4.5 RECEPTOR MODELING OF C_2 – C_{10} VOCS IN HOUSTON, TX DURING TEXAQS II

M. Leuchner * and B. Rappenglück
Institute for Multidimensional Air Quality Studies, Dept. of Geosciences, University of Houston, Houston, TX, U.S.A.

1. INTRODUCTION

In August and September 2006 the comprehensive field campaign TexAQS II (Texas Air Quality Study II) took place in several areas of Texas. This project focussed on photochemical processes and transport in the urban atmosphere and covered a wide range of simultaneous measurements of meteorological parameters and air chemical species at various ground-based sites as well as aboard airborne and marine facilities. Among this extensive campaign the Texas Air Quality II Radical Measurement Project (TRAMP) was located at the urban receptor supersite Moody Tower on the University of Houston campus, approximately 5 km southeast of Downtown Houston and 10 km west from the Houston Ship Channel. This site was built on the rooftop of a 60 m tall student dormitory building without major local sources in the close vicinity.

This paper presents the results of multivariate receptor modeling of continuous online measurements of C_2 – C_{10} volatile organic compounds (VOCs) from 7 Aug. – 30 Sep. 2006 at the urban receptor site Moody Tower utilizing Positive Matrix Factorization (PMF). In addition, PMF analyses of VOC data obtained by the TCEQ and Enhanced Industry Sponsored Monitoring auto-GC networks at Channelview and Wallisville Rd., located near major industrial source areas within the Houston Ship Channel, were used to support the source apportionment for the Houston urban area.

The results of the receptor models reveal a set of factors and source profiles that are associated with several anthropogenic (industrial, traffic) as well as biogenic sources. More than 50% of the total VOCs measured at the urban site can be contributed to sources within the industrial Houston Ship Channel. Despite the overall presence of biogenic sources, only minor contributions to the total measured VOC mass can be observed.

* *Corresponding author address*: Michael Leuchner, Dept. of Geosciences, University of Houston, 4800 Calhoun Rd, Houston, TX 77204-5007, e-mail: mleuchner@uh.edu

2. METHODS

The data used for receptor modeling originates from continuous hourly online measurements of VOCs from 7 Aug. – 30 Sep. 2006 at the Moody Tower urban receptor site as well as the two selected Ship Channel sites Channelview and Wallisville Rd. in northeastly directions. The urban site is unique, because it is affected by a combination of air masses from urban, biogenic, and industrial sources throughout the Houston area, unlike previous studies (Buzcu and Fraser, 2006; Xie and Berkowitz, 2006) that concentrated on the mostly industrial Ship Channel region.

The measurements at the three investigated sites were conducted by similar gas chromatographs based on flame ionization detection (GC/FID) (Perkin Elmer Clarus 500 & Turbomatrix 650 ATD). The sampling frequency is one hour, the sampling time 40 minutes. A set of 67 C_2 – C_{10} VOCs was quantified at the Moody Tower of which 59 could be used for receptor modeling after quality control, 49 C_2 – C_{12} VOCs were measured at both Ship Channel sites of which 43 and 47 were used for PMF at Channelview and Wallisville Rd., respectively.

The applied PMF analysis (EPA PMF 1.1) is based on the multilinear engine ME-2 described by Paatero (1999). Out of the 59 compounds at the Moody Tower site, the influence of 19 compounds that showed a significantly smaller signal to noise ratio and/or had several missing values or values below the detection limit, was reduced, i.e. the uncertainty was increased three times. The selection of the appropriate number of factors was based on the standard criteria such as the value of the minimized sum of squared residuals, residual distribution, and the correspondence to realistic physical phenomena. Missing values were substituted by the median value and their respective uncertainties were increased accordingly. The obtained results were confirmed and supported by estimating the PMF model's uncertainties using a bootstrap technique combined with a method to account for the rotational freedom in the solution. 200 bootstrap runs were performed

showing a high level of confidence in the uncertainty estimates.

3. RESULTS AND DISCUSSION

3.1 *Source apportionment at the urban receptor site*

3.1.1 *Source profiles identified by the Positive Matrix Factorization analysis*

The PMF analysis conducted for the receptor site at the Moody Tower over the almost eight week period during summer 2006 shows a whole set of different anthropogenic and biogenic sources that affect the air quality at this urban location. Fig. 1 displays the source composition profiles determined by the receptor model by total measured VOC mass. An eight factor solution revealed the most plausible results. Out of the eight determined factors, only one (profile A) can be attributed to biogenic sources and consists mainly of isoprene emitted by biomass. All other factors can be ascribed to anthropogenic sources. The composition of profile B with the presence of isopentane, n-pentane, and toluene indicates fuel evaporation as the main source. Since acetylene, a typical marker for combustion processes is also present, the profile is called industrial / fuel evaporative. Most of the acetylene mass is explained by source profile C that can be attributed to vehicular exhaust. In addition, this factor contains further compounds typically associated with vehicular combustion such as toluene, xylenes, other aromatics, and alkenes as well as ethane and propane. Profile D consists mainly of aromatics and smaller amounts of some alkanes, alkenes and isobutane, most of them also found in traffic related sources. The composition profiles E and F are each mostly represented by a single compound: ethylene and propylene, respectively. The liquefied petroleum gas (LPG) compounds isobutane, n-butane, and propane primarily assemble profile G. Natural gas and evaporation, e.g. from crude oil and refining compounds, represent profile H with the main alkane constituents ethane, propane, n-butane, isobutane, n-pentane, isopentane, and some heavier alkanes.

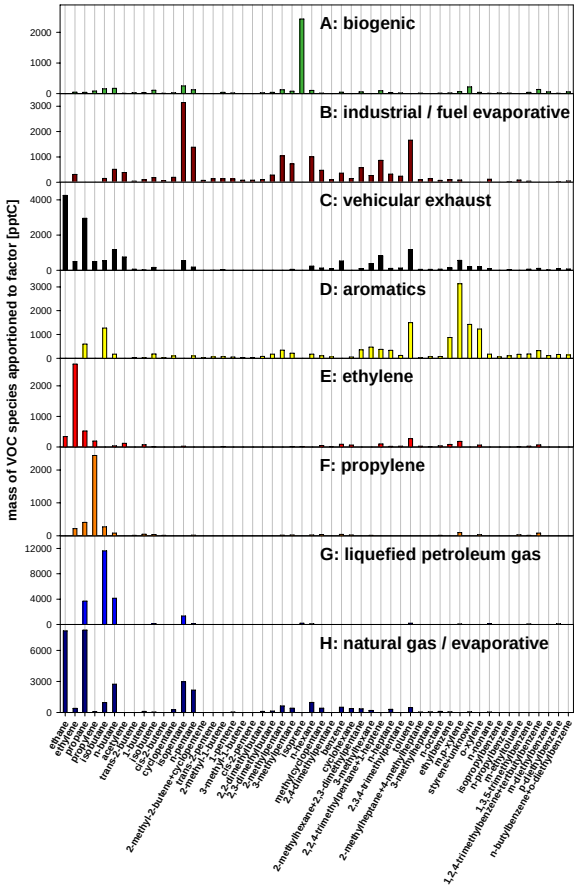

Fig. 1. Source composition profiles for the eight factors resolved by the PMF analysis at the urban site.

3.1.2 *Mass contributions*

Fig. 2 shows the contributions of the different determined factors to the total measured VOC mass at the urban receptor site. The most abundant sources representing 26.6% of the VOC mass are natural gas and evaporation of refining compounds (H). Industrial LPG emissions account for 19.2% (G), vehicular exhaust for 14.9% (C), the mixture of industrial emissions and fuel evaporation for 13.8% (B), aromatics for 13.2% (D) and petrochemical emissions of ethylene (E) and propylene (F) for 4.5% and 3.5%, respectively. Biogenic emissions (A) play only a minor role at the urban site with 4.3% of the total VOC mass despite large areas of photosynthetically active biomass in the Houston area.

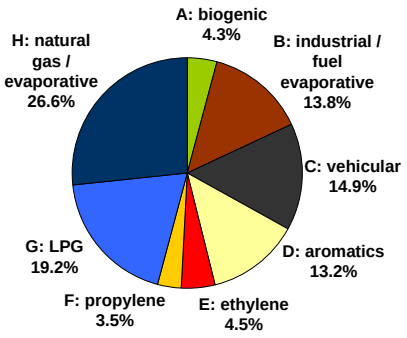

Fig. 2. Source contributions to the VOC mass [in pptC] at the receptor site

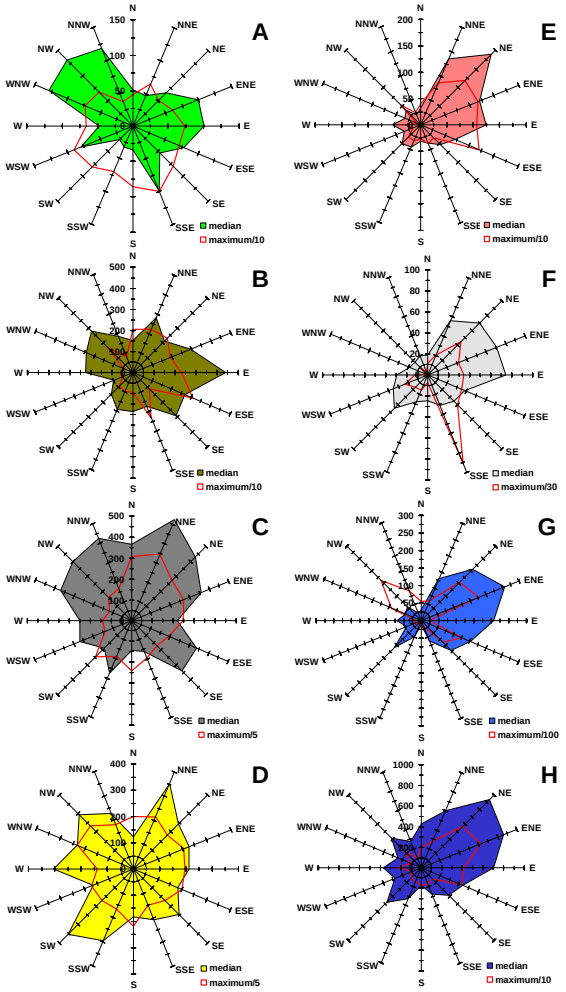

Fig. 3. Wind plots of the resolved factors [pptv]. Number of samples for each sector: N 79, NNE 99, NE 87, ENE 63, E 42, ESE 69, SE 84, SSE 116, S 143, SSW 50, SW 60, WSW 25, W 31, WNW 15, NW 21, NNW 27.

3.1.3 *Wind directional dependency*

When compared to wind directional data, certain source regions for the different factors can be identified. Fig. 3 exhibits the eight wind plots each associated with the respective factor. The median mixing ratio in pptv as well as the maximum value for each of the 16 wind sectors are shown. The four factors that, by their profile composition, can be associated clearly with petrochemical, refining, and evaporative sources (E, F, G, H) show significantly higher mixing ratios with wind directions pointing towards northeasterly regions, identifying the Houston Ship Channel area as their principal source. The overall contribution of these four factors is over 53% of the total VOC mass at the urban site. Mobile and urban sources (B, C, D) do not show such a strong directional dependency, however, the factor mainly associated with vehicular combustion (C), indicates elevated values from all northern directions, pointing towards major freeways. Biogenic sources show higher median mixing ratios with wind directions from northwest and east.

3.2 *Analysis at the industrial sources: the Ship Channel sites Channelview and Wallisville Rd.*

In comparison to the urban receptor site Moody Tower, the two selected TCEQ sites at Channelview and Wallisville Rd. are both located close to several different industrial emission sources (e.g. refineries, petrochemical and chemical facilities, other industrial complexes) within the Houston Ship Channel area. Their location ENE of the receptor site is also the direction associated with those air masses containing the highest median mixing ratios (Fig. 3).

For both sites a six factor solution proved to be the best fit (Fig. 4 and 5). Both sites show similar profiles for biogenic (A), vehicular (C), LPG (G), and evaporative sources (H). At Channelview only one petrochemical profile (E/F) could be derived, while at Wallisville the two main compounds ethylene (E) and propylene (F) show different behavior and thus are split into two separate factors. A mixed profile for industrial and fuel evaporative sources (B) can only be found at Channelview. All profiles shown in Fig. 4 and 5 can also be found at the urban receptor site (Fig. 1). Both sites lack factor D that mainly consists of aromatic species.

The mass contributions of the different source categories for both Ship Channel sites (plot not shown) indicate that the largest fraction of the total measured VOC mass can be ascribed to evaporative

and refinery related sources (E, F, G, H) with more than 75% at both sites. Again, biogenic sources only contribute around 3 - 4% of the mass at all sites.

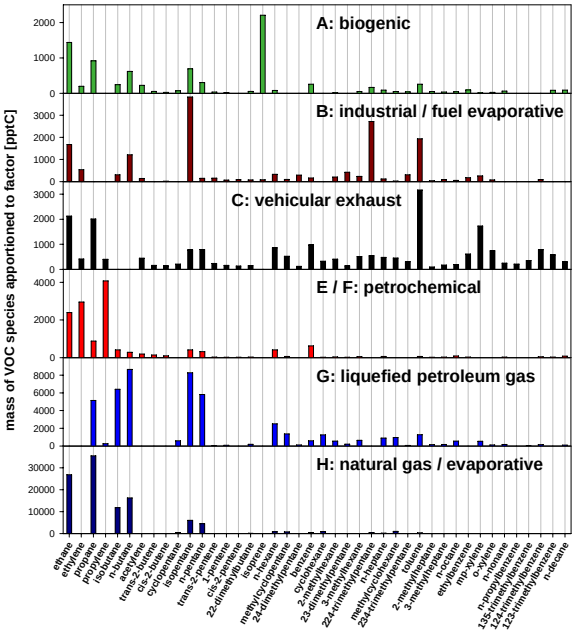

Fig. 4. Source composition profiles of the six resolved factors at the industrial site Channelview.

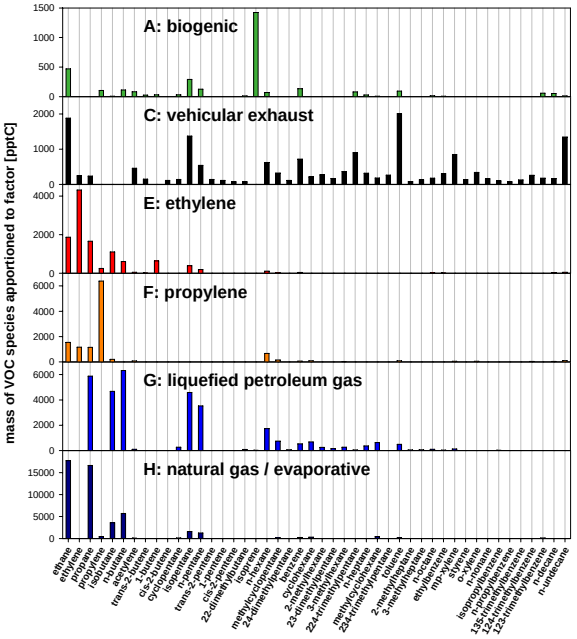

Fig. 5. Source composition profiles of the six resolved factors at the industrial site Wallisville Rd.

3.3 *Identification of the Ship Channel fingerprint at the urban site*

The retrieved source profiles, the wind directional dependencies as well as the mass contributions at the three sites clearly indicate the Ship Channel fingerprint in the urban area, consisting mainly of the factors E, F, G, and H. To confirm this observation another PMF analysis for the urban site was conducted taking solely data with wind from NNE to E directions, i.e. air masses passing with a high probability over the Ship Channel area. The similar eight factors as shown in Fig. 1 could be extracted, but with higher mass fractions of the factors E – H (plot not shown) supporting the identification of the fingerprint.

The mass contribution of these four factors constitute more than 53% of the total measured VOC mass at the urban site (Fig. 2). This shows that the urban site is influenced considerably by Ship Channel emissions, but also significantly by mobile as well as evaporative and industrial point sources from other locations in the Houston area.

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