



## Source apportionment of particulate matter and trace gases near a major refinery near the Houston Ship Channel



Henry W. Wallace<sup>a,\*</sup>, Nancy P. Sanchez<sup>a</sup>, James H. Flynn<sup>b</sup>, Mathew H. Erickson<sup>b</sup>, Barry L. Lefer<sup>b,1</sup>, Robert J. Griffin<sup>a</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005, USA

<sup>b</sup> Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77004, USA

### ARTICLE INFO

#### Keywords:

Particulate matter  
Hazardous air pollutants  
Airborne carcinogens  
Positive matrix factorization  
Principle component analysis  
Petrochemical refinery  
Secondary organic aerosol  
Primary organic aerosol  
BEE-TEX

### ABSTRACT

From February 7 to 27, 2015, a mobile air quality laboratory was deployed to a location proximate to a major refinery, the Port of Houston, and several neighborhoods to conduct measurements of atmospheric trace gases and particulate matter. Two statistical models were utilized to apportion the sources of pollution impacting this site and the denizens of the nearby neighborhoods. Positive matrix factorization (PMF) was performed on the organic signal of the aerosol mass spectra, resulting in five factors totaling an average of  $4.1 \mu\text{g}/\text{m}^3$  of the organic aerosol: hydrocarbon-like ( $0.67 \mu\text{g}/\text{m}^3$ ), cooking ( $0.35 \mu\text{g}/\text{m}^3$ ) biomass burning ( $1.14 \mu\text{g}/\text{m}^3$ ), low-volatility oxidized ( $1.15 \mu\text{g}/\text{m}^3$ ), and semi-volatile oxidized ( $0.78 \mu\text{g}/\text{m}^3$ ). Principal component analysis was performed on daytime and nighttime data, including concentrations from PMF output, of other  $\text{PM}_{10}$  components, and of trace gases. This generated five daytime and five nighttime factors that explained 74.5% and 73.0% of the variance, respectively. The most important factors impacting this site were from mobile source exhaust and petrochemical aromatic compound emissions. Together these two factors also constitute most of the observed carcinogens.

### 1. Introduction

Air pollution impacts human health, reduces visibility, damages crops and ecosystems and forces climate. In order to reduce these effects in the United States (U.S.), the Clean Air Act (CAA) was enacted in 1970. Promulgation of the CAA established the National Ambient Air Quality Standards (NAAQS) for six criteria pollutants and created the U.S. Environmental Protection Agency (EPA) to enforce the NAAQS.

The formation of the U.S. EPA and enforcement of the NAAQS have improved greatly air quality in the U.S. Since 1980, a 32% reduction in the fourth maximum daily 8-h average ozone ( $\text{O}_3$ ) concentration has been achieved nationally, while a 37% decrease in the annual average of particulate matter with a diameter of less than  $2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) also has been achieved (EPA, 2016). While  $\text{O}_3$  is a secondary pollutant, meaning that it is generated in the lower troposphere as opposed to being emitted directly,  $\text{PM}_{2.5}$  has both primary and secondary sources (Robinson et al., 2007; Zhang et al., 2007). As such, the reductions in  $\text{O}_3$  have been achieved through pollution controls targeting precursor nitrogen oxides ( $\text{NO}_x$ ) and volatile organic compounds (VOCs), while both primary emissions and the emissions of secondary PM precursors (including  $\text{NO}_x$  and VOCs, among other species) have been targeted for

reductions of  $\text{PM}_{2.5}$ . Reduction in emissions of VOCs also is important because many VOCs are toxic compounds with mutagenic and carcinogenic properties. The EPA defines 188 compounds as hazardous air pollutants (HAPs).

Houston, the most populous city in Texas and the fourth most populous city in the U.S., has been one of the fastest growing cities in the U.S. over the past decade. Its denizens travel on average over 153 million vehicle miles per day (Lubertino, 2015), and it is also home to the second largest petroleum refining complex in the world, with over 400 chemical plants and over 40% of the U.S. petrochemical capacity (Port Houston, 2017; Sexton and Linder 2015). In addition, the Port of Houston is the second busiest port in the U.S. by tonnage (Port Houston, 2017). Goods coming to and from the Port of Houston utilize ships, rail cars, and heavy-duty diesel vehicles (HDDV). For example, the HDDV are sources of primary PM (including black carbon (BC) and particle-phase polycyclic aromatic hydrocarbons (PAH)), VOCs (including gas-phase PAH) and  $\text{NO}_x$ . In addition to the plethora of emissions from heavy industry near the Houston Ship Channel (HSC), there are numerous other emission sources impacting Houston, including on-road vehicles, non-road vehicles, cooking, biomass burning, and light industry such as paint shops, gasoline stations, and dry cleaning

\* Corresponding author.

E-mail address: [wwallaceiv@gmail.com](mailto:wwallaceiv@gmail.com) (H.W. Wallace).

<sup>1</sup> Now at Division of Tropospheric Composition, NASA, Washington, DC 20024, USA.

operations. This variety of air pollution sources makes Houston an interesting challenge for air quality managers.

A lack of zoning laws in the state of Texas allows residential neighborhoods and petrochemical refineries to exist in close proximity, and significant increases in the occurrence of cancers are found in these areas. Linder et al. (2008) found that 62 out of 647 census tracts in Harris County, TX, were in the top 90<sup>th</sup> percentile nationally for cancer risk from air pollution. With the exception of the north central downtown area, most of the tracts falling in the 90<sup>th</sup> percentile are located proximate to the highly industrialized HSC. Despite implementation of pollution controls in both the on-road fleet and the refineries, it is critical to evaluate the air and to apportion the sources of pollution in neighborhoods located proximate to heavy industry in the HSC.

This work critically examines and apportions the sources of pollution in an area surrounded by refineries, heavily used roads, and residential neighborhoods. We present measurements of non-refractory particulate matter with a diameter no greater than 1  $\mu\text{m}$  (NR-PM<sub>1</sub>), VOCs including known HAPs, reactive inorganic trace gases, and particulate PAHs. To better understand the sources and relationships of the pollution in this location, we employ positive matrix factorization (PMF) on the NR-PM<sub>1</sub> data set and principle component analysis (PCA) to the entire data set.

## 2. Material and methods

Data presented in this manuscript were collected as a part of the Houston Aerosol Characterization and Health Experiment. The University of Houston/Rice University Mobile Air Quality Laboratory (MAQL), previously described in Leong et al. (2017), monitored air from February 1 through February 27, 2015, in the vicinity of the HSC at 29.7184°N, 95.2537°W. The location and time period were selected to coincide with the Houston Advanced Research Center's Benzene and other Toxics Exposure Study (BEE-TEX) (Olague, 2015). The greater aim of BEE-TEX was to study the exposure of nearby neighborhoods to air toxic compounds from the HSC area and to quantify emissions sources using a real-time inverse modeling algorithm fed with concentrations from mobile observations of benzene and other toxics.

### 2.1. Site description

The site was located to the southeast of downtown Houston along the HSC and provided ample opportunity for the instrumentation to sample a variety of emission sources proximate to the nearby neighborhoods (Fig. 1). A major refinery lies to the north and east, while Texas State Highway (SH) 225 and Interstate 610 (I-610) are to the south and west, respectively. The HSC extends due east from the site. Finally, a small neighborhood is located due west, between the sampling site and I-610.

A multitude of emission sources exist within the refineries including stacks, flares, and fugitive leaks from tanks and pipelines. Olague et al. (2016) found that emission rates of benzene from pipelines moving refined products were 2–6 times higher than accounted for in the national emissions inventory. Significant emissions from unloading of crude oil from tankers in the HSC were also noted by Olague et al. (2016). In addition to refinery emissions, both I-610 and SH-225 serve as major freight corridors for goods moving to and from the Port of Houston. This activity results in a high density of HDDV use. Traffic crossing Buffalo Bayou on I-610 is forced to operate under high engine loads due to the steep grade while crossing the Sidney Sherman Bridge.

### 2.2. Measurements

Four sample inlets were used to bring trace gases and PM to the instrumentation in the MAQL for online analysis. With the exception of the PAS2000 (to be described subsequently) inlet, which was mounted above the MAQL trailer at a height of 3 m, the inlets were mounted on a

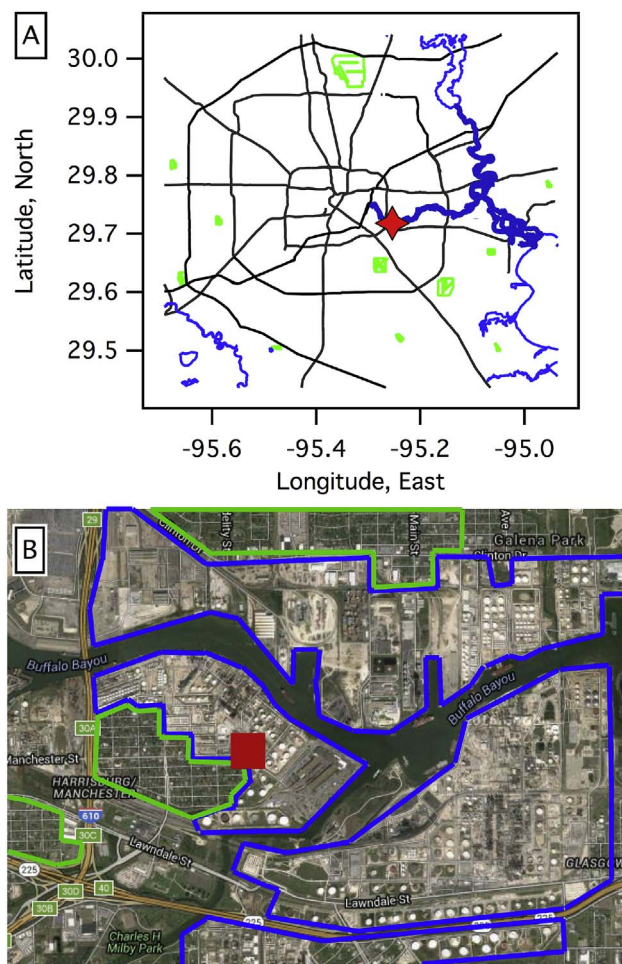


Fig. 1. A) A map showing the site relative to the greater Houston area (center of map). The site location (red star), major roads (black traces), airports (green traces) and rivers or bodies of water (blue traces) are included in the map. The HSC is demarcated from other bodies of water with thicker blue lines. B) A map taken from Google Earth on 3/14/2017, shows a close up of the site area. The site (red square), adjacent neighborhoods (green traces), and industrial/petrochemical complexes (blue traces) are shown. The prominent freeways, I-610 running north to south and SH-225 running east to west, are visible. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

crane hoisted to an elevation of 6 m. Instrumentation for trace gases including nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), total reactive nitrogen (NO<sub>x</sub>), carbon monoxide (CO), O<sub>3</sub>, and sulfur dioxide (SO<sub>2</sub>) shared a common line, while the proton-transfer reaction quadrupole mass spectrometer (PTR-QMS, for VOC measurement) and the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) each had their own inlets. The PTR-QMS inlet consisted of a 1/4" O.D. PFA Teflon tube heated to 65 °C. Flow in the PTR-QMS inlet was maintained at a rate of 10–15 standard liters per minute (SLPM), and a smaller flow of 100 standard cubic centimeters per minute (SCCM) was drawn into the PTR-QMS from the sample flow for analysis. The HR-ToF-AMS inlet consisted of a 2.5- $\mu\text{m}$  cut diameter Teflon<sup>®</sup>-coated cyclone (URG Corporation) followed by approximately 8 m of 1.27 cm O.D. copper tubing. Air was drawn through the inlet at a rate of 16.7 SLPM to achieve the desired aerosol size cut of 2.5  $\mu\text{m}$  in the cyclone. The cyclone was utilized to prevent the critical orifice in the HR-ToF-AMS inlet (100  $\mu\text{m}$  diameter) from clogging. From the main sample flow, approximately 80 SCCM were drawn through a MD-series, Nafion dryer (Perma Pure, LLC) to the inlet of the HR-ToF-AMS. This configuration dried the sample to below 45% relative humidity. The PAS2000 inlet included a cyclone with a 2.5- $\mu\text{m}$  cut diameter, but the flow was not

Download English Version:

<https://daneshyari.com/en/article/8864253>

Download Persian Version:

<https://daneshyari.com/article/8864253>

[Daneshyari.com](https://daneshyari.com)