Forschungszentrum jülich

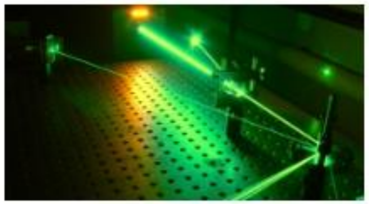
Helmholtz Association

Employs : <5,700 (1,500 scientists)

Forschungszentrum jülich

- Institute for Advanced Simulation (IAS)
- Institute of Bio- and Geosciences (IBG)
- Institute of Biological Information (IBI)
- Institute of Energy and Climate Research (IEK)
- Institute of Neuroscience and Medicine (INM)
- Jülich Centre for Neutron Science (JCNS)
- Nuclear Physics Institute (IKP)
- Peter Grünberg Institute (PGI)

IEK-8 troposphere



Photochemistry and Radicals

Investigation of the chemistry of free radicals (OH, HO_2, RO_2, NO_3) in the atmosphere and their impact on the atmospheric self-cleaning and formation of secondary air pollutants (ozone, aerosols etc). → More

Reactive Trace Gases

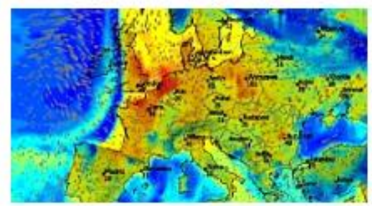
Reactive trace gases like hydrocarbons and nitric oxides are emitted in enormous amounts by natural and anthropogenic sources into the atmosphere. The measurement of their concentrations and the review of their depletion paths help us to understand the complex processes, which are needed to remove the contamination from the atmosphere. → More

Aerosols

Investigations of the sources, the chemical composition, and the micro physical properties of atmospheric aerosols under various aspectes. → More

Global Monitoring

Investigation of cycles and trends of water vapour, aerosols, and clouds as well as of ozone and ozone precursors in the upper troposphere and lowermost stratosphere (UTLS) → More



Modeling

Numerical modelling of atmospheric physics and chemistry provides both key information on so far poorly understood processes and feedback mechanisms, as well as planning and analysis tool for field missions.
→ More

Importance of atmospheric OH, HO_2 and RO_2 radicals in tropospheric Ozone production

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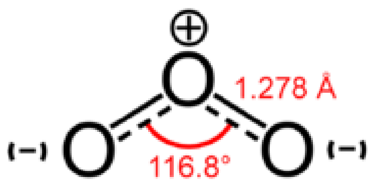
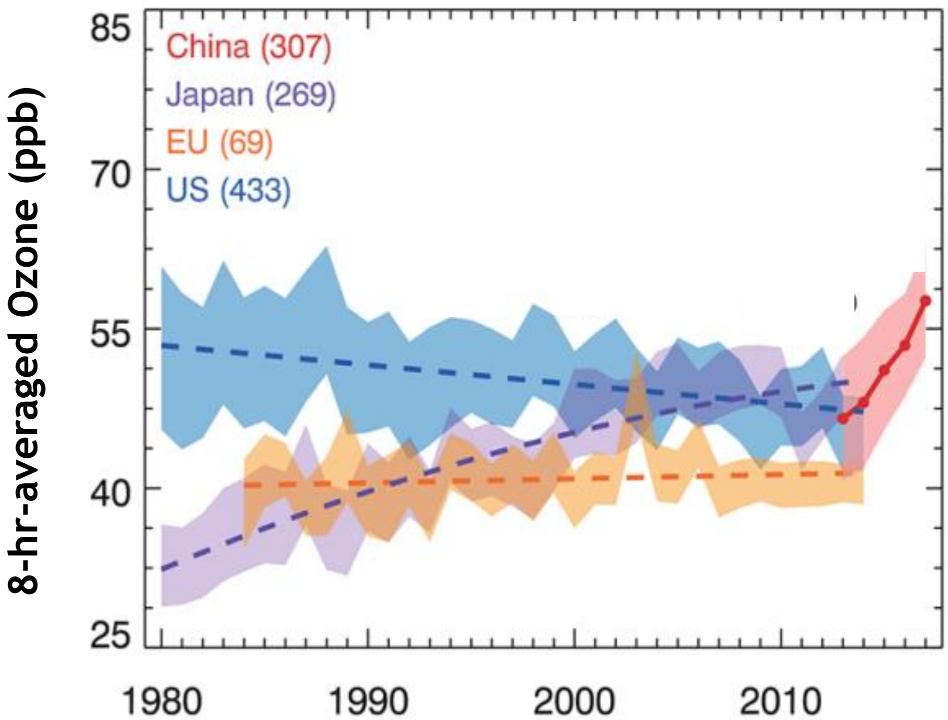
Tropospheric Ozone

Tropospheric Ozone (O_3) is

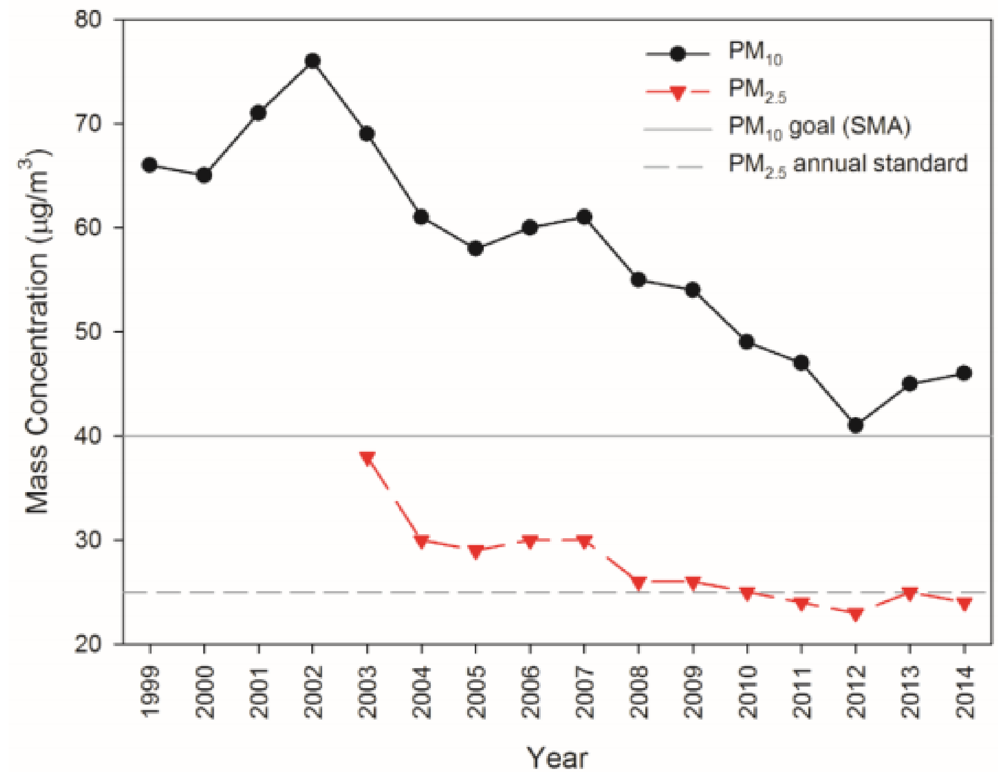


- Greenhouse gas
- Reducing productivity of crops
- Harmful to human health

Increasing Ozone Concerns



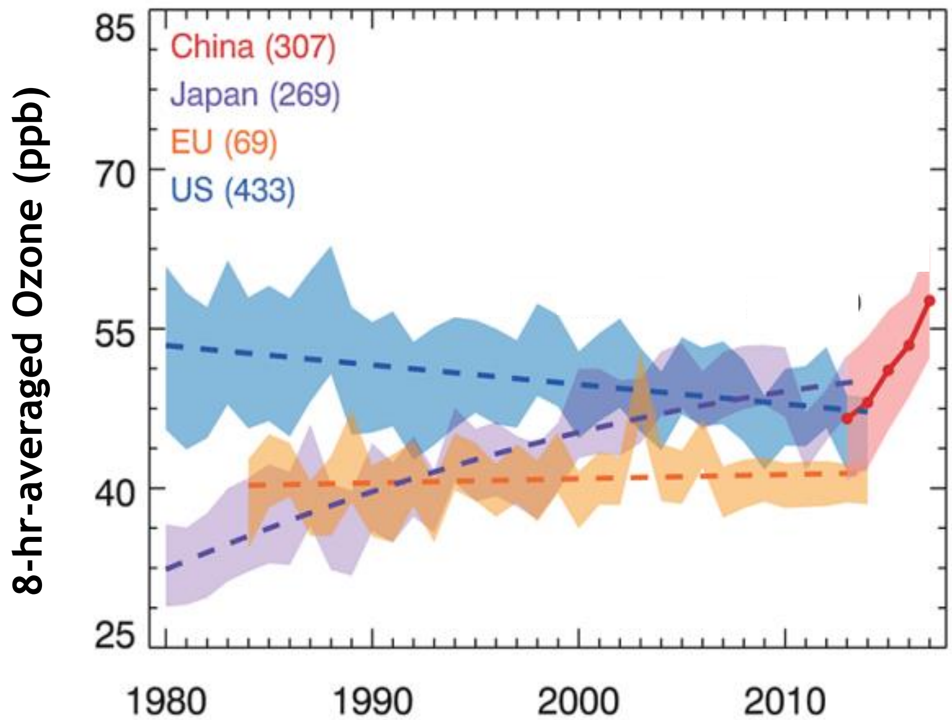
Seoul, South Korea



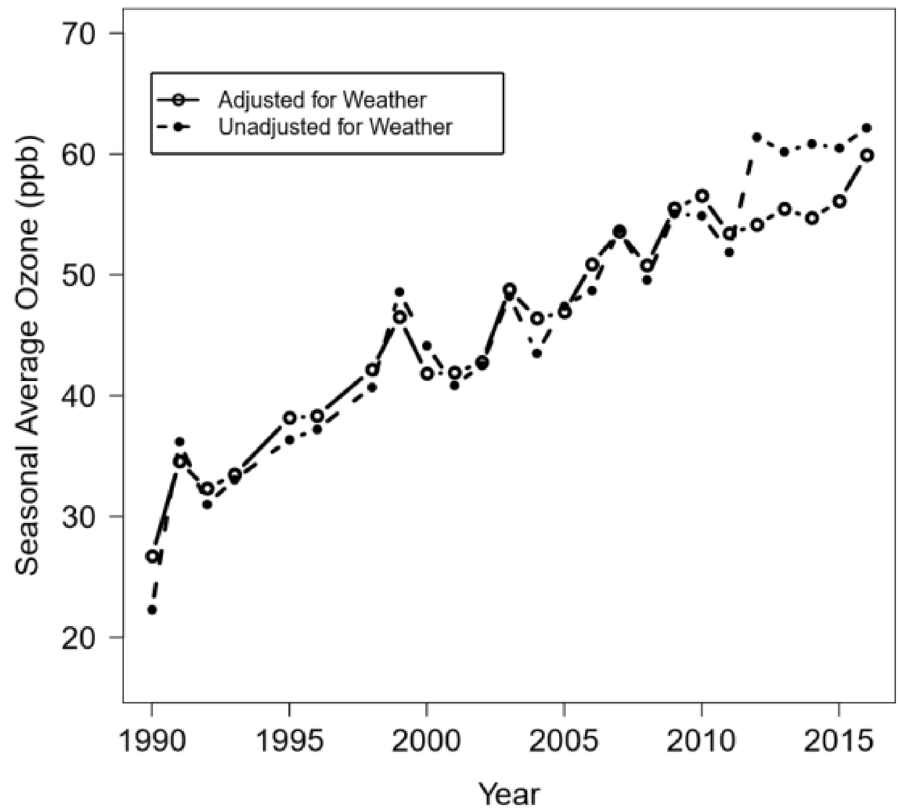
Lu et al.:, Envi. Sci. & Tech., 2021.

Kim et al.:, Aero. Air Qual. Res., 2018.

Increasing Ozone Concerns



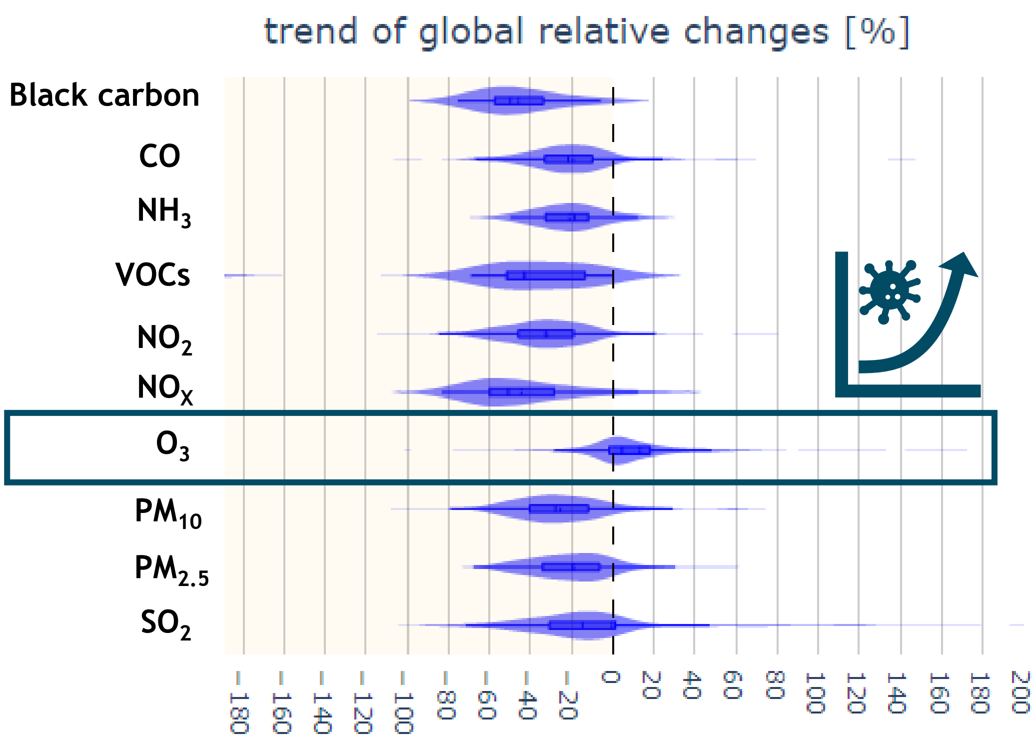
Seoul, South Korea



Lu et al.:, Envi. Sci. & Tech., 2021.

Kim et al.:, Aero. Air Qual. Res., 2018.

Increasing Ozone Concerns

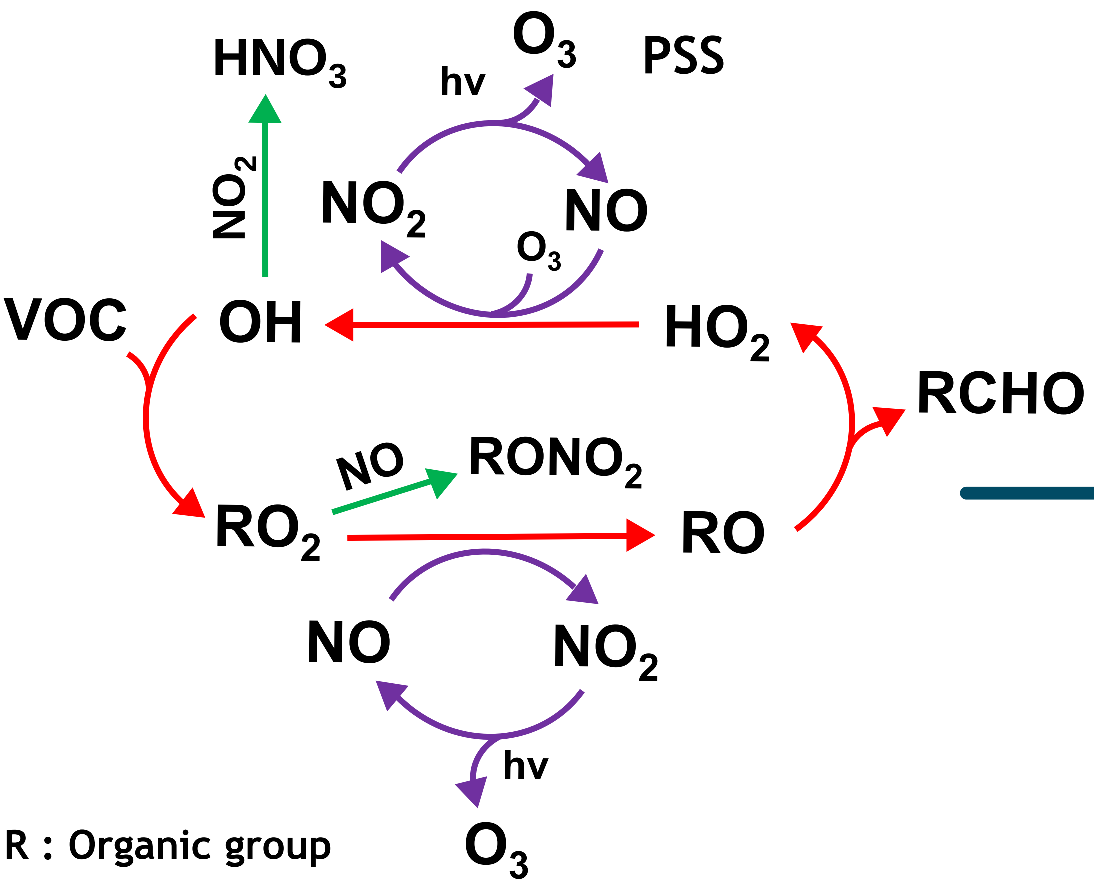


COVID-19 lockdowns decreases O_3 precursor concentrations, but O_3 does not?!

European Green Deal: Commission aims for zero pollution
→ further reduction on NO_X

COVID-19 AQ Data Collection (http://covid-aqs.fz-juelich.de)
Gkatzelis et al.:, Elementa: Sci. Anthrpo., 2021.

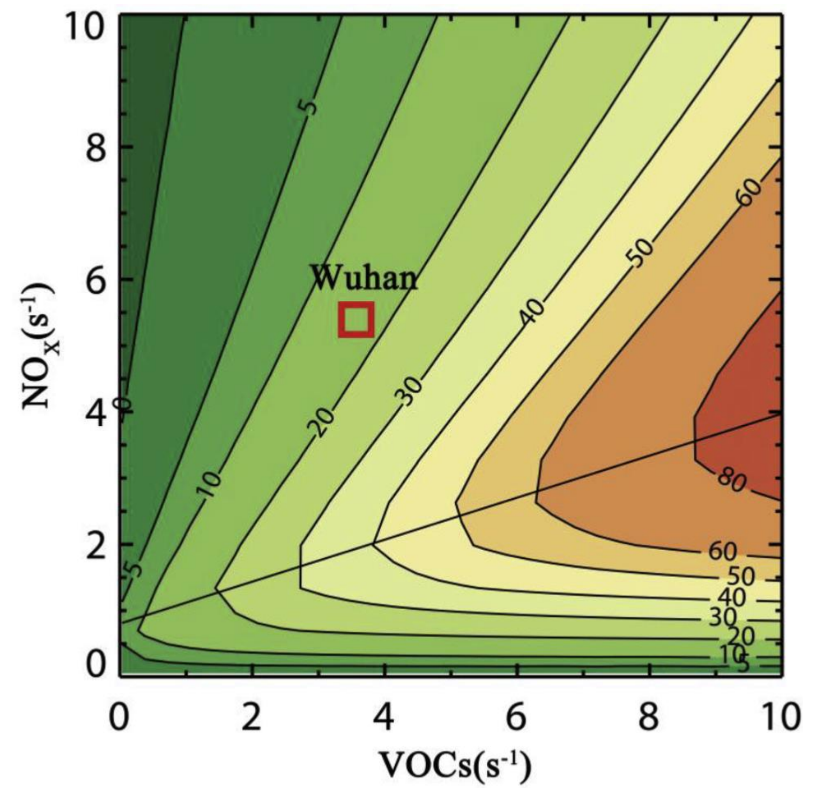
Tropospheric Ozone Formation



R : Organic group

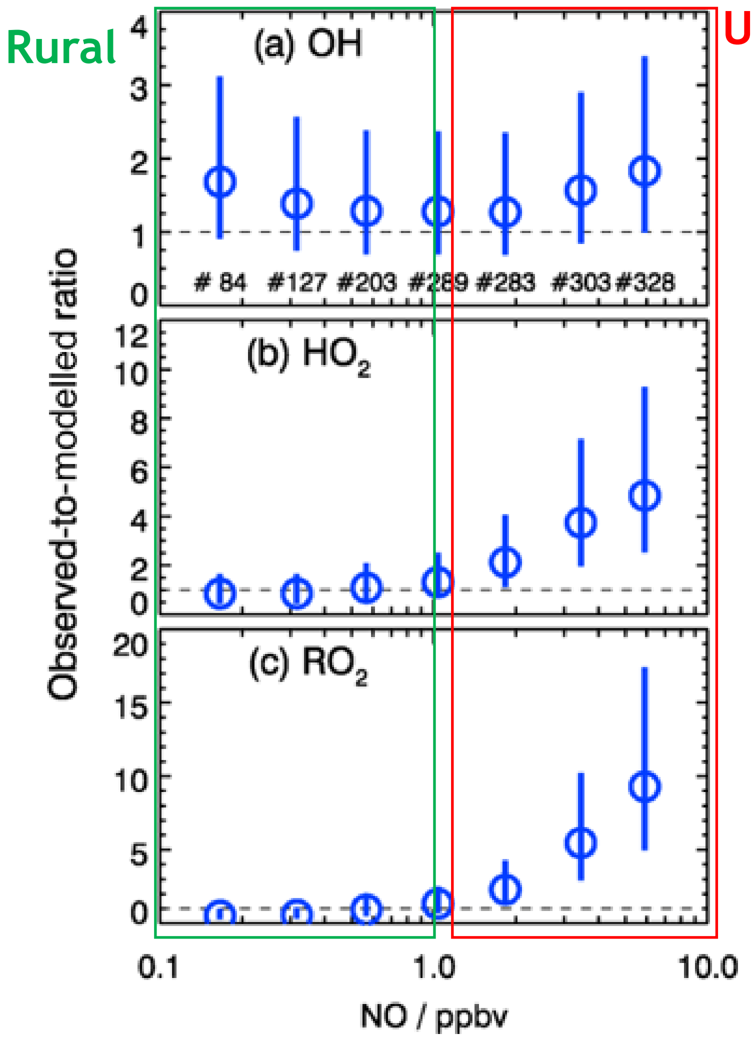
Contour lines : O_3 production rate (ppbv h^{-1})

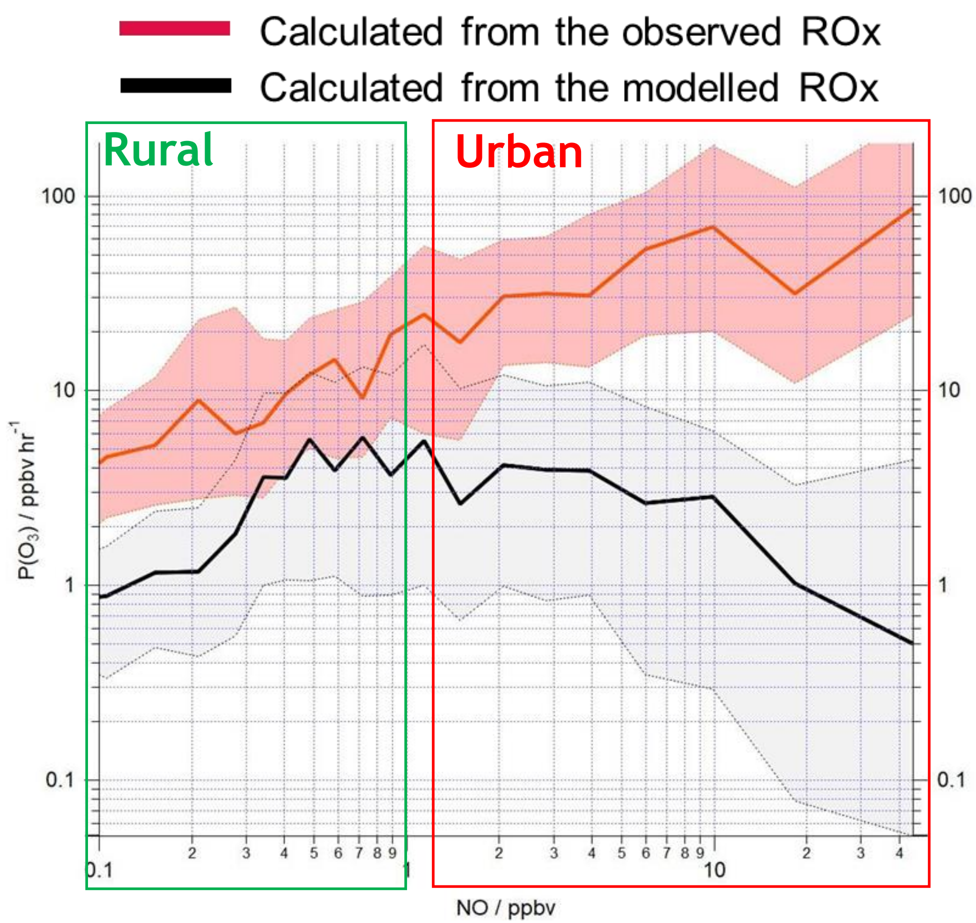
NOx = NO + NO_2



Hui et al.: Atmos. Envi., 2018.

Tropospheric Radical chemistry



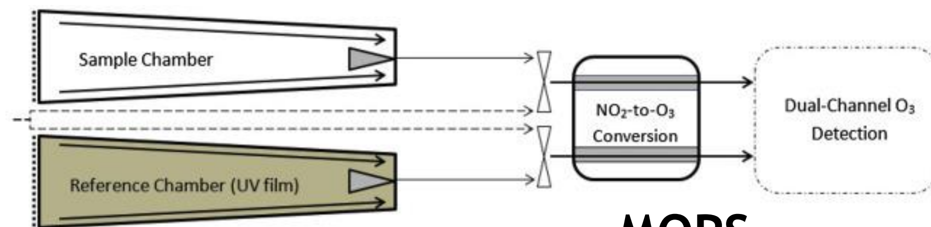


Tan et al.: Atmos. Chem. Phys., 2018.
Whalley et al.: Atmos. Chem. Phys., 2021.

Quantification of Net-Ozone Production Rates

Chemical Source ➡ $NO_2 \underset{NO}{\overset{hv}{\rightleftarrows}} O_3$

$O_X = O_3 + NO_2$



MOPS

1. Direct measurement of POx

$P(O_X)_{meas.}$

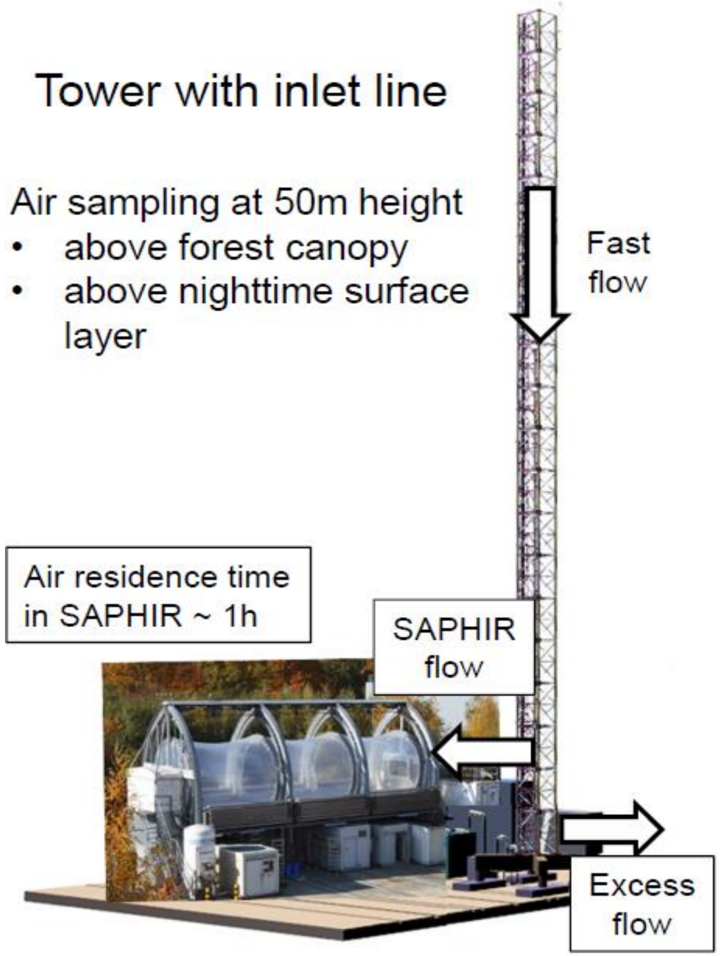
2. Calculation from NO_2-to-NO ratio (photostationary state, PSS)

$P(O_X)_{PSS}$

3. Calculation from NO oxidation rate by RO_2 and HO_2

$P(O_X)_{calc.}$

Jülich Atmospheric Chemistry (JULIAC) 2019



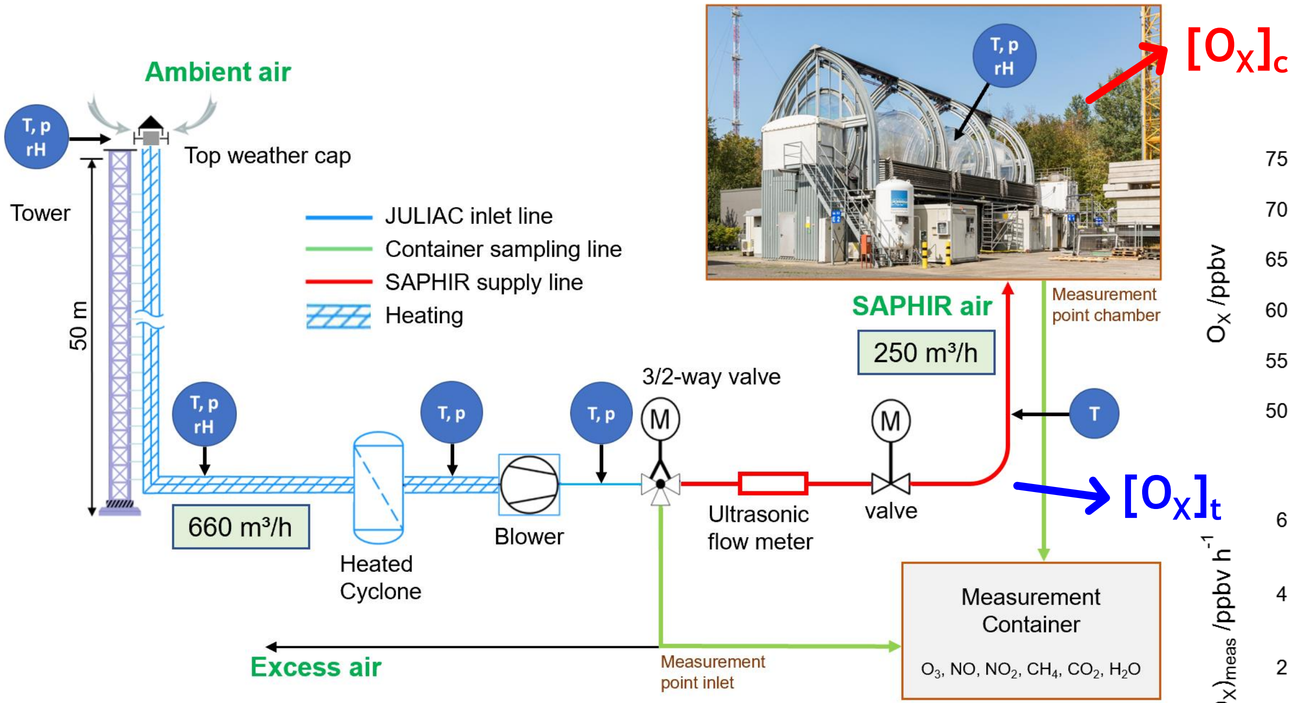
Instrumentation:
- OH, HO_2,RO_2 : CMR – LIF
- k_{OH} : LP-LIF
- OH, HCHO, SO_2, Naphthalene : DOAS
- HONO : LOPAP and CAPS
- NO_3, N_2O_5 : CRDS
- NO, NO_2, O_3 : CLD
- CH_4, H_2O, CO, CO_2 : Picarro
- Photolysis frequencies
- HCHO : Picarro and Hantzsch
- VOCs : GC-FID, PTRMS, VOCUS-PTR
- OVOCs : Br-CIMS and I-CIMS
- $CLNO_2$: CIMS
- GLYOX, $CH_3C(O)CHO$, NO_2, H_2O : CEAS
- PAN : GC
- ANs : CRDS
- Aerosol number density : CPC
- Aerosol size distribution : SMPS
- Aerosol chemical composion: AMS

Investigating atmospheric chemistry in a mixed environment (rural + forest)

Direct Ox (NO_2+O_3) Production Rate Measurement

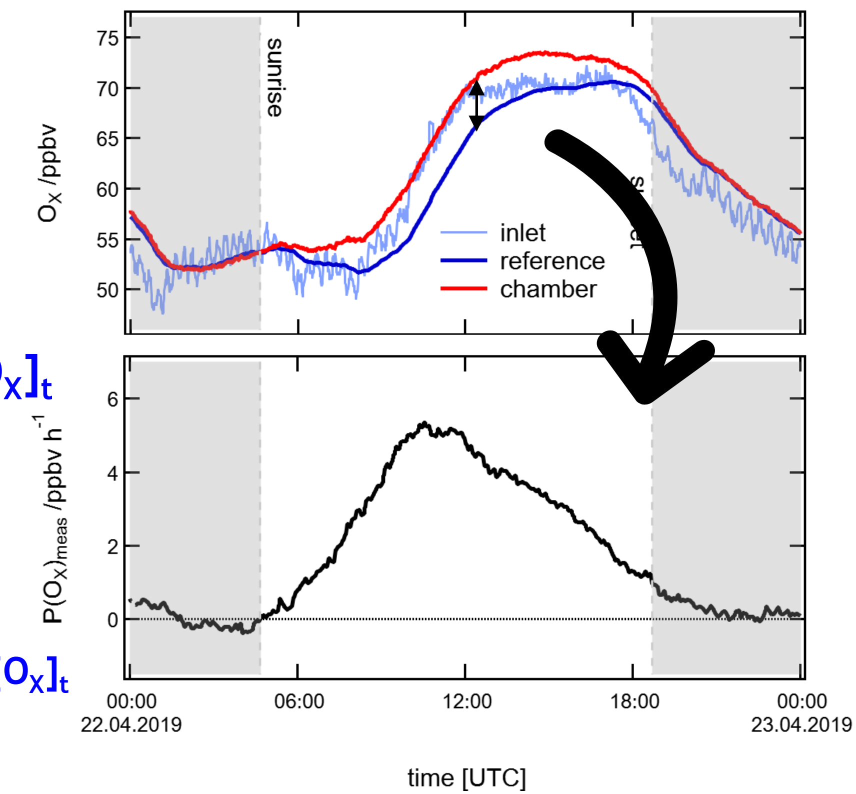
JULIAC-SAPHIR: continuous flow stirred tank reactor (CFSTR)

Air residence time $\tau = 1.13$ h



Measured P(O_X):

$$P(O_X)_{meas.} = \frac{[O_X]_c - [O_X]_t}{\tau}$$



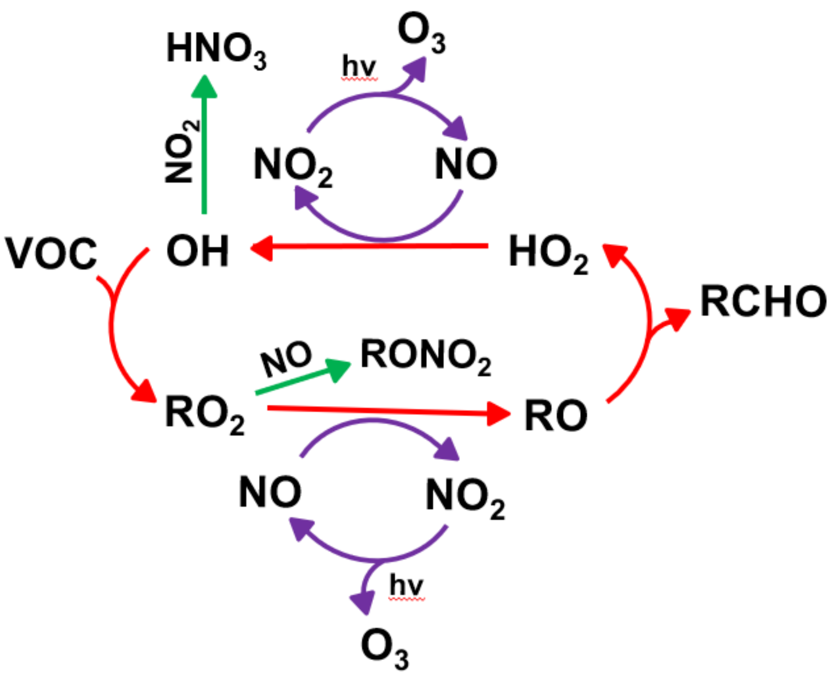
Numerical calculation of transport-based O_X (NO_2 + O_3) concentration $[O_X]_t$

$$[O_X]_t(t) = \frac{\Delta t}{\tau}\cdot[O_X]_i(t-\Delta t) + \left(1-\frac{\Delta t}{\tau}\right)\cdot[O_X]_t(t-\Delta t)$$

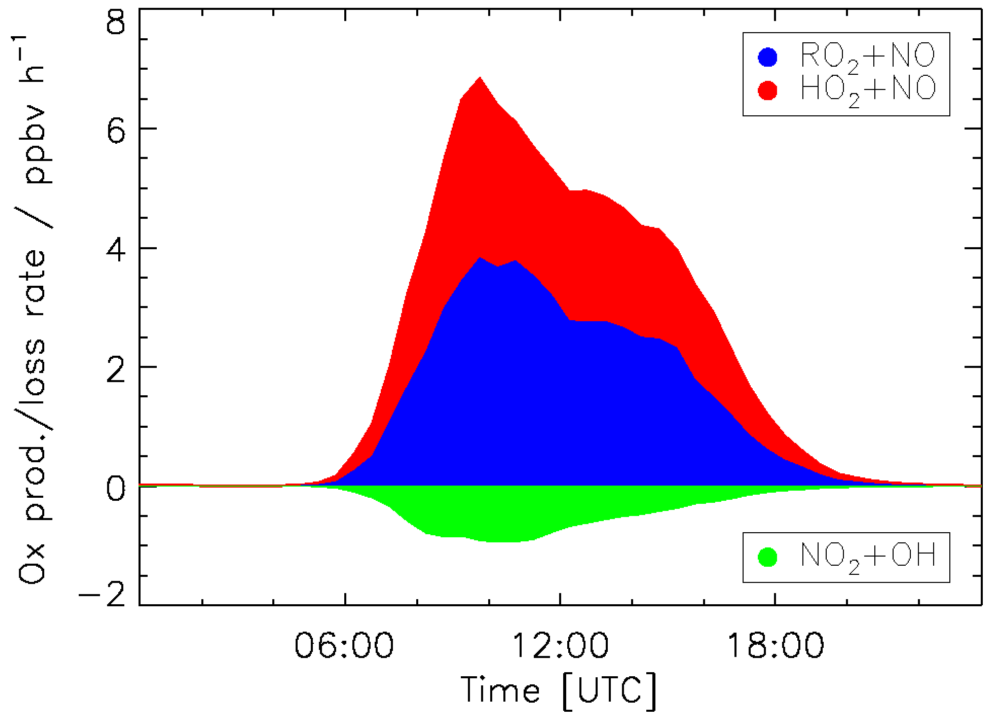
Calculated O_X Production Rate (Radicals)

$$P(O_X)_{calc.} = k_{NO+HO_2}[NO][HO_2] + \alpha k_{NO+RO_2}[NO][RO_2] - k_{NO_2+OH}[NO_2][OH]$$

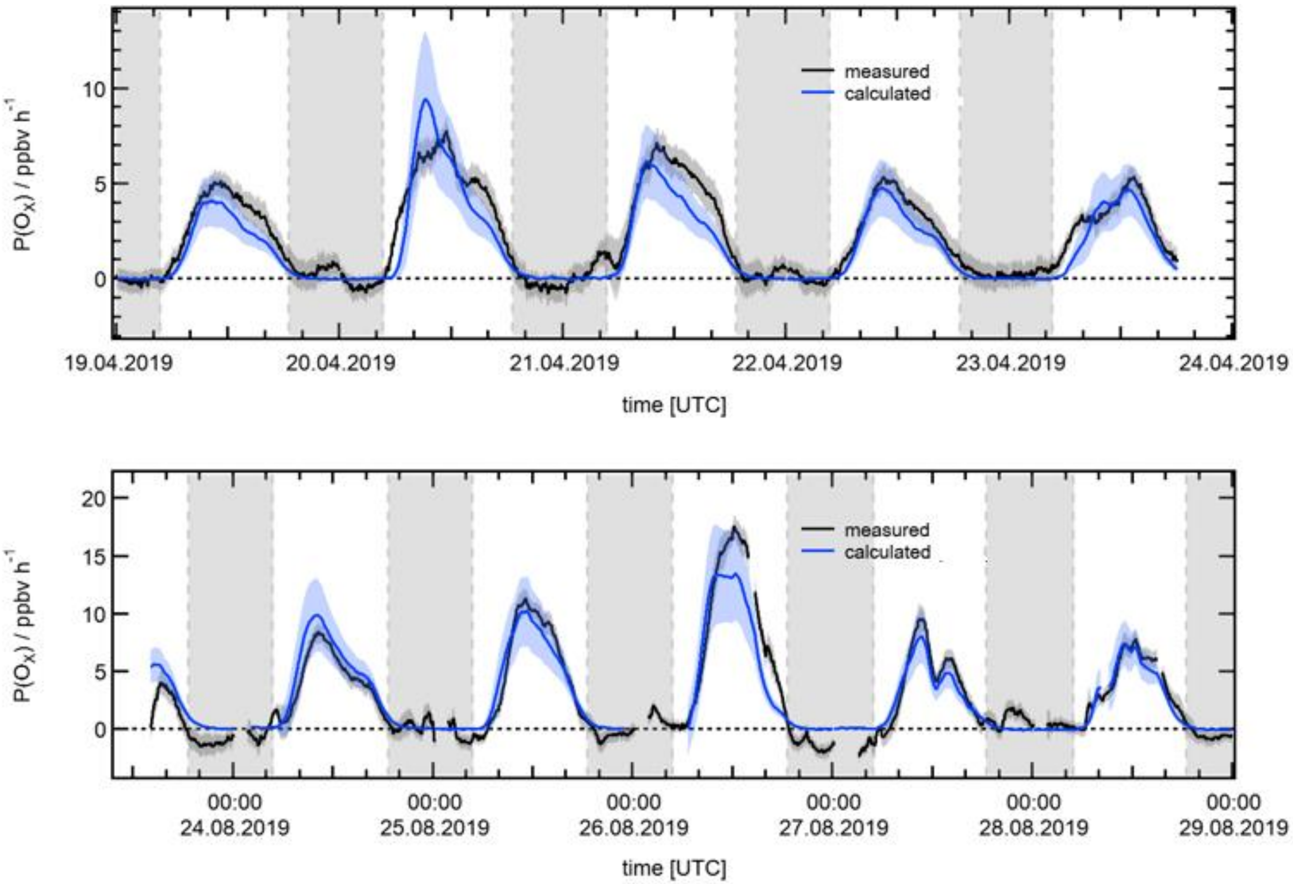
(α=0.95)



Median diurnal during summer (JULIAC-III)



O_X Production Rate Comparisons

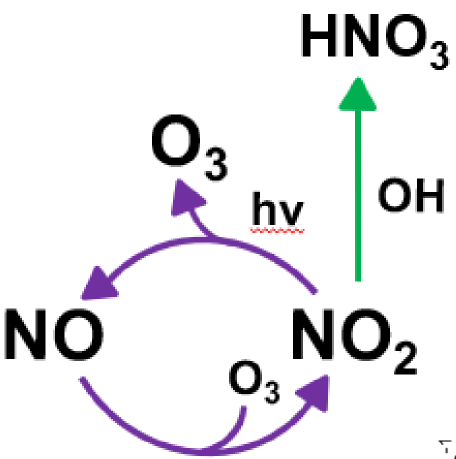


$P(O_X)_{meas.}$ vs $P(O_X)_{calc.}$

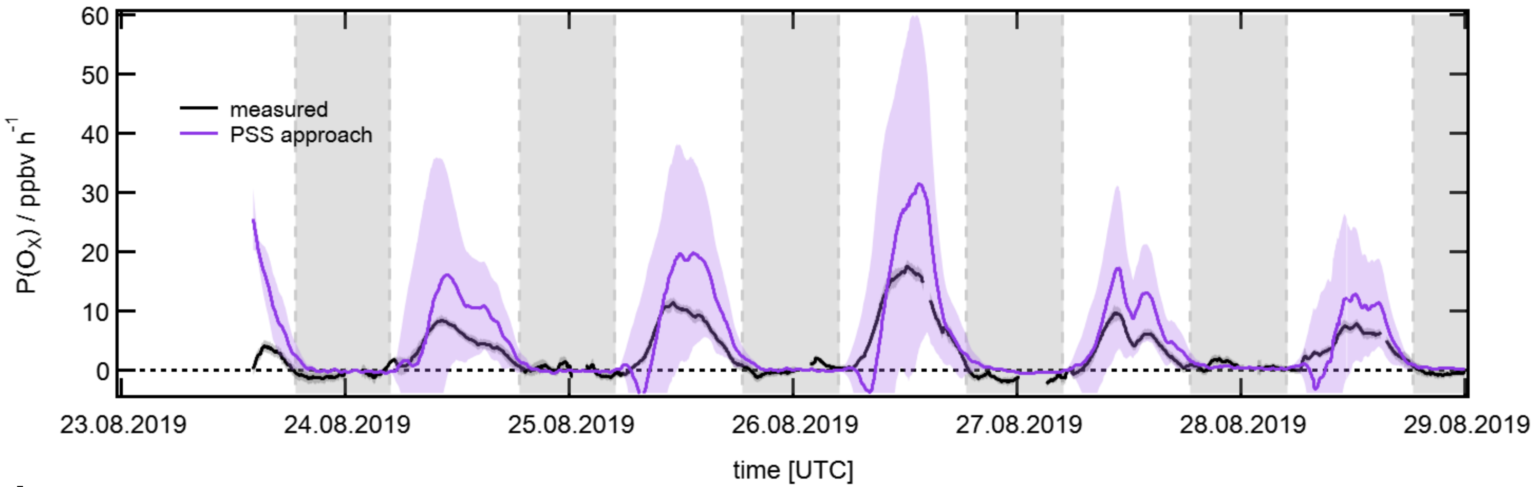
Linear regression:
Slope = 0.877 ± 0.003
Intercept = 0.044 ± 0.004
R^2 = 0.82

Tropospheric ozone production is mostly explained by radical reactions with NO_X

O_X Production Rate Comparisons



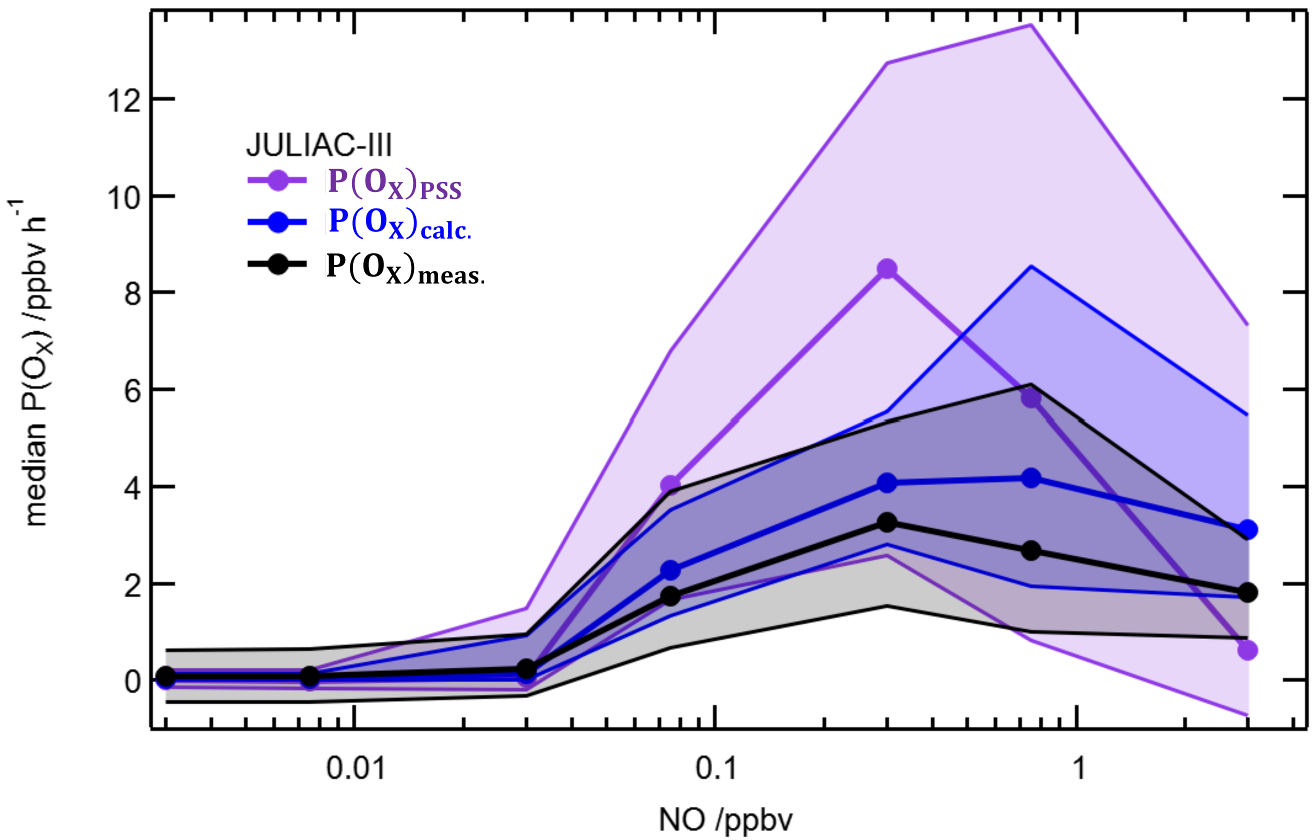
$$P(O_X)_{PSS} = j_{NO_2}[NO_2] - k_{NO+O_3}[NO][O_3] - k_{NO_2+OH}[NO_2][OH]$$



Linear regression:
Slope = 1.85 ± 0.02
Intercept = 0.11 ± 0.0
R^2 = 0.62

Large overestimation of O_X production rate by PSS approach.

O_X Production Rate Comparisons



Large overestimation of O_X production rate by PSS approach.

→ missing oxidant for NO without O_X production.

Summary

- **First long-term direct measurement of ozone production rate ($P(O_X)_{meas.}$) was performed with atmospheric radical measurements during each season in 2019.**

- **The JULIAC measurements confirm our current chemical understanding of ozone formation for air in a rural environment.**

- **Ozone production rate by PSS approach ($P(O_X)_{PSS}$) contains large uncertainty and generally overestimates ozone production rate.**

Outlook

- **Improving knowledge on estimating radical chemistry by chamber experiments or field campaign.**

- **Further investigations on ozone production rate in more polluted environment (by adding NO_X and VOCs to the chamber).**