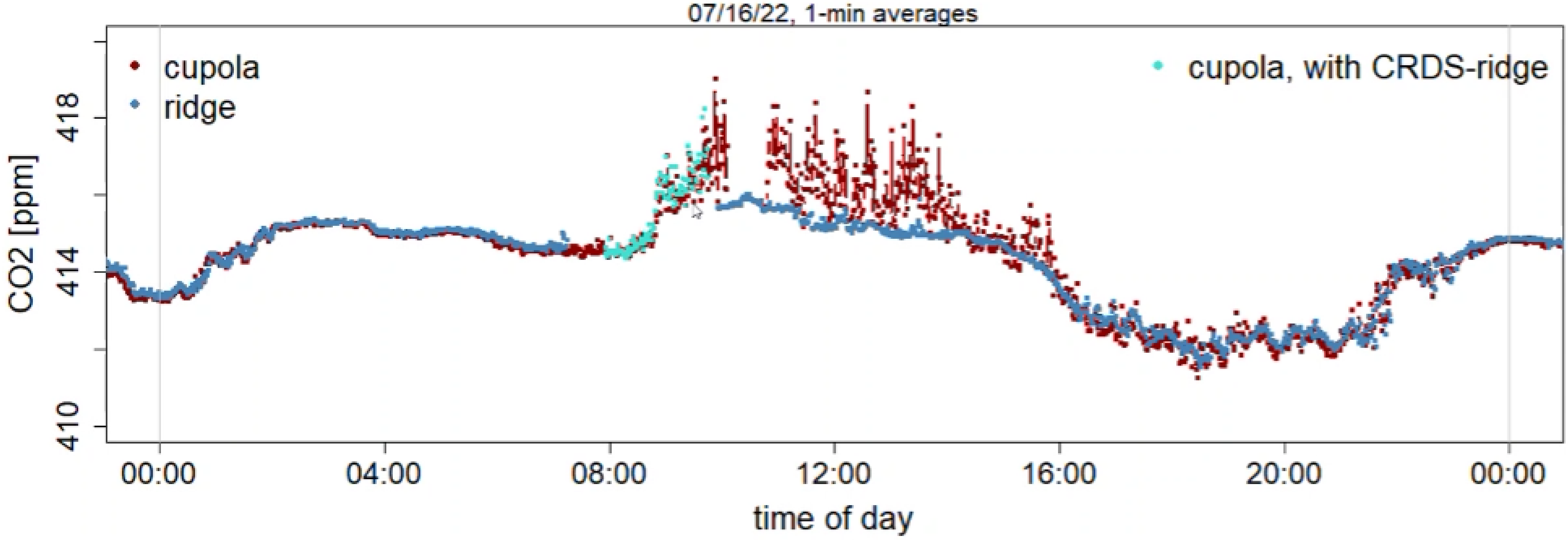
Quality Assurance – Data control

Example 2:
HCFC-142b at Jungfraujoch, Switzerland



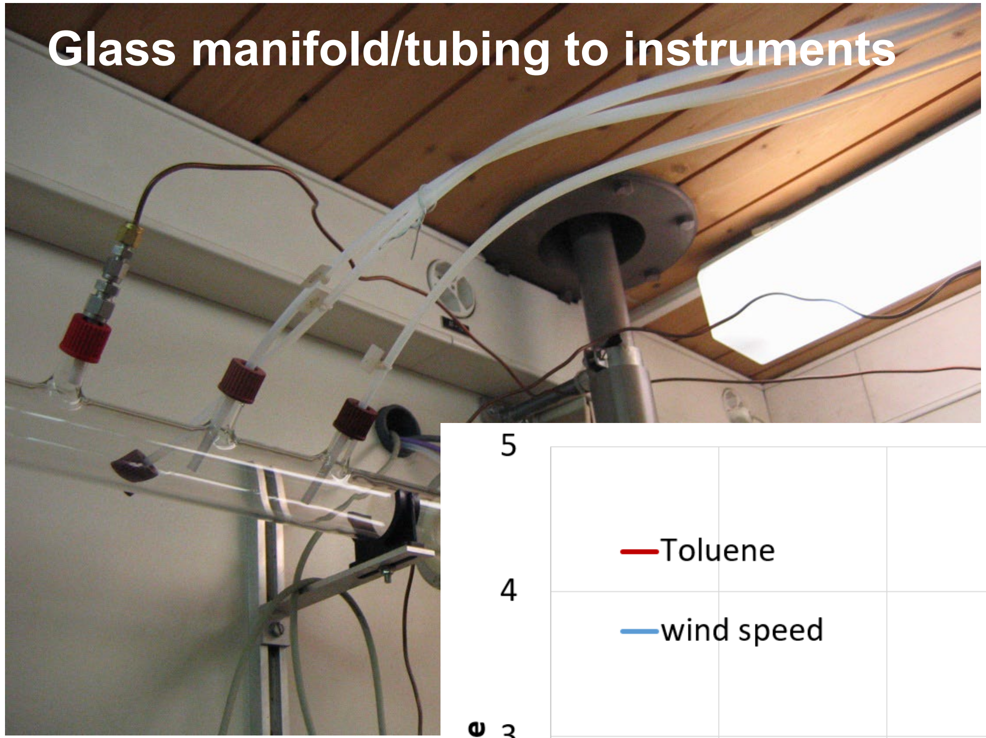


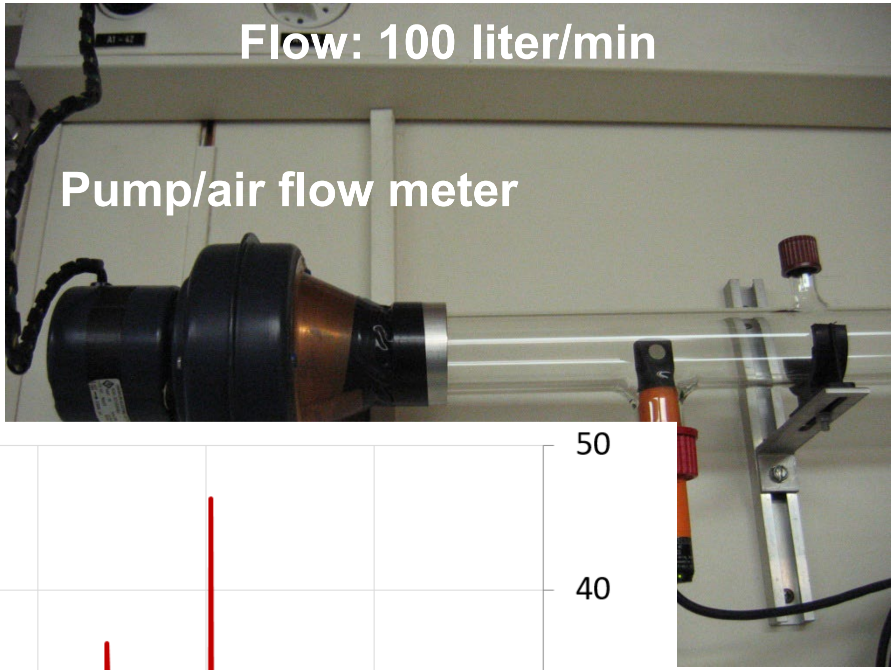
CO2 from the ridge and from the roof

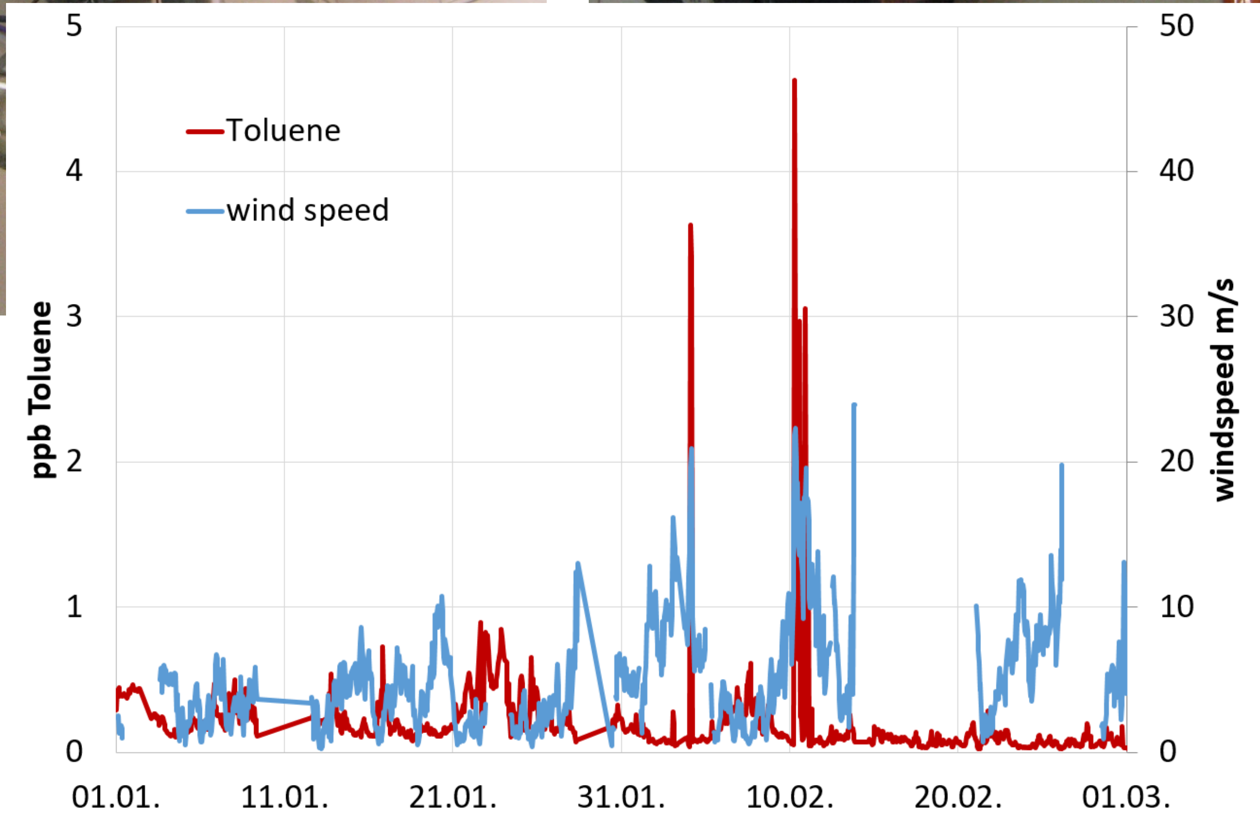


Time series of 1-min averages of CO_2 mole fractions from the cupola (red) and the ridge inlet (blue) for 16 July 2022. Light blue data (between 8 AM and 9:45 AM) show data from the cupola inlet sampled with CRDS-ridge.

NABEL
distribution device/pump



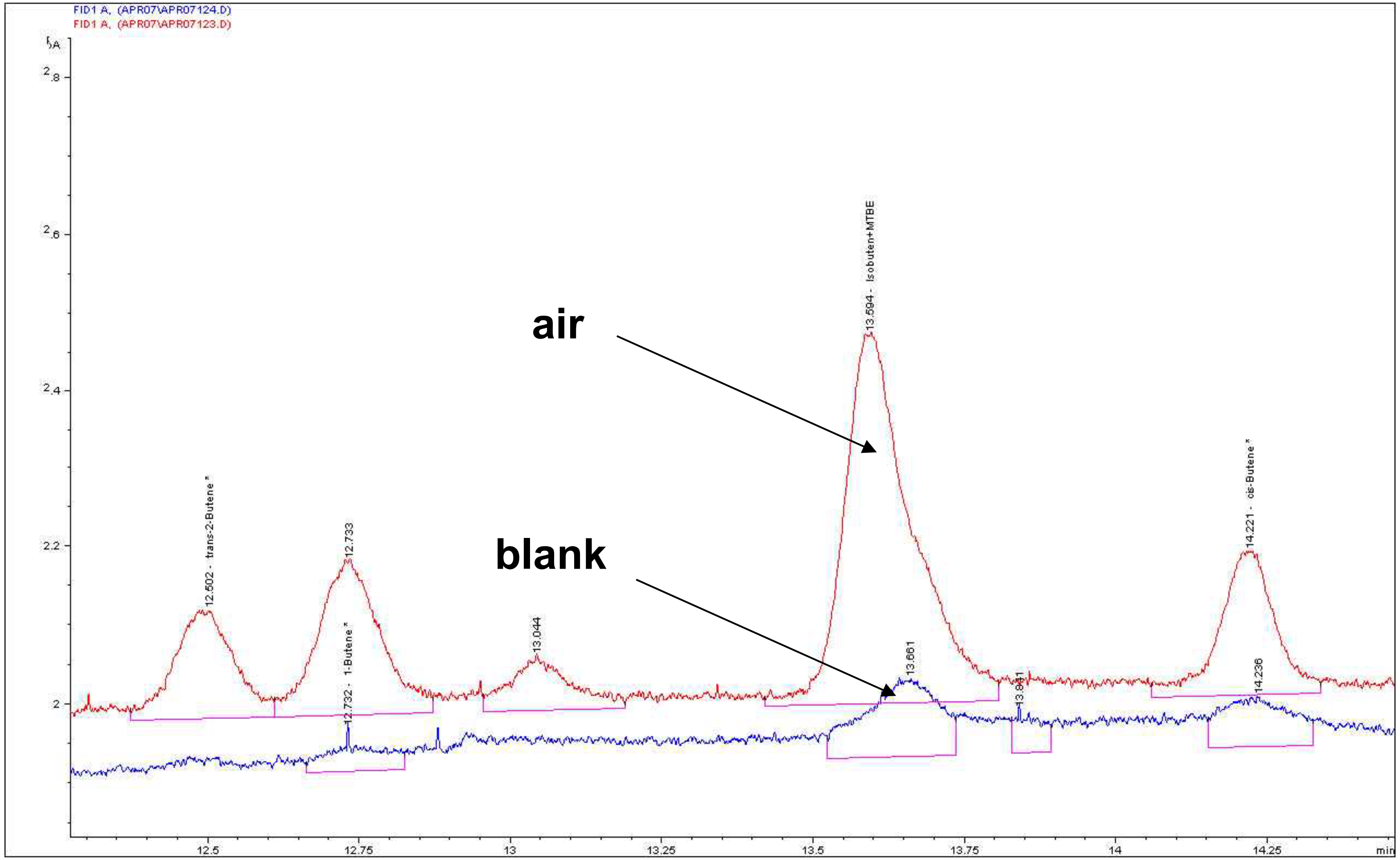




Quality Assurance – Data control

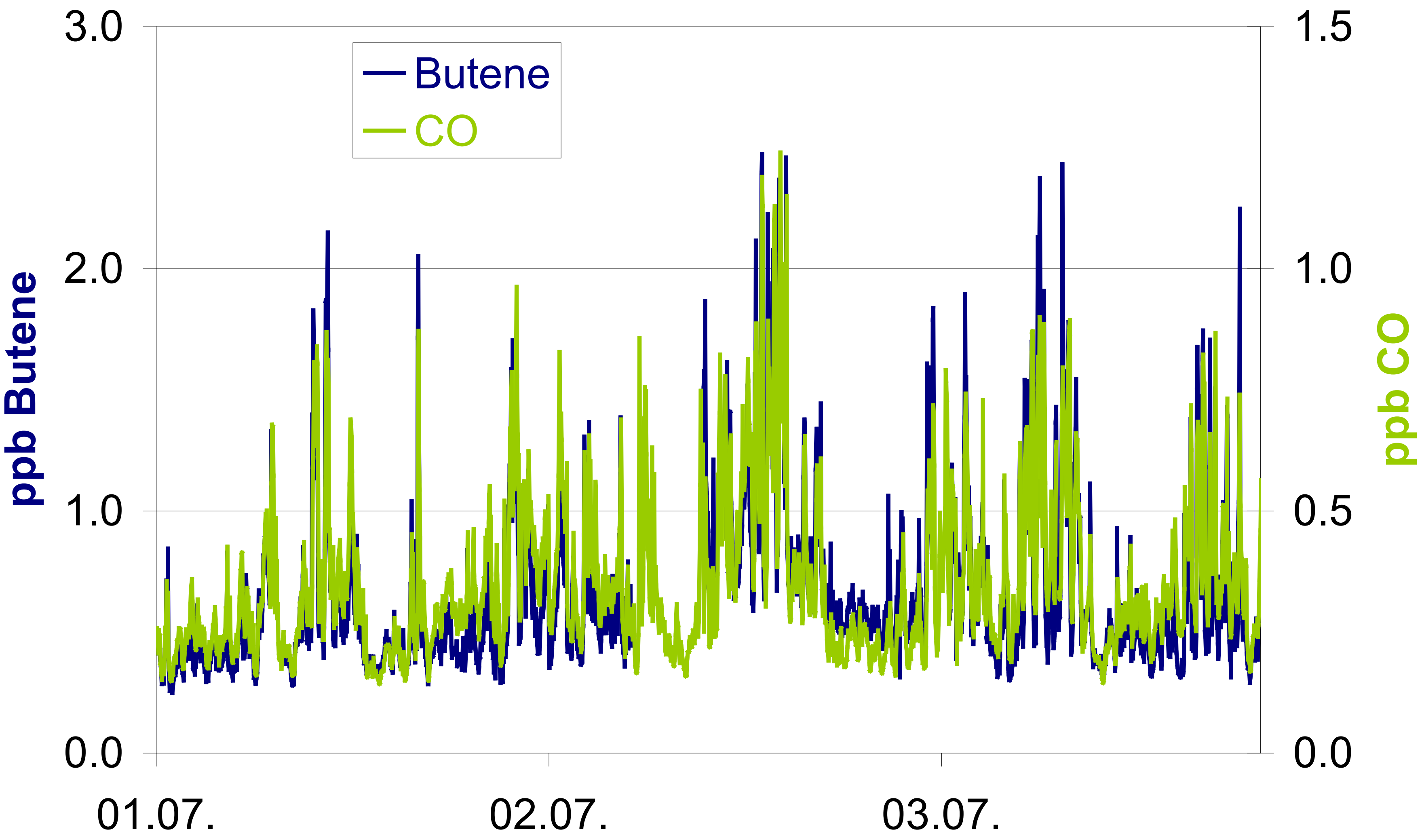
Blanks

Blank of butene (C_4) from the Nafion Dryer: 0.2 ppb



Quality Assurance – Data control

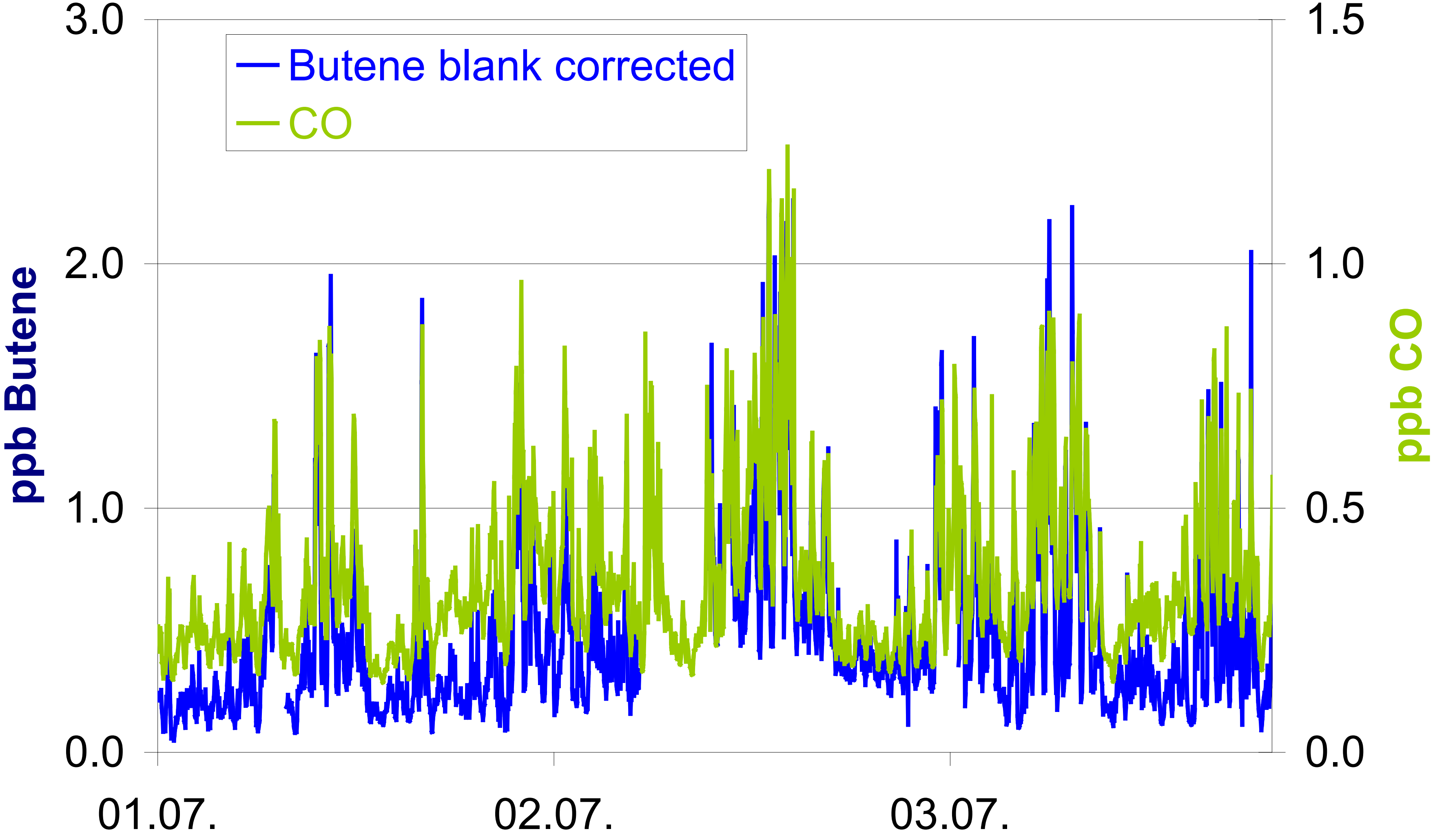
Blanks



Quality Assurance – Data control

Blanks

Blank of butene (C_4) from the Nafion Dryer: 0.2 ppb

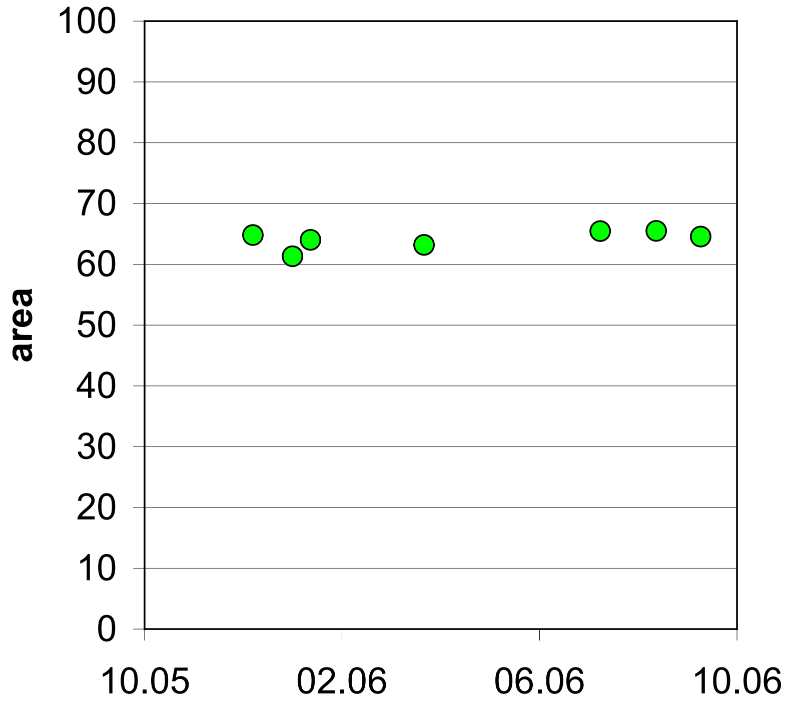


Quality Assurance – Data control

drift in detector stability

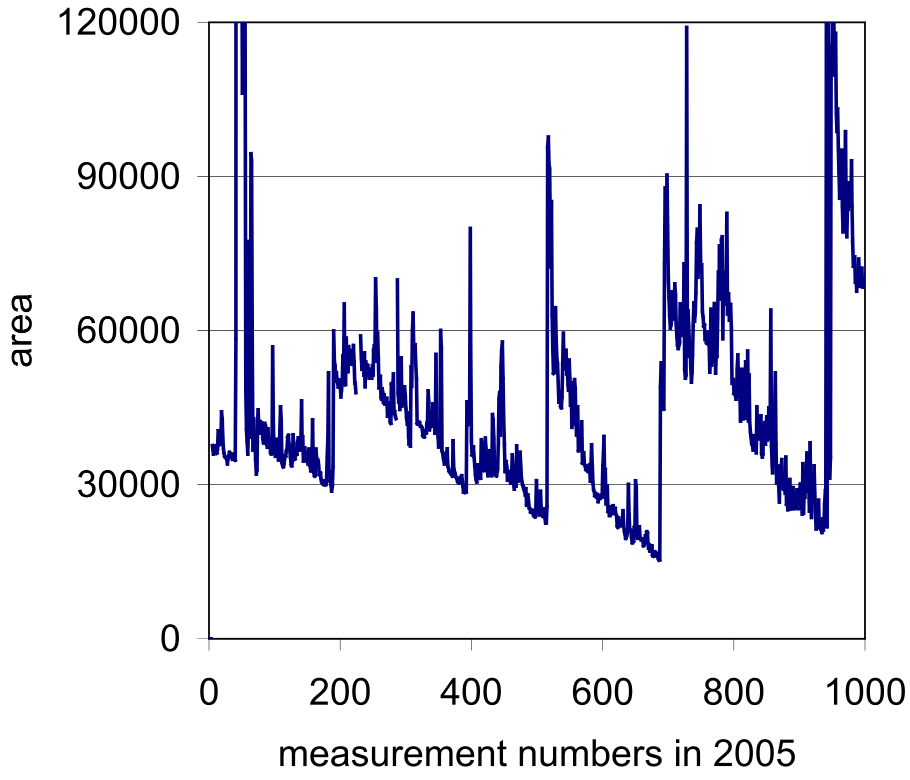
FID (stable)

peak areas of calibration:
- stable over 1 year
- ± 5% std. dev.

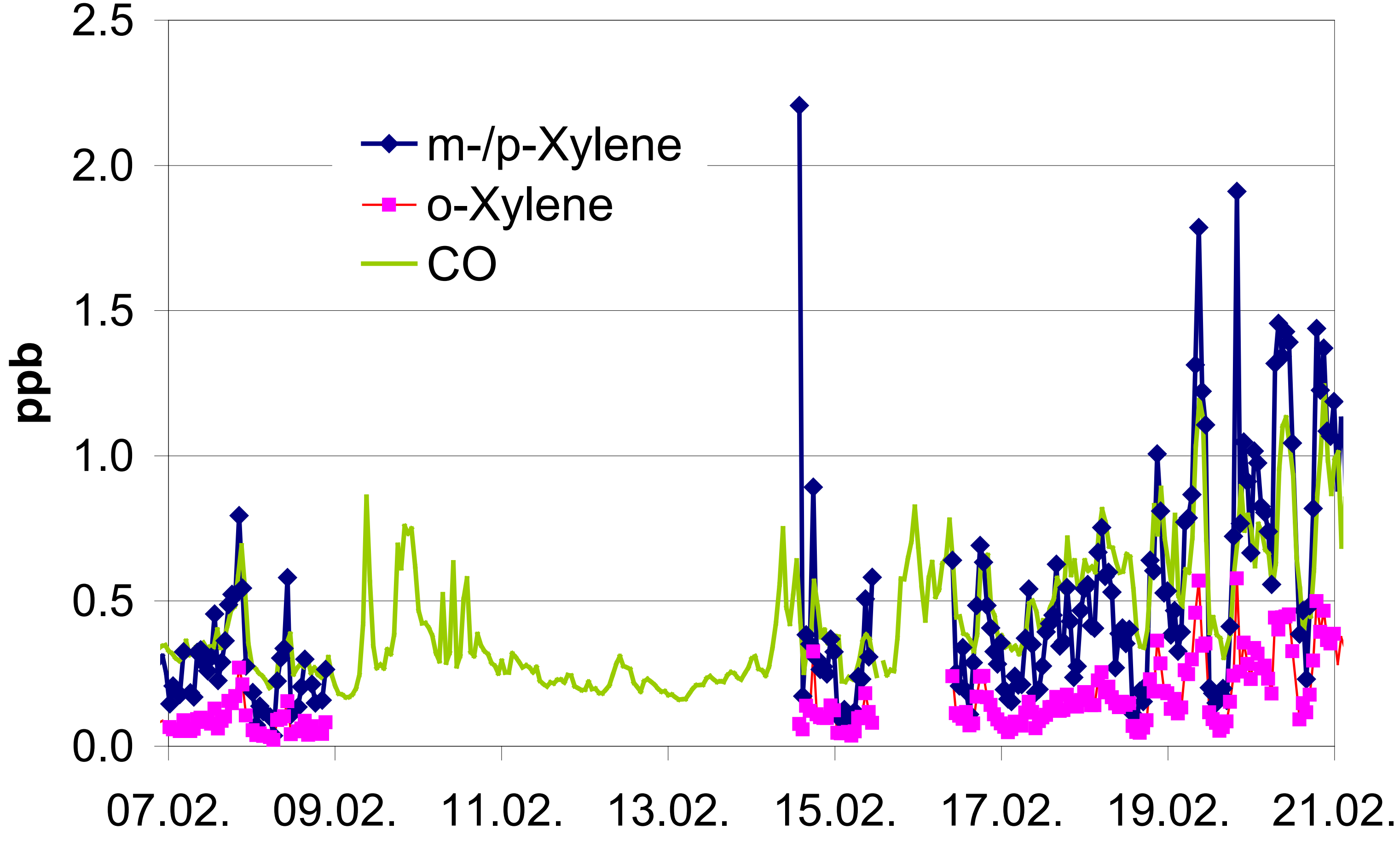


MS (unstable)

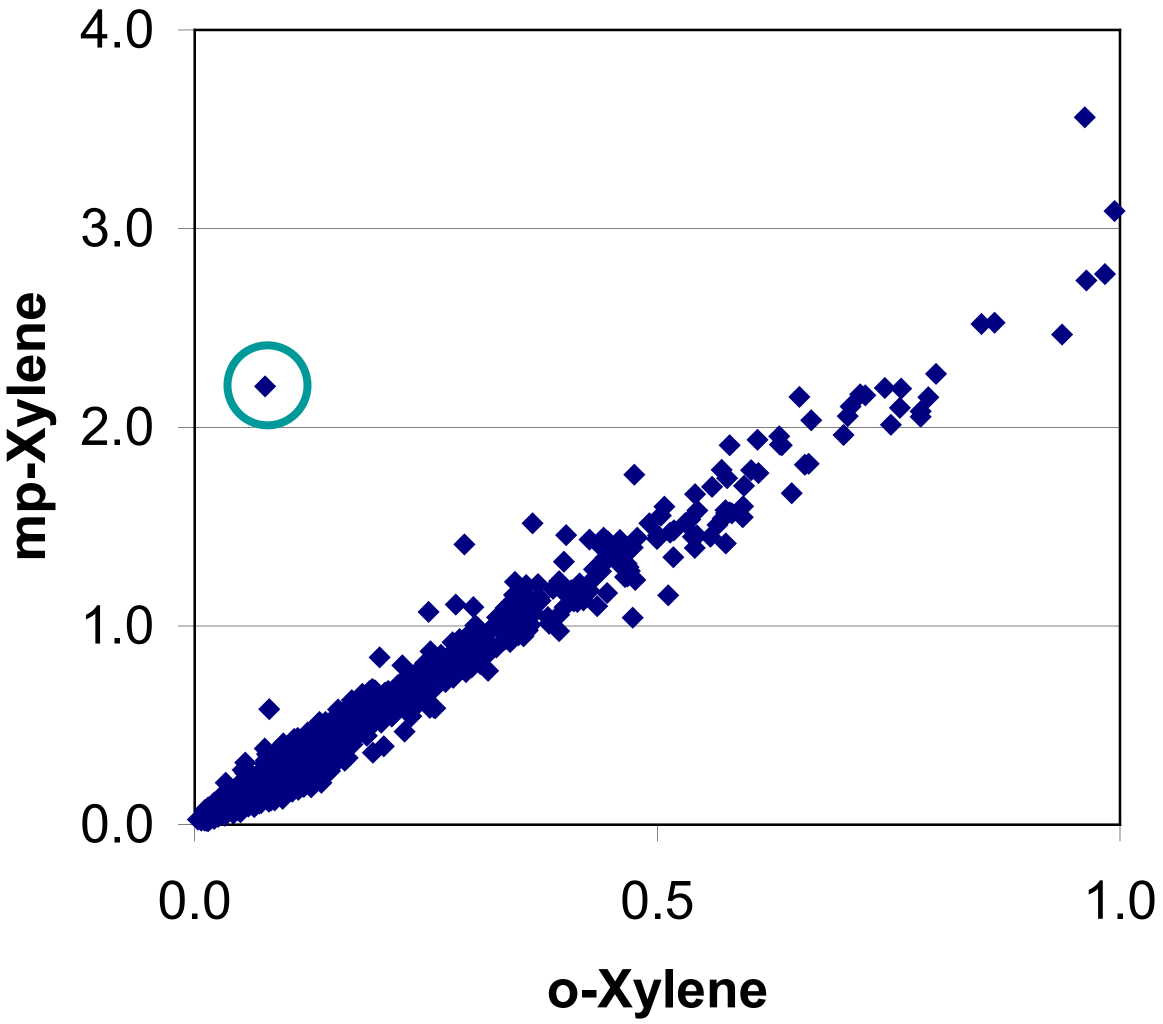
raw peak areas show:
- fast declining sensitivity
- jumps after tuning of source



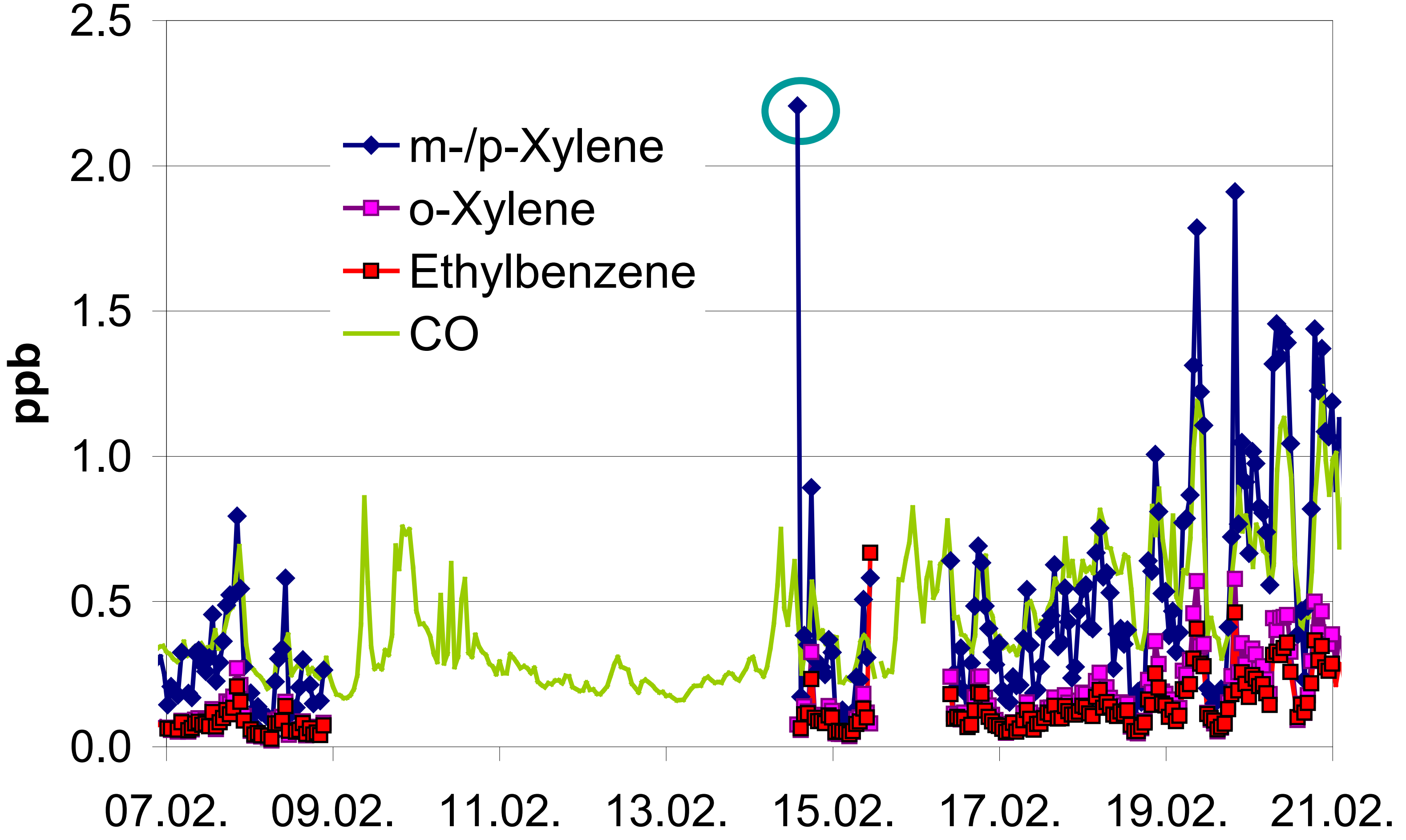
Data quality checks
Interdata comparison (xy-plots)



Data quality checks
Interdata comparison (xy-plots)



Data quality checks
Interdata comparison (xy-plots)



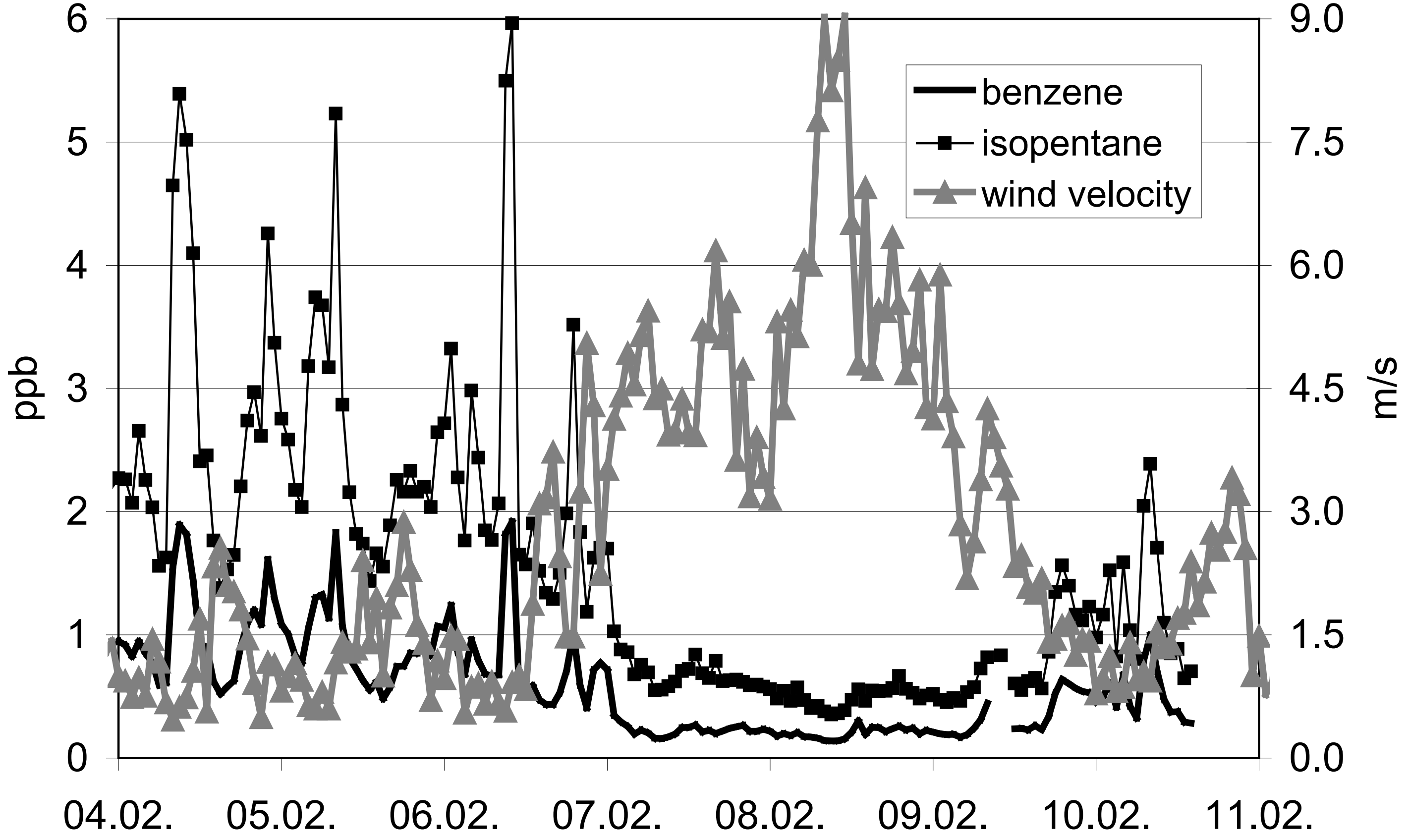
Quality Assurance – Data control

Tools for data verification

2. comparison with meteorological information

Wind speed and direction
important in cities and with known industrial sources

Example: VOCs in the city center of Zurich



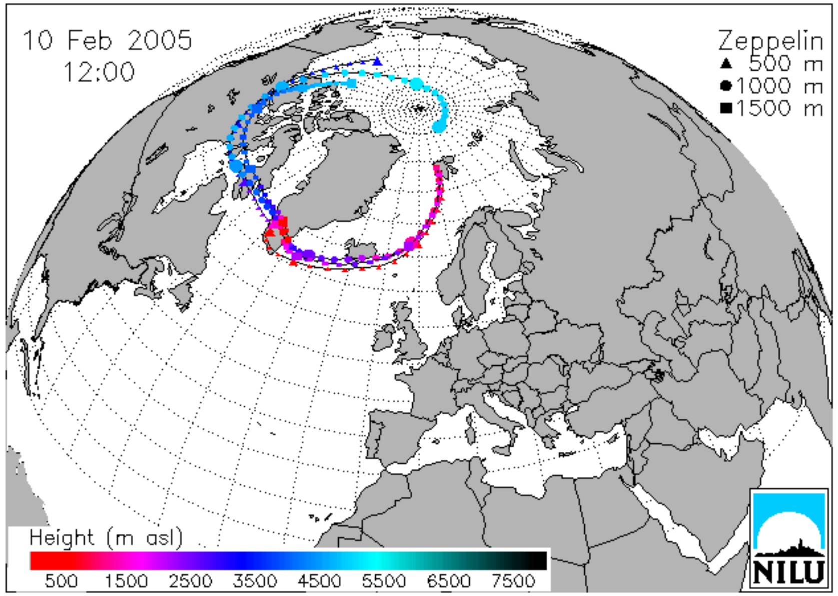
Quality Assurance – Data control

Tools for data verification

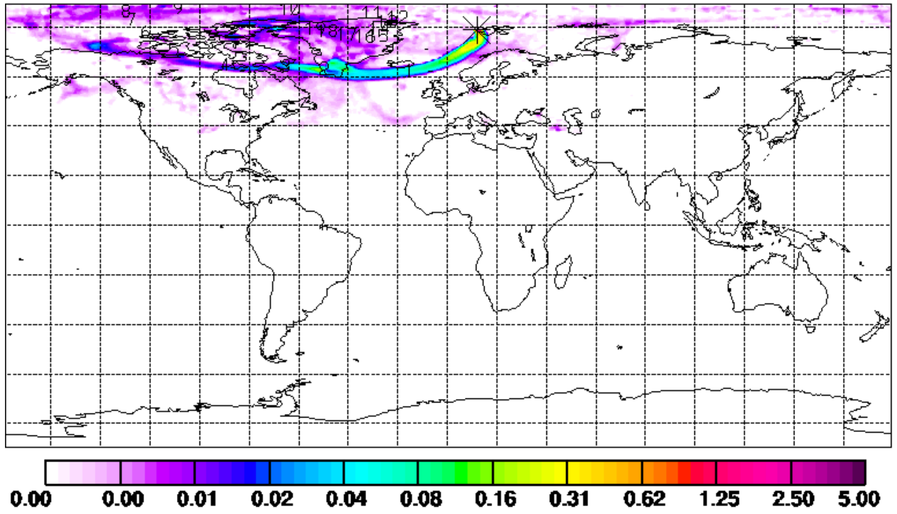
2. comparison with meteorological information

important at remote locations

b) Trajectories



c) Footprints of Lagrangian particle dispersion models (LPDM)

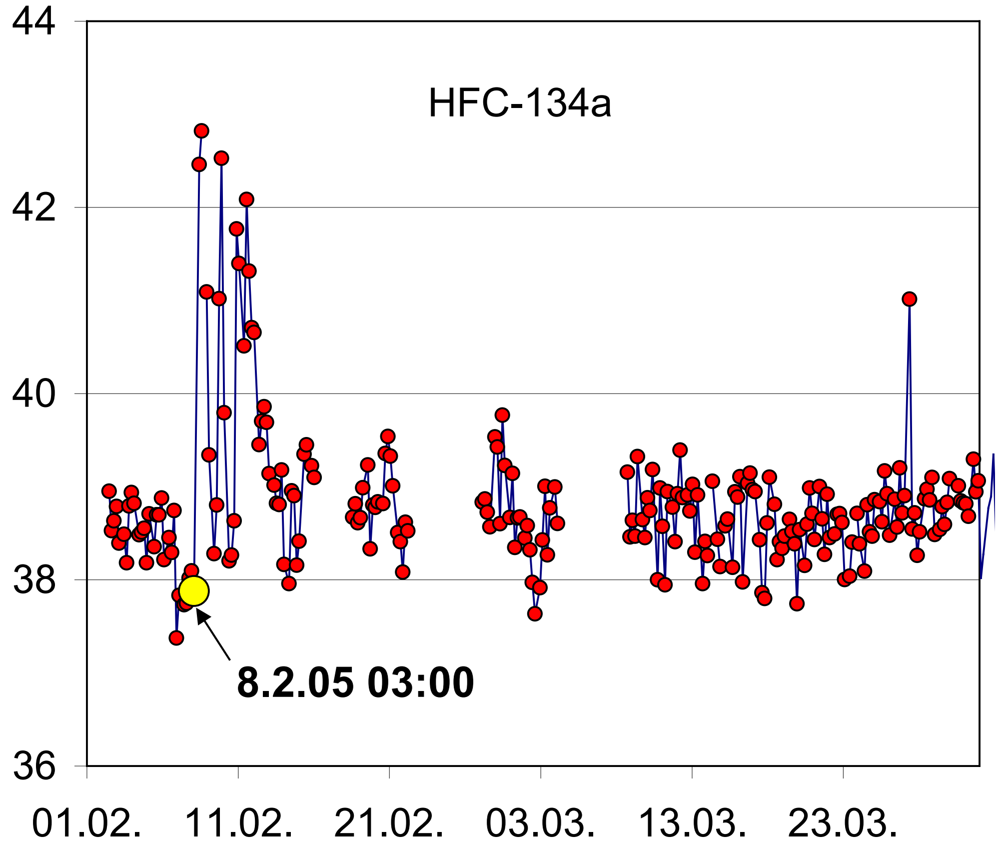


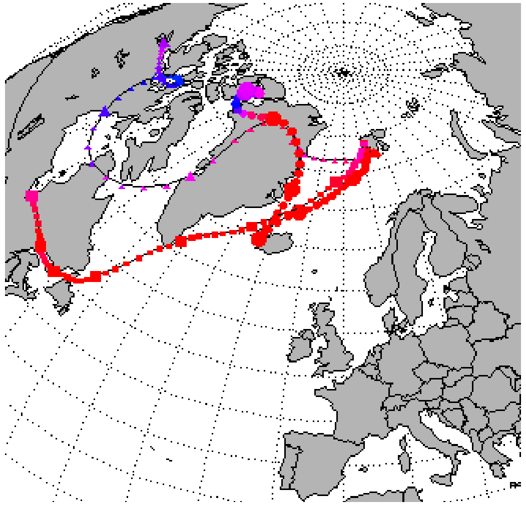
Quality Assurance – Data control

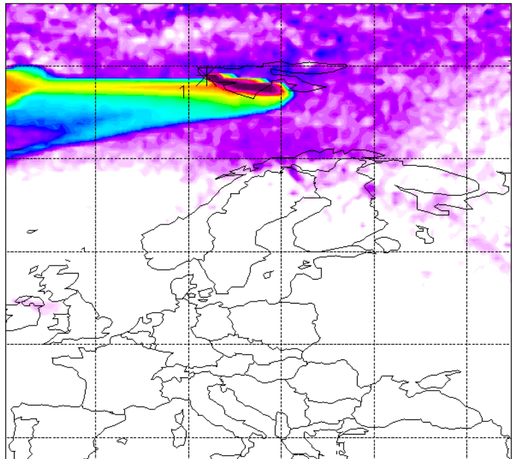
Tools for data verification

2. comparison with meteorological information

Example: Pollution event of HFC-134a in Spitsbergen





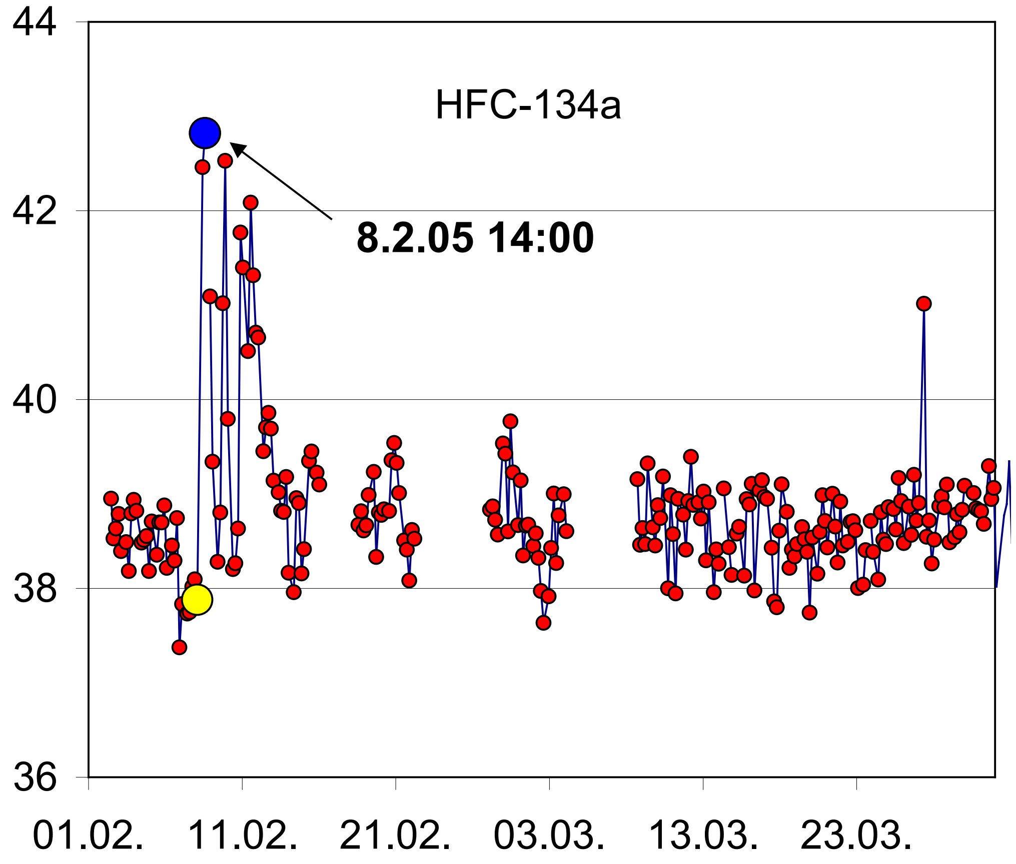


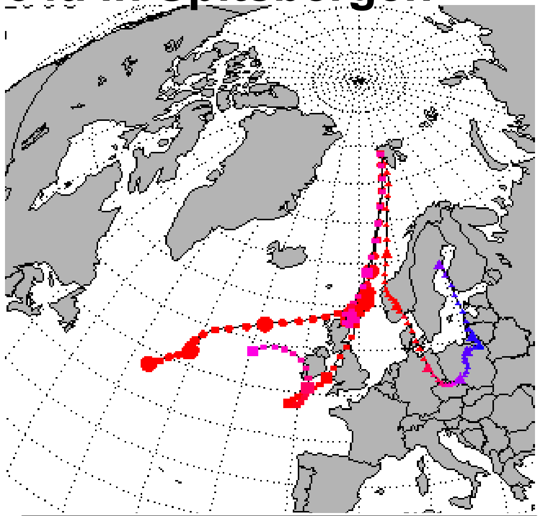
Quality Assurance – Data control

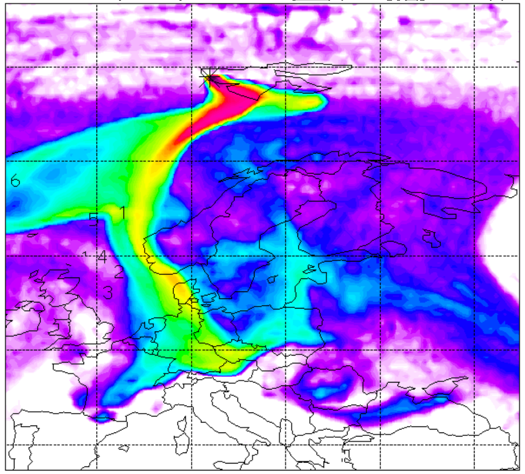
Tools for data verification

2. comparison with meteorological information

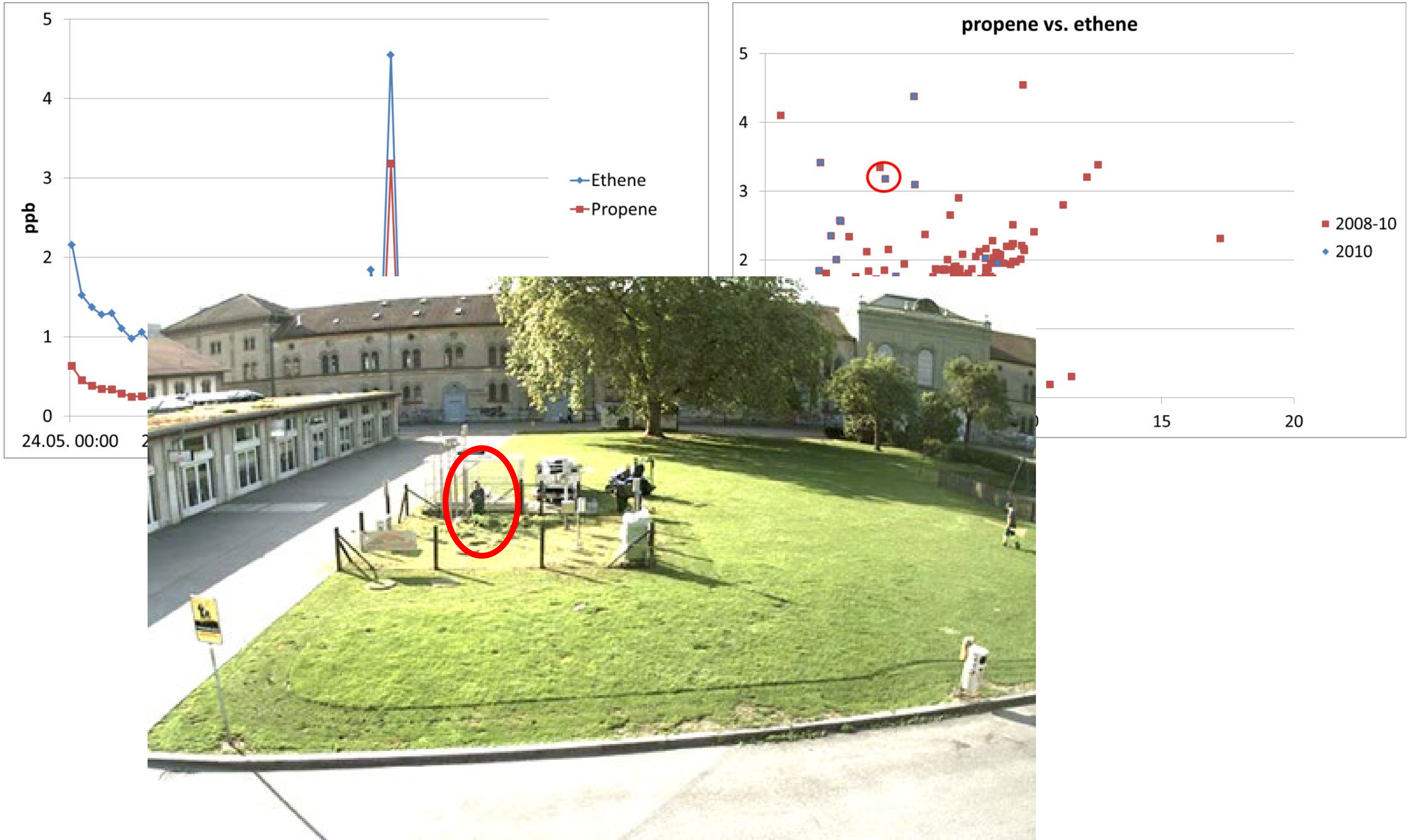
Example: Pollution event of HFC-134a in Spitsbergen



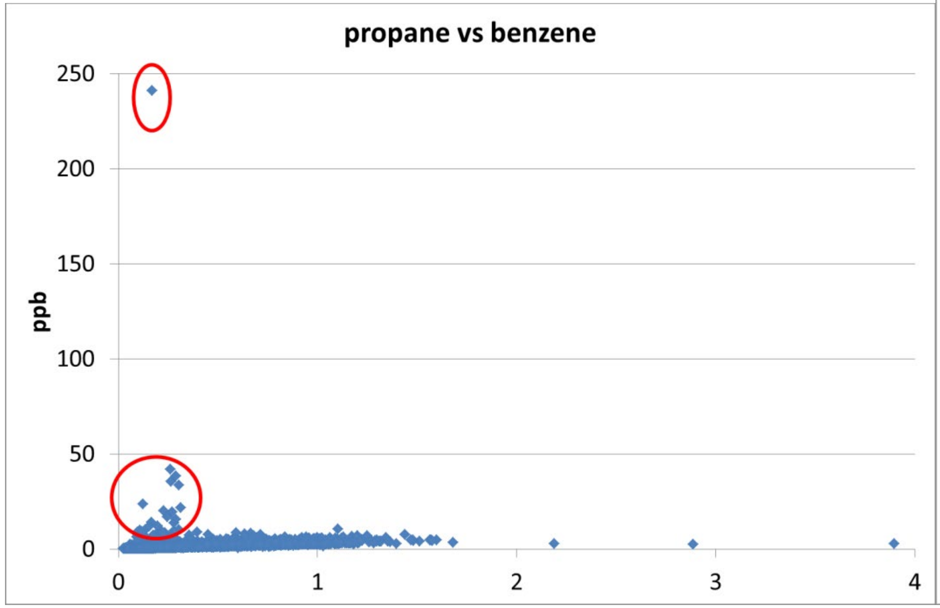


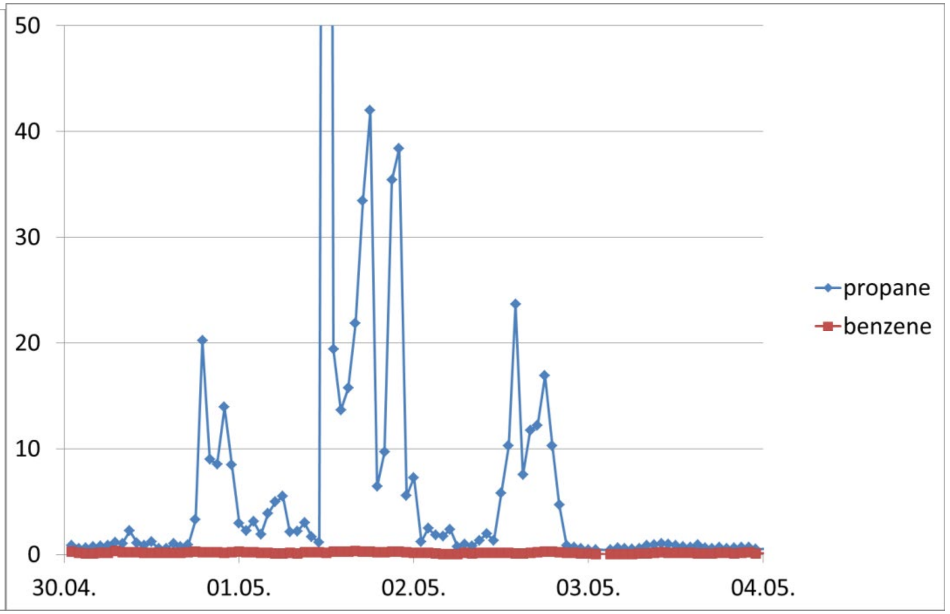


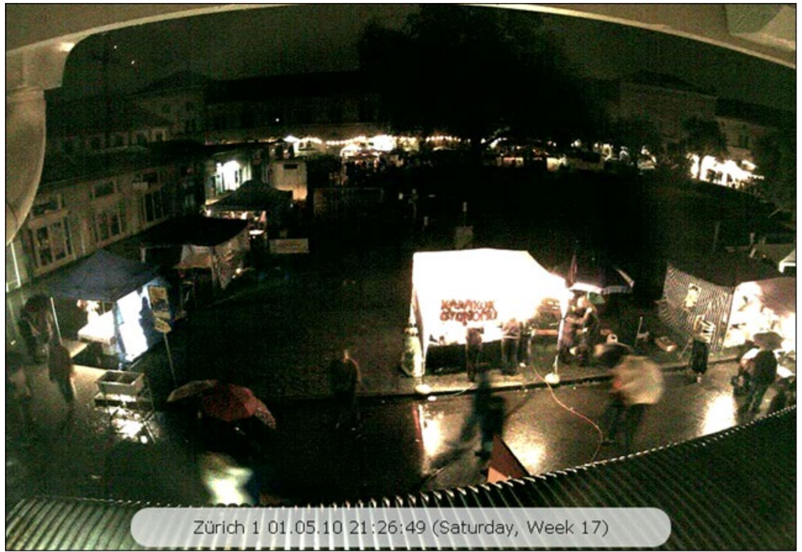
Is this a normal data point?



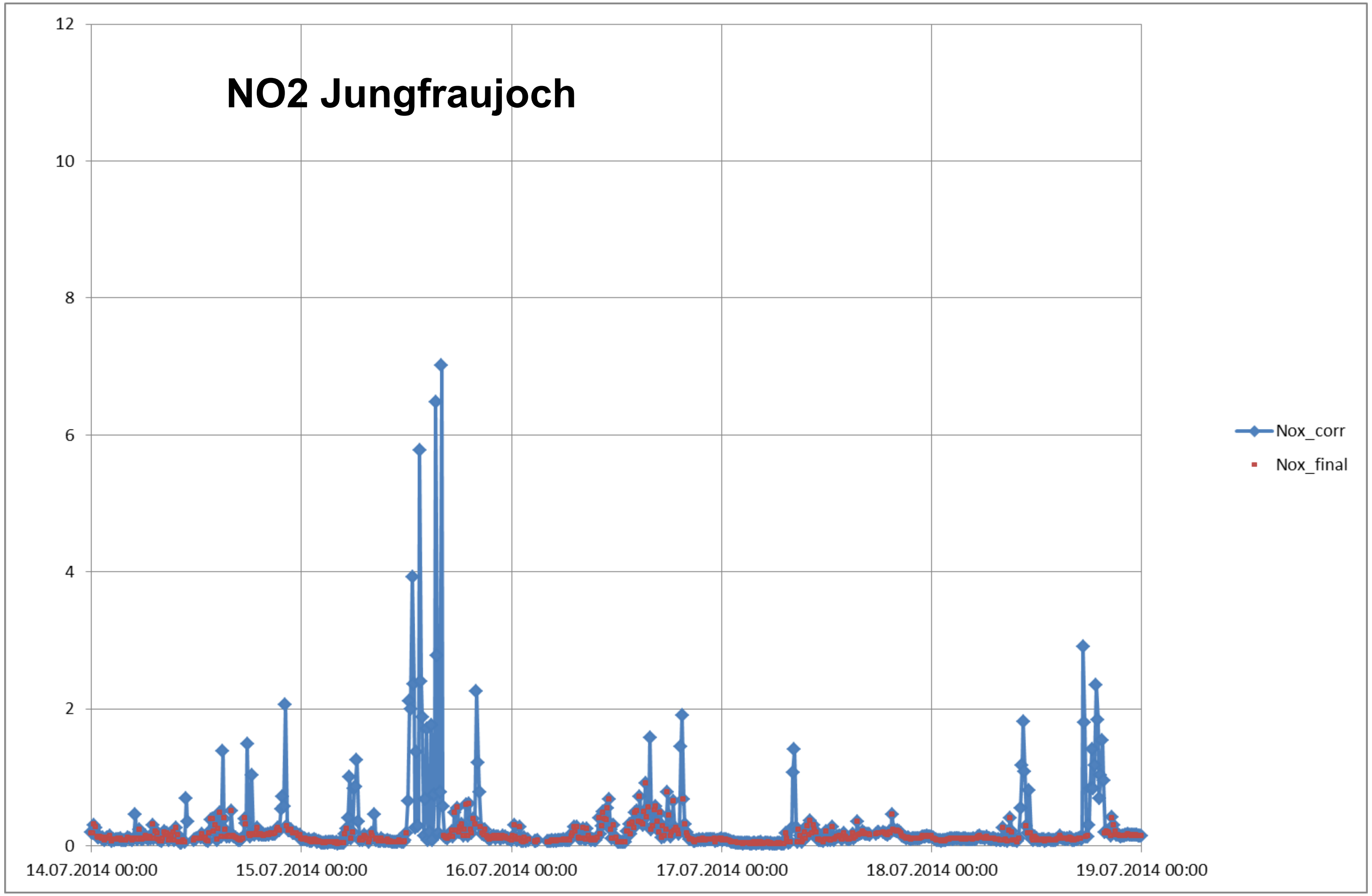
Is this a normal data point?







Is this data ok?



4 different ways to describe the "concentration" in the atmosphere

1. Mixing ratio C_X [mol mol^{-1}]

2. Mass concentration ρ_X [µg m^{-3}]

3. Number density n_X [Moleküle cm^{-3}]

4. Column abundance [Moleküle cm^{-2}]

Mixing ratio C_X [mol mol^{-1}]

$$C_X = \frac{\text{\# moles of X}}{\text{mole of air}}$$

advantage:
Remains constant if pressure and/or temperature changes

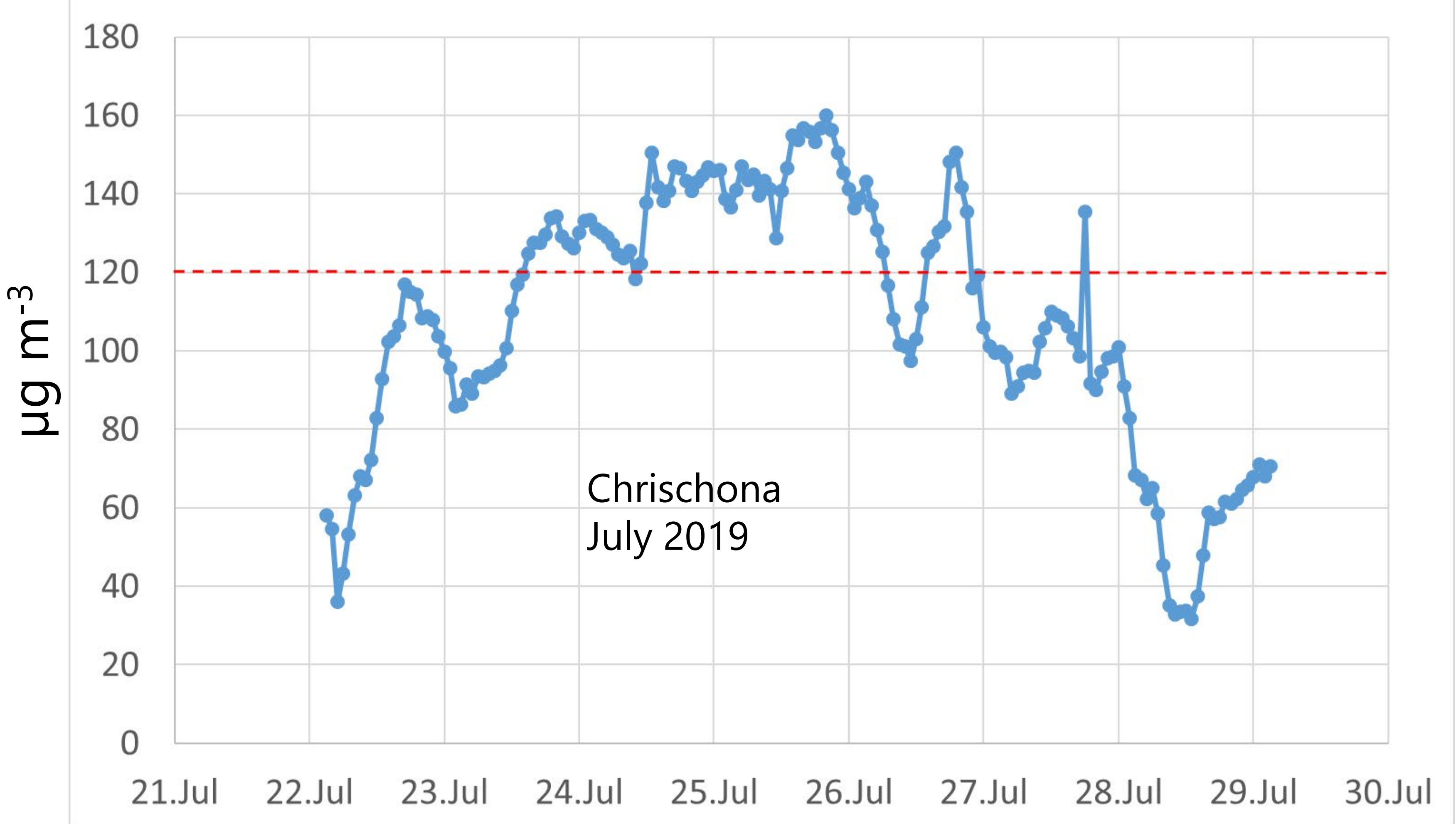
GAS	MIXING RATIO (dry air) [mol mol^{-1}]
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO_2)	420x10^{-6}
Neon (Ne)	18x10^{-6}
Ozone (O_3)	(0.01-10)x10^{-6}
Helium (He)	5.2x10^{-6}
Methane (CH_4)	1.9x10^{-6}
Krypton (Kr)	1.1x10^{-6}

Trace gases

- **units:**
  1 ppm = 1x10^{-6} mol mol^{-1}
  1 ppb = 1x10^{-9} mol mol^{-1}
  1 ppt = 1x10^{-12} mol mol^{-1}
  1 ppq = 1x10^{-15} mol mol^{-1}

Mass concentration ρ_X [µg m^{-3}]

Legal limit values
example: Swiss 1-hour limit value for ozone: 120 µg m^{-3}



Conversion: Mass Concentration and Mixing Ratio

1/24.47
l/mol

25 °C

Mass concentration [μg/m^3]=
Mixing ratio [ppb] x molecular weight [g/mol] x 0.0409[mol/l]

1 ppm => 1 mg/m^3
1 ppb => 1 μg/m^3
1 ppt => 1 ng/m^3

Mixing ratio [ppb] =
Mass concentration [μg/m^3]/ molecular weight [g/mol]/0.0409[mol/l]

1 mg/m^3 => 1 ppm
1 μg/m^3 => 1 ppb
1 ng/m^3 => 1 ppt

Conversion: Mass Concentration and Mixing Ratio

Exercise:

How many µg/m³ are 60 ppb of ozone (MW: 48 g/mol) at 1013 mbar/25 °C

60ppb x 48 g/mol x 1/24.45L = ~120 µg/m³

And at the Jungfraujoch (3580 m)? 1 mol air = 32.4 Liter (700 mbar/ 0° C)

60ppb x 48 g/mol x 1/32.4L = 88 µg/m³

Mass concentration [µg/m³]=
Mixing ratio [ppb] x molecular weight [g/mol] x 1/24.45 [mol/l]

Number density n_X [Molecules cm^{-3}]

$$n_X = \frac{\text{\# molecules of X}}{\text{unit volume of air}}$$

Only used in reaction kinetics

***n_X* can be calculated from mixing ratio relative to the total amount of air molecules**

$$n_X = n_a C_X$$

n_A (total amount of air molecules) = $\frac{\text{\# air molecules}}{\text{ml}}$ **= 2.46 x 10^{19}**

➔ 1 ppm of a substance ➔ 2.46 x10^{13} molecules/ml

1 mol = 24.45 L (25°C, 1013 mbar)

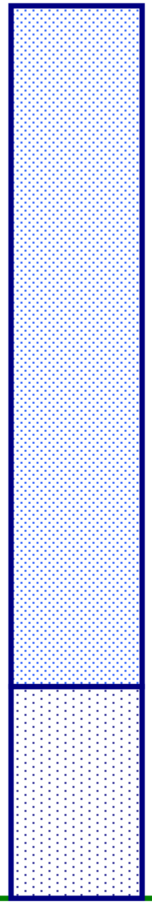
$\Rightarrow$1 ml = 1/24.45/1000 = 4.09 x 10^{-5} mol

$\Rightarrow$ 4.09 x 10^{-5} * 6.022 x 10^{23} = 2.46 x 10^{19} air molecules/ml

Column abundance: molecules/cm^2
Example: Measurement of total ozone from space

Stratosphere

Troposphere

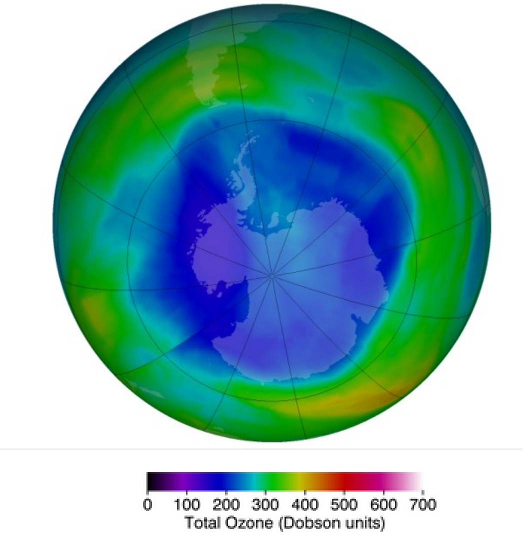


Unit of the column density of ozone is measured in (DU) gemesssen

1 Dobson-Unit (DU) = 2.7 x 10^{16} molecules/cm^2.

1 DU = 10µm layer of pure ozone

How thick is 300 DU?
(normal column abundance of ozone)

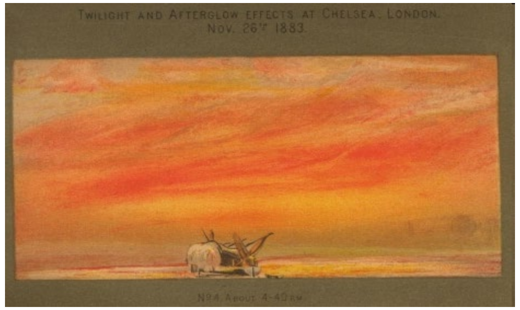


SO_2 in the atmosphere

First local anthropogenic air pollution due to SO_2:
1306: **King Edward** I tried to ban coal from being used in London
16th century: Replacing of smelters outside of towns

Effects on human health
- labored breathing
- permanent pulmonary damage
- Production of aerosols ("London smog")

Effects on the environment (Production of H_2SO_4, sulfuric acid)
- Forest decline
- Acidification of lakes and soils (Scandinavian lakes, 1970s)
- Global cooling (negative greenhouse effect)



Fluxes and effects of SO_2 in the atmosphere

Sources (Tg/y): **tons?**

Anthropogenic (~100 Tg/y)

Power plants:	35 Tg/y
Oil and gas production	10 Tg/y
Metal smeltering:	10 Tg/y
Small scale use:	45 Tg/y

Natural

Volcanoes:	18 Tg/y
Degradation of oceanic DMS, H_2S, OCS :	50 Tg/y

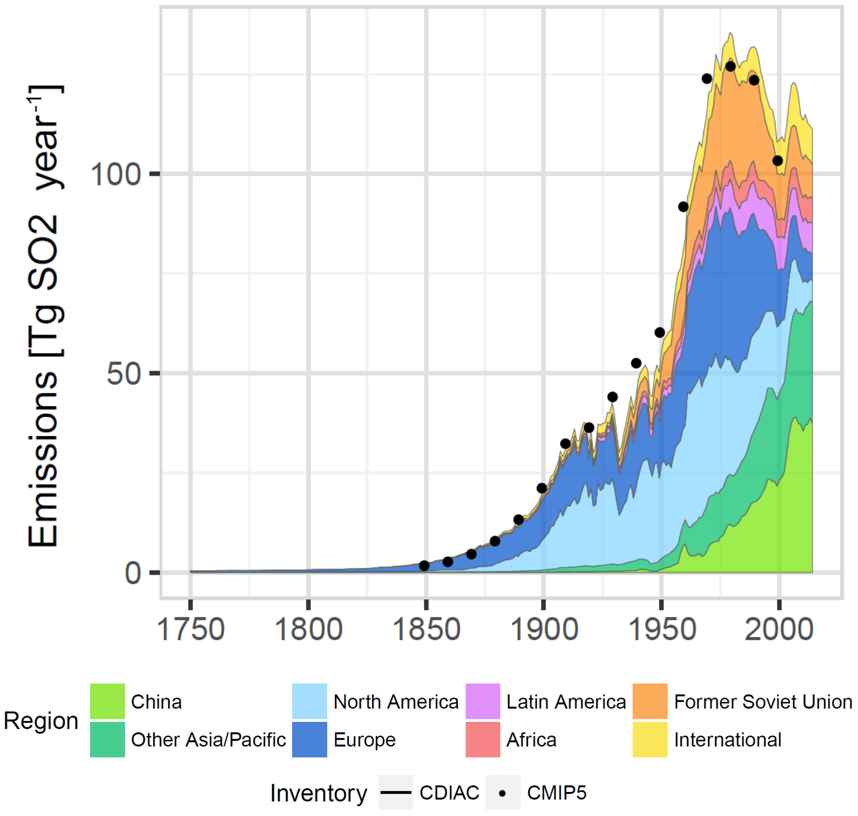
Sinks:

1. Dry deposition (40%)

2. Wet deposition (60%)

$SO_2 + H_20 \Rightarrow H_2SO_3 + \text{Oxid.} \Rightarrow H_2SO_4$

$H_2SO_4 \Rightarrow$ deposition



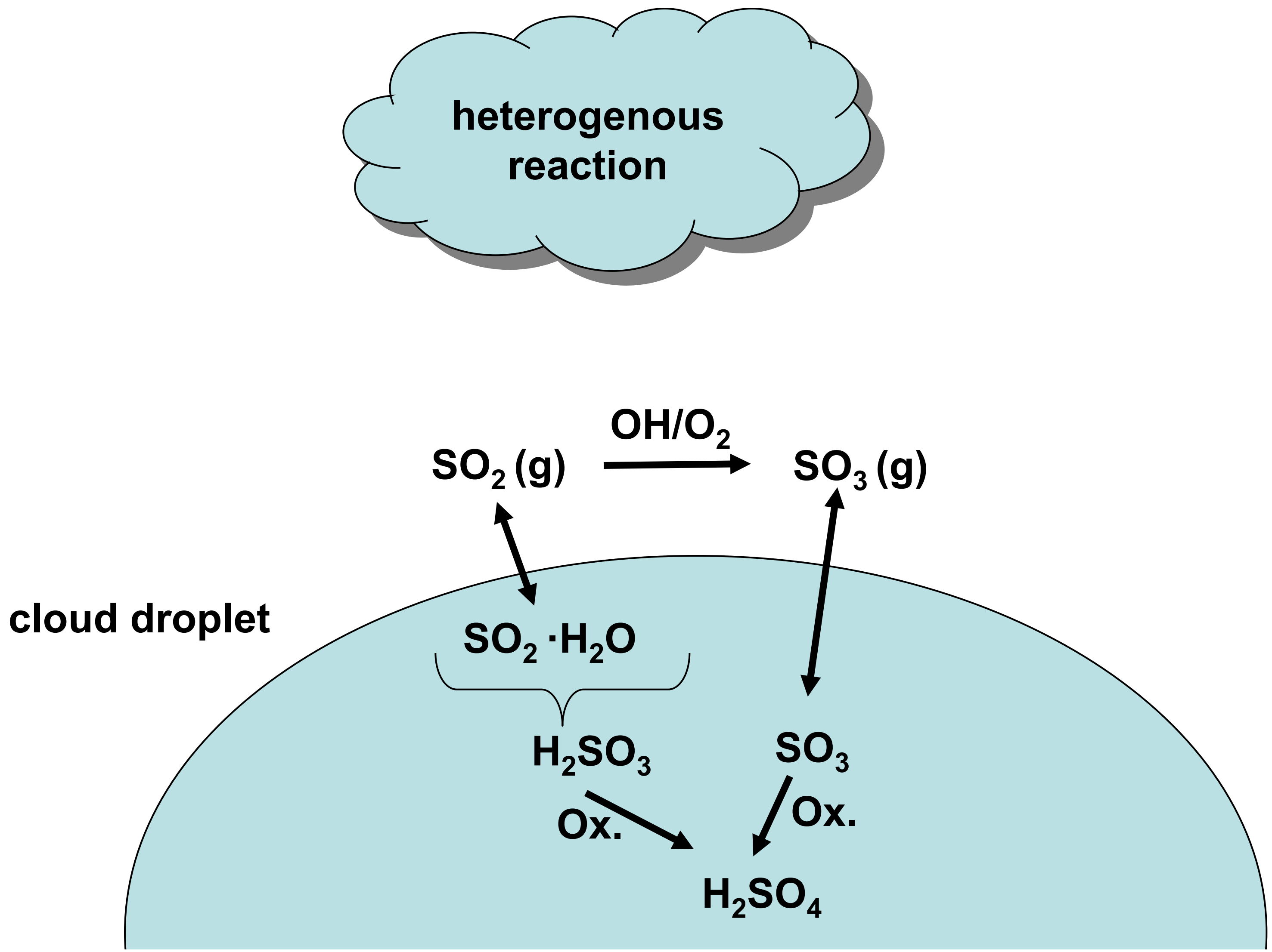
Hoesly et al., Geosci. Model Dev., 11, 369–408, 2018

Lifetime:

<3 days

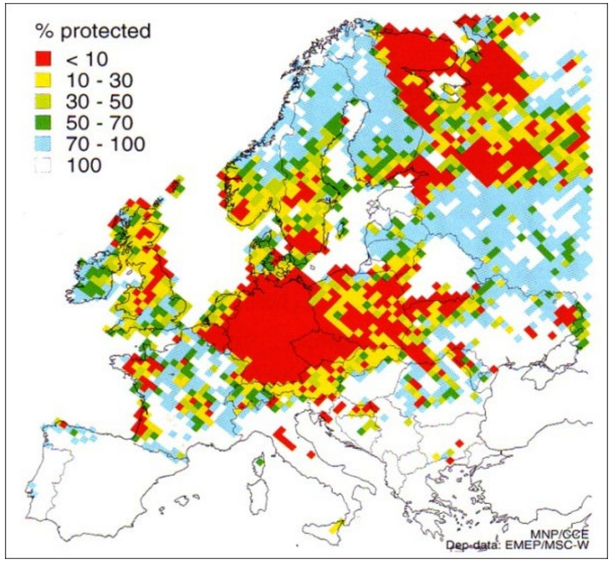
Fiotelev et al., Atmos. Chem. Phys., 16, 11497–11519, 2016

Formation of H_2SO_4 from SO_2 in the atmosphere

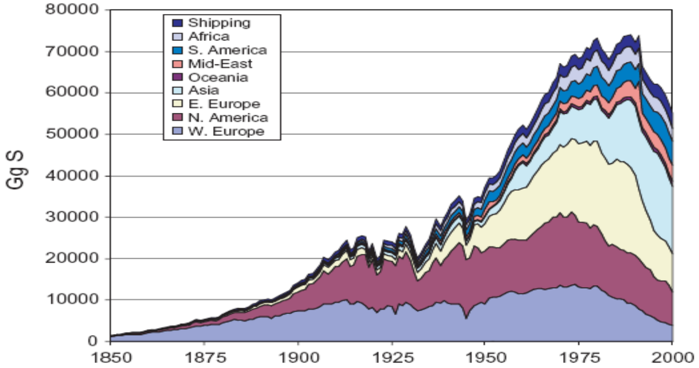


regional effects: Influence of acid rain
Exceedance of critical loads for acidification

1980

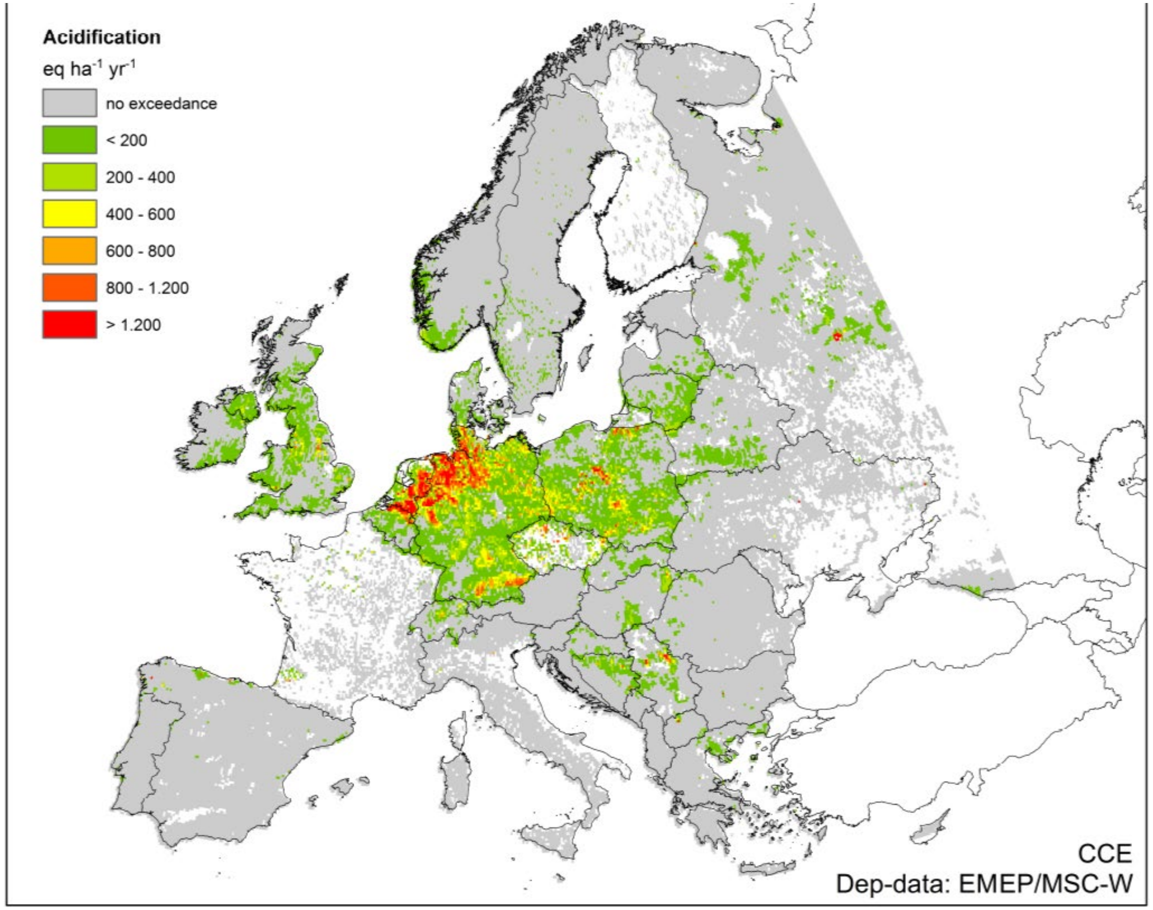


Global anthropogenic SO_2 emissions



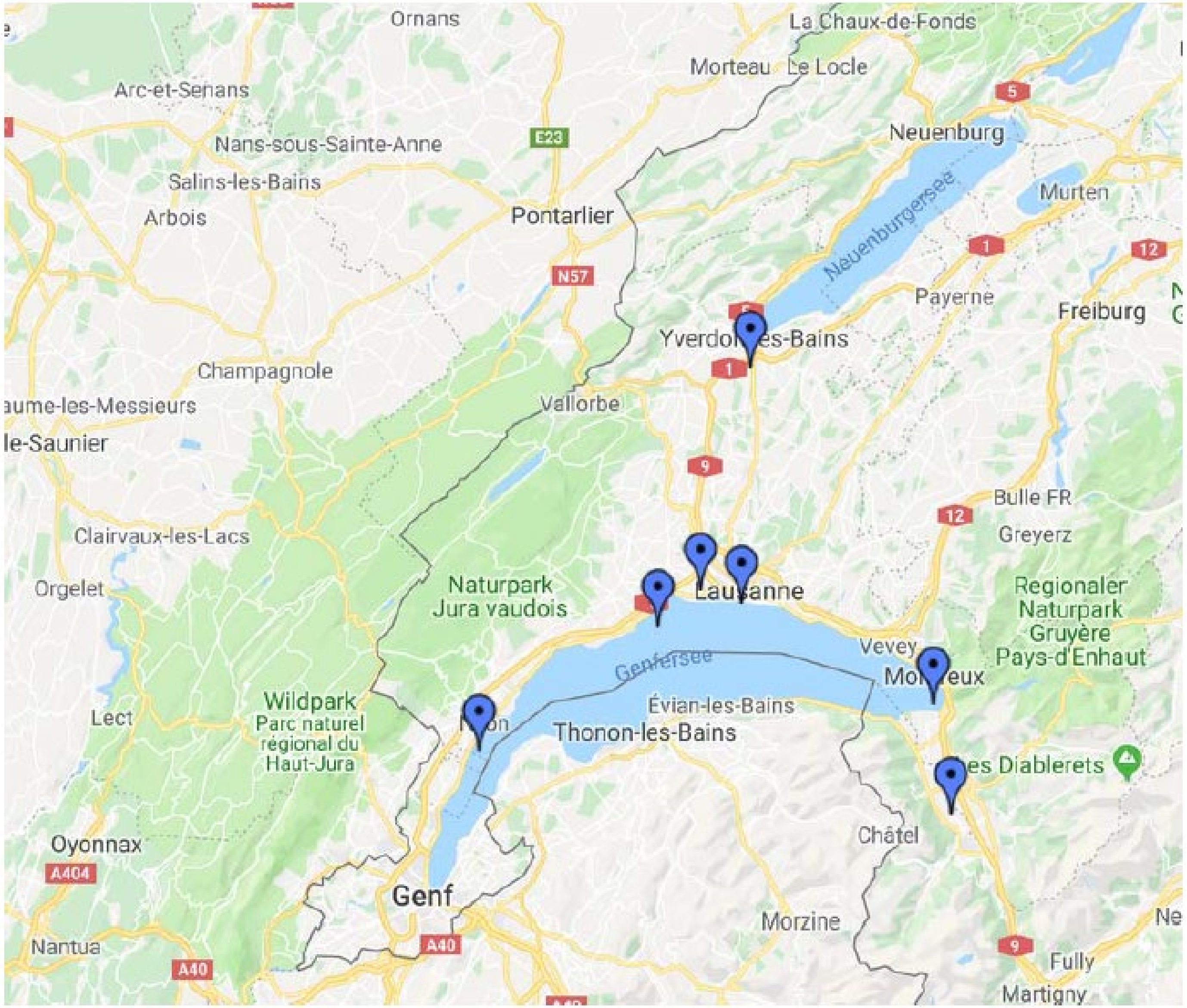
Stern, Chemosphere, 2004

2017



EMEP status report 2018

Exercise 1
The Canton Vaud is looking for a new background site where would you place it and why?

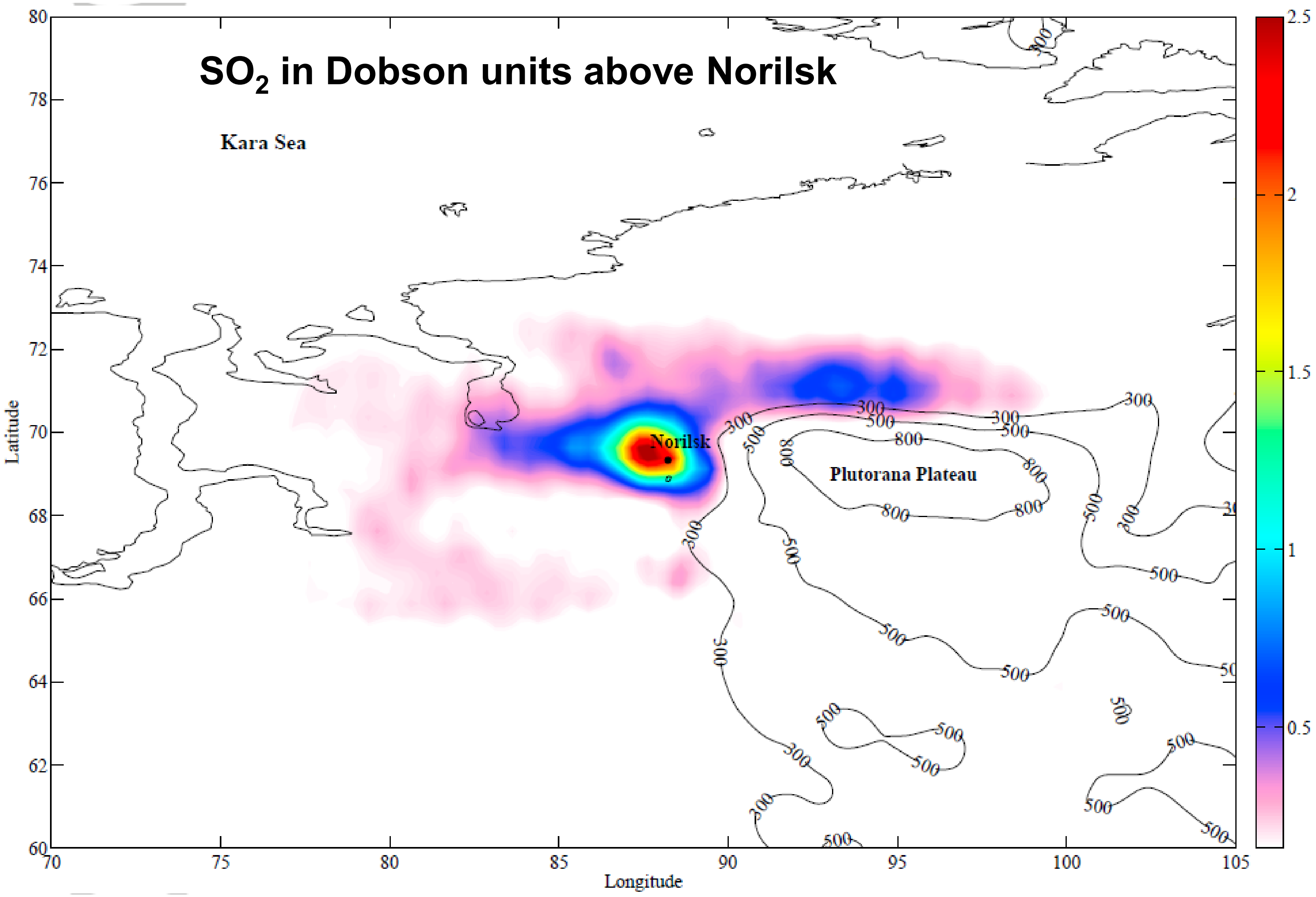


SO_2 Emissions from metal smelters

Norilsk (Russia)
2% of global emissions (2 Mio t/yr)

Pyrit: $4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$
Zinkblende: $2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$
Zinnober: $HgS + O_2 \rightarrow Hg + SO_2$

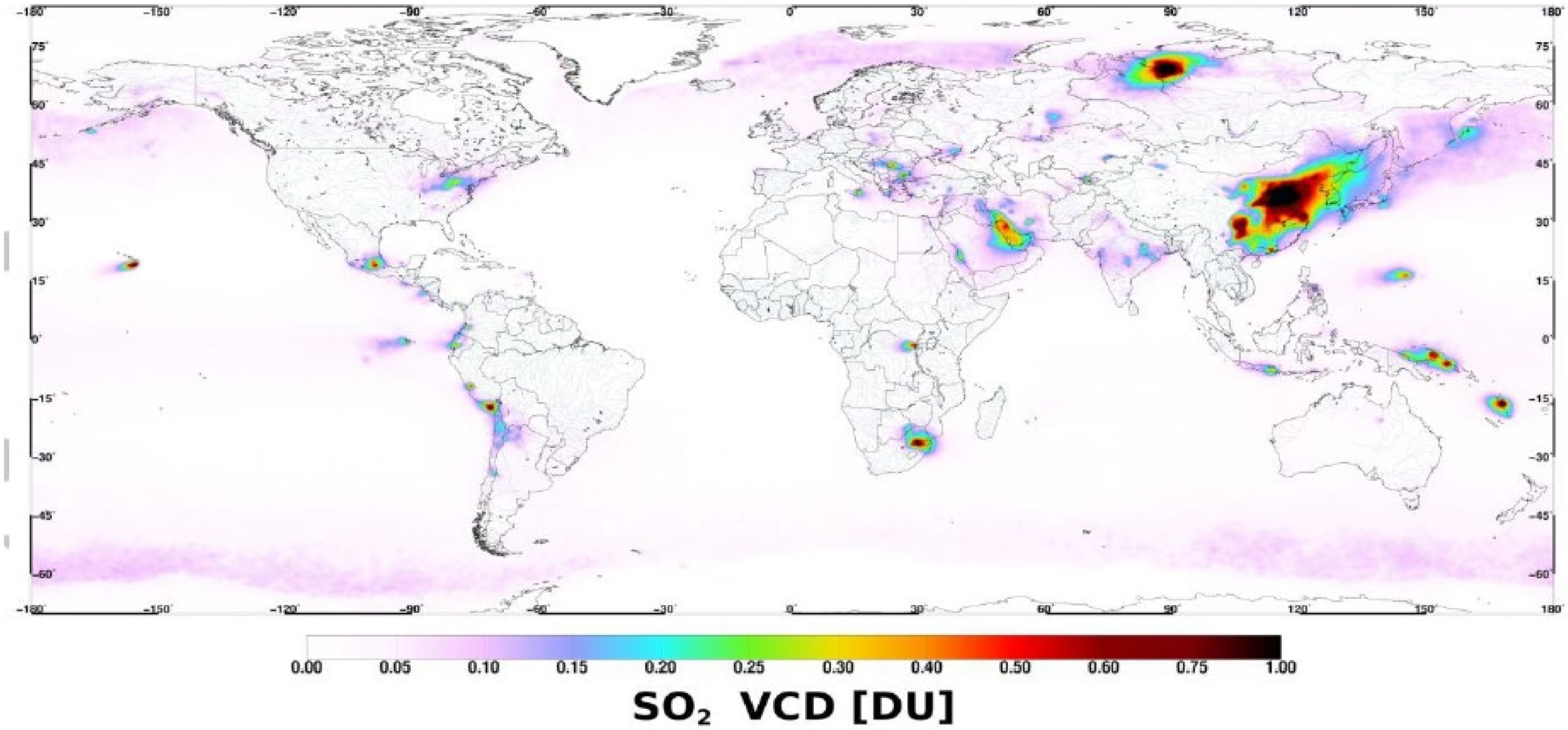
SO_2 Emissions from metal smelters



Baudin et al., JGR, 2014

SO_2 emissions anthropogenic sources and volcanos

(Theys et al, JGR, 2015)



Coal-Fuelled Power Plants
Oil and Gas Refineries

Coal-Fuelled Power Plant, South Africa

Aghar Oil and Gas Refinery, Iran

SO_2 from Coal Power Plants

Coal contains sulfur from the sulfur-containg proteins in the old biomass. Of biomass is oxidised to CO_2, sulfur is oxidised to SO_2.

Good practice: Stripping of SO_2 from chimneys and usage of produced H_2SO_4 for chemical processes.

SO_2 from Refineries

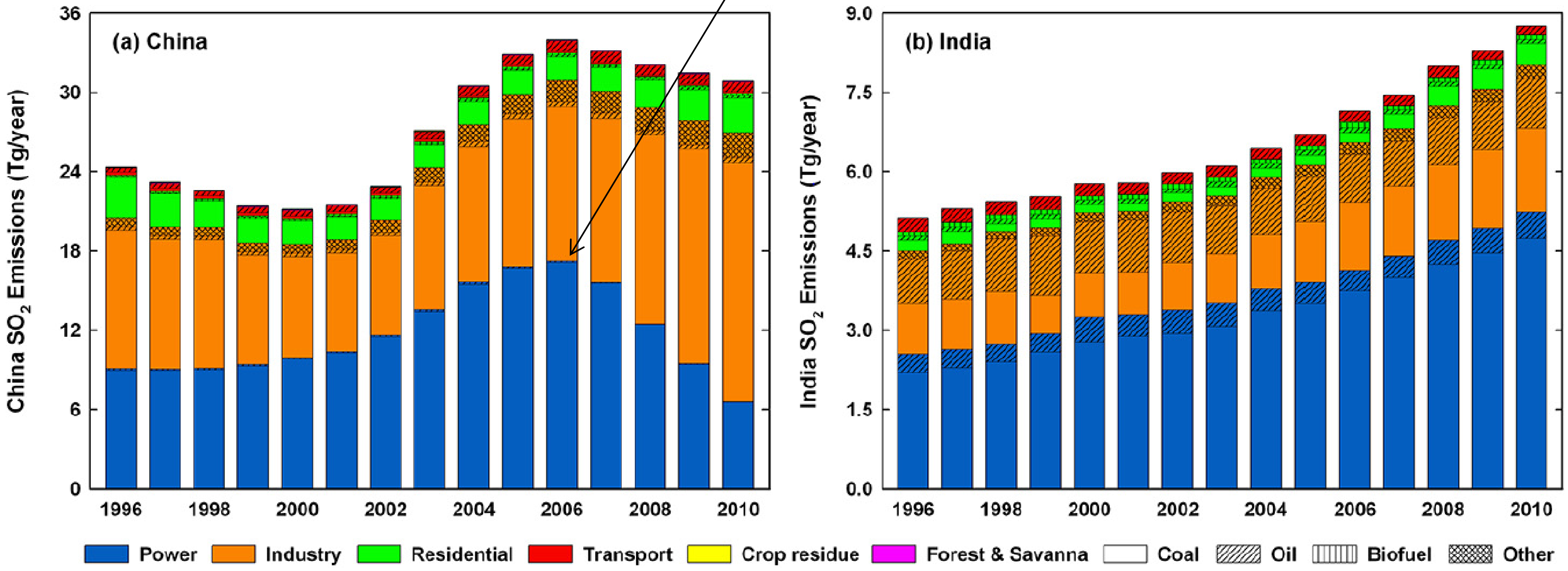
1. Regeneration of catalysts from cracking by oxidizing adsorbed coke to carbon monoxide. During regeneration, sulfur and sulfide deposits that also accumulated on the catalyst are oxidized to SO_2.

2. Hydrogen sulfide (H_2S) flaring. Good practice: > 95 % are stripped from the gas before it is are burned. If not, SO_2 is formed

3. Burning of sulfur-containing oil and gas on the spot for energy consumption.

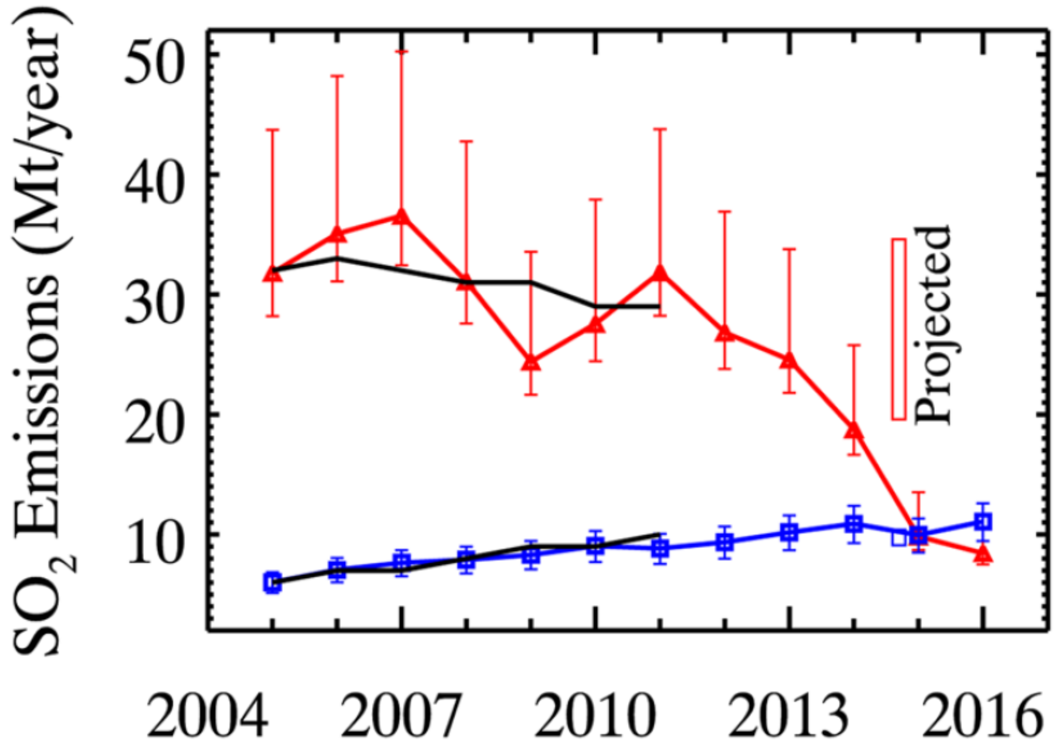
SO_2 emissions from China and India

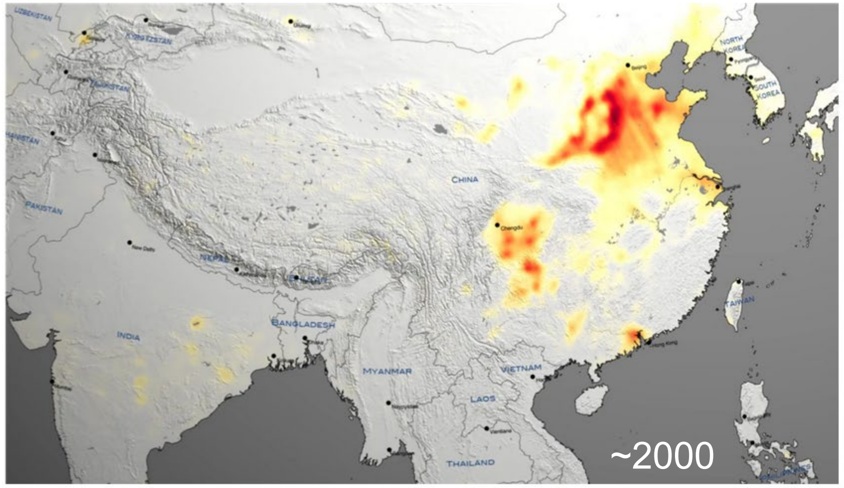
flue-gas desulfurization
in power plants



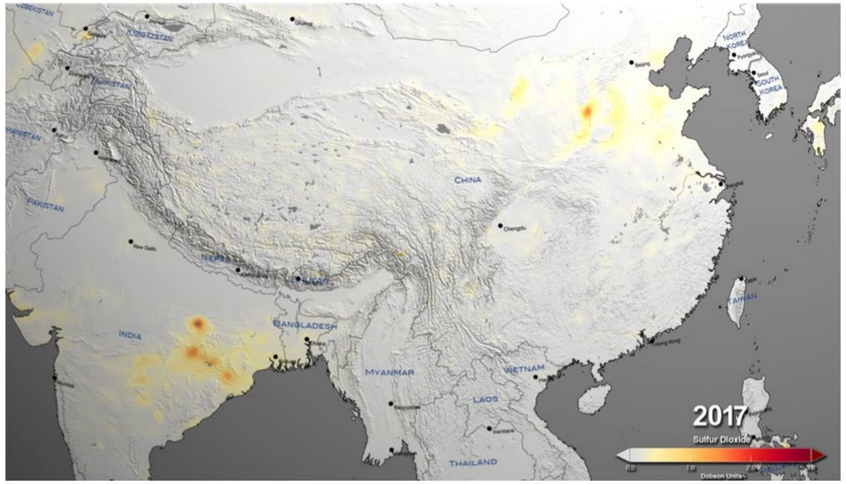
Sulfur dioxide and primary carbonaceous aerosol emissions in China and India, 1996–2010, Lu et al., ACP, 2011

In 2016 India Overtook China, based on Satellite Measurements)





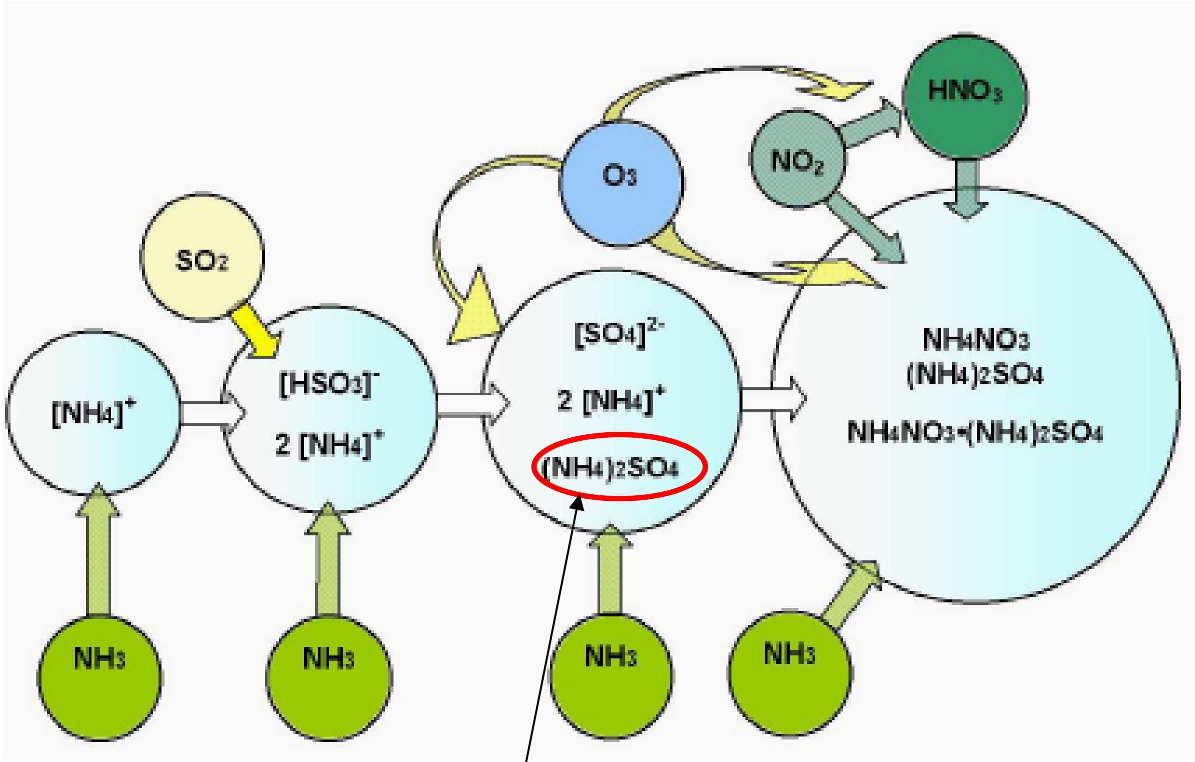
NASA



Li et al., Scientic Reports, 2017

Particle formation with the inclusion of SO_2

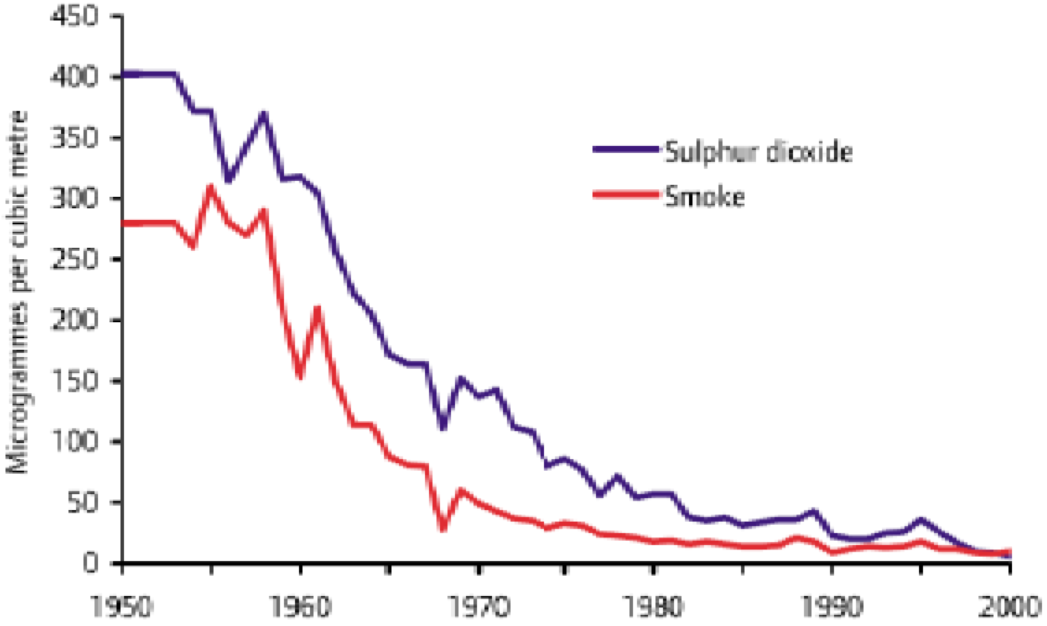
Key to secondary particle formation is NH_3 (ammonia) mainly emitted from agriculture (manure/fertilizer)



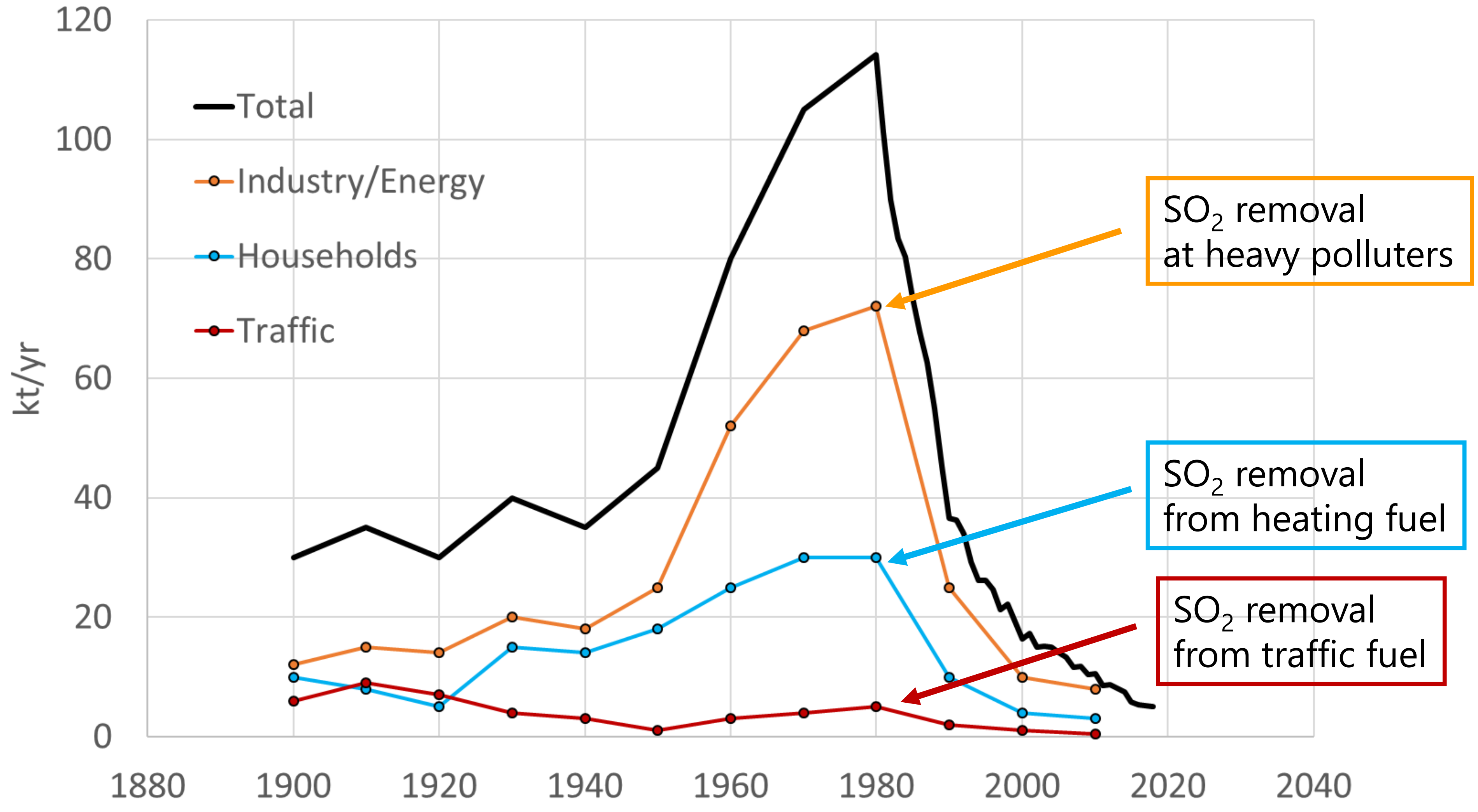
Ammoniumsulfate

regional effects:
The London smog (winter smog)

London, 1952

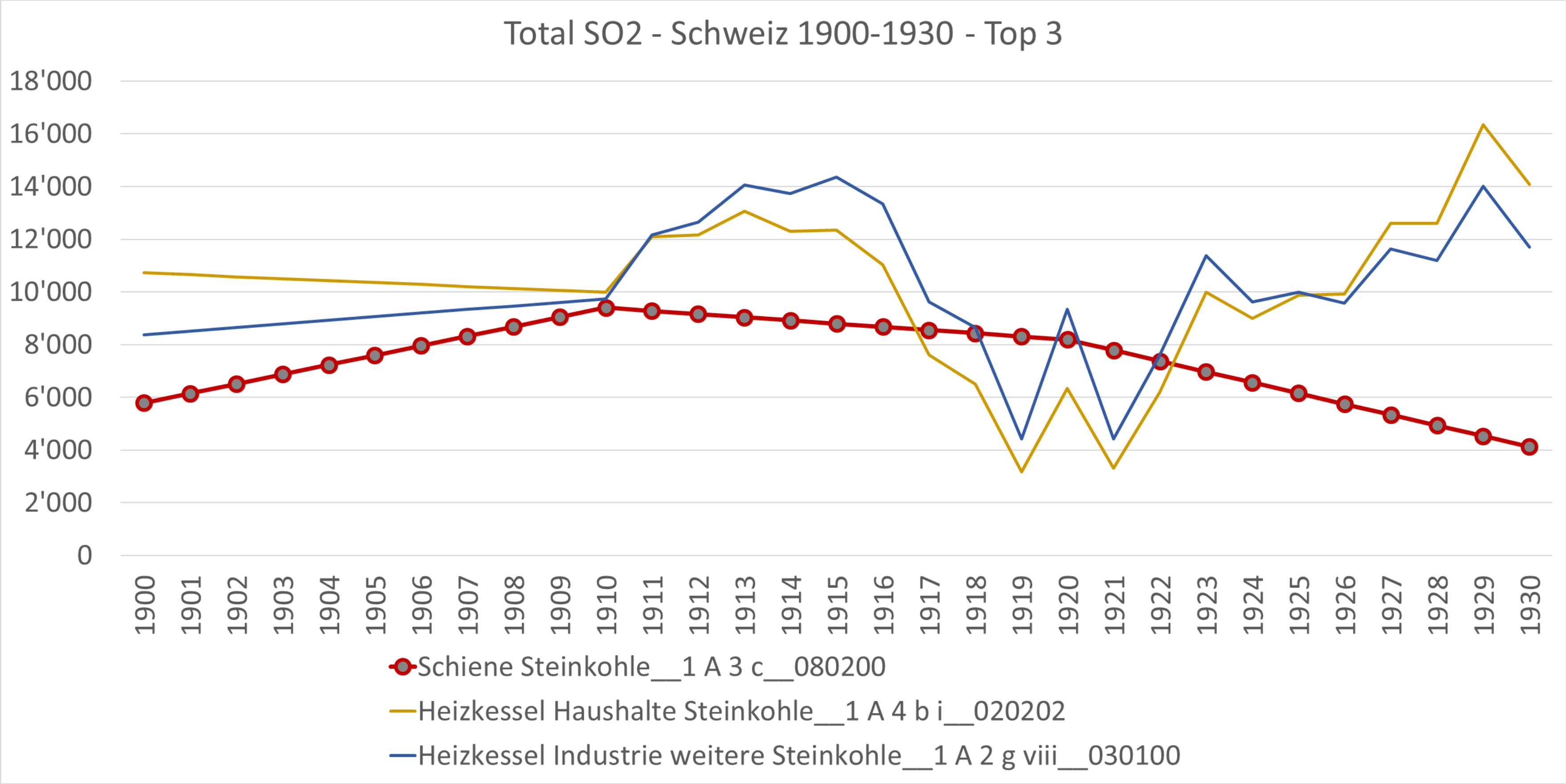


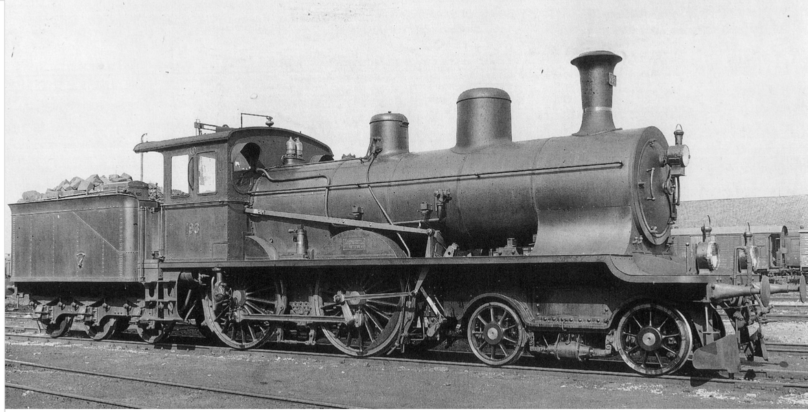
SO_2 emissions in Switzerland



Switzerland's Informative Inventory Report 2020 (IIR)

SO_2 peak from traffic in 1910 in Switzerland



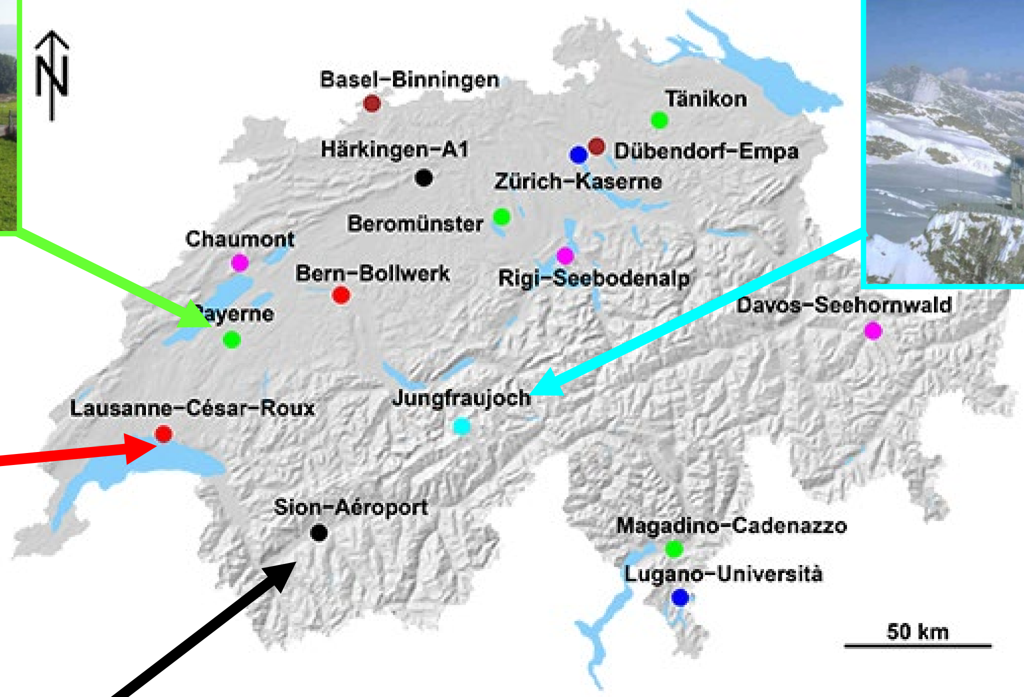


A2/4: Schnellzuglokomotive 1906
6t Kohle; bis 100 km/h

AE 3/6: ab 1920
bis 110 km/h

Antwort BAFU: Schaut man aber die Emissionen aus dem Schienenverkehr an, erkennt man tatsächlich einen schwachen Peak im Jahr 1910. Die Vermutung mit der Elektrifizierungswelle um und ab 1920 dürfte also korrekt sein.

Swiss Network for Air Pollution Monitoring
NABEL



- City center, street
- City center, park
- Rural, highway
- rural, below 1000 m
- rural, above 1000 m
- agglomeration
- high-Alpine

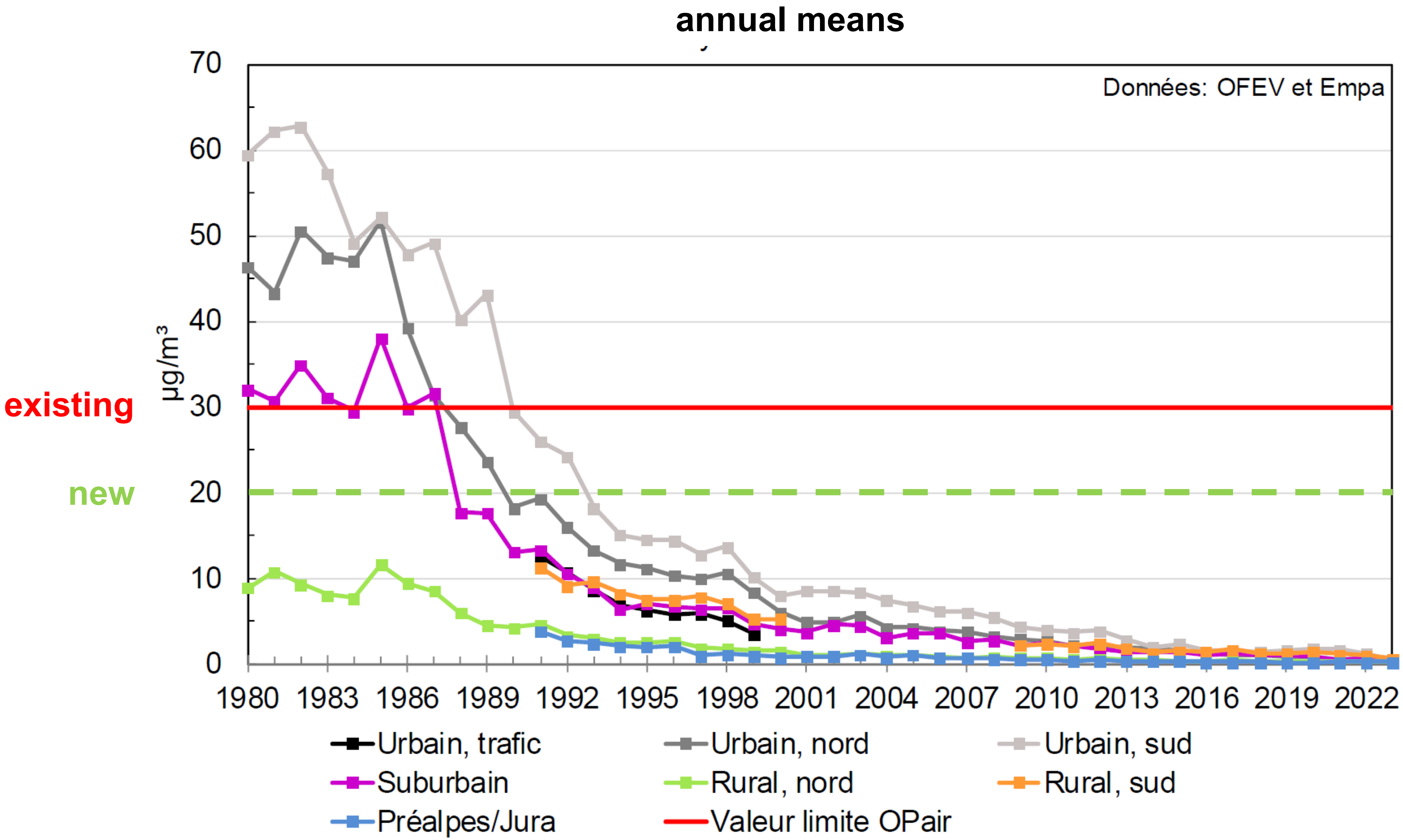
Swiss Legal Air Pollution Limits

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

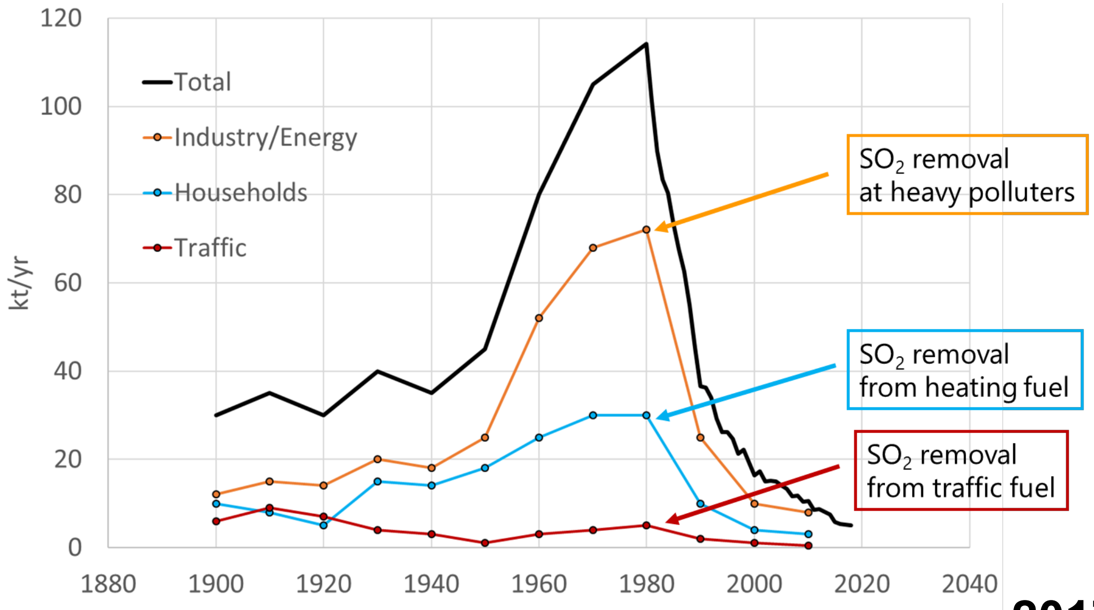
Pollutant	Averaging time	WHO AQG 2021	Current OAPC ambient limit value	FCAH recommen-dation 2023
Sulphur dioxide (SO_2), µg/m³ (see Chapter 8)	Annual average and new mean value over winter half-year	–	30[a]	20[b]
	95 % of ½ h mean value for a year	–	100	remove
	24h mean value	40[c]	100[d]	40[c]
Nitrogen 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.

SO_2 concentrations in Switzerland (1980-2023)



Do-it yourself: SO_2 in Switzerland



2017: 5'000t/yr

Back-of-the envelope calculation

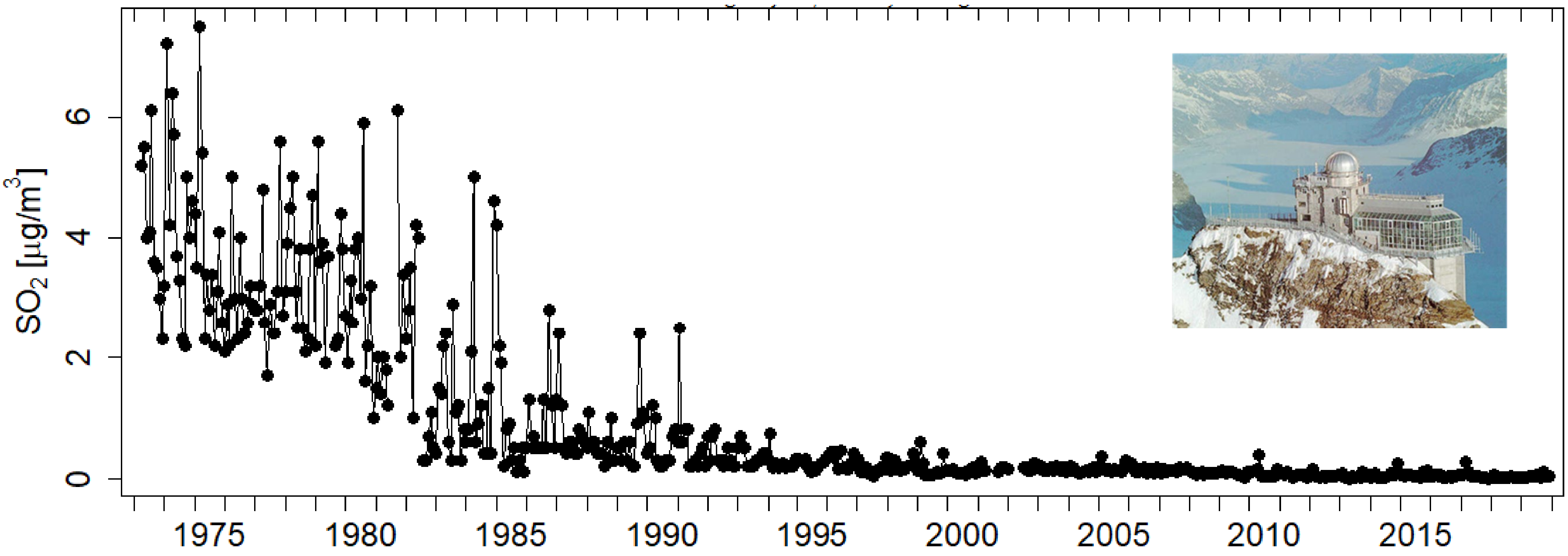
Assumption:
Lifetime: 3 days
(all emissions are replaced)

Mixing height: 1 km

Area CH: 42'000 km²

Concentration in µg/m³?
1985 and 2017

Effect of restrictions on SO_2 in the atmosphere
Jungfraujoch 1973 – 2019



Overview of measurement-techniques for tropospheric trace compounds

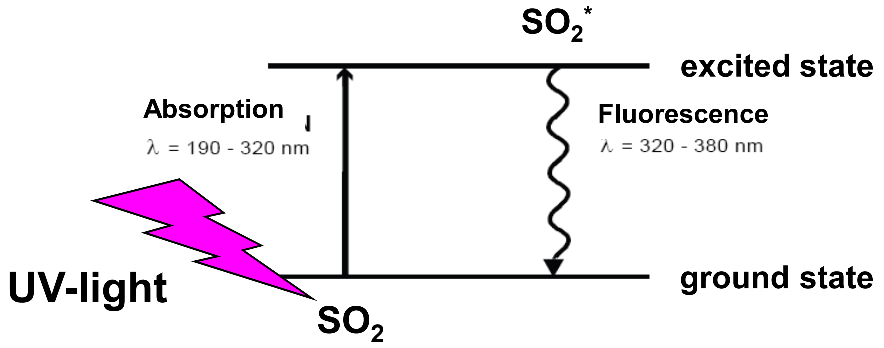
	Compound	Monitor	GC – (MS)	Laser	Satellite
air pollutants in OPair	**SO_2**	**XX**			**X**
	NO_x	XX			X
	CO	XX	X	X	X
	O_3 (Troposph.)	XX			(X)
	Particles	X			(X)
	VOCs	(X)	X		
greenhouse gases in Kyoto Protocol	CO_2	XX	X	XX	(X)
	CH_4	X	XX	XX	X
	N_2O		XX	X	(X)
	Halocarbons*		X		(X)

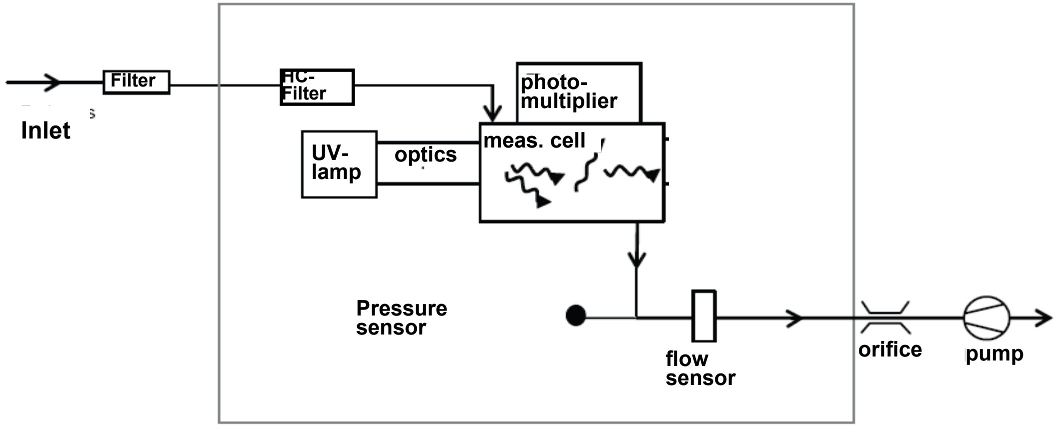
XX: best available method
X: good method
(X): possible

* also causing ozone depletion

Measurements of SO_2 in the atmosphere
Measurement principle: UV-fluorescence (monitor)

UV-fluorescence (monitor)
APSA-370





Swiss Legal Air Pollution Limits
Luftreinhalteverordnung bestehend und neu empfohlen

Schadstoff	Mittelungszeit	WHO AQG 2021	LRV IGW derzeit	Empfehlung EKL 2023
Schwefeldioxid (SO_2), µg/m³ (siehe Kapitel 8)	Jahresmittelwert und neu Mittelwert über das Winterhalbjahr	–	30[a]	20[b]
	95 % der ½-h-Mittelwerte eines Jahres	–	100	streichen
	24-h-Mittelwert	40[c]	100[d]	40[c]
Stickstoffdioxid (NO_2), µg/m³ (siehe Kapitel 7)	Jahresmittelwert	10	30	10
	95 % der ½-h-Mittelwerte eines Jahres	–	100	streichen
	24-h-Mittelwert	25[c]	80[d]	25[c]
Kohlenmonoxid (CO), mg/m³ (siehe Kapitel 9)	24-h-Mittelwert	4[c]	8[d]	4[c]
Ozon (O_3), µg/m³ (siehe Kapitel 6)	Sommersaison[e]	60	–	60
	98 % der ½-h-Mittelwerte eines Monats	–	100	100
	8-h-Mittelwert	100[c]	–	–
	1-h-Mittelwert	–	120[d]	120[d]
Schwebestaub / Feinstaub (PM10), µg/m³ (siehe Kapitel 4)	Jahresmittelwert	15	20	15
	24-h-Mittelwert	45[c]	50[c]	45[c]
Schwebestaub / Feinstaub (PM2.5), µg/m³ (siehe Kapitel 5)	Jahresmittelwert	5	10	5
	24-h-Mittelwert	15[c]	–	15[c]

[a] Immissionsgrenzwert, welcher auch den Schutz von Tieren und Pflanzen, ihren Lebensgemeinschaften und Lebensräumen nach USG Art. 1 Abs. 1 einschliesst und dem Stand des Wissens zum Zeitpunkt des Erlasses der Luftreinhalte-Verordnung im Jahre 1985 entspricht.
[b] Wert der WHO-Luftqualitätsleitlinien 2000 (WHO, 2000), welcher zum Schutz von Wäldern und weiteren naturnahen Ökosystemen festgelegt wurde. Er gilt als Jahresmittelwert sowie auch für das Winterhalbjahr. (Oktober–März).
[c] 99. Perzentil (d. h. 3 Überschreitungen pro Jahr sind zulässig).
[d] Darf höchstens einmal pro Jahr überschritten werden.
[e] Durchschnitt der maximalen täglichen 8-h-Mittelwerte der Ozon-Konzentration in den sechs aufeinanderfolgenden Monaten mit der höchsten Ozon-Konzentration im Sechsmonatsdurchschnitt. Für die Schweiz entspricht dies April bis September.

Rationale for CO measurements

- CO is toxic to humans

- CO is an intermediate product of the VOC degradation on the way to CO_2 (the final product)

- CO is a good tracer for anthropogenic pollution (e.g. in Europe) and for biomass burning (e.g. in Africa)

- CO sources are known well => relative emission of other anthropogenic pollutants can be estimated

Carbon monoxide (CO): global budget

Sources [Tg/y] (Duncan et al., 2007)

Fossil fuel combustion	476
Biofuel	189
Biomass burning	512
Oxidation of methane	812
Oxidation of hydrocarbons	177
Total	2166

Sinks (approx.)

Oxidation by OH	78%
Soil uptake	17%
Stratosphere	4%

Lifetime:
2 months

CO oxidation by OH

$CO + OH \rightarrow CO_2 + H$

$H + O_2 \rightarrow HO_2$

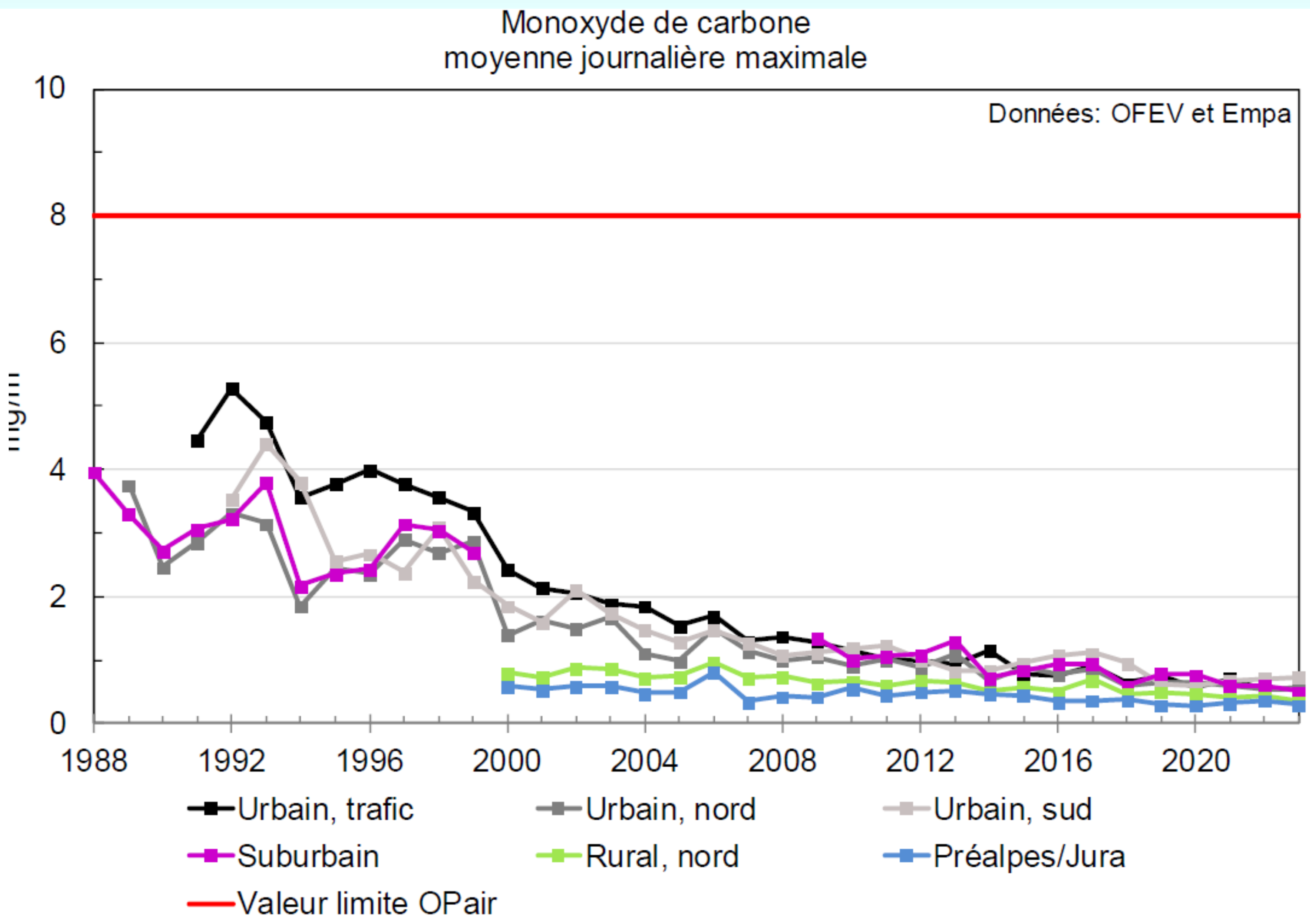
$HO_2 + NO \rightarrow OH + NO_2$

$NO_2 + h\nu \rightarrow NO + O$

$\underline{O + O_2 \rightarrow O_3}$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

CO: Switzerland (yearly averages)



Limit value: 24-h average should not exceed 8 ug/m^3

No exceedance in the last decades

Overview of measurement-techniques for tropospheric trace compounds

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

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

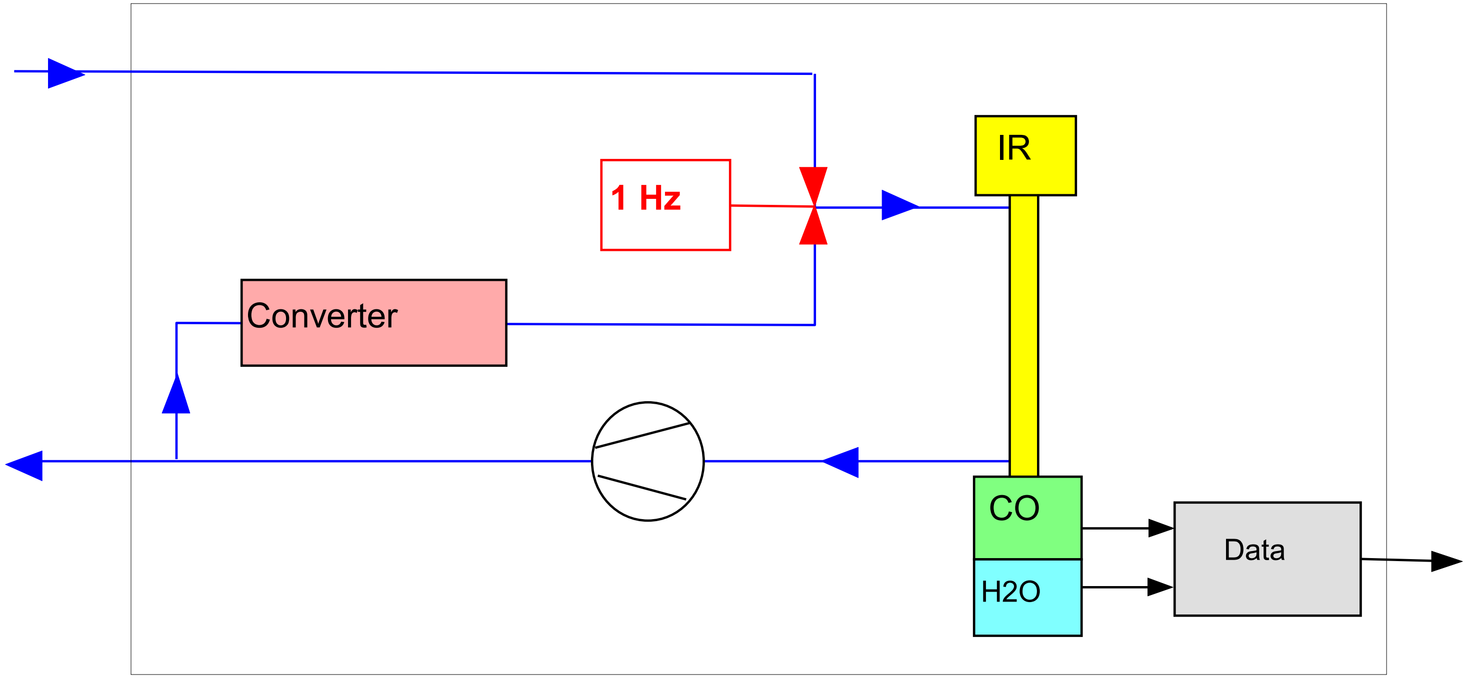
CO: measurement principles

1. **NDIR Spectrometry** (Non-dispersive infrared)
   The absorbed amount of light is direct proportional to the CO mixing ratio

2. **Quantum cascade laser/cavity ring-down laser**

CO and CO_2 measurement principles
1. NDIR: Non-dispersive infra red

Horiba APMA-360

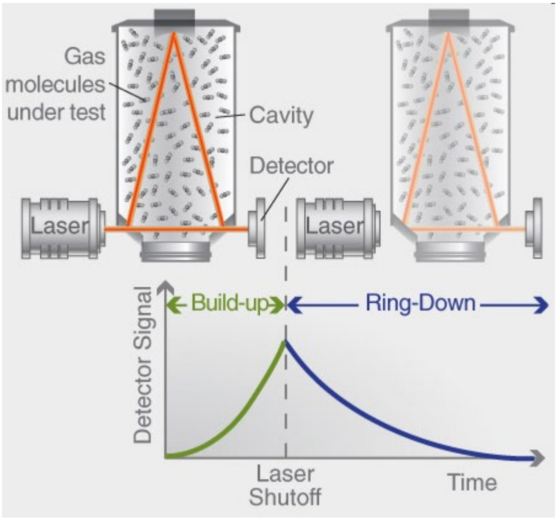


Linear, robust

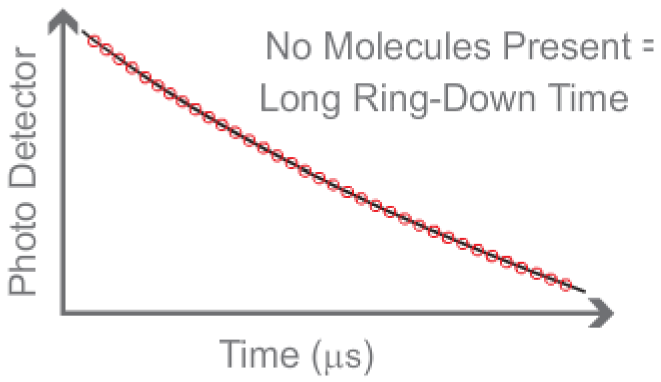
Linearity: 0-100 ppm
Detection limit: ~10 ppb
needs zeroing about every week

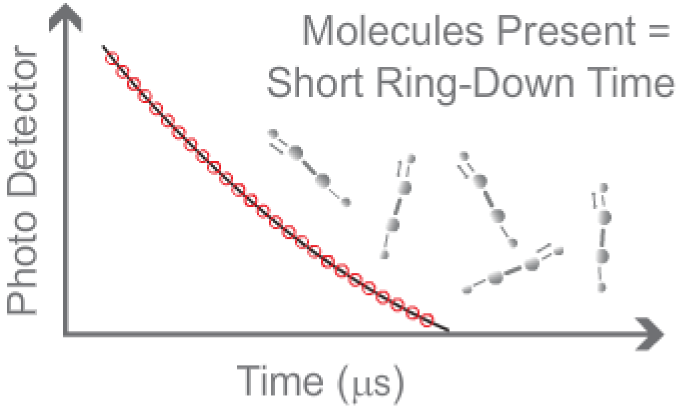
2. Laser-based: Cavity-ring down laser (CRD)

Picarro G1302



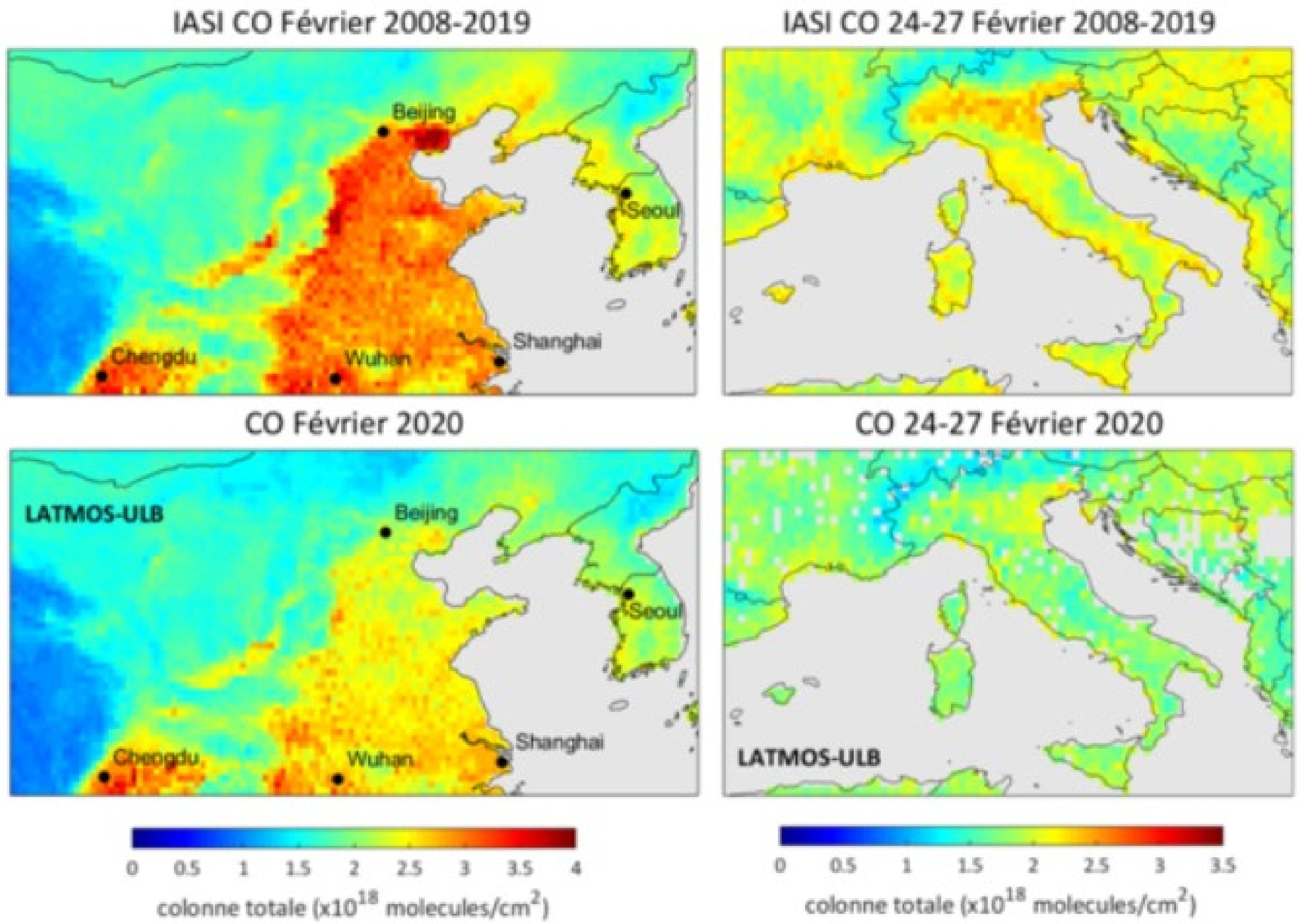
detection limit (1s)	<2 ppb
linearity	0-1000 ppm
time resolution	5s – 5 min.
time coverage	integral





http://www.picarro.com/gasanalyzers/carbondioxide.php

CO before and after Corona



https://www.ipsl.fr/Actualites/Actualites-scientifiques/Coronavirus-chute-de-la-pollution-en-Chine-et-en-Italie-vue-depuis-l-espace-avec-IASI