Multi-instrumental analysis of the influence of boundary layer depth variability on the vertical distribution of nitrogen oxides in Paris region

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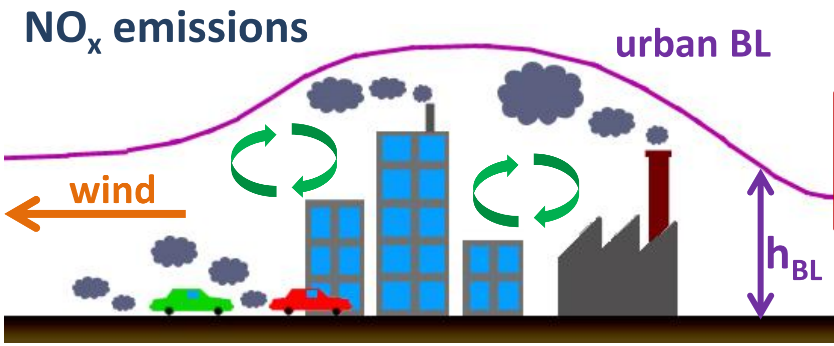
Under the direction of
François Ravetta & Jacques Pelon

Summary

- Context and methodology
- Database and variability analyses
  - Boundary layer depth
  - Concentration of NO_2
  - Integrated content of NO_2
- Linking surface concentration and integrated content of NO_2
  - Statistical relationship
  - Case study
  - Consequences on NO_2 profile
  - Discussion: 3 boxes model
- Conclusions and perspectives

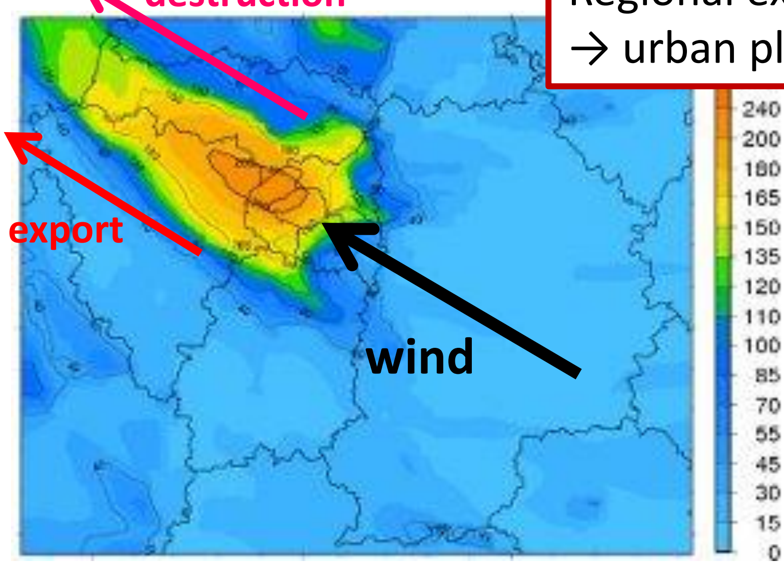
Cities emissions of NO_x(≡$NO+NO_2$): local to global impact



Local pollution
→ air quality issues

feedback

Chemical destruction



Regional export
→ urban plume

Long range transport
→ global impact on
environment / climate

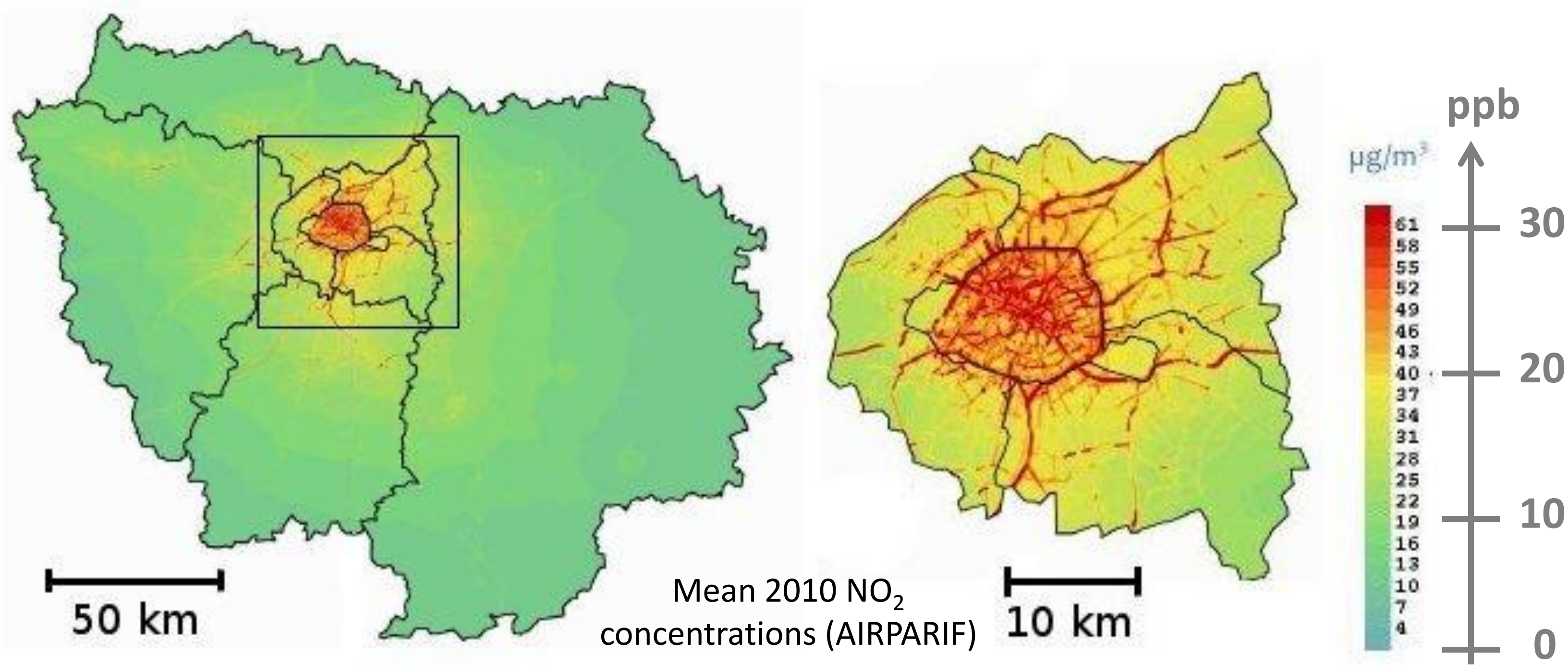
NO_x measurements needed to estimate emissions and quantify the impact of cities at all scales.

NO_2 concentration forecast by
CHIMERE model (ESMERALDA project)

Horizontal variability of NO_x concentrations

Horizontal distribution = competition between

Turbulent mixing + wind advection	and	Heterogeneous emission distribution + NO_x short lifetime

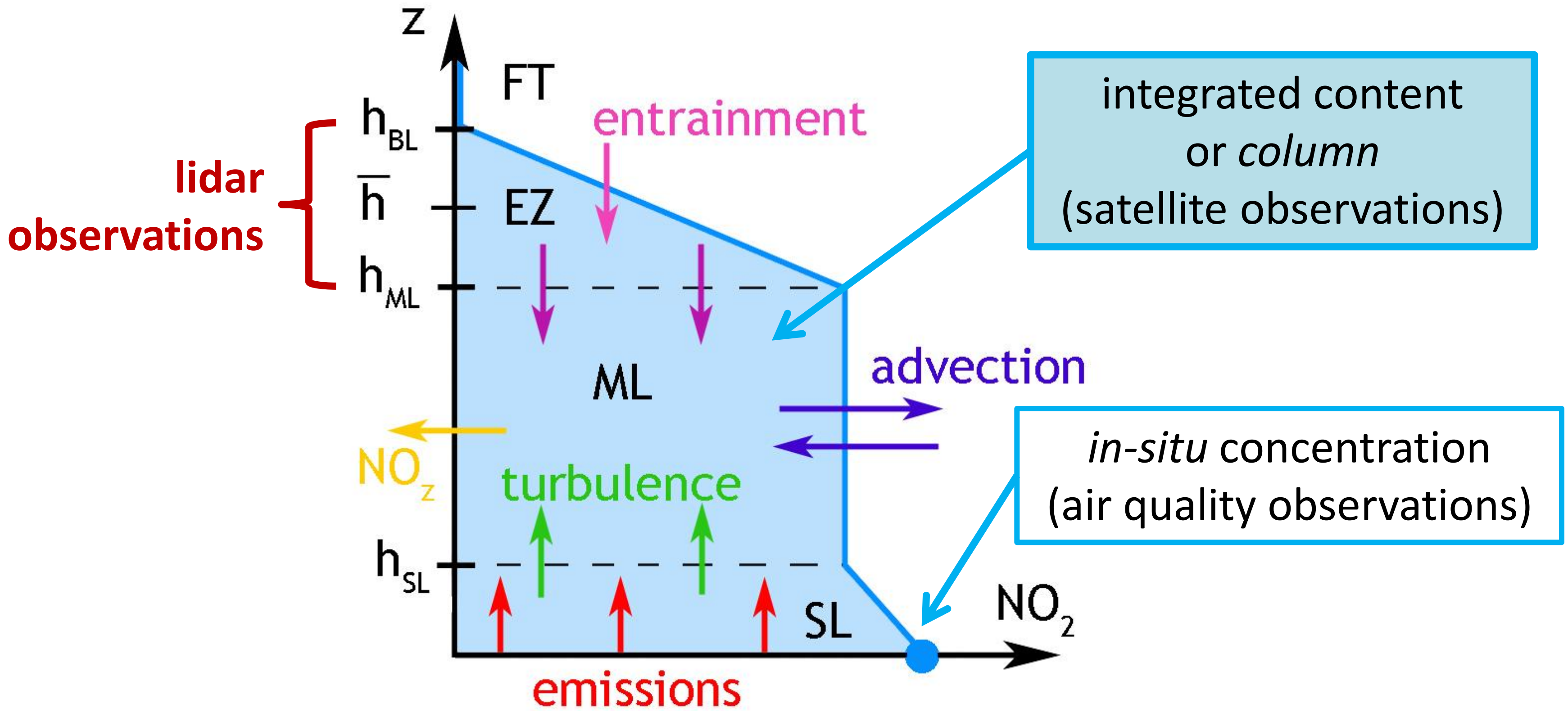


Mean 2010 NO_2 concentrations (AIRPARIF)

Strong horizontal gradients following source distribution (roads)

→ horizontal representativeness of *in-situ* measurements

NO_2 vertical distribution in the convective urban boundary layer



- Vertical representativeness of *in-situ* observations?
- Satellite validation / space-borne air quality monitoring?

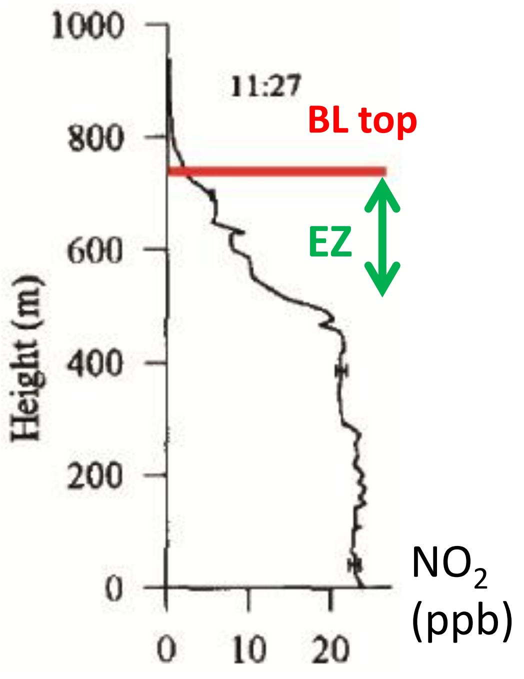
→ linking surface concentration to integrated content

Profiles in the urban boundary layer

No measured urban NO_x profiles, only periurban profiles:

→ EZ gradient but no SL gradient (low emissions)

Pisano et *al.* (AE, 1997)



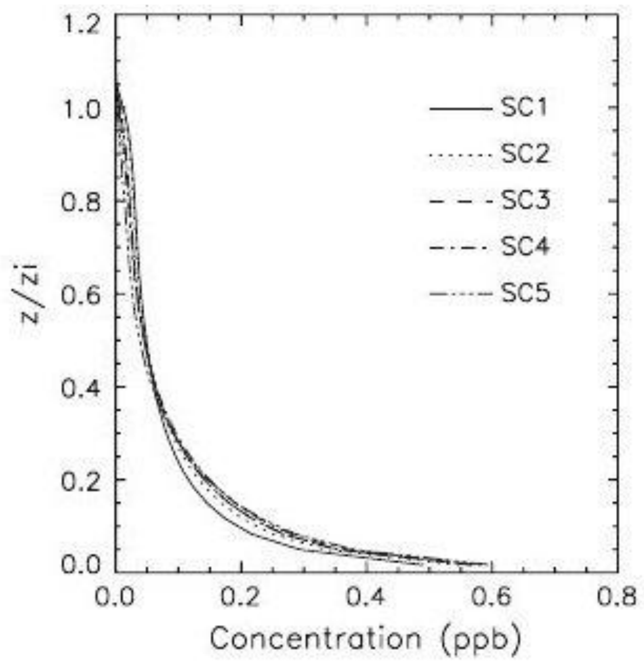
Modeled tracer dispersion above emission zone:

→ advection depleting SL and ML

→ strong gradient

But real emissions vary in time

Vinuesa et al. (BLM, 2010)



→ what is the influence of BL depth variability on NO_2 surface concentrations?

→ what processes govern NO_2 vertical distribution above emission zones?

Comparing surface concentrations and columns

Problems:

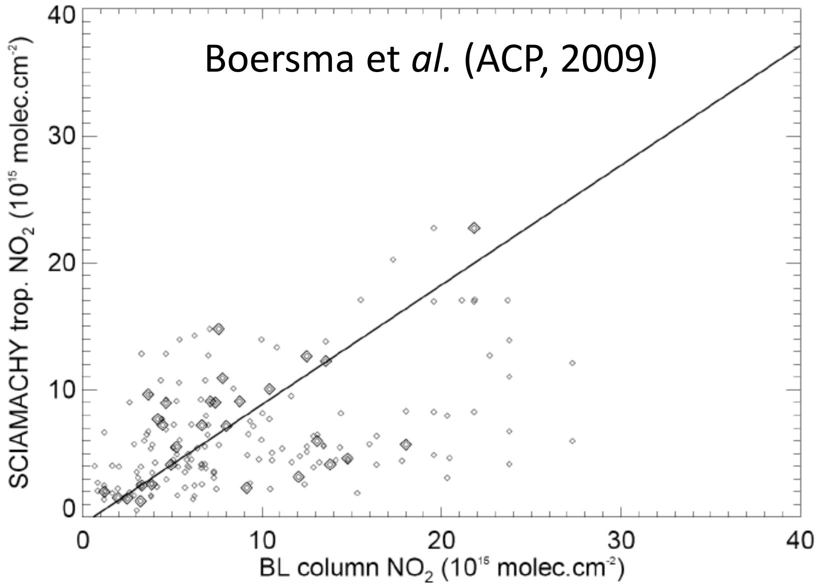
- Unknown NO_2 profile and BL depth

"Solutions":

- Direct comparison *in-situ*/integrated
- Hypotheses on NO_2 profile
- Using CTM modeled profiles

- BL homogeneous concentration
- BL depth from climatology or model

→ large dispersion



see also:

- Ordonez et al. (JGR, 2006)
- Kramer et al. (JGR, 2008)
- Lamsal et al. (JGR, 2008) etc.

→ can spectroscopic and *in-situ* observations be related over urban sites?

→ what is the influence of BL depth on the concentration/column relationship?

Observation campaigns

Satellite validation campaigns:

INTEX-A/B → gulf of Mexico

DANDELIONS → Dutch periurban site

→ airborne NO_2 profiles, 200 m tower

but no urban profile

Paris campaigns:

ECLAP → BL variability

ESQUIF → ozone

MEGAPOLI → organic aerosols

→ airborne O_3, NO and NO_y profiles in Paris plume

but no really urban profile and no NO_2

→ incomplete picture of NO_2 vertical distribution over source areas

→ study of NO_2 vertical distribution in Paris urban BL

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Qualair station

Observation platform in Paris city center

Objectives:

- Complement air quality network with vertically resolved measurements
- Study pollutants vertical dispersion, transport and processing in the urban BL
- Develop new instrumental synergies

Qualair roof on Jussieu campus

Parameters:

- BL depth
- Aerosol extinction profile
- Aerosol optical depth
- Ozone concentration profile
- Wind profile
- NO_2, O_3, CO, CH_4… integrated content

Instruments:

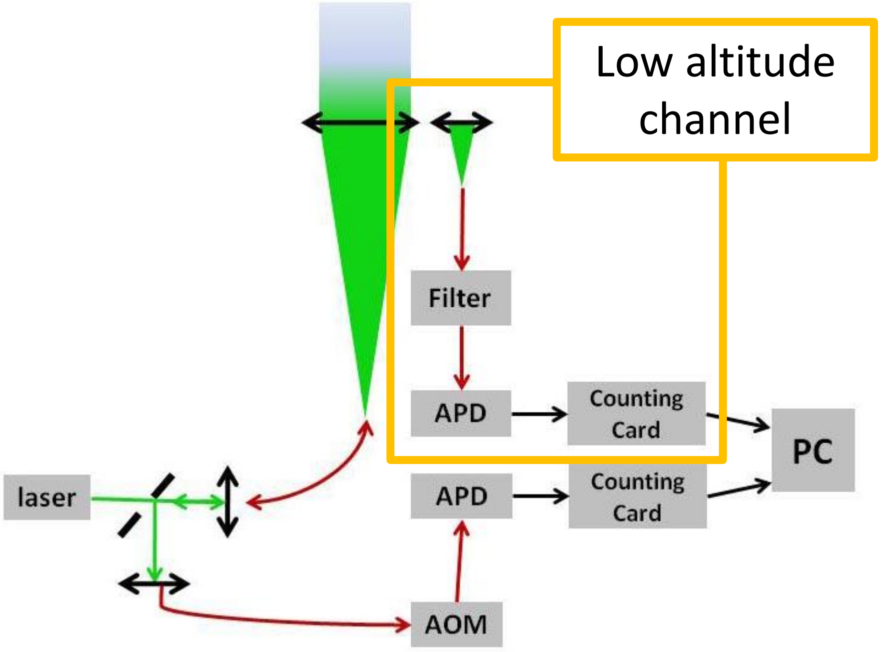
- Backscatter microlidar (CAML)
- Ozone lidar
- Sun photometer
- Wind radar
- Zenith-sky UV-vis spectrometer (SAOZ)
- Direct-sun IRTF spectrometer

The CAML microlidar

The instrument:

Initial configuration (AMMA campaign) not suited for urban observations

→ addition of a low altitude channel



Algorithmic developments:

- Implementation of low altitude channel
- Sun photometer closure
- Atmospheric stratification (BL depth) monitoring

→ to be submitted to *Applied Optics* (Feb. 2012)

Aerosol monitoring:

worldwide sun photometer network measuring AOD (AERONET)

but need for vertically resolved information

→ lidar networks (US MPLNET, German DWD…)

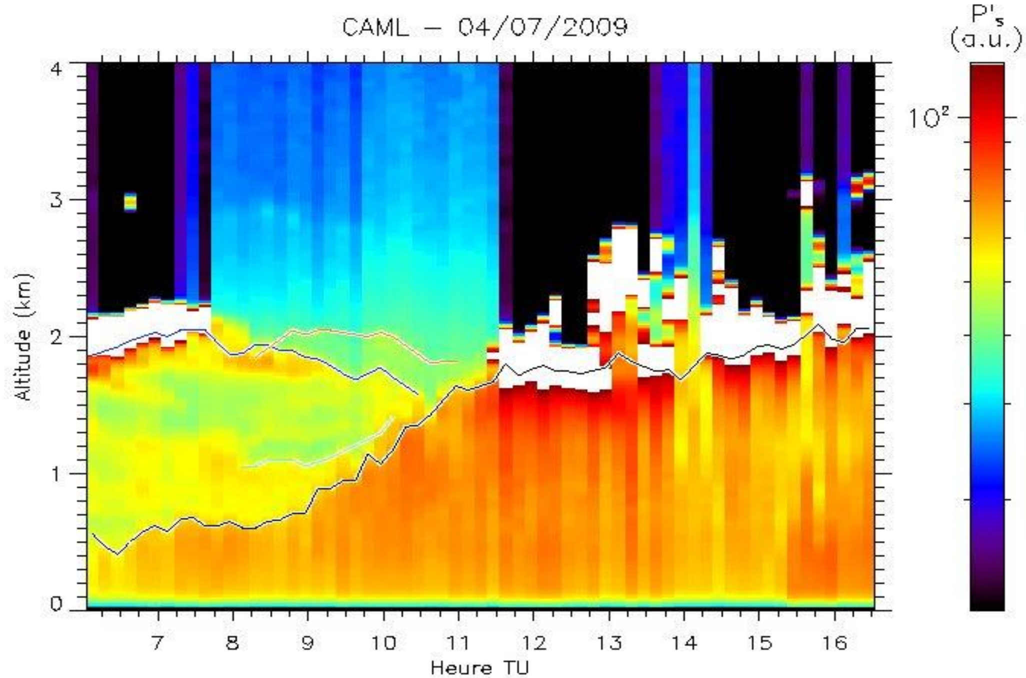
Network instruments requirements:

→ robust, autonomous and eye-safe

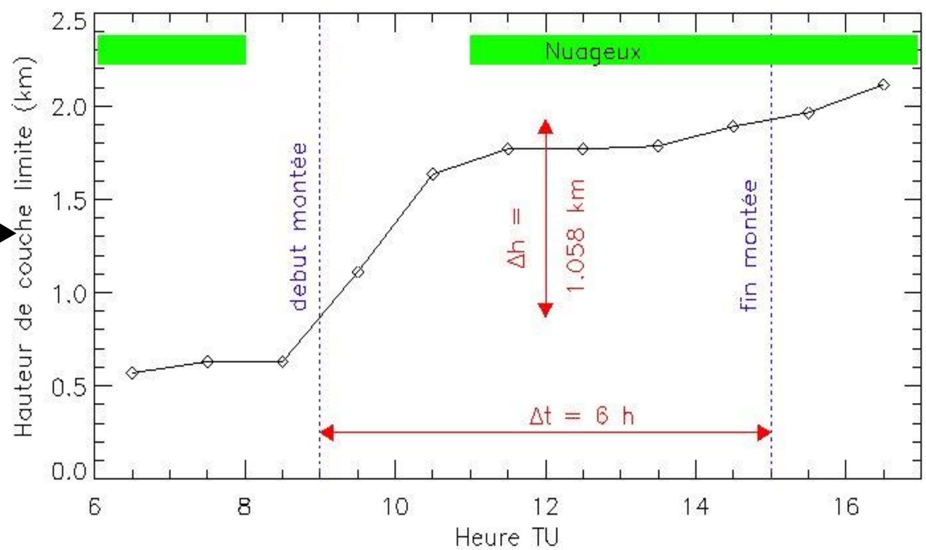
Measuring boundary layer depth by lidar

Automated gradient detection with thresholds + temporal continuity

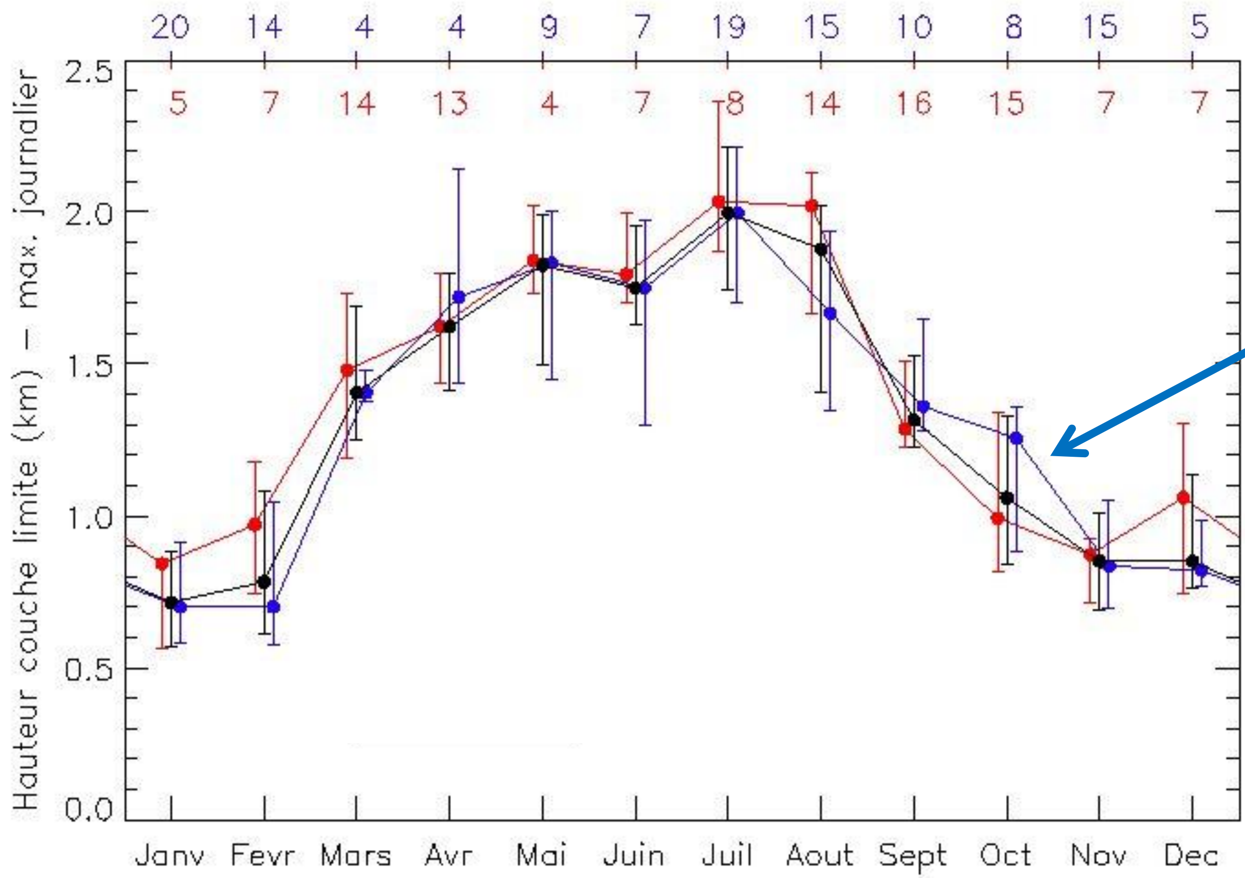
Use of cloud base if low level clouds



For NO_2 studies, 20 months database of hourly mean h_{BL} covering ½ of days



Seasonal variability of boundary layer depth



h_{BL} daily max.

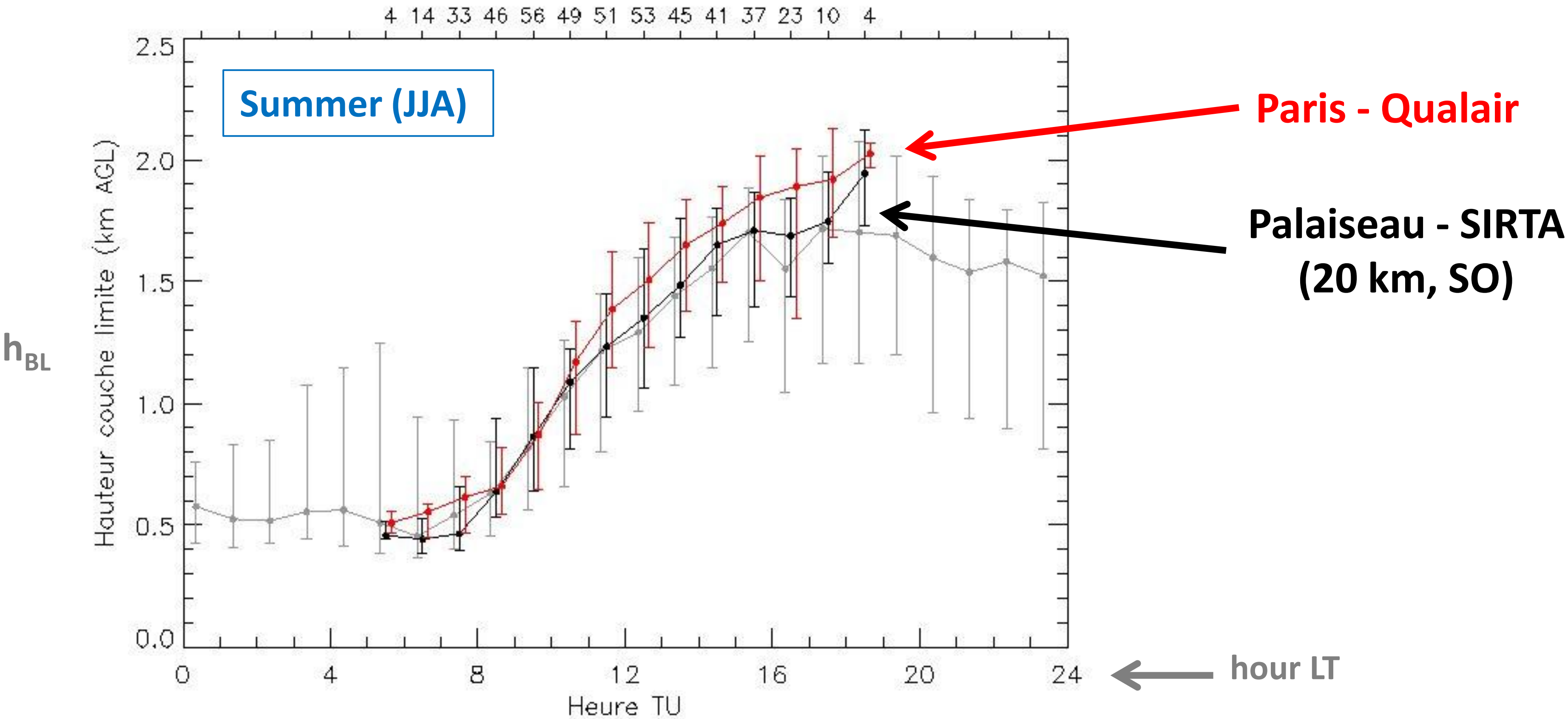
mostly cloudy days (cloud base)

mostly clear sky days

month

Strong seasonal cycle of h_{BL} → **dilution factor >2 for trace gases**

Diurnal variability of boundary layer depth



- Slightly deeper BL over Paris (≈125 m)
- Similar variability downtown and in the suburbs

→ no BL influence on NO_2 daytime horizontal gradients

In-situ NO_2 concentrations: AIRPARIF network

6 Paris stations

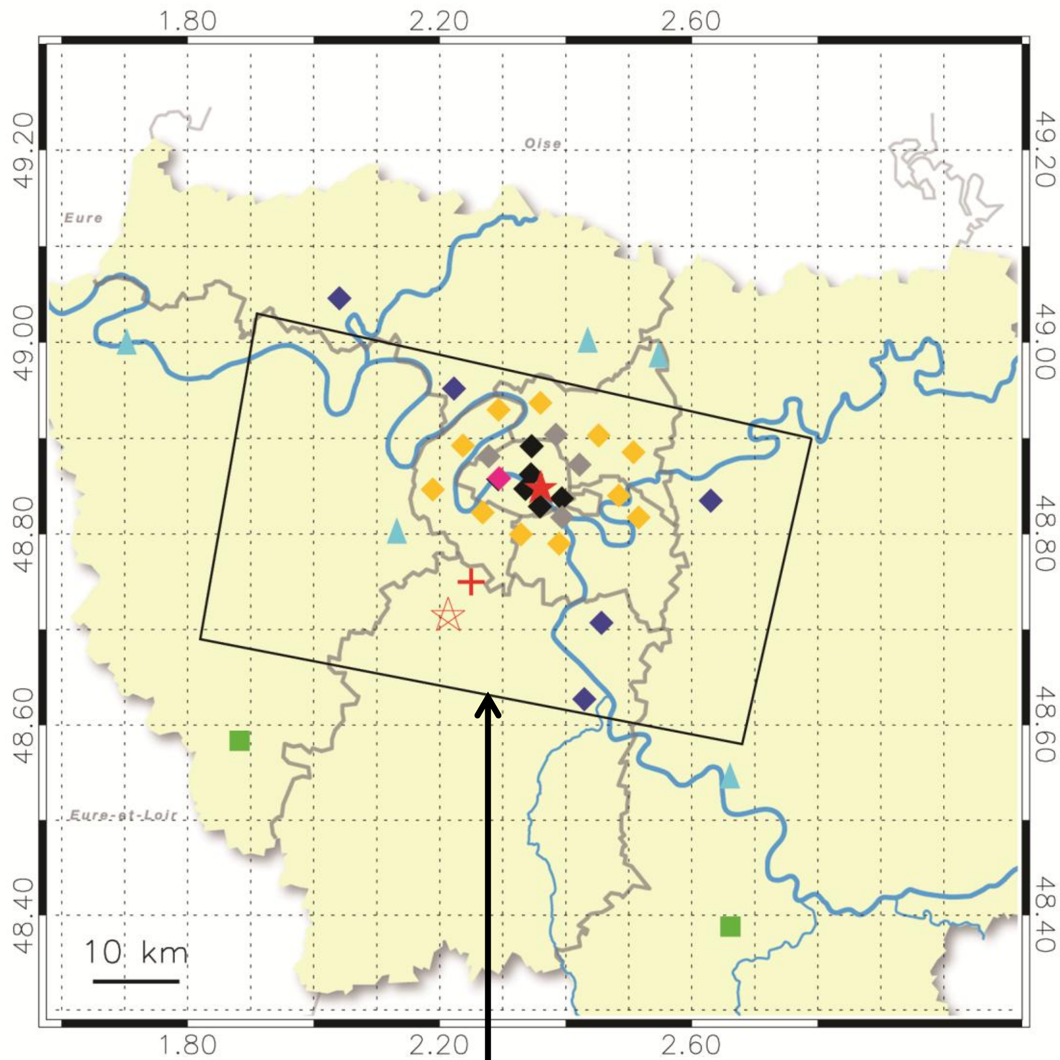
11 suburbs stations

Eiffel Tower (300 m a.g.l.)

↓

NO_2 local, horizontal and vertical variability

/!\ possible overestimation of NO_2 caused by NO_z interference



SCIAMACHY pixel

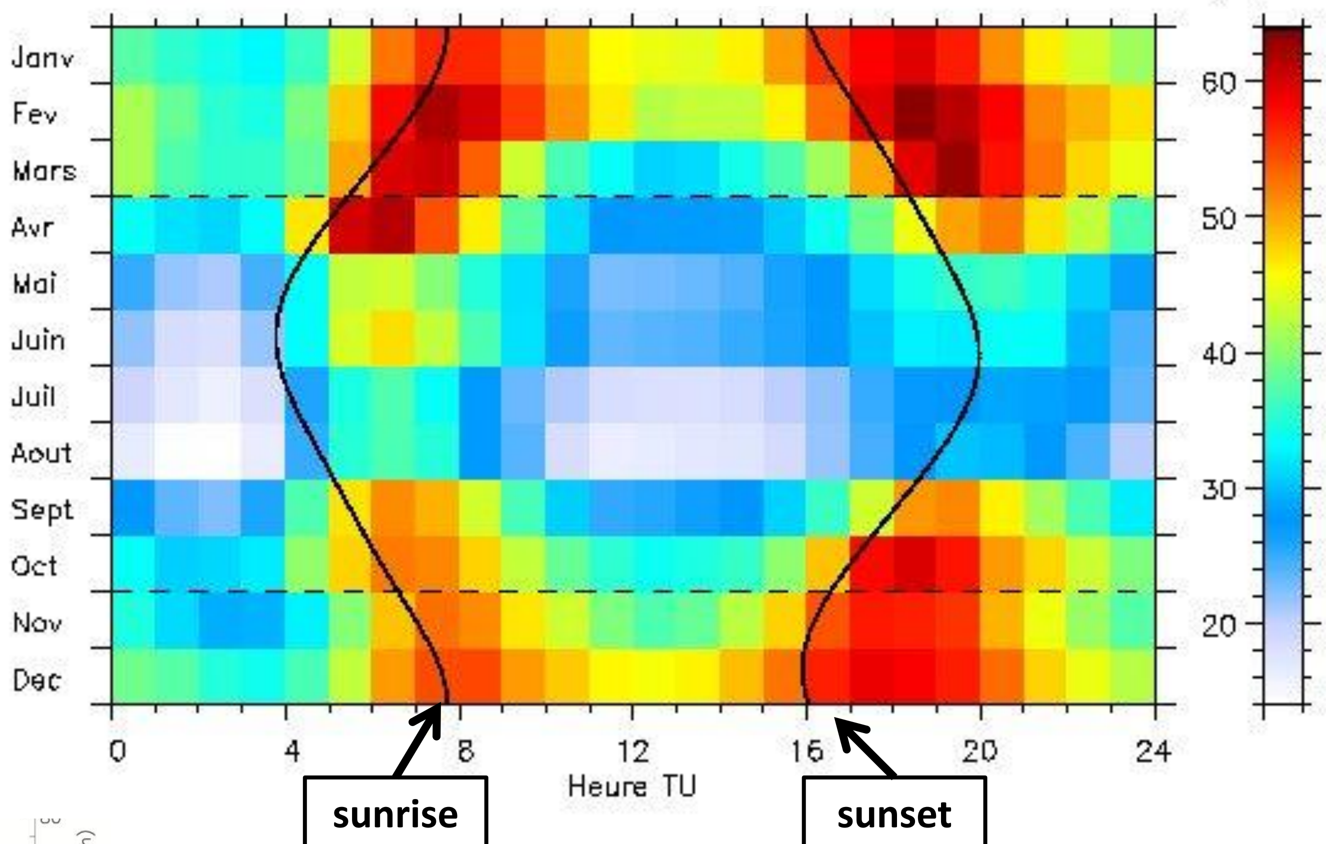
NO_2 concentrations: local variability

Diurnal cycle controlled by emission variability (traffic) :

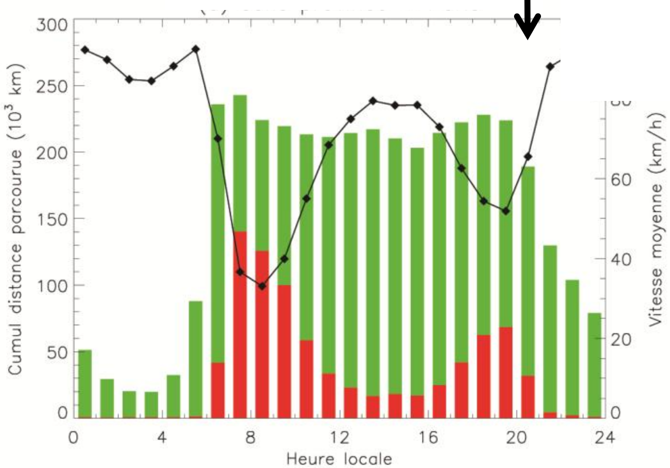
Peaks at 7-10h
and 17-20h LT

+ influence of BL: evening peak diluted

Average of 6 Paris ground stations

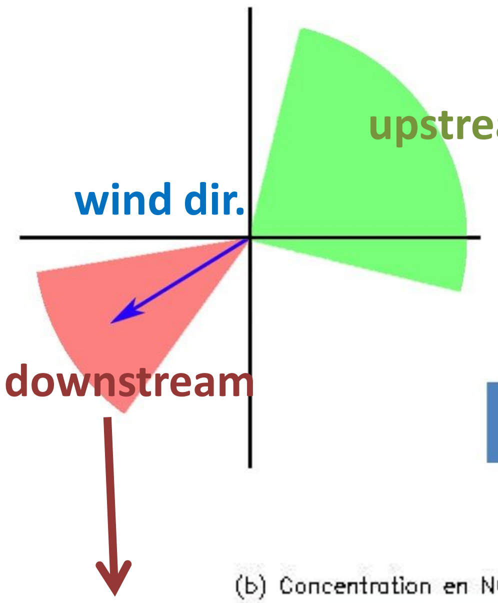


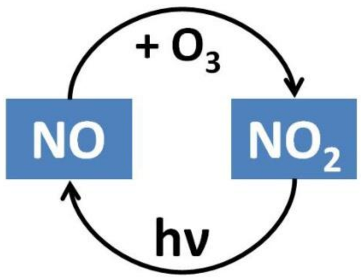
Traffic stats.

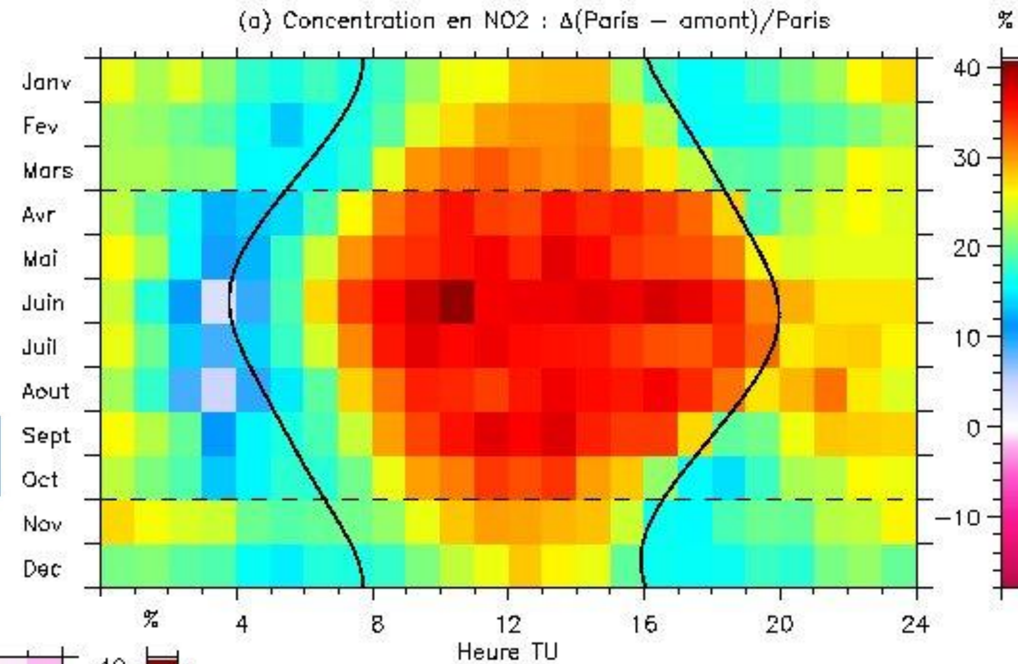


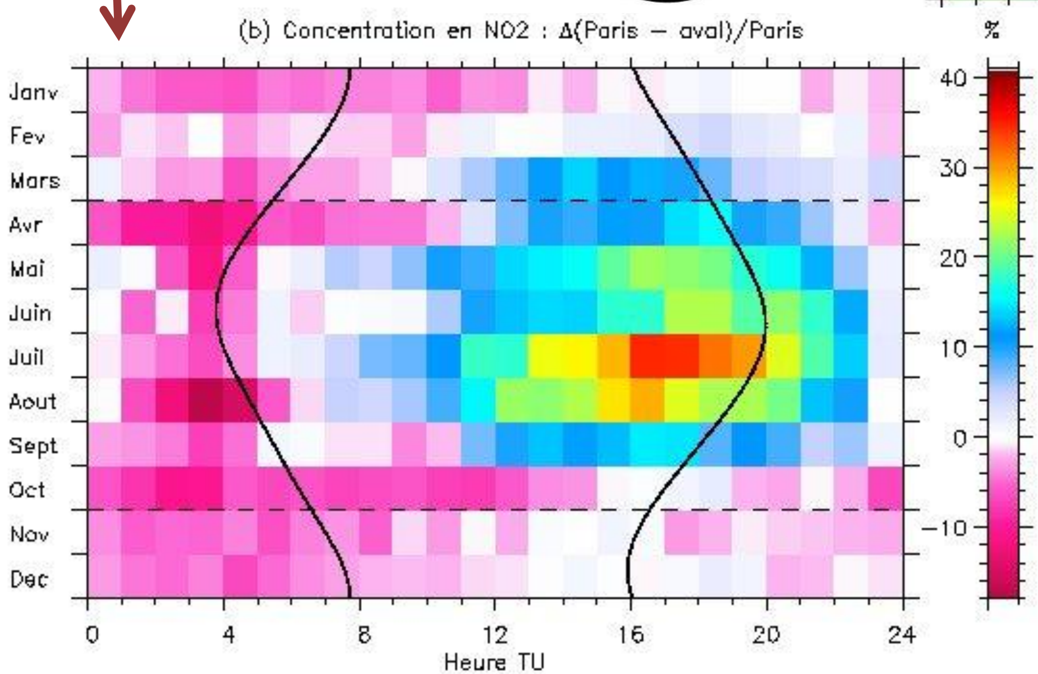
Annual cycle controlled by photochemical lifetime
+ emission variability
(winter heating, summer holidays ↘ traffic)

NO_2 concentrations: horizontal variability









Upstream: major influence of

- emissions level (↘$\nabla_h C$)
- ozone concentration (↗$\nabla_h C$)

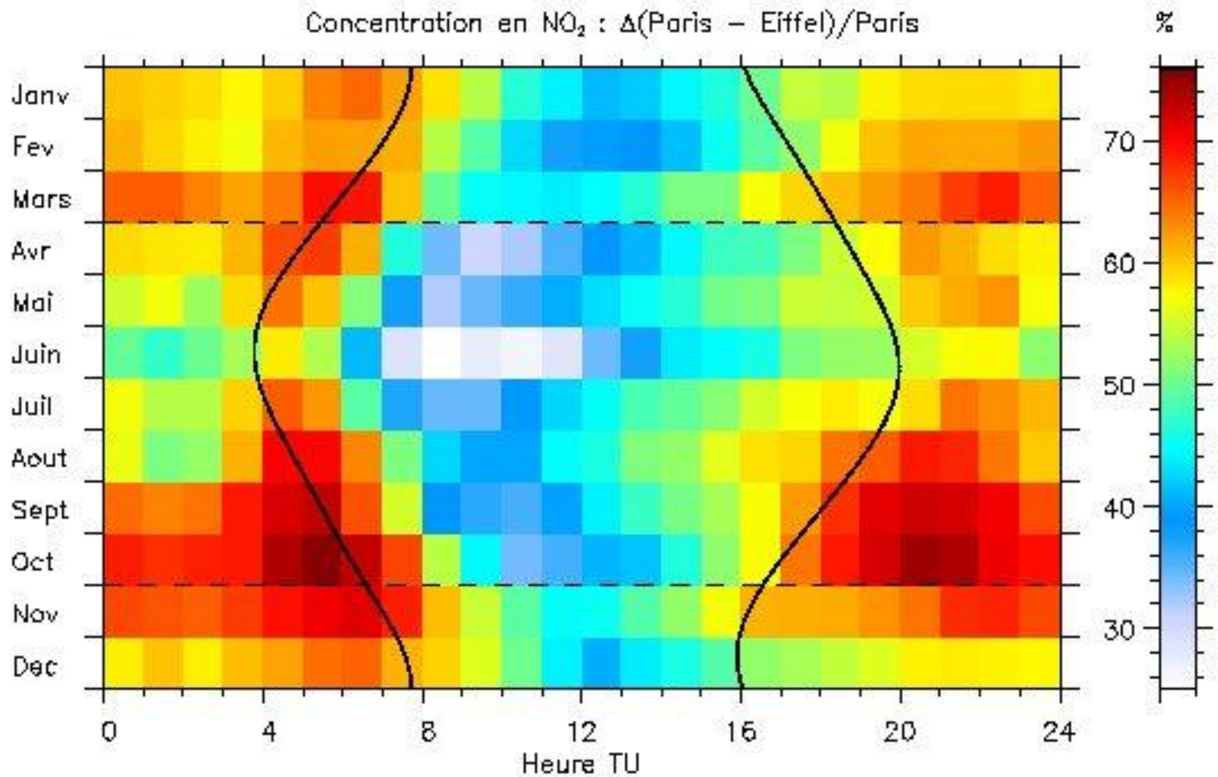
Downstream: major influence of vertical dilution
→ accumulation in thin BL

NO_2 concentrations: vertical variability

Ground / Eiffel Tower gradient (0-300 m)

Night: surface / residual layer gradient.

Day: surface / mixed layer gradient.

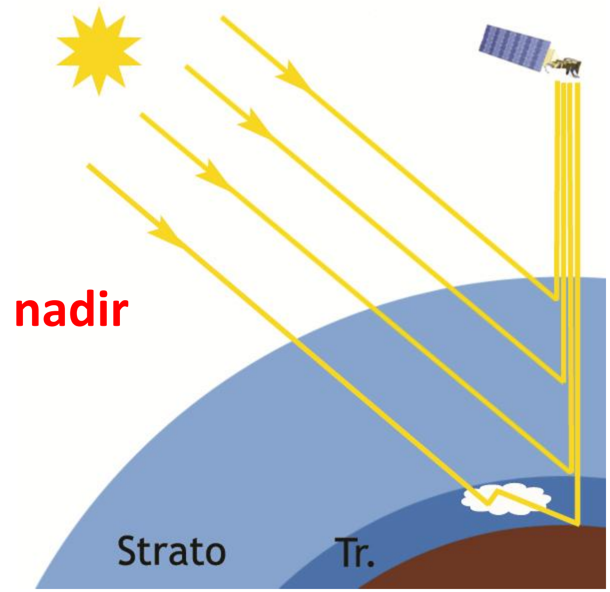


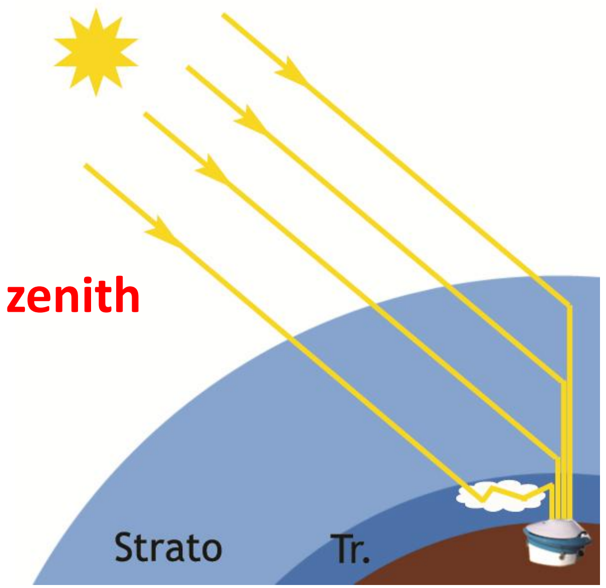
Strong SL/ML gradient and <u>very variable</u>:

→ ground-level measurements not representative of ML concentrations

→ hypothesis of homogeneous profile (i.e. for satellite validation) unrealistic

Measuring NO_2 integrated content: the instruments





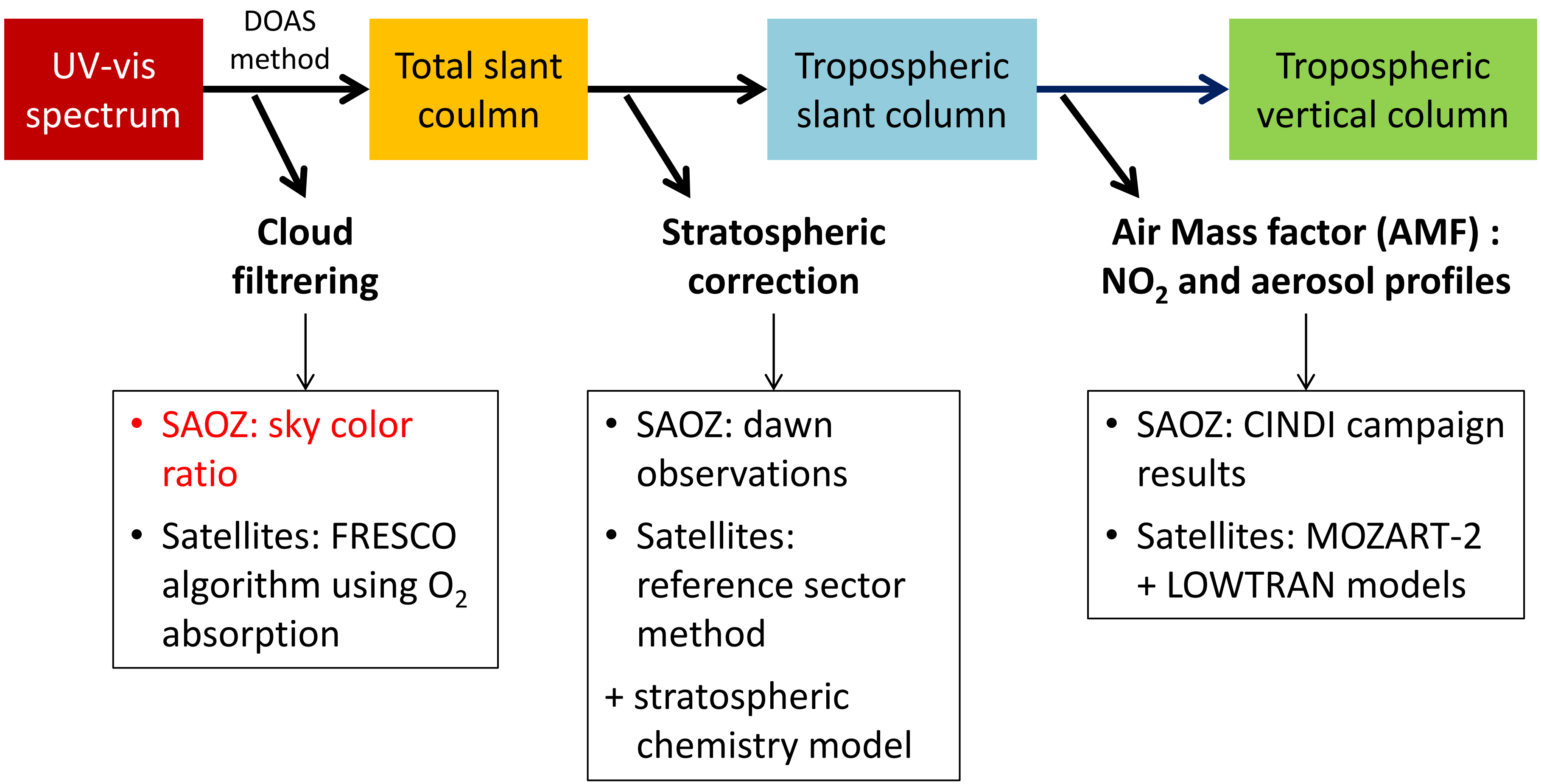
3 UV-vis spectrometers using DOAS retrieval method

	SAOZ	SCIAMACHY	GOME-2
Platform	ground	Envisat	MetOp-A
Geometry	zenith	nadir	nadir
Footprint	<city scale	30x60 km²	40x80 km²
Meas. hour	daytime	≈10h25 TU	≈9h55 TU
Coverage	all days	1/6 days	1/3 days
Deployment	Jan. 2005	Mar. 2002	Oct. 2006

→ different space and time scale

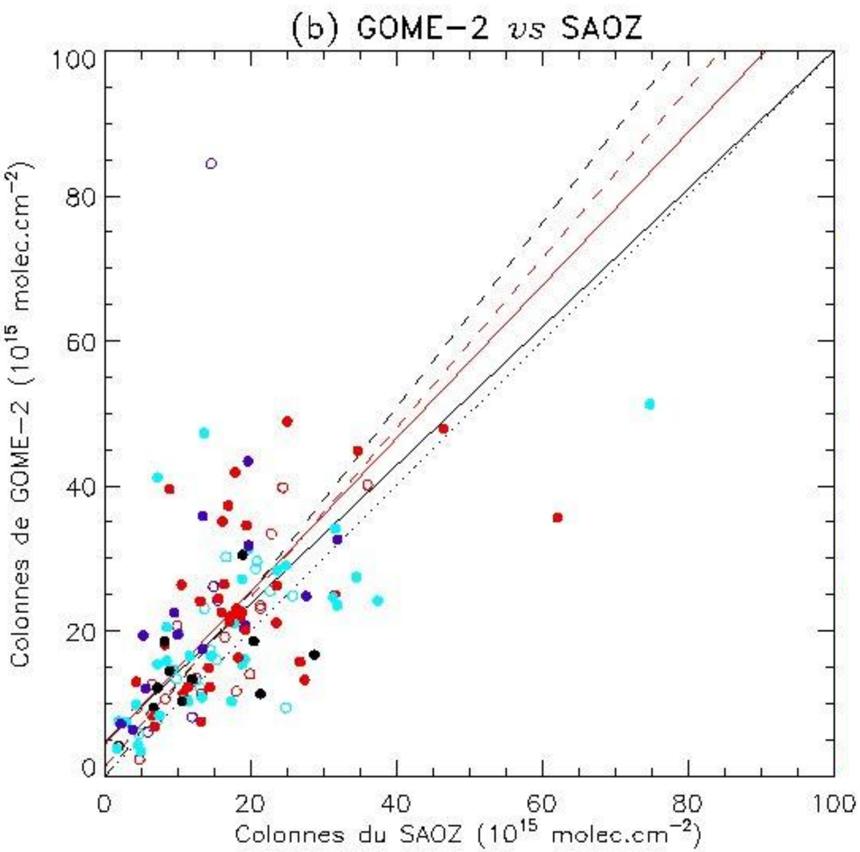
→ different light path

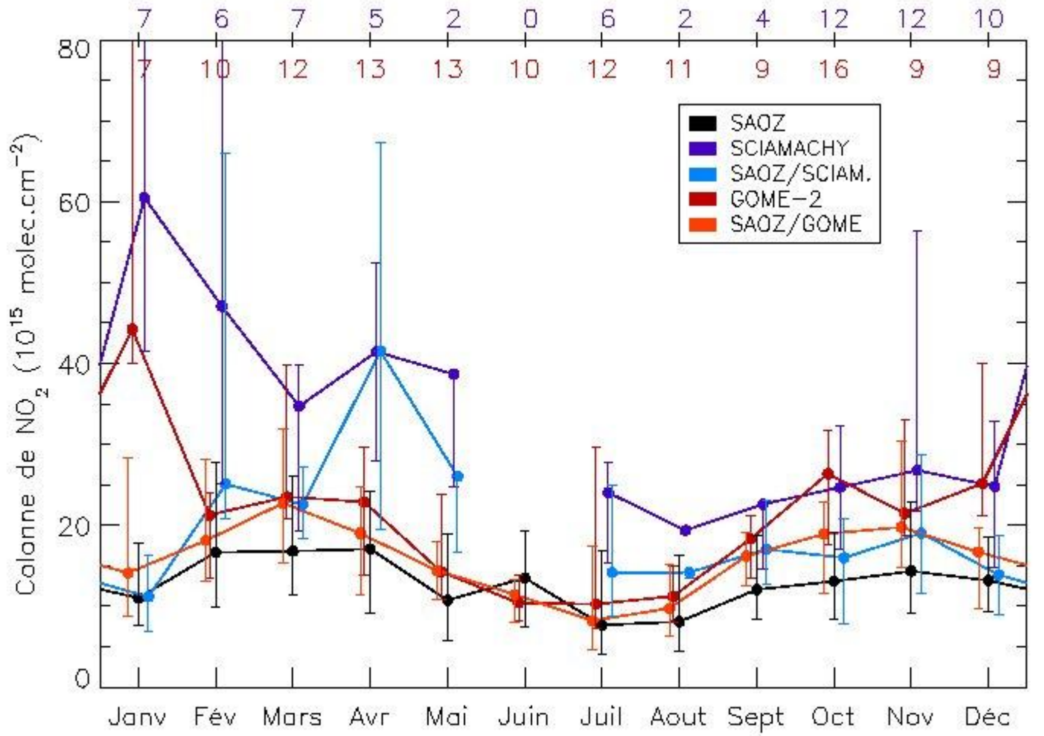
Measuring NO_2 integrated content: inversion process



SAOZ / satellites comparison

Co-localization criterion :
Paris city center included in the pixel.



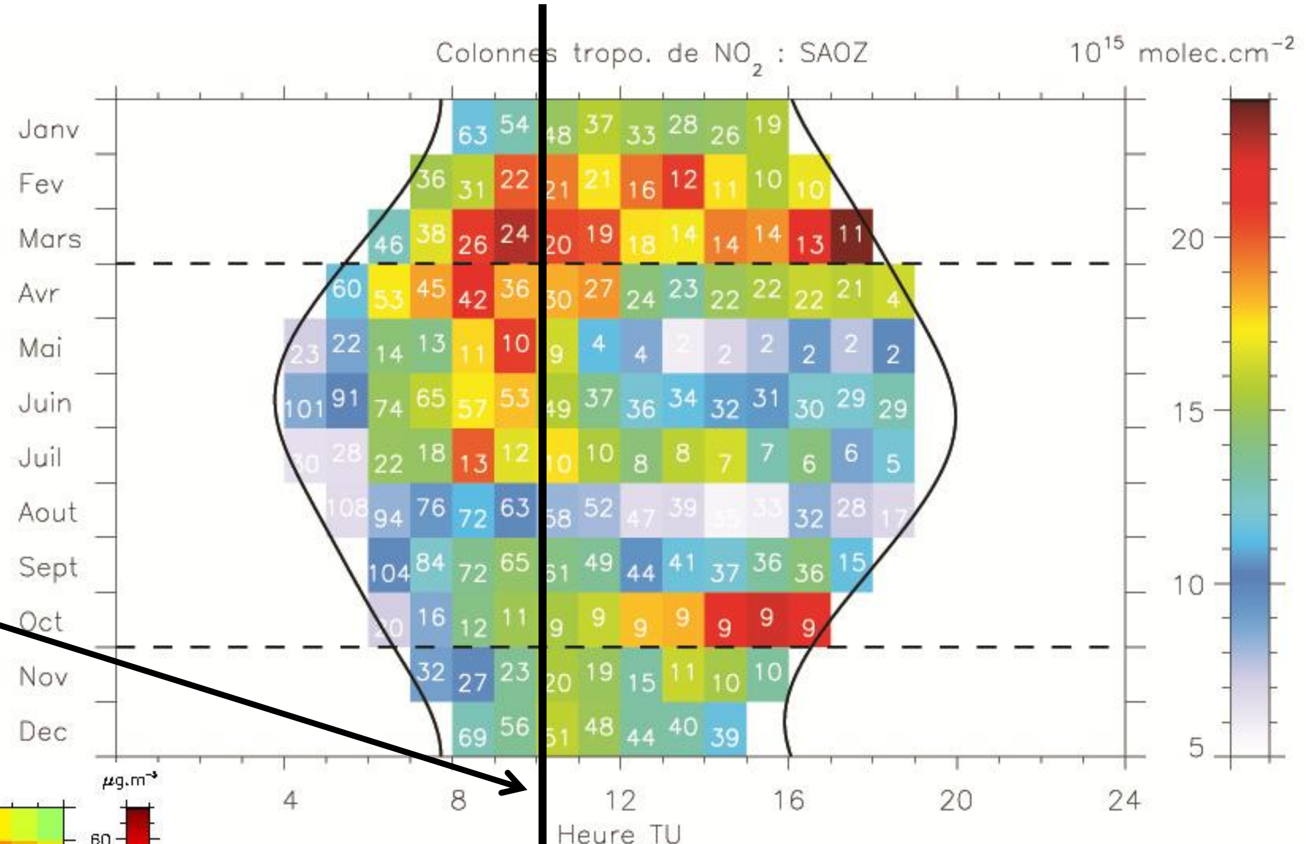


SAOZ / GOME-2 in good agreement except December / January

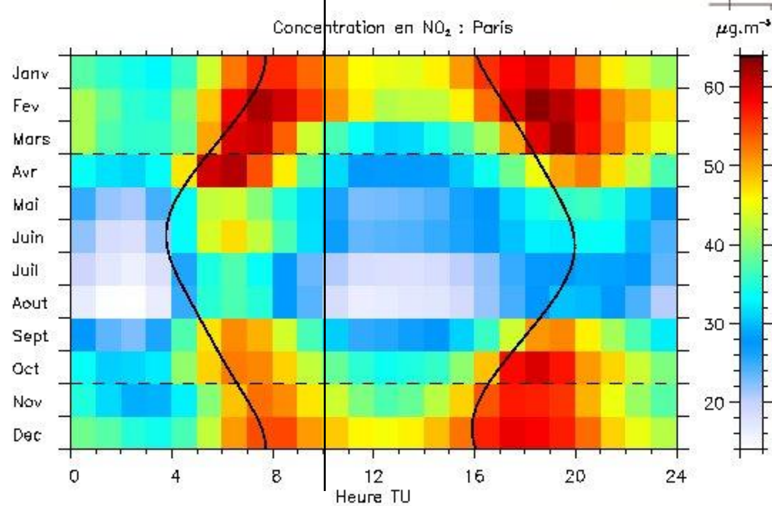
SAOZ / SCIAMACHY → less coincidences

NO_2 integrated content variability

Diurnal cycle of columns and concentrations is very different.



SCIAMACHY / GOME-2 overpass time



Accumulation in the BL after peak end at ground level, max. column around 10-11h TU

→ morning satellites best suited to monitor emissions

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Statistical relationship: concentration *vs* integrated content

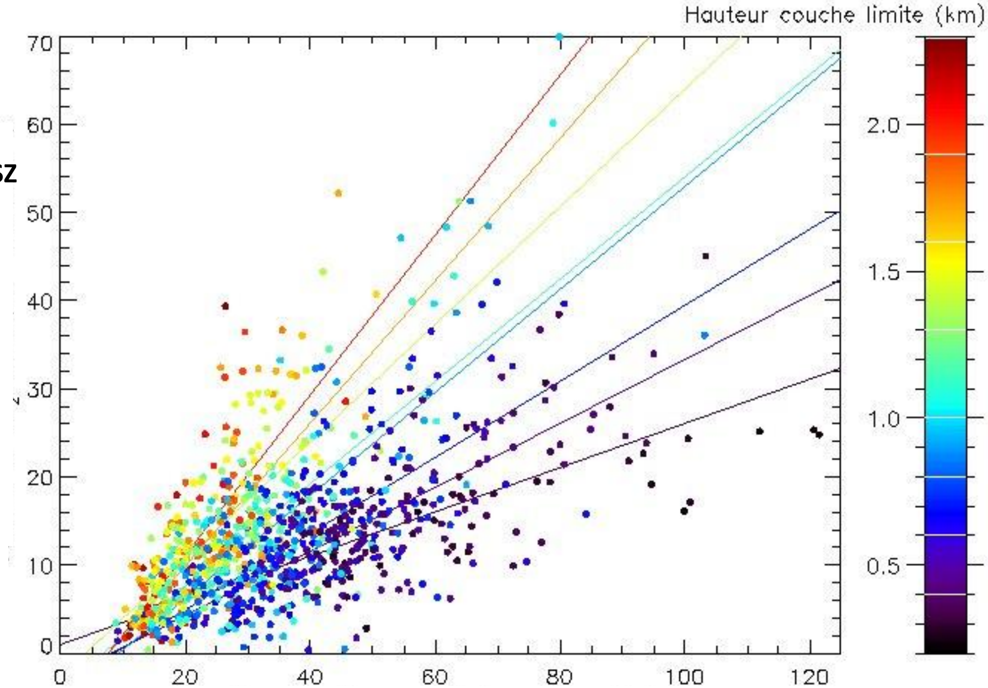
956 coincident measurements of Ω_{SZ}, C_{im} and h_{BL}

→ division in 8 classes of BL depth

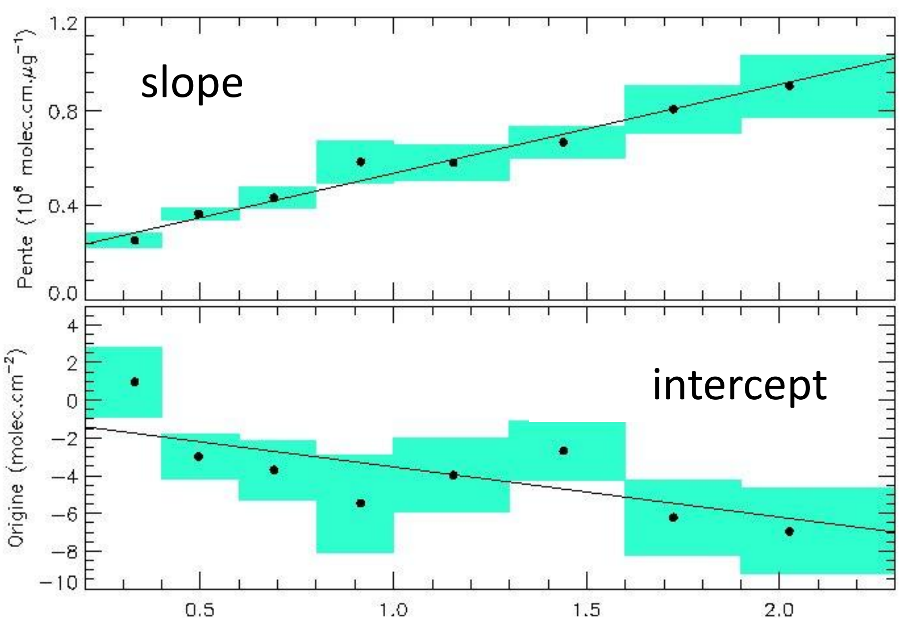
→ linear regression $\Omega_{SZ} = f(C_{im})$ for each class

Ω_{SZ}

SAOZ column



C_{im} = ground level concentration



h_{BL} = BL depth

Slope/intercept depending on h_{BL}

→ relationship $\Omega_{SZ} = f(C_{im}, h_{BL})$

Statistical relationship: concentration *vs* integrated content

Units conversion coefficient

Effective concentration (C_{cor} ≈ 7 µg.m^{-3} or 3.5 ppb)
→ NO_z or horiz. inhomogeneity correction

SAOZ column

$$\Omega_{SZ} = K\,[(0.29\,h_{BL} + 0.12) \times (C_{im} - C_{cor})\,]$$

Average concentration in **ML + EZ**
→ only 29% of SL concentration

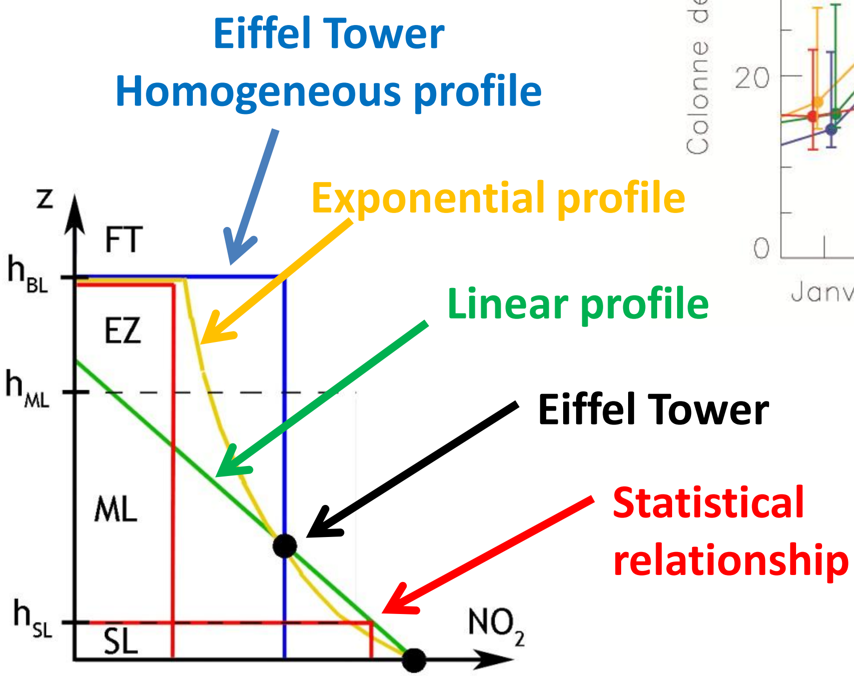
SL: constant height h_{SL} ≈ 120 m
→ fixed by surface roughness

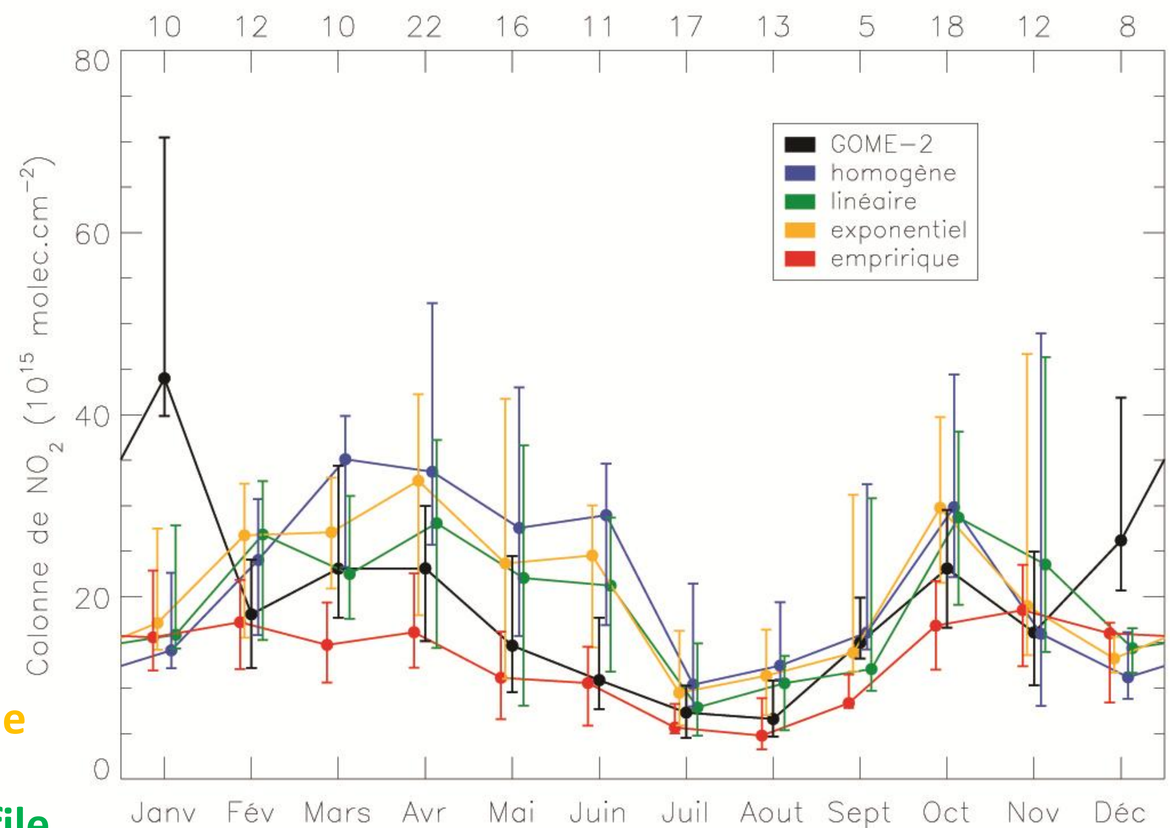
→ Is this relationship robust: application to satellite observations?

→ Which process is responsible for the low concentrations in ML + EZ?

Validation of statistical relationship against GOME-2

GOME-2 columns seasonal variability better reproduced by statistical relationship than profile hypotheses





Homogeneous profile
→ overestimation, even using 300 m a.g.l. concentration

MEGAPOLI project and campaigns

Project objectives:

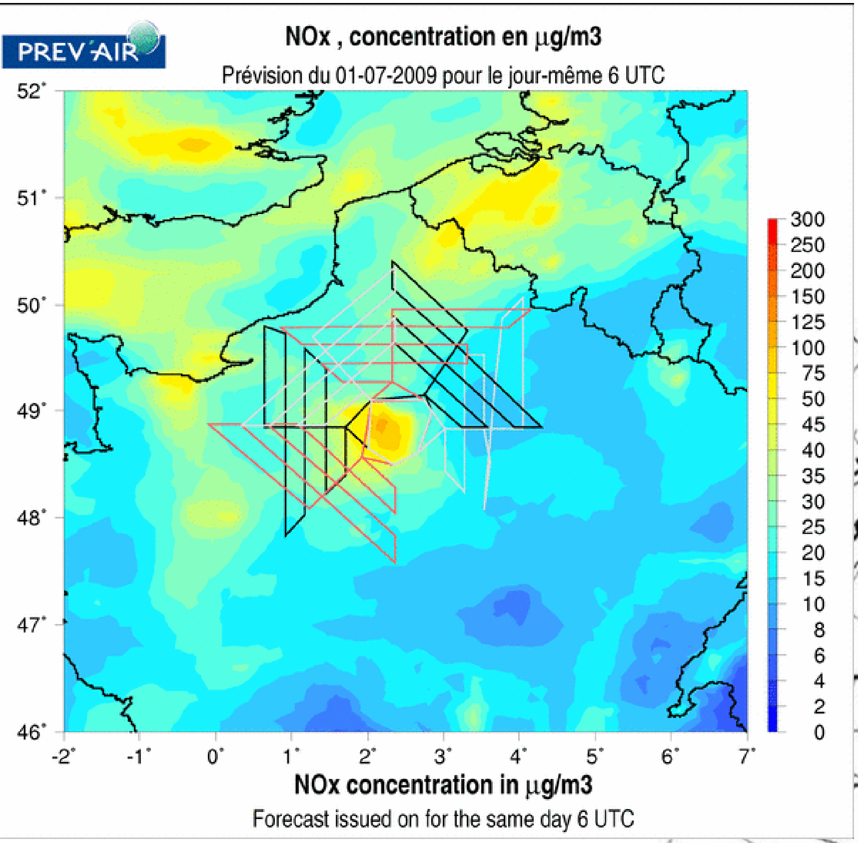
- Assess **impacts of megacities** on local to global air quality
- Quantify **feedbacks** among megacity air quality and climate change
- Develop tools for predication of air pollution

Focus on Paris with 2 **field campaigns: July 2009** + Jan.-Feb. 2010

Campaign objectives:

- Better quantification of primary and secondary **aerosol sources**
- Focus on **secondary organic aerosols** formation mechanisms

MEGAPOLI summer campaign case study

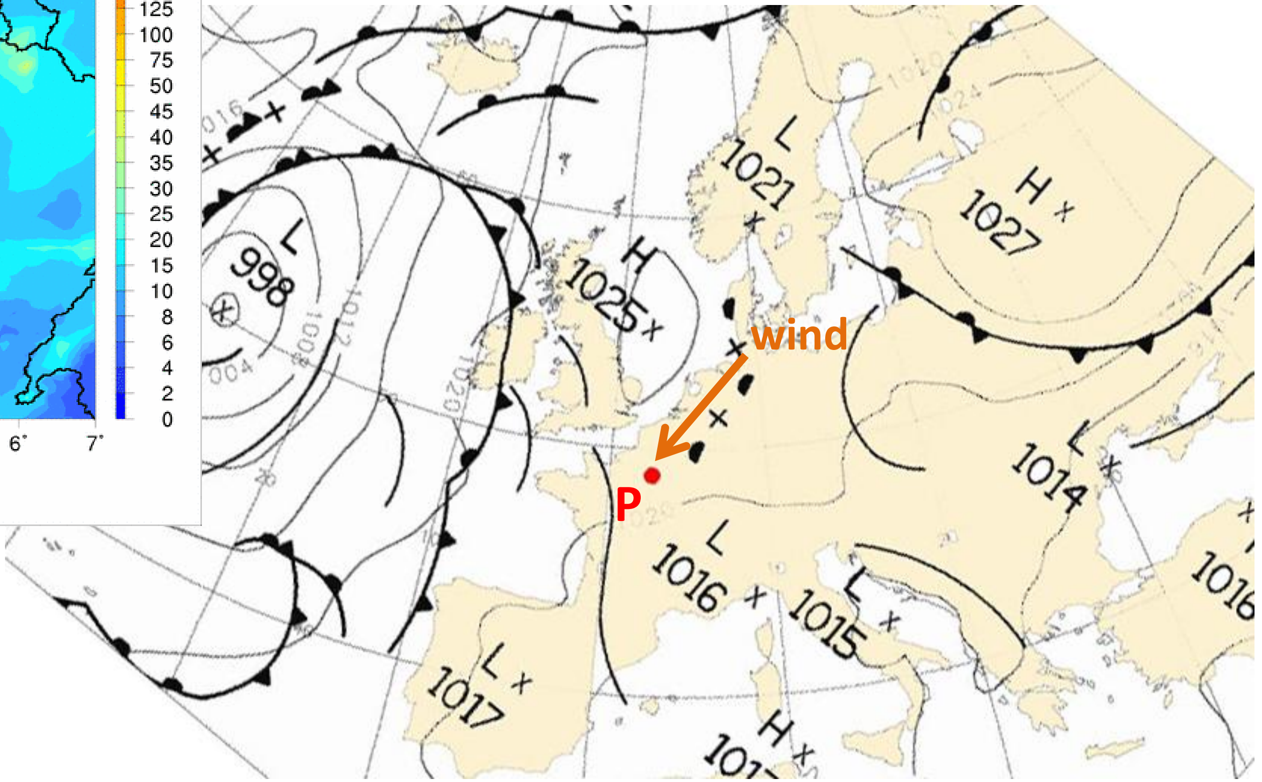


NO_x forecast for July 1st 2009
(CHIMERE model)

June 26th – July 4th 2009

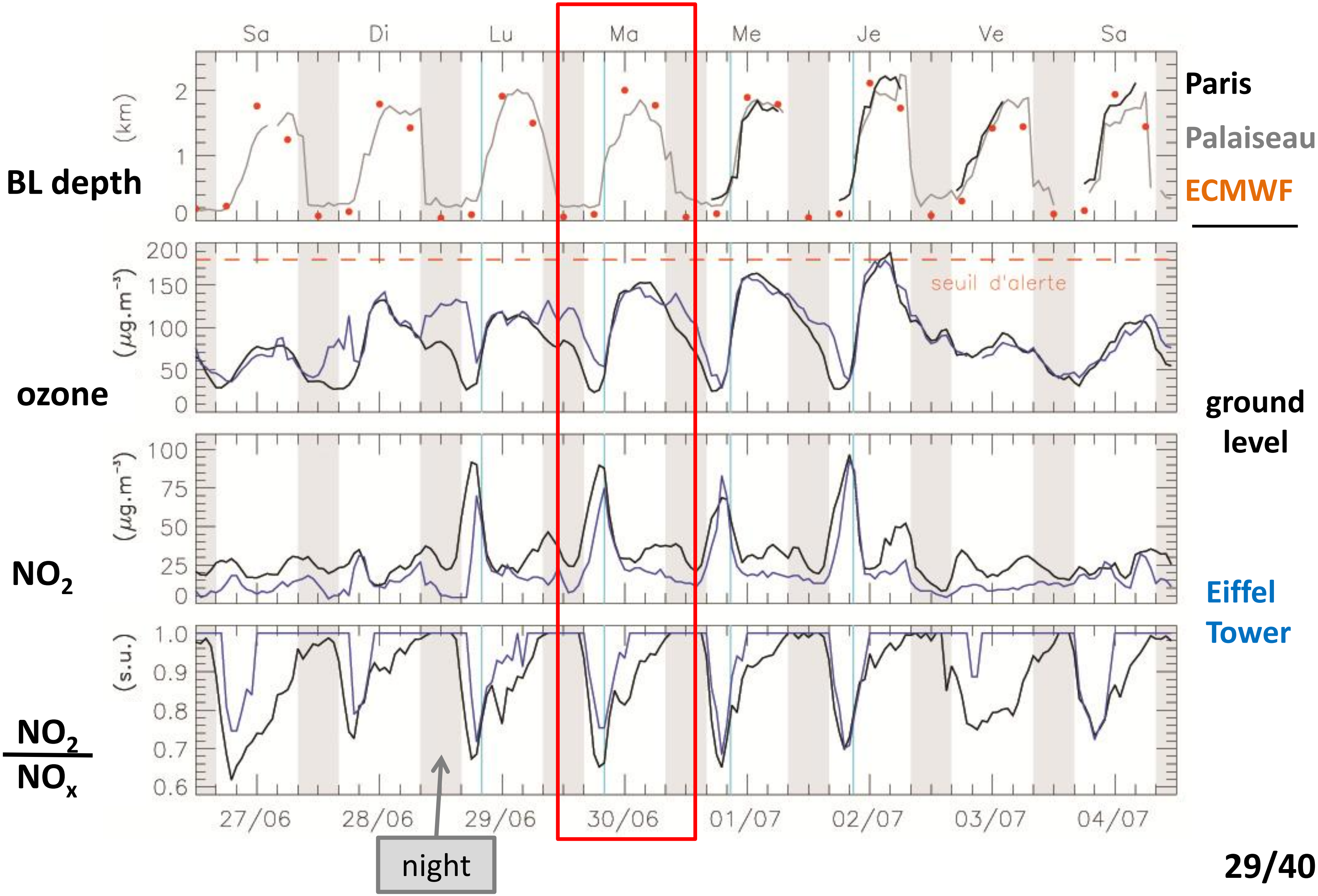
Summer pollution episode: June 29th – July 2nd

Hot and sunny weather, weak NE wind

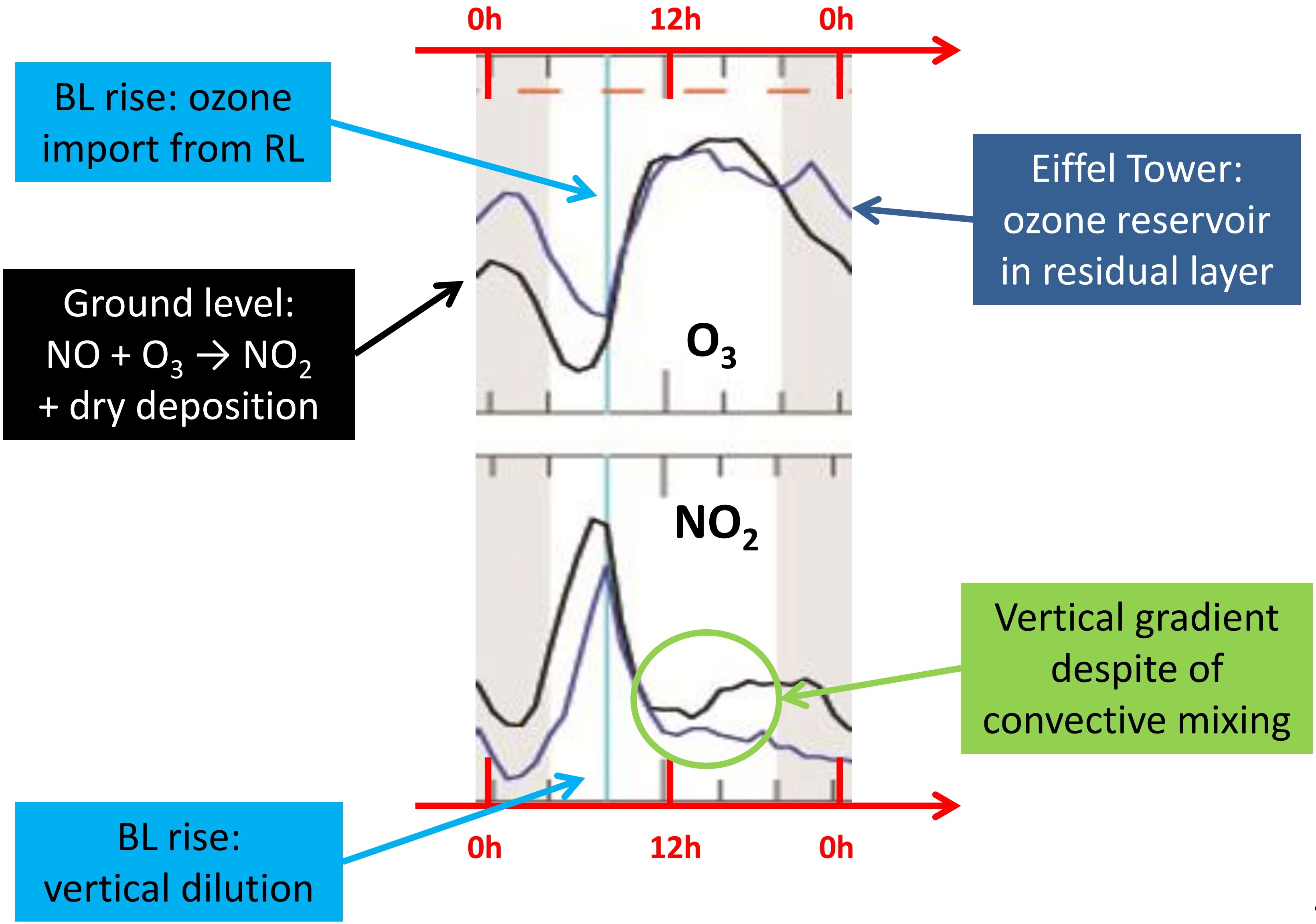


Sea-level pressure forecast on July 1st 2009

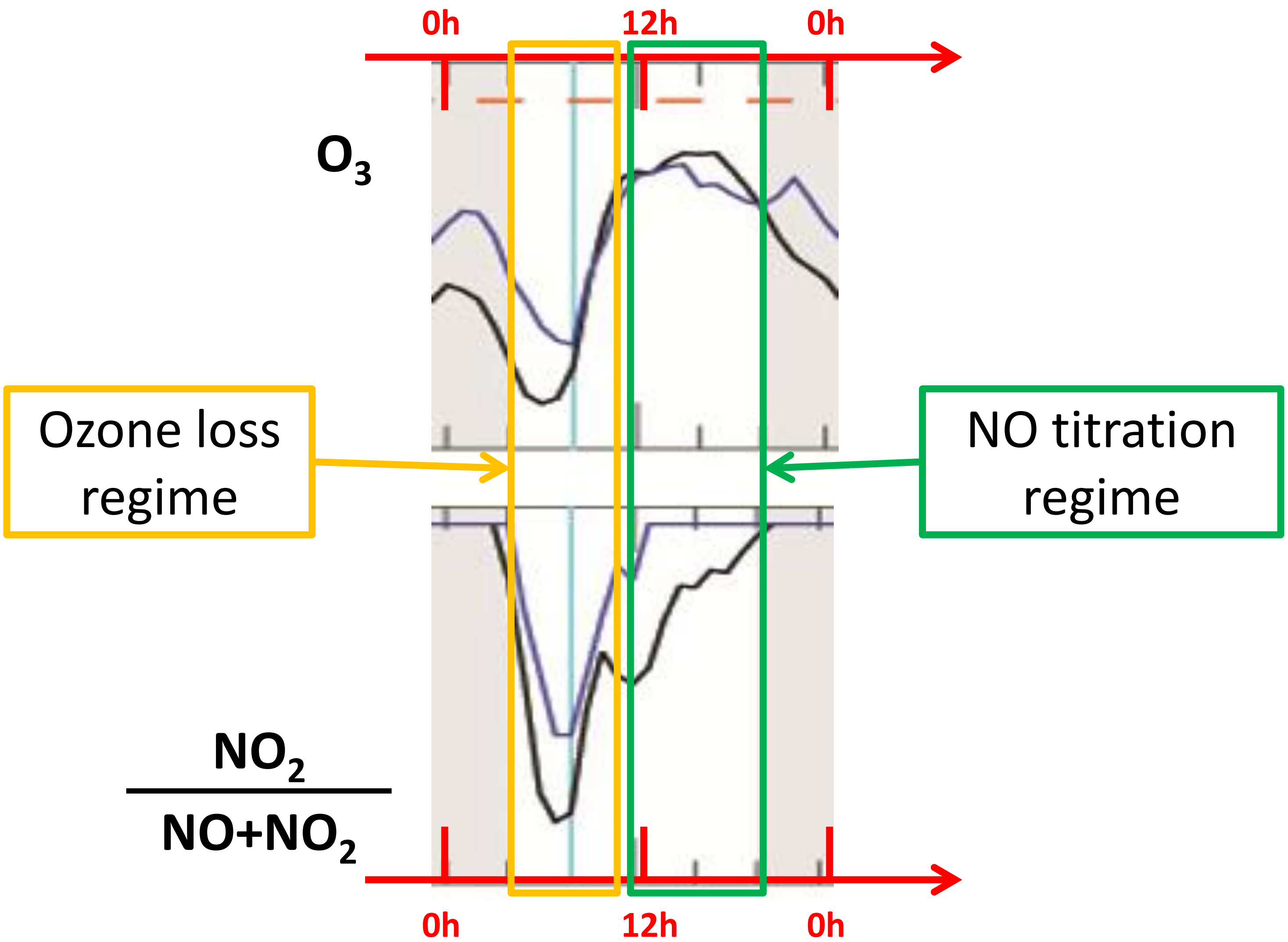
MEGAPOLI case study: chemical regimes



MEGAPOLI case study: chemical regimes



MEGAPOLI case study: chemical regimes



Influence of chemical regime on concentration / column relationship

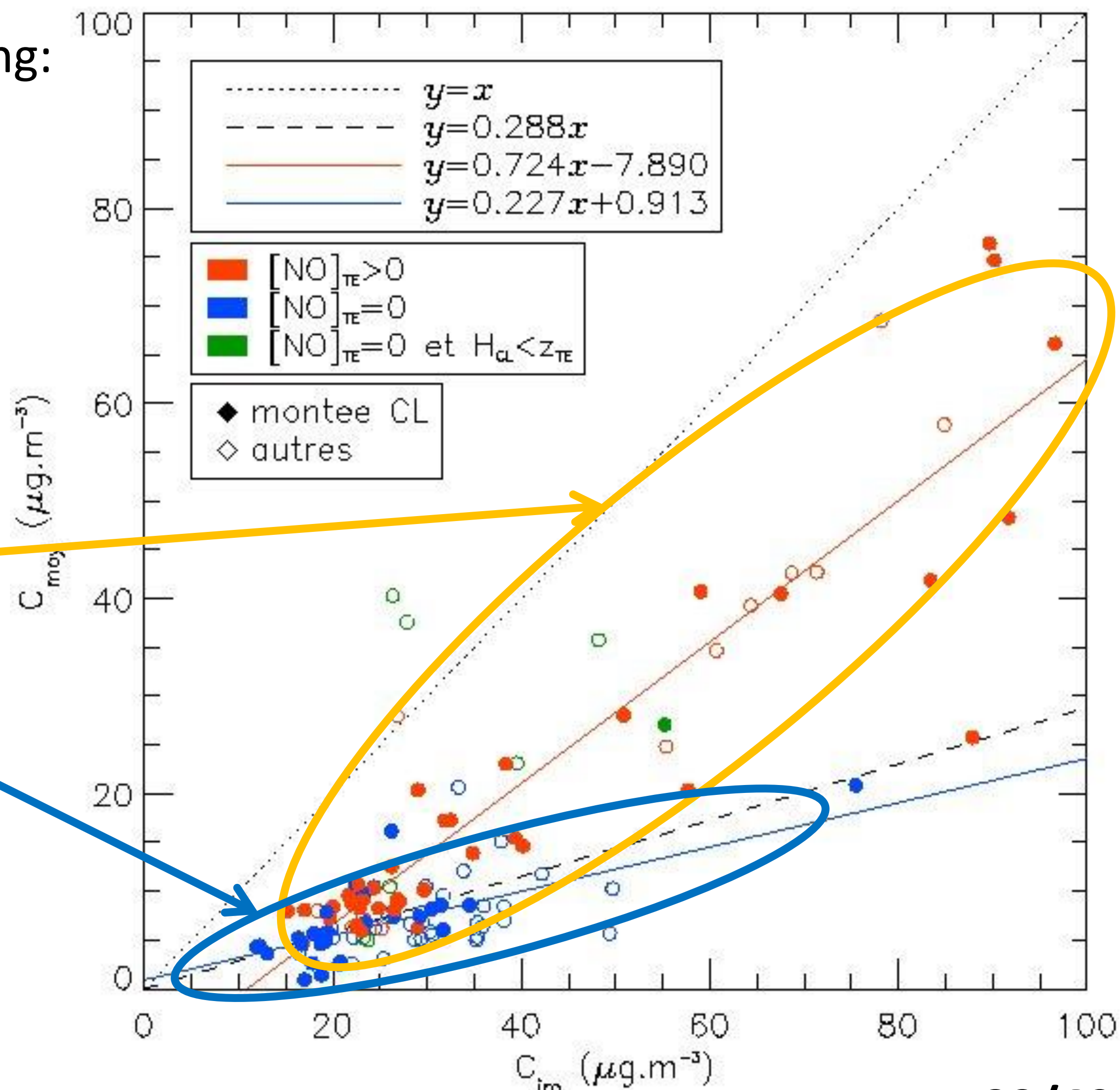
Not enough points for class-splitting:

→ ratio $\frac{\Omega_{SZ}}{h_{BL}} = C_{moy}$ against

ground level concentration C_{im}

O_3 loss regime
→ slope = 0.72

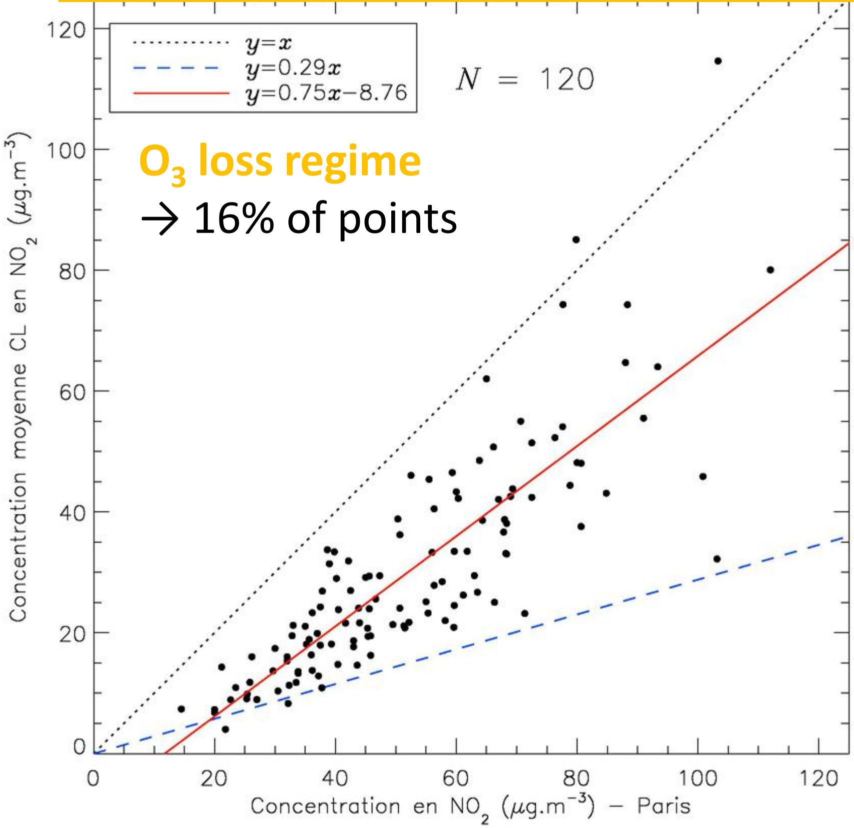
NO titration regime
→ slope = 0.23



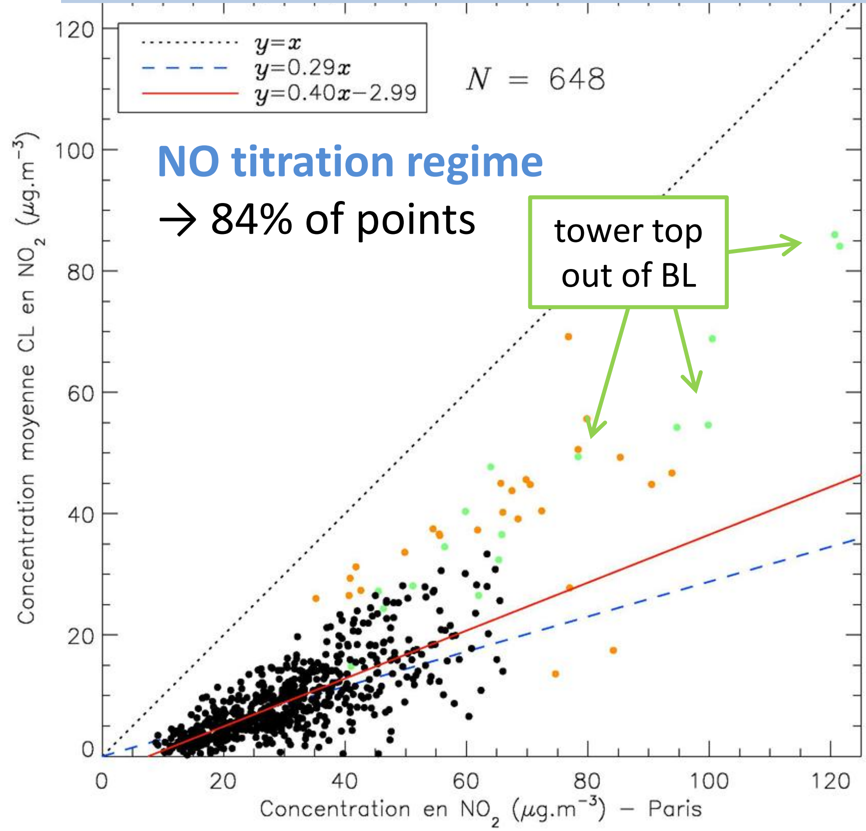
→ Statistical relationship representative of NO titration regime

Influence of chemical regime on concentration / column relationship

Eiffel NO_2/NO_x < threshold → slope 0.75



Eiffel NO_2/NO_x > threshold → slope 0.39

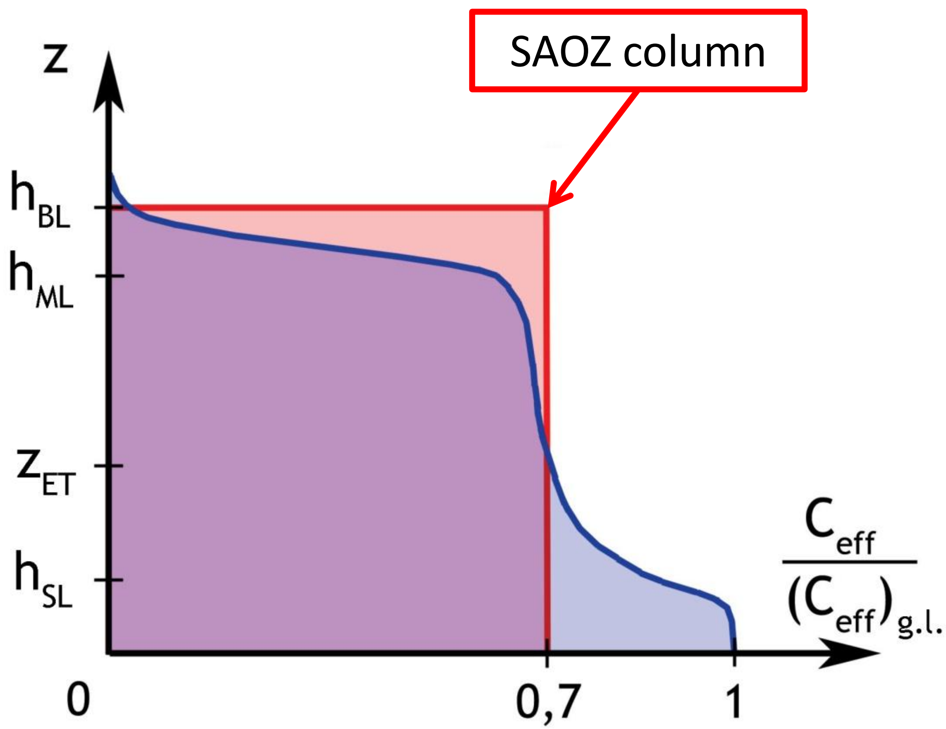


All year observations → seasonally modulated NO_2/NO_x threshold (monthly median value of 12-13h ratio at ground level)

Resulting NO_2 profile

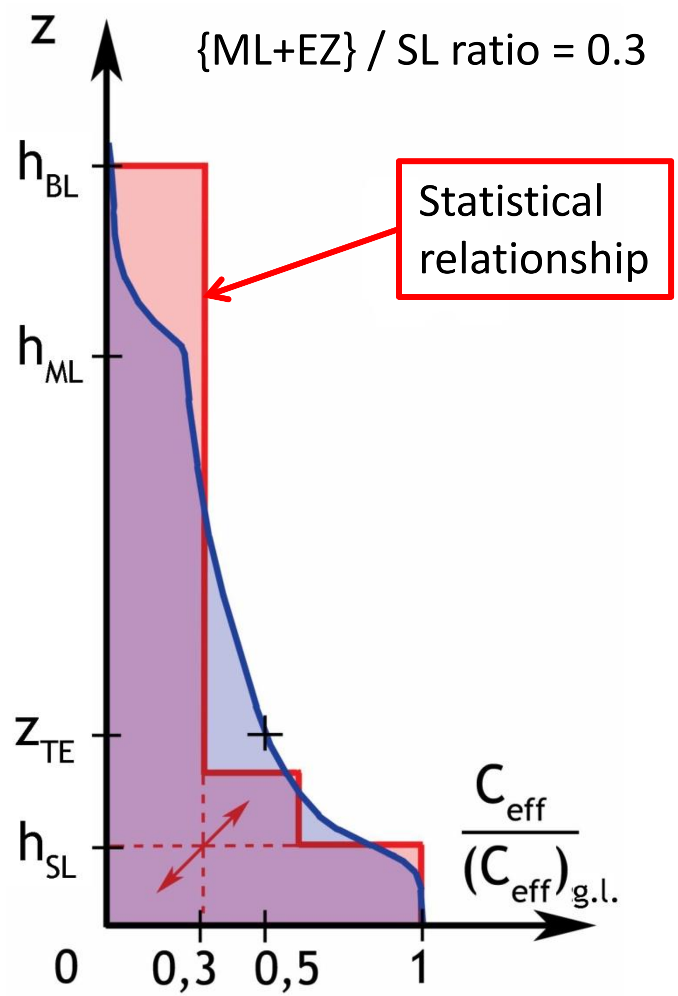
Ozone loss regime

{ML+EZ} / SL ratio = 0.7



NO titration regime

{ML+EZ} / SL ratio = 0.3



Preliminary analysis of MEGAPOLI case study: box modeling approach

Can ML/SL ratio in NO_2 profiles be reproduced by a simple model ?

entrainment speed dh/dt
(lidar time series)

O_3 titration → 0,50 km/h
NO titration → 0,15 km/h

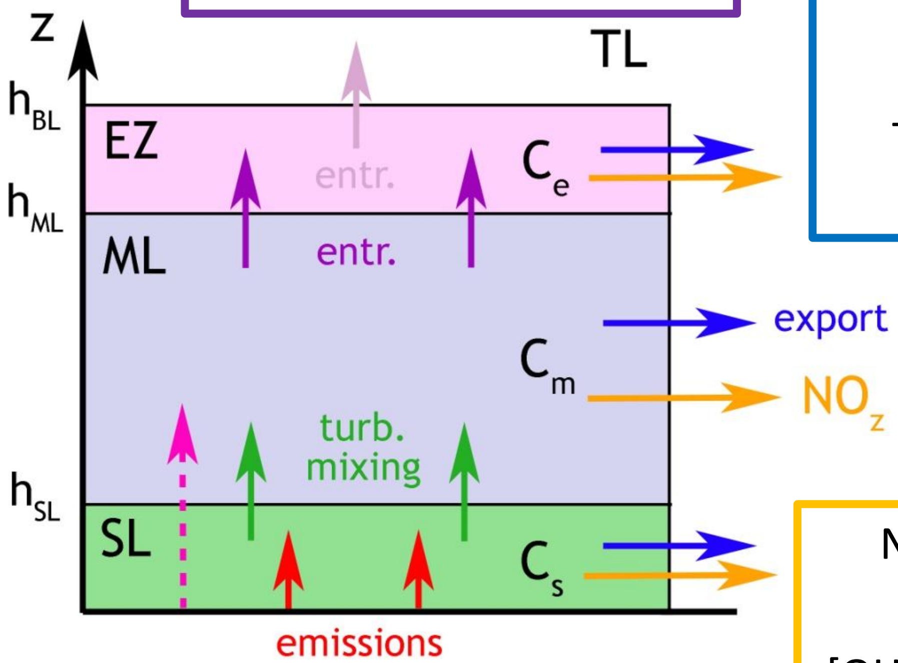
horizontal wind speed
(Météo-France radiosondes)

v_h = {1 ; 2.5 ; 4} m/s
in {SL ; ML ; EZ}

+ background conc. = 0

+ box size L = 20 km

Layers depth from previous profiles



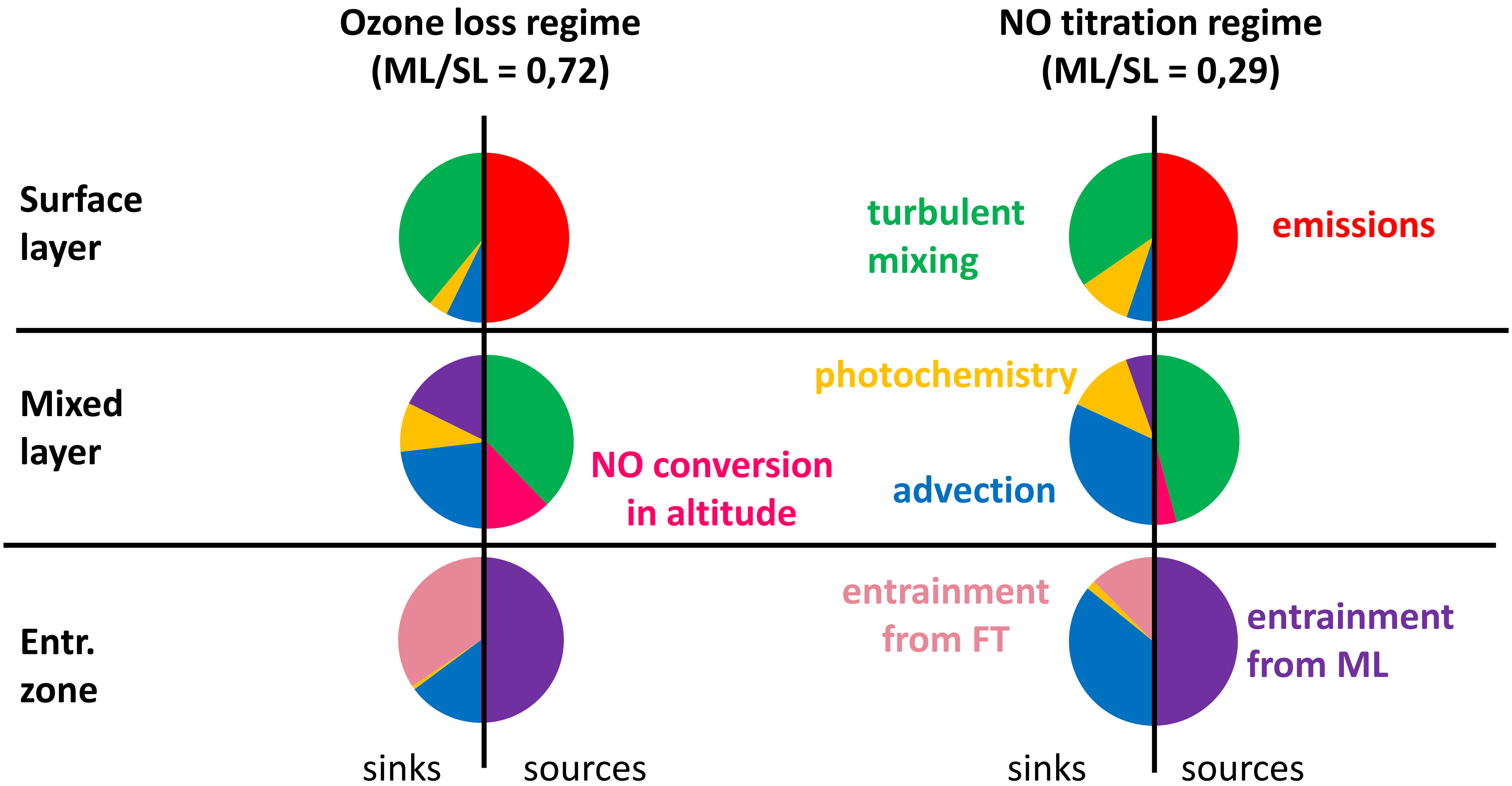
turbulent mixing :
vertical wind
speed $\boldsymbol{v_z}$ **to tune**

NO_2 destruction by OH:
$NO_2 + OH \rightarrow HNO_3$
[OH] = {10^7 ; 5.10^6 ; 10^6} cm^{-3}
→ OH obs. in Tokyo
by Kanaya et *al.* (JGR, 2007)

remaining NO
converted in ML

fraction of NO
converted to NO_2 in SL:
O_3 titration → 80 %
NO titration → 94 %

Box model: NO_2 net fluxes in the three layers



Dominant role of **export**, even at low wind speed

→ as in Vinuesa et al. (BLM, 2010)

Box model: processes characteristic time and sensitivity

		O_3 loss regime	NO titration regime
Turbulent mixing SL→ML:	$\tau_{tur} = \frac{h_m}{v_z}$	**0,52 h** (0,82 – 0,29 h) v_z = 23 cm/s	**3,8 h** (6,8 – 2,4 h) v_z = 5,6 cm/s
Photochemistry:	$\tau_{\chi,m} = \frac{1}{k_m}$	**5,6 h** (1,25 – ∞ h)	**5,6 h** (1,33 – ∞ h)
Advection :	$\tau_{adv,m} = \frac{L}{v_{h,m}}$	**2,2 h** (1,0 – 4,9 h)	**2,2 h** (1,0 – 4,9 h)
Entrainment ML → EZ :	$\tau_{ent,m} = \frac{h_m}{dh_m/dt}$	**1,7 h** (0,61 – ∞ h)	**10,4 h** (0,92 – ∞ h)

Mostly sensitive to transport processes: turbulent mixing and export

Uncertainties
→ varying ML/SL by ±0.1

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- Conclusions and perspectives

Conclusions

- Contribution of urban BL depth and NO_2 column measurements to NO_x emission monitoring and process studies
- Development of new instrumental synergies to compensate for the lack of trace gas urban profiles
- Existence of a robust relationship between surface concentration and integrated content, over NO_x source areas
- Influence of BL depth and chemical regime on the concentration/column relationship
- Inhomogeneous NO_2 vertical distribution in urban BL + dominant role of transport processes in the ML

Perspectives

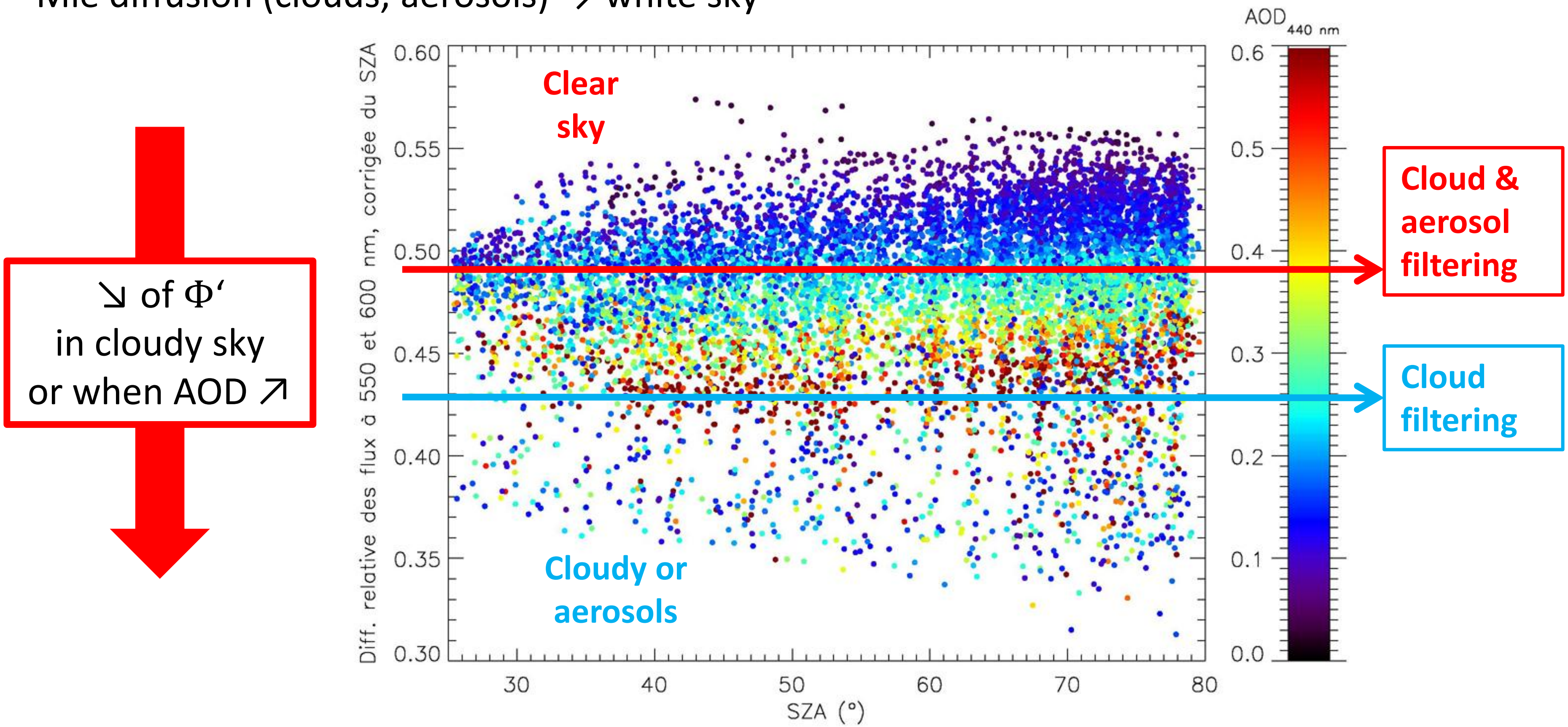
- Robustness of concentration/column statistical relationship:
  - lidar + ground-based DOAS in other cities (GEOMON network?)
  - further satellites validation
  - geostationary satellites?
- Quantifying chemical and dynamical effects:
  - other species with variable lifetimes (O_3, $O_x \equiv NO_2 + O_3$, HNO_3, CO_2…)
  - trace gas profile measurements in urban BL

Thank you for your attention!!

Filtration of cloudy SAOZ spectra

Rayleigh diffusion (clear sky) → blue sky

Mie diffusion (clouds, aerosols) → white sky



Selection criterion : $$\Phi' = \frac{F_{550} - F_{600}}{F_{550}} + 8.10^{-4}(90 - SZA) > 0{,}43 \text{ or } 0{,}48$$

Three boxes model: continuity equations

photochemistry

$NO_2 + OH \rightarrow HNO_3$

advection

In surface layer (SL):

$$\frac{dC_s}{dt} = \frac{\alpha E}{h_s} - k_s C_s - \frac{v_z}{h_s}(C_s - C_m) - \frac{v_{h,s}}{L} C_s = 0$$

emissions

turbulent mixing

SL→ML

In mixed layer (ML):

$$\frac{dC_m}{dt} = \frac{(1-\alpha)E}{h_m} - k_m C_m + \frac{v_z}{h_m}(C_s - C_m) - \frac{v_{h,m}}{L} C_m - \frac{1}{h_m}\left(\frac{dh_m}{dt}\right)(C_m - C_e) = 0$$

$NO \rightarrow NO_2$ conversion in altitude

entrainment EZ→ML

In entrainment zone (EZ):

$$\frac{dC_e}{dt} = -k_e C_e - \frac{v_{h,e}}{L} C_e + \frac{1}{h_e}\left(\frac{dh_m}{dt}\right)(C_m - C_e) - \frac{1}{h_e}\left(\frac{dh_e}{dt}\right) C_e = 0$$

entrainment FT→EZ