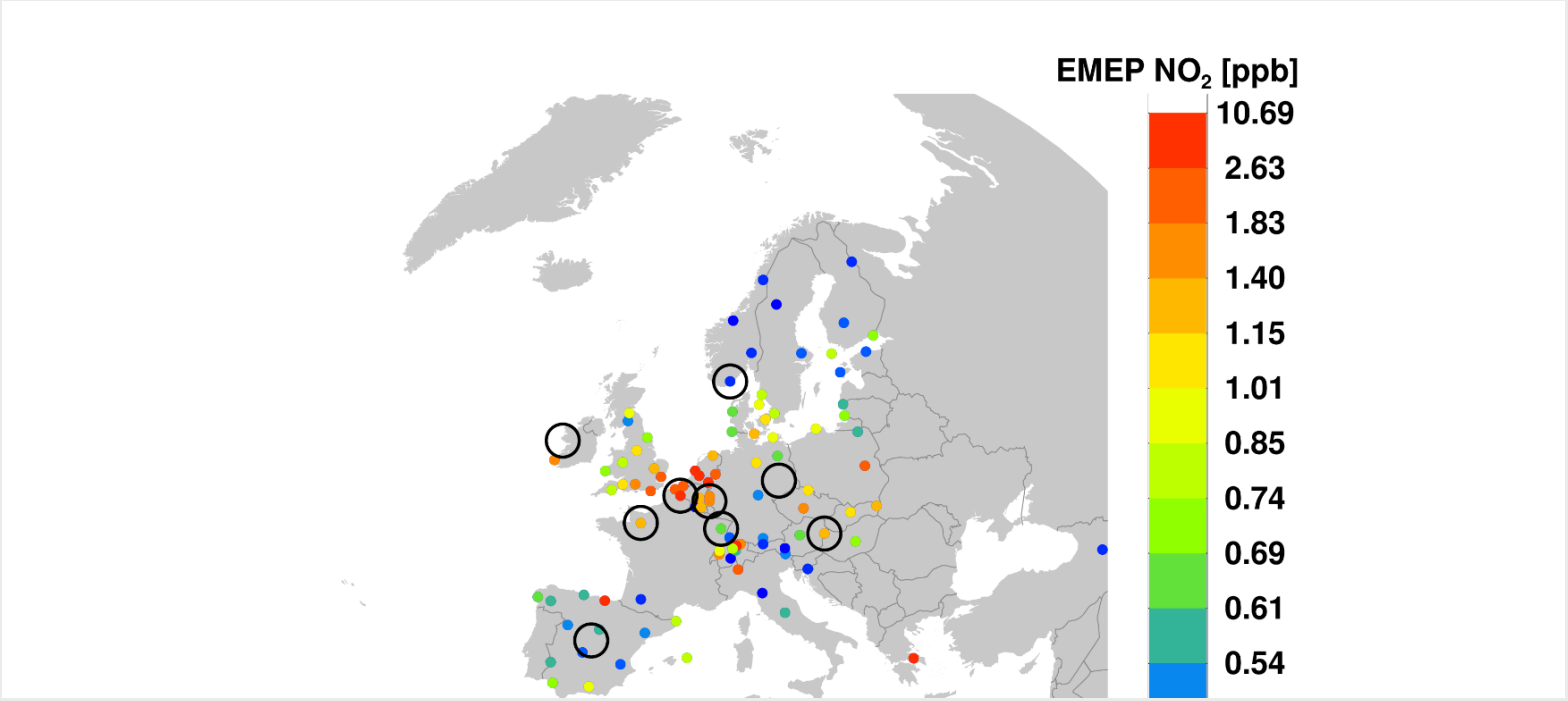
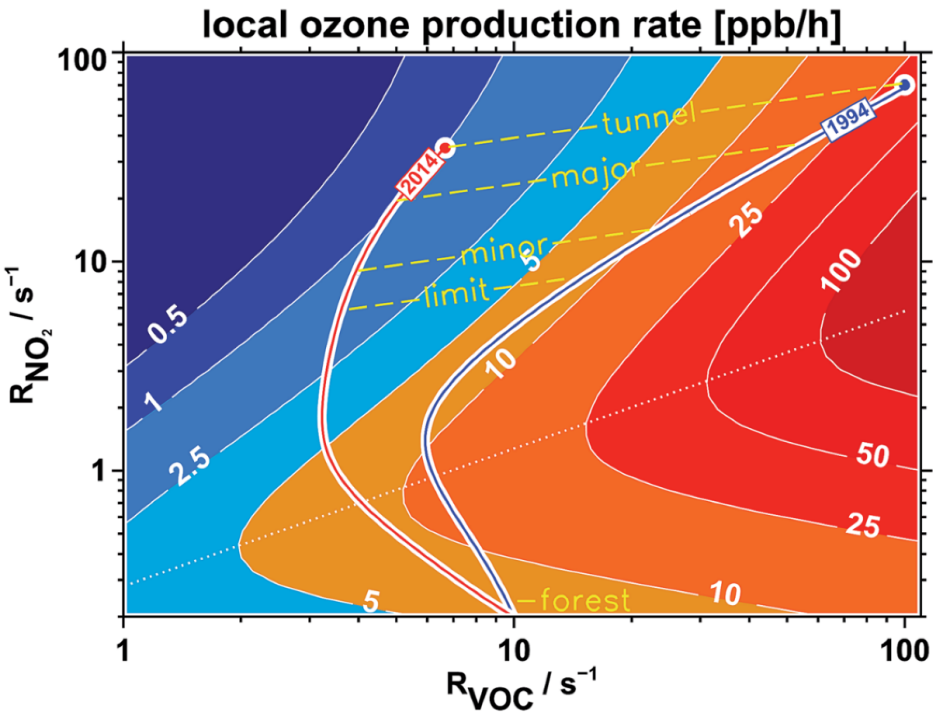


Ozone production deduced from offline precursor measurements in Europe

2024/06/07 I ROBERT WEGENER, RENÉ DUBUS, LIA KARDURMUS, BENJAMIN WINTER, LUKAS KESPER, THÉRÈSE SALAMEH, HEIDI HELLÉN, STEFAN REIMANN FRANZ ROHRER, DIETER KLEMP

Introduction

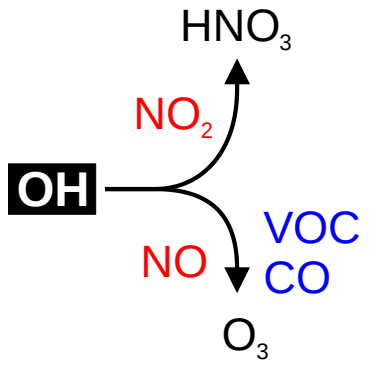


MCM3.2, 10min runtime, Summer conditions in Germany, J_{O1D}=2.9x10^{-5}s^{-1}, J_{NO2}=8.4x10^{-3}s^{-1}

- Local ozone production is determined by the ratio of VOC / NO_2

$$R_{VOC} = \sum k_{OH+VOC_i} \times [VOC_i]$$

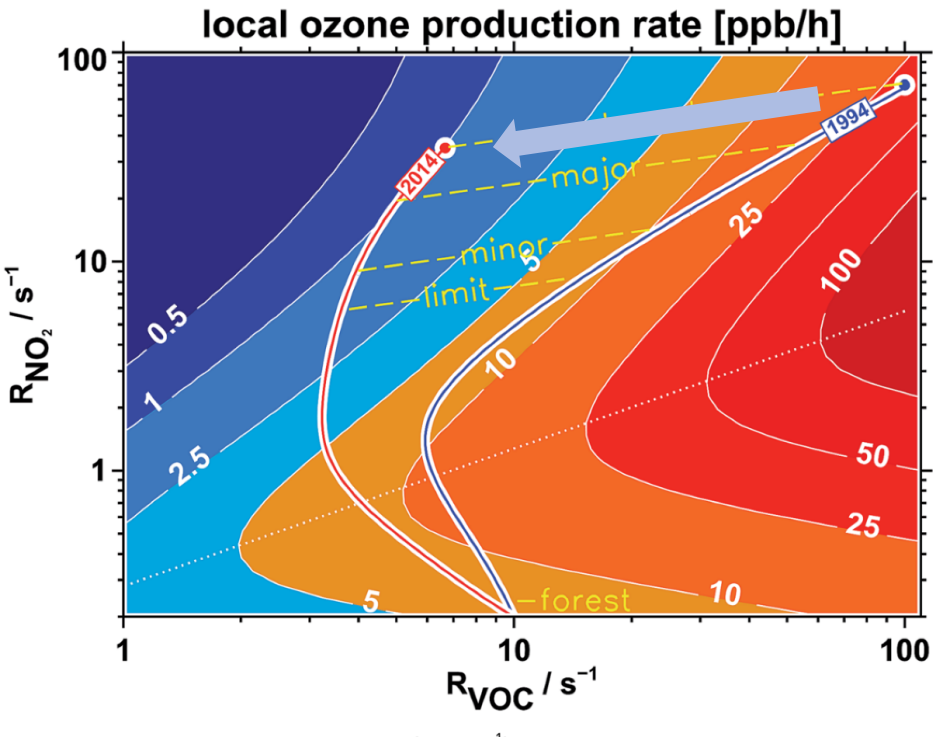
$$R_{NO_2} = k_{OH+NO_2} \times [NO_2]$$

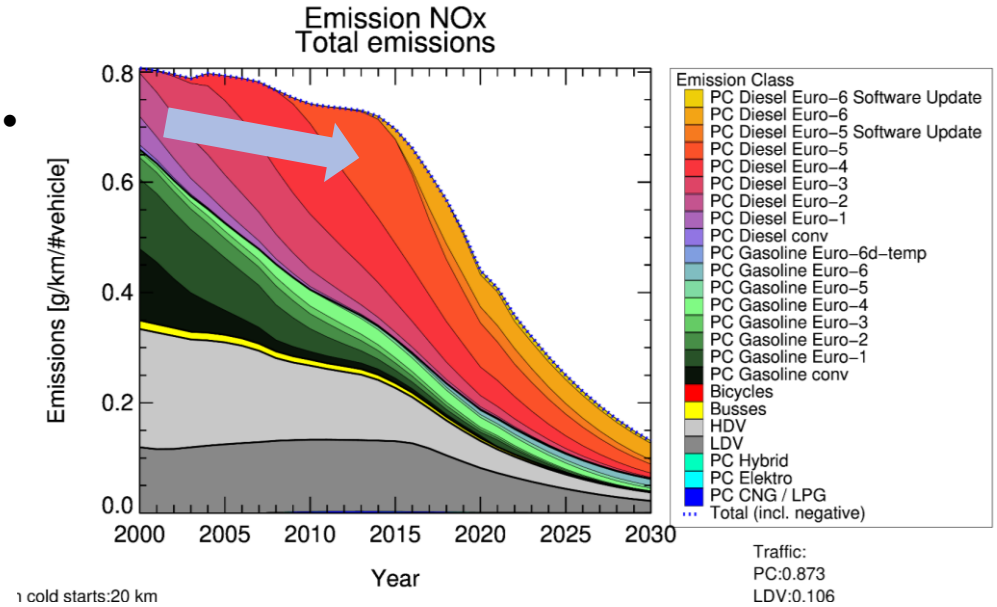


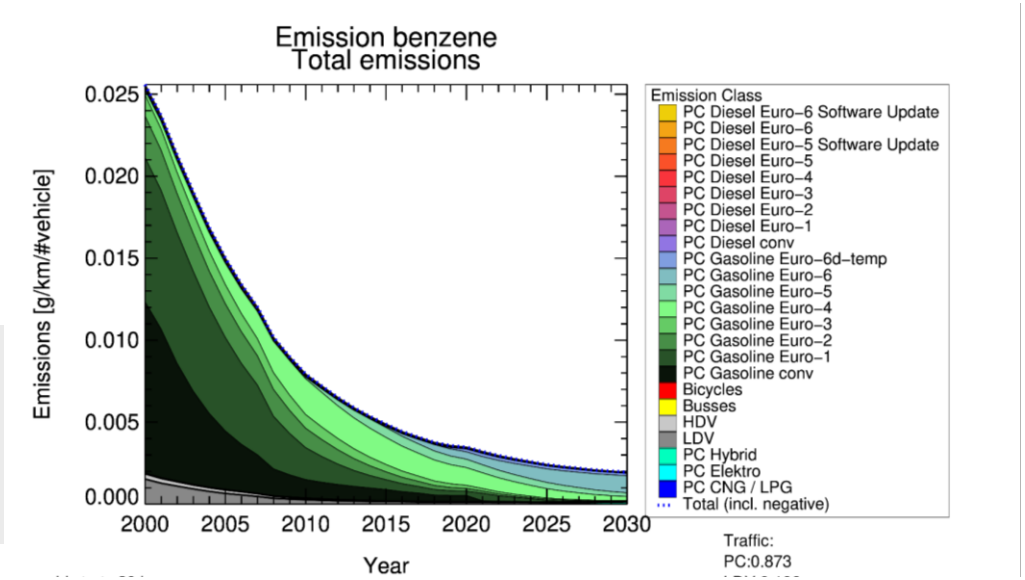
From: Ehlers, C., et al. (2016). "Twenty years of ambient observations of nitrogen oxides and specified hydrocarbons in air masses dominated by traffic emissions in Germany." Faraday Discussions 189: 407-437.)

Local ozone production

In German inner cities



- 

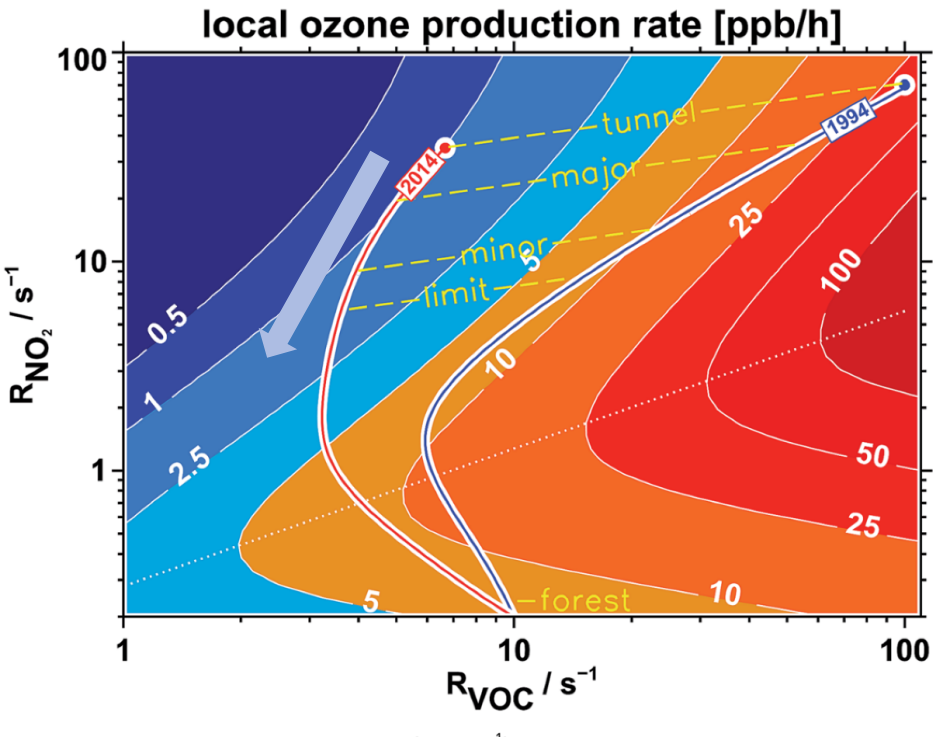


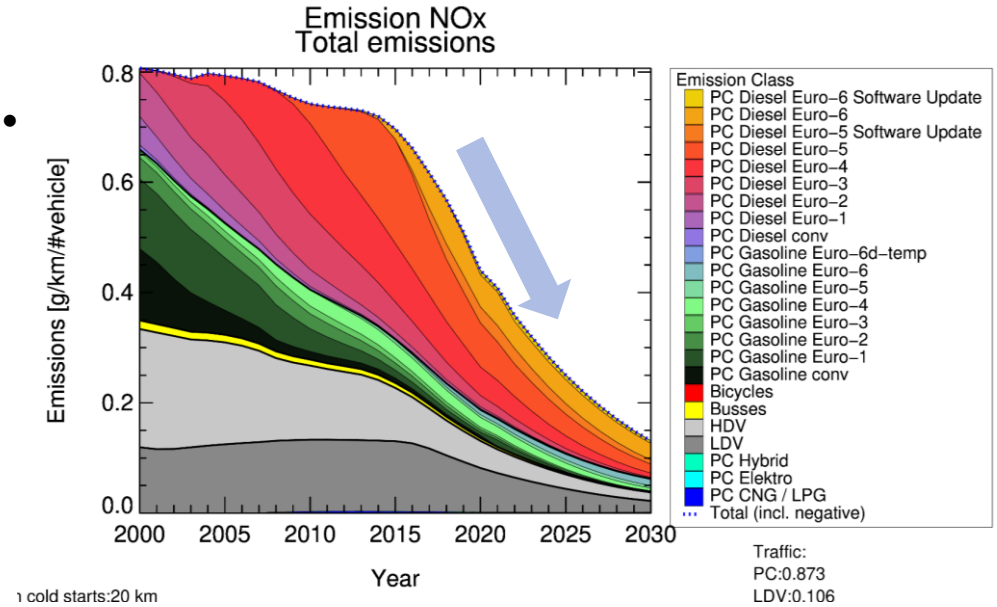
Before 2016: Small decrease in traffic NOx emissions compared to the decrease in VOC emission

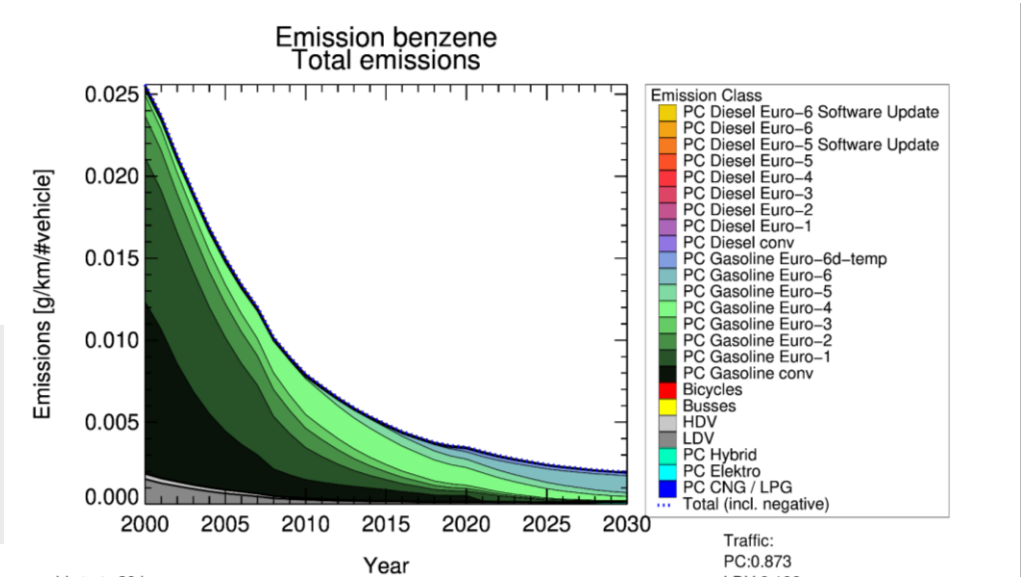
Traffic emission in German Inner Citites (HBEFA4.2)

Local ozone production

In German inner cities



- 

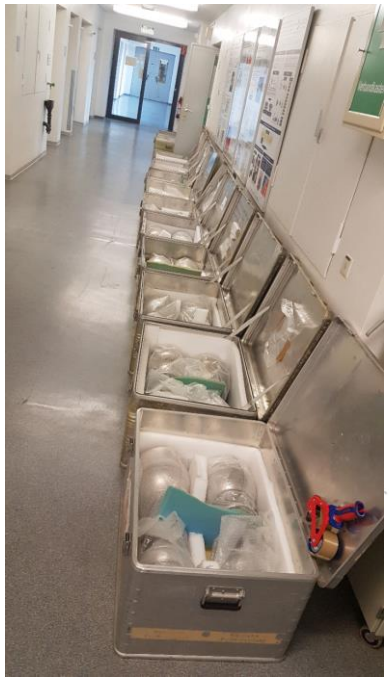


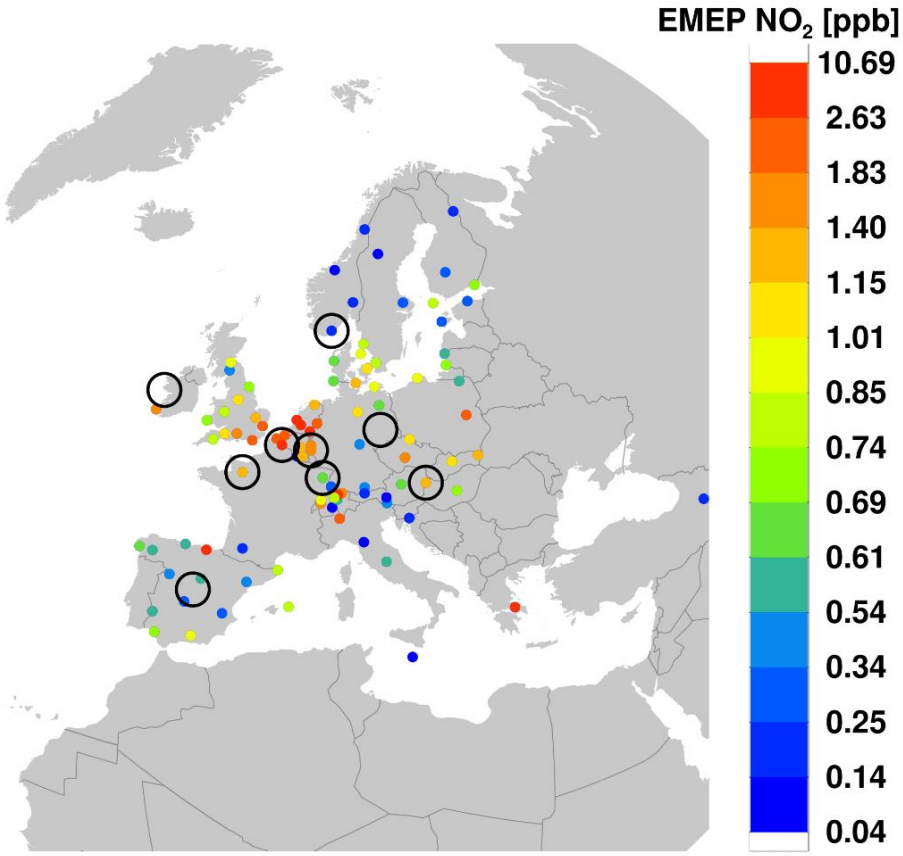
After 2016: Faster decrease in traffic NOx emissions compared to the decrease in VOC emission

Traffic emission in German Inner Citites (HBEFA4.2)

The EMEP 2022 intensive campaign

Offline canister measurements

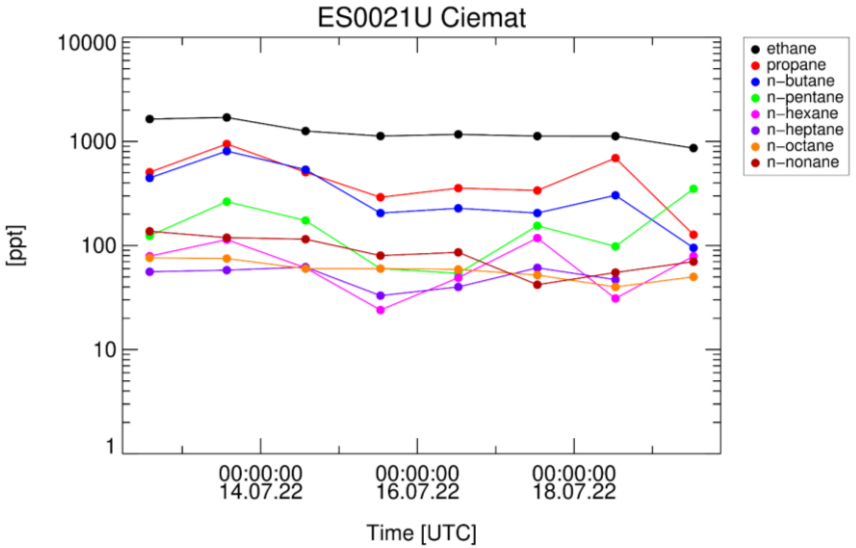


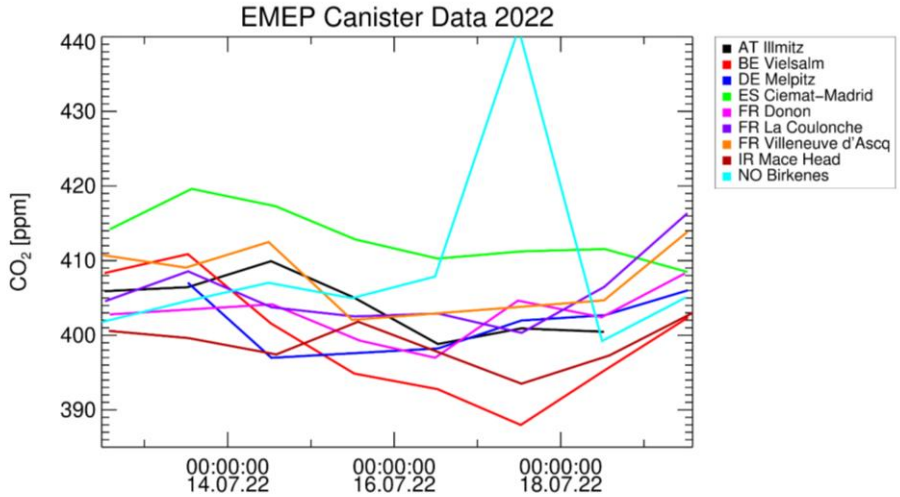


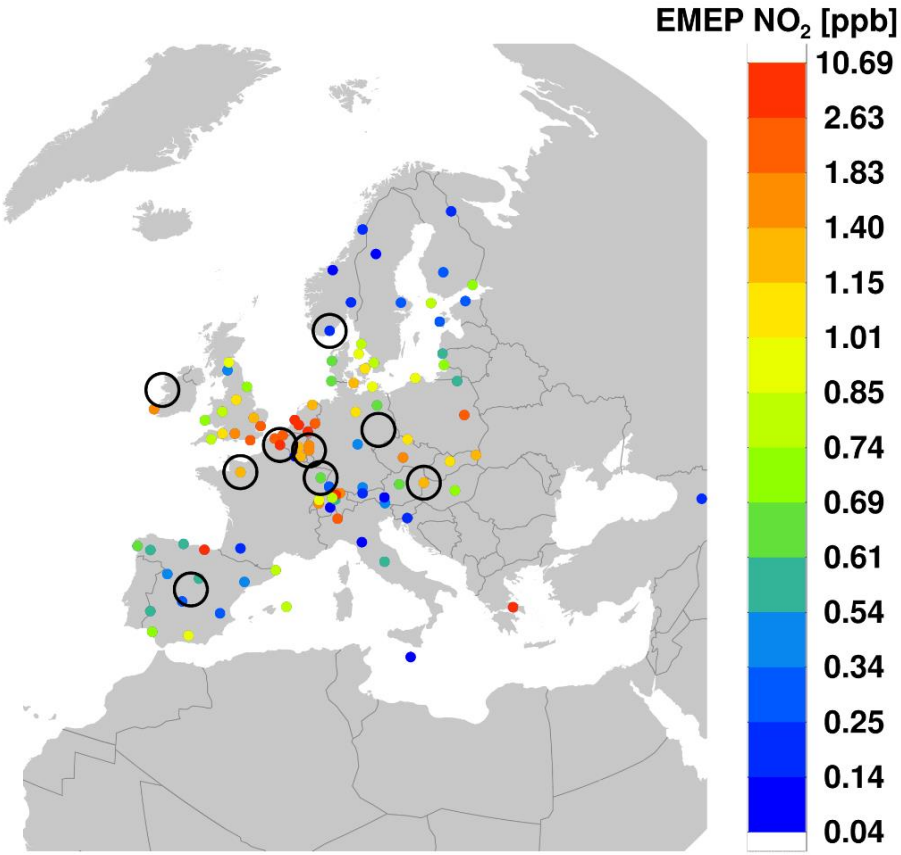
Mean summer NO_2 mixing ratio

The EMEP 2022 intensive campaign

Offline canister measurements





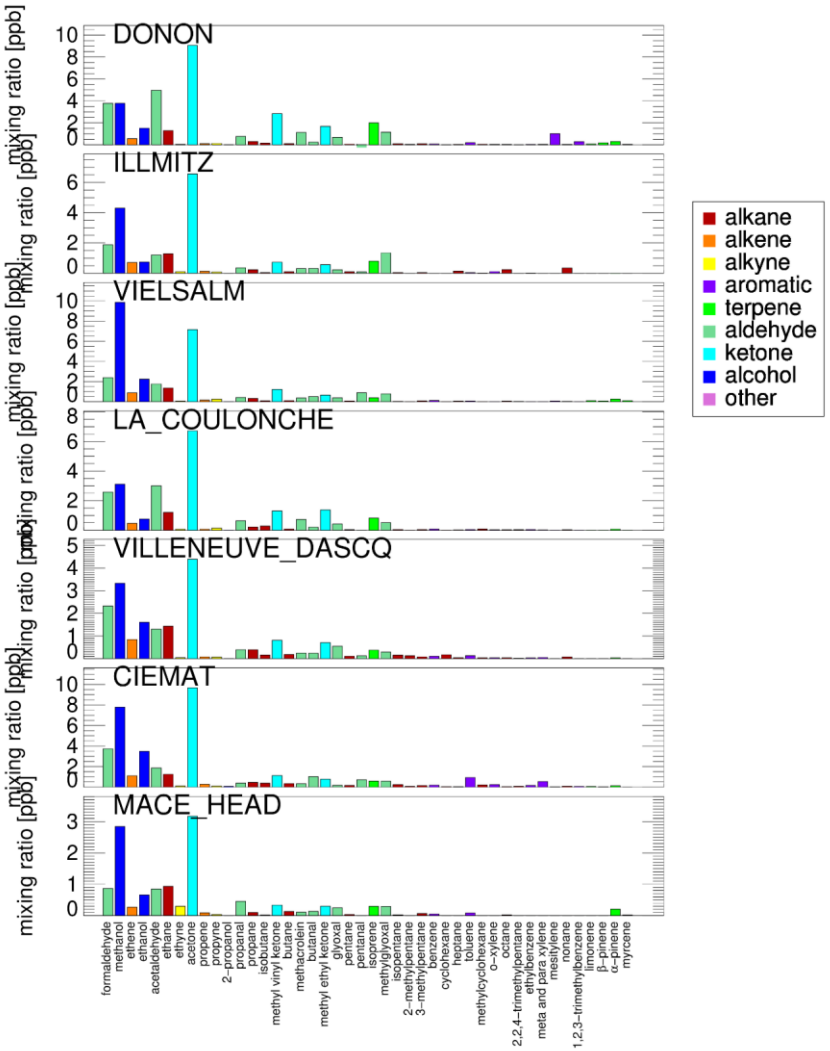


Mean summer NO_2 mixing ratio

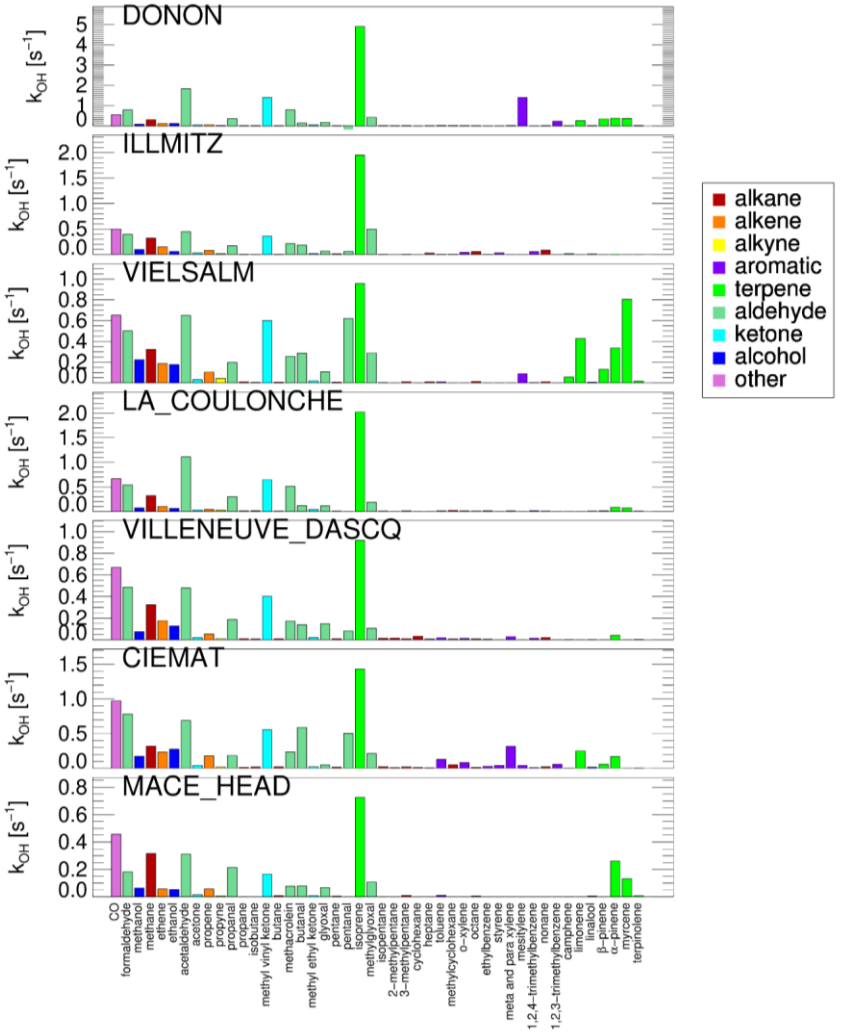
Mean VOC concentrations

Canister data + data from tenax tubes + OVOC DATA

Mean mixing ratios

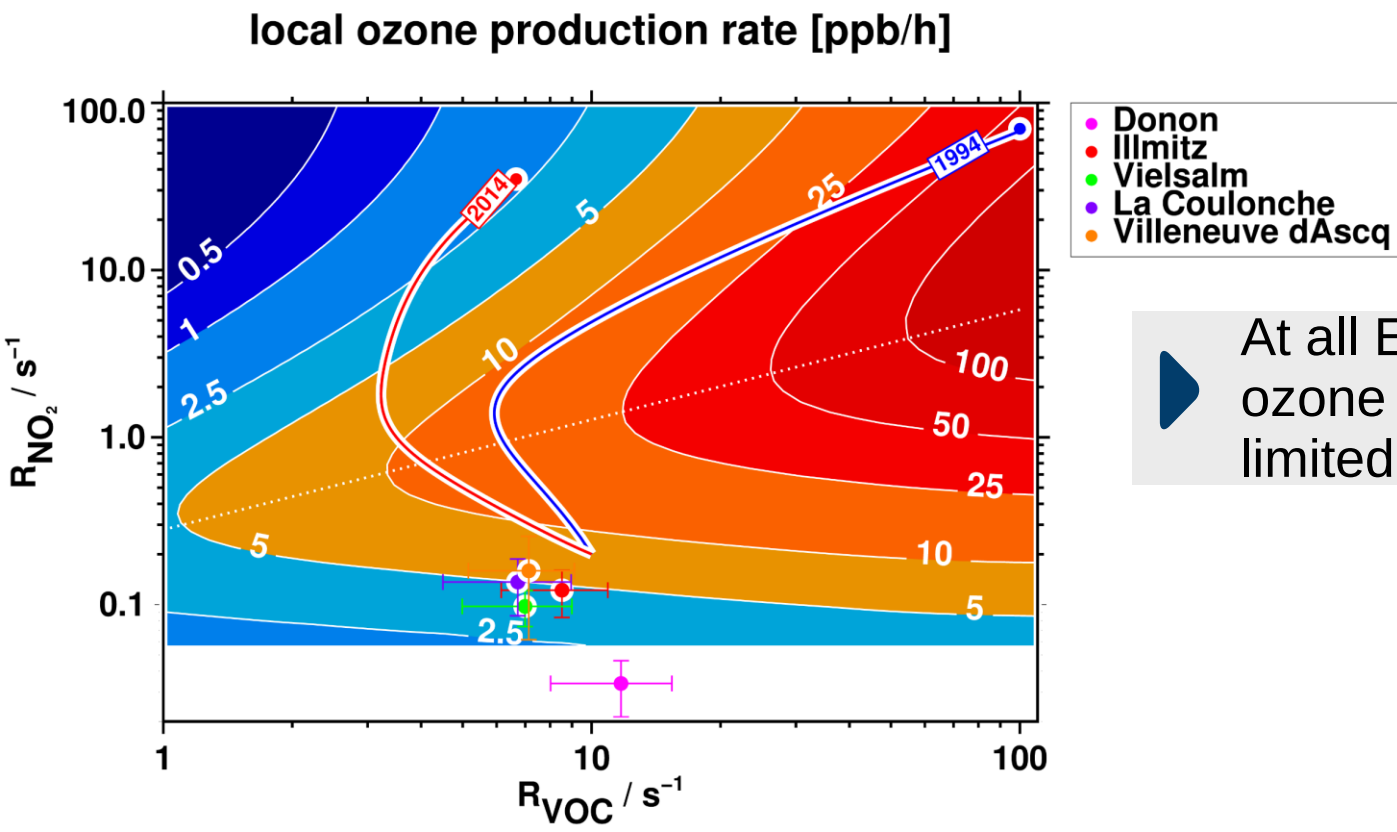


Mean OH reactivity



Local ozone production

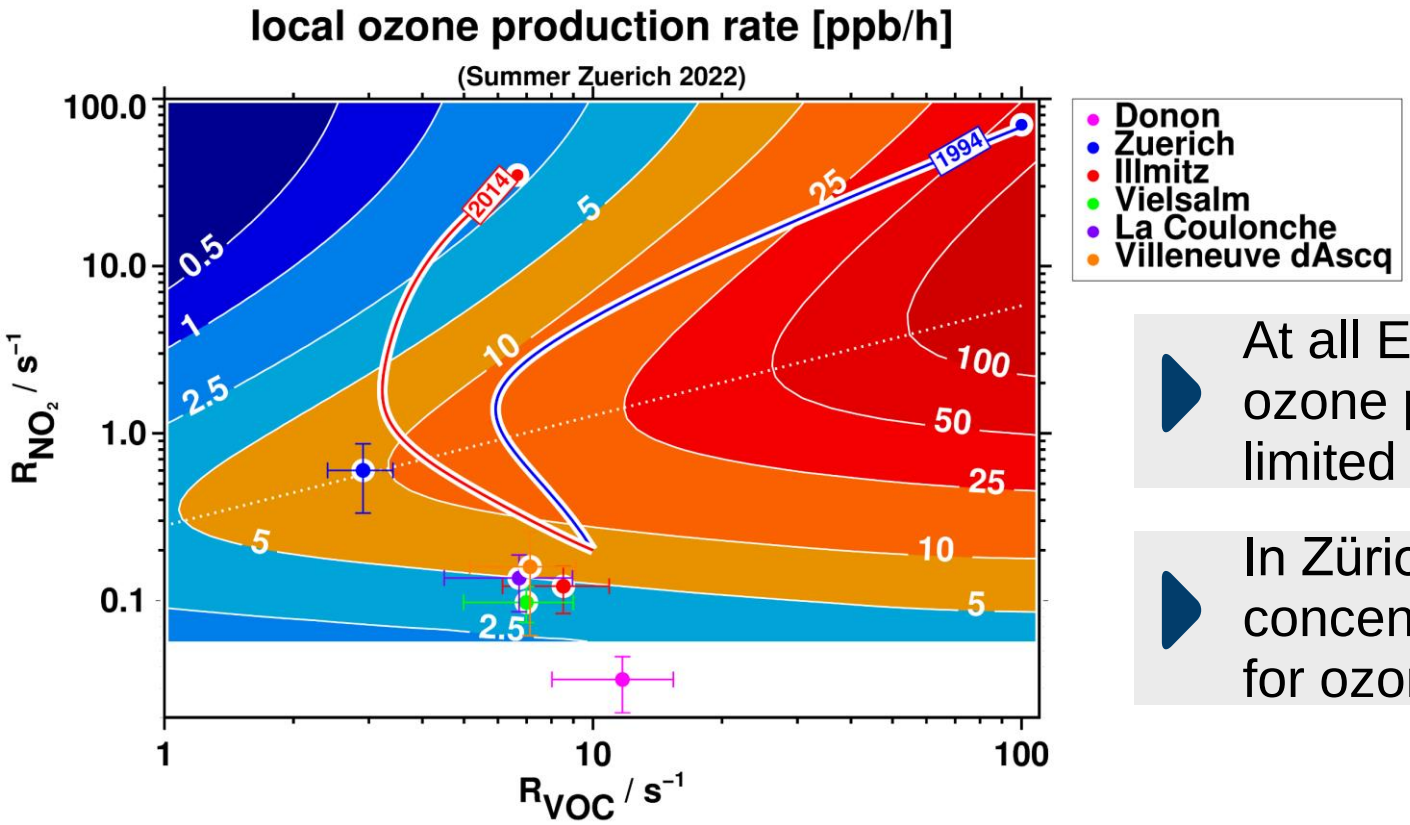
Averaged values 2022/07/12-2022/07/20 noon



- At all EMEP sites the ozone production is NOx limited

Local ozone production

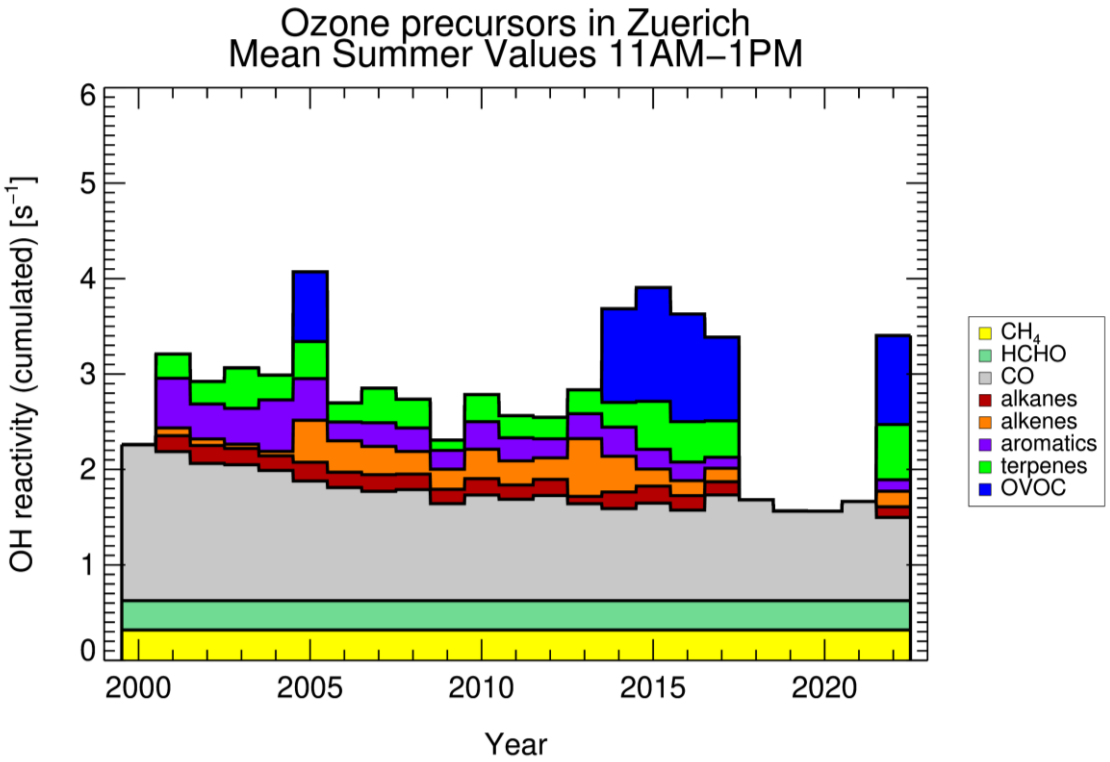
Averaged values EMEP and Zürich



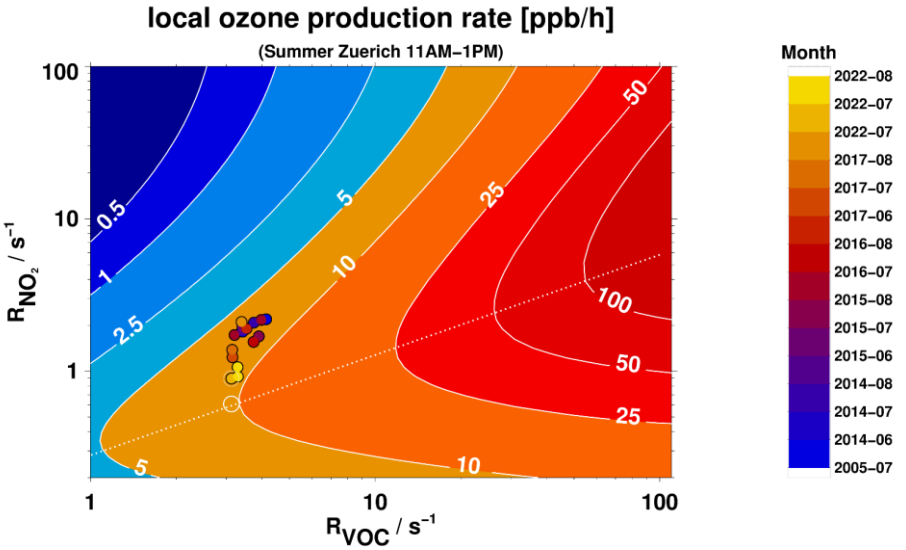
- At all EMEP sites the ozone production is NOx limited
- In Zürich NOx concentration is optimal for ozone production

Local ozone production in Zürich

Long term trend



- Zürich has a long record of VOC and OVOC measurements



- Measurements shows a trend towards a higher ozone production rates
- Similiar to obserations in China

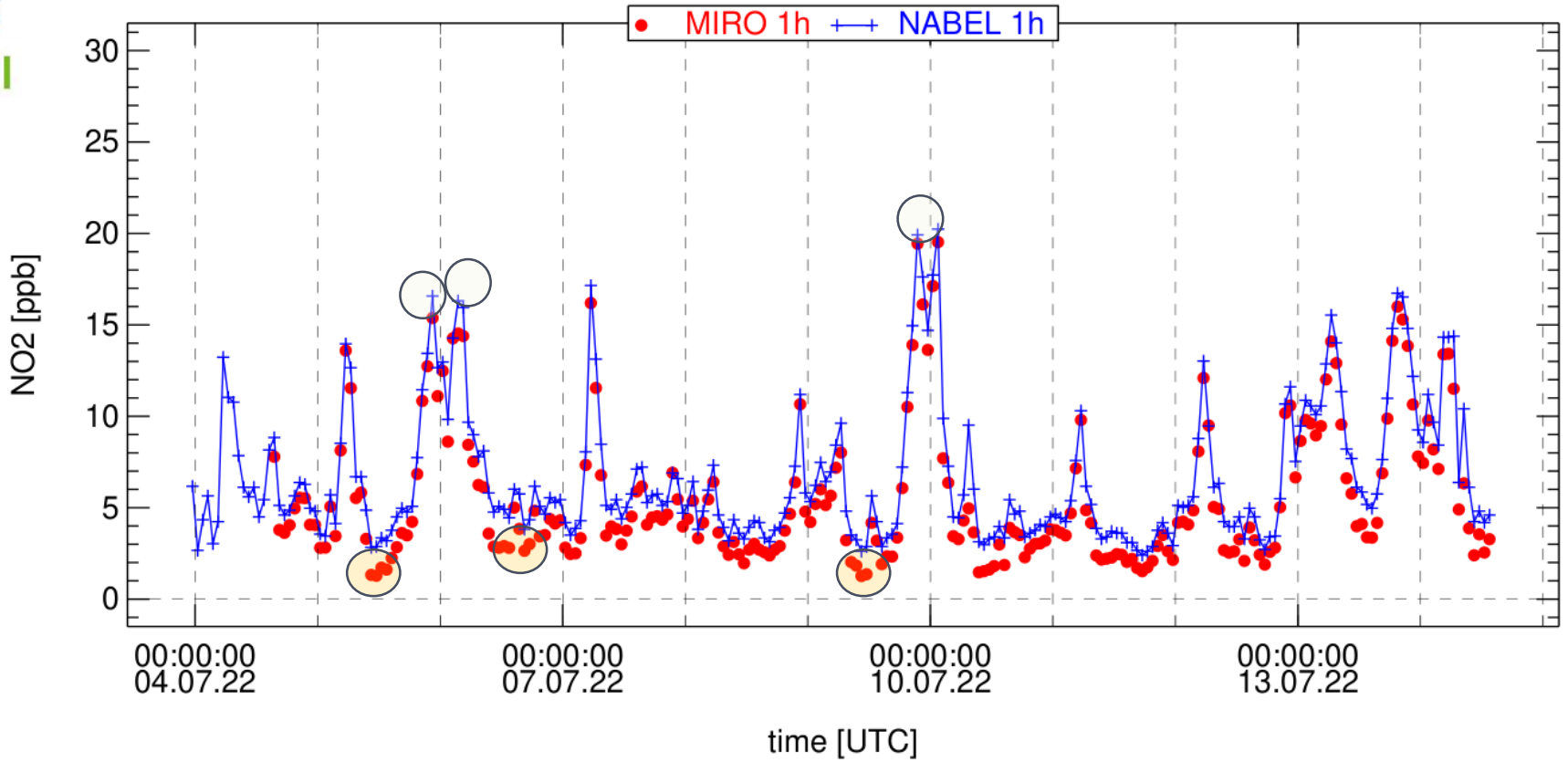
Wang, W., et al. (2024). "Ozone pollution mitigation strategy informed by long-term trends of atmospheric oxidation capacity." Nature Geoscience **17**(1): 20-25.

NO_2 measurements in Zürich

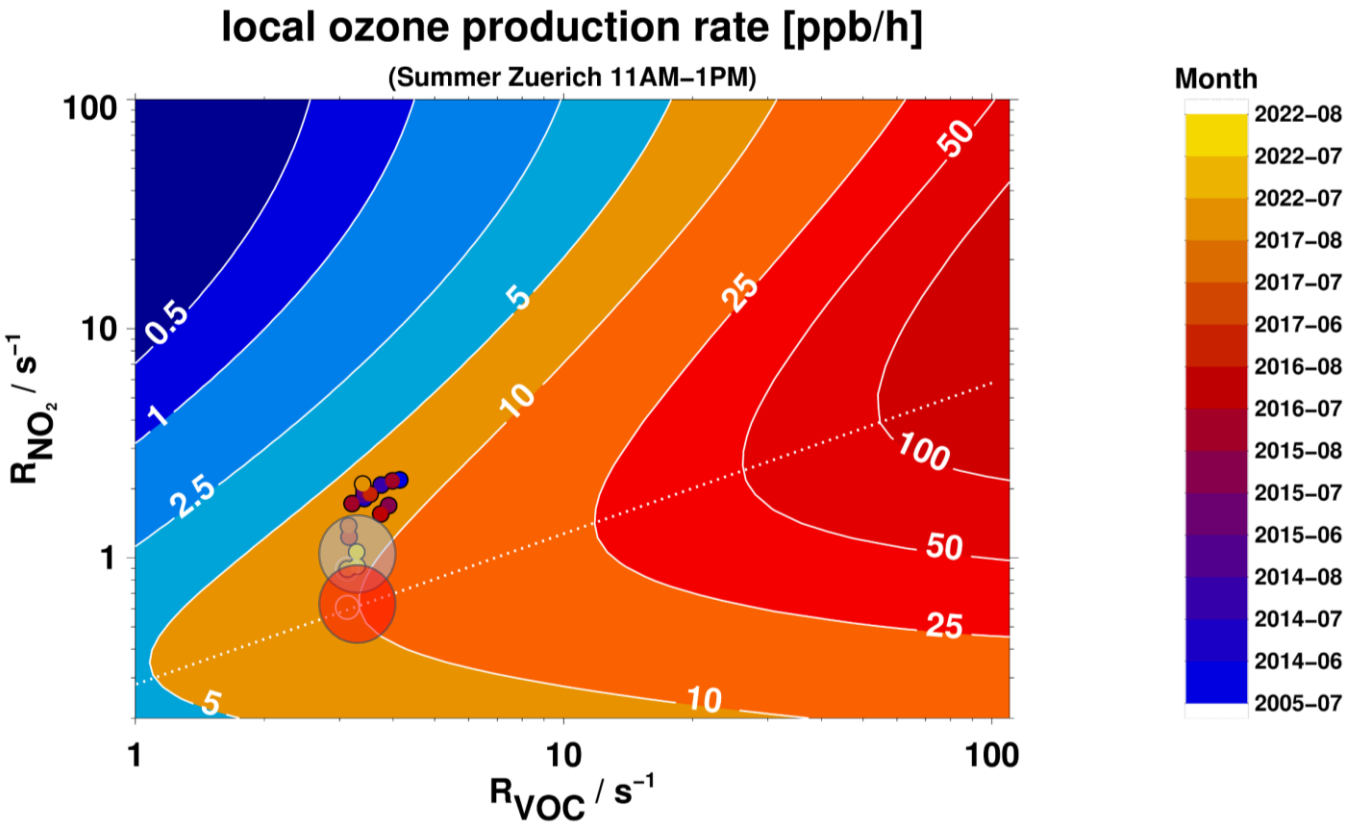
Comparison of TDL data (MIRO FZJ) and data from molybdenum converters

Good agreement at night

Overestimation during the day



Effect of the NO_2 measurement technique on the calculated ozone production

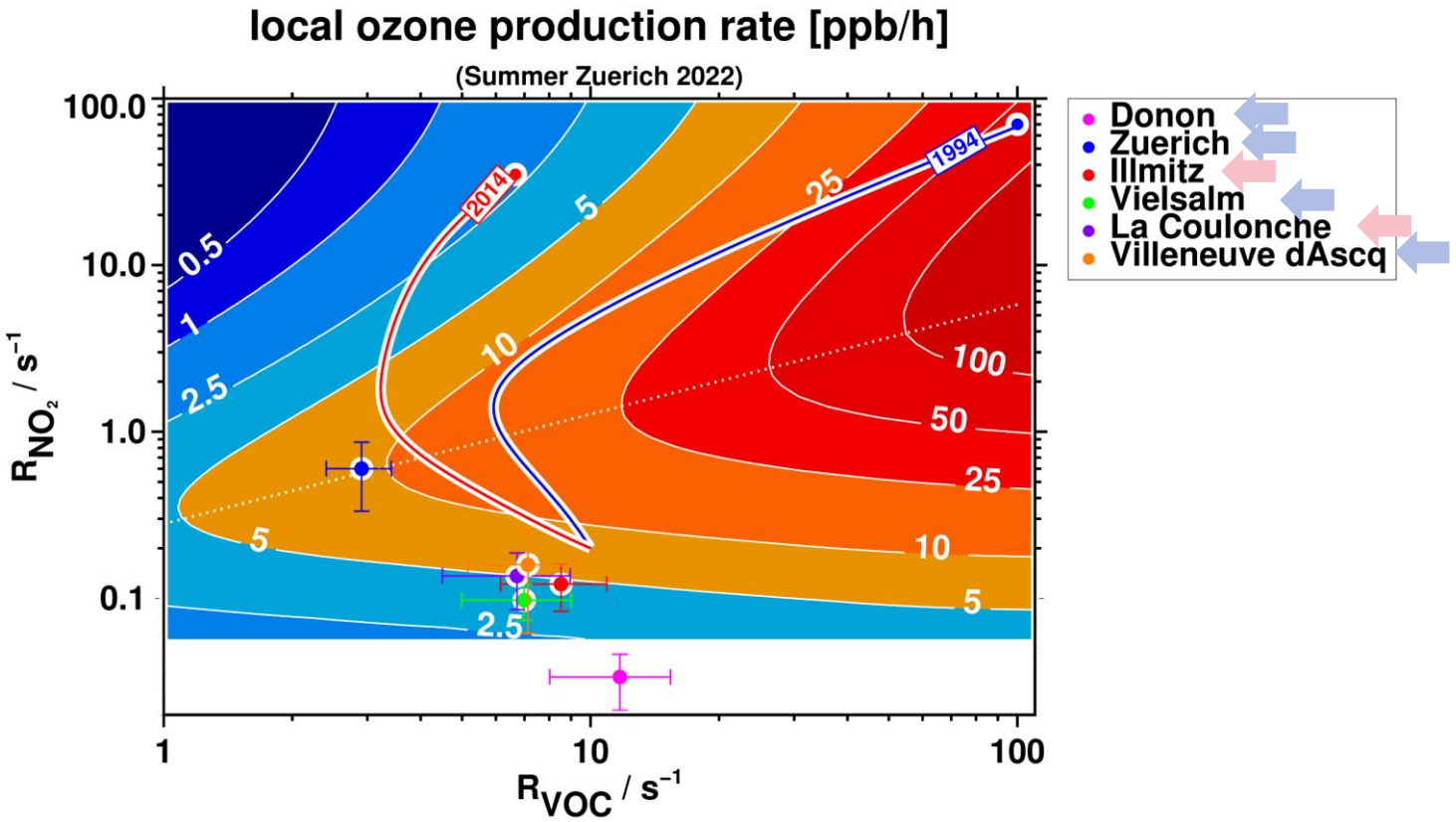


Measurments with molybdenum convertes lead to an underestimation of ozone production at high NOx

2022 with Molybdenum Converter

2022 wiith NO2 from TDL

Effect of the NO_2 measurement technique on the calculated ozone production



Measurments with molybdenum convertes lead to an overestimation of ozone production at low NOx

Molybdenum Converter

Photolytical Converter

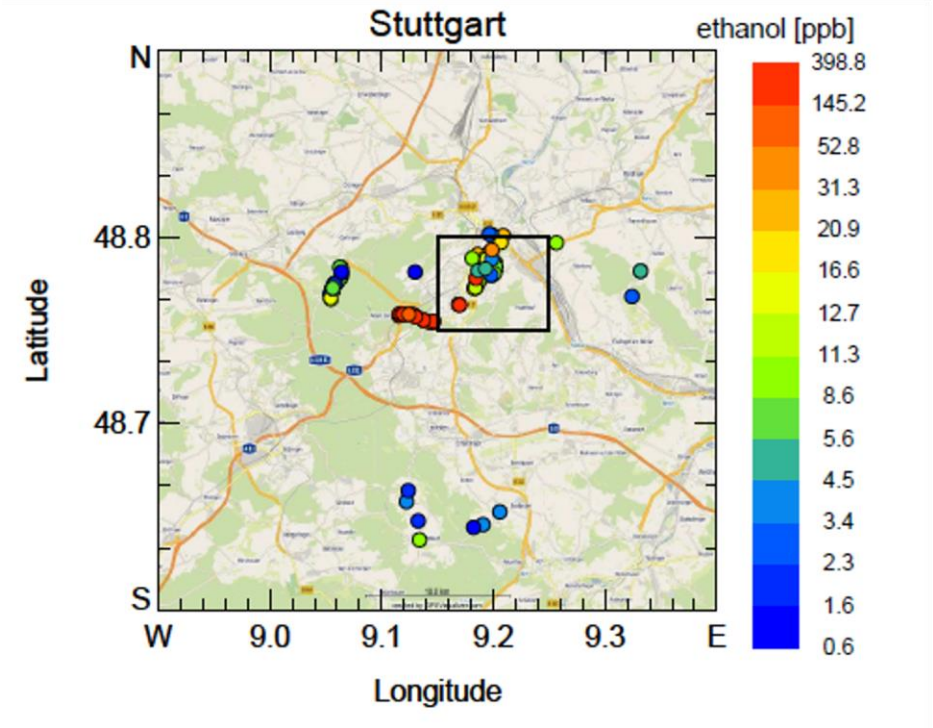
EMEP intensive campaign 2022 summary

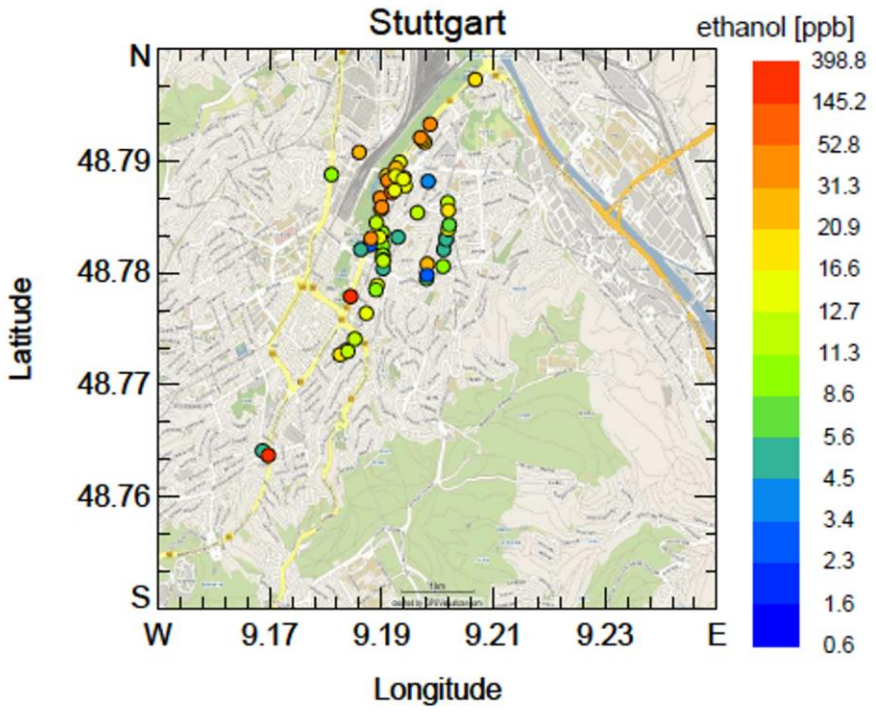
- **Biogenic compounds (mainly isoprene) and OVOCs are the main contributors of the OH loss at the EMEP sites**
- **Ozone production at the EMEP sites are NOx limited**
- **In Zürich, the VOC to Nox ratio is optimal for ozone production**
- **Using NO_2 data from Molybdenum CL instruments lead to an over- or underestimation of ozone production**

VOC in German inner cities

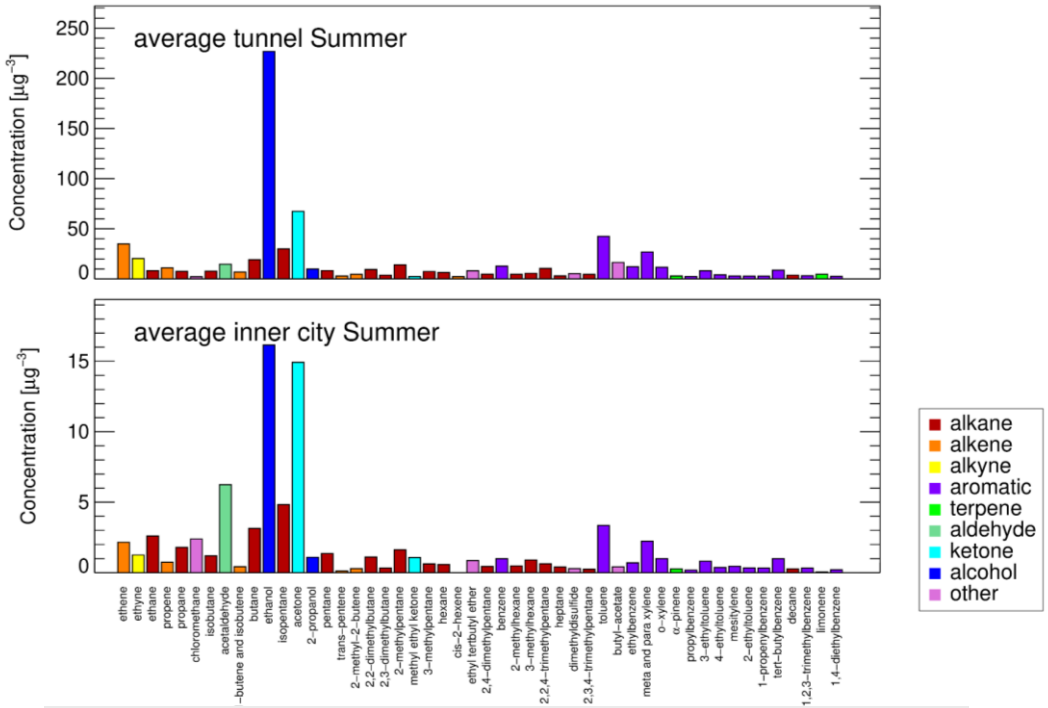
From mobile measurements

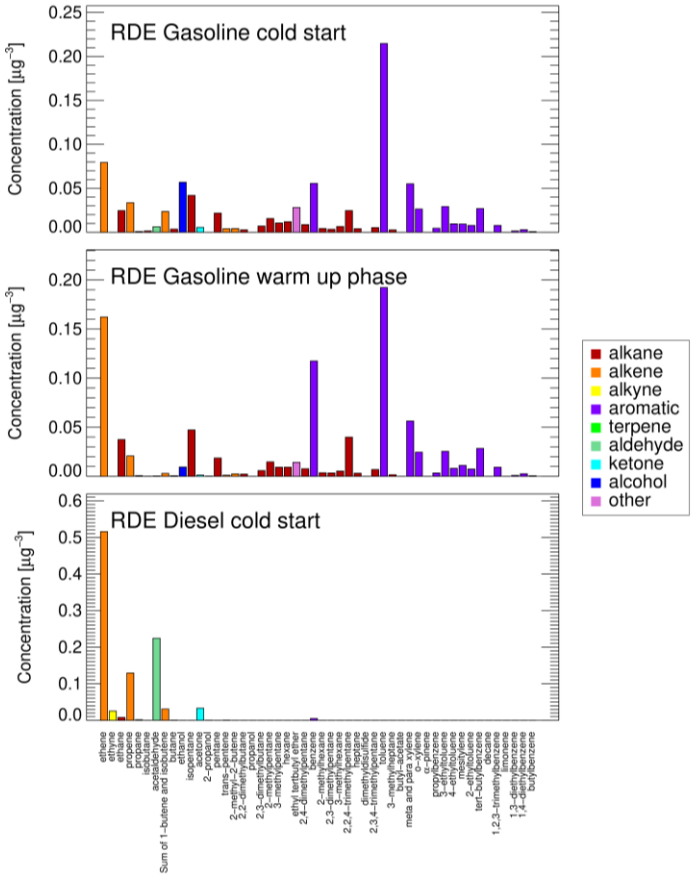
Distribution of VOCs can be deduced by mobile measurements





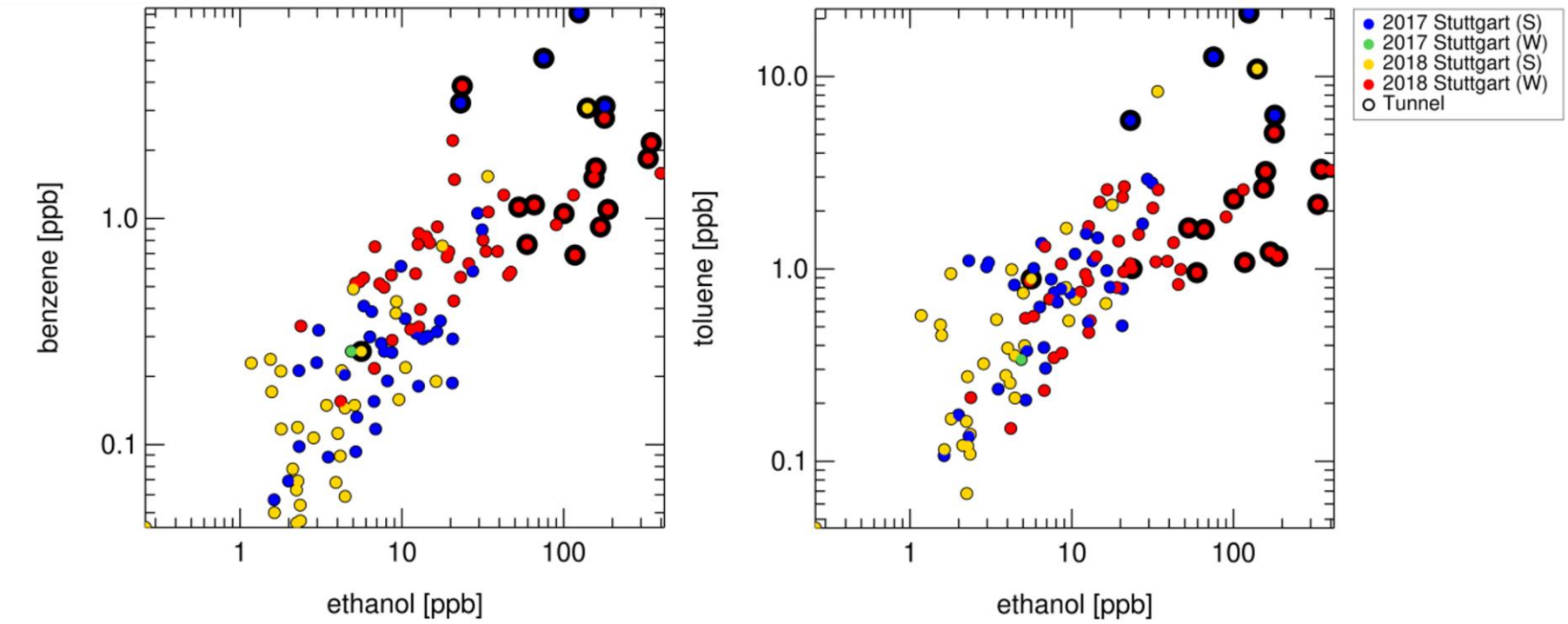
VOC in German inner cities





- OVOCs (especially Ethanol) are abundant in inner cities but are only minor components in exhaust data

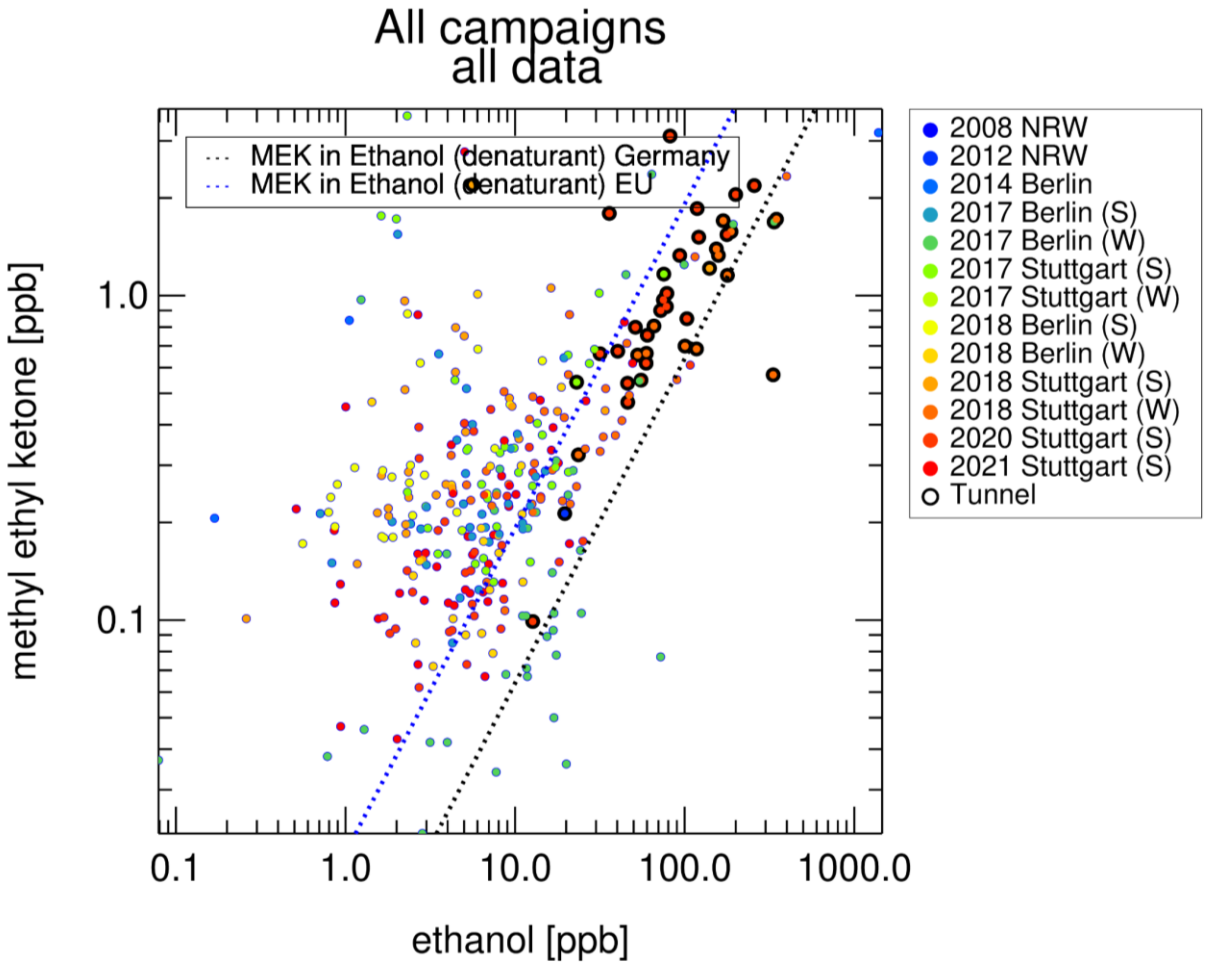
Ethanol correlates well wittraffic-related emissions



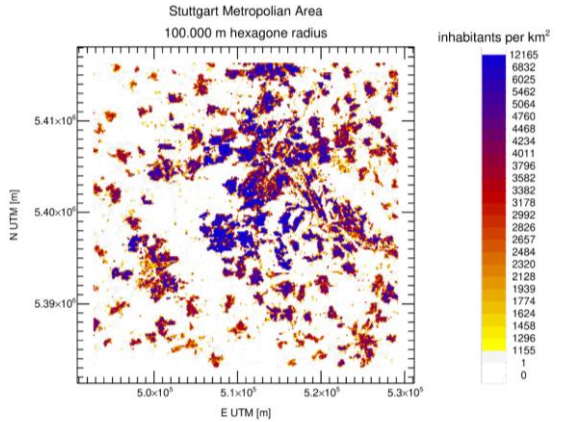
- Still, ethanol correlates well with, e.g, benzene and toluene

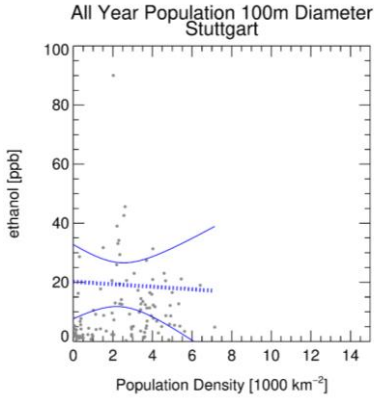
Ethanol is a technical product

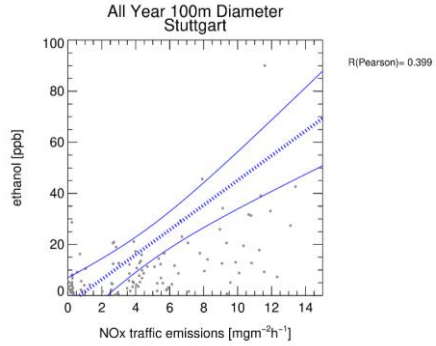
The ratio of ethanol to to its denaturating agent methyl ethyl ketone agrees to the values prescribed in EU and Germany



Ethanol concentration corelates with traffic







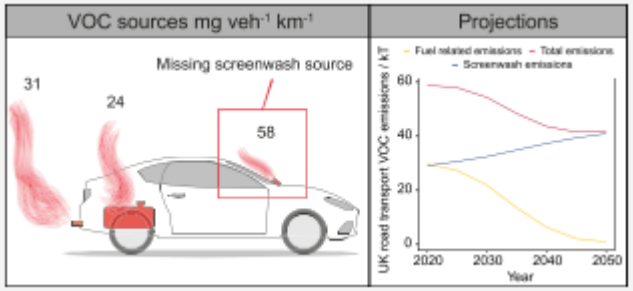
- The spatial distribution is reflected by traffic model data rather then by population density data

- The situation is different to the US where population density is higher

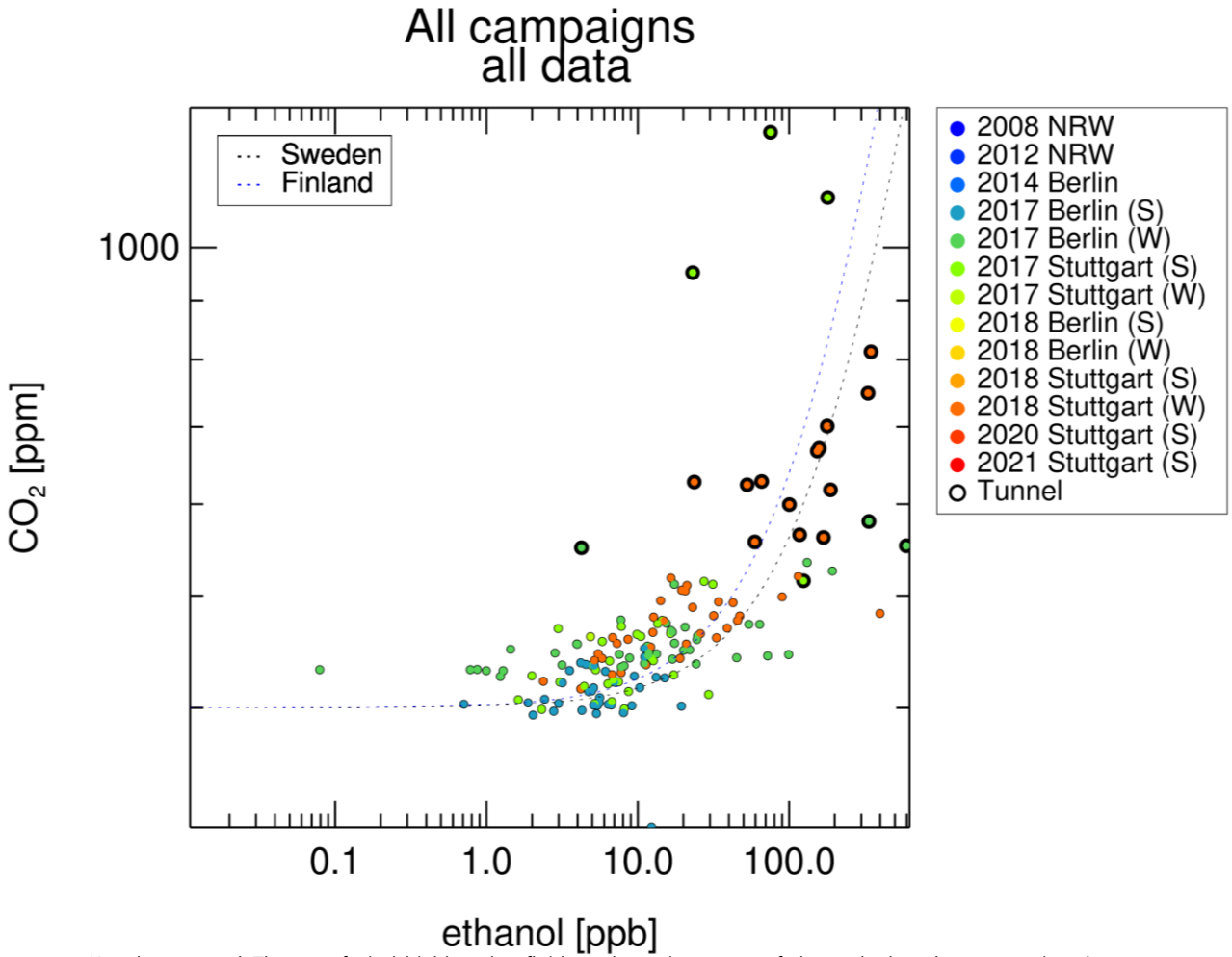
Gkatzelis, G. I., Coggon, M. M., McDonald, B. C., Peischl, J., Aikin, K. C., Gilman, J. B., Trainer, M., and Warneke, C.: Identifying Volatile Chemical Product Tracer Compounds in U.S. Cities, Environ. Sci. Technol., 55, 188-199, 10.1021/acs.est.0c05467, 2021.

Ethanol from windscreen washer fluid

- The ratio of Ethanol to CO_2 corresponds to the ratio of Ethanol consumption in windscreen washer fluid to traffic CO_2 emission as reported by Finland and Sweden to the EU



Cliff, S. J., et al. (2023). "Unreported VOC Emissions from Road Transport Including from Electric Vehicles." Environmental Science & Technology 57(21): 8026-8034.



Karadurmus et al. The use of windshield washer fluids as the major source of elevated ethanol concentrations in German urban air (In Preparation)

Thank you / Dzięki

Thérèse Salameh, Heidi Hellén, Stefan Reimann for providing data

Iris Buxbau, Marie Dury, Laurent Poulain, Elias Diaz, Emmanuel Stuart Ritchie the sites for sampling

EMEP, ACTRIS and German Federal Ministry of Education and Research for Funding

EMEP Task Force on Measurements and Modelling (TFMM) for organising the campaign

Bundesministerium für Bildung und Forschung

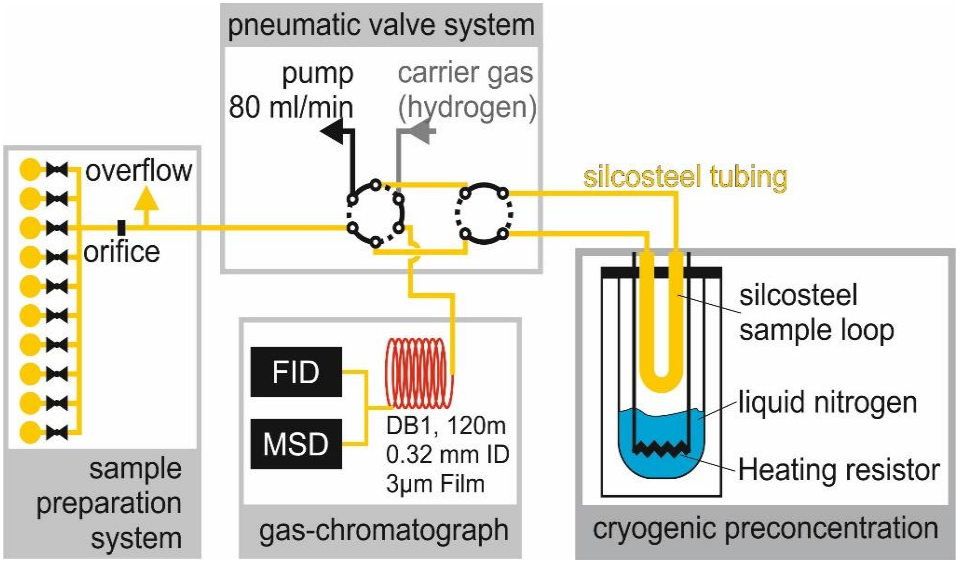
[UC]²: B-3DO

emep

ACTRiS
Exploring the Atmosphere

Analysis

- Canisters were be pressurized and analysed with GC/MS/FID Quantification was done by FID (according to SOP for VOC)
- Separation is done with a 120 m DB1 column
- Calibration: 74-component standard nmhc gas standard
- OVOC gas standard NPL



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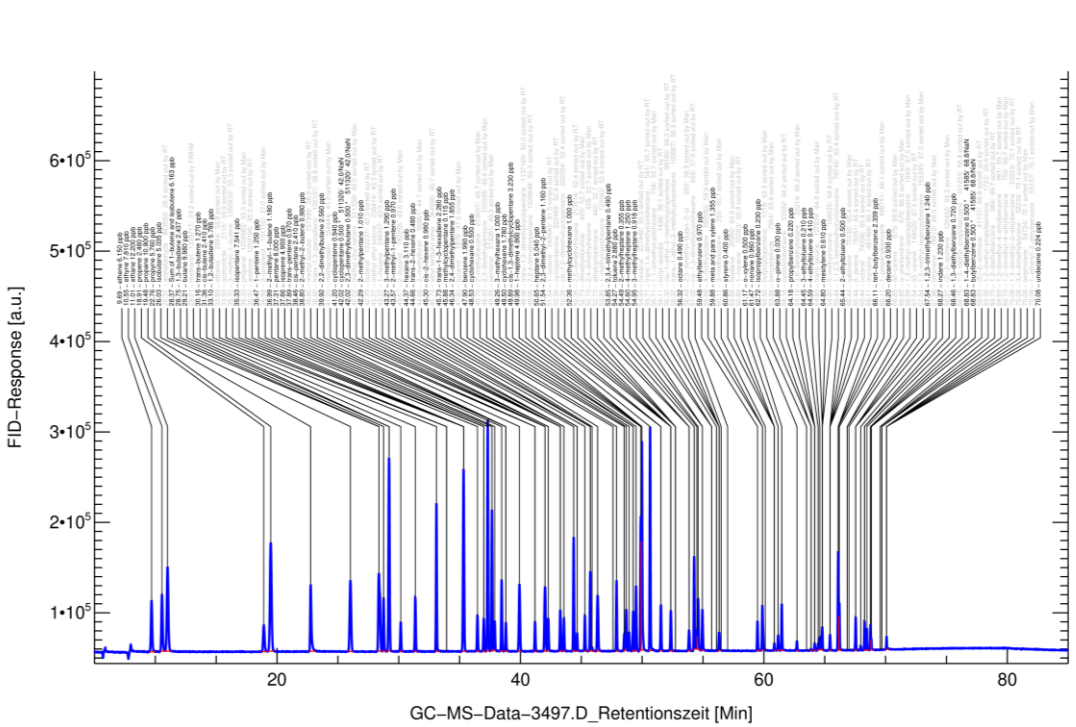
- VOCs from C2 to C12 are separated



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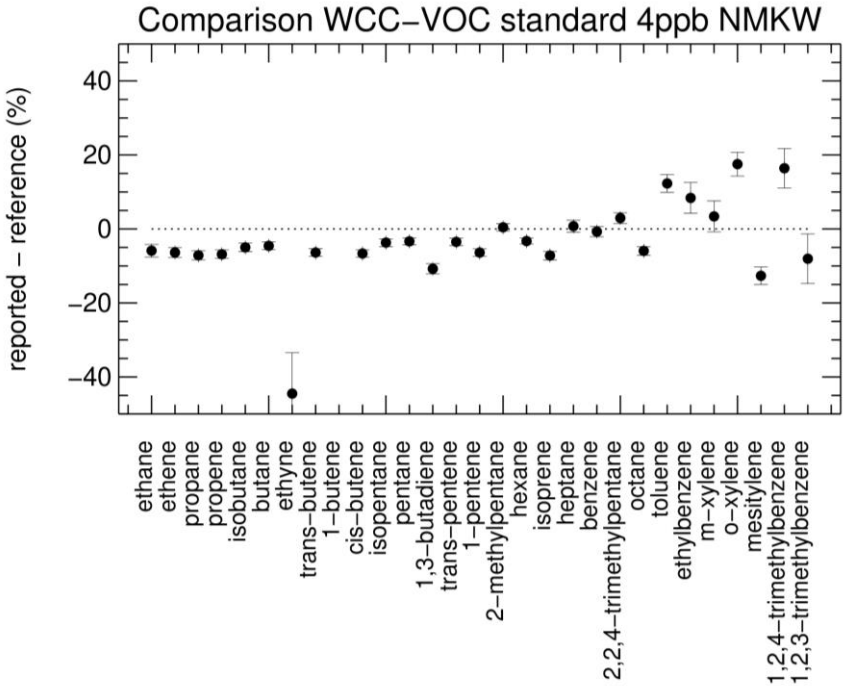
- Standard agrees for most of the compound to the WCC-VOC standard



Ozone interference

- Ozone can react in the canister
- Use of an ozone scrubber with Sodium thiosulfate prevents ozone from entering into the canister according to Helmig et al.

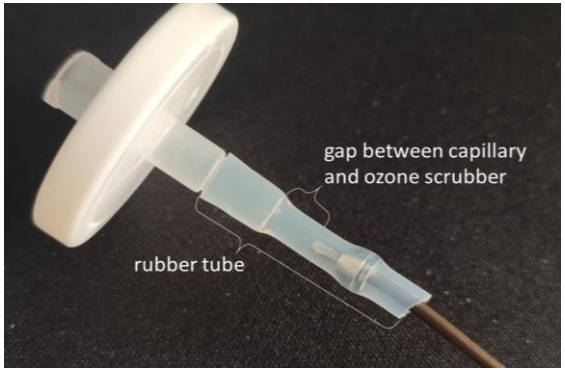


Fig. 1