



# **NO<sub>2</sub> seasonal evolution in the background North Subtropical free troposphere**

*M. Gil-Ojeda, M., Navarro-Comas, L. Gómez-Martín, A. Saiz-López (CSIC), J. A. Adame, Yenny González, O. Puentedura and E. Cuevas (AEMET)*

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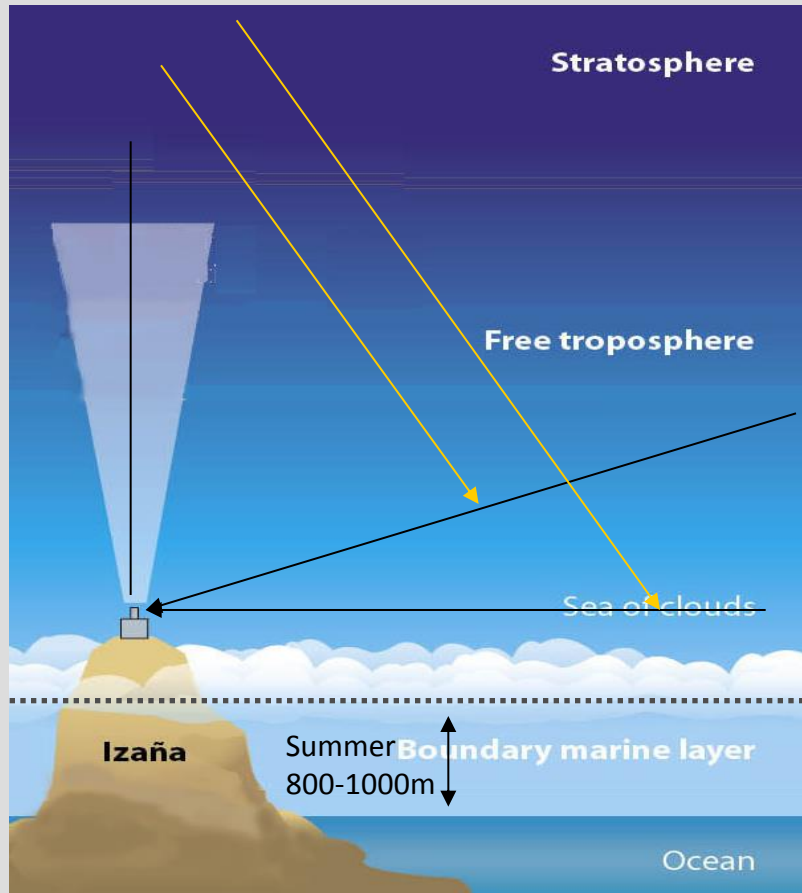
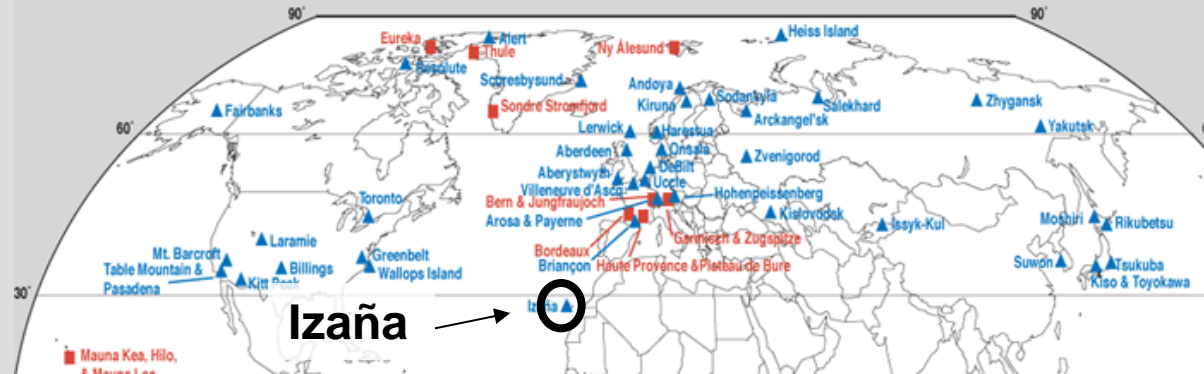
# The IZAÑA MAXDOAS

Latitude:  $28^{\circ}18' \text{ N}$

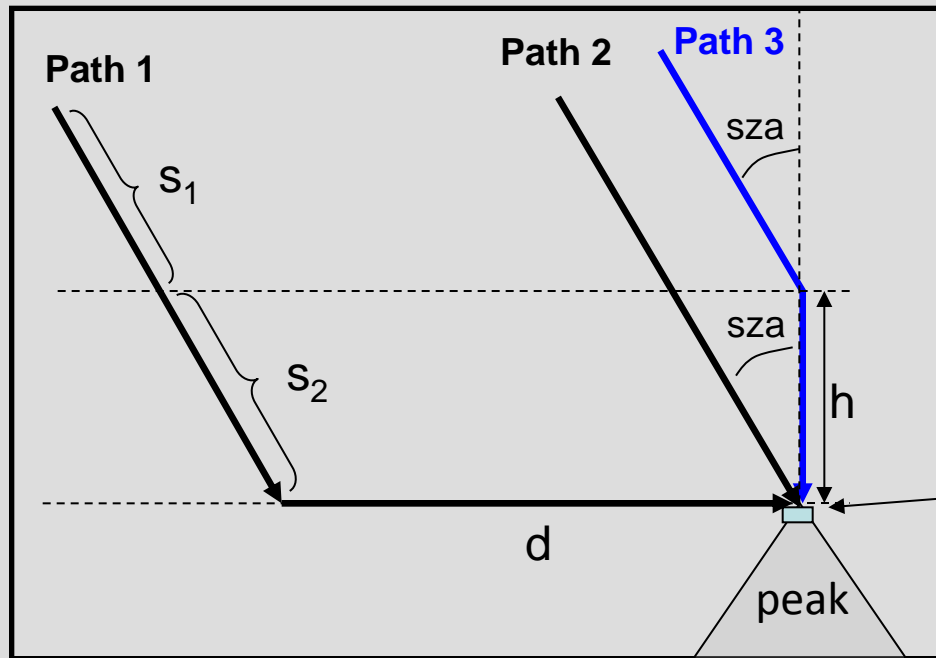
Longitude:  $16^{\circ}29' \text{ W}$

Height: 2360 masl.

## NDACC Sites



# Method *(Gómez et al. AMT, 2014)*



$$\text{Slant Path} = s_1 + s_2$$

$d$  = Horizontal Path

$h$  = effective scattering height

$$NO_2(vmr) = \frac{NO_2 DSCD}{path} = \frac{NO_2 DSCD}{\frac{O_4 DSCD}{[O_4]_{surface}} + h \cdot (R \cdot g - R' \cdot g')}$$

$NO_2 DSCD$ ,  $O_4 DSCD$  = Columns along the path  
 $[O_4]_{surf}$  = Modeled concentration

$h$  = Effective height

$R, R' = (\text{mean\_} \rho \text{ in\_layer}) / (\text{surface } \rho)$

$g, g' = (AMF(sza) - 1)$

Relative error

2.3% ( $sza=50^\circ$ )

9% ( $sza=70^\circ$ )

# Uncertainty

Uncertainty in NO <sub>2</sub> due to fit	15-20%
Uncertainty in path due to the O <sub>4</sub> fit	< 1%
Uncertainty of the method (related to unknown vertical distribution of NO <sub>2</sub> and actual effective path)	< 9% (for sza < 70°)
Error in horizontal path due to O <sub>4</sub> cross-sections temperature dependence	2%
<b>OVERALL UNCERTAINTY</b>	<b>25-32%</b>

*Approx. 10-12 pptv*



Spinei et al. ATMD 2014

*9% temperature dependence in 44K*

*Izaña temperature change along the year = 10K (277K-287K)*

O4 analysis done with Hermans et al XS

# Range of Validity

- The method is only valid in places where aerosol content is low
- At high  $\text{sza}$  there is difficult to completely remove the stratospheric contribution and the error in the tropospheric path increases as well.
- Occasionally the horizontal path is reduced (cloud/fog or a very narrow dust/smoke layer) exactly at the level of the station. Those cases are removed.

## Filtering

- a) AOD at 500 nm < 0.1
- b)  $\text{Sza} < 70^\circ$
- c) Path at 477 nm > 30 km
- d)  $\text{Rmse} < 2 \times 10^{15} \text{ molec.cm}^{-2}$
- e) Negative values, removed.

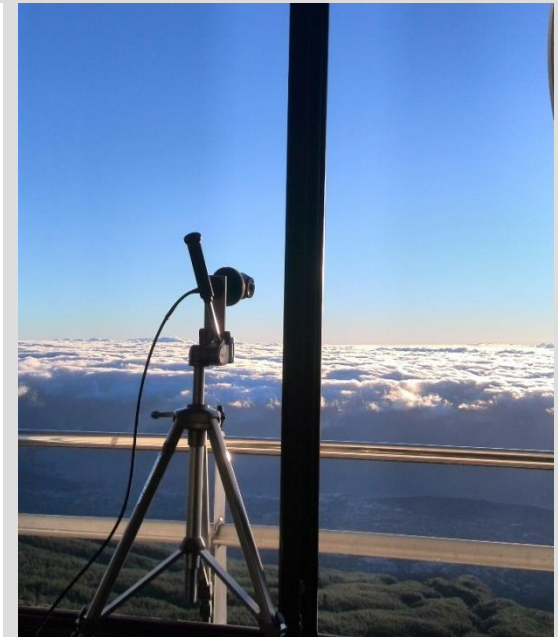
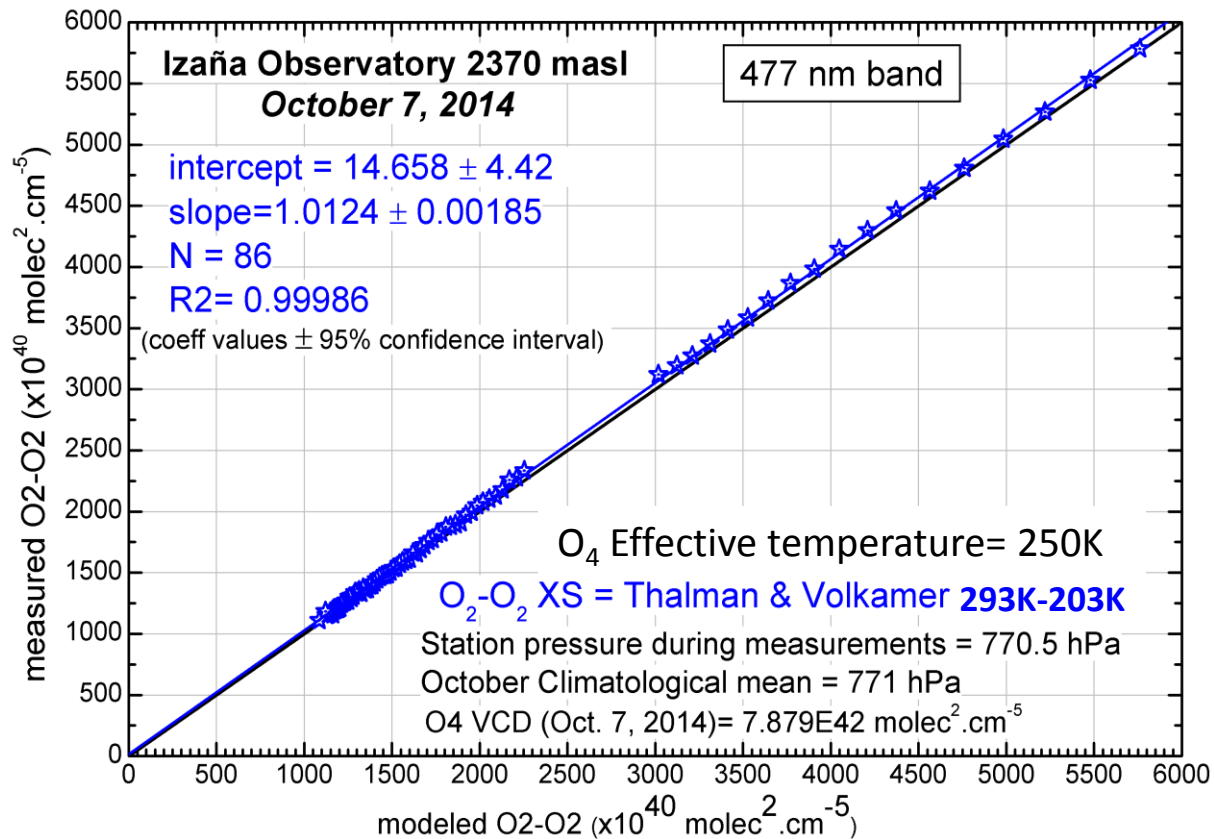
Data analyzed: 2011-2013: Over 15.000 data pairs passed the filtering

# O<sub>4</sub> XS accuracy: Direct Sun measurements & model in actual atmosphere (radiosounding of the day)

Meas. O<sub>4</sub> = O<sub>4</sub>(203K) + O<sub>4</sub>(293K)

Reference content from Langley plot

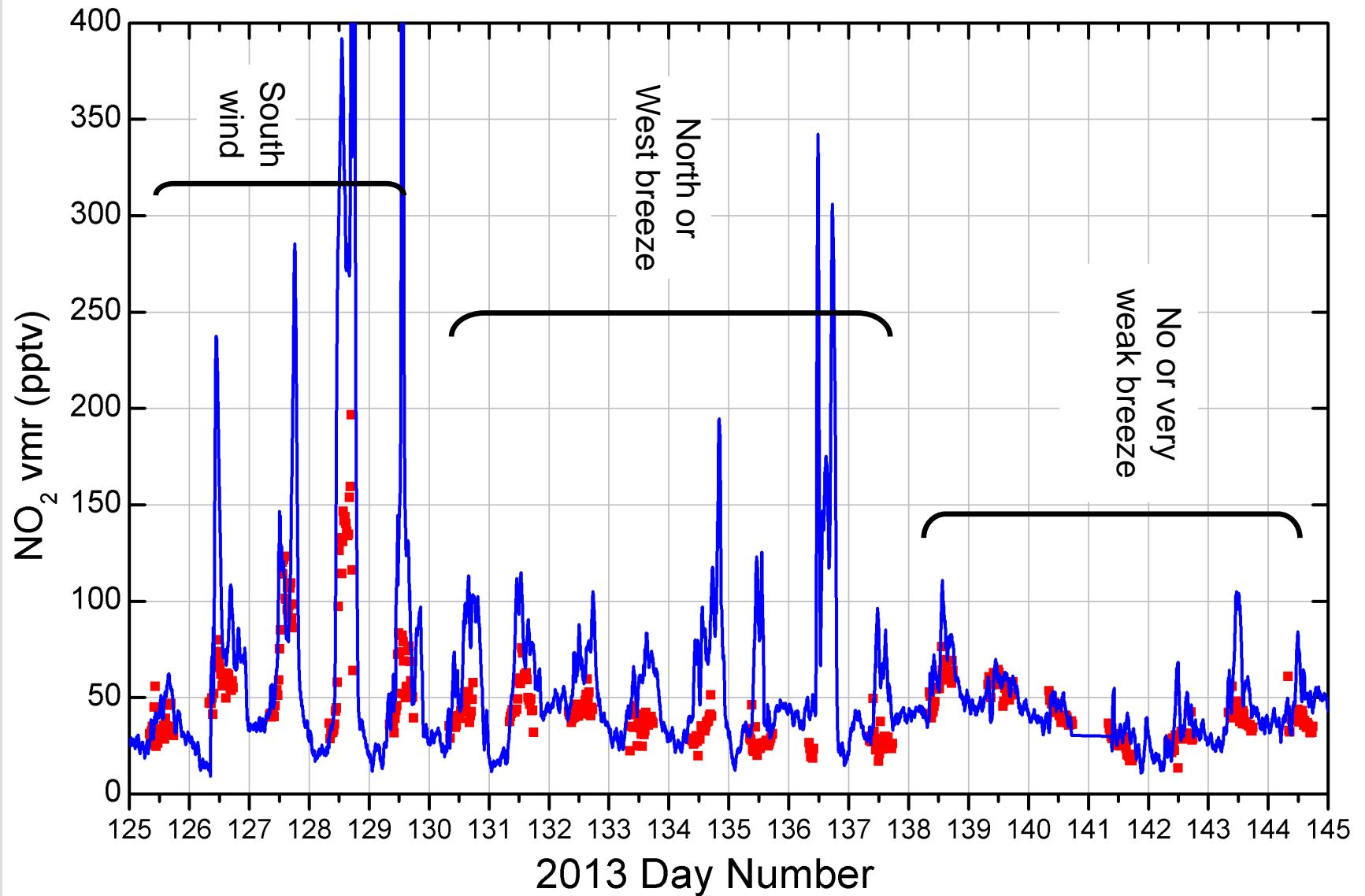
AOD (500 nm) = 0.0071



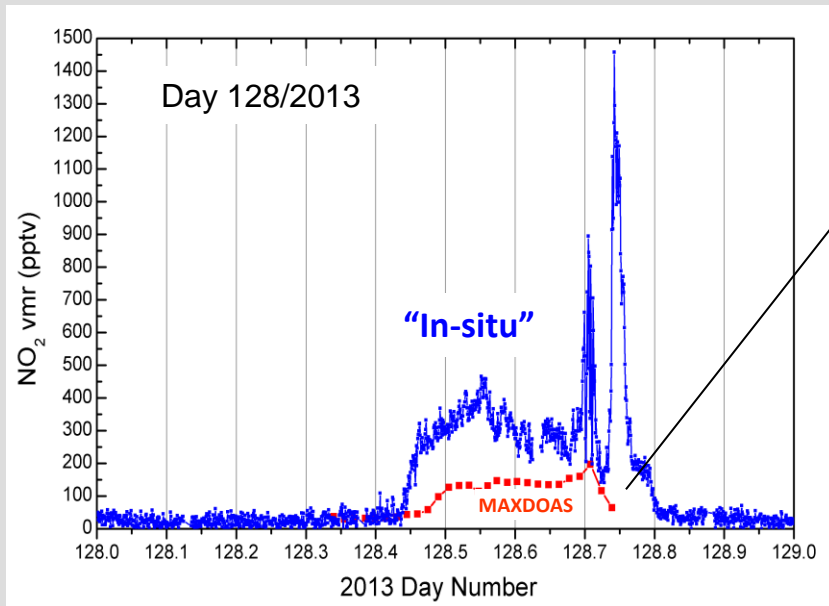
No problem in Cross-sections -> Path not corrected

# NO<sub>2</sub> vmr MAXDOAS & “In-situ”

— “In-situ” Chemilum. TECO 42C  
■ MAXDOAS

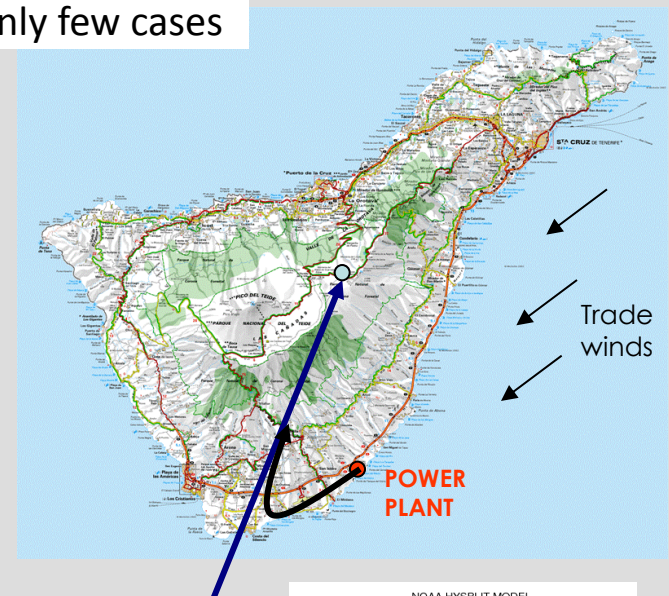






Very large MAXDOAS signal

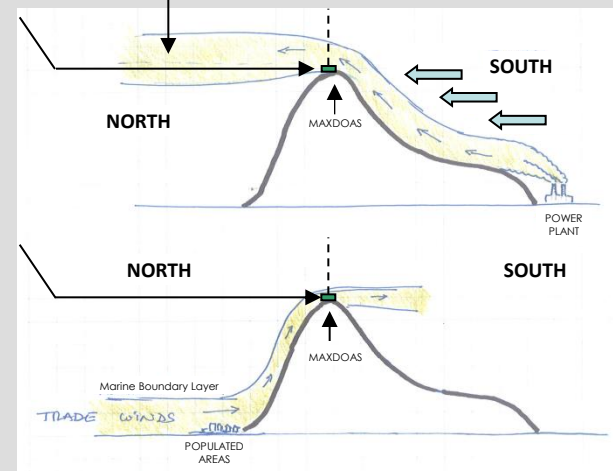
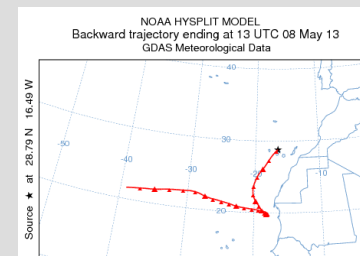
Only few cases



Very large concentration observed with South wind -> Pollution from Power Plant (25 km distance, emission/year =  $4.7 \times 10^6$  Kg of NO<sub>x</sub>)

Irreversible transport from surface to FT in a little more than 1 hour

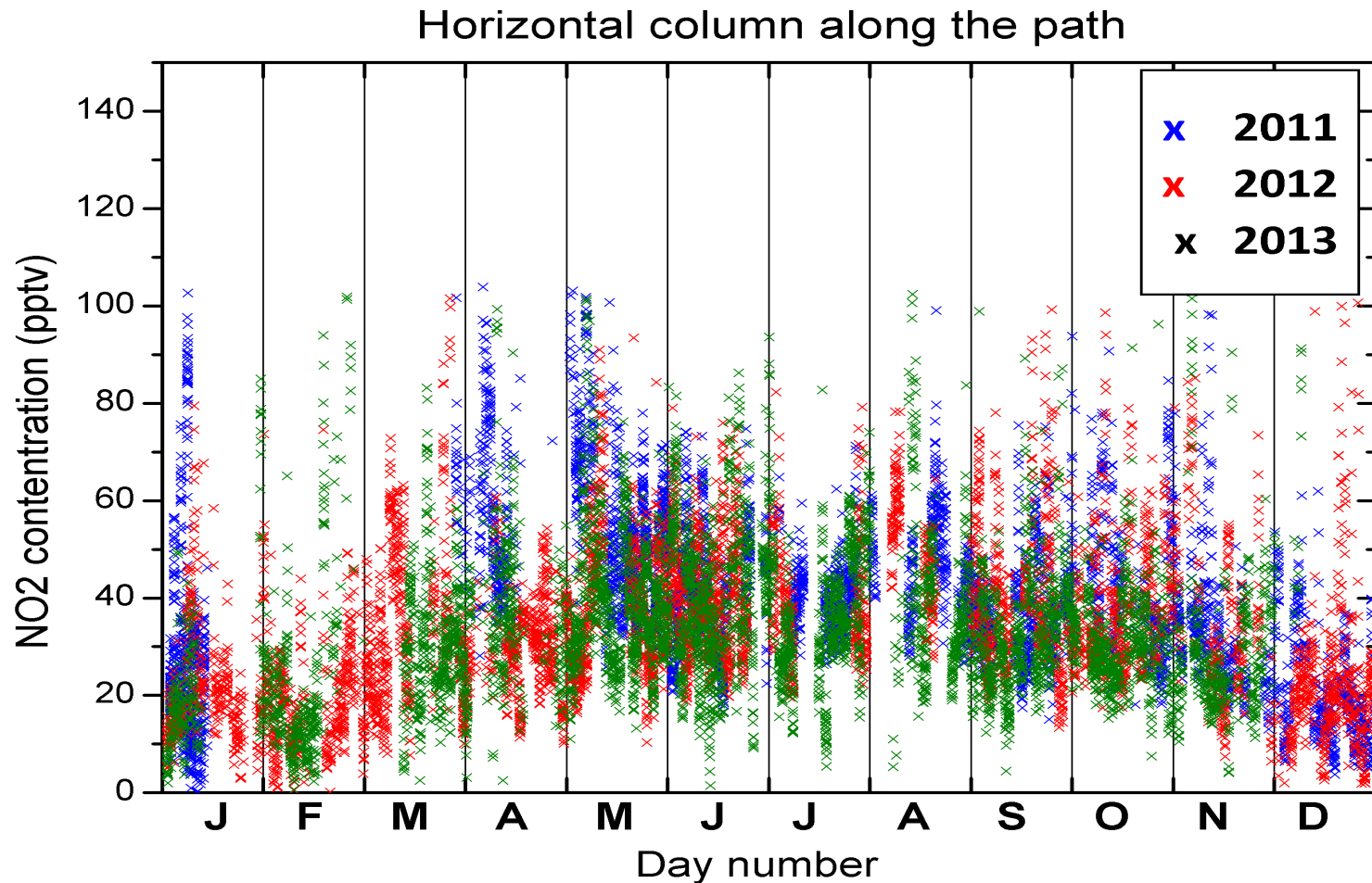
Instrument points North



Implications for other species such as IO, BrO



# Seasonal evolution of the individual data NO<sub>2</sub> vmr.



Little inter-annual variability

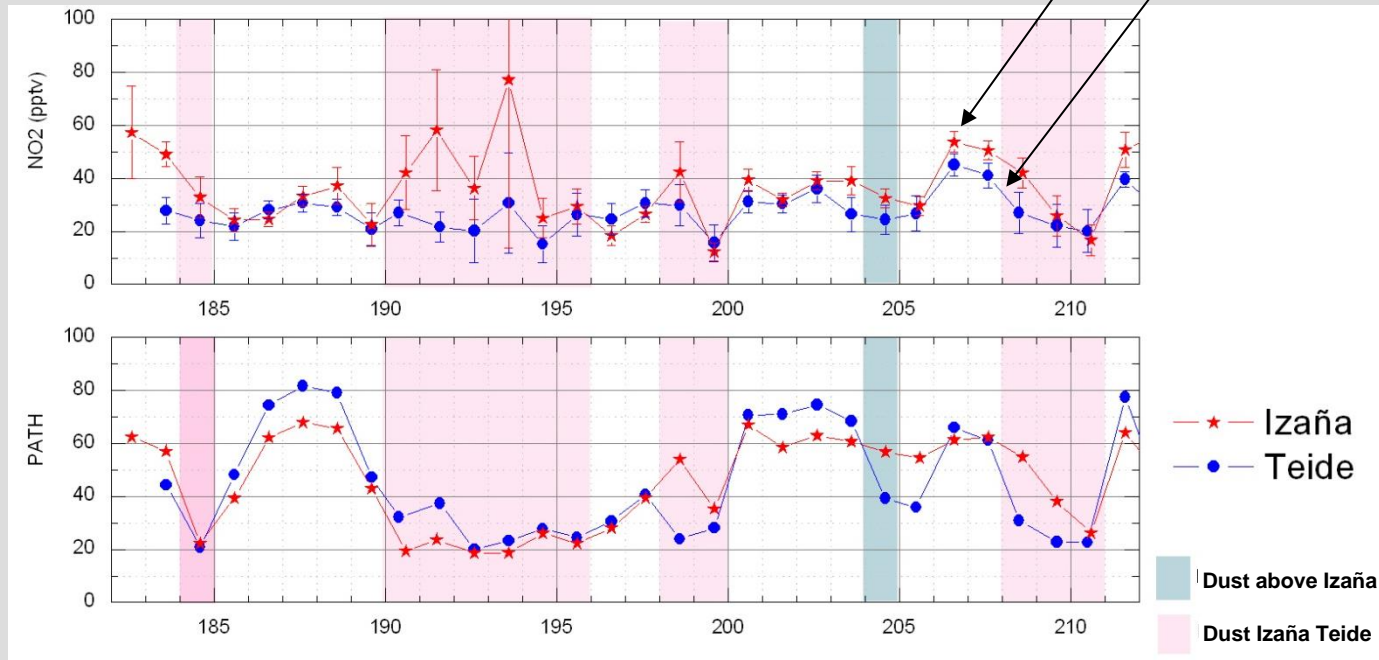
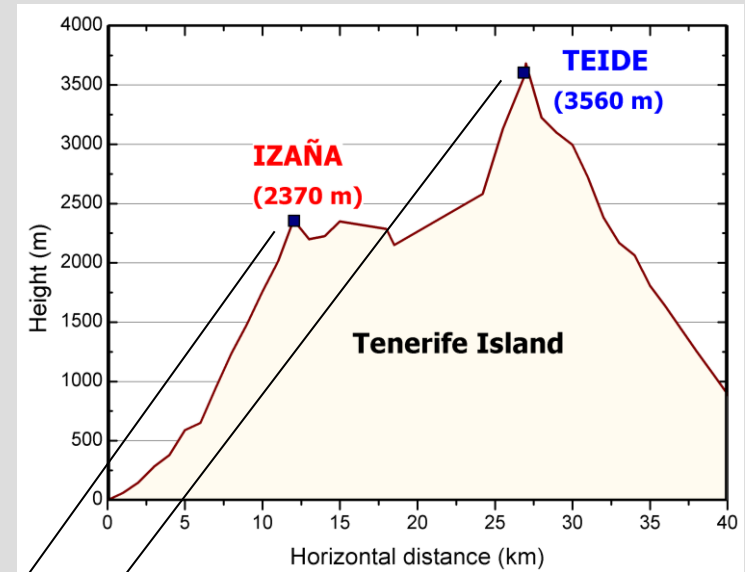
Summer NO<sub>2</sub> -> A minimum expected due to high radiation and declining ozone

Possible reasons for the summer maximum

- A) Supply from upper levels -> The subtropical subsidence is larger in summer (25 m/h) than in winter (7 m/h) (*E. Cuevas, private communication*)
- B) Contamination by anabatic winds -> If MBL concentration is high enough and the vertical extension of the layer is large, the contribution from below could account for the observed increase.
- C) Long range transport from North America. -> NO<sub>x</sub> has long enough lifetime to reach Canary islands.
- D) Natural change in the partition of the NO<sub>y</sub> chemistry

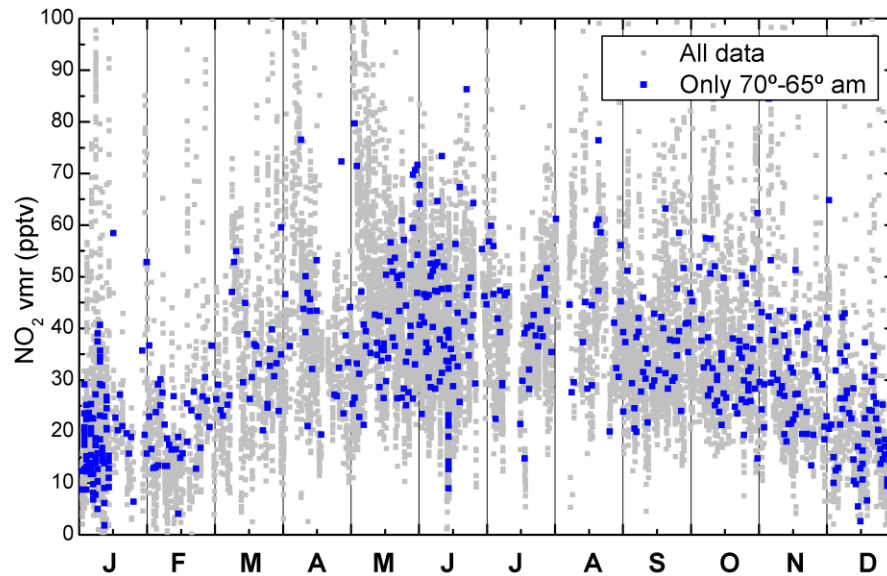
## A) Supply from upper levels

*During the AMISOC-2013 project, NO<sub>2</sub> vmr was measured at two levels in the Free Troposphere (2370m and 3550 m)*

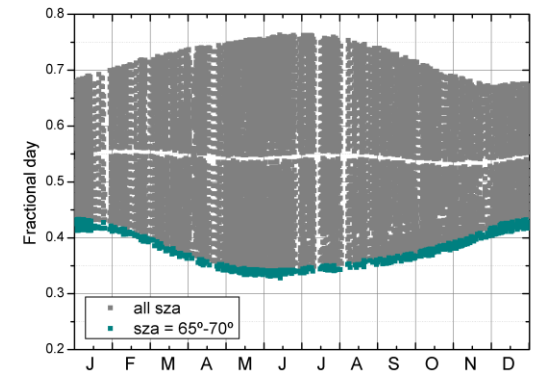


During the Non-dust periods NO<sub>2</sub> is lower at Teide (3550 masl) than at Izaña (2370 masl) -> *Subsidence cannot explain the seasonal wave*

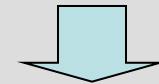
## B) Contamination by anabatic winds



*Contamination by anabatic winds is not the reason of the seasonality*

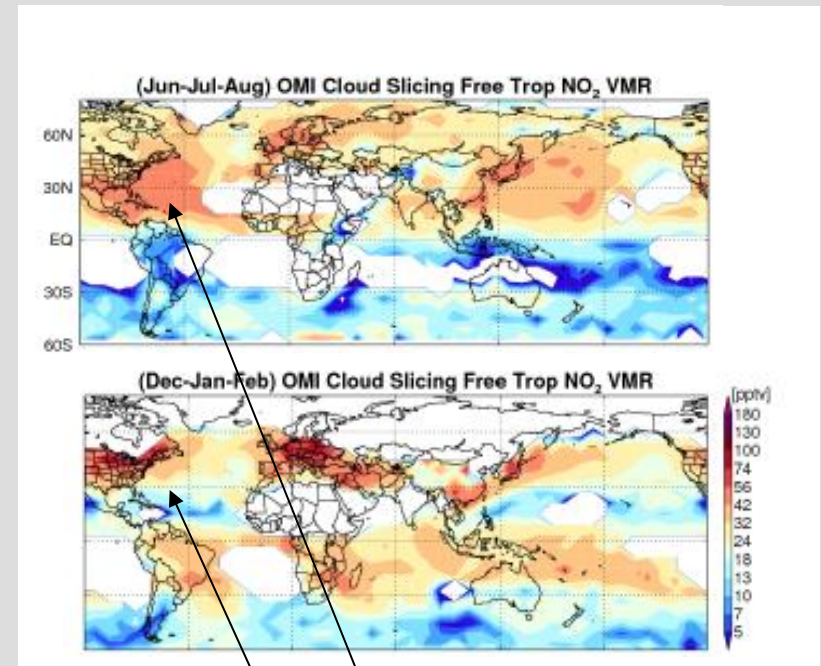
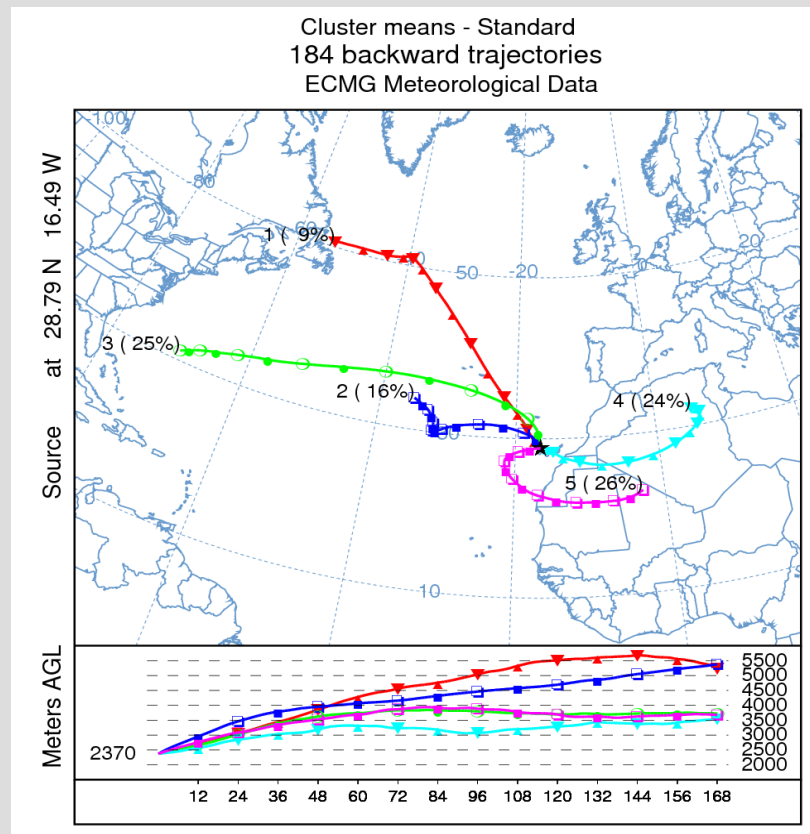


70°-65° -> 0.41 FD in winter  
0.32 FD in summer



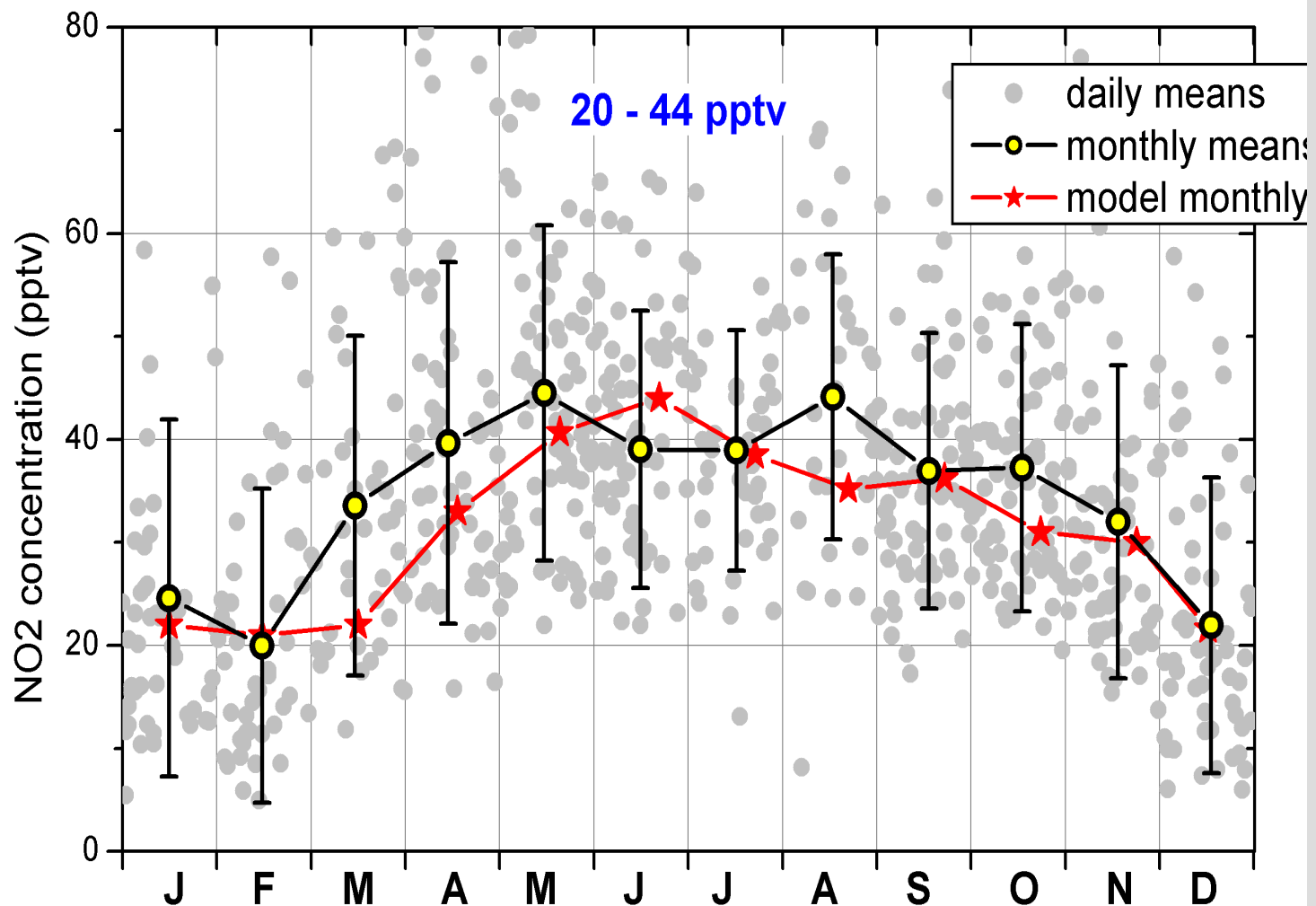
At this time of the day a maximum of only 20% is expected

C) Long range transport from North America. -> NO<sub>x</sub> has long enough lifetime to reach Canary islands. Zien et al. (2014) found no plumes in tropical regions but -> Choi et al., (2014) from GOME-2 cloud slicing technique show larger concentrations in Caribbean and N. America East coast than in East Atlantic.



**Larger vmr in summer  
(42-56 pptv)**

HYSPLIT clusters of backtrajectories arriving to Izaña Observatory for the summer months (JJA)



Monthly means of  $\text{NO}_2$  vmr observations at the level of Izaña Observatory (open circles and black lines) and the CAM-Chem model for the level (Red stars and lines). Individual solid grey circles are the 3-years diurnal mean.

Model result shows increase in  $\text{NO}_y$  during the summer months



# Summary

- + Mountain MAXDOAS under low aerosol loading ( $AO < 0.1$ ) is useful for  $NO_2$  vmr long-term observation at the level of the station
- + Two advantages over “in-situ” instrumentation:
  - a) Contamination by MBL- $NO_2$  (upslope breeze) is minimized.
  - b) Very low concentration can be measured (few pptv)
- + 3-years of  $NO_2$  measurements (over 15.000 cycles) have been used to establish the  $NO_2$  seasonal evolution over the station
- + A clear seasonality in  $NO_2$  vmr has been found, with the maximum in summer months. Background monthly means range between 20 and 44 pptv. Cam-CHEM model reproduce the observations
- + Only occasionally, large  $NO_2$  from coastal industry are recorded. During these events, upward flow transports MBL airmasses to the FT. This is a mechanism for fast irreversible injections of pollution and surface/ocean minor species to the FT.
- + Few possibilities have been explored: Vertical movements (subtropical subsidence and upslope breeze) are excluded. Long-range transport from Western Atlantic most feasible

**THANK YOU**

