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Spatial gradients and source apportionment of volatile organic compounds near roadways

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ABSTRACT

Concentrations of 55 volatile organic compounds (VOCs) (C_2–C_{12}) are reported near a highway in Raleigh, NC. Thirty-minute samples were collected at eight locations, ranging from approximately 10–100 m perpendicular from the roadway. The highest concentrations of VOCs were generally measured closest to the roadway, and concentrations decreased exponentially with increasing distance from the roadway. The highest mean concentration for individual VOCs were for ethylene (3.10 ppbv) (mean concentration at $x = 13$ m), propane (2.27 ppbv), ethane (1.91 ppbv), isopentane (1.54 ppbv), toluene (0.95 ppbv), and *n*-butane (0.89 ppbv). Concentrations at the nearest roadway location ($x = 13$ m) were generally between 2.0 and 1.5 times those from the farthest roadway location ($x = 92$ m). The data were apportioned into four source categories using the EPA Chemical Mass Balance Model (CMB8.2): motor vehicle exhaust, compressed natural gas, propane gas, and evaporative gasoline. The majority of the VOCs resulted from motor vehicle exhaust (67 ± 12%) (% of total VOC at $x = 13$ m ± S.D.). Compressed natural gas, propane gas, and evaporative gasoline accounted for approximately 15%, 7% and 1% of the total VOC emissions, respectively, at $x = 13$ m.

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1. Introduction

Motor vehicles constitute a major source of emissions in urban areas, comprising a variety of pollutants, including volatile organic compounds (VOCs) (29% of emissions in the U.S. as estimated in U.S. Environmental Protection Agency, 2001), nitrogen oxides (NO_x) (34%), and carbon monoxide (CO) (51%). Several approaches have been used to estimate the contribution of vehicle emissions to ambient concentrations. These include source tests, where emission factors and/or detailed chemical profiles are developed for different vehicles and operating conditions, typically using a dynamometer under controlled test conditions. For example, source tests have reported that VOCs comprise >95% (by mass) gasoline-powered motor vehicle exhaust (Schauer et al., 2002) and >50% medium-duty truck exhaust (Schauer et al., 1999). Numerous gas-phase organic compounds have been identified and quantified, including aromatic hydrocarbons, alkanes, and alkenes. Because source profiles are limited to the sources and conditions tested, these studies can been supplemented by measurements collected in roadway tunnels (e.g., Legreid et al., 2007; McGaughey et al., 2004) to represent a composite vehicle fleet in an actual urban area. Advances in sampling and analytical techniques have expanded the library of source profiles such that source markers have been widely used in receptor modeling of PM concentrations (e.g., Schauer and Cass, 2000, Schauer et al., 1996). In addition, several source apportionment studies (Wittig and Allen, 2008; Hellen et al., 2006, 2003; Choi and Ehrman, 2004; Mukerjee et al., 2004) have estimated the contributions of various sources to ambient VOC levels.

Studies have reported various PM size fractions (nano, ultrafine, fine, coarse) near roadways (e.g., Zhu et al., 2006, 2002; Charron and Harrison, 2005; Lin et al., 2005), but reports of spatial variability near roadways have generally been limited to surrogate measurements (PM, CO, etc.) as opposed to source markers for receptor models. Particle number concentrations have been reported to decay exponentially with distance from the roadway, e.g., an approximately 5-fold decrease in particle number concentration from 30 m to 300 m near a Los Angeles highway during daytime (Zhu et al., 2006).

Although dozens of organic compounds have been reported from source tests of motor vehicles, studies reporting VOC concentrations in near road environments have been limited. Chan et al. (2002) reported concentrations of VOCs from 16 near roadway sites (21,000–50,000 daily traffic counts) in urban and industrial areas. Concentrations for most VOCs were higher in the industrial as compared with the residential area (e.g., mean benzene concentrations of 31.8 and 17.6 μg m^{-3} in the industrial and

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residential areas, respectively). Chang et al. (2006) measured VOCs from two roadway sites to evaluate the suitability of different vehicle source markers, including aromatic and aliphatic hydrocarbons.

Exposure to elevated VOC concentrations near roadways may be an important contributor to total VOC exposures for populations that live near major roadways. Data from the U.S. Census indicate that 36 million people in U.S. live within 300 feet of a four-lane highway, railroad, or airport (U.S. Census Bureau, 2005). Recently, the U.S. EPA has incorporated the influence of living near a major roadway into exposure modeling conducted as part of the National Air Toxics Assessment (NATA) using the limited data available for providing an estimate of roadway impact (U.S. Environmental Protection Agency, 1999a; Rosenbaum and Huang, 2007). The exposure model used in this assessment estimates the relative increase in chemical concentrations based on proximity to roadway. Studies that characterize the spatial pattern of elevated VOC concentrations near roadways are needed to improve exposure and risk assessment for urban populations living near major roadways.

The objective of this study is to quantify spatial differences in VOCs near roadways. Although numerous studies have reported VOC concentrations in urban areas, few have focused on VOC gradients near roadways. Studies have reported spatial variability of bulk parameters (e.g., CO, NO_x, PM size fractions) in near roadway environments, but none have quantified spatial differences in VOCs. This research reports concentrations of 55 VOCs near a highway in Raleigh, NC using sampling locations at eight different horizontal distances perpendicular to the road (10–100 m) and three vertical distances (0.5–2 m) to examine spatial variability in VOCs near roadways.

2. Experimental methods

2.1. Site description

VOC measurements were collected at eight horizontal distances and three vertical distances near a highway in Raleigh, NC (Fig. 1). U.S. Interstate 440 (I-440) is an 8-lane, limited access highway carrying a daily weekday traffic volume of approximately 125,000 vehicles day^{-1}. The highway, which surrounds the perimeter of north Raleigh, predominately carries local traffic. Average heavy-duty truck volume on I-440 was approximately 4% during the study. A secondary road carrying approximately 200 vehicles day^{-1} was located parallel to I-440 (approximately 10 m north of I-440). The site was an open field that extended 120 m north from I-440; the field was at grade with the highway. No physical structures were present at the study location other than a guardrail adjacent to the highway and sparse shrubbery (all <1 m in height). A one-story building (height <10 m) was located at the study site; for all monitoring locations, samples were collected at least 20 m from this building. Fewer than 100 passenger cars per day were estimated to use the parking lot and adjacent access road to the building in a typical day. No other sources of VOCs were identified within 1 km of the study site. Additional details on the site description are given elsewhere (Baldauf et al., 2008).

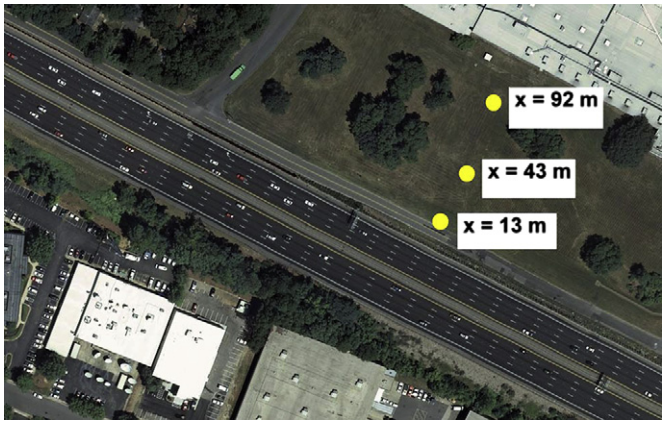

Fig. 1. Map of sampling locations.

The eight horizontal distances were located at 13, 19, 25, 31, 43, 58, 74, and 92 m from the roadway (Fig. 1); all samples were collected along the same transect perpendicular from the road. One VOC sample was collected at each of the eight sampling locations for each sampling period. Sampling sites located farther from the roadway were not selected so that all samples were collected at grade with the highway and unobstructed from the one-story building. At the 13 m site, samples were also collected at three different vertical distances ($z = 0.5$, 1.0 and 1.5 m). VOC samples were collected for 5 different sampling periods; given the comparatively small number of sampling periods, sample collection focused on rush hour traffic periods on weekdays. Sampling periods included a mix of morning (collected at approximately 8:00 AM) and afternoon (collected at approximately 5:00 PM) samples. Weather conditions during sampling were generally clear with wind speeds ranging from 1 to 1.5 m s^{-1}. All measurements were collected during August 2006.

2.2. Sample collection and analytical methods

Samples were collected for 30 min in 6-L, evacuated, internal surface treated (Summa electropolished), stainless steel canisters; four different sampling days were completed over the course of the study. Canister cleaning and sample preparation were performed using U.S. EPA compendium method TO-14A (U.S. Environmental Protection Agency, 1999b).

Traffic volume was measured using traffic surveillance cameras mounted within 5 m of I-440. Vehicle counts, speed, and size class (motorcycles, light-duty cars, light-duty trucks, and heavy-duty trucks) were estimated using TigerEye software (DTS Inc.). Additional details on traffic measurements are described elsewhere (Baldauf et al., 2008).

Wind speed and wind direction data were collected using sonic anemometers (Model 81000 Ultrasonic Anemometer, R.M. Young Co.). Additional details on meteorological measurements are described elsewhere (Baldauf et al., 2008).

Canister samples were analyzed for C_2–C_{12} VOCs using a gas chromatograph (GC, Hewlett–Packard 5890 Series) equipped with flame ionization detector (FID) with cryogenic preconcentration. Analytical procedures were completed using U.S. EPA compendium method TO-14A (U.S. Environmental Protection Agency, 1999b). A 60-m, 0.32-mm i.d., fused silica capillary column with 1.0-μm film thickness (DB-1, J&W Scientific, Rancho Cordova, CA) was used for separation of target analytes. Additional details describing cryogenic concentration of samples, peak identification and quantitation are provided elsewhere (U.S. Environmental Protection Agency, 1999b; Seila et al., 2001). A repeat analysis was completed for each canister sample collected.

A compound list consisting of 55 VOCs was used for all samples described in this study, based on a hydrocarbon target list used at the U.S. EPA Photochemical Assessment Monitoring Station (PAMS) network sites (U.S. Environmental Protection Agency, 2003). Similar target lists have been used in previous source apportionment studies (e.g., Mukerjee et al., 2004; Fujita, 2001; Watson et al., 2001). Several of the compounds measured in this study are also classified