VOC speciation during the morning rush hour

On three weekdays in August and September 2006 (08/27, 09/19, 09/26), data has been collected for typical speciation patterns during the morning rush hours (06:00 – 09:00 a.m. CDT). Days have been chosen that were characterized by a stable boundary layer height of 300 m and an average wind direction in the planetary boundary layer between 270º and 360º with a standard deviation smaller than 15º. The source area is shown in the upper left. The samples were taken at the Moody Tower site (60 m a.g.l.) on campus of the University of Houston with a sampling period of 40 mins per sample.

A special event occurred in the early morning hours on 09/29/06 lasting for about 80 mins. Significant enhancement of the mixing ratios of formaldehyde, SO2, NOx, PAN, and PPN, as well as slight enhancement of NO and CO can be observed. O3, CO, and NO remained almost unchanged. This increase of distinct compounds correlates highly with a shift towards easterly wind directions during that period, moving air masses that derive from the industrially very heterogeneous Houston Ship Channel, to the receptor station. The plume of this source seems to be containing primarily formaldehyde, SO2, VOCs, and PANs. This specific behavior of those compounds could also be observed in similar ways at different time periods. Preliminary conclusions suggest that sources from refineries are the possible source. Further contribution to F2 comes from several alkenes, C6-alkanes and aromatic species. Further contribution to F2 comes from several alkenes, C6-alkanes and aromatic species.

Principal component analysis and correlation matrix of selected compounds

A principal component analysis with varimax rotation was performed to extract a number of factors that support the source apportionment of C2-C8 VOCs in Houston (see right). The investigated period covers 09/15-09/30. A larger dataset from 08/07-06 until the end of September including hydrocarbons up to C11 will be added after quality control. In addition, a correlation matrix (see below) of selected C2-C8 VOCs, formaldehyde, ozone, CO, NO, NOx, PAN and PPN was calculated for the last two weeks of September n = 450 (bulk) n = 60 (CO).

A number of five factors (F1-F5) met the criteria of an eigenvalue > 1, and thus were extracted. In total ca. 85% of the total variance could be explained. For those five factors F1 and F2 explained most of the variance, the former including alkanes, several alkenes and benzene which did not show a very strong correlation with F1. Possible sources for F1 could be all kinds of industrial processes as well as evaporation. F2 could be linked to combustion processes such as vehicular exhaust, indicating acetylene and CO that was included as an indicator for combustion. Further contribution to F2 comes from several alkenes, C6-alkanes and aromatic species. Further contribution to F2 comes from several alkenes, C6-alkanes and aromatic species. C8- and C9-alkenes constitute F3. Only n-butane and n-pentane might derive from liquid petroleum gas, correlate with F4. Exclusively isoprene is associated with F5, accounting for biogenic sources.

The correlation matrix gives further support for the detection of common emission sources and connections between VOCs and other compounds. Formaldehyde shows its highest correlations with PAN, PAN, benzene, and most of the alkenes. Higher HCHO, PAN, and PPN also correlate well with ozone, but don’t show any correlations with the other compounds. In general, aromatics usually correlate well amongst field own groups and to some extent with the others. Despite not contributing to F1, CO shows quite high correlation coefficients also with aromatics from F1, indicating combustion processes as a possible source for this factor. Unsaturated, as a mostly biogenic compound, does not show any significant correlation. No coefficient > 0.50 can be observed by isoprene, that primarily relates to F5.