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Source apportionment of VOCs in the Los Angeles area using positive matrix factorization

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Abstract

Eight 3-h speciated hydrocarbon measurements were collected daily by the South Coast Air Quality Management District (SCAQMD) as part of the Photochemical Assessment Monitoring Stations (PAMS) program during the summers of 2001–03 at two sites in the Los Angeles air basin, Azusa and Hawthorne. Over 30 hydrocarbons from over 500 samples at Azusa and 600 samples at Hawthorne were subsequently analyzed using the multivariate receptor model positive matrix factorization (PMF). At Azusa and Hawthorne, five and six factors were identified, respectively, with a good comparison between predicted and measured mass. At Azusa, evaporative emissions (a median of 31% of the total mass), motor vehicle exhaust (22%), liquid/unburned gasoline (27%), coatings (17%), and biogenic emissions (3%) factors were identified. Factors identified at Hawthorne were evaporative emissions (a median of 34% of the total mass), motor vehicle exhaust (24%), industrial process losses (15%), natural gas (13%), liquid/unburned gasoline (13%), and biogenic emissions (1%). Together, the median contribution from mobile source-related factors (exhaust, evaporative emissions, and liquid/unburned gasoline) was 80% and 71% at Azusa and Hawthorne, respectively, similar to previous source apportionment results using the chemical mass balance (CMB) model. There is a difference in the distribution among mobile source factors compared to the CMB work, with an increase in the contribution from evaporative emissions, though the cause (changes in emissions or differences between models) is unknown.

Keywords: Source apportionment; PMF; VOC; PAMS; Receptor modeling

1. Introduction

Volatile organic compounds (VOCs) are important precursors to ozone (Carter, 1994; Chameides et al., 1992). Understanding the temporal and spatial characteristics of VOCs gives insight into likely VOC emissions sources and sources to which emissions controls should be applied for ozone reductions. To comply with the 1990 Clean Air Act Amendments, the US Environmental Protection Agency (EPA) initiated the Photochemical Assessment Monitoring Stations (PAMS) program for ozone nonattainment areas. This network was established to provide information about the effectiveness of control strategies, trends, and exposure on ozone precursors (Demerjian, 2000). The Los

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Angeles South Coast Air Basin (SoCAB) was designated a "severe" ozone nonattainment area, and has extensive PAMS monitoring.

Some PAMS target compounds such as isoprene, which is primarily emitted by biogenic sources in the SoCAB, are useful as markers for specific source types. Other VOCs, such as i-pentane, are emitted by a number of sources. Source apportionment techniques can be applied to better understand the contribution of the principal VOC emissions sources to ambient concentrations in the SoCAB. Previous source apportionment efforts of VOCs in the SoCAB have used the chemical mass balance (CMB) model (Fujita et al., 2003a, 1994; Harley et al., 1992; Schauer et al., 2002), which fits ambient data to specific source profiles. Drawbacks of this type of model are that only source profiles used in the model can be resolved (i.e., if coatings emissions are not included in the model, they cannot be identified), and up-to-date profiles are needed. In the past decade, source apportionment tools such as positive matrix factorization (PMF) (Paatero and Tapper, 1994) have been developed that require only ambient data, and assumptions of sources or specific profiles are not explicitly needed. The primary drawback of models such as PMF is the need for a large data matrix. However, the data collected over several years as part of the PAMS program is more than adequate for application of PMF.

2. Methods

2.1. Data

As part of the PAMS program, eight 3-h canister samples were collected every third day at a number of sites in the SoCAB during the ozone season (generally July–September) from 2001 to 2003. Sample start times are used throughout this discussion. Site locations are shown in Fig. 1. Azusa and Hawthorne were selected for source apportionment analysis because they have a large, good-quality data set and are typical of sites in the SoCAB. The canisters were analyzed with gas chromatography-flame ionization detection (GC-FID) by the South Coast Air Quality Management District (SCAQMD) for 56 target hydrocarbons, with minimum detection limits (MDLs) of 0.2 ppbC. Sampling and analytical methods are fully described in the PAMS technical assistance document (Code of Federal Regulations, 1997; US Environmental Protection Agency, 1999). Data were then validated using a standard approach developed for the PAMS program (Cardelino and Chameides, 2000; Lewis et al., 1996; Main and Haste, 1997).

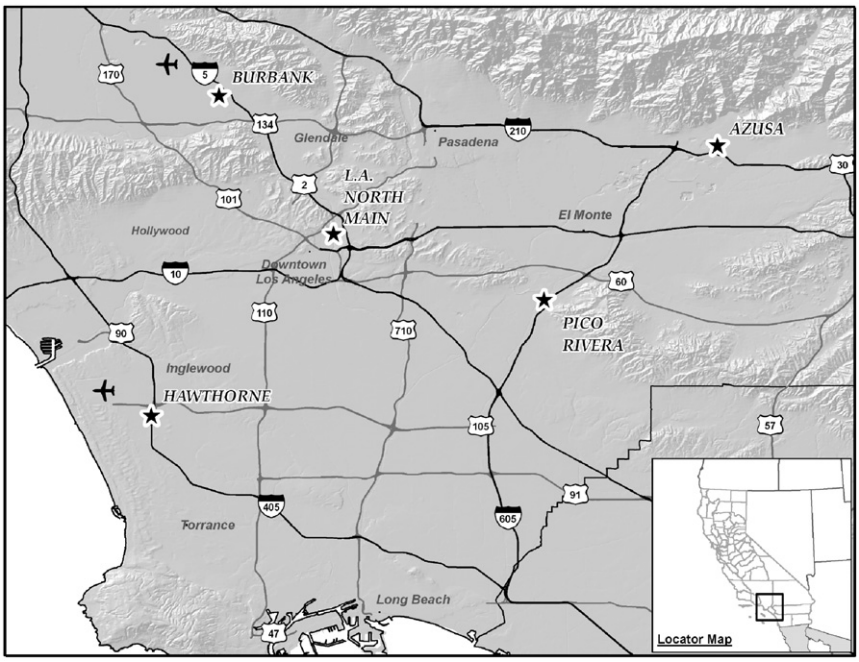

Fig. 1. Location of selected PAMS and PAMS-like monitoring sites in the SoCAB area.