ITINERIS

NO_x near-surface measurements (science & techniques)

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Italiadomani

Outline

- ❑ **Introduction on nitrogen oxides**
  - Definitions
  - Sources
  - Chemical reactions
- ❑ **Measurements of NO_x**
  - Chemiluminescence technique
  - Other techniques
  - Interferences by ozone and relative humidity, zero offset correction
  - Calibration
  - How to setup NO_x measurements
- ❑ **NO_x measurements at Monte Cimone**
  - Experimental setup
  - Diel and seasonal variability

Nitrogen oxides

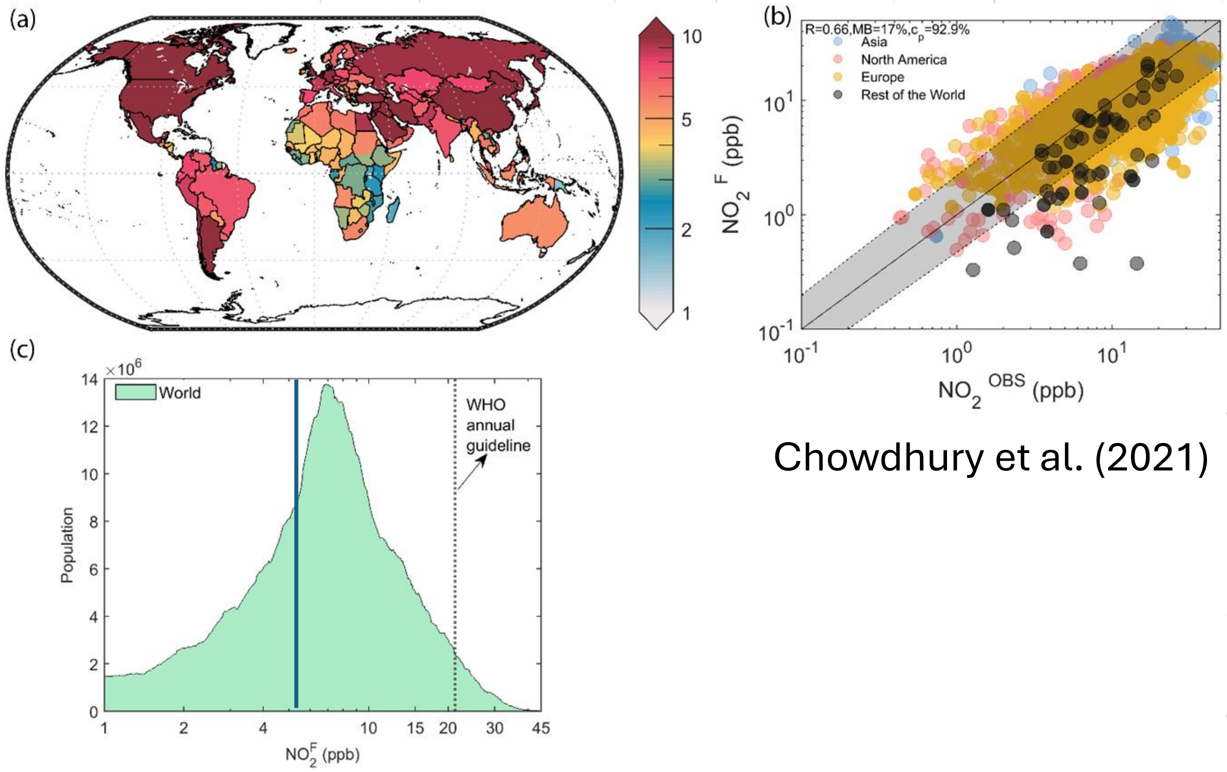
NO	Nitric oxide	$\left.\right\}$ NO_x
NO_2	Nitrogen dioxide	
	Lifetime of hours (NO), hours to days (NO_2)	
	Health effects: respiratory irritation, aggravation of asthma, respiratory infections	
	Environmental effects: NO_x react with VOCs to produce O_3, control OH, acid rain	
N_2O	Nitrous oxide	
	Lifetime > 100 years	
	Powerful greenhouse gas, controls O_3 variations in the stratosphere	
NO_3	Nitrate radical	
	Lifetime of seconds to hours	
	Important for the degradation of VOCs during night-time	
N_2O_5	Dinitrogen pentoxide	
N_2O_4	Dinitrogen tetroxide	
	Night-time sources of nitric acid; reservoirs for nitrate radical and NO_x	

WMO (2011)

Nitrogen oxides

NO	Nitric oxide
NO_2	Nitrogen dioxide

} NO_x



Chowdhury et al. (2021)

90% of the World's NO_2-related asthma incidence is found in regions that meet the WHO guideline of 21.25 ppb (40 μg m^{-3})

2021: the WHO reduced the guideline to 10 μg m^{-3}

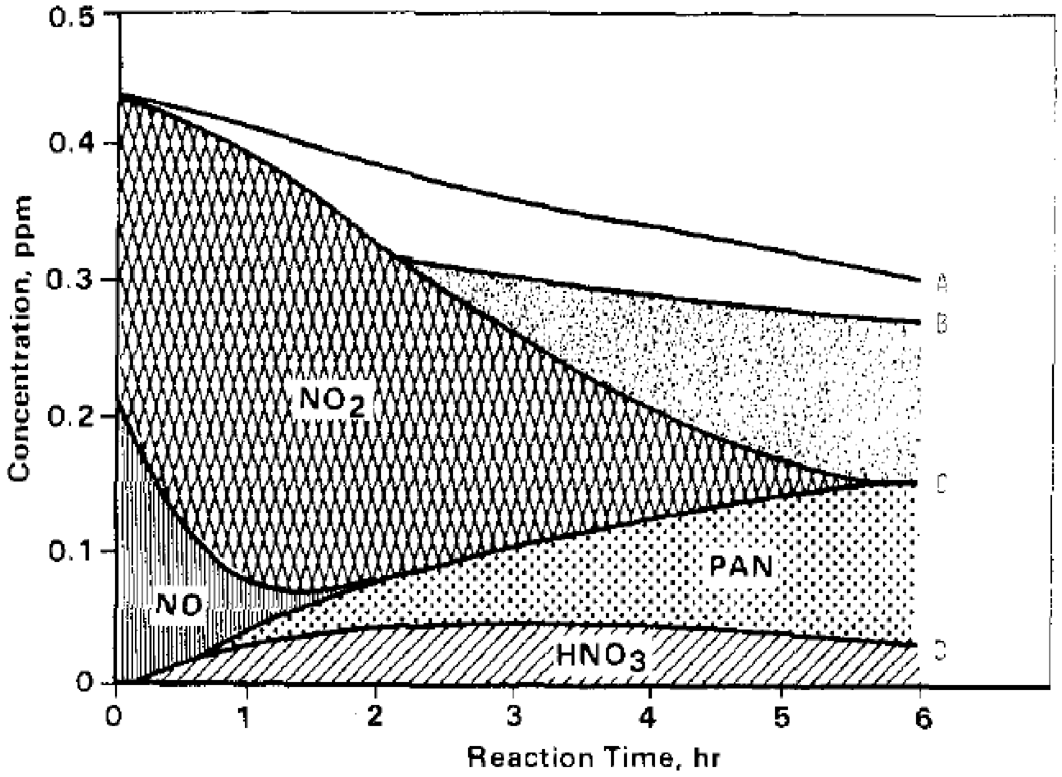
→ **Most of the World's population lives in unhealthy conditions**

Nitrogen oxides

NO	Nitric oxide	NO_x
NO_2	Nitrogen dioxide	
N_2O	Nitrous oxide	
NO_3	Nitrate radical	NO_z
N_2O_5	Dinitrogen pentoxide	
N_2O_4	Dinitrogen tetroxide	
HNO_3	Nitric acid	
HONO	Nitrous acid	
$RONO_2$	Alkyl nitrates	
$RCOONO_2$	Peroxyacyl nitrates, PANs	

$$NO_z + NO_x = NO_y$$

odd nitrogen



Spicer (1983)

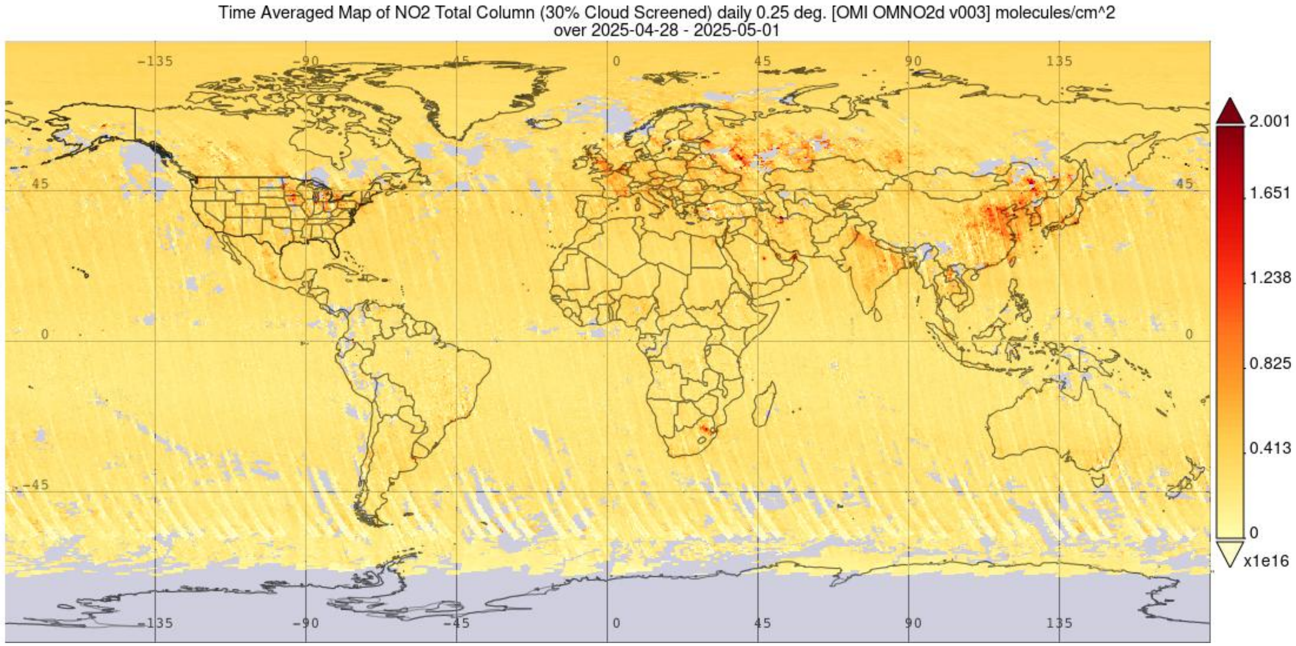
- NO and NO_2 have rather short lifetime
- Closer to the source, NO_y is dominated by NO and NO_2
- More remote you get, more important influence from NO_z

Sources of nitrogen oxides (NO_x)

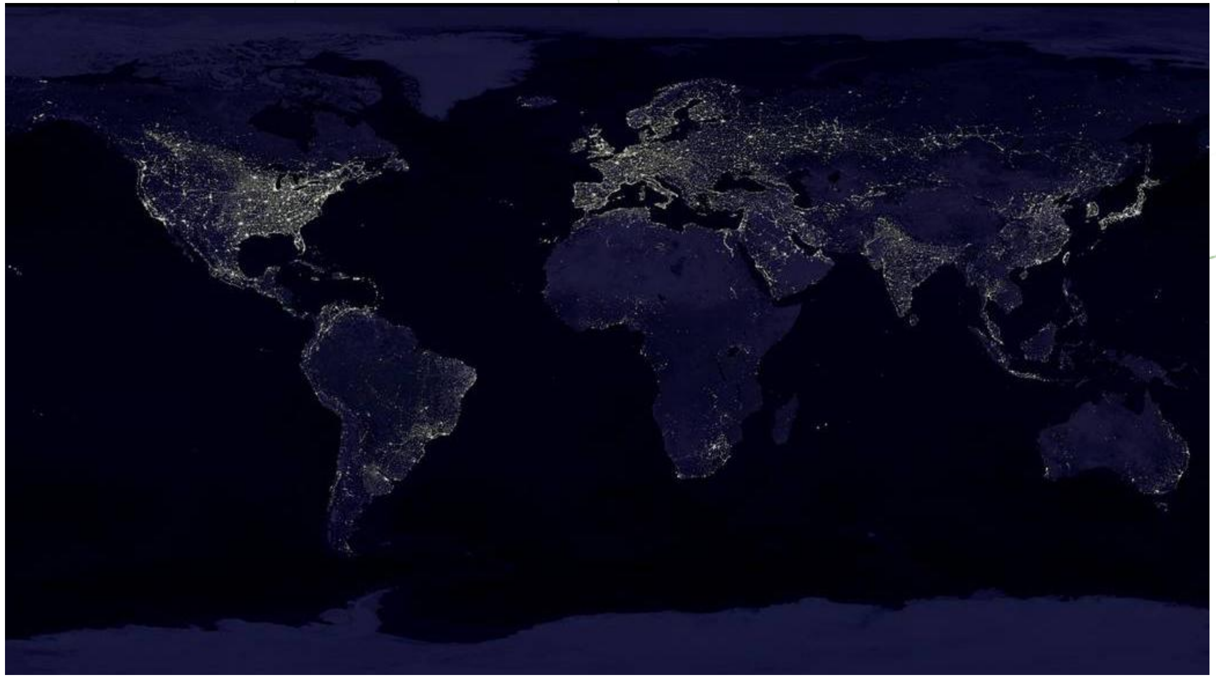
Biogenic sources	22 Tg/y
Lightning	10-20 Tg/y
Biomass Burning	18 Tg/y
Anthropogenic	72 Tg/y

Müller (1992)

- NO_x are mainly formed in combustion processes, at high temperatures, at excess oxygen, produced mainly as NO (not as NO_2)

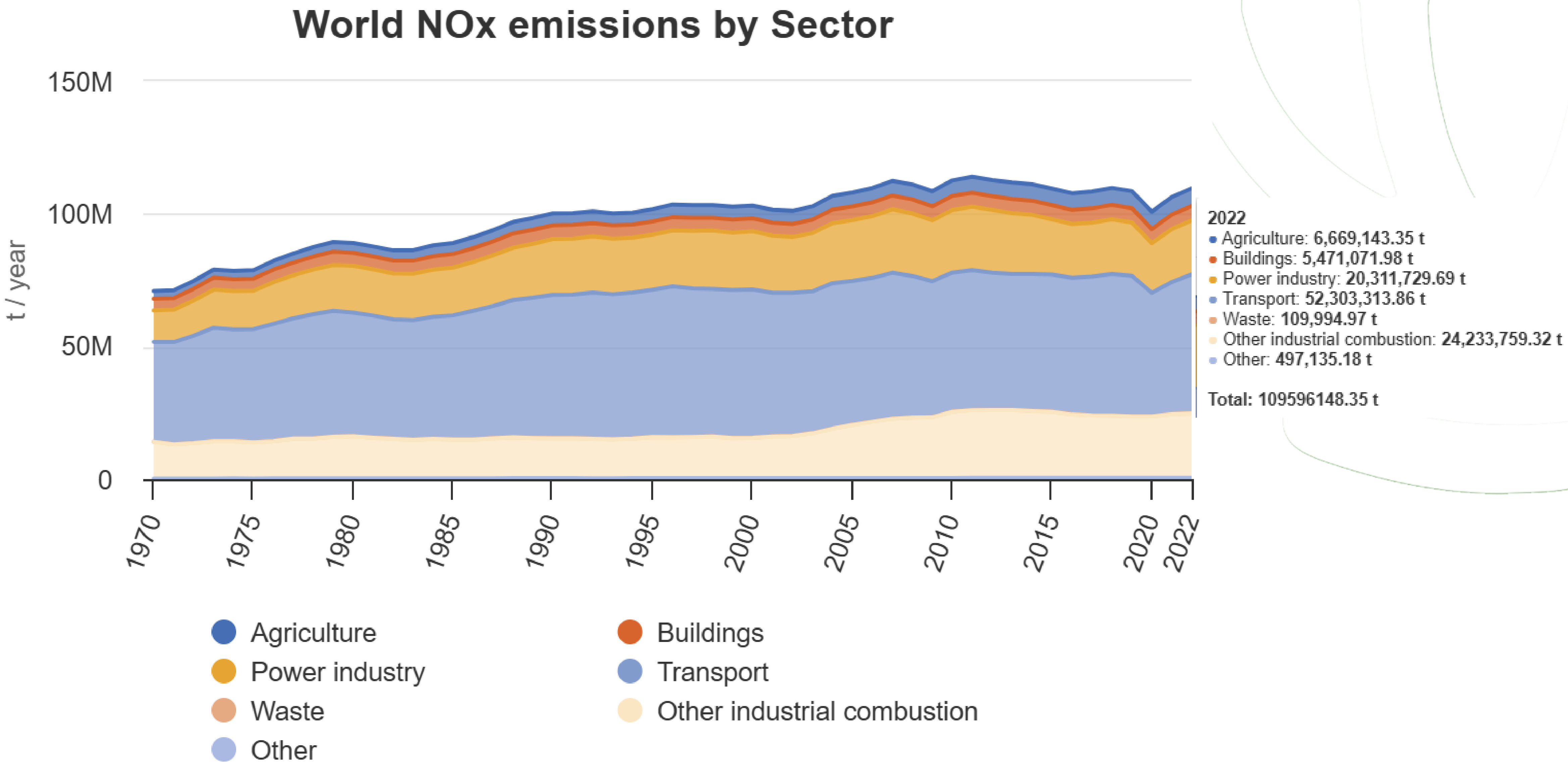


NASA/GSFC/HSL



NASA/NOAA

Sources of nitrogen oxides (NO_x)



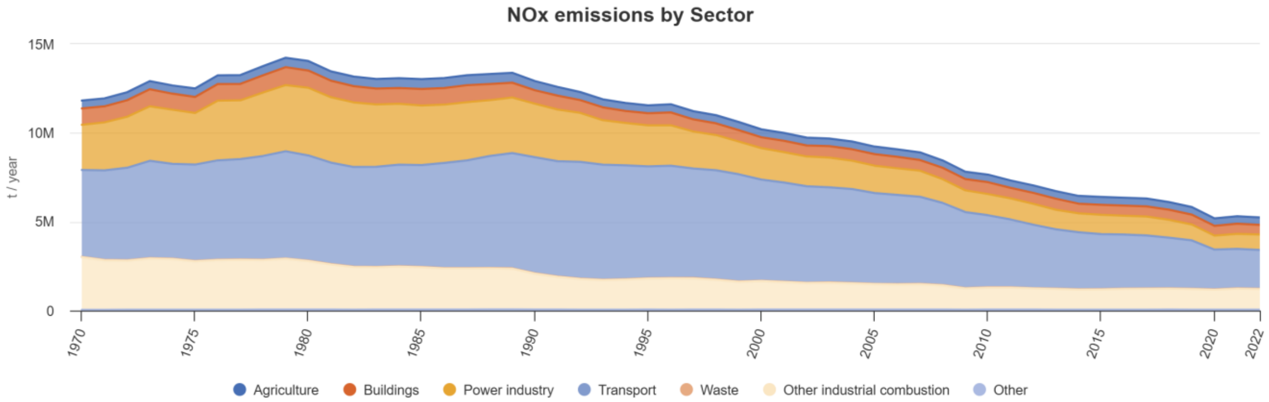
2022
- Agriculture: 6,669,143.35 t
- Buildings: 5,471,071.98 t
- Power industry: 20,311,729.69 t
- Transport: 52,303,313.86 t
- Waste: 109,994.97 t
- Other industrial combustion: 24,233,759.32 t
- Other: 497,135.18 t

Total: 109596148.35 t

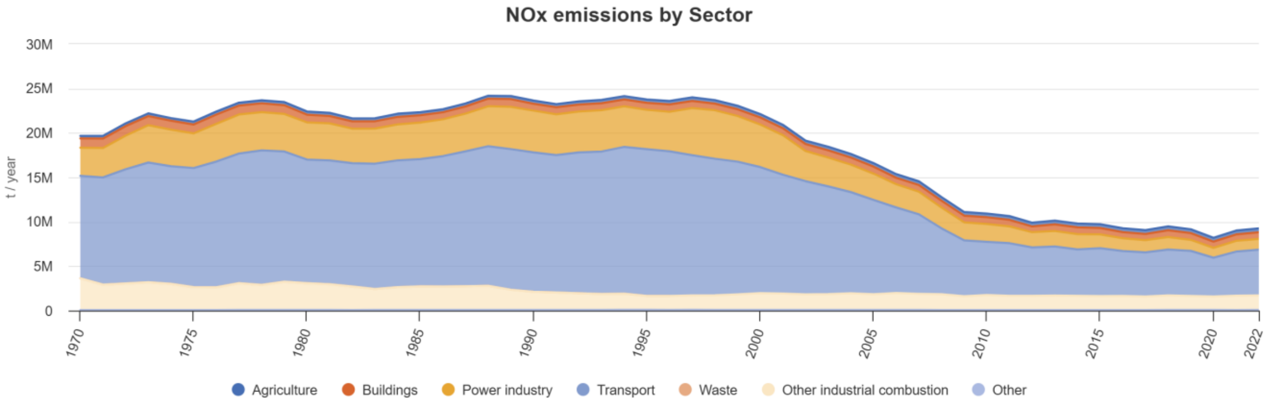
EDGAR v8.1 database

Sources of nitrogen oxides (NO_x)

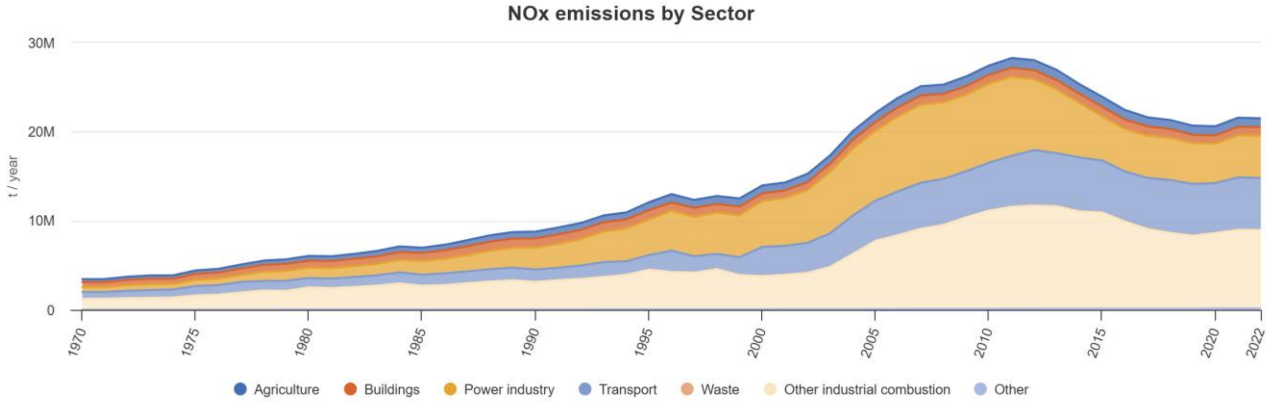
EU27



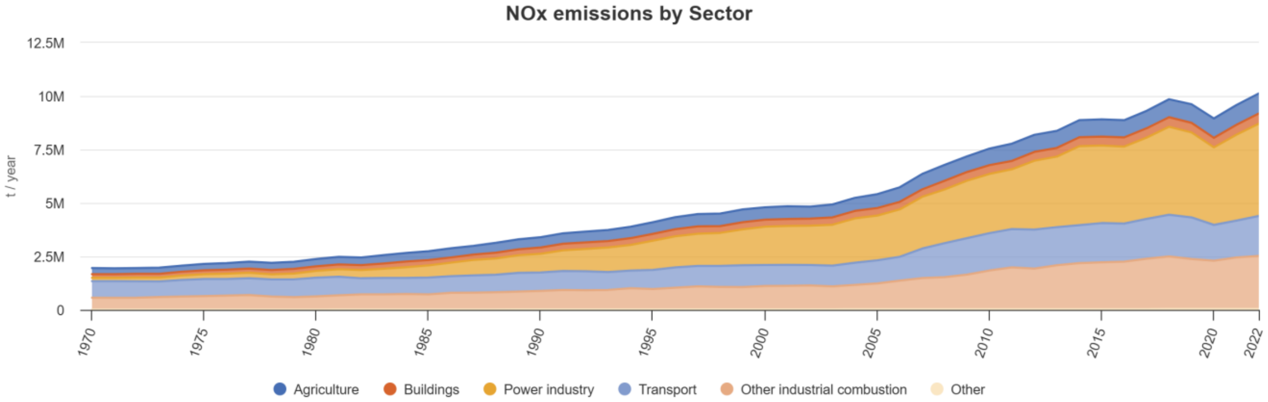
USA



China



India



EDGAR v8.1 database

Chemical reactions: the photostationary state

NO_2 photolysis	$NO_2 + h\nu$	$\rightarrow$	$NO + O(^3P)$	$j_{5.1}$ *($\lambda < 420$ nm)*
O_3 formation	$O(^3P) + O_2 + M$	$\rightarrow$	$O_3 + M$	$k_{5.2}$
O_3 destruction	$O_3 + NO$	$\rightarrow$	$NO_2 + O_2$	$k_{5.3}$

$$\boxed{NO_2 \overset{hv}{\rightleftarrows} NO + O_3}$$

$$[O_3]_{PSS} = \frac{j_{5.1} \cdot [NO_2]}{k_{5.3} \cdot [NO]}$$

In the absence of other pollutants (like VOCs), the reactions reach a **dynamical equilibrium**

Measurements of NO_x by chemiluminescence

The **chemiluminescence** occurs when NO is exposed to O_3. It is a two-step process.
First, the NO and O_3 molecules collide and react to produce O_2 and one molecule of NO_2. Part of this reaction gives excited NO_2

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO + O_3 \rightarrow NO_2^* + O_2$$

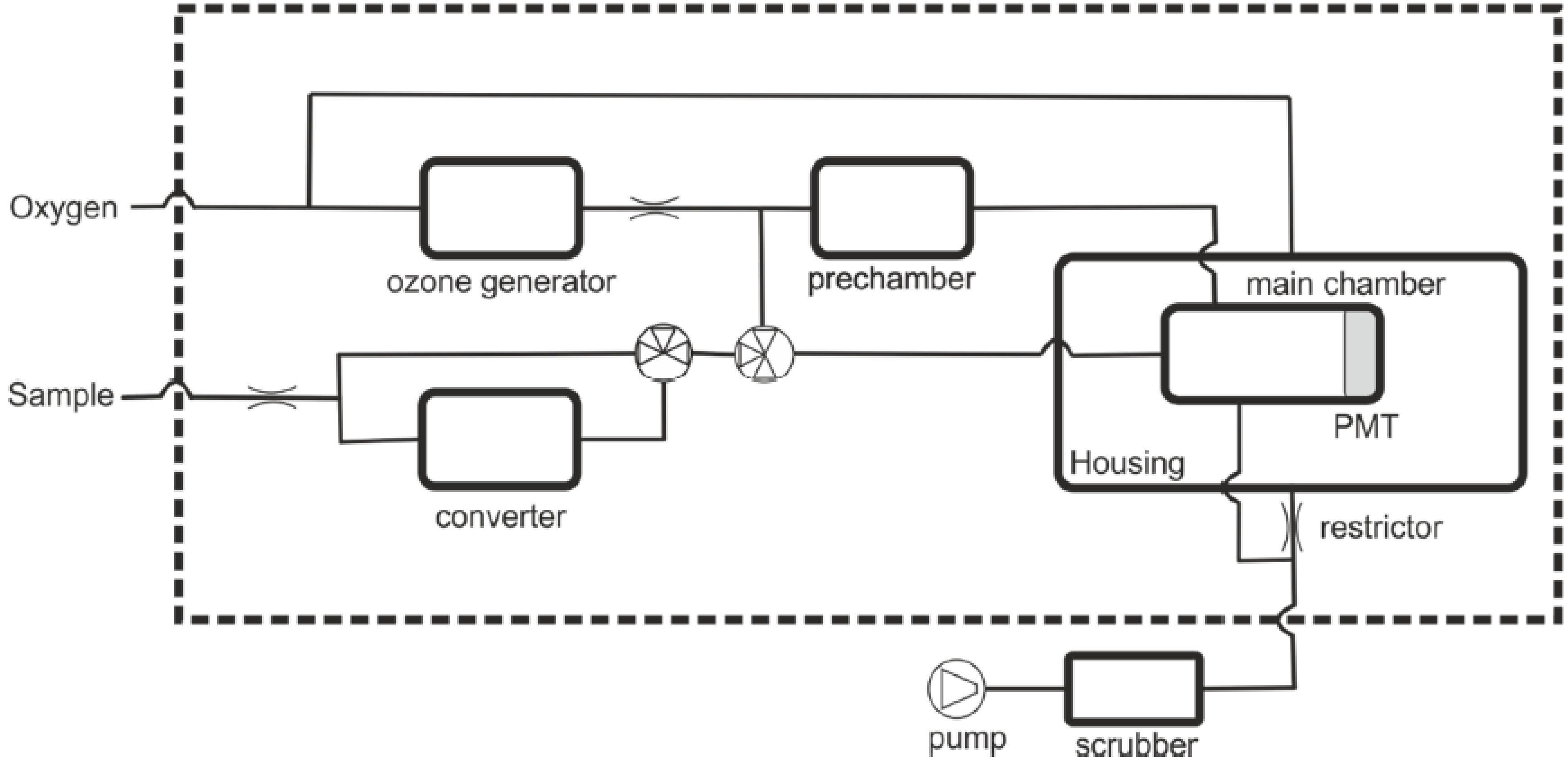
The excited NO_2 can be quenched by other molecules, or can quickly return to its ground state, **releasing excess energy**, in the form of a quantum of light

$$NO_2^* + M \rightarrow NO_2 \quad , \mathrm{M} = \mathrm{N_2, O_2, H_2O, Ar}$$
$$NO_2^* \rightarrow NO_2 + h\upsilon_{1200nm}$$

All things being constant (i.e., T, P, amount of O_3, …), the relation between NO and the amount of light emitted is **very linear**. If more NO is present, more IR light is produced. By measuring the amount of IR light produced with a sensor sensitive in the infra-red spectrum, the amount of NO present can be determined.

Measurements of NO_x by chemiluminescence

The NO **chemiluminescence** detector (CLD) has been invented in 1970 (Fontijn et al., 1970)



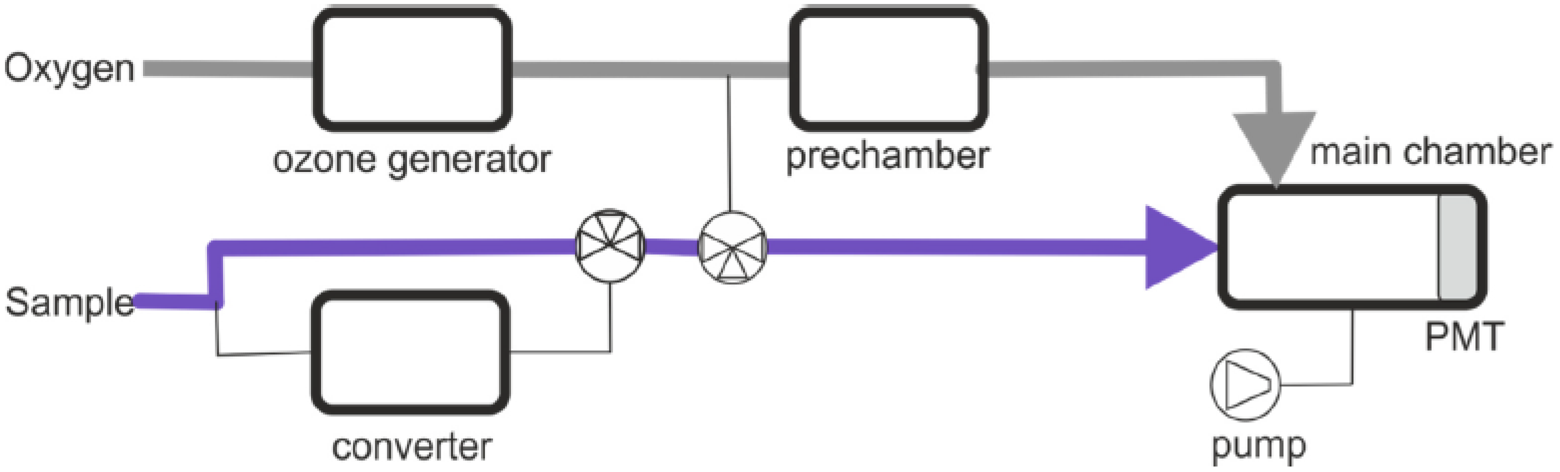
By altering both the converter mode and the chamber mode, a measurement cycle consists of **4 steps**

Measurements of NO_x by chemiluminescence

Measuring the zero is necessary because a **detector background** is always present (in the absence of NO) due to:

- Dark current (thermoionic emission of electrons across the stages in the PMT). A solution is to operate the PMT at low temperature
- Ozone reacting on cell walls
- Other molecules reacting with ozone, e.g. alkenes, which lead to an excited OH* radical, which fluoresces at a similar wavelength to NO_2*

To measure the detector background, the CLD uses the **pre-chamber mode**.



Flow goes directly to the main chamber

Measurements of NO_x by chemiluminescence

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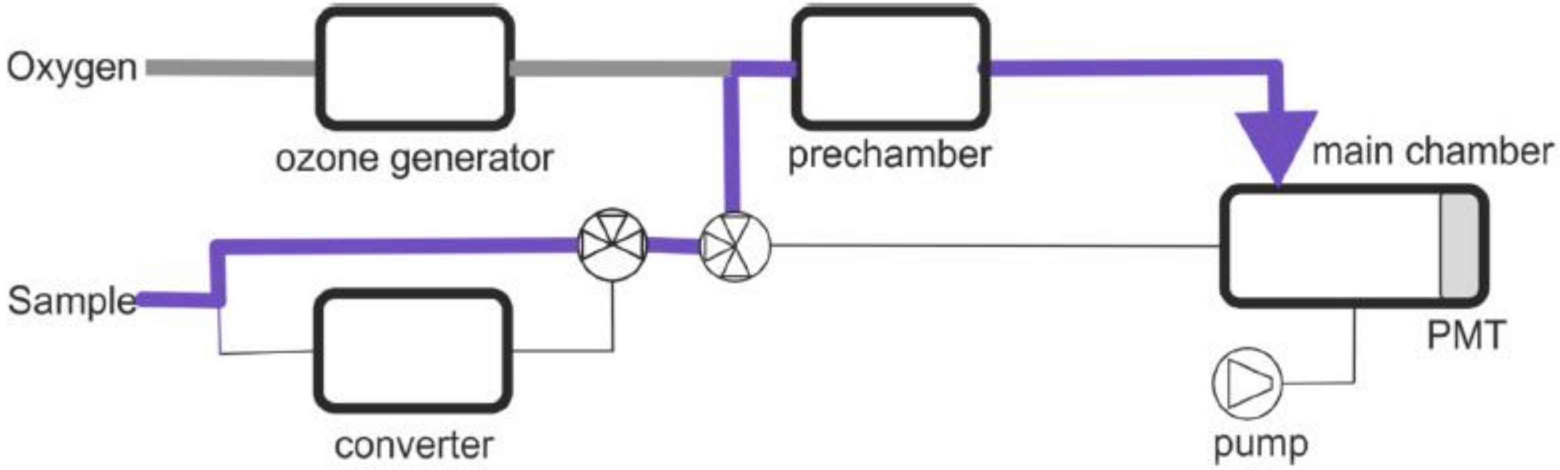


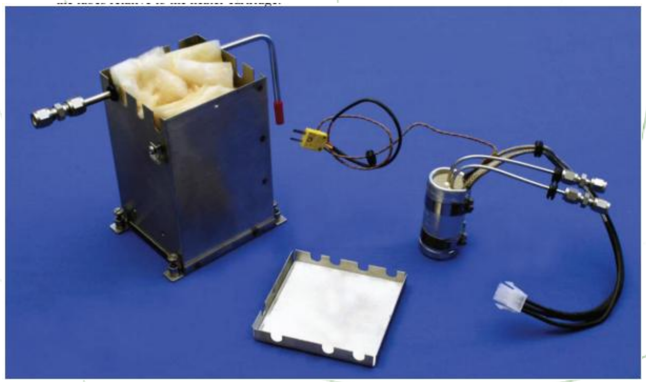
- $NO+O_3$ reaction 100 times faster than NO+alkene
- NO_2^* already been decayed when passing the prechamber

Measurements of NO_x by chemiluminescence

NO_2 to NO conversion: molybdenum converters

$$3NO_2 + Mo \rightarrow MoO_3 + 3NO$$

300-350 °C



MLU Recordum manual

Pros:

- Method approved by EPA and EEA
- High conversion efficiency (>95%)
- Conversion efficiency is very stable

Cons:

- Conversion of HNO_3, PANs, alkylnitrate can also be >95%

Grosjean and Harrison (1985)

Overestimate of measured NO_2:

- ~15-20% at a suburban site in Korea (Jung et al., 2017)
- ~17-30% at a rural site and 24-57% at a high-mountain site in Switzerland (Steinbacher et al., 2007)
- ~30% at a peatland monitoring site in Scotland (Cowan et al., 2024)

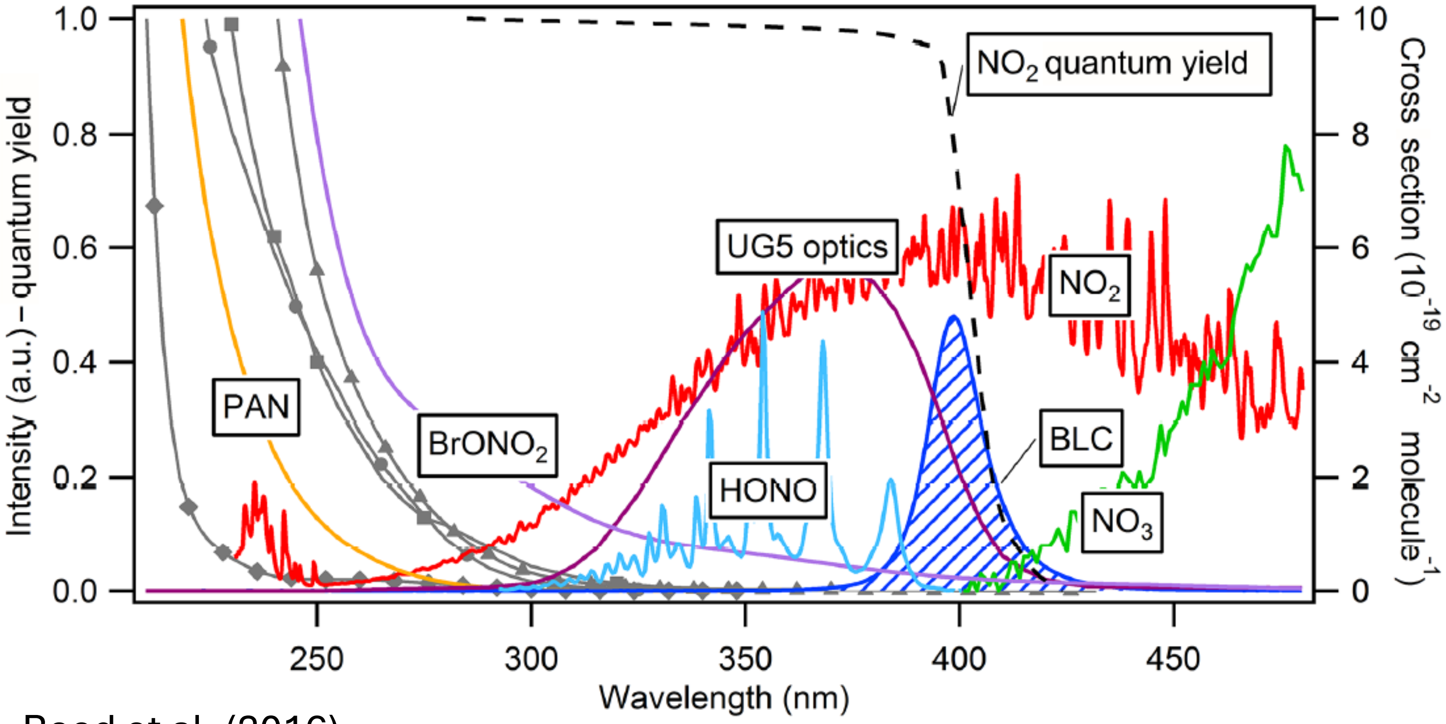
GAW does not recommend the use of molybdenum converters at its stations

Measurements of NO_x by chemiluminescence

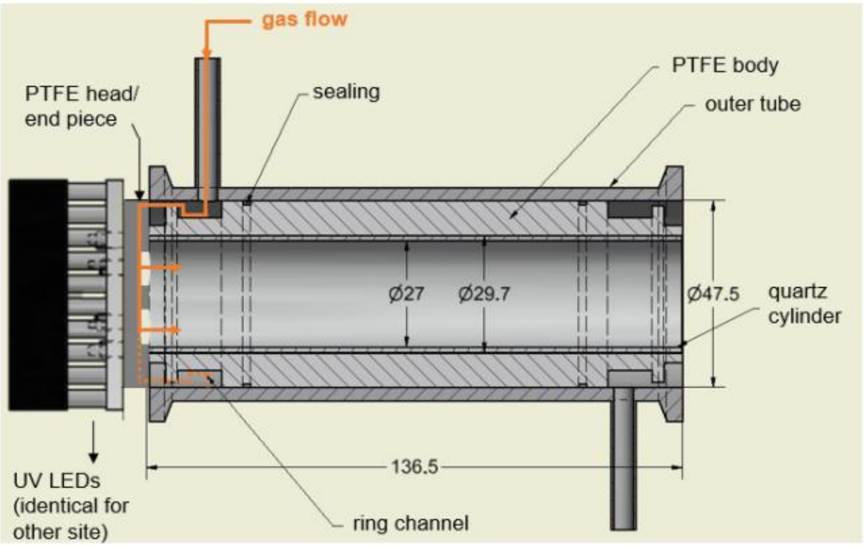
NO_2 to NO conversion: photolytic converters

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

Xenon lamps or UV emitting diodes («blue light converters»)



Reed et al. (2016)



(a) type 1 blue light converter

Nussbaumer et al. (2021)

- Spectral band width should be small
- No overlap with PAN
- Some overlap with HONO and $BrONO_2$

Other techniques for NO_x measurements

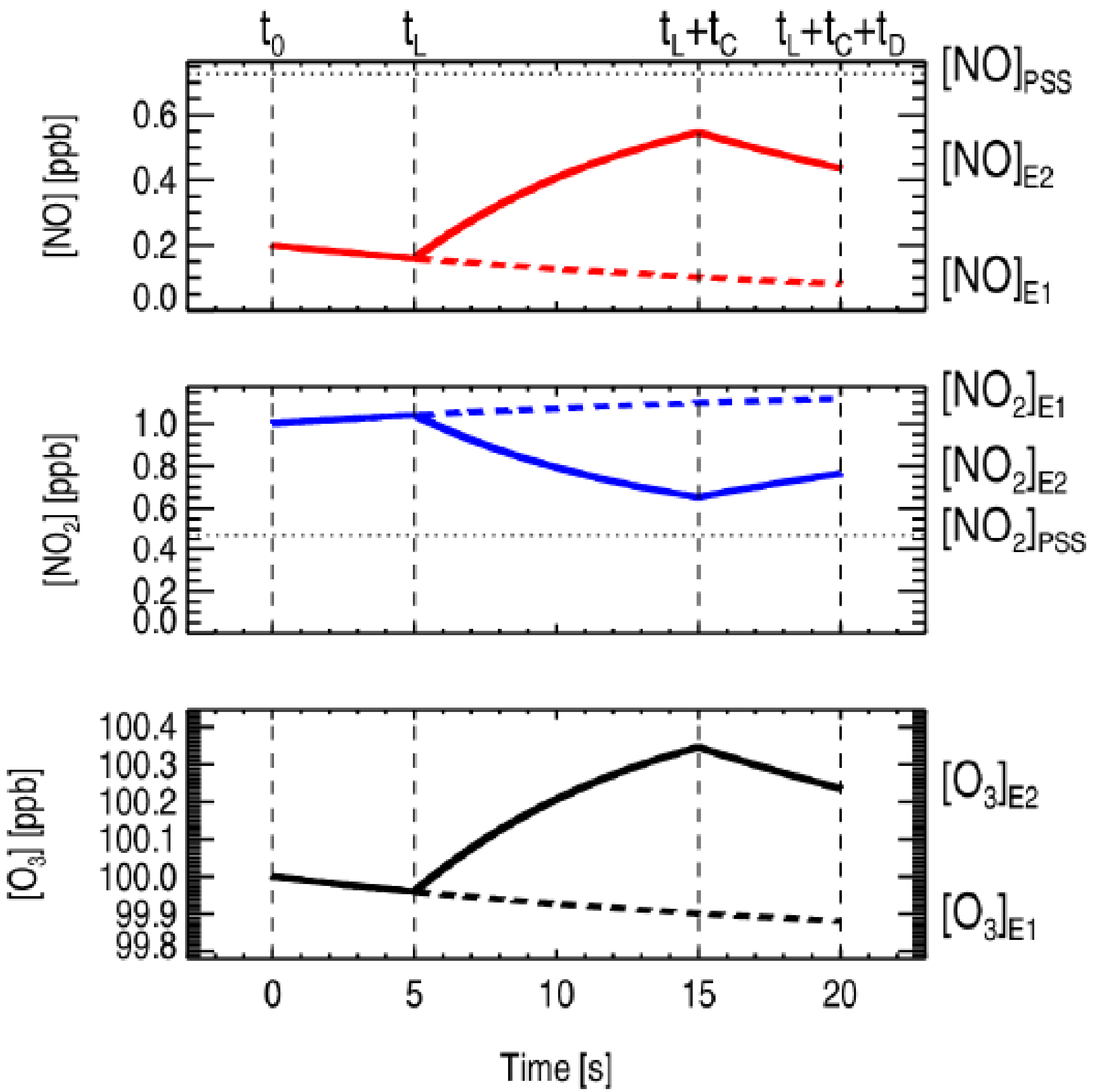
A direct spectroscopic measurement of NO_2 circumvents the conversion of NO_2 and reduces the possibilities of interferences.

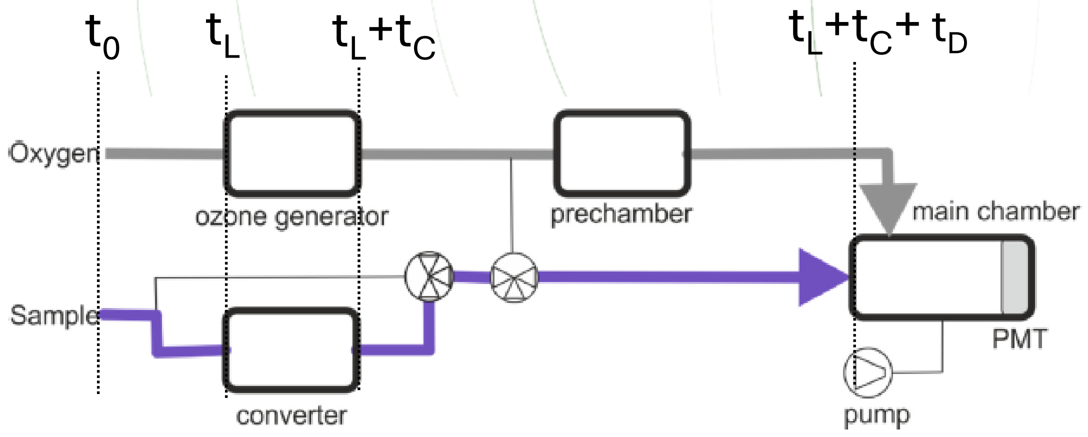
- **Cavity attenuated phase shift** spectroscopy (CAPS, Ge et al., 2013; Kebabian et al., 2008)
- **Quantum cascade laser** (QCL) absorption spectroscopy (Sobanski et al., 2021)
- **Iterative cavity-enhanced DOAS** (Horbanski et al., 2019)
- **Single-photon laser-induced fluorescence** (Rollins et al., 2020). This has been applied to measure NO at mixing ratios with a detection limit of better than 1 pptv for an integration time of 1 s

The advantage is that you can directly measure NO_2; however, most of these instruments are insensitive to NO, so the conversion of NO to NO_2 is needed. They are also sensitive to O_3 and humidity interferences.

Although these instruments are used in campaigns and perform well in intercomparisons, they are only rarely used for continuous measurements at remote or pristine sites and experience in the long-term behavior of these instruments are lacking. This is why the NO_x ACTRIS/GAW measurement guidelines do not yet include a SOP for spectroscopic systems.

Chemistry in the inlet



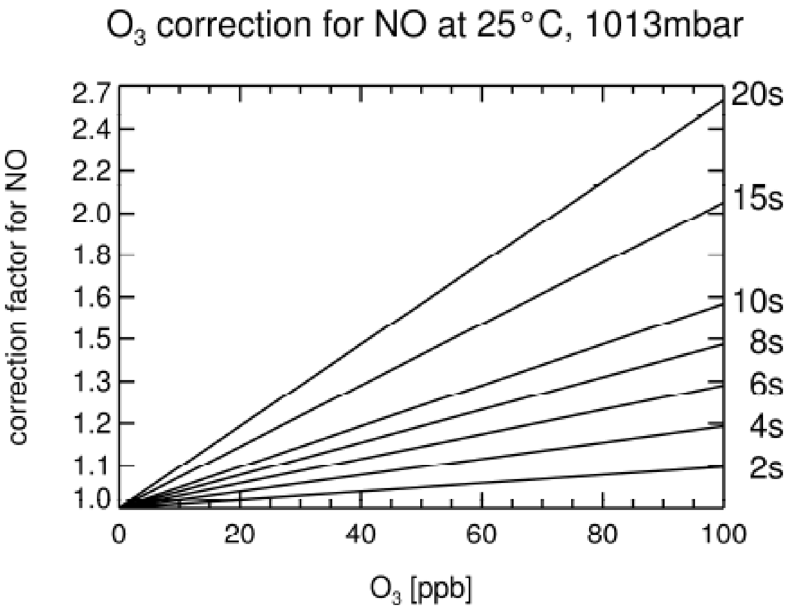


$$[NO]_0 = [NO]_{E1} \times e^{k_{O_3L} \times (t_L + t_B + t_D)}$$

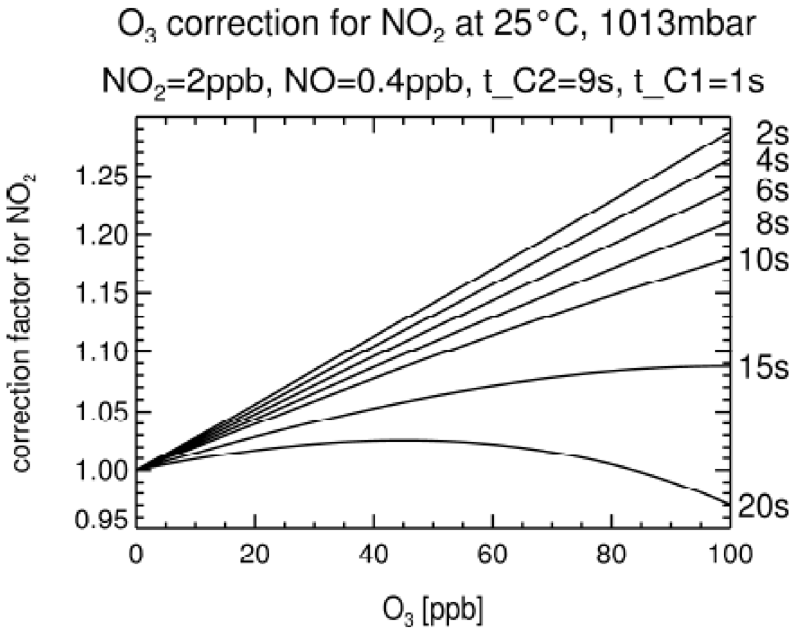
$$\boxed{NO_2 \rightleftarrows NO + O_3}$$

- NO reacts with O_3 in the inlet manifold, in the photolytical converter and after passing the converter before the detection in the CLD
- O_3 is also produced in the converter, which can oxidize NO on its way to the detector

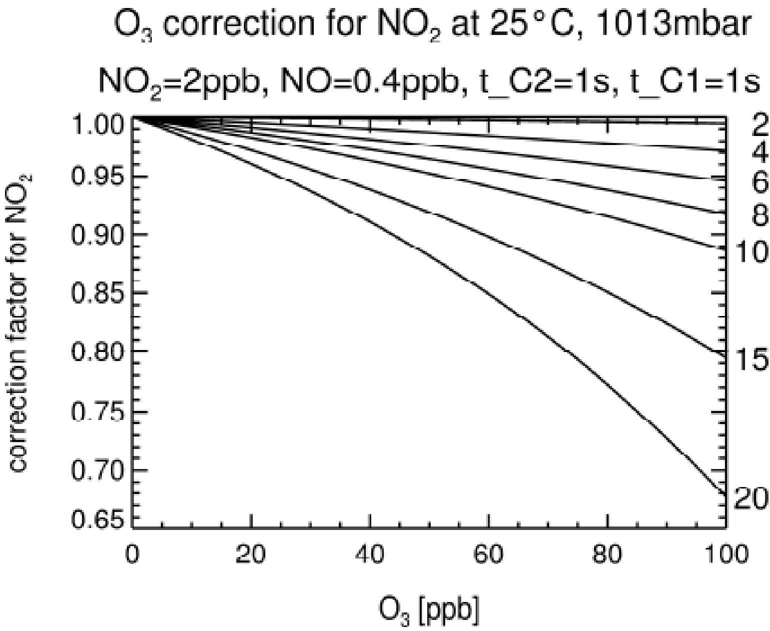
Chemistry in the inlet



Correction factor for NO at different residence time in sampling line



Correction factor for NO$_2$ at different residence time in sampling line



Correction factor for NO$_2$ at different residence time in sampling line

- Correction is necessary even with high sampling flows
- NO correction gets larger with larger O$_3$ concentration and longer residence time
- NO$_2$ correction gets larger/smaller with larger O$_3$ concentration (+−), longer inlet line (−), larger converter volume (+), larger NO concentration (−), better converter efficiency (-)

Inlet correction is needed for all NOx instruments, not only CLD

The humidity effect

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

$$NO_2^* + M \rightarrow NO_2 \quad , \mathrm{M} = \mathrm{N_2, O_2, H_2O, Ar}$$

$NO_2^* + N_2 \rightarrow NO_2$	$k(NO_2^* + N_2)$
$NO_2^* + O_2 \rightarrow NO_2$	$k(NO_2^* + N_2) * 1.115$
$NO_2^* + CO_2 \rightarrow NO_2$	$k(NO_2^* + N_2) * 2.05$
$NO_2^* + Ar \rightarrow NO_2$	$k(NO_2^* + N_2) * 0.5$
$NO_2^* + H_2O \rightarrow NO_2$	$k(NO_2^* + N_2) * 4.42$

Matthews et al. (1977)

Factor for quenching in ambient air

21% → 1.034

400 ppm → 1.000

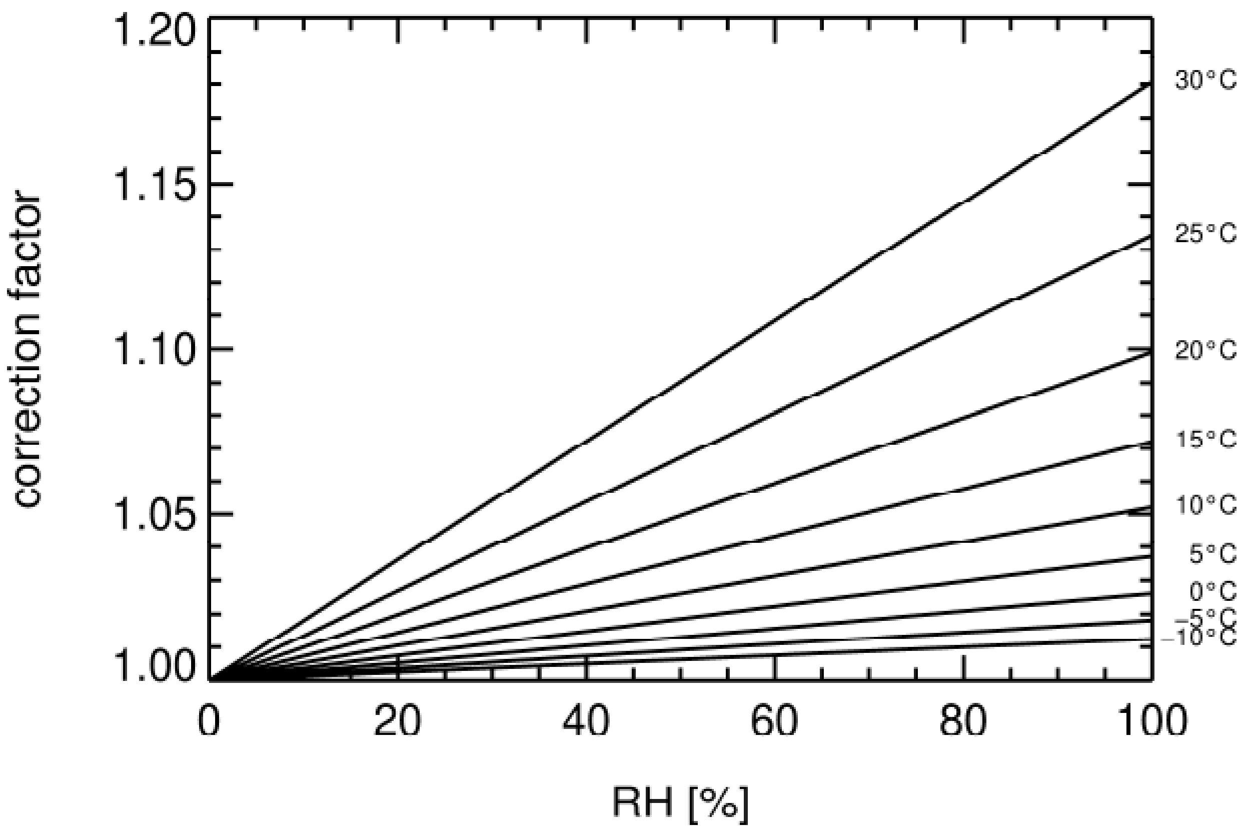
1% → 0.995

1% → 1.043

Consequences (for CLD instruments)

- No correction needed when frequent spiking of ambient air is performed
- 0-10% correction needed for calibrations using NO/N_2 diluted by synthetic air
- No water correction needed if the ambient air is dry or dried

The humidity effect



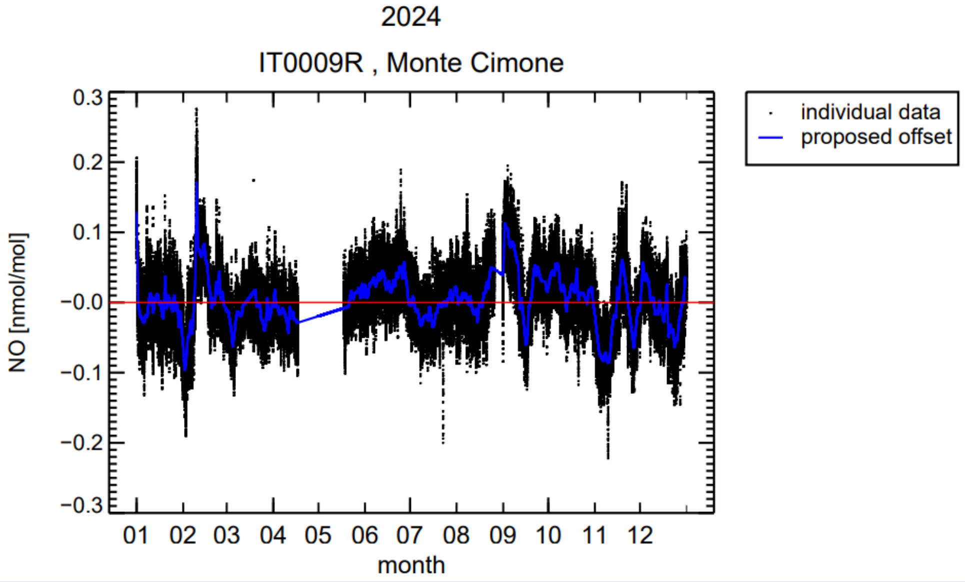
Ridley et al. (1992)

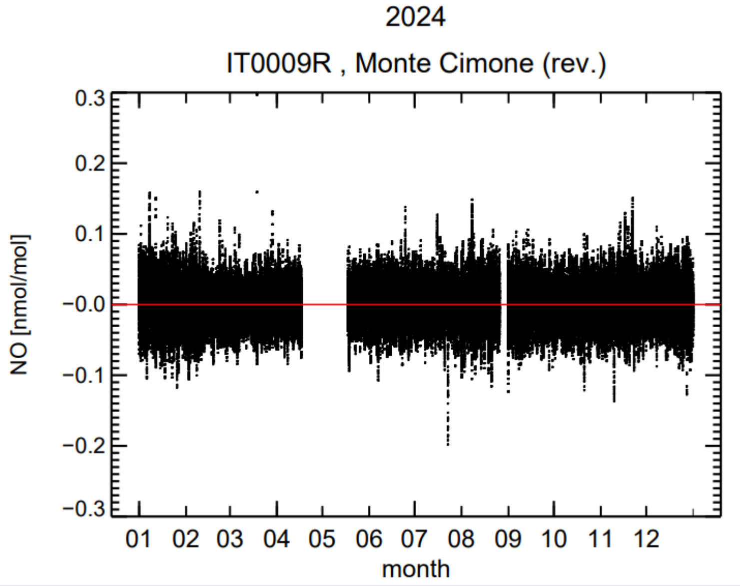
$$[NO_2]_{H20} = [NO_2]_M \times \ (1 + \alpha \times [H_2O])$$

$$\alpha = (4.3 \pm 0.3) \times 10^{-3} \times \frac{flow_{sample}}{flow_{sample} + flow_{ozone}}$$

Zero offset correction

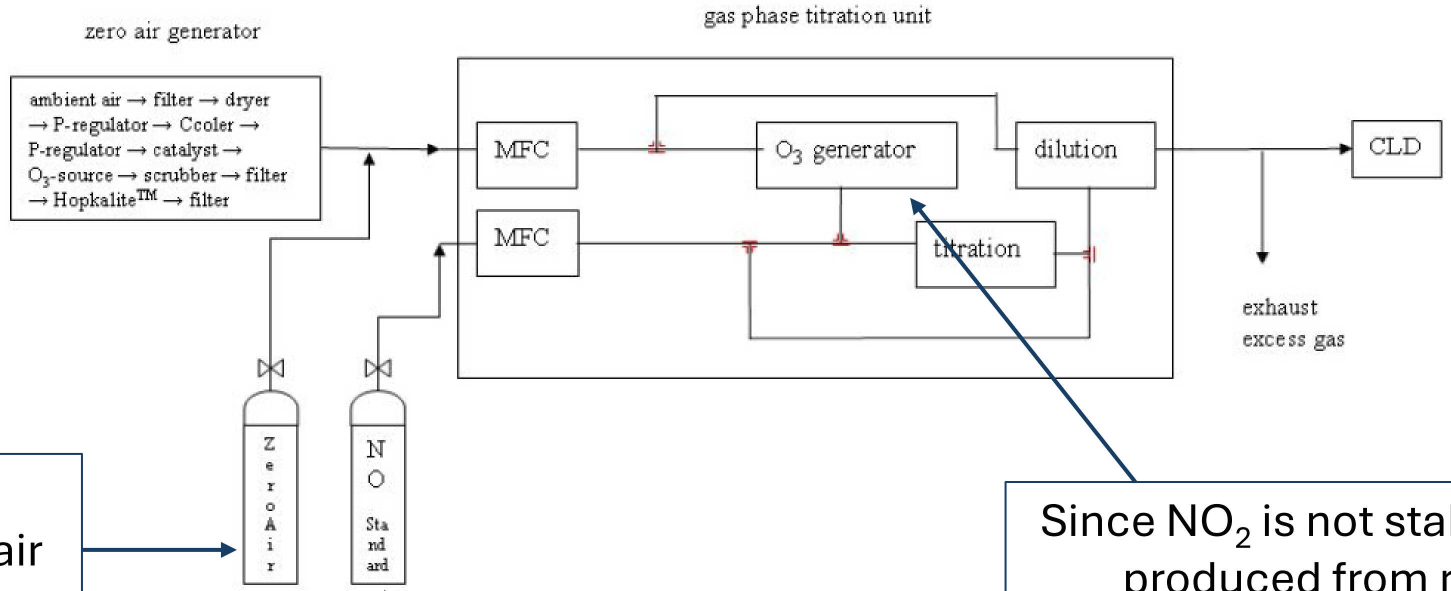
- In remote environments where NO_x concentrations are low (<0.1 ppb) it is recommended to use the measured night-time NO signal as the **detector artefact** (Lee et al., 2009; Galbally et al., 2020)
- Ambient night-time NO concentrations are expected to equal zero due to reaction with ambient O_3
- To assess valid zero offset corrections, the following conditions must be met:
  - ○ A level of $O_3 > 20$ ppb
  - ○ Low ozone variability with a variation coefficient of < 0.1
  - ○ No local sources of NO
  - ○ Absence of sunlight
  - ○ Steady meteorological conditions with wind speed > 2 m/s
  - ○ Absence of high levels of VOCs





Calibration by gas phase titration (GPT)

The chemiluminescence method is not an absolute method, therefore **periodic calibration** of the instrument is required. Sensitivity depends on parameters like cell temperature or pressure, photon count efficiency of the PMT, contamination or degradation of optical components, etc. which can change with time.

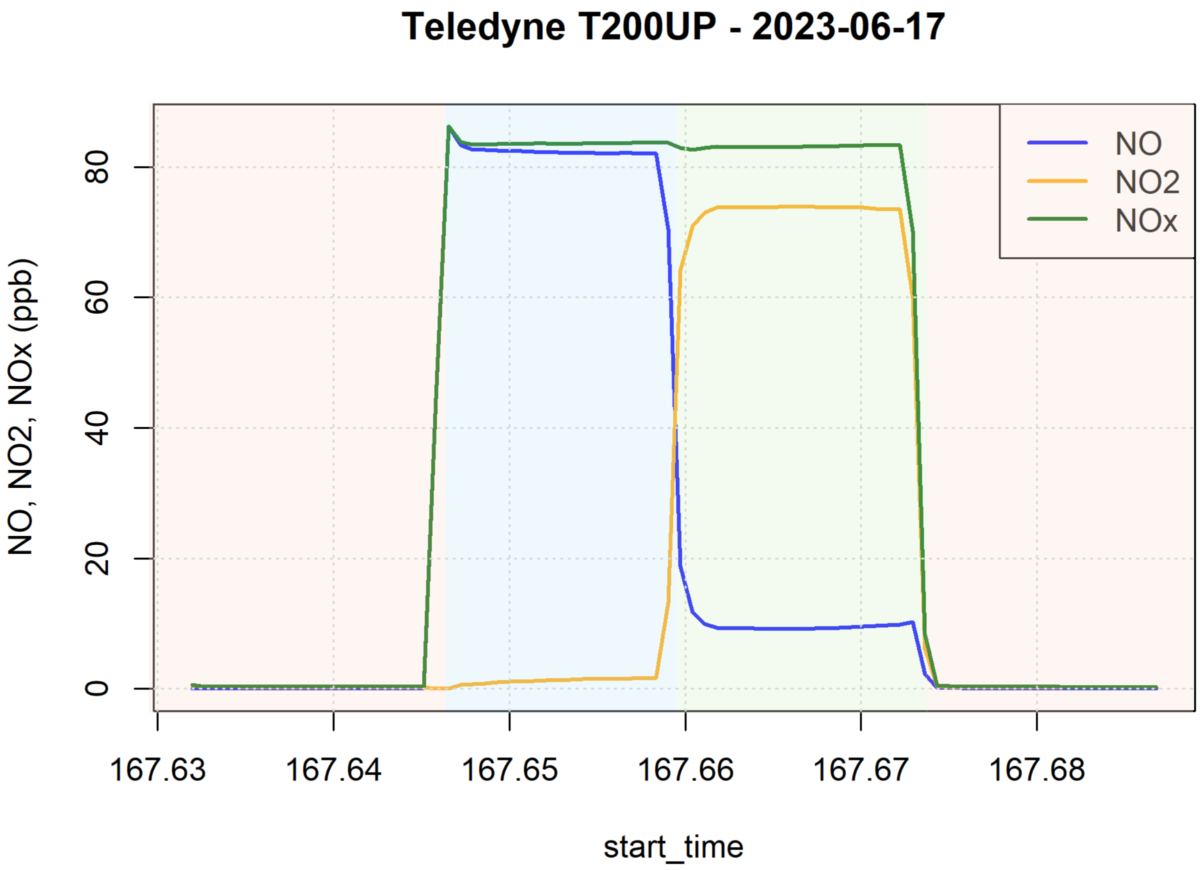


Zero air (from cylinder/generator), i.e., air without significant amounts of NO in it

Since NO_2 is not stable in cylinders, it is produced from reaction with O_3

Calibration standard from the CCL (Central Calibration Lab), with NO stable in the ppm range, diluted before entering the CLD

Calibration by gas phase titration (GPT)



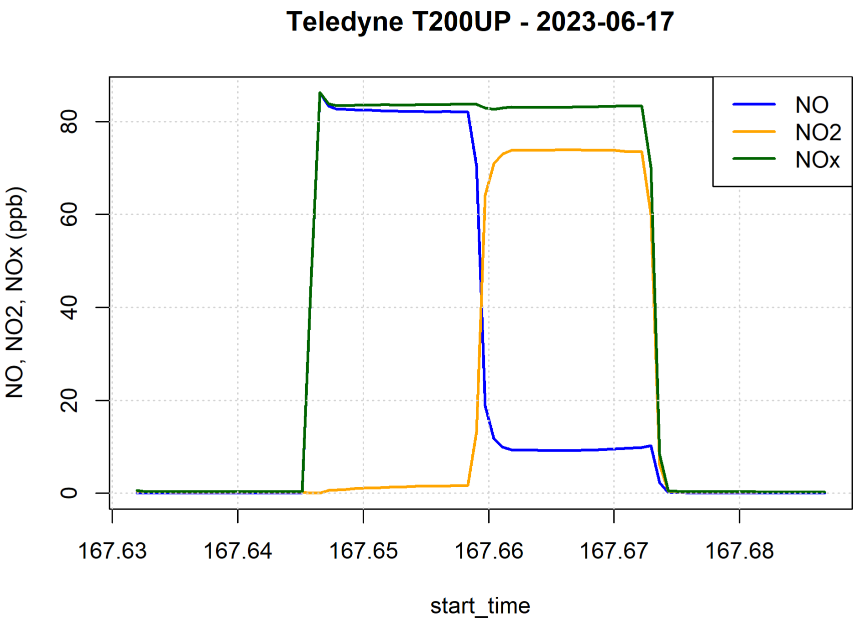
ZERO PHASE
Only synthetic air is added, it is for determining NO and NO_2 artifacts

NO SPAN PHASE
NO added from standard cylinder. The NO sensitivity is determined

GPT PHASE
NO_2 is produced from NO after O_3 is added, by GPT. In this phase, NO_2 is measured to determine the conversion efficiency (Sc)

Each calibration phase should last at least 15-20 min to allow the instrument to stabilize

Calibration by gas phase titration (GPT)



1) As a first step, we calculate the NO and NO_x calibration coefficients

$$NO_{COEF} = \frac{gas\_conc_{SPAN}}{NO_{SPAN} - NO_{ZERO}}$$

$$NOx_{COEF} = \frac{gas\_conc_{SPAN}}{NOx_{SPAN} - NOx_{ZERO}}$$

2) From these, we can get calibrated NO and NO_x values (NO_x is only temporarily calibrated, being now based only on NO)

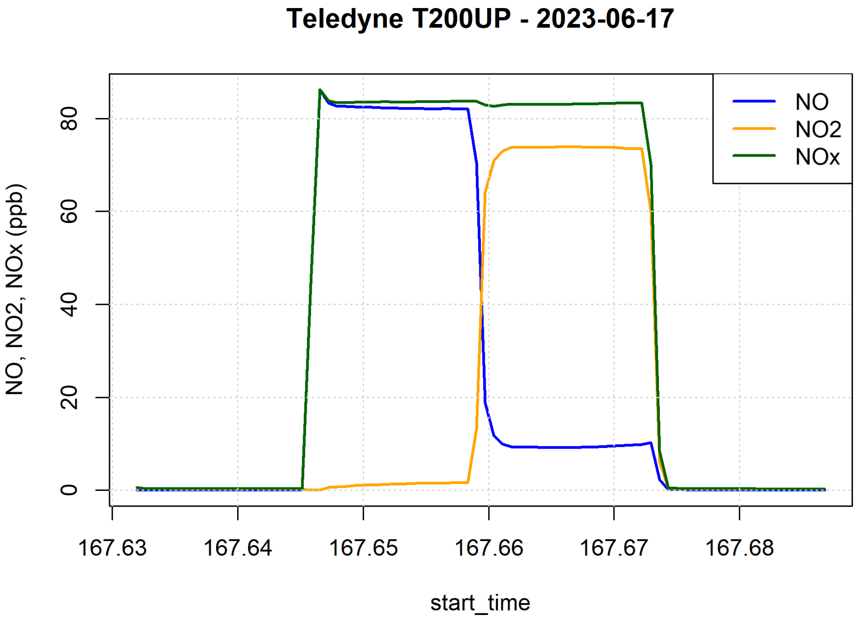
$$NO_{CALIB} = (NO \cdot NO_{COEF}) - NO_{ZERO}$$

$$NOx_{CALIB} = (NOx \cdot NOx_{COEF}) - NOx_{ZERO}$$

3) Then, we can derive conversion efficiency (Sc)

$$Sc = \frac{(NOx_{GPT} - NO2_{SPAN} - NOx_{ZERO}) - (NO_{GPT} - NO_{ZERO})}{NO_{SPAN} - NO_{GPT}}$$

Calibration by gas phase titration (GPT)



4) Given the Sc, we can now compute NO_2 calibrated data, and the final NO_x calibrated value

$$NO_{2\,CALIB} = \frac{NOx_{CALIB} - NO_{CALIB}}{Sc}$$

$$NOx_{CALIB} = NO_{2\,CALIB} + NO_{CALIB}$$

- Always check how calibration parameters (e.g., NO_{ZERO}, NO_{COEF}, ...) vary over time, to see that no drifts are present
- Do calibration results vary within acceptable limits?
- If NO_2 conversion efficiency falls below 40% or lamp intensity fluctuates excessively, check/change the lamps or the converter

How to setup NO_x measurements

Location:

- Regionally-representative for the measured species
- Unaffected from local contamination sources; upwind from any emission sources
- Infrastructure available

Site requirements:

- Controlled laboratory temperature (air-conditioning)
- Instrumentation not exposed to direct sunlight
- Network connection for (automated) data transfer and remote access is recommended

Inlet and sample line design:

- At least 2 m from the closest surface
- It is recommended to shield the sample against light to prevent $NO_2 + h\nu \rightarrow NO + O$
- Residence time should be as little as possible to reduce the reactions of O_3 and RO_2 with NO
- Inlet should be heated to prevent condensation of water, organic and inorganic volatile compounds
- Inlet materials should be smooth, non-porous and inert. The use of NAFION sample driers is **not recommended** due to their conversion of HONO to NO causing a bias in measurements
- The analyzer should be equipped with an inlet line filter made of Teflon with a pore size of 5 µm

How to setup NO_x measurements

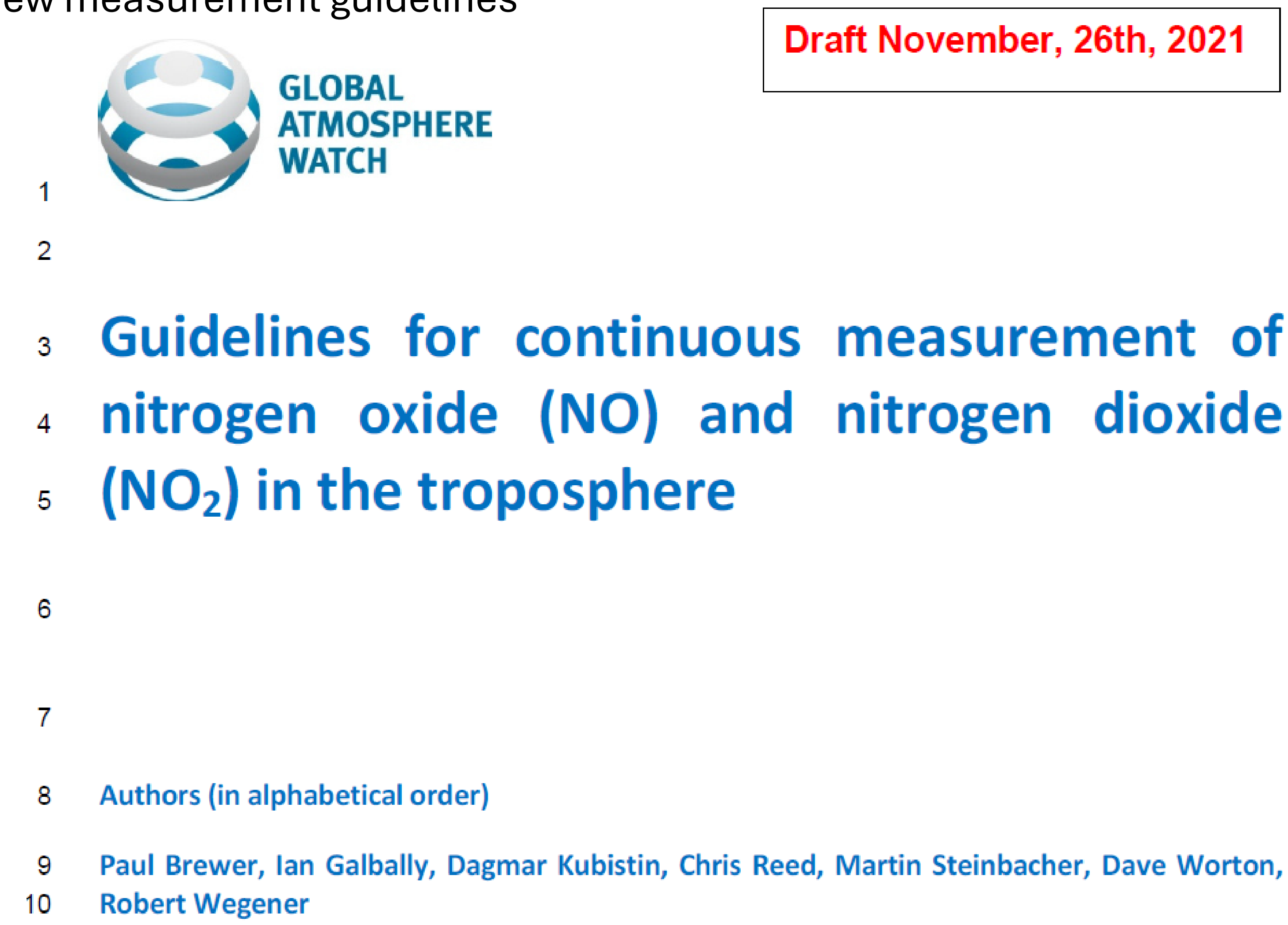
Instrumentation:

- *Analyzer*:
  - NO chemiluminescence detection technique (CLD), with photolytic converter
- *Calibration*:
  - A traceable source of NO calibration gas, generally in a cylinder containing a gas mixture
  - A gas dilution system
  - A source of zero air
  - A gas phase titration system (GPT), using an ozone generator to generate O_3 for reaction with NO to calibrate NO_2 converters
- *Ancillary instrumentation*:
  - Ozone measurements, for ozone interference correction
  - Water concentration measurements, for humidity interference correction

NO$_x$ guidelines

https://ebas-submit.nilu.no/SOPs

GAW has prepared new measurement guidelines



Draft November, 26th, 2021

GLOBAL
ATMOSPHERE
WATCH

Guidelines for continuous measurement of nitrogen oxide (NO) and nitrogen dioxide (NO_2) in the troposphere

Authors (in alphabetical order)

Paul Brewer, Ian Galbally, Dagmar Kubistin, Chris Reed, Martin Steinbacher, Dave Worton, Robert Wegener

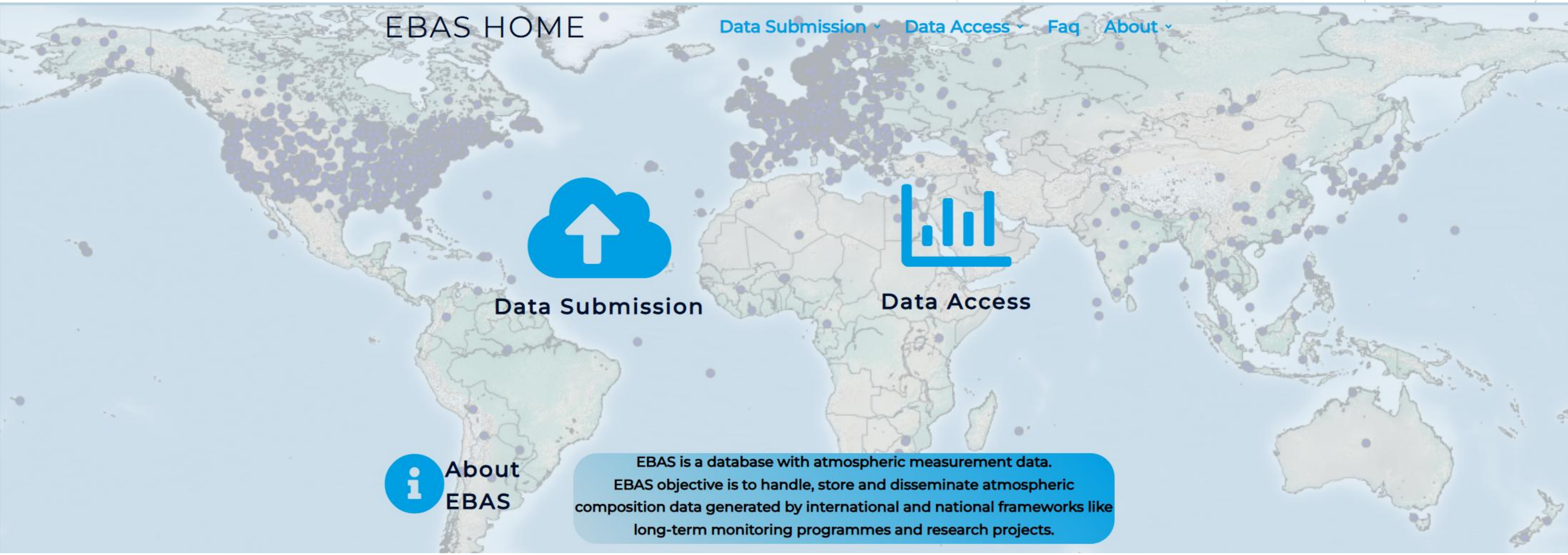
Instrumental setup at Monte Cimone

- Unmanned observatory (visits every 2/3 weeks)
- *Sampling head*: composed by Teflon and Pyrex (glass) with residence time of about 3s from the tube entrance to instrument inlet. From 2025, active flow control and T, RH, P measurements
- *Analyzer*:
  - **Jan. 2015–Aug. 2023**: Thermo 42i-TL equipped with a Photolytic Converter (Air Quality Design Inc.) to convert NO_2 to NO
  - **August 2023–now**: Teledyne T200UP equipped with a Blue light Converter to convert NO_2 to NO

  Inlet particle filter (Teflon); no dryer
- *Calibration unit*: Thermo 146i (dilution and GPT). Calibrations performed every 7 days
- *NO standard* (5 ppm). Several standards have been used throughout the years.
- *Zero air source*: Thermo 1160 dry air generator (activated charcoal and Purafill)
- NRT data delivery capacity
- Automatic procedures (R, Python) for application of calibrations and flags, and for EBAS file creation (lev0, lev1, and lev2)

NO$_x$ data submission

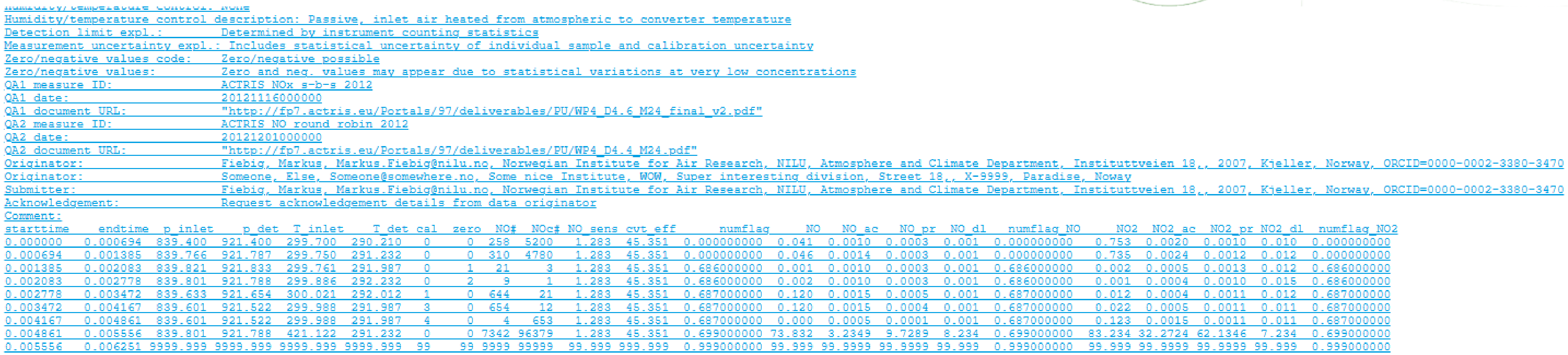
- **World Data Centre for Reactive Gases (WDCRG)**
- Database hosted by **NILU:** https://ebas.nilu.no/



EBAS is a database with atmospheric measurement data.
EBAS objective is to handle, store and disseminate atmospheric composition data generated by international and national frameworks like long-term monitoring programmes and research projects.

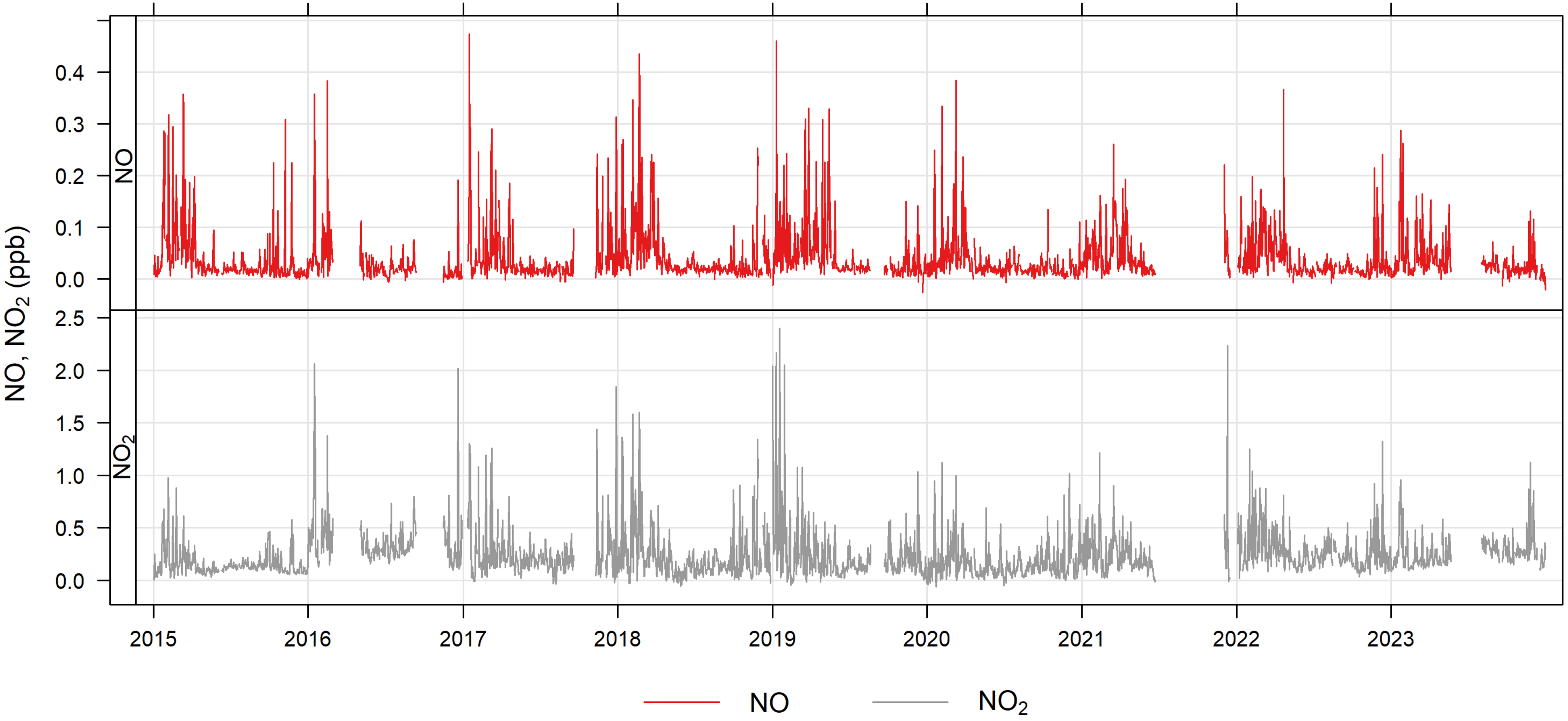
NO$_x$ data submission

- Data format is EBAS NASA Ames 1001 (ASCII text)
- Data levels to be submitted:
  - **Level 0**: data as provided by instrument, amount fraction and raw counts (when available), flags applied
  - **Level 1**: calibrations applied, original time resolution, flags applied
- Data produced by the Topical Centre (TC), from 2024:
  - **Level 2**: hourly averages, offset correction applied, not sample line corrected
  - **Level 3**: hourly averages, offset correction applied, sample line corrected
- To perform corrections, the TC also requires ozone (lev1) and meteo (lev0, lev2) data, if available



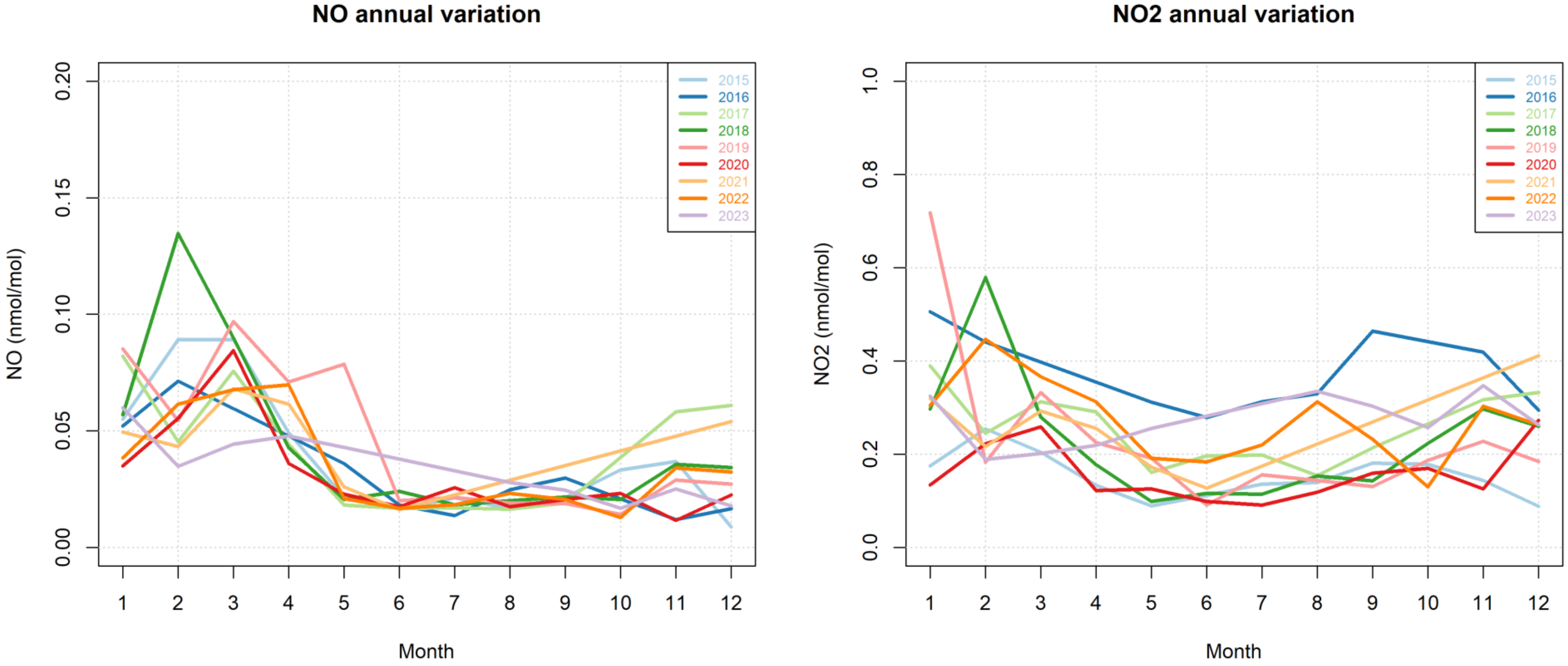
```
Humidity/temperature control: None
Humidity/temperature control description: Passive, inlet air heated from atmospheric to converter temperature
Detection limit expl.:        Determined by instrument counting statistics
Measurement uncertainty expl.: Includes statistical uncertainty of individual sample and calibration uncertainty
Zero/negative values code:    Zero/negative possible
Zero/negative values:         Zero and neg. values may appear due to statistical variations at very low concentrations
QA1 measure ID:               ACTRIS NOx s-b-s 2012
QA1 date:                     20121116000000
QA1 document URL:             "http://fp7.actris.eu/Portals/97/deliverables/PU/WP4_D4.6_M24_final_v2.pdf"
QA2 measure ID:               ACTRIS NO round robin 2012
QA2 date:                     20121201000000
QA2 document URL:             "http://fp7.actris.eu/Portals/97/deliverables/PU/WP4_D4.4_M24.pdf"
Originator:                   Fiebig, Markus, Markus.Fiebig@nilu.no, Norwegian Institute for Air Research, NILU, Atmosphere and Climate Department, Instituttveien 18,, 2007, Kjeller, Norway, ORCID=0000-0002-3380-3470
Originator:                   Someone, Else, Someone@somewhere.no, Some nice Institute, WOW, Super interesting division, Street 18,, X-9999, Paradise, Noway
Submitter:                    Fiebig, Markus, Markus.Fiebig@nilu.no, Norwegian Institute for Air Research, NILU, Atmosphere and Climate Department, Instituttveien 18,, 2007, Kjeller, Norway, ORCID=0000-0002-3380-3470
Acknowledgement:              Request acknowledgement details from data originator
Comment:
starttime    endtime  p_inlet    p_det  T_inlet    T_det cal  zero  NO#  NOc# NO_sens cvt_eff      numflag     NO   NO_ac   NO_pr  NO_dl   numflag_NO     NO2  NO2_ac  NO2_pr NO2_dl  numflag_NO2
0.000000   0.000694  839.400  921.400  299.700  290.210   0     0  258  5200   1.283  45.351  0.000000000  0.041  0.0010  0.0003  0.001  0.000000000   0.753  0.0020  0.0010  0.010  0.000000000
0.000694   0.001385  839.766  921.787  299.750  291.232   0     0  310  4780   1.283  45.351  0.000000000  0.046  0.0014  0.0003  0.001  0.000000000   0.735  0.0024  0.0012  0.012  0.000000000
0.001385   0.002083  839.821  921.833  299.761  291.987   0     1   21     3   1.283  45.351  0.686000000  0.001  0.0010  0.0003  0.001  0.686000000   0.002  0.0005  0.0013  0.012  0.686000000
0.002083   0.002778  839.801  921.788  299.886  292.232   0     2    9     1   1.283  45.351  0.686000000  0.002  0.0010  0.0003  0.001  0.686000000   0.001  0.0004  0.0010  0.015  0.686000000
0.002778   0.003472  839.633  921.654  300.021  292.012   1     0  644    21   1.283  45.351  0.687000000  0.120  0.0015  0.0005  0.001  0.687000000   0.012  0.0004  0.0011  0.012  0.687000000
0.003472   0.004167  839.601  921.522  299.988  291.987   3     0  654    12   1.283  45.351  0.687000000  0.120  0.0015  0.0004  0.001  0.687000000   0.022  0.0005  0.0011  0.011  0.687000000
0.004167   0.004861  839.601  921.522  299.988  291.987   4     0    4   653   1.283  45.351  0.687000000  0.000  0.0005  0.0001  0.001  0.687000000   0.123  0.0015  0.0011  0.011  0.687000000
0.004861   0.005556  839.801  921.788  421.122  291.232   0     0 7342 96379   1.283  45.351  0.699000000 73.832  3.2349  9.7289  8.234  0.699000000  83.234 32.2724 62.1346  7.234  0.699000000
0.005556   0.006251 9999.999 9999.999 9999.999 9999.999  99    99 9999 99999  99.999 999.999  0.999000000 99.999 99.9999 99.9999 99.999  0.999000000  99.999 99.9999 99.9999 99.999  0.999000000
```

The NO_x dataset at Monte Cimone



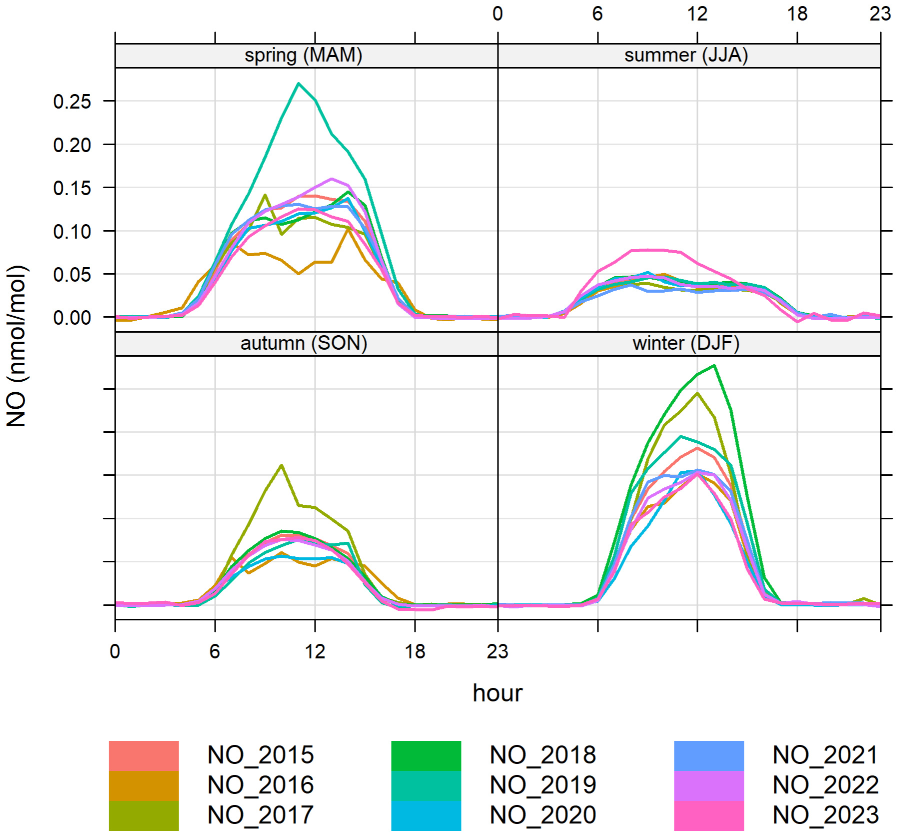
- Data coverage: **77.5%** for NO and **78.8%** for NO_2 (valid data)
- Large gaps for construction works at CMN, intercomparison in Jülich, instrumental problems
- 2024 data are under revision
- Monte Cimone observations are generally representative of baseline atmospheric conditions

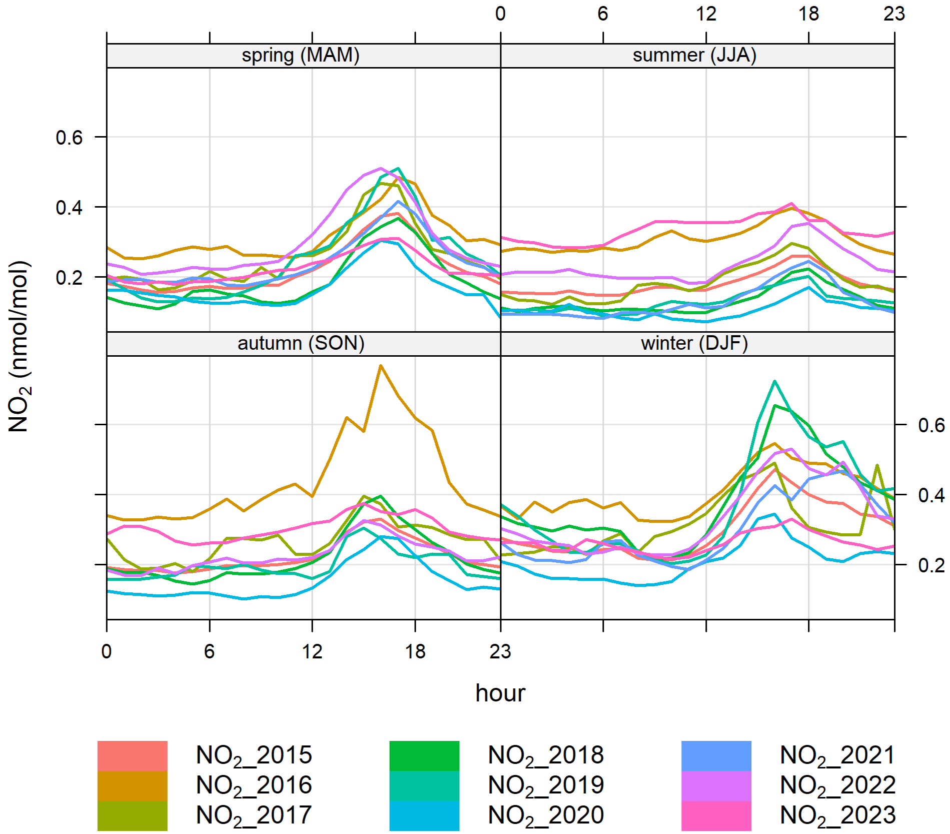
The NO_x dataset at Monte Cimone



- NO characterized by a peak in Feb.-Mar. and a minimum in July
- NO_2 maximized in winter (peak in Jan.-Feb.) and minimized in June
- This is due to a major accumulation in the lower atmospheric layers associated to the stable boundary layer, and less destruction by photochemical processes in winter with respect to summer

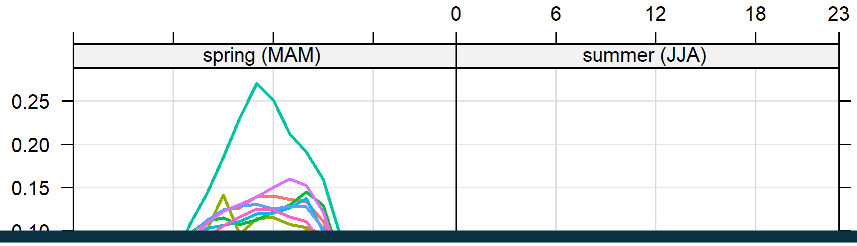
The NO_x dataset at Monte Cimone

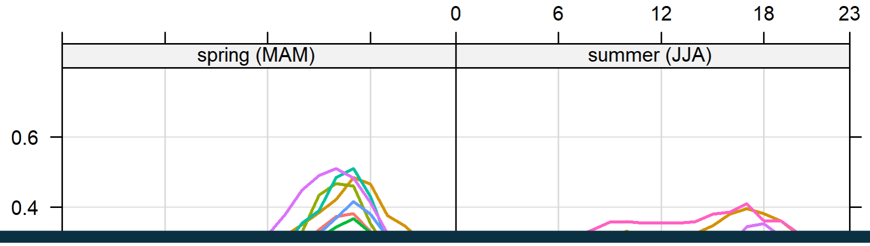


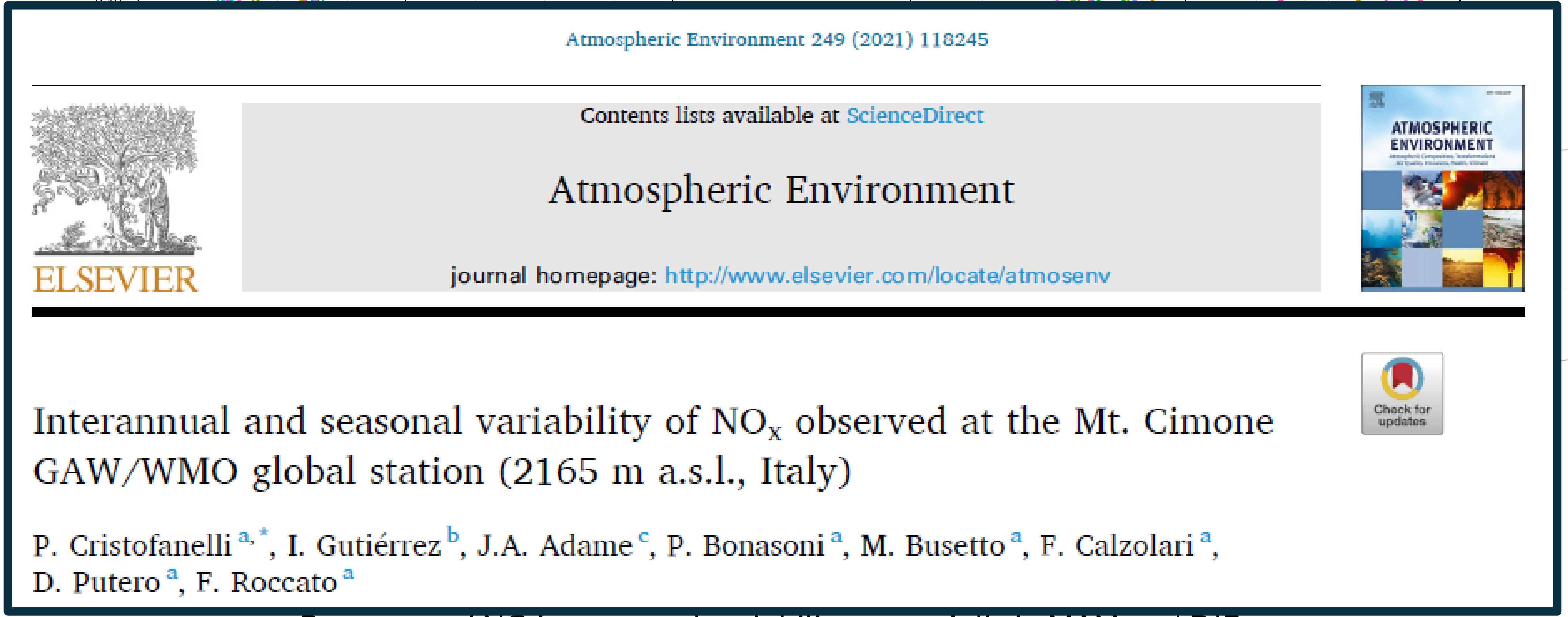


- Diel and seasonal variability consistent throughout the years
- Peak of NO during mid-day due to photolysis of NO_2 to NO
- NO_2 increase from late morning to evening, due both to photochemistry and PBL dynamics
- Pronounced NO interannual variability, especially in MAM and DJF

The NO$_x$ dataset at Monte Cimone







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Interannual and seasonal variability of NO$_x$ observed at the Mt. Cimone GAW/WMO global station (2165 m a.s.l., Italy)

P. Cristofanelli [a,*], I. Gutiérrez [b], J.A. Adame [c], P. Bonasoni [a], M. Busetto [a], F. Calzolari [a], D. Putero [a], F. Roccato [a]

- Pronounced NO interannual variability, especially in MAM and DJF

THANKS!

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Ministero dell'Università e della Ricerca

Italiadomani

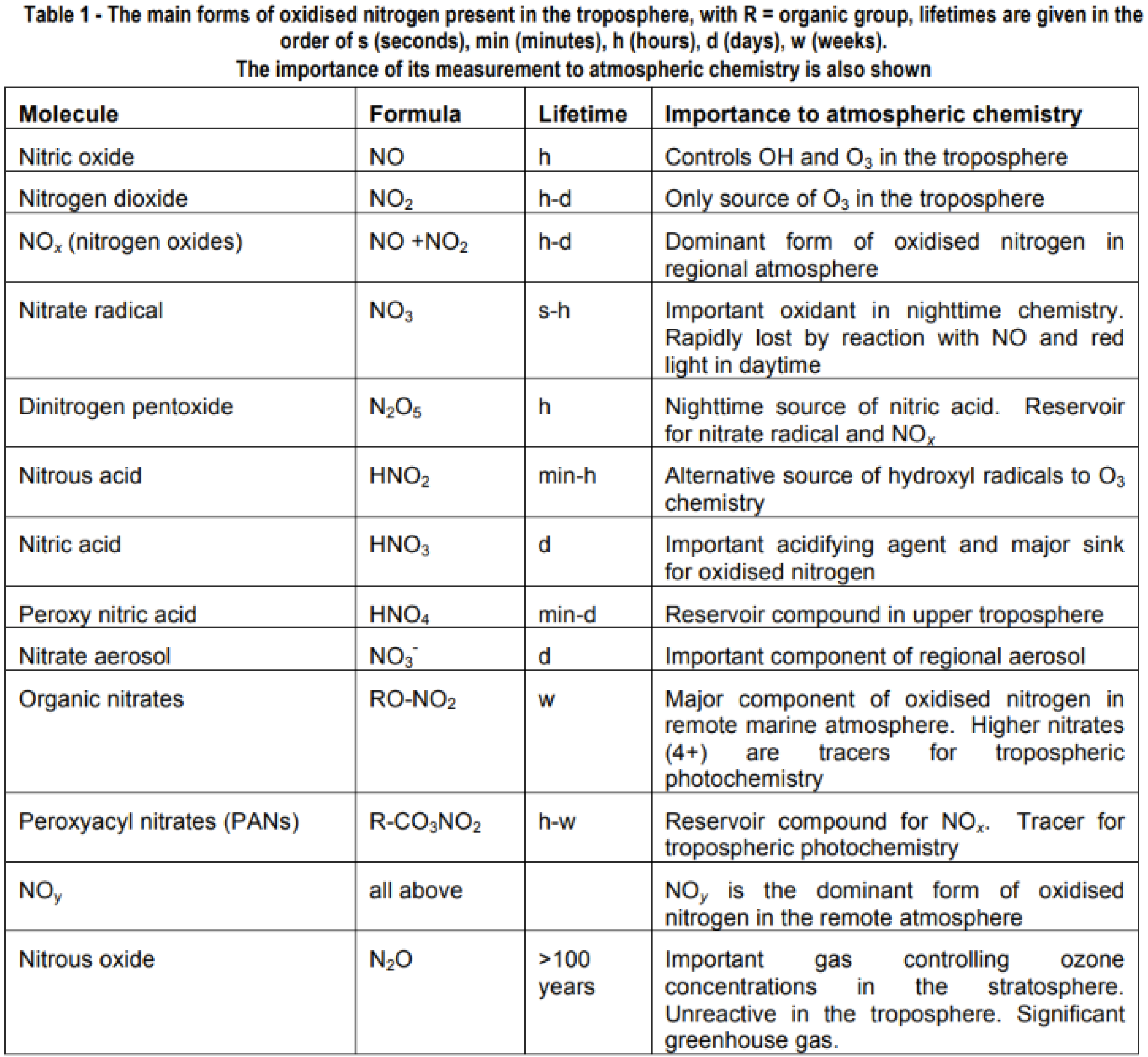

Table 1 - The main forms of oxidised nitrogen present in the troposphere, with R = organic group, lifetimes are given in the order of s (seconds), min (minutes), h (hours), d (days), w (weeks).
The importance of its measurement to atmospheric chemistry is also shown

Molecule	**Formula**	**Lifetime**	**Importance to atmospheric chemistry**
Nitric oxide	NO	h	Controls OH and O_3 in the troposphere
Nitrogen dioxide	NO_2	h-d	Only source of O_3 in the troposphere
NO_x (nitrogen oxides)	$NO + NO_2$	h-d	Dominant form of oxidised nitrogen in regional atmosphere
Nitrate radical	NO_3	s-h	Important oxidant in nighttime chemistry. Rapidly lost by reaction with NO and red light in daytime
Dinitrogen pentoxide	N_2O_5	h	Nighttime source of nitric acid. Reservoir for nitrate radical and NO_x
Nitrous acid	HNO_2	min-h	Alternative source of hydroxyl radicals to O_3 chemistry
Nitric acid	HNO_3	d	Important acidifying agent and major sink for oxidised nitrogen
Peroxy nitric acid	HNO_4	min-d	Reservoir compound in upper troposphere
Nitrate aerosol	NO_3^-	d	Important component of regional aerosol
Organic nitrates	$RO\text{-}NO_2$	w	Major component of oxidised nitrogen in remote marine atmosphere. Higher nitrates (4+) are tracers for tropospheric photochemistry
Peroxyacyl nitrates (PANs)	$R\text{-}CO_3NO_2$	h-w	Reservoir compound for NO_x. Tracer for tropospheric photochemistry
NO_y	all above		NO_y is the dominant form of oxidised nitrogen in the remote atmosphere
Nitrous oxide	N_2O	>100 years	Important gas controlling ozone concentrations in the stratosphere. Unreactive in the troposphere. Significant greenhouse gas.