RELATIONSHIPS BETWEEN SPECIFIC VOC FINGERPRINTS AND RATIOS OF PEROXYACYLNITRATE (PAN) COMPOUNDS IN HOUSTON, TX DURING TEXAQS II

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1. INTRODUCTION

In August and September 2006 the Texas Air Quality Study II (TexAQS-II) took place in the Houston-Galveston Brazoria Area. 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 ground-based sites as well as aboard airborne and marine facilities. Within the framework of this extensive campaign the Texas Air Quality II Radical Measurement Project (TRAMP) was performed at the urban receptor site Moody Tower on the University of Houston (UH) campus, approximately 5 km southeast of Downtown Houston and 10 km west of the Houston Ship Channel. This site was located on the rooftop of a 60 m tall student dormitory building. There are no major local sources in the close vicinity. This urban site is unique, because it can be affected by different air masses impacted by urban, biogenic, and industrial sources or a complex combination of those.

This paper presents the results of continuous online measurements of speciated PANs, and $C_2 - C_{10}$ volatile organic compounds (VOCs) at the Moody Tower supersite on the UH campus. In addition, offline canisters for the VOCs were sampled within the Houston-Galveston metropolitan area for determination of industrial, vehicular and biogenic fingerprints. Starting from the characterization of measured VOC source profiles, Positive Matrix Factorization (PMF) was applied to establish the source apportionment of ambient VOCs and relate those VOC fingerprints to PAN data. The analyses of the measured compounds indicate complex mixtures from various sources. Case studies for two time periods with different wind regimes in August and September 2006 are presented.

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2. METHODS

The PAN compounds (peroxiacetic nitric anhydride [PAN], peroxipropionic nitric anhydride [PPN], peroxymethacrylic nitric anhydride [MPAN], peroxyacrylic nitric anhydride [APAN], peroxisobutyric nitric anhydride [PiBN]) were measured continuously by a Metcon gas chromatograph based on electron capture detection (GC/ECD) in a ten minute sampling frequency. The respective limits of detection are 30 pptv (PAN), 35 pptv (PPN), 100 pptv (MPAN), 40 pptv (APAN), and 85 pptv (PiBN). The calibration of PAN and PPN is performed by their synthesis through the reaction of NO with peroxyradicals produced by photolysis of acetone (for PAN) and propionaldehyde (for PPN). For APAN, PiBN, and MPAN response factors relative to the PAN response according to Flocke et al. (2005) were used.

The VOC measurements were conducted by a gas chromatograph 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 were quantified at the Moody Tower of which 59 could be used for receptor modeling after quality control. The applied PMF analysis is described in more details in Abstract 4.5 "Receptor Modeling of $C_2 - C_{10}$ VOCs in Houston, TX during TexAQS II". In addition to the online measurements, a set of canister samples (five simultaneous samples per site) were taken at different locations within the Houston area to validate the results from the receptor model.

3. RESULTS AND DISCUSSION

3.1 *VOC source apportionment at the urban receptor site*

The PMF analysis conducted for the receptor site at the Moody Tower over the almost eight week period during summer 2006 shows a set of different anthropogenic and biogenic sources that affect 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. 2 shows the contributions of the different source factors to the total measured VOC mass at the Moody Tower. 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) appear to play only a minor role at the urban site with 4.3% of the total VOC mass.

When compared to wind direction data, 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 (B, C, D) as well as biogenic sources (A) do not show such a strong directional dependency.
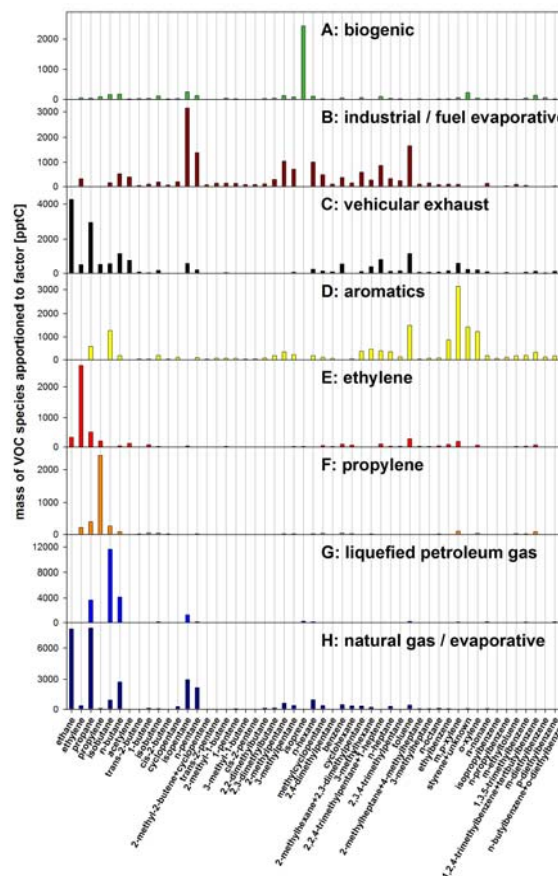

Fig. 1. Source composition profiles for the eight factors resolved by the PMF analysis at the Moody Tower, which can be considered an urban site.
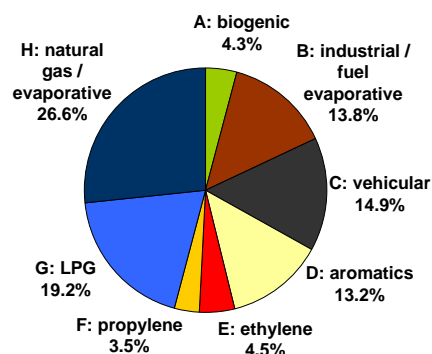

Fig. 2. Source contributions to the VOC mass [in pptC] at the Moody Tower.

In Fig. 3. VOC fingerprints at different sources within the Houston area for biogenic, vehicular

combustion, and crude oil evaporative emissions, determined from canister samples, are presented. The three obtained fingerprints at the sources agree well with the modeled profiles A, C, and H (Fig. 1).
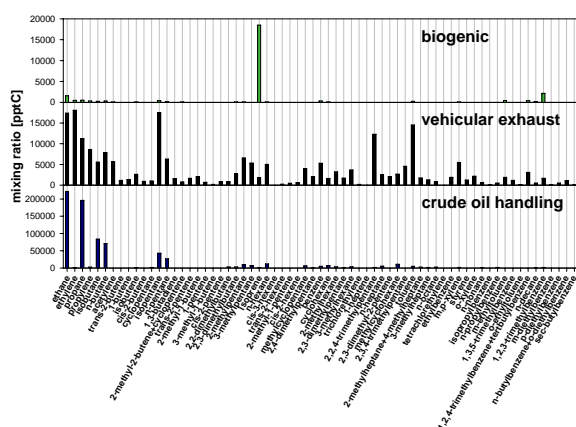

Fig. 3. Measured source profiles within the Houston area for biogenic, vehicular combustion, and crude oil evaporative emissions.

3.2 *Statistics and wind directional dependency of PAN and its homologues*

Besides the main compound PAN, a set of homologous species was additionally measured during the campaign. The quantified compounds are PPN, APAN, PiBN, and MPAN. Some stats for the five PANs are presented in Tab. 1. Only 147, 35, and 225 values above the limits of detection could be obtained for APAN, PiBN, and MPAN, respectively, while PPN and PAN could be measured very frequently with 4905 and 10824 values, respectively. Tab. 1 also shows the median, arithmetic mean, and maximum mixing ratios during TexAQS II.

	PAN	APAN	PPN	PiBN	MPAN
#Measurements	10824	147	4905	35	225
Median [pptv]	278	73	94	114	128
Mean [pptv]	587	87	148	116	138
Maximum [pptv]	7639	299	1623	161	293

Tab. 1. Selected statistics for measured PAN compounds during TexAQS II

In Fig. 4 and 5 the wind directional dependency for the five compounds as well as the PPN/PAN ratio is displayed. The median and maximum mixing ratios of PAN and PPN, the median PPN/PAN ratio is shown in Figure 4, while in Figure 5, due to the small number, all data points of APAN, PiBN, and MPAN in relation to the wind directional data are shown in both figures. The highest median PAN, PPN, APAN, and PiBN

mixing ratios can be observed under easterly wind directions from the industrial Houston Ship Channel. In addition, PPN exhibits a second maximum from southwesterly directions. MPAN has its highest mixing ratios under north and northeasterly wind directions. The ratio of PPN to PAN shows its highest values with flows from SW and lowest from NE.
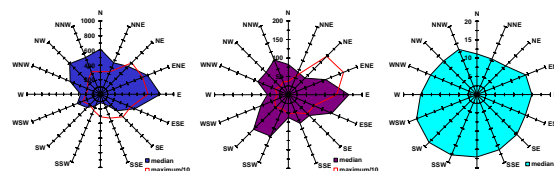

Fig. 4. Wind plots of the median and maximum PAN and PPN mixing ratios [pptV] and the median PPN/PAN ratio [%] for August and September 2006.
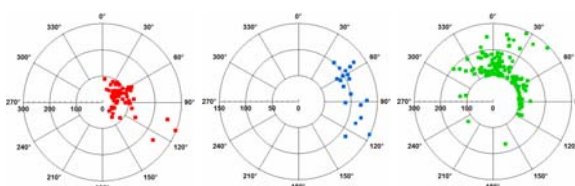

Fig. 5. Wind plots of APAN (red), PiBN (blue), and MPAN (green) mixing ratios [pptV] for August and September 2006.

3.3 *Contribution of different anthropogenic and biogenic sources to the formation of PANs*

Ratios of different PAN homologues are used for the differentiation of anthropogenic and biogenic precursor pools for the formation of PANs, in particular the ratios of PPN and MPAN to PAN. While PPN has only anthropogenic precursors, the precursor for MPAN is exclusively isoprene that is emitted mainly by biogenic sources. Thus, a high PPN/PAN ratio indicates anthropogenic precursor pools, a high MPAN/PAN ratio biogenic influence. In the following, two case studies with different anthropogenic and biogenic precursors in August and September 2006 are presented.

Fig. 6 shows a time series from the morning of Sept. 12 to the morning of Sept. 14, 2006. Besides the PAN mixing ratio, also the two ratios PPN/PAN and MPAN/PAN are plotted. In addition, the mixing ratios of the biogenically emitted isoprene (factor A) and the factor C from Fig. 1, representing vehicular combustion, are displayed. Whenever there is no data point for the MPAN/PAN ratio, MPAN was below the limit of detection of 100 pptv. In particular on Sept. 13, both the PPN/PAN as well as the MPAN/PAN ratio agree well with the mixing ratios of vehicular

combustion and isoprene, respectively. While in the morning and afternoon biogenic precursors seem to have some importance to PAN formation, anthropogenic sources are responsible for the main PAN peak around noon. A shift in wind direction from NNE to SSE and later to SW is indicated by the solid vertical line. The wind shift is accompanied by a change from biogenic influence to mostly anthropogenic precursors to PAN formation.
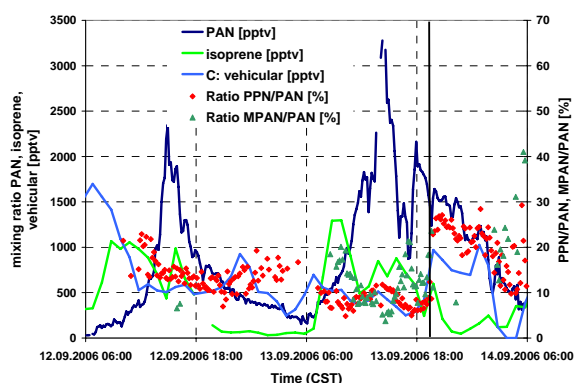

Fig. 6. Time series of PAN, isoprene, PPN/PAN and MPAN/PAN ratio, and the VOC source profile C from Fig. 1 representing vehicular combustion sources. The solid vertical black line indicates a change in wind direction from NNE to SSE and then to SW.

A time series of Aug. 31 is presented in Fig. 7. While there was no MPAN detectable, the anthropogenically formed PPN, APAN, and PiBN were present. The plot also shows the APAN precursor 1,3-butadiene, isoprene, and the modeled factors G and H from Fig. 1, representing LPG and natural gas / evaporative sources. In the morning hours rather high mixing ratios of APAN, PiBN, PPN, and PAN as well as 1,3-butadiene could be observed. In addition, high values of the two factors G and H that consist mainly of evaporated alkanes, indicate industrial origin of the precursors. During the whole time, back trajectories point towards the Houston Ship Channel (not shown here). In the afternoon increased isoprene mixing

ratios are accompanied by a slight increase in PAN. Although no MPAN could be measured, biogenic sources are likely to contribute to this minor peak.
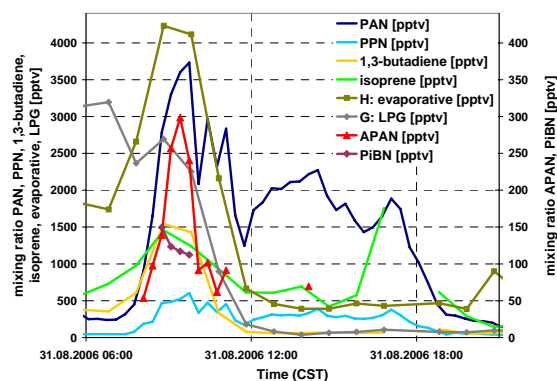

Fig. 7. Time series of PAN, PPN, APAN, PiBN, isoprene, 1,3-butadiene, and the VOC source profiles G and H from Fig. 1. The wind direction remains constant from NE throughout the entire displayed period, indicating air masses from the Ship Channel.

4. REFERENCES

Flocke, F.M., Weinheimer, A.J., Swanson, A.L., Roberts, J.M., Schmitt, R., Shertz, S., 2005: On the Measurement of PANs by Gas Chromatography and Electron Capture Detection. *J. Atmos. Chem.*, 52, 19-43.