Investigation of the photochemical activity in different MPC outflows during EMeRGe

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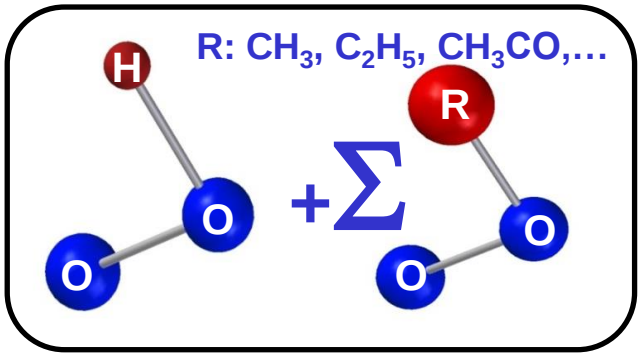
Peroxy Radicals

- Peroxy radicals are $HO_2 + RO_2$
- Accurate measurement of peroxy radicals is essential to understand:
  - Photochemical activity of air masses
  - Local and regional production of O_3
  - Radical chemistry in the urban pollution
  - Variation in primary and secondary pollutants



R stands for an organic chain

- **Pe**roxy **R**adical **C**hemical **E**nhancement and **A**bsorption **S**pectrometer (PeRCEAS)
  - **P**eroxy **R**adical **C**hemical **A**mplification + CRDS NO_2 Detector
  - $RO_2^* = HO_2 + \sum RO_2$ reacting with NO to produce NO_2.
  - $[RO_2^*] = \frac{\Delta[NO_2]}{e\mathrm{CL}}$, where eCL is the amplification factor known as effective chain length and is determined from lab calibrations.

Selected indicators for the photochemical activity

- A proxy for production, $P_p(RO_2^*)$, is calculated by considering following photochemical reactions of the radical precursors measured simultaneously on board.
  - $O_3 + h\upsilon\ (\lambda < 320nm) \rightarrow O(^1D) + O_2$
  - $O(^1D) + H_2O \rightarrow 2OH$
  - $CH_3CHO + h\upsilon(\lambda < 340nm) + 2O_2 \rightarrow CH_3O_2 + HO_2 + CO$
  - $CH_3COCH_3 + h\upsilon(\lambda < 340nm) + 2O_2 \rightarrow 2CH_3O_2 + CO$ (generally RO_2^* to take into account all branching ratios)
  - $HONO + h\upsilon\ (\lambda \leq 400nm) \rightarrow OH + NO$
  - $HCHO + h\upsilon\ (\lambda < 340nm) + 2O_2 \rightarrow 2HO_2 + CO$

$$P_p(RO_2^*) = 2\,J_{O^1D}[O_3]\frac{k_{O^1D+H_2O}\,[H_2O]}{k_{O^1D+O_2}[O_2]\,k_{O^1D+N_2}[N_2]} + 2\,J_{CH_3COCH_3}[CH_3COCH_3] + 2\,J_{CH_3CHO}[CH_3CHO] +$$

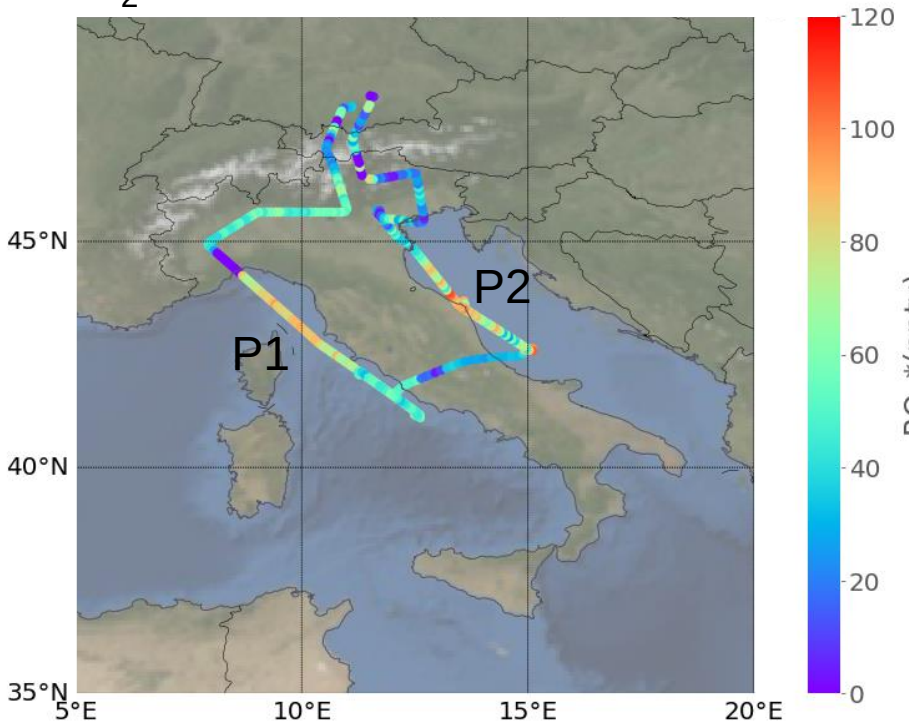
$$2\,J_{HCHO}[HCHO] + J_{HONO}[HONO]$$

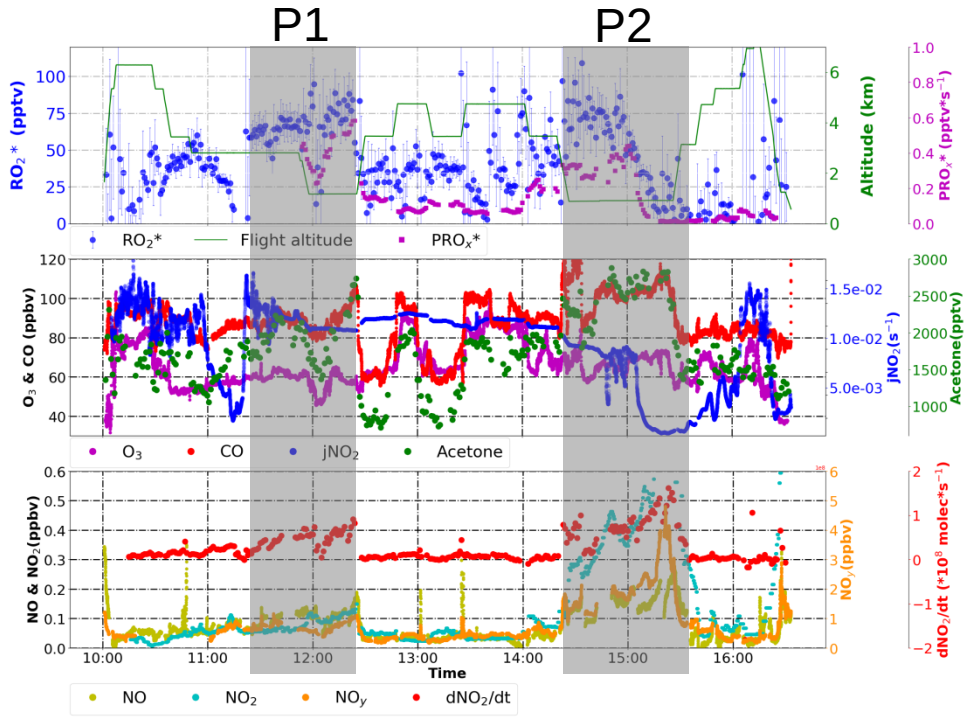
- $\frac{d[NO_2]}{dt}$ is calculated from the reactions involved in the tropospheric O_3 production.

$$\frac{d[NO_2]}{dt} = k_{NO+O_3}[NO][O_3] + k[NO][RO_2^*] - j_{NO_2}[NO_2]$$

HALO flight E_EU_F#3 (11.07.2017)

RO_2* measurement from PeRCEAS





- The temporal variation of the calculated P_p RO_x* and the measured RO_2* shows reasonable agreement.
- Estimated $\frac{d[NO_2]}{dt}$ is higher in highly polluted air masses (P1 and P2).

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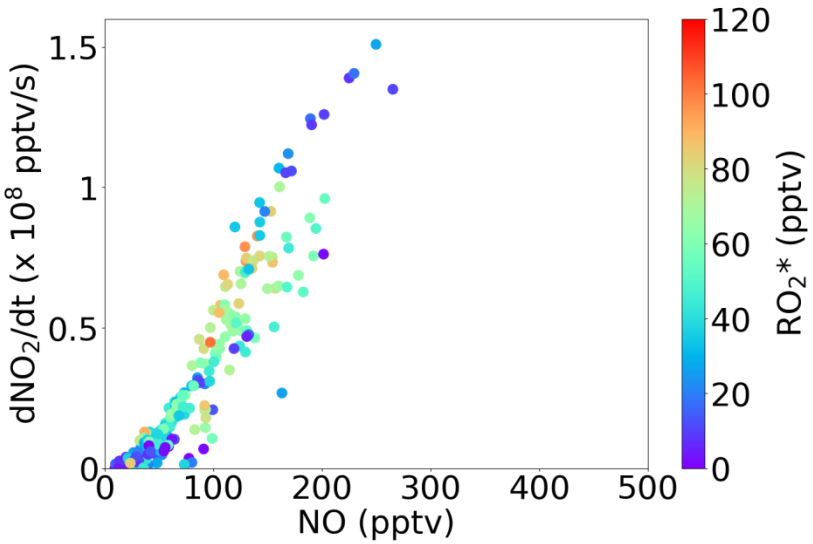

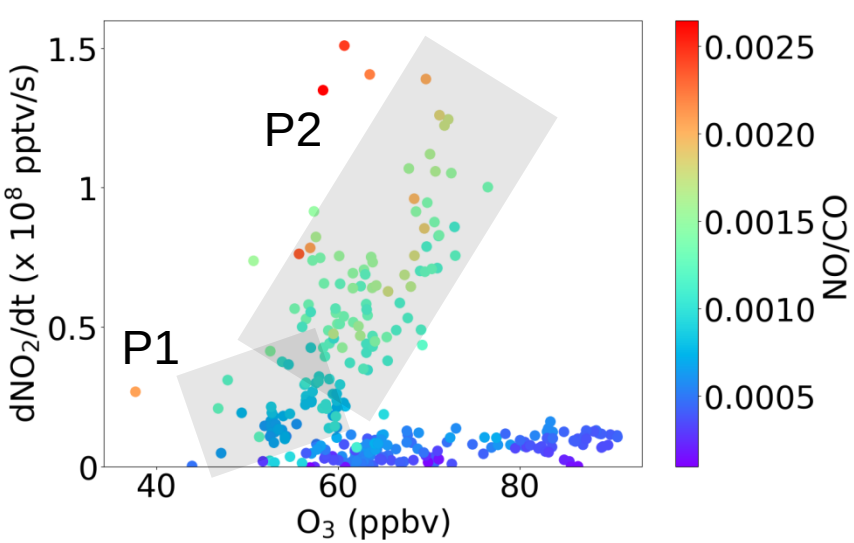

- $\frac{d[NO_2]}{dt}$ and NO are clearly correlated.
- The correlation between $\frac{d[NO_2]}{dt}$ and O_3 depends on the NO/CO ratio.
- High values of $\frac{d[NO_2]}{dt}$ at high NO/CO ratios for high O_3 mixing ratios indicate air masses of high photochemical activity.
- Low values of $\frac{d[NO_2]}{dt}$ at low NO/CO ratios for high O_3 mixing ratios indicate long range transport of polluted air masses.

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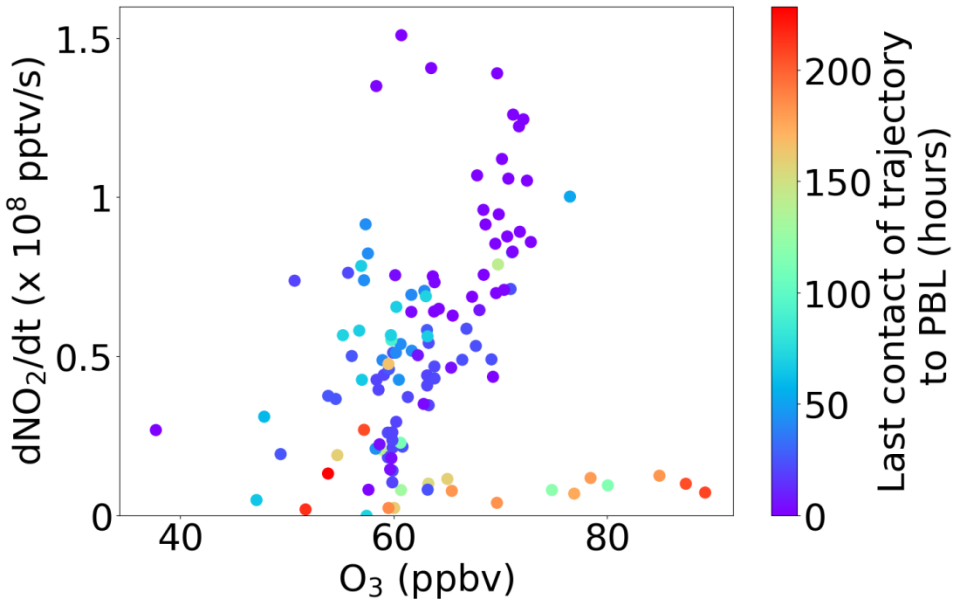
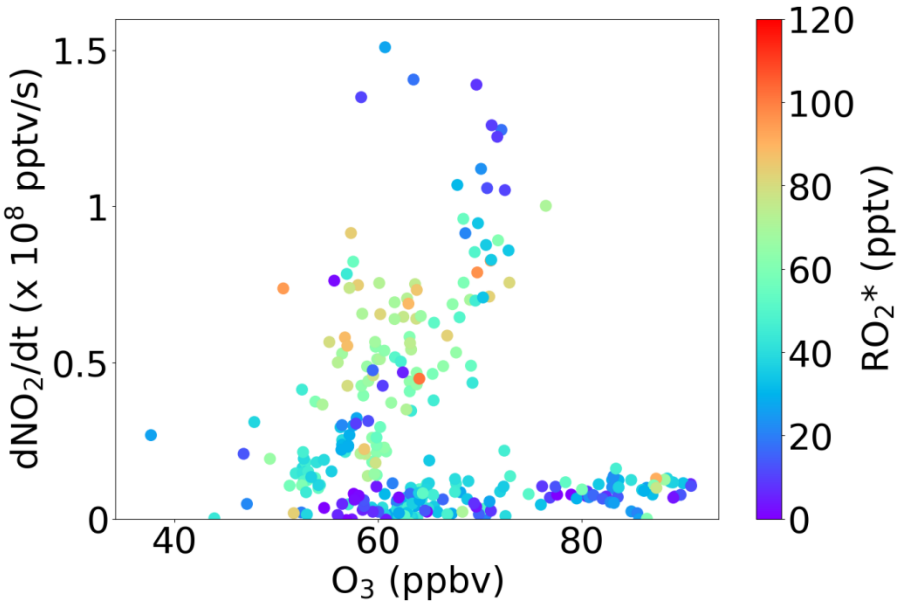
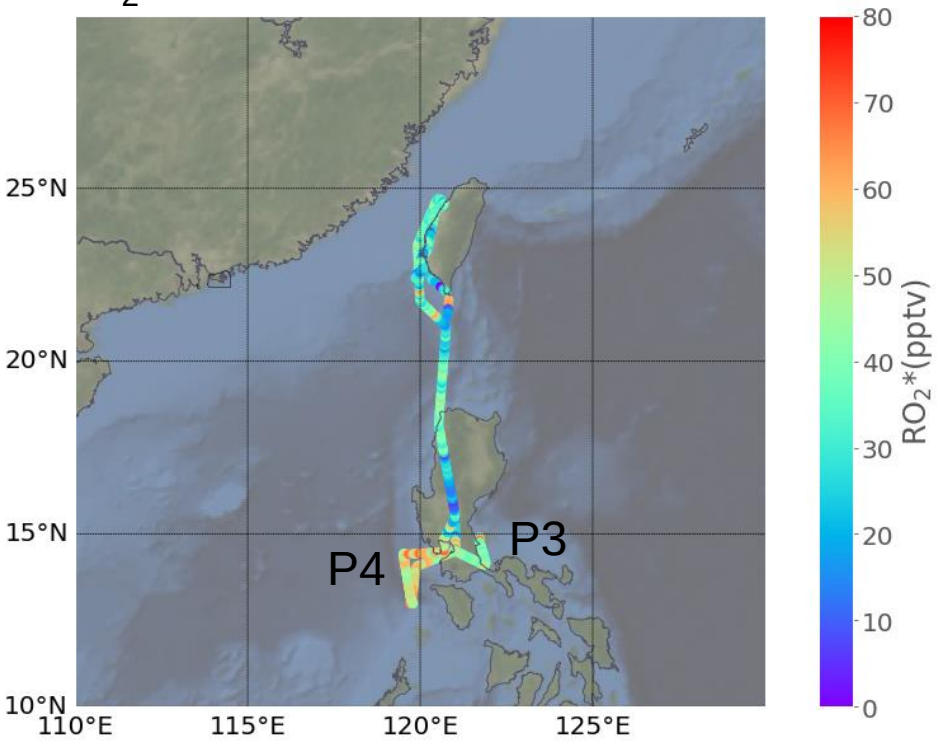


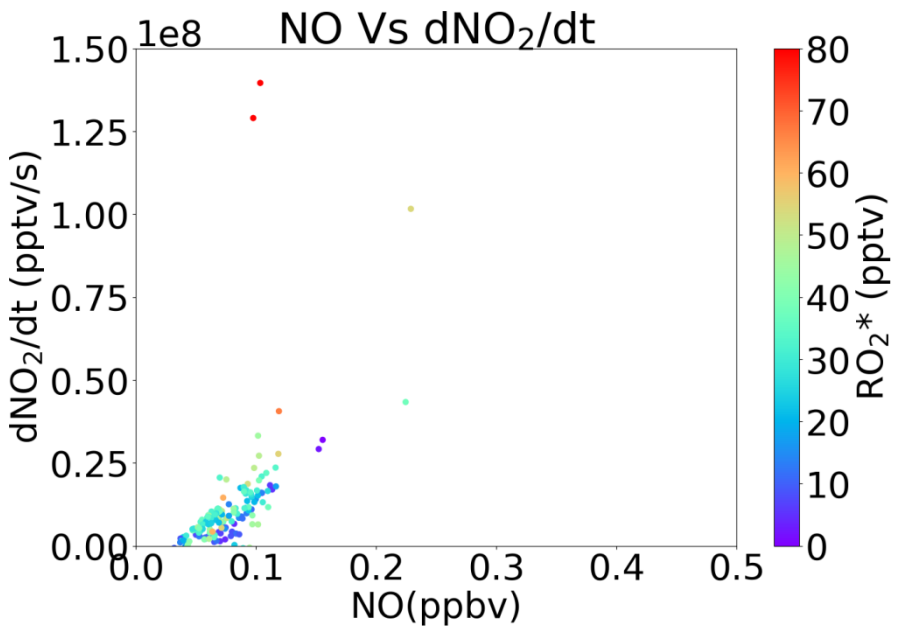


- The last contact to the planetary boundary layer calculated with the FLEXTRA back trajectories shows a positive relation with the photochemical activity of the air mass as indicated by the $\frac{d[NO_2]}{dt}$ and the RO_2^* mixing ratios measured.

HALO flight E_AS_F#10 (28.03.2018)

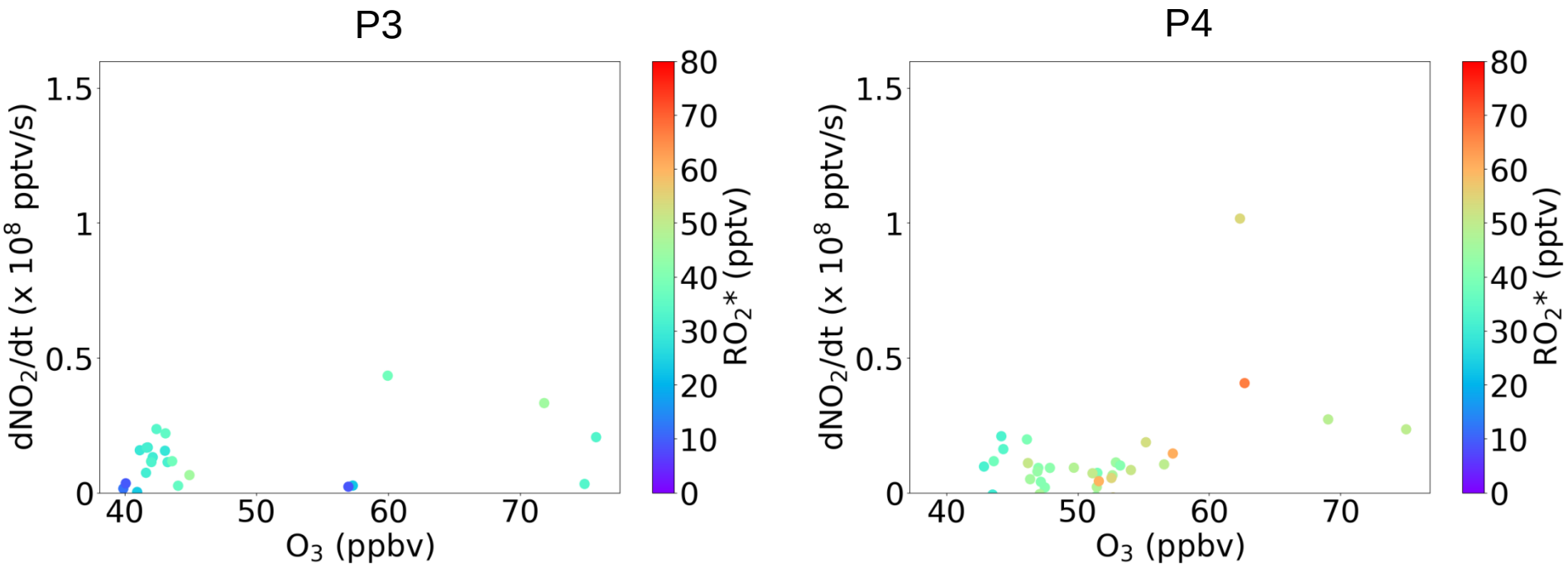
RO_2* measurement from PeRCEAS





- The absolute value of $\frac{d[NO_2]}{dt}$ estimated around Manila (P3 and P4) is lower than in the case studies around Italy (P1 and P2) but is also highly correlated with NO.

HALO flight E_AS_F#10 (28.03.2018)



- The NO/CO ratio is lower over Manila (P3 and P4) than over Italy (P1 and P2).
- Similarly, lower RO_2^* mixing ratios which eventually result in low $\frac{d[NO_2]}{dt}$ are measured in P3 and P4.

Summary

- The relationship between RO_2^* to radiation and precursors was investigated for air masses probed during EMeRGe.
- Photochemically active air masses were identified using RO_2^* mixing ratios, a proxy for the radical formation, $P_p(RO_2^*)$, and $\frac{d[NO_2]}{dt}$ as indicators.
- O_3 measured during the flight in Europe shows:
  - O_3 is correlated to $\frac{d[NO_2]}{dt}$ (local photochemical production).
  - O_3 is independent of $\frac{d[NO_2]}{dt}$ (long transport).
- High amount of O_3 measured around Manila with low $\frac{d[NO_2]}{dt}$ shows the importance of the long transport of O_3.

Outlook

- Further correlation studies in individual pollution plumes.
- New correlation studies with aerosol loading in different pollution plumes measured during EMeRGe.