

VOC source–receptor relationships in Houston during TexAQS-II

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ABSTRACT

During the TRAMP field campaign in August–September 2006, C₂–C₁₀ volatile organic compounds (VOCs) were measured continuously and online at the urban Moody Tower (MT) site. This dataset was compared to corresponding VOC data sets obtained at six sites located in the highly industrialized Houston Ship Channel area (HSC). Receptor modeling was performed by positive matrix factorization (PMF) at all sites. Conditional probability functions (CPF) were used to determine the origin of the polluted air masses in the Houston area. A subdivision into daytime and nighttime was carried out to discriminate photochemical influences. Eight main source categories of industrial, mobile, and biogenic emissions were identified at the urban receptor site, seven and six, respectively, at the different HSC sites. At MT natural gas/crude oil contributed most to the VOC mass (27.4%), followed by liquefied petroleum gas (16.7%), vehicular exhaust (15.3%), fuel evaporation (14.3%), and aromatics (13.4%). Also petrochemical sources from ethylene (4.7%) and propylene (3.6%) play an important role. A minor fraction of the VOC mass can be attributed to biogenic sources mainly from isoprene (4.4%). Based on PMF analyses of different wind sectors, the total VOC mass was estimated to be twofold at MT with wind directions from HSC compared to air from a typical urban sector, for petrochemical compounds more than threefold. Despite the strong impact of air masses influenced by industrial sources at HSC, still about a third of the total mass contributions at MT can be apportioned to other sources, mainly motor vehicles and aromatic solvents. The investigation of diurnal variation in combination with wind directional frequencies revealed the greatest HSC impact at the urban site during the morning, and the least during the evening.

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1. Introduction

Volatile organic compounds (VOCs) are important in the formation of secondary air pollutants such as ozone, peroxy-carboxylic nitric anhydrides, aldehydes, and secondary organic aerosols in photochemical processes. In addition, many VOC species act directly as air toxics or hazardous air pollutants. Thus, monitoring and modeling of the spatiotemporal distribution of those species, in particular in industrialized urban areas with high emission rates, is important for mitigation strategies concerning human health.

The Houston metropolitan area is a highly industrialized urban region with the largest number of petrochemical facilities within the United States, large number of other industrial, and significant mobile emission sources due to a very limited public transportation system. Extensive areas of deciduous and coniferous vegetation cover along with subtropical climate conditions make biogenic

sources another significant VOC emission source in this region. Previous studies (e.g. Jobson et al., 2004; Zhao et al., 2004; Buzcu and Fraser, 2006; Xie and Berkowitz, 2006) have shown that the VOC mixture in Houston is very complex, due to numerous different sources such as evaporation of oil, gasoline and solvents, petrochemical manufacturing and refining, and motor vehicle exhaust. In order to identify the different source categories and estimate their respective contributions, advanced multivariate receptor models have been developed and applied successfully in many air pollution studies. Out of the four most widely applied source apportionment techniques that are principal component analysis/absolute principal component scores (PCA/APCS) (e.g. Guo et al., 2004, 2006; Chan and Mozurkewich, 2007), chemical mass balance (CMB) (e.g. Na and Kim, 2007; Badol et al., 2008), UNMIX (e.g. Jorquera and Rappenglück, 2004; Olson et al., 2007), and positive matrix factorization (PMF) (e.g. Paatero, 1997; Lingwall and Christensen, 2007), the latter has been tested successfully in comparison with the other receptor models for both VOCs (Anderson et al., 2002; Miller et al., 2002) and PM (Viana et al., 2008a) and has shown to provide robust results for VOCs in the Houston industrial areas (Kim et al., 2005; Buzcu and Fraser, 2006; Xie and Berkowitz, 2006).

Within the framework of the comprehensive Texas Air Quality Study-II (TexAQS-II) which covered a wide range of simultaneous

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measurements of meteorological parameters and air chemical species in the Houston–Galveston area during August and September 2006, the TexAQS-II Radical and Aerosol Measurement Project (TRAMP) comprised the only ground-based supersite (further details see Lefer and Rappenglück, in this issue). It was located at the Moody Tower (MT) on the University of Houston campus, approximately 5 km southeast of Downtown Houston and 10 km west from the western edge of the Houston Ship Channel (HSC) (Fig. 1). The monitoring site was built on the rooftop of a 60 m tall student dormitory building without major local emission sources. The site is unique, because depending on meteorological conditions it may be affected by different air masses from urban, biogenic, and industrial sources throughout the Houston area in contrast to previous receptor modeling studies that focused exclusively on highly industrialized sites located within HSC (Buzcu-Guven and Fraser, 2008; Buzcu and Fraser, 2006; Xie and Berkowitz, 2006; Kim et al., 2005).

For the determination of different source categories, the whole set of C_2 – C_{10} VOCs was measured at this urban site. In addition, VOC data from six sites within the HSC were analyzed to identify industrial source contributions.

This study focuses on a comparative analysis and apportionment of industrial, urban, and biogenic source contributions at the urban and industrial sites, with the objective of assessing the impact of HSC emissions on the urban Houston air, utilizing multivariate receptor modeling of continuous online measurements of VOCs in the summer of 2006.

2. Methods

2.1. Experimental setup

During TRAMP (Aug. 07–Sept. 30, 2006), continuous online measurements of C_2 – C_{10} VOCs were performed at MT. In addition, VOC data were obtained by the TCEQ and Enhanced Industry

Sponsored Monitoring auto-GC networks, which form part of the photochemical assessment monitoring stations (PAMS), within HSC where similar automated gas chromatographic (GC) systems were used. These sites included Channelview, Wallisville Road (Wallisville), Clinton Drive (Clinton), Haden Road (HRM3), Milby Park, and Lynchburg Ferry (Lynchburg) (Fig. 1). The standard methods for instrument calibration, operation, and data quality assurance at these sites follow the PAMS procedures as described by USEPA (1999).

Here, we briefly report the GC instrumentation deployed at MT: the analysis of the VOCs is performed based on developments by Veillerot et al. (1998) using gas chromatography coupled to flame ionization detectors (FID). It includes a Perkin–Elmer VOC-system consisting of a Clarus 500 GC equipped with two FIDs and two columns for multi-dimensional gas chromatography. VOCs are sampled every hour for 40 min at 15 ml min^{-1} flow through a 6 m long $1/8''$ glass-lined stainless steel tube and preconcentrated on a Peltier-cooled cold trap at -30°C . Subsequently the sample is desorbed at 325°C in a backflush mode by a Turbomatrix 650 Automatic Thermal Desorber and injected into the GC with high purity helium (99.995%) as the carrier gas. Prior to preconcentration, water is removed through a Nafion[®] dryer. For separation two columns run in series are used: high molecular weight VOCs are separated by a BP-1 column ($50 \text{ m} \times 0.22 \text{ mm I.D.}$; methyl silicone, SGE International, Australia), low molecular weight VOCs are transferred into a PLOT fused silica column ($50 \text{ m} \times 0.32 \text{ mm I.D.}$; $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$, Varian, USA). Both are placed in the same oven with a 47.8 min multiramp temperature program: 46°C (15 min hold), 5°C min^{-1} to 170°C , $15^\circ\text{C min}^{-1}$ to 200°C (6 min hold). FIDs are kept at 250°C and supplied with high purity hydrogen (PG-H₂ 250, Perkin–Elmer, USA) and synthetic air (TOC gas generator 1250, Parker Balston, USA).

The MT GC system is calibrated using a 30 component EU Directive ozone precursor mixture provided by the UK National Physical Laboratory (NPL, UK). This certified mixture contains

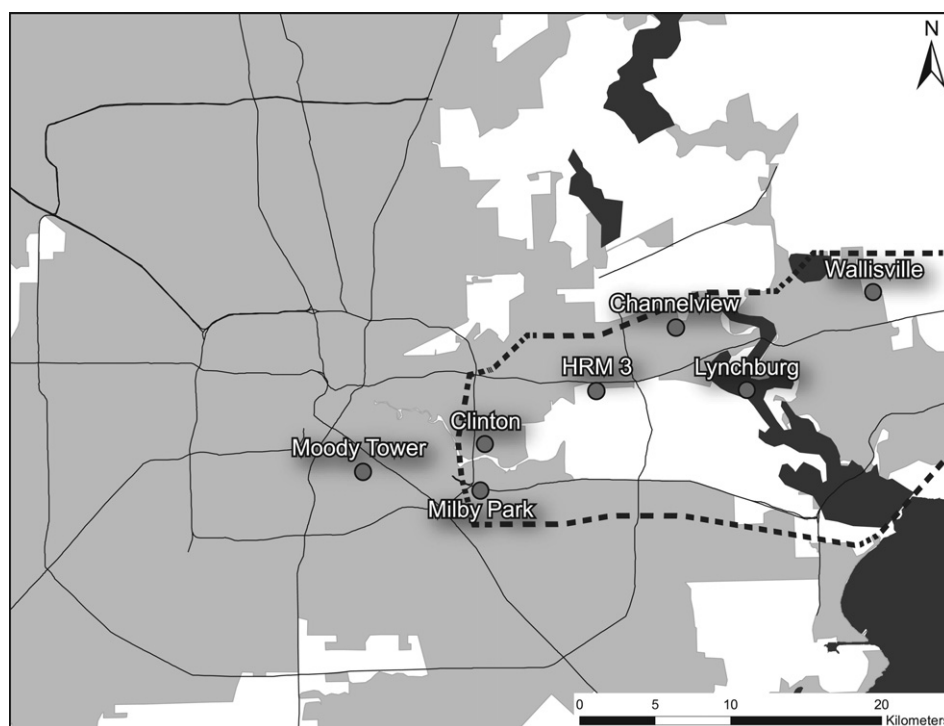


Fig. 1. Locations of the investigated sites in the Houston area during the TexAQS-II campaign. The dashed line shows roughly the extended industrial area surrounding the Houston Ship Channel.

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