

Abstract

Volatile organic compounds (VOCs) comprise a large number of different species, estimated to 10^4 - 10^6 . They are emitted on the Earth's surface from a variety of biogenic and anthropogenic sources. VOCs are removed by multiple pathways from the atmosphere, by oxidation and finally by dry or wet deposition. Most primary emitted VOCs are non-polar and therefore have a low solubility in water. Oxidation facilitates efficient VOC removal by wet deposition. In the atmosphere the main photochemical VOC oxidation agent is the OH radical. As a consequence the polarity of the VOCs is increased and they can be removed faster. The oxidation of VOCs proceeds in several steps until the VOCs are deposited or are eventually oxidized to carbon dioxide. A downside of the VOCs oxidation process lies in the production of significant amounts of ozone if nitrogen oxide is present which is a serious health hazard.

Most of the VOC oxidation takes place in lower part of the atmosphere between the altitudes of 100 to 1000 m, which is only sparsely analyzed. Therefore, fast VOCs measurements by GC-MSD on board the Zeppelin NT offered new important insights in the distribution of VOCs. The measurements were performed within the PEAGSOS campaigns in the Netherlands and in Italy in 2012. For the implementation of the GC-MSD system (HCG) on board the Zeppelin it was reconstructed to enhance its performance and to meet aviation requirements. The system was optimized to measure VOCs ranging from C4 to C10 as well as oxygenated VOCs (OVOCs) with a detection limit below 10 ppt.

The analyzed VOCs for both parts of the campaigns showed low mean concentration below 5 ppb for all VOCs. Especially, the mixing ratios of the primary emitted VOCs were very low with mean values lower than 200 ppt. Higher concentrations could be observed for the OVOCs with mean concentrations up to 5 ppb. The most abundant OVOCs apart from formaldehyde were methanol, ethanol, acetone and acetaldehyde.

The total measured OH (k_{OH}) reactivity showed low values and the comparison to the calculated OH reactivity from the individual trace gas measurements revealed only very small differences due to unmeasured trace gases. In the Netherlands the mean difference was $1.0 \pm 1.4 \text{ s}^{-1}$ at a mean measured with a mean of $6.13 \pm 1.23 \text{ s}^{-1}$ and in Italy $0.1 \pm 2.2 \text{ s}^{-1}$ at a measured total OH reactivity of $3.8 \pm 1.4 \text{ s}^{-1}$.

These results showed that the sampled air in the height range 100m -1000m was not very polluted from primary emitted trace gasses for both parts of the campaign. The analysis revealed that the OVOCs were the major OH sinks by contributing 30 % in the Netherlands and 40 % in Italy to the total OH reactivity. The sources of OVOCs are manifold ranging from primary emissions to photochemical productions. Calculations revealed that the measured OVOCs did not entirely originate from photochemical production; a significant amount originated from primary emissions and advected OVOCs. Primary emitted alcohols were analyzed at one instance in the

plume of the Mannheim/Ludwigshafen region. As the most abundant OVOCs have OH lifetimes ranging between hours and days they are widely distributed and thus have regional to global effects on the air quality and thus climate.