PhD-thesis Andrea Schaub, July 2007

Abstract: Isoprene and its oxidation products in and above a mixed deciduous forest

Isoprene is the most abundant biogenic volatile organic compound (VOC), emitted mainly from deciduous trees, and its oxidation in the atmosphere can significantly contribute to local ozone formation. An estimate of the ozone formation related to isoprene oxidation requires knowledge of to what extent isoprene is oxidized close to its source. The scope of this thesis is to explain measured mixing ratios of isoprene and the ratio of its two oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR), MVK/MACR, as a consequence of photochemical and meteorological processes in a mixed deciduous forest. This enables the MVK/MACR ratio to be used as an indicator to asses the extent of isoprene oxidation on a local scale. Within the ***ECHO*** project (***E***mission and ***Ch***emical transformation of biogenic volatile ***o***rganic compounds) a 36m high tower was erected in a mixed deciduous forest, upon which profile measurements of isoprene, its oxidation products and 8 other VOCs were carried out continuously in summer 2002 and 2003.

In summer 2002 (June and July) the mean daytime (10-18h) volume mixing ratio (VMR) of isoprene was ~ 200 pptv and 3.5 times lower than the mean daytime VMR of 710 pptv in summer 2003 (July to September). The mean daytime MVK/MACR ratio in summer 2002 was 0.8 to 1 and in summer 2003 between 1 and 1.2. This ratio is lower than the MVK/MACR ratio (~ 1.4) expected from laboratory studies of isoprene oxidation. Analysis of meteorological data revealed that the MVK/MACR ratio was dependent on the wind direction. With prevailing westerly winds the mean daytime MVK/MACR ratio was 0.6 (July 2003) and was fairly variable, whereas with an easterly wind the ratio was ~1.5 (July 2003). According to photochemical processes a MVK/MACR ratio of 0.8 arises due to isoprene oxidation under NO-limited conditions. The VMR of NO measured above canopy at the ECHO main tower in summer 2003 was sometimes lower than 100 pptv and therefore the MVK/MACR ratio can be deduced to result from isoprene oxidation under low NO conditions.

Isoprene was found to contribute 60-90% to the local OH reactivity of all VOCs, which supports evidence for the important contribution of isoprene to local photochemistry. A simulation of the ozone formation based on the measured trace gas and radical composition of the ECHO forest site showed that an increase in NO_x-conditions would enhance ozone formation stronger than an increase in VOC reactivity, e.g. by higher isoprene emission.