Urban NO_x Chemistry

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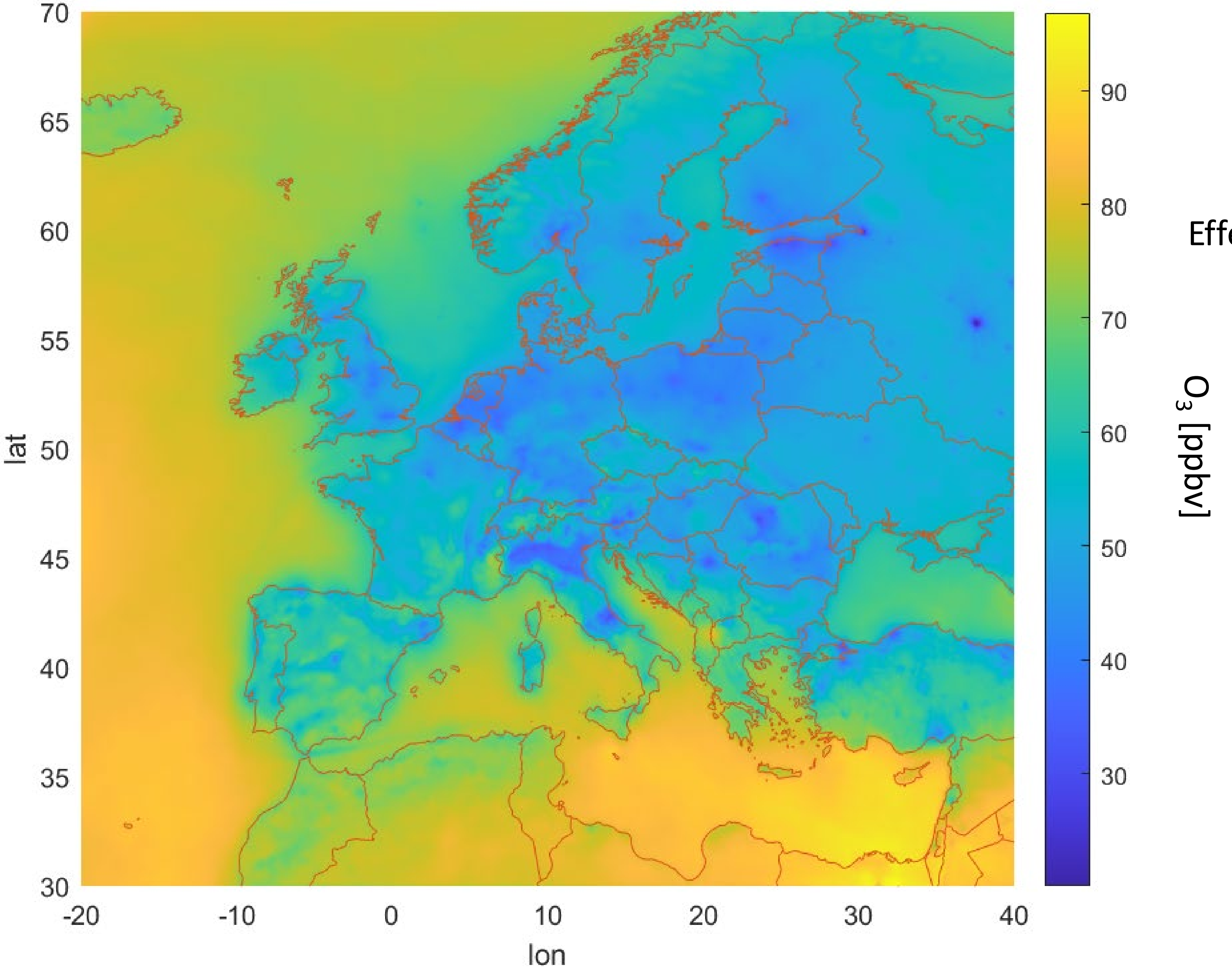
ESA/EUMETSAT/ECMWF, 2023

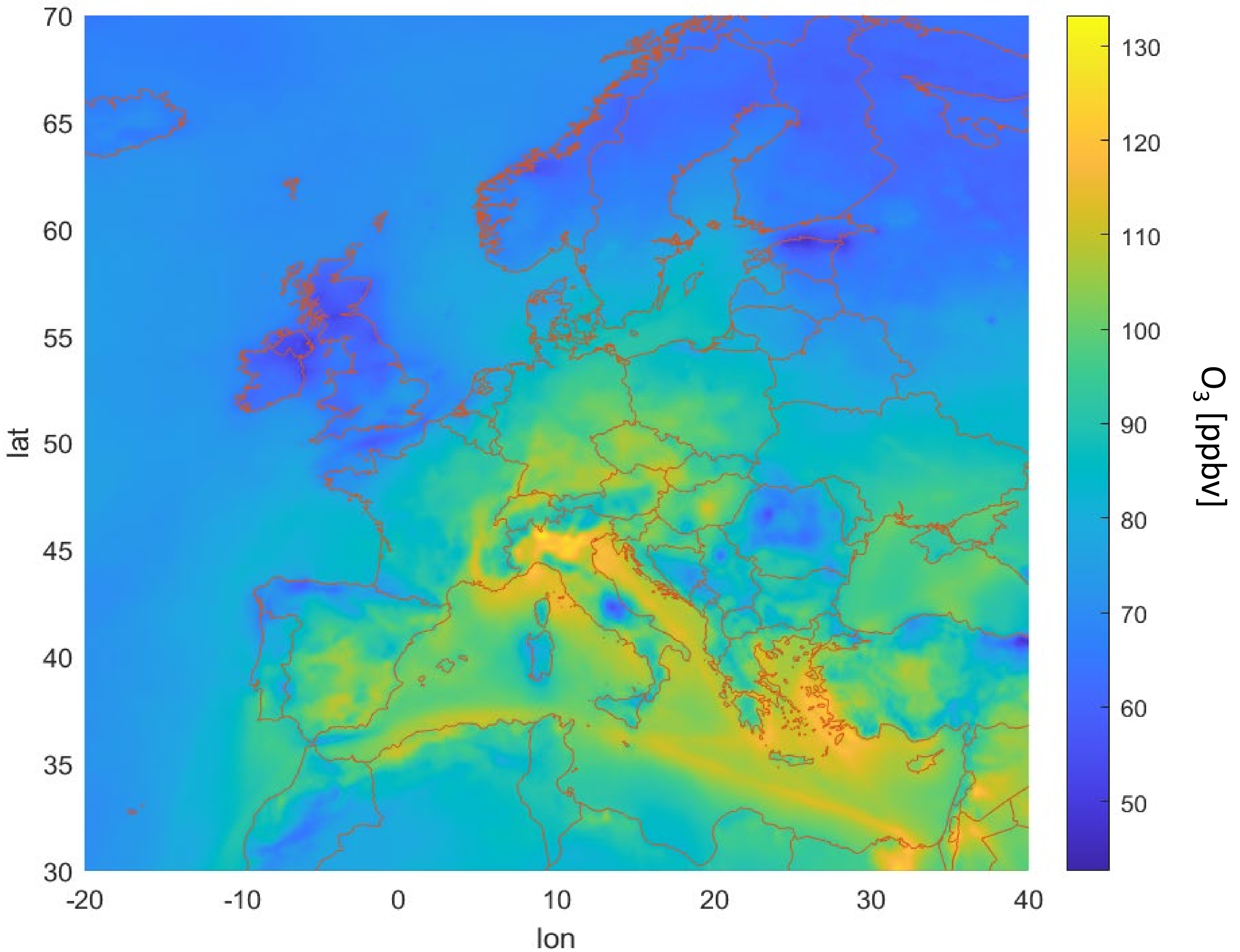
Ozone in the EU - CAMS

Ozone ppbv – all year



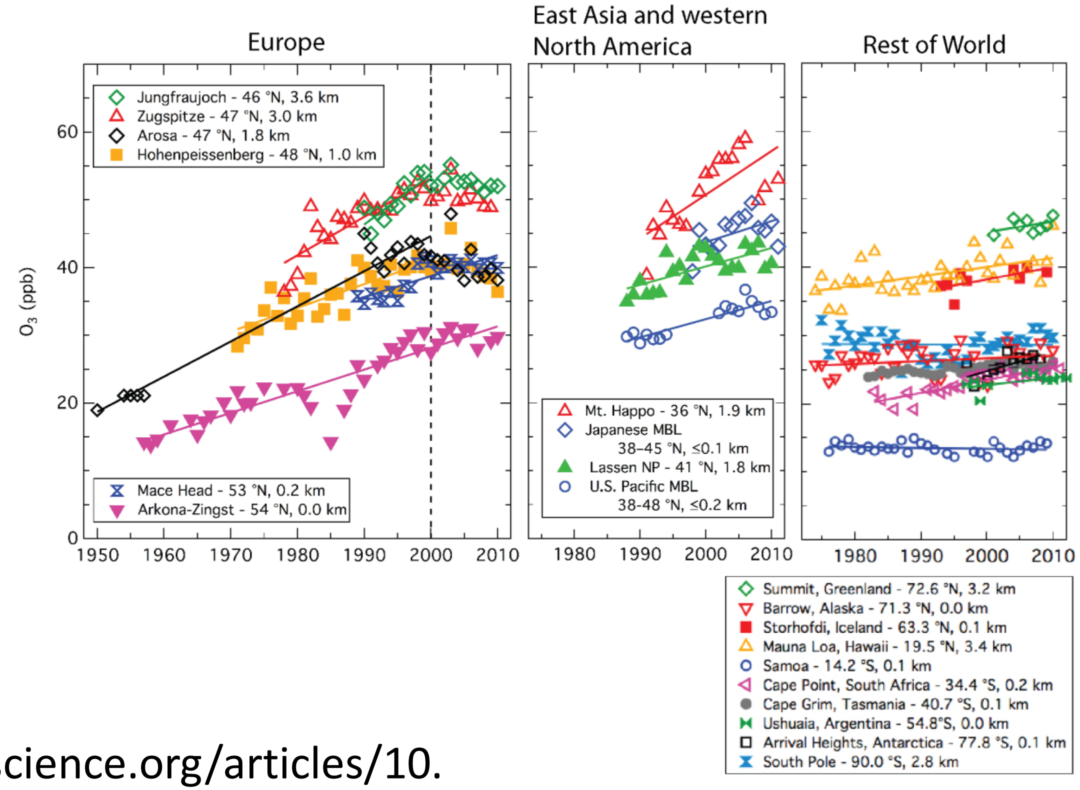
Effect of excessive NO_x in Europe

Ozone ppbv – JJA



Summer Time Ozone

Historical Trends for trop. O_3



https://www.elementascience.org/articles/10.12952/journal.elementa.000029/

NO_x all year

European NO_2 AQ penalty due to climate policy dating back to Kyoto

The Dieselengine

Climate benefit

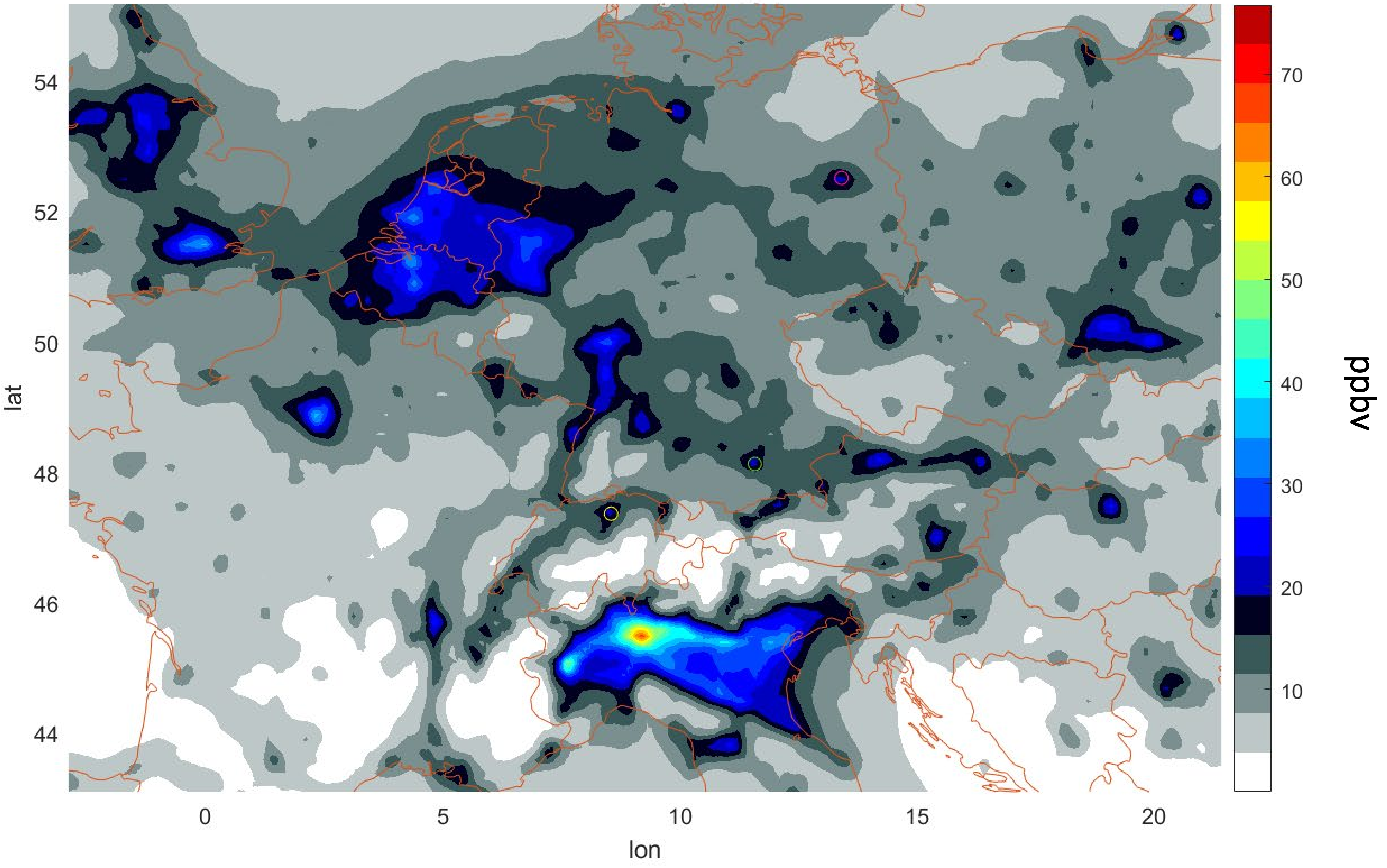
Less CO_2

More NO_x

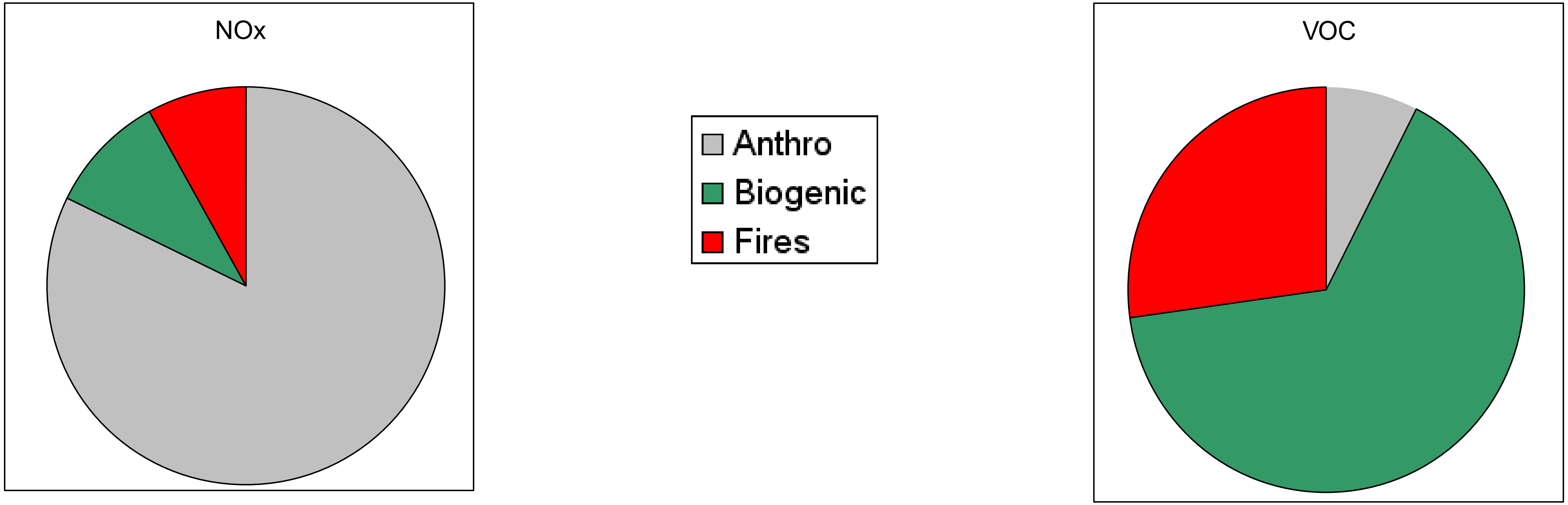
AQ penalty

Excessive NO_2

NO_2 is one of the few regulated pollutants that is out of compliance across most EU cities



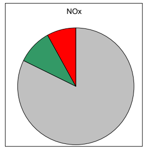
Global Emission Estimates: Trace Gases



Total Emission
26-142 Tg/y

Total Emission
600-1500 Tg/y

EDGARFT2000
Yan et al, GBC, 2005
Guenther et al., 1995; 2006; pers. comm.
GFEDv2
Andreae and Merlet, GBC, 2001
Yokelson et la., ACP, 2008



OXIDATION STATES OF NITROGEN

N has 5 electrons in valence shell ⇨9 oxidation states from –3 to +5

Increasing oxidation number (oxidation reactions) →

-3	0	+1	+2	+3	+4	+5
NH_3 **Ammonia** NH_4^+ **Ammonium** $R_1N(R_2)R_3$ **Organic N**	N_2	N_2O **Nitrous oxide**	NO **Nitric oxide** *radical*	$HONO$ **Nitrous acid** NO_2^- **Nitrite**	NO_2 **Nitrogen dioxide** *radical*	HNO_3 **Nitric acid** NO_3^- **Nitrate**

← Decreasing oxidation number (reduction reactions)

Tropospheric Reactive Nitrogen

- NO_x (**NO** + NO_2)
- N_2O_5
- HNO_3 ($HONO_2$)
- HONO
- $HOONO_2$
- PANs ($RC(O)OONO_2$)
- Alkyl Nitrates ($RONO_2$)
- XONO2 (X = halogen)

$NO_z = NO_y - NO_x$
NO_y reservoir species

NO_y, or odd nitrogen

- NO_3 radical
- NO_3^- nitrate aerosol

- NH_3, Amines

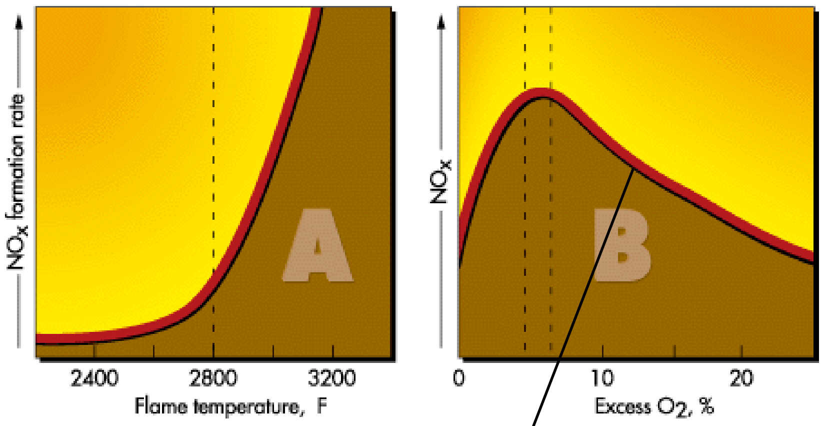
Combustion source for NOx

- No nitrogen in fuel

$N_2 + O = NO + N \quad +314\ kJ/mol$

$N + O2 = NO + O$

$N + OH = NO + H$ (not important)



Alentec Inc.

- Nitrogen in Fuel

$HCN_{(g)}$, $RCN_{(g)}$, NH_3, etc + OH/O →→ NOx

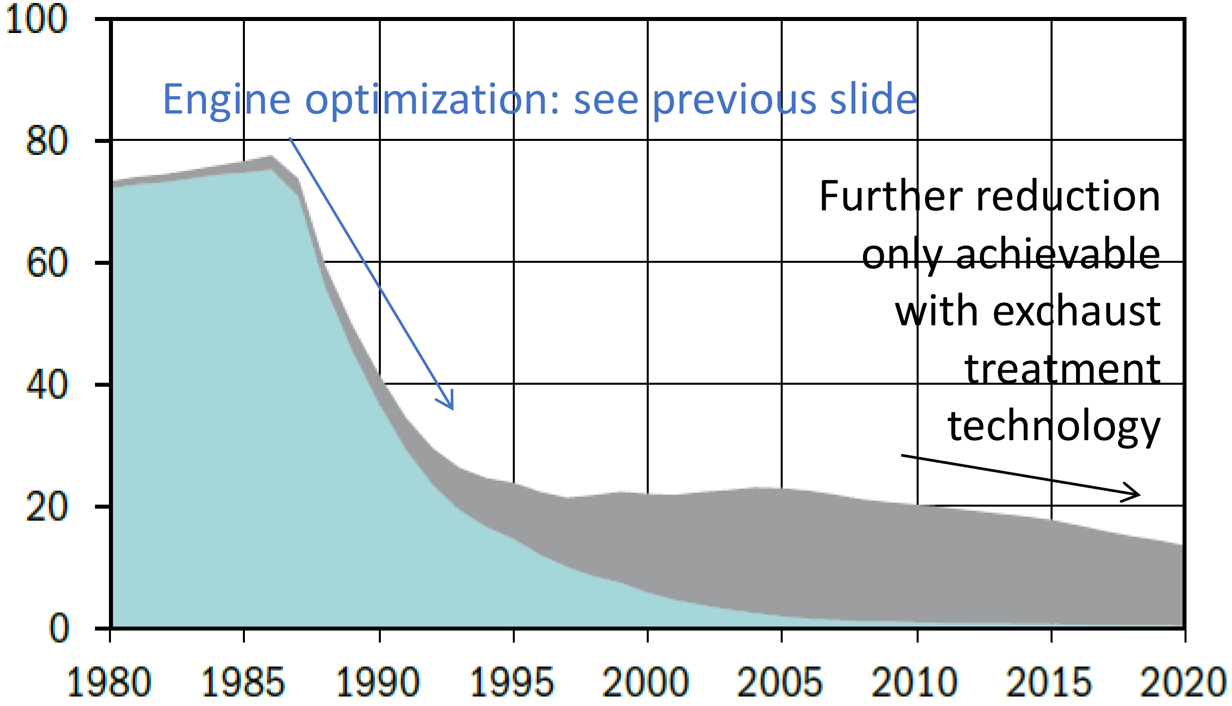
This is why most modern car engines have an exhaust gas recirculation (EGR) system („Abgasrueckfuehrung“)

Note: The easiest tuning method in cars: close the „Abgasrueckfuehrungsventil“ – will give you more PS

NO_x

STICKSTOFFOXID (NOX) – EMISSIONEN DES PKW - BESTANDES

(in 1000 Tonnen = 10^3t)



	1980 10^3 t	1990 10^3 t	2000 10^3 t	2010 10^3 t	2020 10^3 t
PKW-Diesel	1,1	4,6	16,2	19,3	13,1
PKW-Benzin	72,1	36,8	5,8	0,9	0,3
Summe	**73,2**	**41,5**	**21,9**	**20,2**	**13,4**

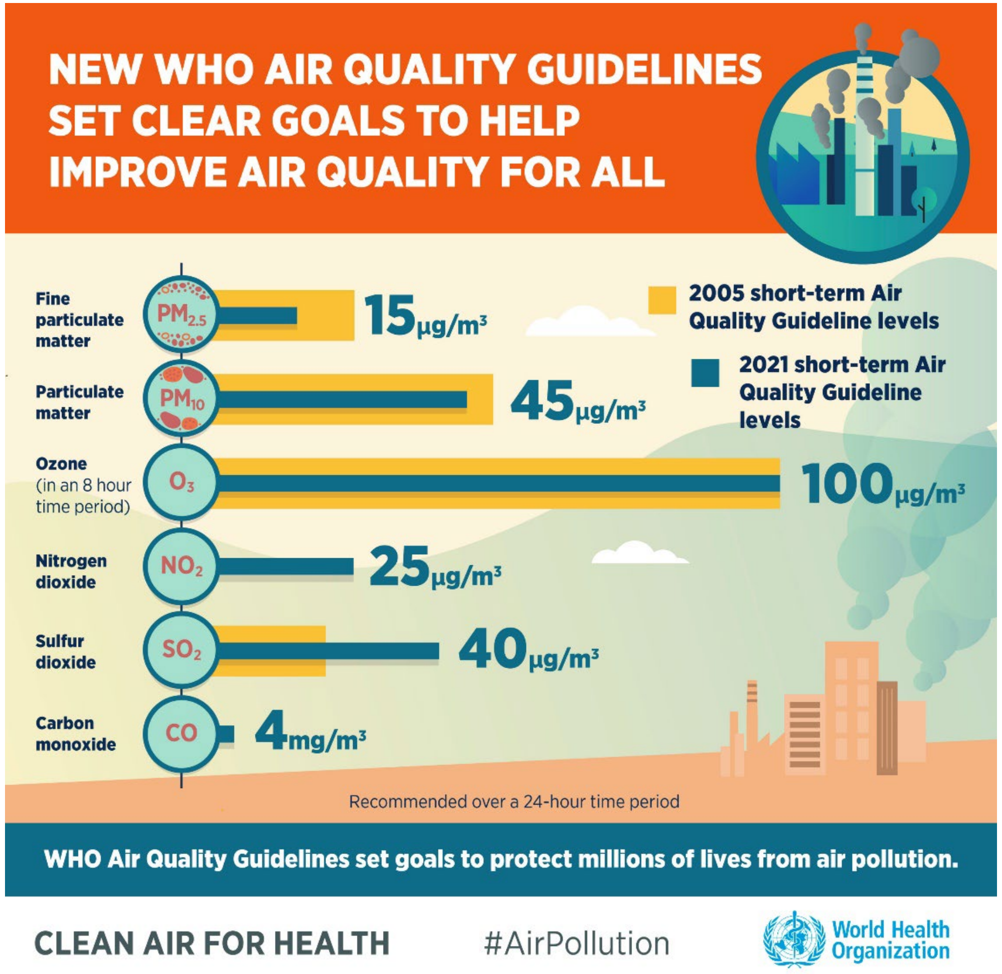
Blue: gasoline
Gray: Diesel

Austria wide: about 50% from mobile sources

Note that locally these numbers could be quite different!

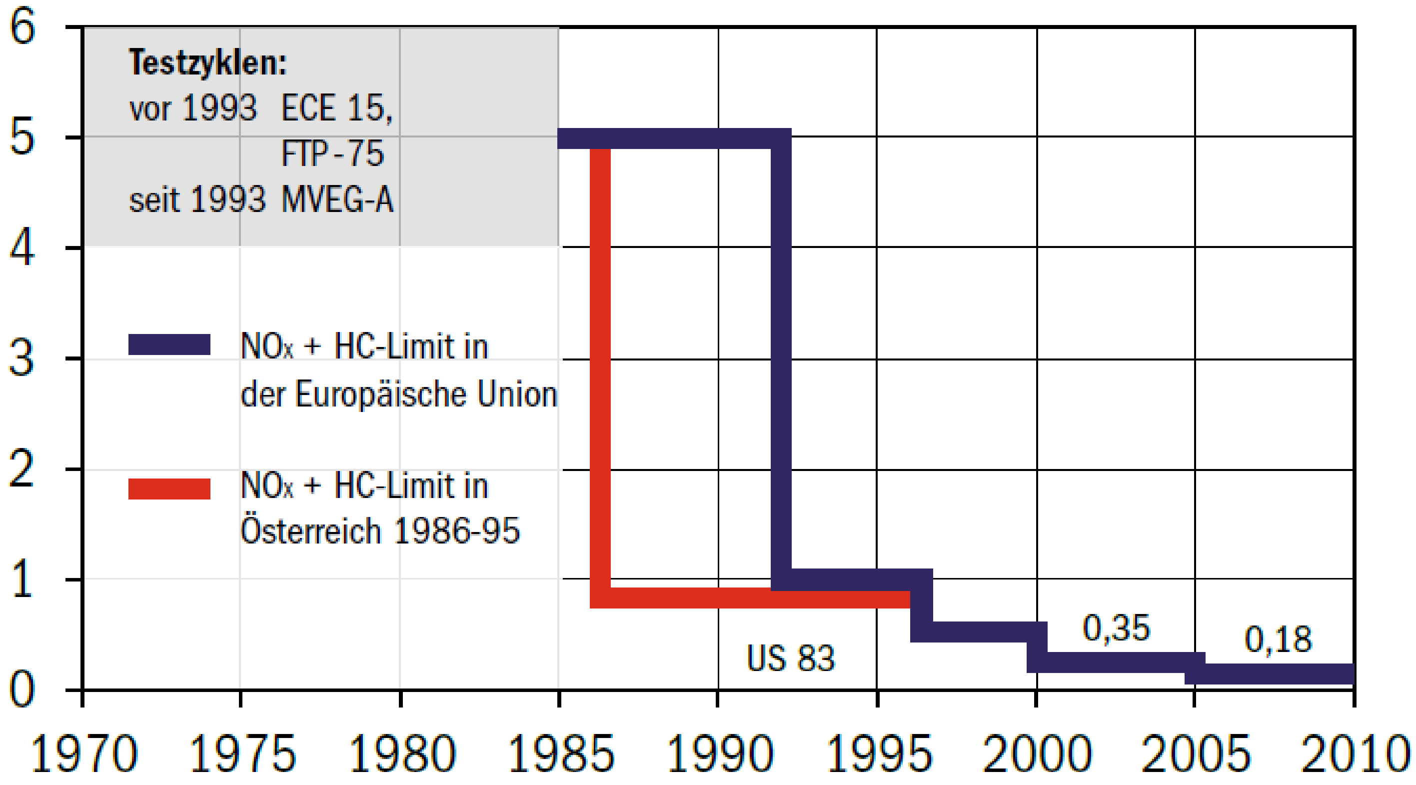
Source, ÖAMTC, 2014, UBA, 2013

Recent update:WHO recommends lower AQ standards



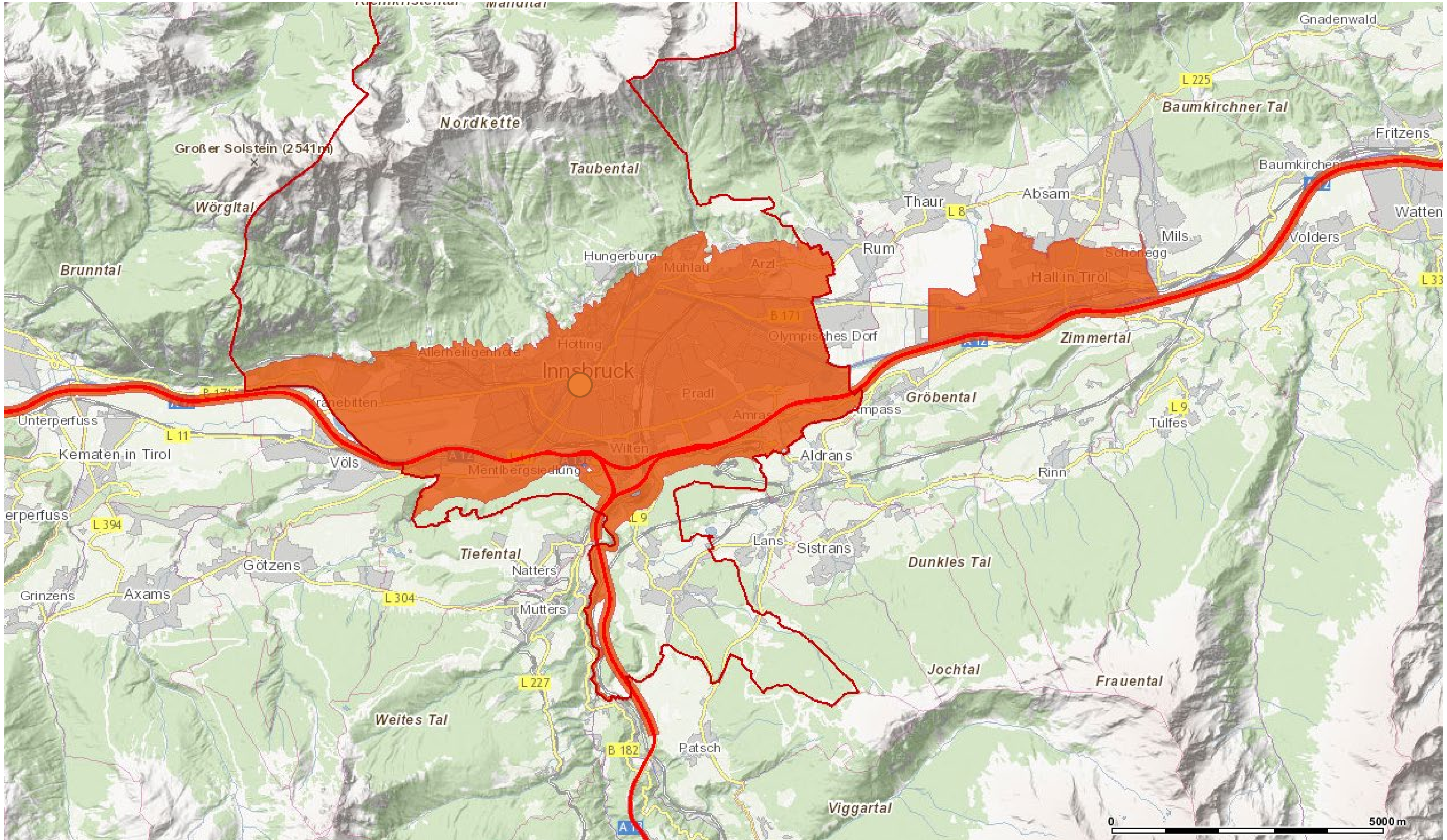
Historical Note on AQ management in Austria

- Austria was among the first European countries to adopt rigorous US emission vehicle standards in 1987

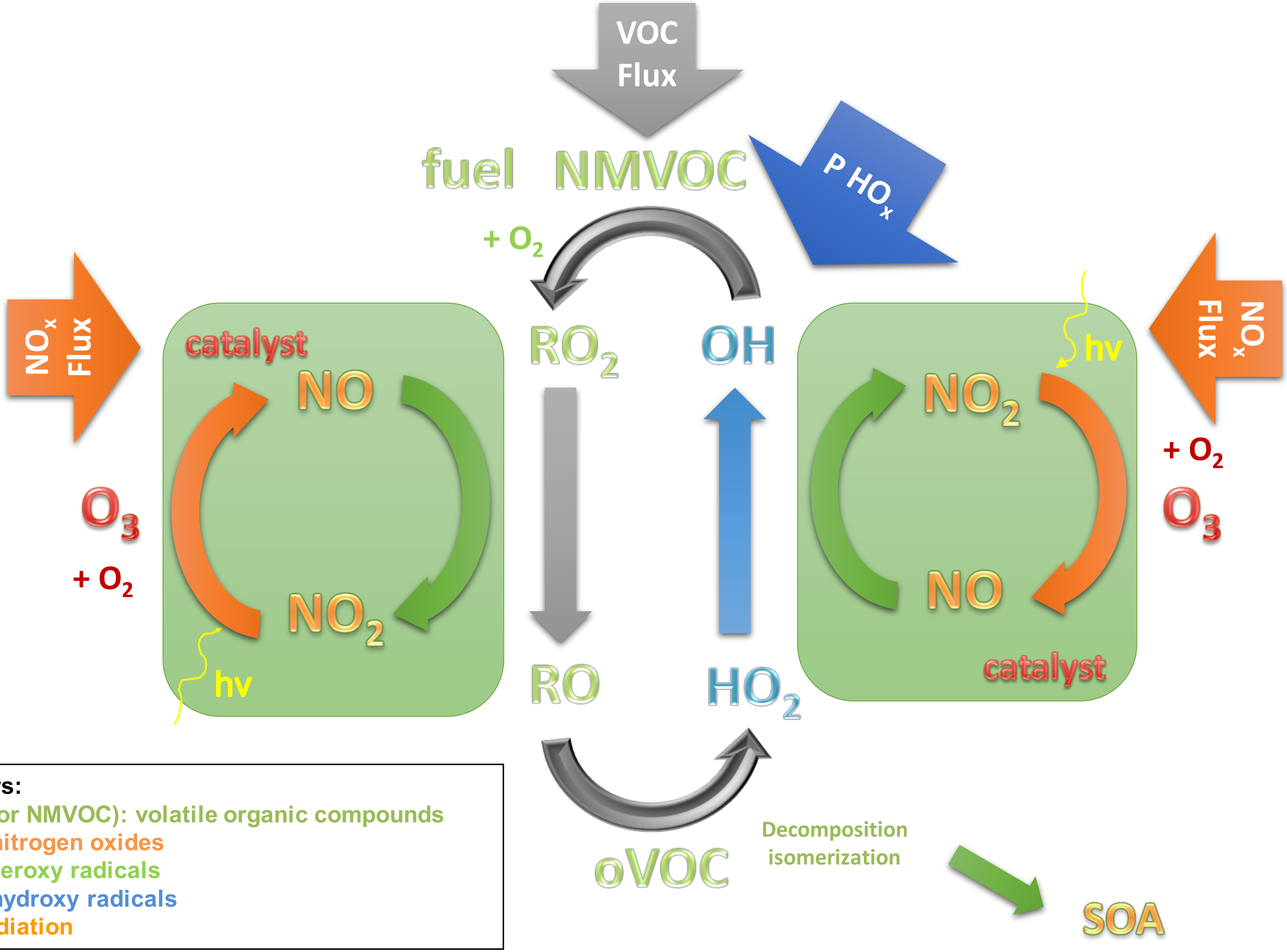


Source, ÖAMTC, 2014

Non-attainment area for NO_2



The photochemical engine



Players:

VOC (or NMVOC): volatile organic compounds

NO_x: nitrogen oxides

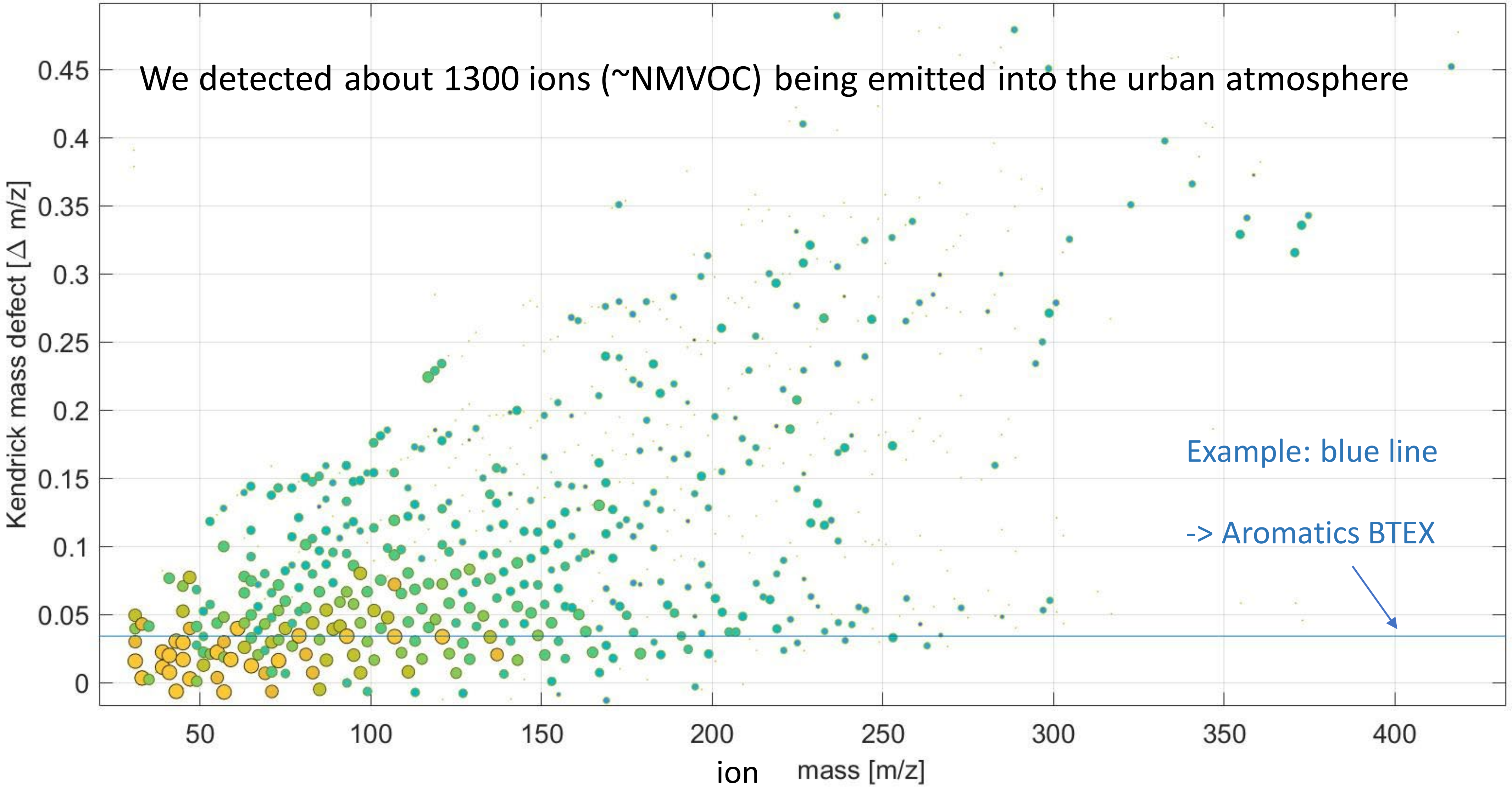
RO_x: peroxy radicals

HO_x: hydroxy radicals

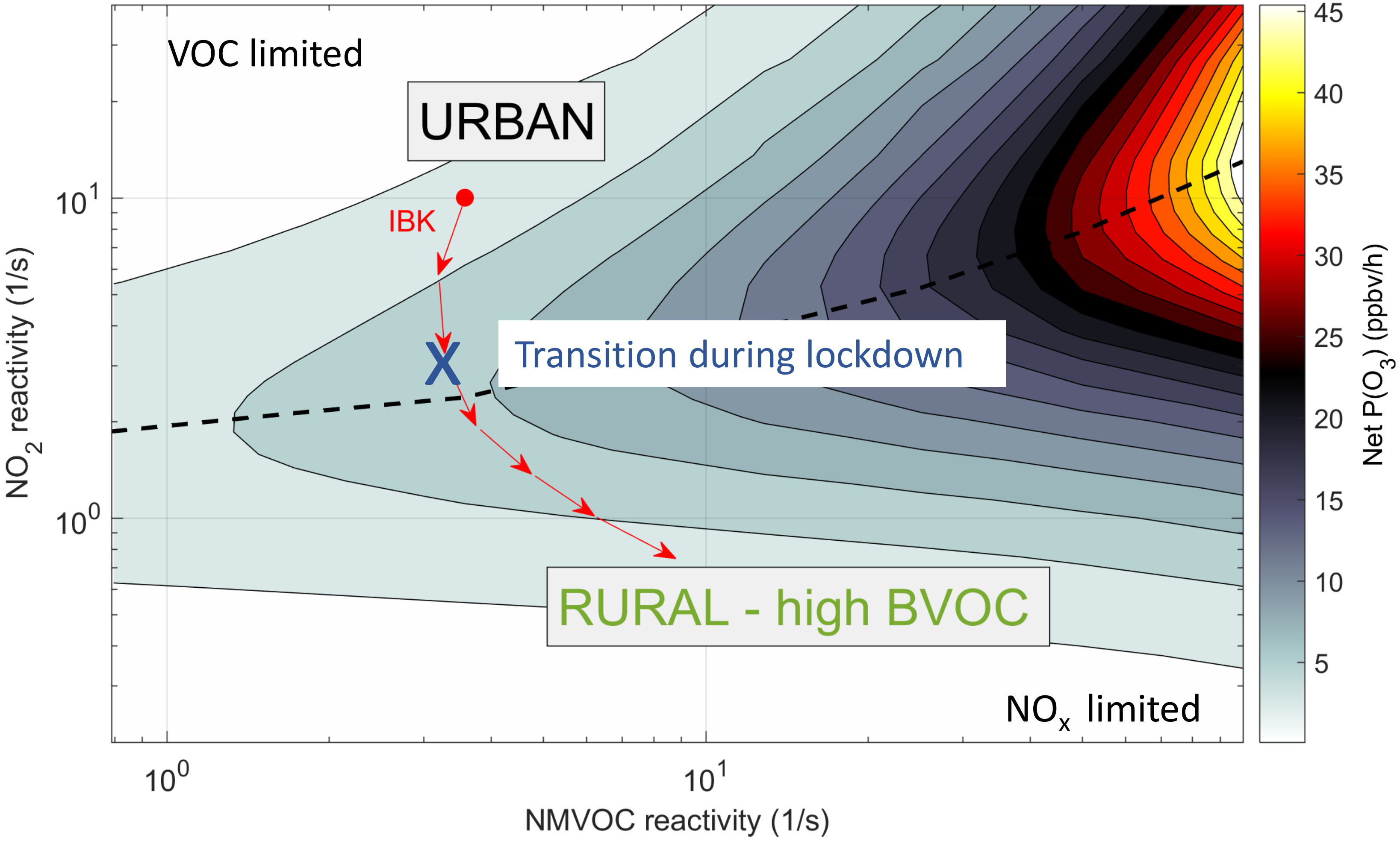
hv: radiation

2021 Spring Campaign

Total median NMVOC flux ~ 8-12 nmol/m^2/s
Total median CH_4 flux: 10 nmol/m^2/s
Total median NO_x flux: 7-8 nmol/m^2/s



Net Ozone Production in Innsbruck

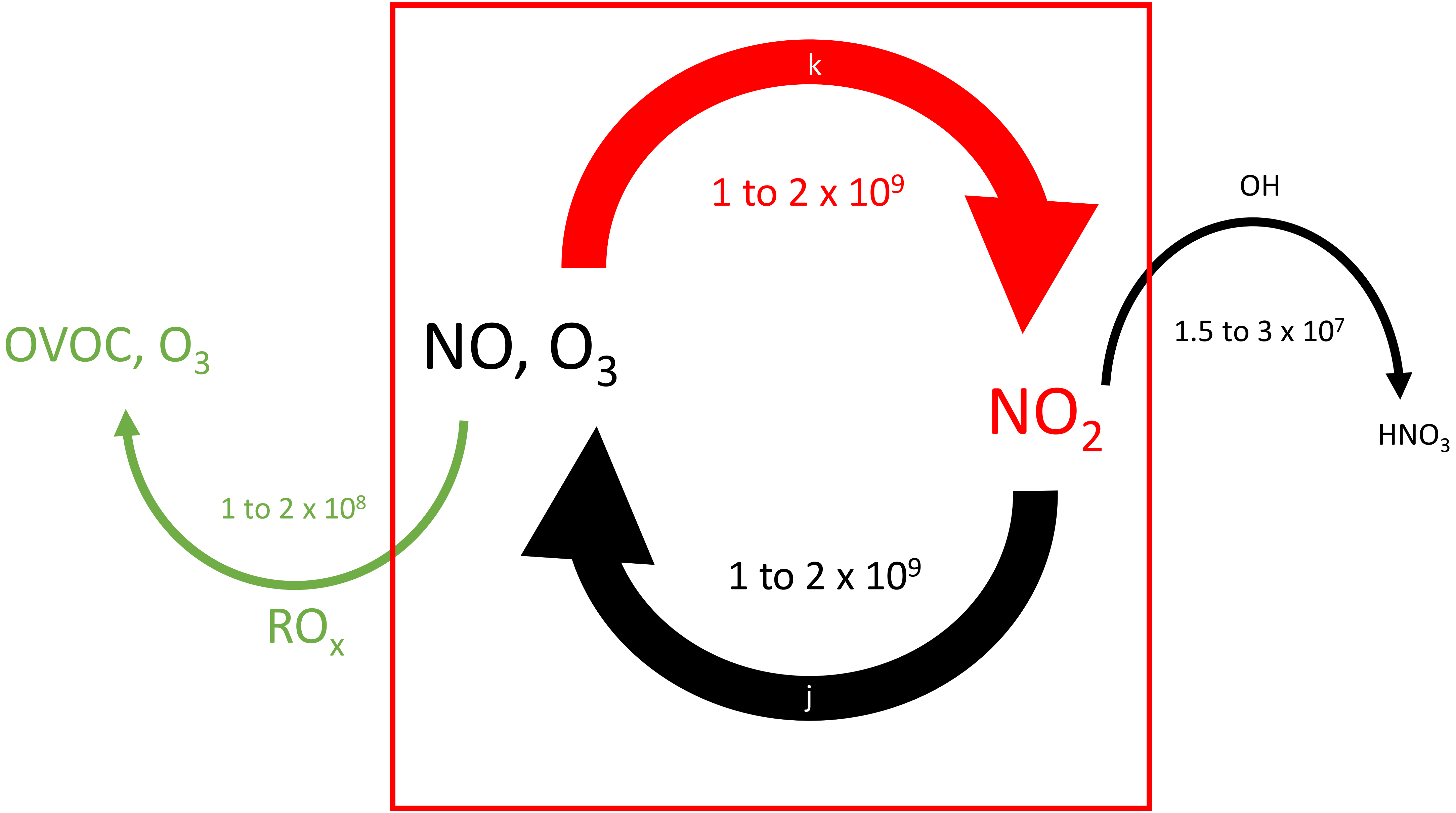


O_x mixing ratio no change

O_3 mixing ratio +24%

$O_x = O_3 + NO_2$

IAO – Urban conditions: Rates in [molecules/cm³/s]



The Photostationary State (PSS) of $NO\text{-}NO_2\text{-}O_3$

$$NO_2 + h\nu \rightarrow NO + O \qquad \phi k_a(NO_2) \qquad \text{(V-1)}$$
$$O + O_2 + M \rightarrow O_3 + M \qquad \text{(V-3)}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad k_1(NO)(O_3) \qquad \text{(VI-1)}$$

In the absence of other competing reactions, and in the absence of rapid changes in light intensity or reactant concentrations, the rates of these two processes must approach equality. Setting them equal gives

$$\frac{(NO)(O_3)}{(NO_2)} = \frac{\phi k_a}{k_1} \qquad \text{(VI-3)}$$

Leighton, P., Photochemistry of Air Pollution, 1961

“O_3 and NO_x live in photostationary state”

„Under daylight in polluted conditions the photolysis of NO_2 and the reaction of $NO+O_3$ occur at higher rates than most other reactions, and the ratio approaches 1.“

τ_{chem} = 100-200 s at IAO

LA, Urban Atmosphere, 1973

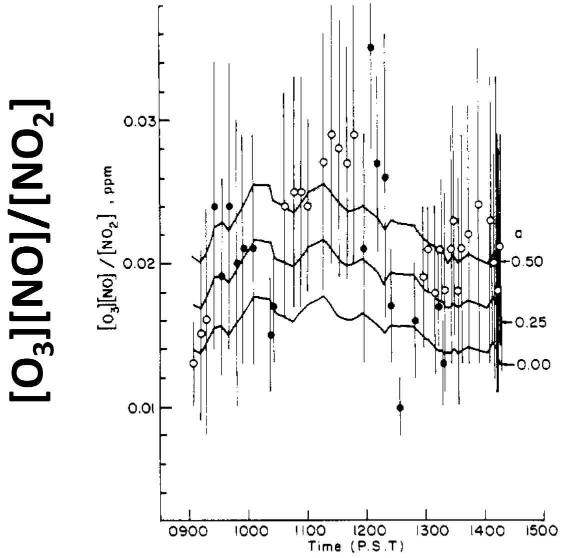
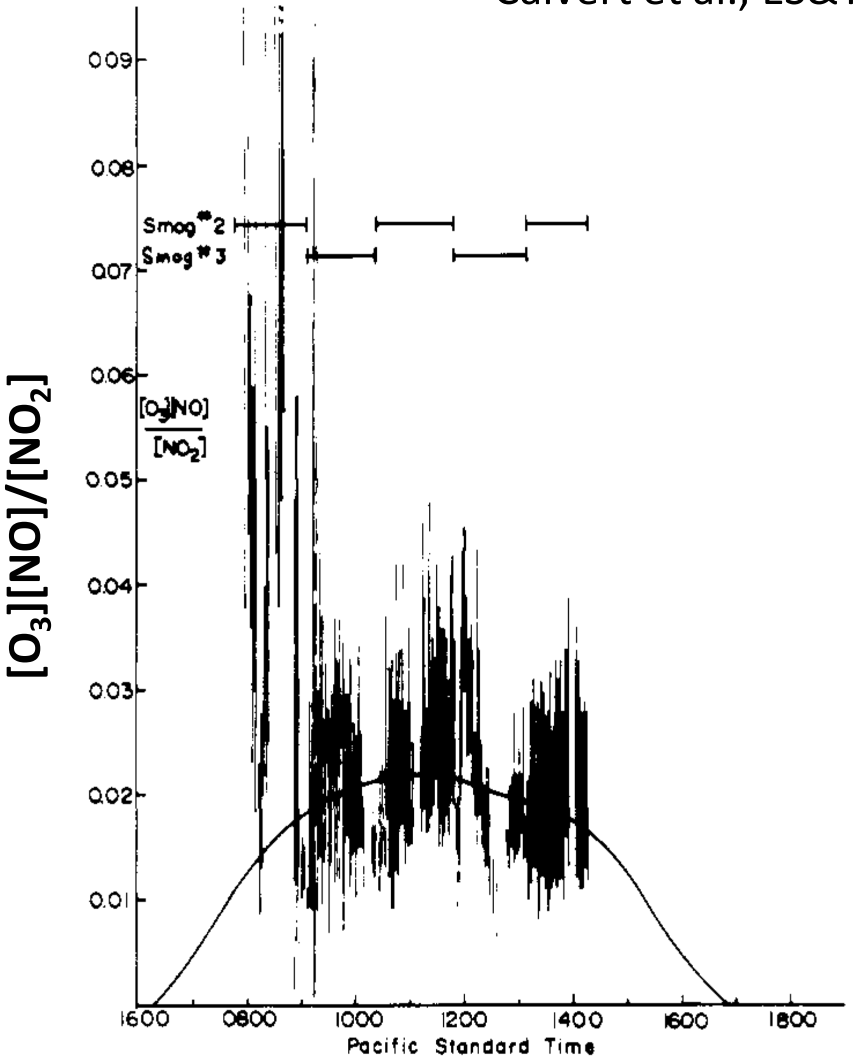


Figure 15. Plot of function $[O_3][NO]/[NO_2]$ as estimated from experimental data from operation #33
Open circles and darkened circles are data from Smog #2 and Smog #3, respectively; lengths of vertical lines indicate range of standard deviation of average over the four legs of the given constant elevation run; the solid curves give the theoretically expected values of k_1'/k_3 for three different assumed values of the surface albedo, a = 0, 0.25, and 0.50. Theoretical model in this case includes attenuation of ultraviolet within the polluted layer

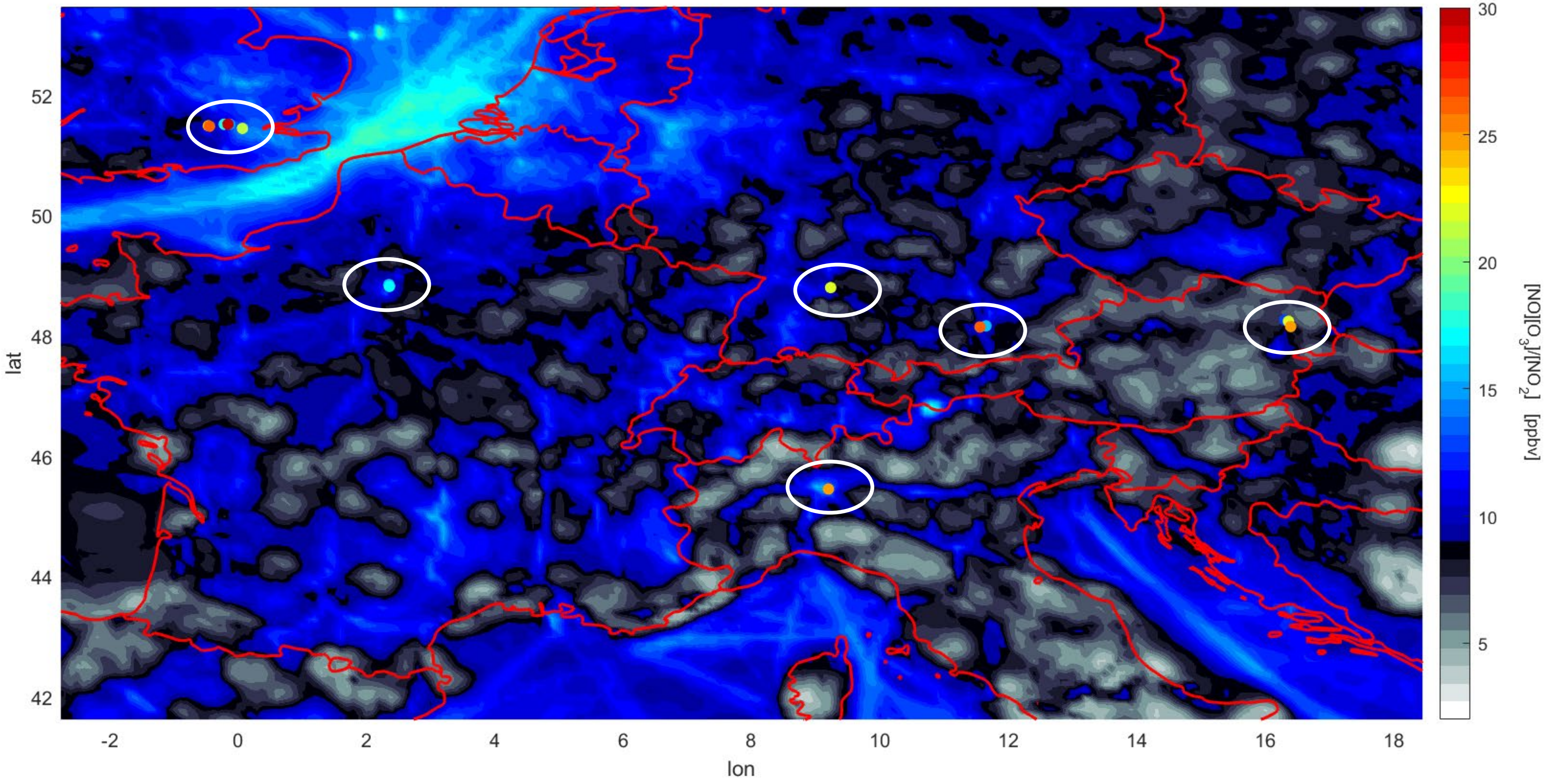
Calvert et al., ES&T, 1976



Early observations of the LRatio in LA

CAMS vs EEA (midday JJA)

Obs/Model = 1.85 ± 0.43 ~ 1/PSS
Models overestimate PSS

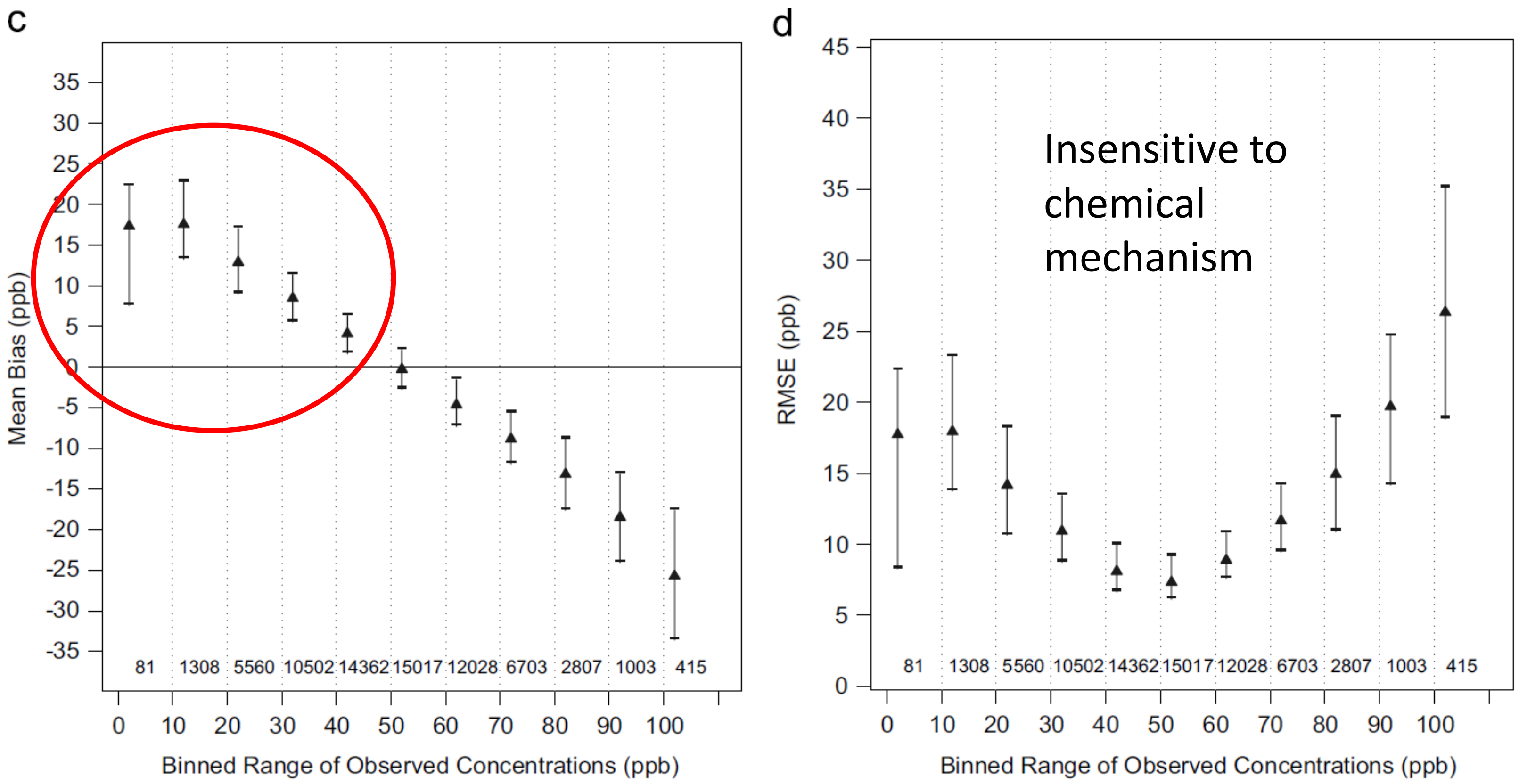


CMAQ – US - JJA

Models overpredict mixing and PBL in SBL ?

But 8h O3 average

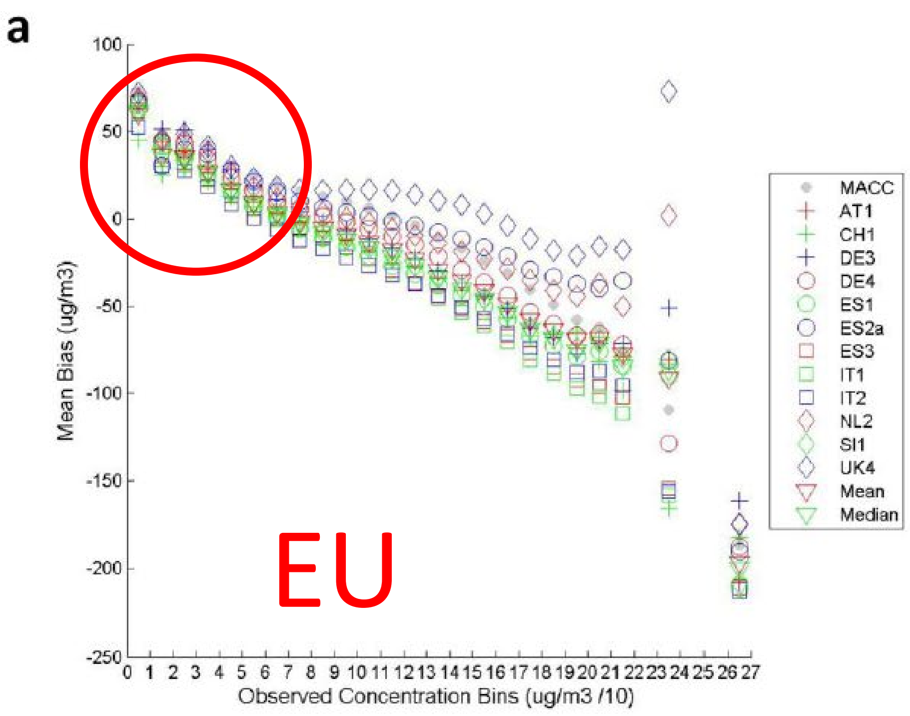
-> biased towards daytime convective conditions

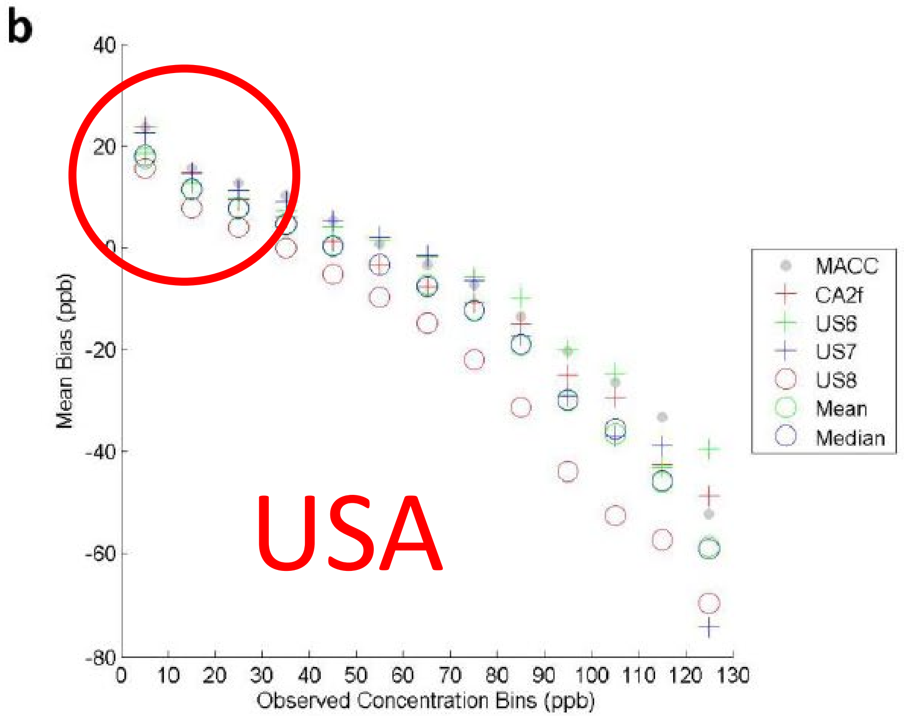


Appel et al., 2007

„ Overprediction biases at low O_3 levels are more sensitive to the boundary condition (BC) O_3 levels near the surface than BC concentrations aloft „

AQMEII: AQM intercomparision





Only May – September 8h maximum data – skewed towards daytime

Im et al., Atm. Env., 2015

From Emission to Concentrations

Science to support decisions

A complicated problem

- From a modeling point of view: need accurate ***emissions, chemistry and transport***

- High end observations can address some issues in support of modeling activities (e.g. city scale top down constraints on emissions)

- Big uncertainty is the **spatial and temporal distribution** of pollutants

Different approaches to estimate emissions

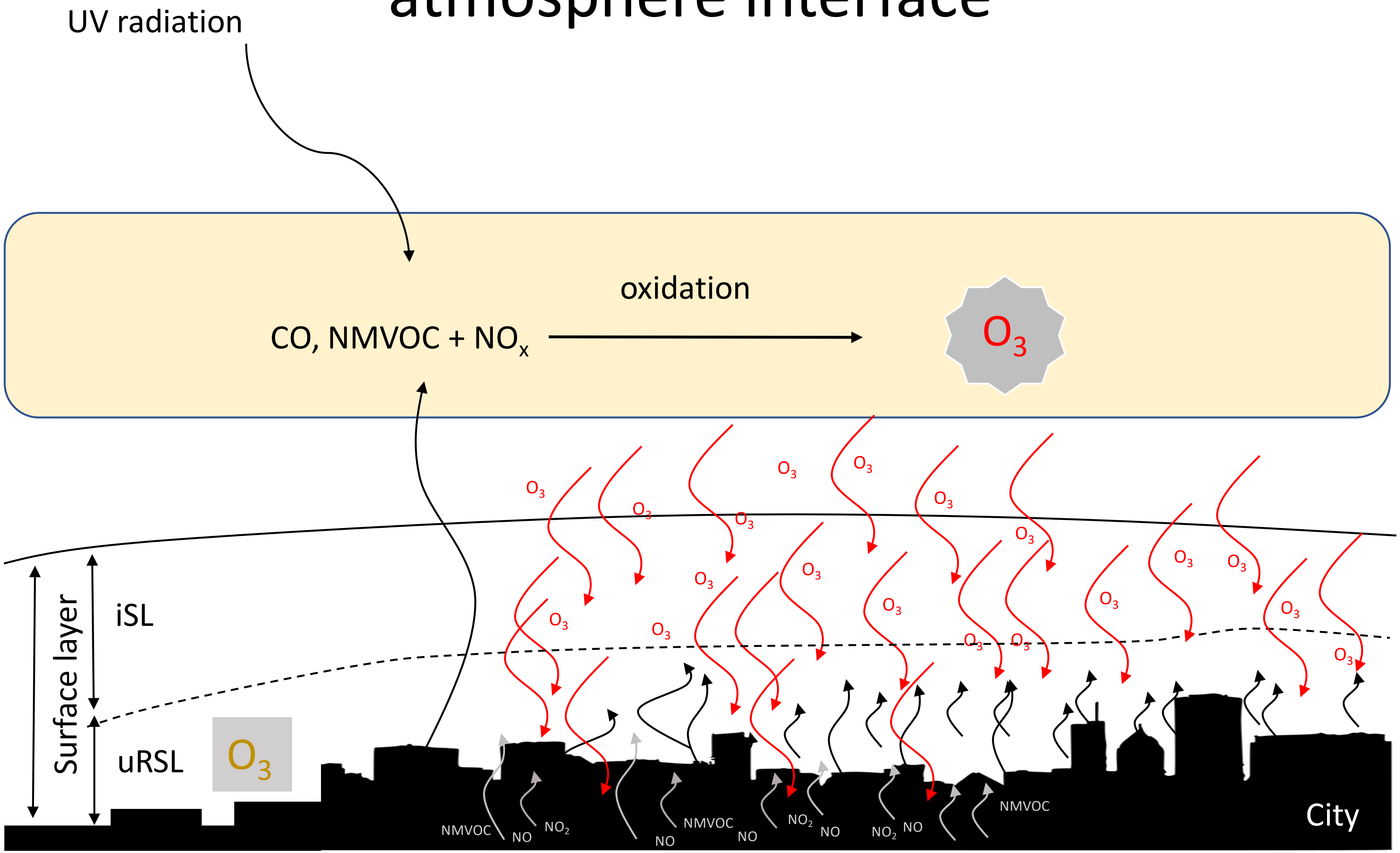
- Bottom-up emission modeling (local – global)

- Inverse modeling (regional – global)

- Direct flux observations (local – regional)

Atmospheric chemical cycles at the urban – atmosphere interface

Atmospheric chemical cycles at the urban – atmosphere interface



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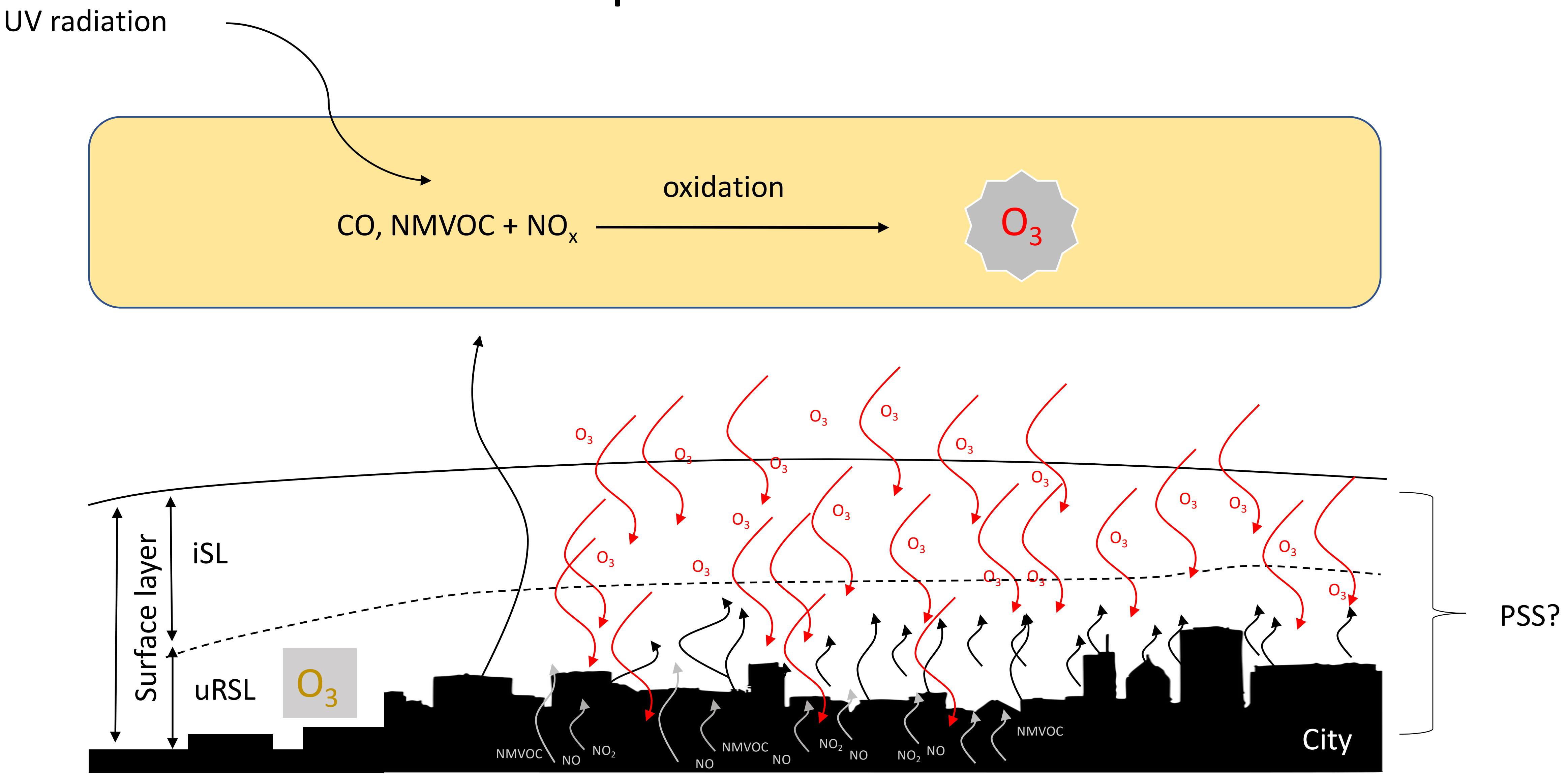


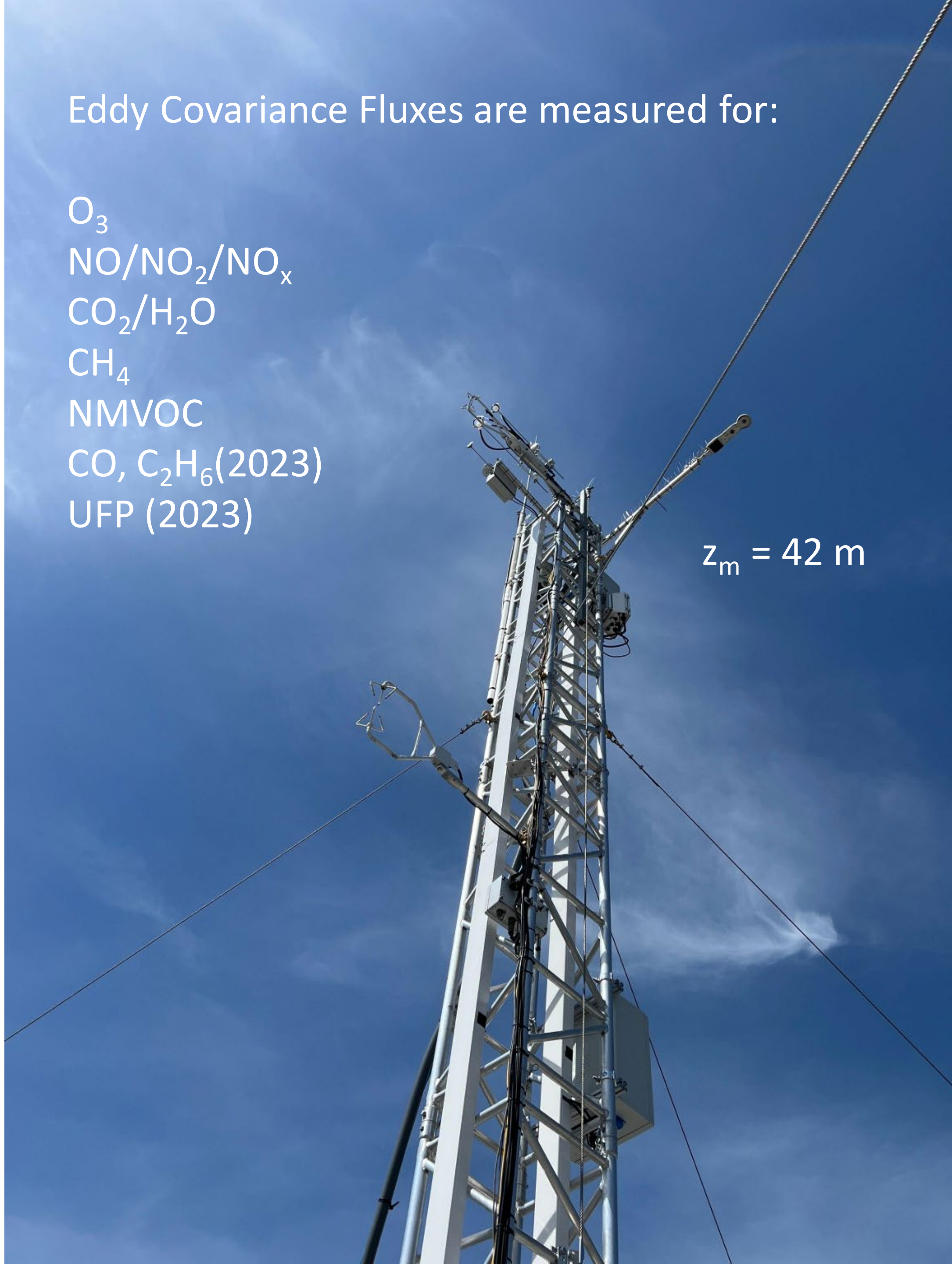
BAMS Article

Studying Urban Climate and Air Quality in the Alps

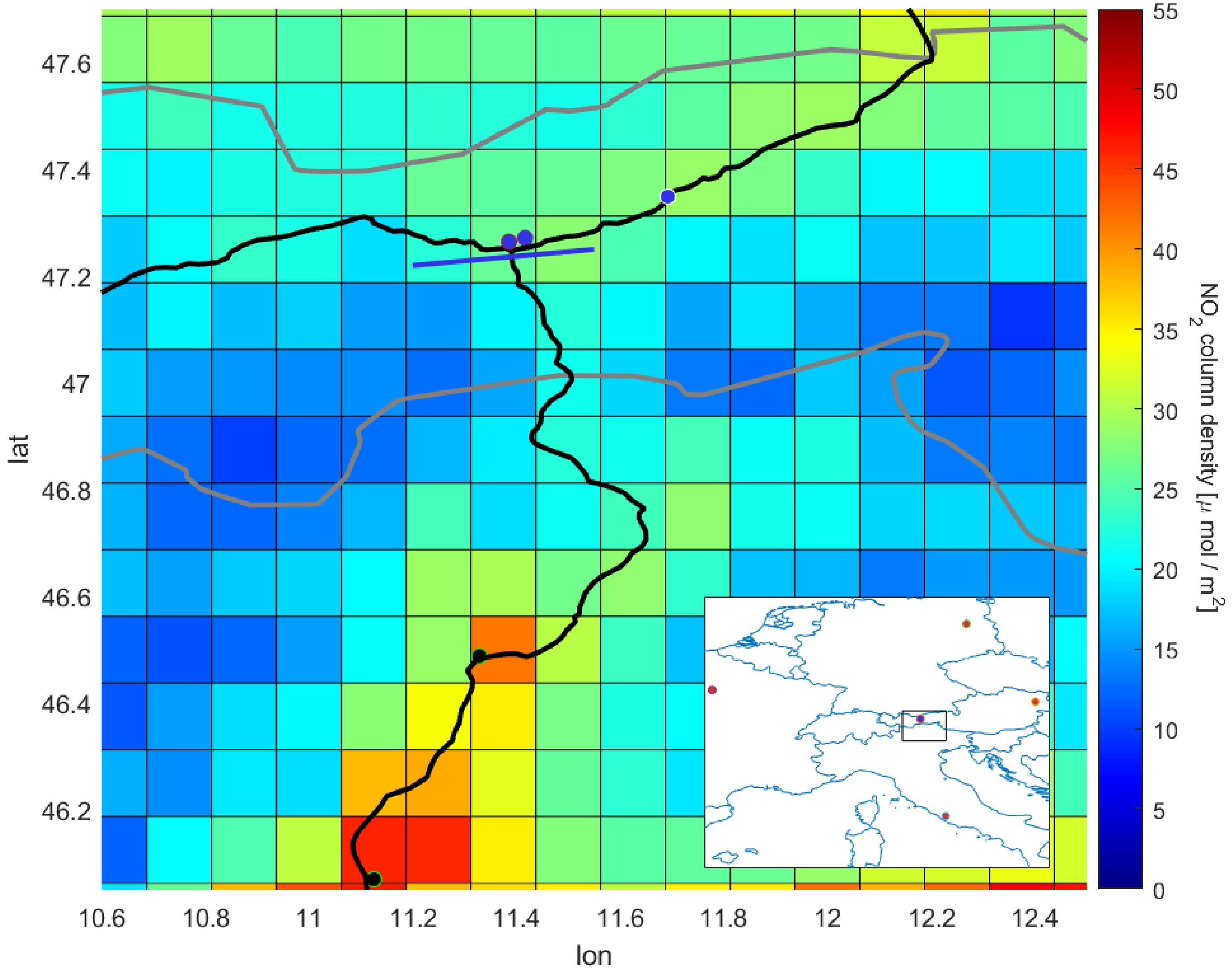
The Innsbruck Atmospheric Observatory

Thomas Karl, Alexander Gohm, Mathias W. Rotach, Helen C. Ward, Martin Graus, Alexander Cede, Georg Wohlfahrt, Albin Hammerle, Maren Haid, Martin Tiefengraber, Christian Lamprecht, Johannes Vergeiner, Axel Kreuter, Jochen Wagner, and Michael Staudinger

https://doi.org/10.1175/BAMS-D-19-0270.1

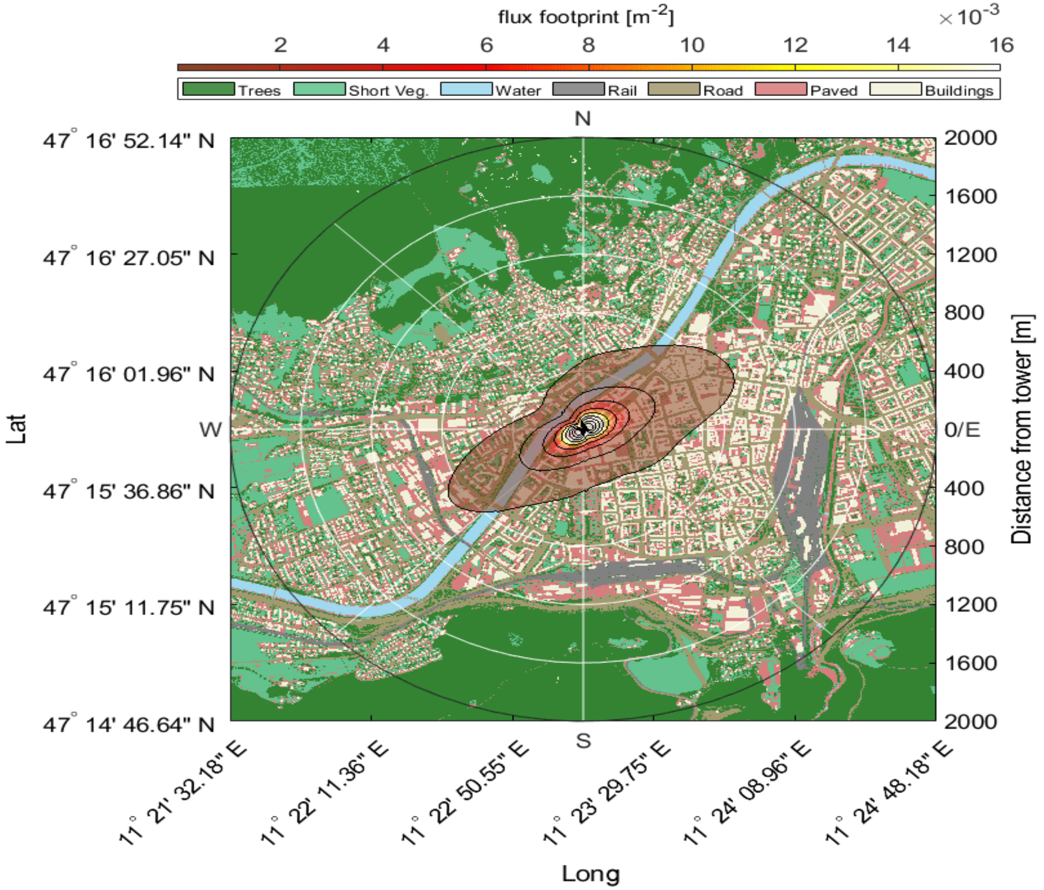


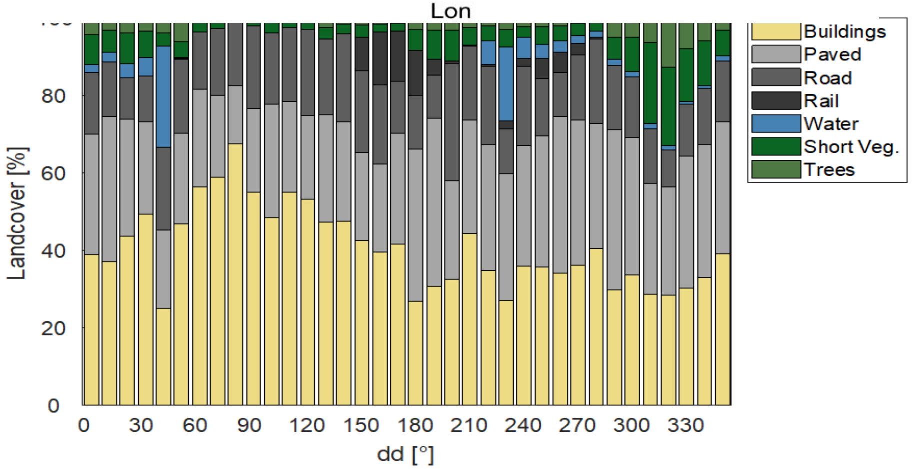
TROPOMI NO_2 Euregio (Ti-STi-Tr)



Turbulence Observations

„Eddy Covariance Measurements“





Ward et al., ACP, https://doi.org/10.5194/acp-22-6559-2022

Mountaintop cubesat demonstrator for urban AQ monitoring at sub-hectometer spatial resolution

Mapping NO_2

KARLOS
Mountaintop cubesat demonstrator
HafeleKAR Line Of Sight AQ monitoring
for urban AQ monitoring

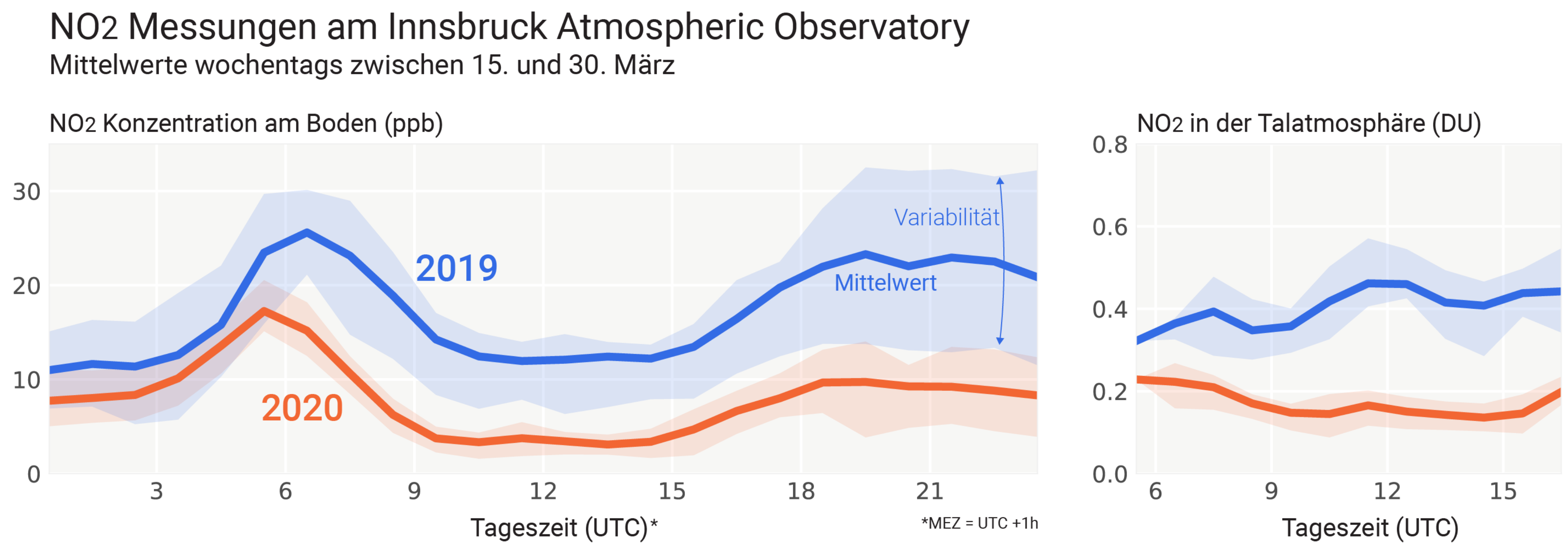
LUFTBLICK
EARTH OBSERVATION TECHNOLOGIES

BIRA • IASB

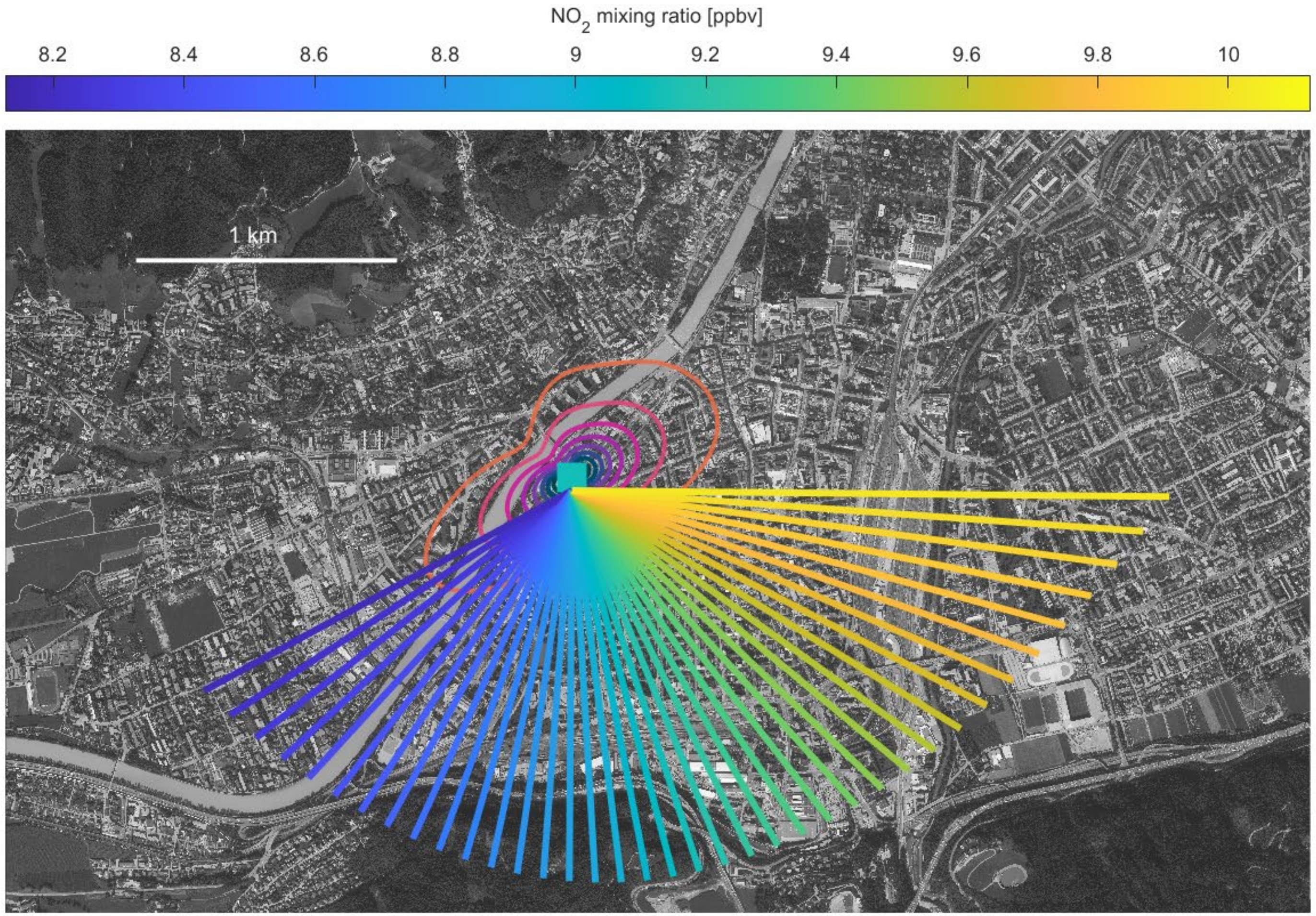
esa
European Space Agency

universität innsbruck

How comparable are surface and valley average observations - comparison between in-situ and remote sensing concentrations of NO2

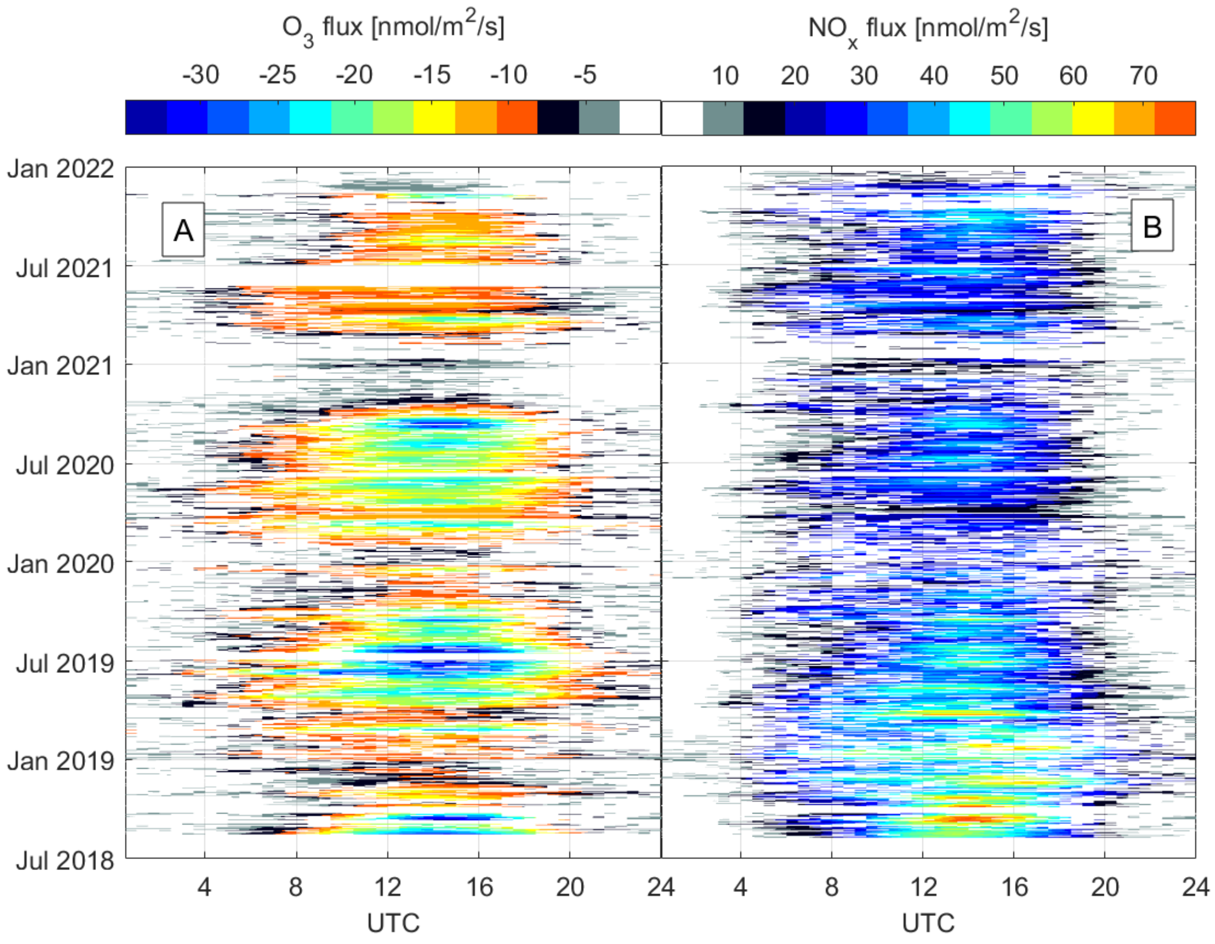


PANDORA PBL NO_2



Longterm O_3 and NO_x Eddy Covariance Observations

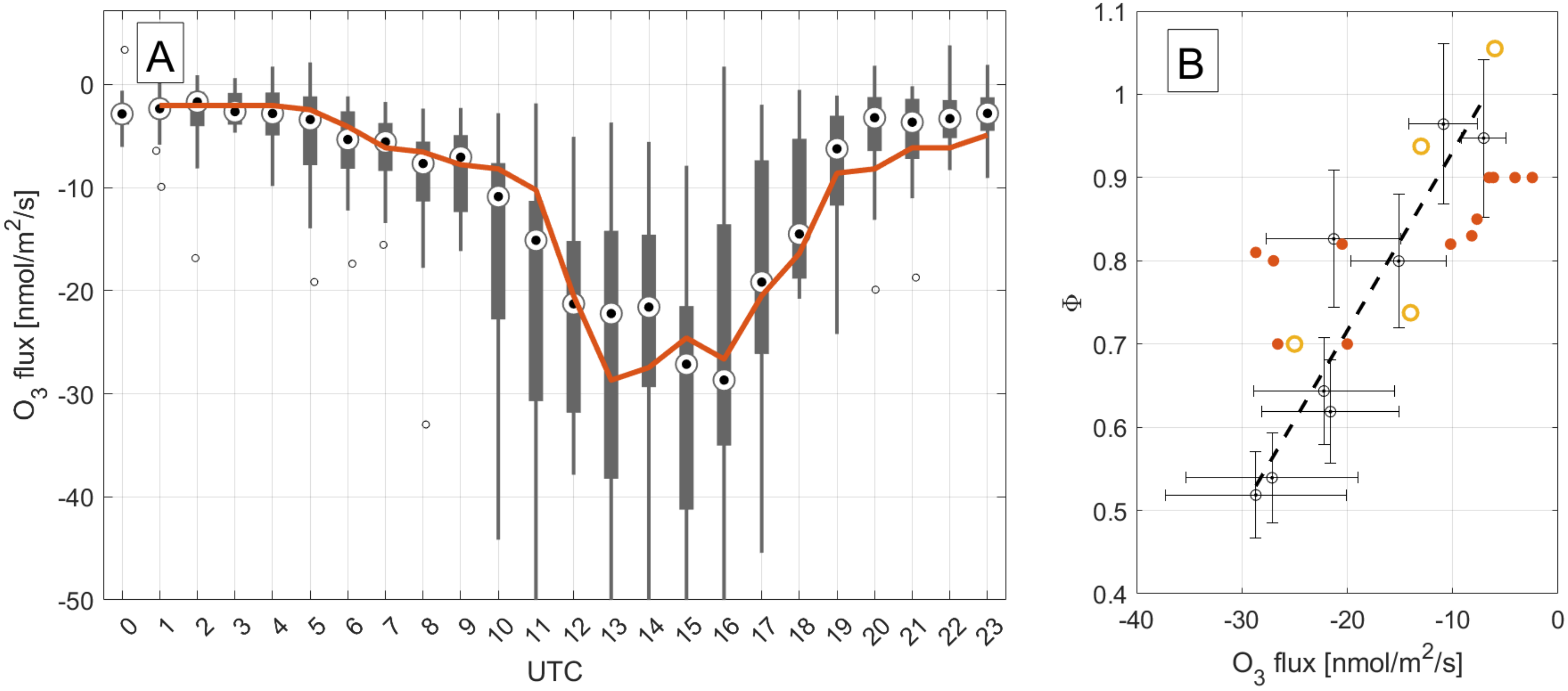
$O_3 – NO – NO_2$ Fluxes



High urban NOx triggers a substantial chemical downward flux of ozone

https://www.science.org/doi/full/10.1126/sciadv.add2365

Observations at IAO



Karl et al., Sci Adv., 2023

Dahmköhler numbers = 0.3- 1.15
Flux Dahmköhler numbers = 0.3-0.55

→ Impact of chemistry on diffusion gradients

PSS Assumption

$$0 = \frac{\partial \overline{[NO]}}{\partial t} = j_{NO2}\overline{[NO_2]} - k_3\overline{[NO]} \cdot \overline{O_3}$$

Steady state = 0 and well mixed

$$\Phi = \frac{j_{no2}[NO_2]}{k_3[NO][O_3]}$$

Leighton, P. 1961

Karl et al., Sci Adv., 2023

Revisit PSS Assumption

…after Reynolds decomposition

$$\frac{\partial\overline{[NO]}}{\partial t} = -\frac{\partial\overline{F_{NO}}}{\partial z} + j_{NO2}\overline{[NO_2]} - k_3\overline{[NO]}\cdot\overline{O_3} - k_3\overline{[NO]'[O_3]'}$$

Steady state = 0

Flux Divergence

Incomplete mixing

$$\frac{\partial\overline{F_{NO}}}{\partial z} = j_{NO2}\overline{[NO_2]} - k_3\overline{[NO]}\cdot\overline{O_3} - k_3\overline{[NO]'[O_3]'}$$

Karl et al., Sci Adv., 2023

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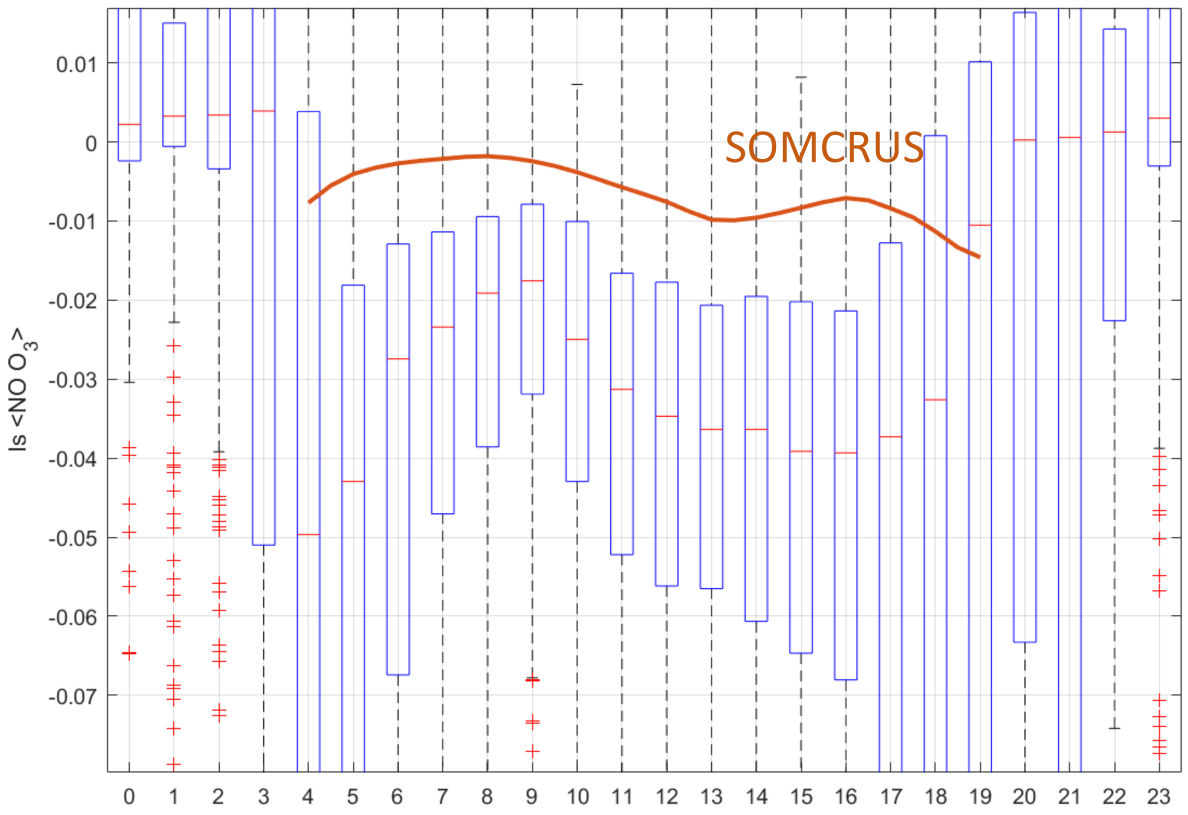
Karl et al., Sci Adv., 2023

Effect of Segregation between NO and O_3

$$\frac{\partial \overline{F_{NO}}}{\partial z} = j_{NO2}\overline{[NO_2]} - k_3\overline{[NO]} \cdot \overline{O_3} - k_3\overline{[NO]'[O_3]'}$$

$$I_S = \frac{\overline{[NO]'[O_3]'}}{\overline{[NO]} \cdot \overline{O_3}}$$



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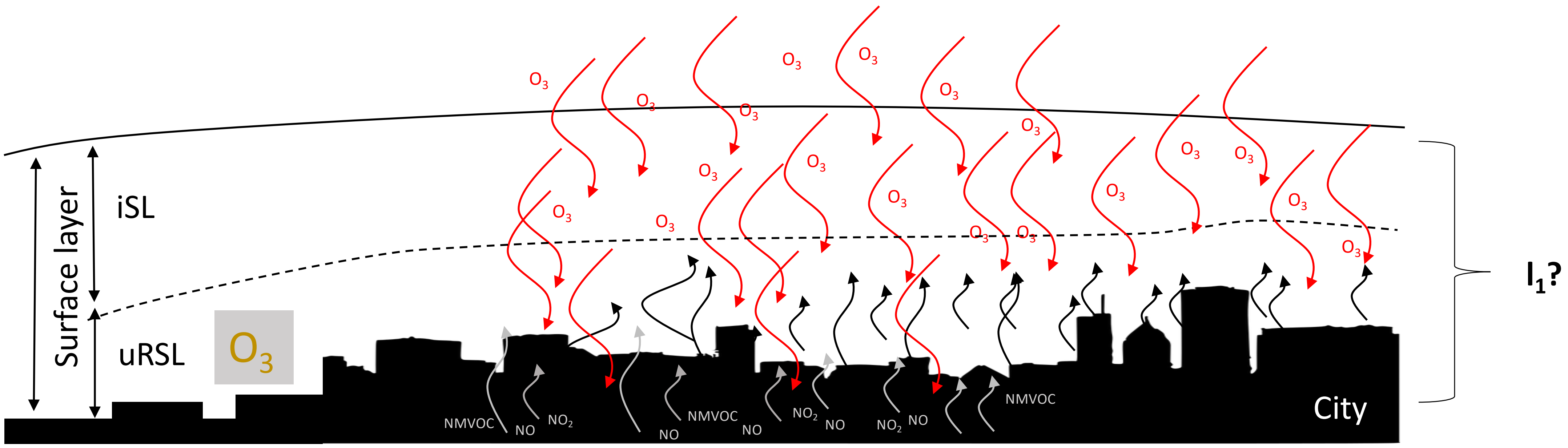
Flux divergence

$$\frac{\partial\overline{F_{NO}}}{\partial z} = j_{NO2}\overline{[NO_2]} - k_3\overline{[NO]}\cdot\overline{O_3} - k_3\overline{[NO]'[O_3]'}$$

Karl et al., Sci Adv., 2023

So where does the flux divergency go to zero and PSS approaches 1?

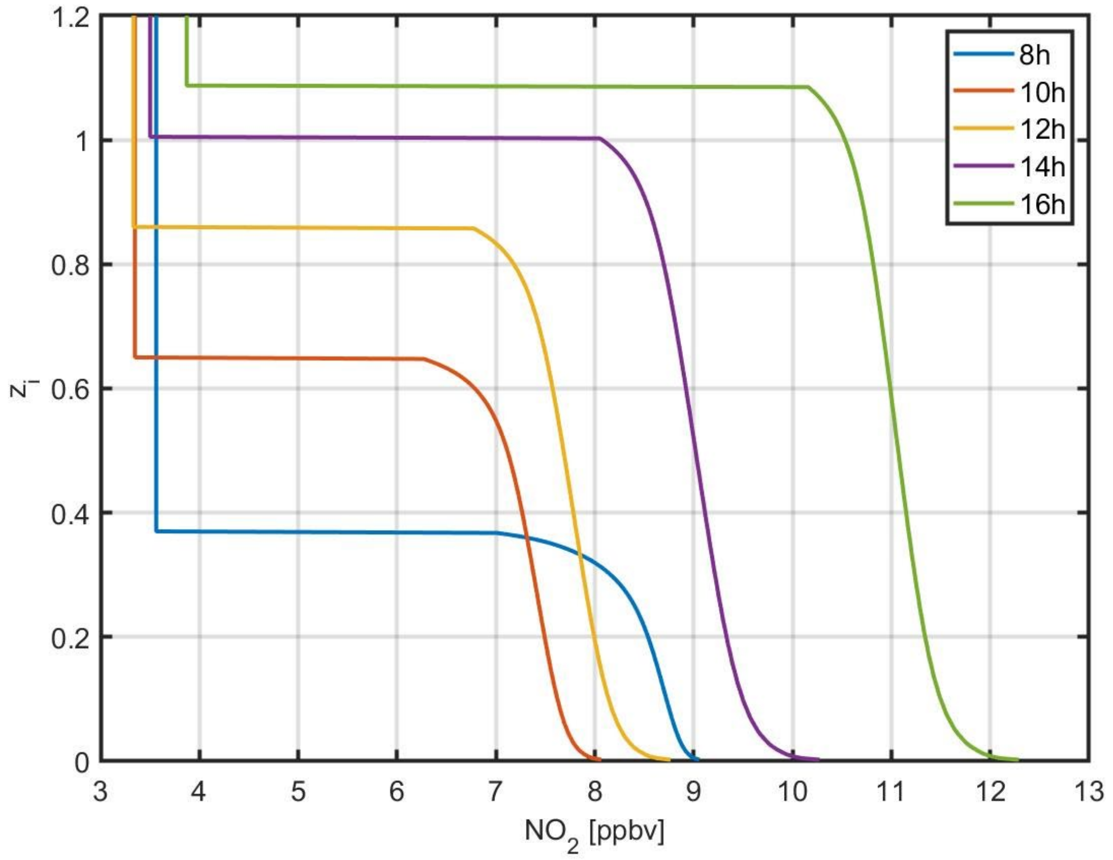
Look at length scale l_1 for the triad reaction



l_1 ~100-200 m

Comparing In-situ and Remote Sensing Data

Summer Scenario

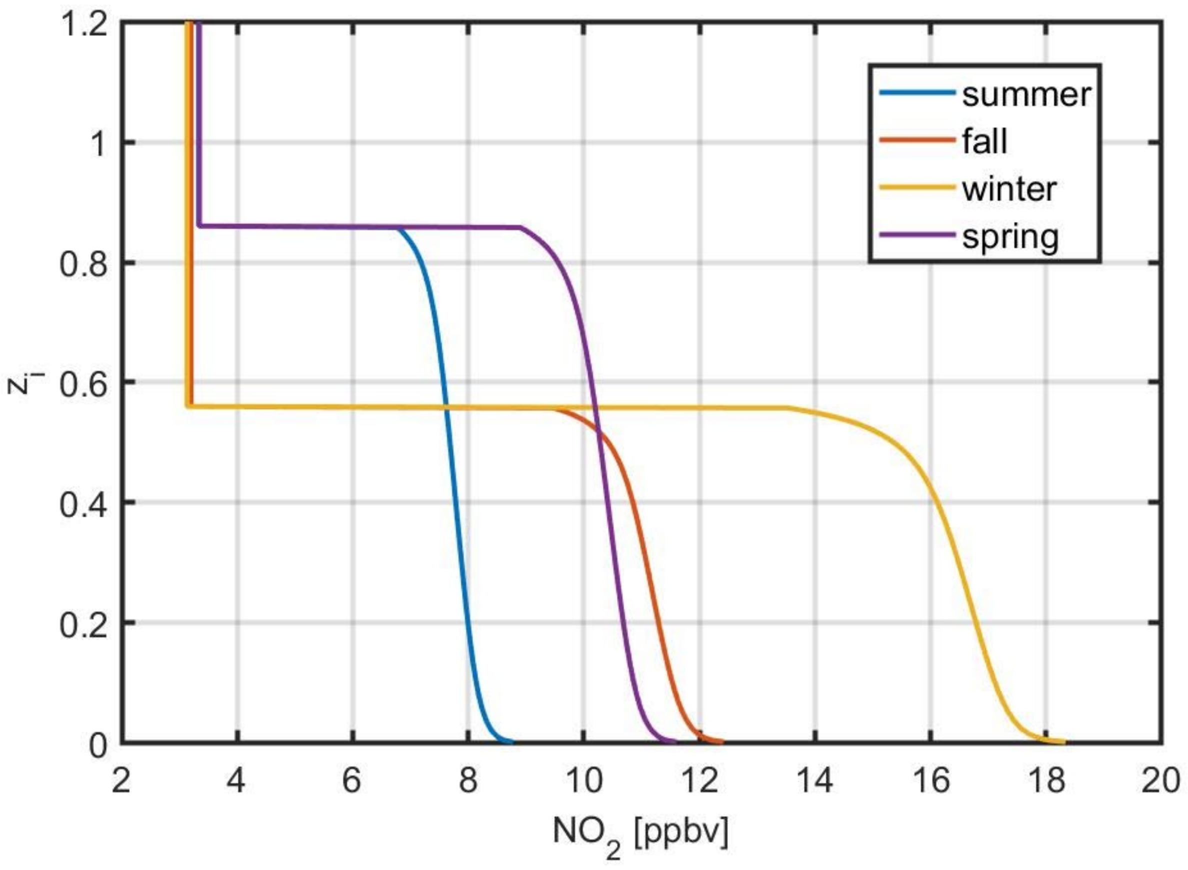


2nd order closure model SOMCRUS **driven by in-situ fluxes** scaled by flux footprint

IAO

Season for Noon (12LT)

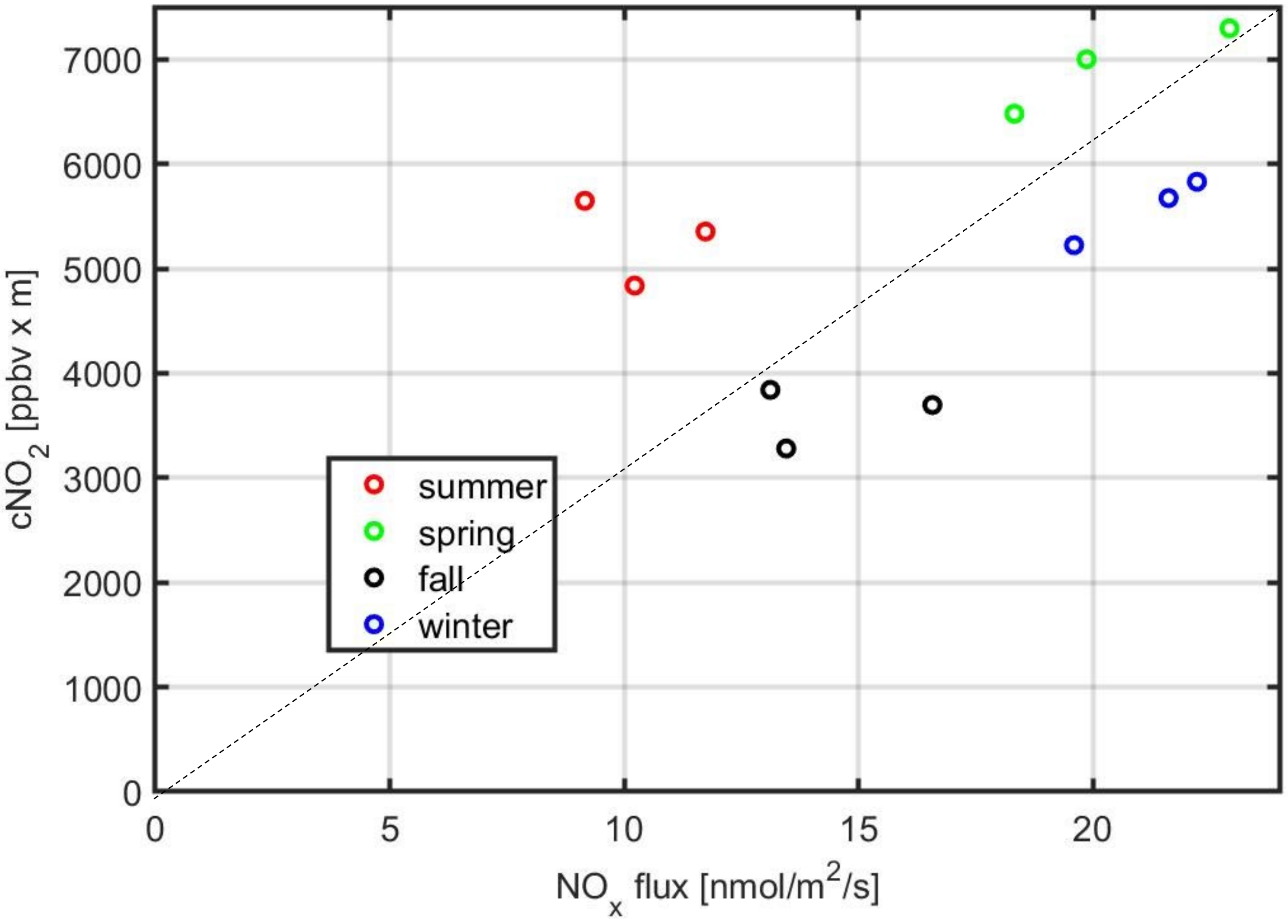
Summer Scenario



2nd order closure model SOMCRUS **driven by in-situ fluxes** scaled by flux footprint

IAO

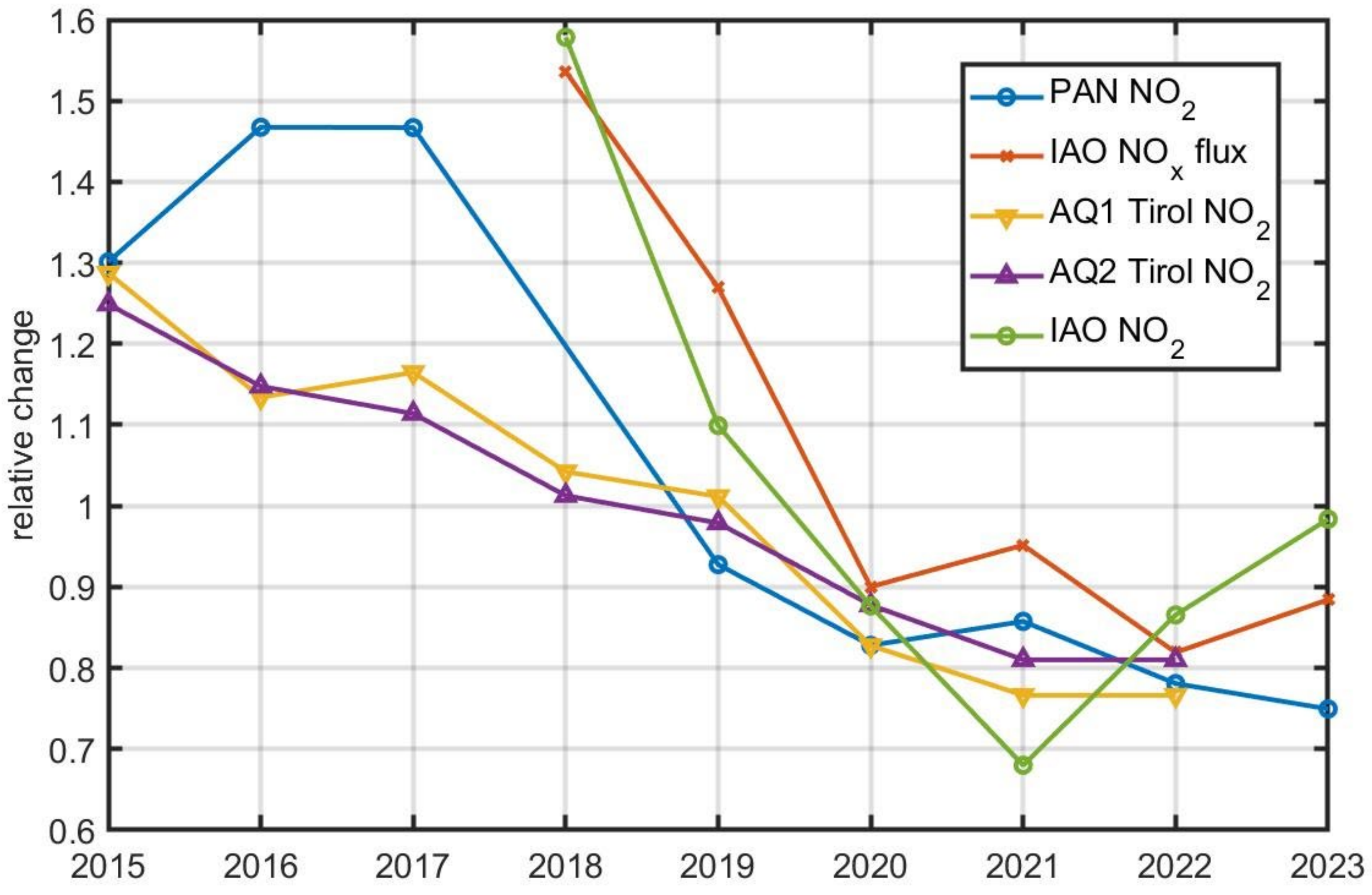
Outlook



Can we find a relationship between NO_x Emissions and NO_2 columns above the urban Area of Innsbruck?

SOMCRUS – IAO Flux

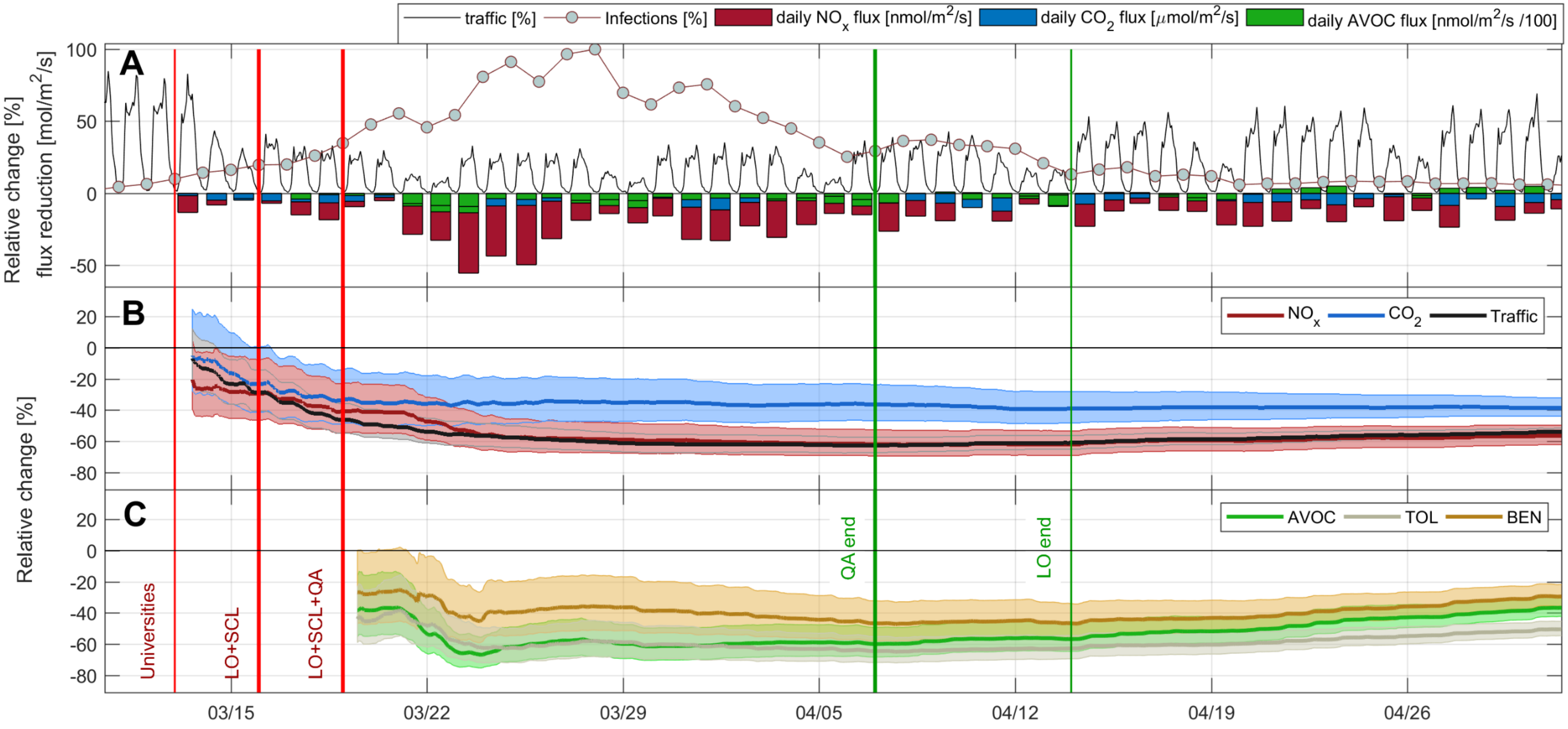
Evolution of NO_2 and NO_x in IBK



Remote sensing vs in-situ OBS

Air pollution decline during COVID lockdown in 2020

Traffic activity reduction: -61%
NO_x flux reduction: -59%
CO_2 flux reduction: -38%
AVOC flux reduction: -56%



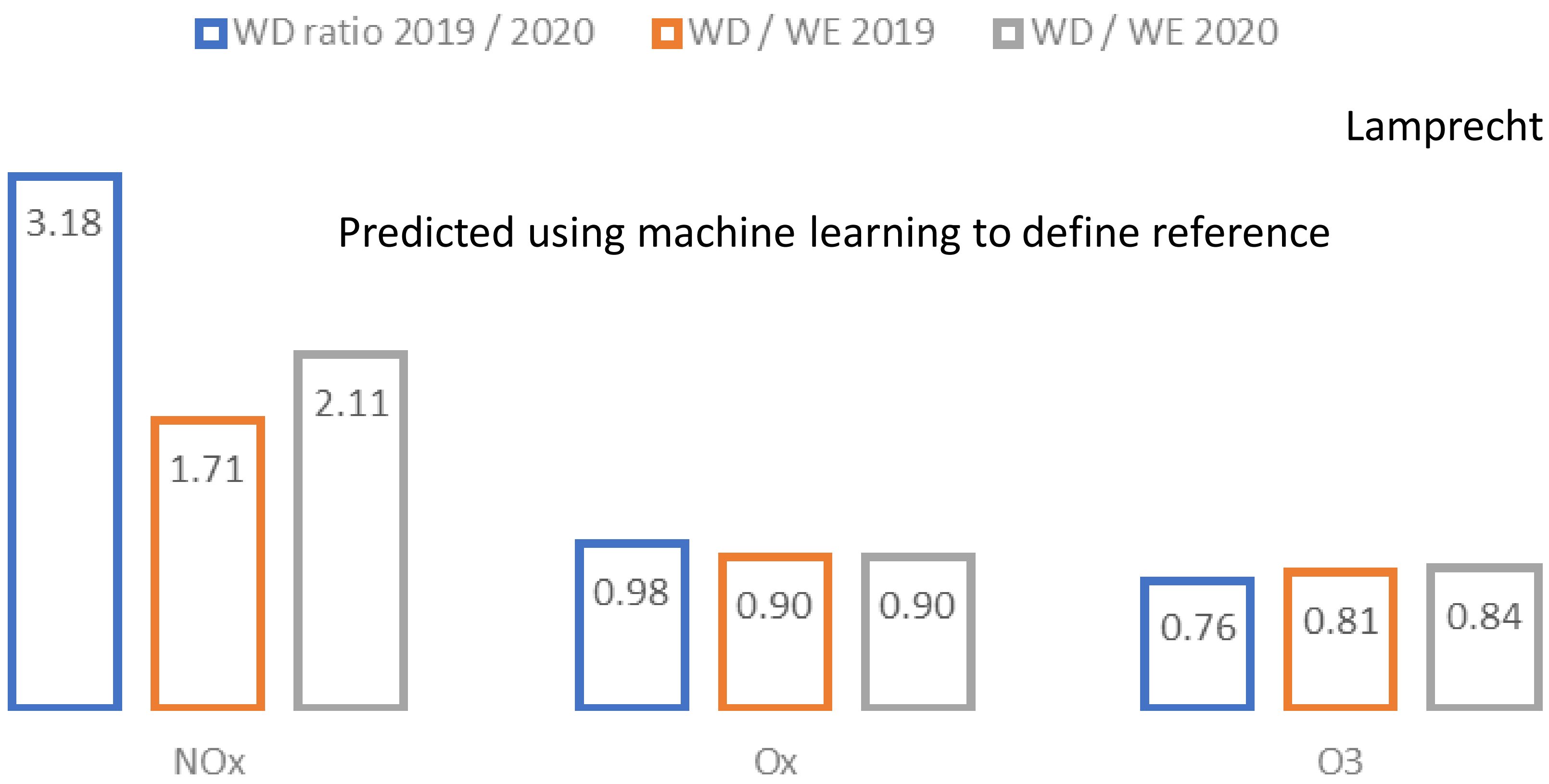
Lamprecht et al., ACP, 2021

Modeling the Impact on Urban O_3 Pollution

Mixing Ratio Changes of NO_x, O_x and O_3

Lockdown and Weekday / Weekend ratios

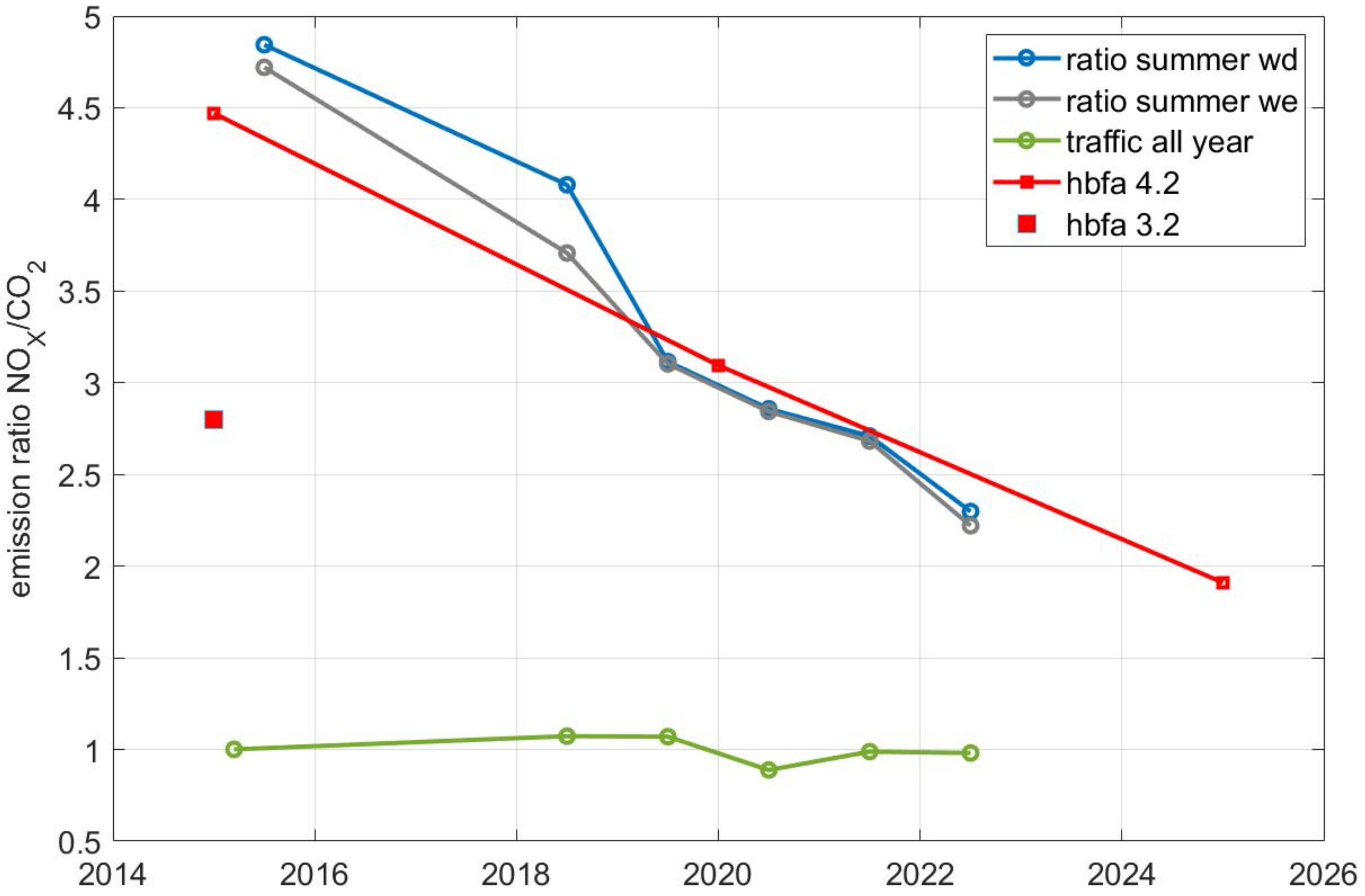
Lamprecht et al., ACP, 2021



Lockdown repartitioning $NO_2 \leftrightarrow O_3$ – **little change in O_x** 24% increase in O_3 (+11 ppbv)

Have NO_x Emissions Changed?

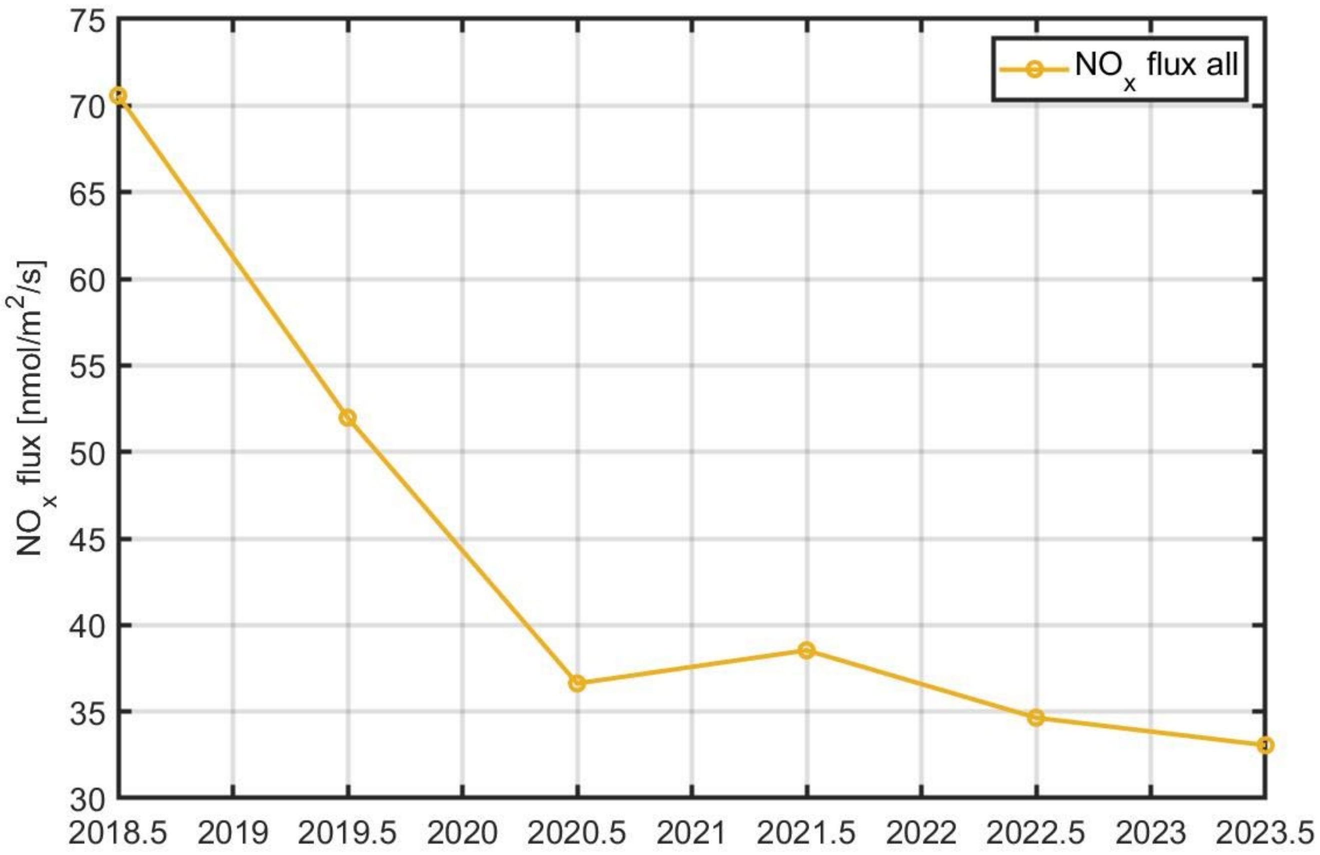
Evidence from in-situ flux observations



Look at NO_x / CO_2 flux and emission ratios

Ratio decreases by 2.5 between 2015 and 2023

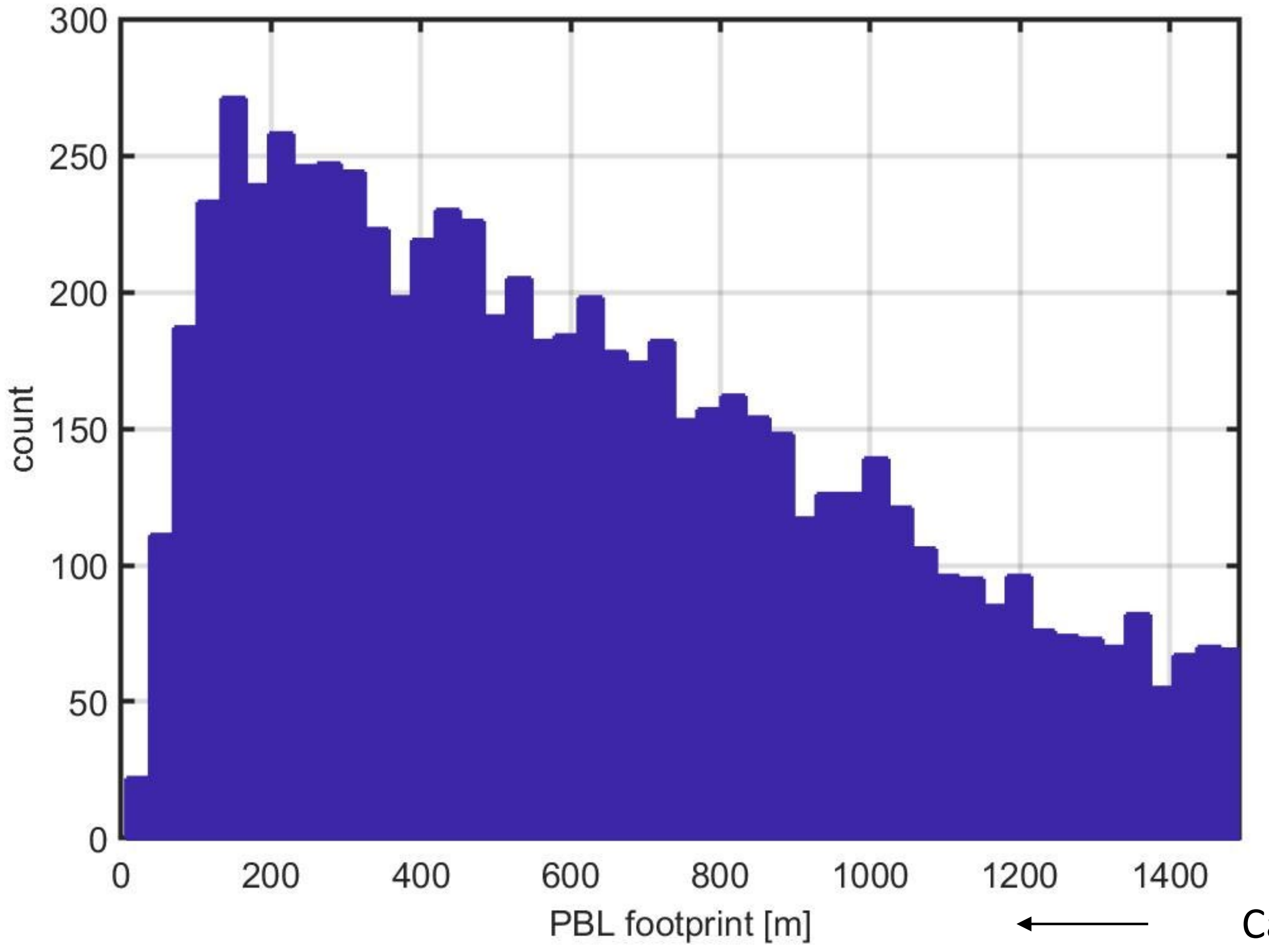
Other Evidence for decreasing NO_x



Direct NO_x Flux decreases from 70 to about 33 $nmol/m^2/s$

NO_2 Footprint @ IAO

Spatial Resolution

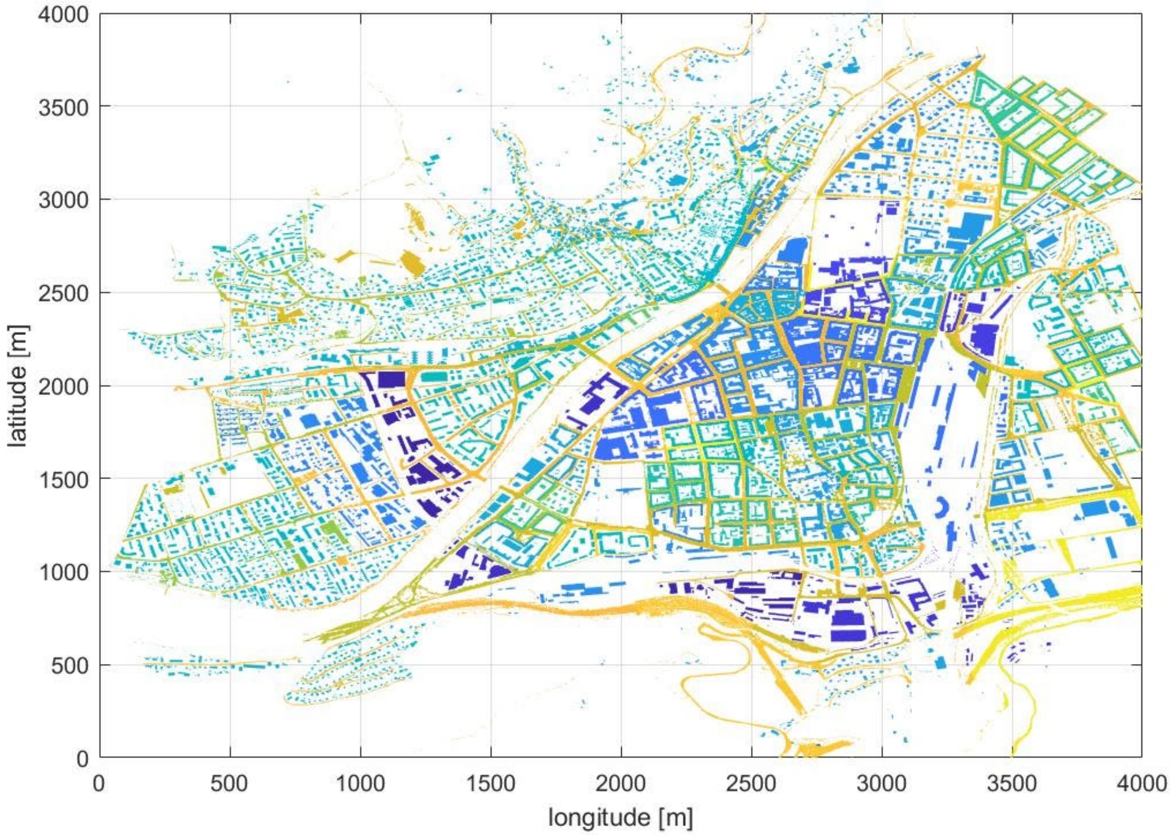


Can be calculated from EC flux obs

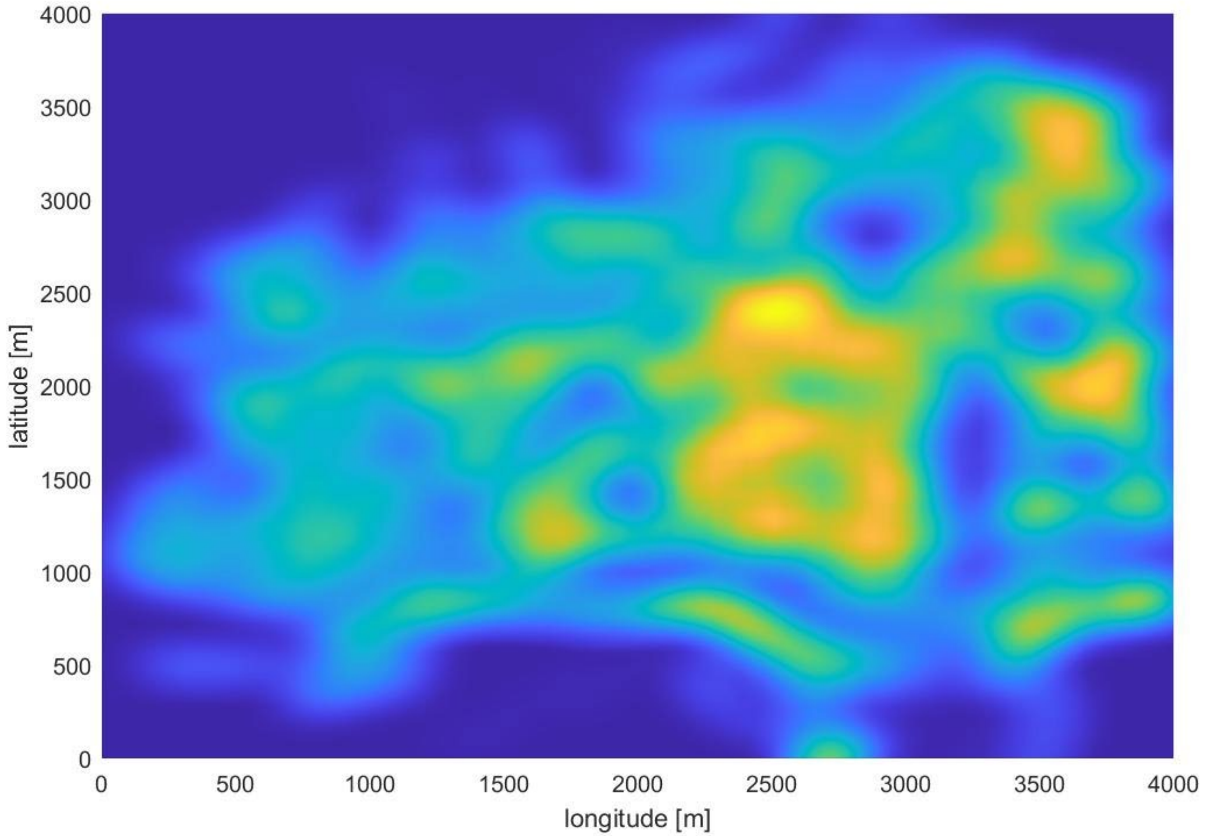
Mapping URBAN NO_x

What is the physical limit of horizontal resolution

URBAN NO_x Emissions validated at IAO



Synthetic KARLOS product: Gaussian filter size 100



Summary

- Urban air pollution is still largely controlled by NO_x and remains a key regulatory pollutant in Europe
- As a consequence urban/suburban O_3 production is largely VOC sensitive
- Urban NO_x emissions are still largely controlled by the mobility sector and emissions seem to go down
- We are currently in a transitional regime
- Integrated longterm remote sensing and in-situ observations can help to validate models and test AQ projections
- Direct Eddy Covariance Observations can provide a ground-truth for emissions

IAO funding

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ZAMG Zentralanstalt für Meteorologie und Geodynamik

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LUFTBLICK EARTH OBSERVATION TECHNOLOGIES

Project related funding

FWF Der Wissenschaftsfonds.

esa European Space Agency