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Detailed emission profiles for on-road vehicles derived from ambient measurements during a windless traffic episode in Baltimore using a multi-model approach

Haohao Ke [a], John M. Ondov [a, *], Wolfgang F. Rogge [b]

[a] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA
[b] School of Engineering and Sierra Nevada Research Institute, University of California Merced, USA

HIGHLIGHTS

- Chemical profiles of motor vehicle emissions were determined using 4 methods.
- The profiles contain 51 molecular markers and 14 other traffic-related species.
- Gasoline-vehicles dominated vehicular emissions on I-895 in Baltimore, MD.

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ABSTRACT

Composite chemical profiles of motor vehicle emissions were extracted from ambient measurements at a near-road site in Baltimore during a windless traffic episode in November, 2002, using four independent approaches, i.e., simple peak analysis, windless model-based linear regression, PMF, and UNMIX. Although the profiles are in general agreement, the windless-model-based profile treatment more effectively removes interference from non-traffic sources and is deemed to be more accurate for many species. In addition to abundances of routine pollutants (e.g., NO_x, CO, $PM_{2.5}$, EC, OC, sulfate, and nitrate), 11 particle-bound metals and 51 individual traffic-related organic compounds (including n-alkanes, PAHs, oxy-PAHs, hopanes, alkylcyclohexanes, and others) were included in the modeling.

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1. Introduction

In the Mid-Atlantic region, motor vehicle exhaust is known to be an important source of air pollution (Lambe et al., 2009; Larsen and Baker, 2003; Ogulei et al., 2005, 2006; Ondov et al., 2006; Park et al., 2006; Suarez and Ondov, 2002). For example, in urban Baltimore, 27% of the annual fine particulate matter ($PM_{2.5}$) was attributed to vehicular emissions (Ogulei et al., 2005), among which the majority was emitted during traffic rush-hours creating the potential for high short-term human exposures. The effects of human exposures to vehicular exhaust is of growing concern (Finkelstein et al., 2004; Jacobs et al., 2010; Kaur et al., 2007; Lipfert et al., 2006; Nawrot et al., 2011; Park et al., 2009; Schwartz, 2005) with more evidence suggesting that high short-term exposure levels are responsible for acute health effects, including increased cardiovascular mortality (Chuang et al., 2007; O'Connor et al., 2008) and respiratory infections (Brauer, 2002; Karr et al., 2009). To a large extent, exposure assessment relies on the availability of detailed emission profiles for on-road vehicles with fossil fuel powered internal combustion engines (Glaser et al., 2005; Nielsen, 1996; Oliveira et al., 2010). Although a substantial number of motor–vehicle profiles are available (e.g., EPA's SPECIATE database, U.S.EPA, 2006), most were derived from dynamometer tests using a relatively small number of vehicles and highly prescribed operating conditions and driving patterns, often differing from actual on-road driving conditions (Cadle et al., 2009; Casati et al., 2007; Holmen and Niemeier, 1998). Very few of these profiles include much beyond abundances of elemental carbon (EC), organic carbon (OC), several metals, and relatively few organic compounds known to be markers of various classes of motor vehicle emissions (Khalili et al., 1995; Landis et al., 2007; Rogge et al., 1993a; Rönkkö et al., 2006; Watson, 1979). And most are not representative of traffic emissions in the Eastern US, wherein lies 58% of the US population.

* Corresponding author. Tel.: +1 301 405 1859; fax: +1 301 314 9121.
E-mail addresses: haohaoke@umd.edu, ke.haohao@gmail.com (H. Ke), jondov@umd.edu (J.M. Ondov), wrogge@ucmerced.edu (W.F. Rogge).

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Fig. 1. The Road map around the Baltimore PM supersite at Ponca St. (provided by *Google* Earth). The tunnel toll facilities are located at the convergence of I895 and I95 at the point marked with an asterisk.

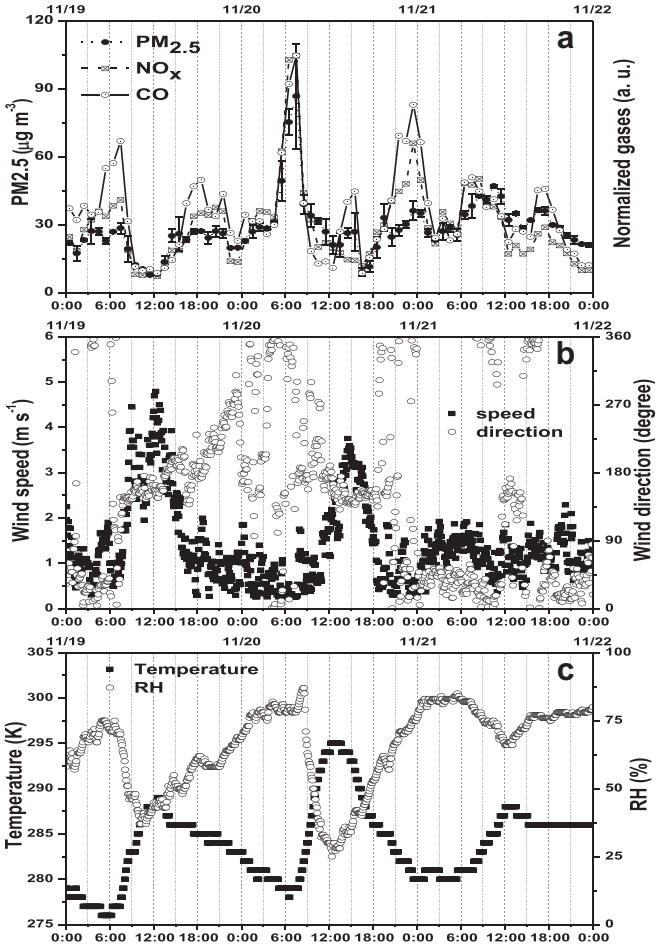

Fig. 2. Time series of a) concentrations of $PM_{2.5}$, NO_x, and CO (normalized to the maximum concentration of $PM_{2.5}$); b) wind profile; and c) ambient temperature and relative humidity (RH) from November 19th through 22nd, 2002 at the Ponca street supersite.

Organic compounds from motor vehicle emissions have been extensively investigated by GC–MS in the late 1990s by Rogge et al. (1996, 1993a), Schauer and Cass (2000); and Schauer et al. (1996). Nevertheless, the measurements were made on relatively few (<20) vehicles and these early studies were conducted in California where different emission standards were enforced and environmental and regulatory factors (e.g., temperature, humidity, altitude, engine inspection frequency) differ markedly from urban areas in the Mid-Atlantic States. Moreover, these are somewhat outdated because gasoline composition and engine and emission control technologies have changed substantially since then (e.g., the Clean Air Act completely banned the sale of leaded fuel since 1996 and gasoline typically now contains up to 10% ethanol). There are few profiles (Fitz et al., 2004; Zielinska et al., 2004) containing a large number of semi-volatile organic compounds (SVOCs), in addition to EC, OC, metals, and VOCs, along with criteria gas emissions of NO, NO_2, and CO available for the eastern US and the Mid-Atlantic States in particular. Fewer still were collected in urban areas or traffic tunnels such that emissions from large numbers of vehicles could be examined during real-world driving conditions. Even fewer were collected at high time resolution, i.e., such that motor vehicle emissions could be better isolated from interfering sources.

Previously, Park et al. (2006) described a cool-weather $PM_{2.5}$ episode that was monitored at the Baltimore Supersite on Ponca street in November of 2002, when stagnant conditions prevailed during a weekday morning commute period resulting in a severe excursion of $PM_{2.5}$ and traffic related pollutants. As this site was located only 50 m away from the highly trafficked Baltimore harbor tunnel throughway (I-895), it was ideally suited to assess the influence of traffic on urban air quality and, in particular, to determine motor vehicle chemical emission profiles. Herein, we present a comprehensive profile of motor vehicle emissions including both semi-volatile and particle-phase organic compounds (TSVOCs), in addition to routine species (i.e., NOx, CO, sulfate, nitrate, EC, OC, and metals) using highly-time resolved data collected during this episode. Four independent modeling approaches, including simple peak analysis, a windless open-terrain regression model (Ke, 2012), positive matrix factorization (PMF), and UNMIX, were used to extract the profiles. As Baltimore exited the oxygenated gasoline program in the mid-1990s and the composition of gasoline, such as the levels of ethanol and methyl tert-butyl ether (MTBE), has barely changed since 2002, these speciation profiles likely represent the current fuel use across the eastern US and allow future assessment of vehicle emission controls.

2. Site and episode description

As shown in Fig. 1, the Ponca street site was located in close proximity to two major interstate highways, I-895 and I-95, and about 1 km north of two tunnel toll facilities (i.e., Fort McHenry and Baltimore Harbor tunnels), through which more than 180,000 motor vehicles passed daily. In this area, the terrain gradually slopes downwards from 33 m above sea level on the roadway near the site to nearly 0 m at the Baltimore Harbor. For more details, see Ondov et al. (2006) and Ke (2012).

The three-day episode considered herein lasted from November 19th through the 21st, 2002. During this period, the time series of $PM_{2.5}$ concentrations were generally in a synchronous pattern with those of traffic-related gaseous pollutants (i.e., NO_x and CO), especially during the morning rush hours (Fig. 2a). Northerly to northeasterly low-speed (<2 m s^{-1}) winds prevailed during the entire episode (Fig. 2b), except around noon on the 19th and the late afternoon of the 20th, when average wind speeds exceeded