Airborne measurement of peroxy radicals during EMeRGe

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Introduction

The project EMeRGe (Effect of Megacities on the Transport and Transformation of Pollutants on the Regional to Global Scales, www.iup.uni-bremen.de/emeRge) focuses on the understanding of the transport and transformation of polluted plumes of air flowing from selected megacities (MPC) in Europe and Asia using the HALO (High Altitude and Long Range Aircraft, www.halo.dlr.de) platform.

One key issue with respect to transformation is the amount and role of peroxy radicals, HO2 and RO2 (where R is an organic group), as their reactions play a key role in oxidation processes and determine the O3 budget and the oxidation capacity of the atmosphere (OCA).

Within EMeRGe, airborne measurements of the total sum of peroxy radicals, \( \text{RO}_2 = \text{HO}_2 + \sum \text{RO}_2 \), were conducted by using PeRCEAS (Peroxy Radical Chemical Enhancement and Absorption Spectrometer) which is part of the HALO EMeRGe payload.

PeRCEAS combines the PeRCA (Peroxy Radical Chemical Amplification) measurement technique, for the amplified conversion of radicals entering the reactor into NO2 in a chain reaction involving NO and CO, with the sensitive detection of NO2 by cw-CRDS (continuous wave – Cavity Ring Down Spectroscopy) technique. The instrument shares a common inlet for two identical measurement lines (reactor-detector) to improve time resolution and sensitivity.

The amplification factor (chain length) and the detection limit were determined in the lab.

PeRCEAS airborne \( \text{RO}_2 \) measurements within EMeRGe

PeRCEAS successfully participated in the EMeRGe HALO campaigns in summer 2017 and spring 2018. A total of 180 flight hours were distributed among seven mission flights over Europe (Figure 2, left), fourteen mission flights over Asia (Figure 2, right) and six transfer flights.

In Europe the MPC outflows of London, Rome, Po Valley, Paris, Benelux/Ruhr, South France, Madrid and Barcelona were investigated.

The outflows of Bangkok, Manila, Taipei, and the transport of MPC emissions from China, South Korea and Japan over the Yellow Sea were in turn a main focus of the campaign in East Asia.

Overall significant \( \text{RO}_2 \) mixing ratios up to 80 pptv were measured in both campaign phases.

Figure 3 shows exemplary the \( \text{RO}_2 \) mixing ratios measured on flight #9 over Europe. HALO shuttles between 500m and 3000m asl. were carried out at the expected downwind areas of South France, Madrid and Barcelona.

Generally, layers of different photochemical activity and origin were identified confirming the effect of convective and long range transport processes on the composition of air masses in the boundary layer and beyond.

Figure 4 and 5 shows \( \text{RO}_2 \) mixing ratios measured during the EMeRGe flights in Asia investigating the outflow from Manila in March 2018. HALO shuttles at altitudes between 800m and 3000m asl. were carried out upwind and downwind of Manila as confirmed by the FLEXPART sensitivity maps shown in Figure 6.

The higher \( \text{RO}_2 \) mixing ratios encountered downwind Manila are in agreement with the expected input of precursors and photochemical processing in within the MPC plume.

Further investigation of the OCA and the regional \( \text{O}_3 \) production upwind and downwind of the selected MPCs is required. Moreover, laboratory experiments are presently being performed to improve the accuracy of the chain length used at different measurement conditions.

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