Night-time vertical profiles of nitrate radical concentrations in urban environment (Paris, France)

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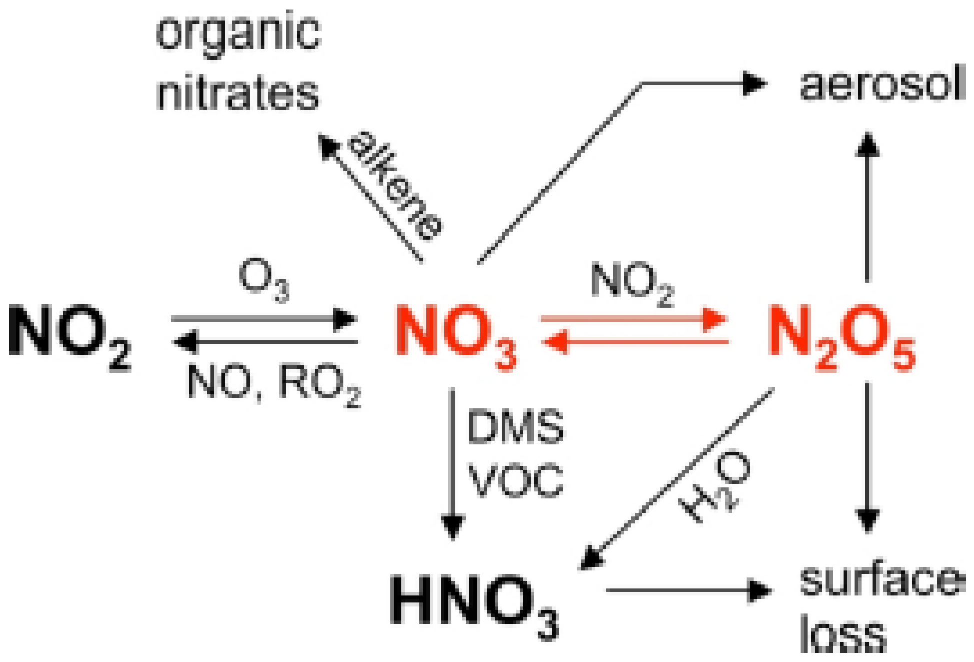
The nitrate radical



Simplified schematic of nocturnal NOy chemical processes, Benton et al., 2010

- **NO_3 plays an important role in night-time chemistry**
- Non-negligible impact on night-time polluted area and daytime chemistry in low sunlight conditions (*Geyer et al, 2003*; *Brown et al, 2005; Forkel et al, 2006)*
- NO_3-oxidation of VOCs produces large amount of organic nitrates (*eg. 50% of isoprene nitrates (Horowitz et al, 2007))* and secondary organic aerosols *(Brown and Stutz, 2012)* → **impact on the air quality and climate**

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The nitrate radical in urban environment

- NO_3 radical is important in the suburban area far from NOx sources
- Urban atmosphere is **less favorable for NO_3 radical occurrence because of the presence of NO_3 sinks (specially NO)**

$NO_3 + NO \rightarrow 2\ NO_2$

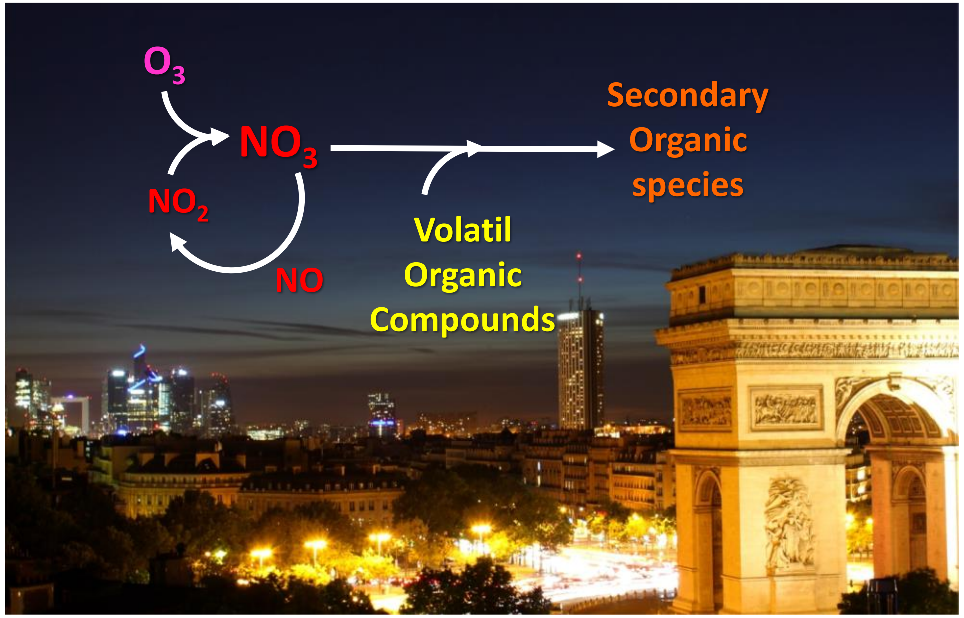
→ Local consumption of NO_3

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O_3 \rightarrow NO_3 + O_2$

→ Slow formation of NO_3

N_2O_5 losses on surfaces



But: What about vertically ?

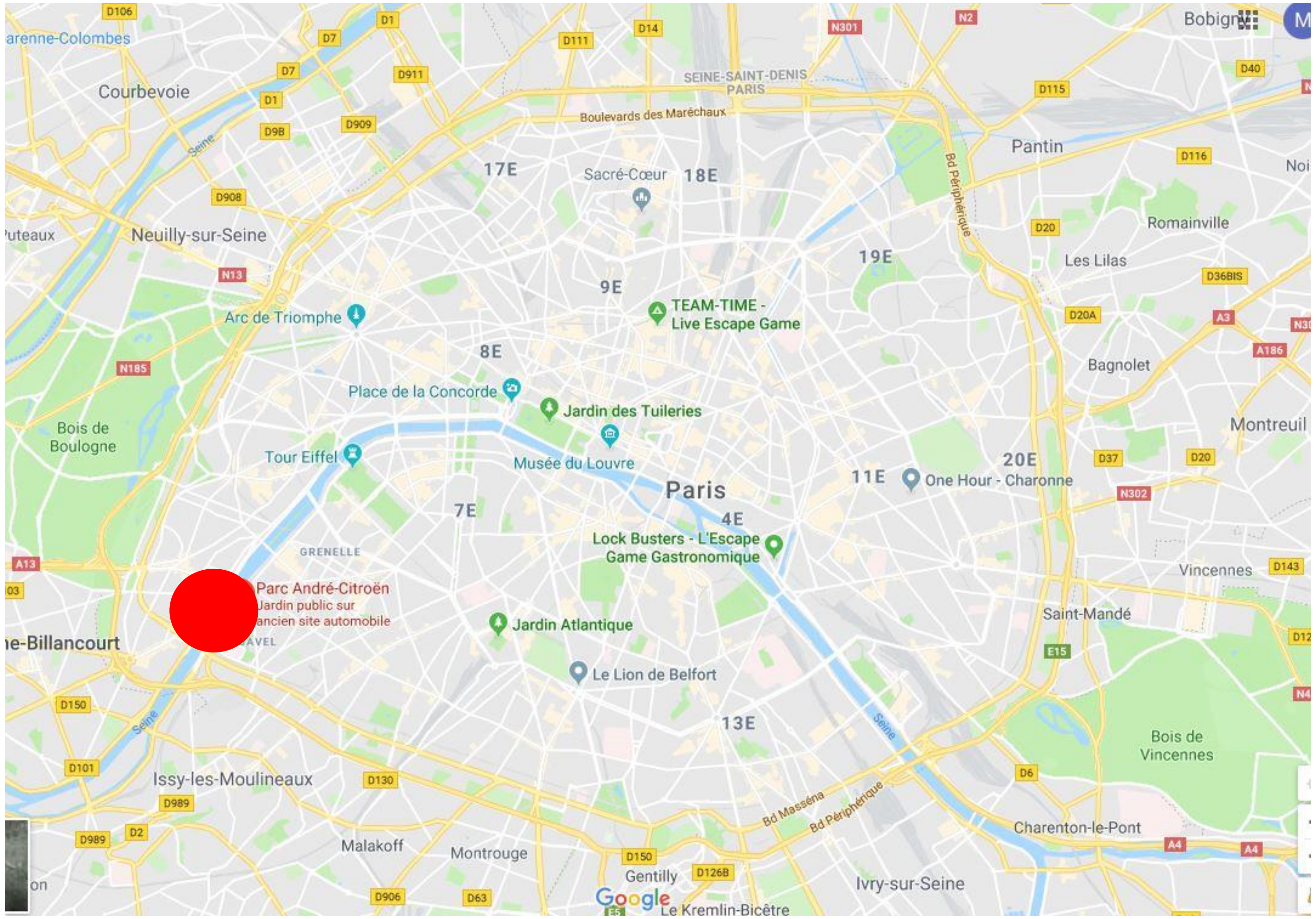
- Atmospheric nitrogen chemistry near the earth surface is strongly linked to the dynamics of the boundary layer
- In summer, in altitude:
  - Levels of O_3 increase
  - Rapid conversion of NO in NO_2 (NO rapidly depleted by ozone)
  - NO_3 and N_2O_5 formation

Large variability of NO_3 mixing ratios as a function of height expected and NO_3 peak concentrations may exists *(Brown et al., 2005)*

What about verticaly ?

Using « Ballon de Paris » to vertically explore the night-time urban atmosphere

Balloon de Paris Generali - high payload touristic tethered balloon located within the André Citroën park, on the banks of the Seine, in inner Paris.



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What about verticaly ?

Using « Ballon de Paris » to vertically explore the night-time urban atmosphere

Possibility to go up to 300 m high above Paris, far away from surfaces and NOx emissions → Far away from NO_3 sinks

Objectives

- ✓ NO_3 vertical profils in Paris urban area
- ✓ Role of NO_3 radical chemistry above Paris

What about vertically ?

Using “Ballon de Paris” to vertically explore the night-time urban atmosphere

- Measurements during nights with clear whether conditions, no wind, high O_3 concentrations and low Relative Humidity (RH) : July 6, 7 and 13, 2018
- Vertical profiles up to a height of 150 m, and up to 300 m in very calm wind conditions:
  - 6 profiles up to 300 m
  - 6 profiles up to 150 m

  Speed: 6 meters.min^{-1} to 13 meters.min^{-1}
- Scientific equipment was installed every evening after the last tourist flight → time of installation ~1 hour

What about vertically ?

Using Ballon de Paris to vertically explore the night-time urban atmosphere

- **The instruments deployed on board:**

✓ IBBCEAS (Incoherent Broad Band - Cavity Enhanced Absorption Spectroscopy) for the concentration measurement of the NO_3 radical (LISA)
✓ Mo Environnement SA analyzer for NOx measurement (LISA)
✓ UV Environment SA absorption analyzer for O_3 measurement (LISA)
✓ CAPS Environnement SA analyzer for NO_2 measurement (ICARE)
✓ OPC GrimmTM for the measurement of particle number concentrations (LISA)
✓ RH probe and temperature

- **Additional measurements at the ground:**

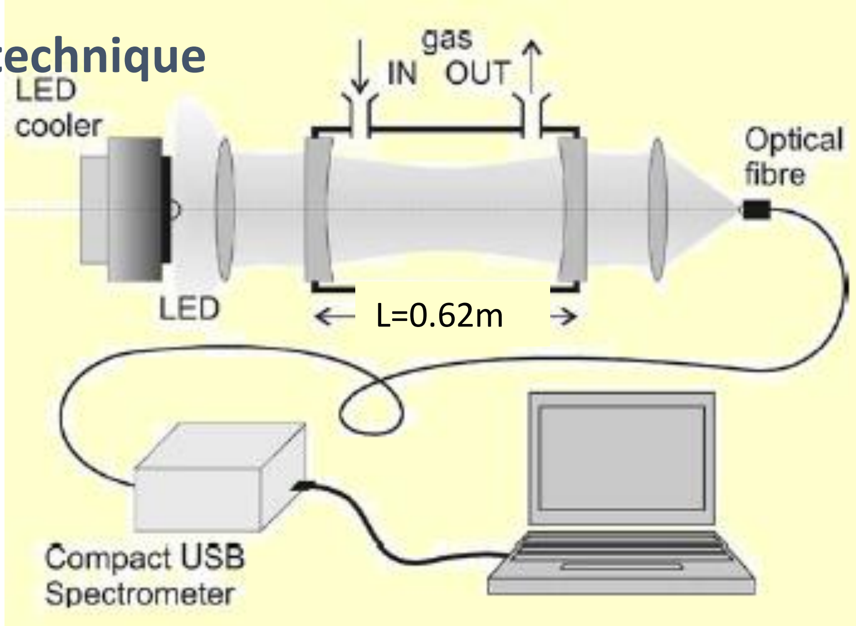
O_3, NOx, Particle counter Meteo parameter (RH, P, T, Wind speed and direction), boundary layer height

MILEAGE station

LIDAR (boundary layer height)

The IBBCEAS instrument for NO_3 radical concentration measurements

Incoherent Broad Band Cavity Enhanced Absorption Spectroscopy technique



Adapted from Ventrillard-Courtillot et al., 2010

→ Broad band emission lamp (LED) centered on the strong absorption band of NO_3 at 662 nm and allowing detection of several gas absorbing in the emission region of the LED (NO_3, NO_2, H_2O)

→ Enhance of the optical path of the light in the cavity up to 4,5 km by 2 high reflective mirrors ($R(\lambda)$ = 99.98%)

→ The absorption coefficient of the sample is determine as follows:

$$\alpha(\lambda) = [X]\sigma(\lambda) = \frac{1}{L}\left(\frac{I_0}{I} - 1\right)(1 - R)$$

→ Quantification of absorbing species:

$$\alpha(\lambda) = [NO_3]\sigma_{NO3}(\lambda) + [NO_2]\sigma_{NO2}(\lambda) + [H_2O]\sigma_{H2O}(\lambda) + p(\lambda)$$

$\alpha(\lambda)$ = absorption coefficient of the sample in the cavity (cm^{-1})
L = effective length between the two mirrors of the cavity
I, I_0 = the intensity of the light in the presence and absence of absorbing sample respectively
$R(\lambda)$ = mirrors reflectivity
$\sigma(\lambda)$ = cross section of the absorbing gaz n(cm^2.molecule^{-1})
[X] = concentration (molecule. cm^{-3})
$p(\lambda)$ = cubic polynomial to correct baseline deformations due to small LED intensity variations

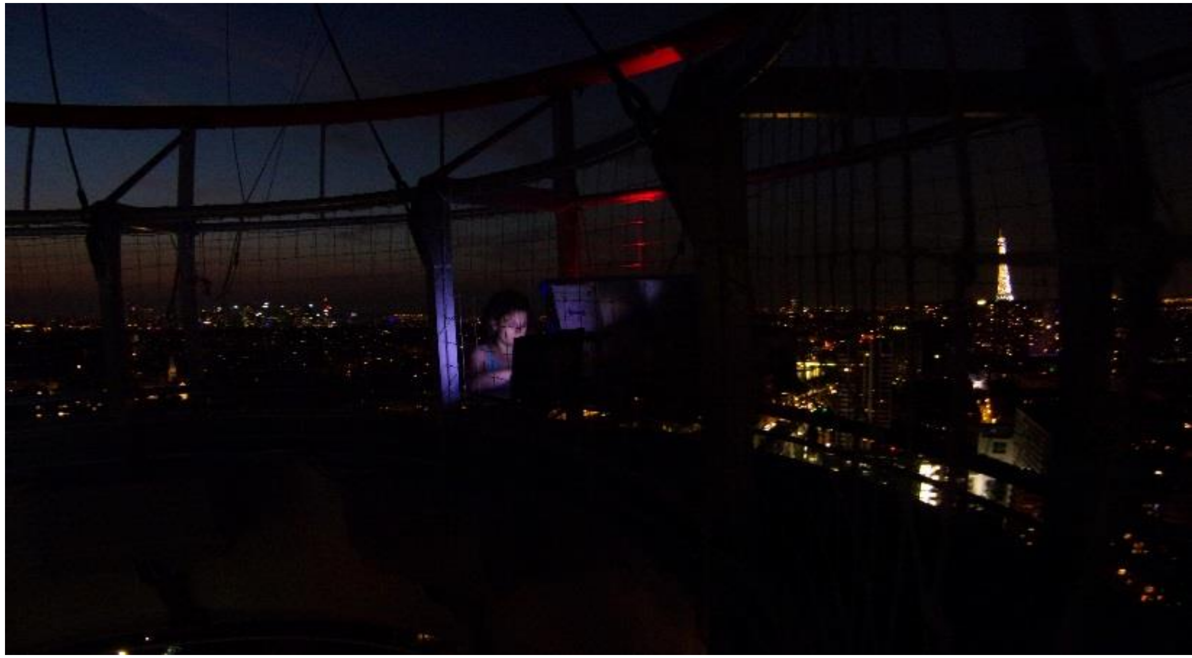
Performances:

- **Detection limit: up to 3 - 4 ppt/10 seconds**
- **High optical stability → easy and quick to install**

The IBBCEAS instrument for NO_3 radical concentration measurements – Balloon deployment

Characteristics:

- Calibration with an accurate known concentration of NO_2 (AirLiquide cylinder, 600 ppb) for reflectivity determination
- Protection of the mirrors to avoid reflectivity degradation:
  - N_2 flush on the mirror surfaces (50 sccm)
  - PTFE filter for particles on the sample line
- PFA coated cavity and line to minimize NO_3 wall losses



Balloon deployment

→ **Installed every evening after the last tourist flight**
→ **Calibration at ground level every evening before measure**
→ **$I_0(\lambda)$ recorded at ground level and every 20 to 30 minutes during flights**
→ **$I(\lambda)$ recorded every minute**

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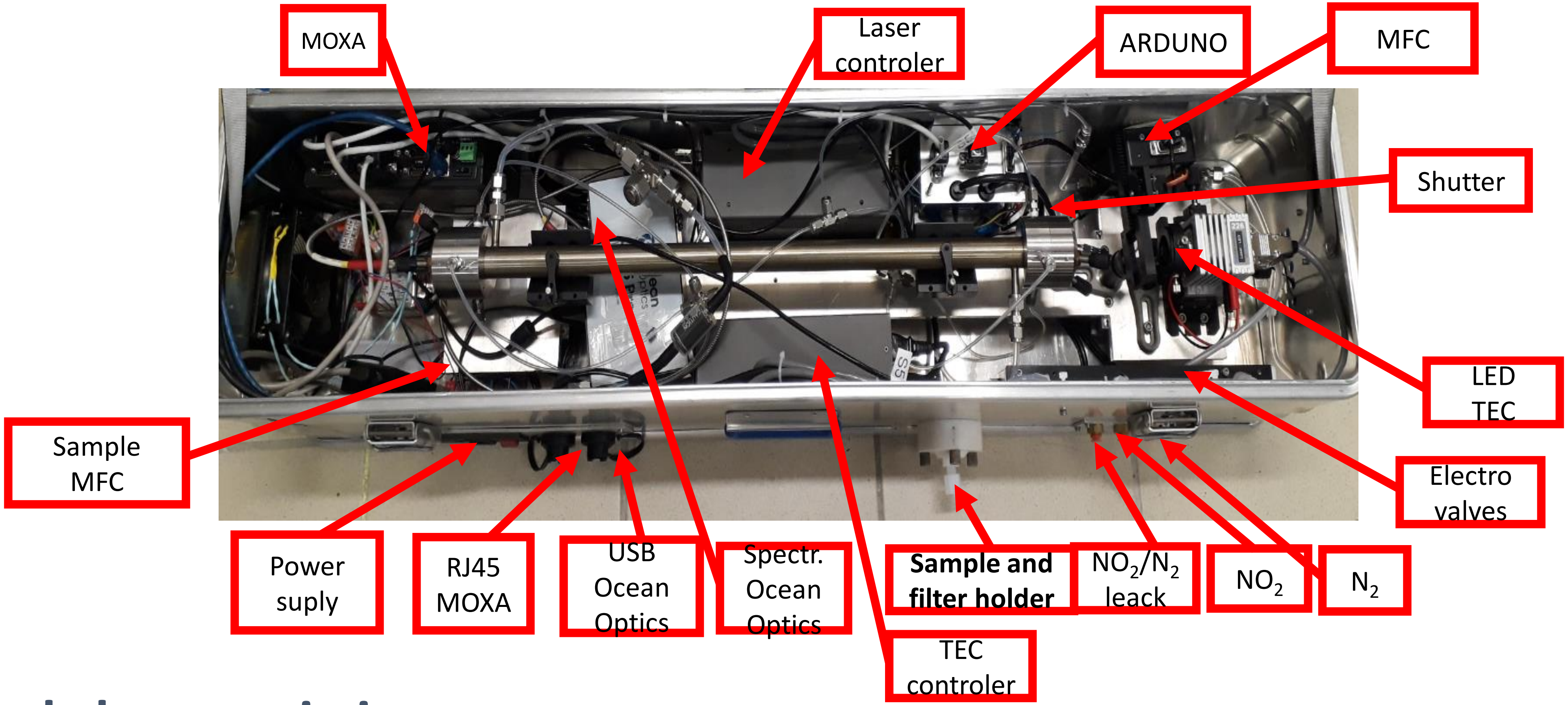
The IBBCEAS instrument for NO_3 radical concentration measurements

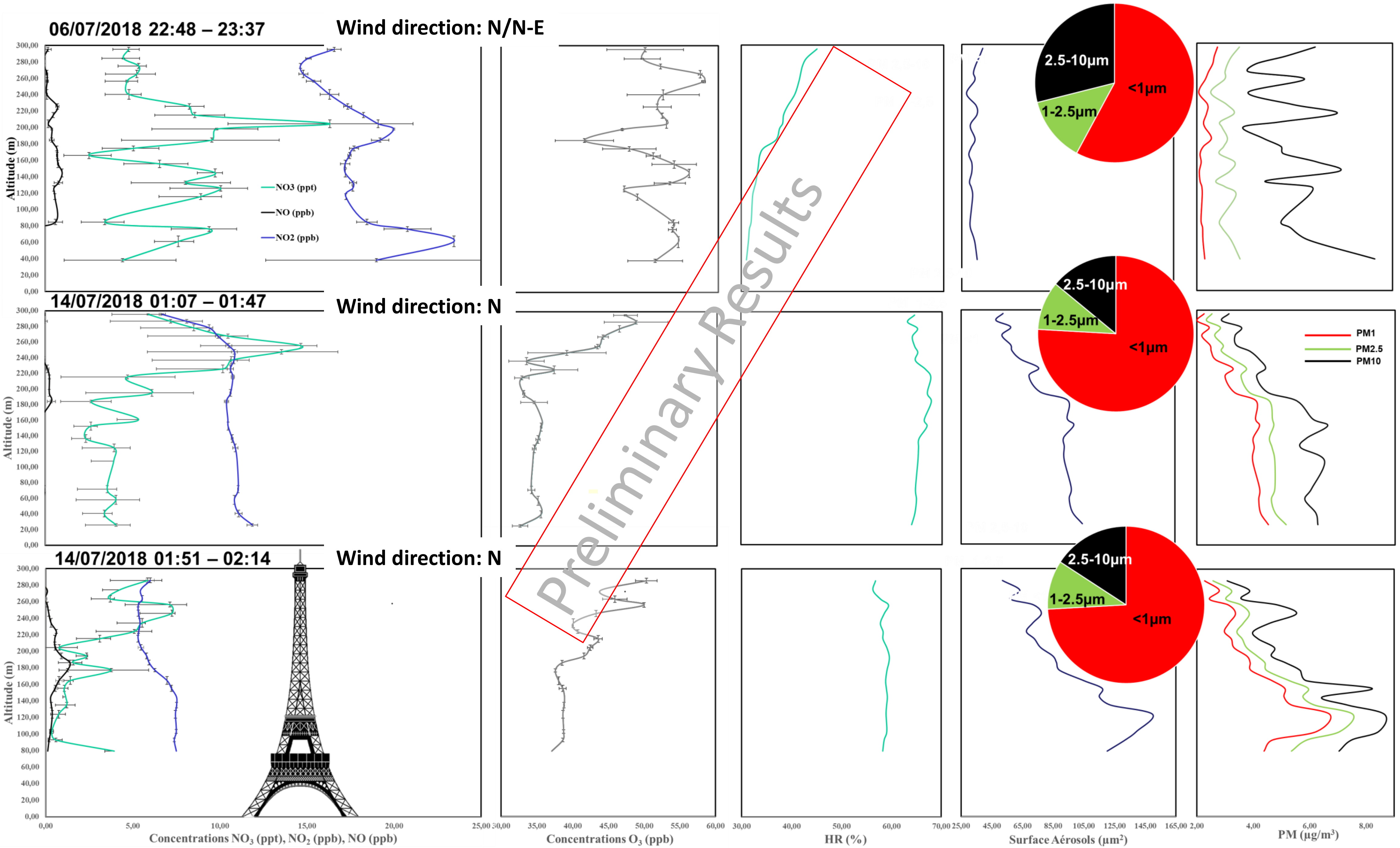


Technical characteristics:

Dimension = 1350 x 220 x 220 cm

Weight = 30 kg

Vertical profiles
Preliminary results



Vertical profiles of gas species
Preliminary results

In altitude:

→ NO_3 radical and N_2O_5 formation

→ Strong correlation between vertical profiles of $[NO_3]$ radical and precursors $[O_3]$ and $[NO_2]$

→ $[NO_3]$ radical maximal concentration at 200 m of altitude

Near ground level :

→ Competition between sources and sinks of NO_3 (NO and surfaces)

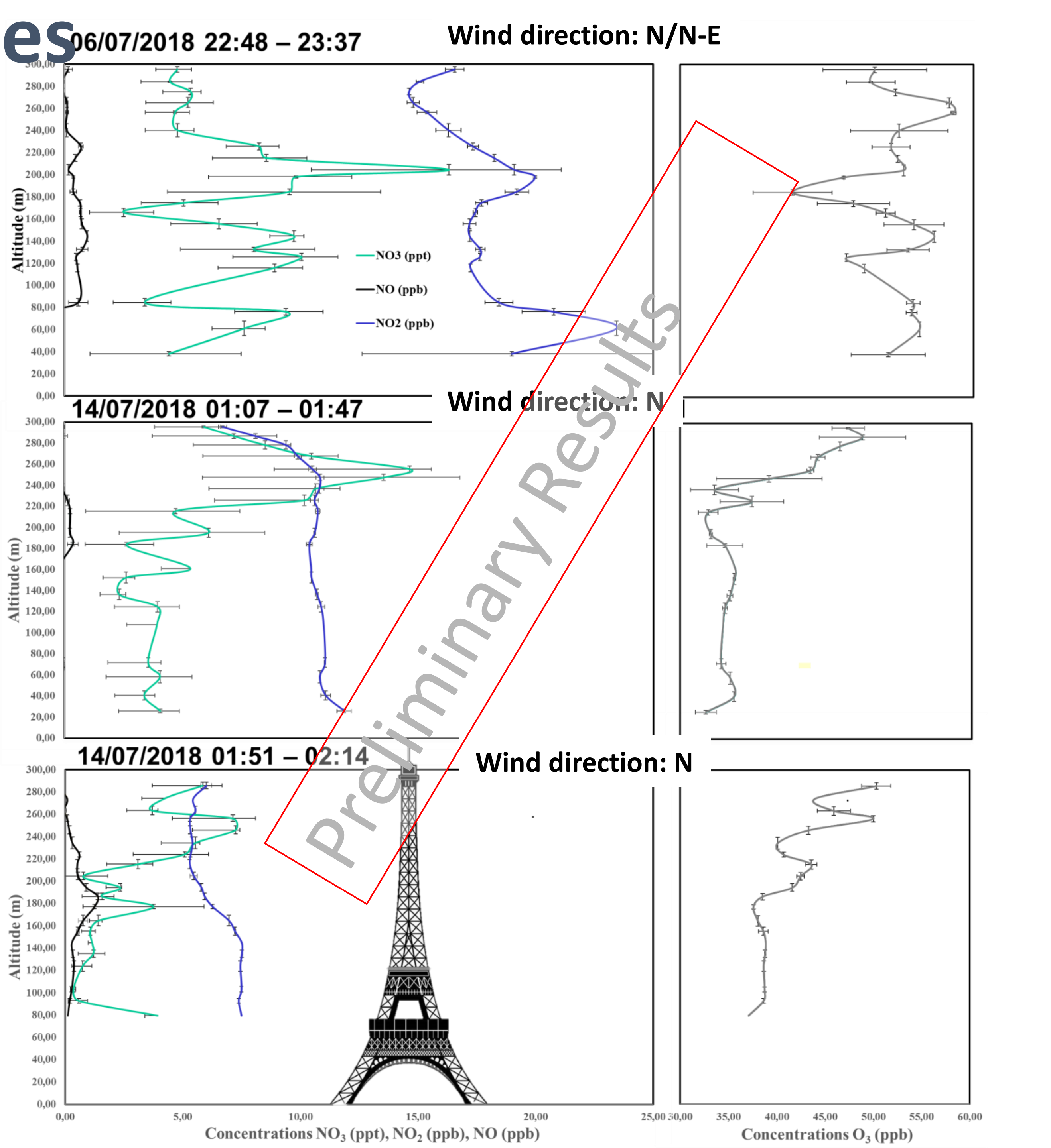
$$\mathbf{NO_3} + NO \rightarrow 2\,NO_2$$

$$\mathbf{N_2O_5} + H_2O \rightarrow HNO_3$$

$$NO + O_3 \rightarrow \mathbf{NO_2} + O_2$$

$$NO_2 + O_3 \rightarrow \mathbf{NO_3} + O_2$$

→ NO_3 radical in ppt range



Overview

✓ Successful deployment of an IBBCEAS instrument for NO_3 radical measurement on a tethered balloon possible due to the high optical stability of the instrument;

✓ First results show a vertical profile of NO_3 radical concentrations over Paris with a peak concentration at 200 m of altitude

✓ IBBCEAS data treatment still in progress:

- loss corrections
- more precise treatment of the strong absorption by water vapor that spectrally overlaps with NO_3 absorption in the 662 nm region,
- NO_2 cross section in the 655 – 665 nm region - source of uncertainties