Available online at www.sciencedirect.com
ScienceDirect
Atmospheric Environment 41 (2007) 6715–6728
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Chemical mass balance receptor model applied to ambient C_2–C_9 VOC concentration in Seoul, Korea: Effect of chemical reaction losses

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Received 15 September 2006; received in revised form 24 April 2007; accepted 25 April 2007

Abstract

A chemical mass balance (CMB) receptor model was used for estimating the diurnal contributions of VOC emission sources to the ambient C_2–C_9 VOC concentration in Seoul, Korea. For this purpose, the VOC concentrations were measured in the morning, the afternoon, and the evening. The samples were collected using a 2-h integrated SUMMA canister. The source profiles were developed for the CMB calculation in the Seoul area. To investigate the effect of the chemical reaction loss of VOCs on the CMB calculation, the modified model employing a decay factor and the standard model that considers no loss were compared. The modified model estimated that the vehicle exhaust (52%) was the largest leading source of VOCs in the Seoul atmosphere, followed by the use of solvents (26%), gasoline evaporation (15%), the use of liquefied petroleum gas (LPG) (5%), and the use of liquefied natural gas (LNG) (2%). Relative source contribution for vehicle exhaust showed a clear diurnal variation with a high in the morning and evening and a low in the afternoon, while the contribution of evaporative emissions (gasoline evaporation and solvent usage) showed a different diurnal pattern from that of the vehicle exhaust, exhibiting a high in the afternoon and evening and a low in the morning. It was found that the difference between the total source contribution ($\mu g\,m^{-3}$) estimated from these two models was not statistically significant. However, when the paired-sample *t*-test is applied to the individual sources, a significant difference was found for the vehicle exhaust and the solvent use. In addition, the modified model brought forth a better performance with high R^2 and low χ^2 as compared to those obtained from the standard model in the CMB calculation. The vehicle exhaust and solvent use were estimated to be the largest and the second largest contributors to ambient benzene as well as ozone formation potential (OFP), respectively. Based on above results we believe that incorporating the reaction loss in the CMB calculations helps to better fit the source profile to the ambient VOC concentrations. However, the reaction loss does not significantly affect the estimation of source contributions.

Keywords: Benzene; CMB; Diurnal source contribution; Ozone formation potential; Photochemical loss; VOCs

1. Introduction

The chemical mass balance (CMB) receptor model has been used to establish air quality

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doi:10.1016/j.atmosenv.2007.04.054

management programs to control VOCs or to evaluate the accuracy of VOC emission inventory (Hellén et al., 2003; Srivastava, 2004). This technique uses the pattern of speciated emissions from major source categories to determine the contributions of those sources to a given sample of ambient air. Because the method is based on a top-down analysis of ambient measurements, it provides an independent verification on emission inventories developed by the more traditional bottom-up approach from emission factors and source-test techniques.

The emission inventories for VOCs have been an important factor to evaluate the effectiveness of strategies for reducing ground-level ozone and hazardous organic compounds (Fujita et al., 1994; Chung et al., 1996). Previous studies pointed to a large underestimation of vehicle emissions (Pierson et al., 1990; Fujita et al., 1992) and demonstrated the need to evaluate emission rate uncertainties when photochemical air quality models were applied (Harley and Cass, 1995). This problem has brought about considerable interest in using ambient measurements to inspect VOC emission estimates.

The CMB receptor model provides a variety of approaches for improving emission estimates that have been widely and successfully used for particulate matter. However, relatively few receptor modeling studies have been conducted for VOCs, mainly due to the problem that VOCs emitted from sources are degraded by photochemical reactions (Lin and Milford, 1994). In an attempt to minimize the effect of chemical loss on source estimates in the CMB modeling, VOC samples obtained during winter or in the early morning in which chemical loss effect is less significant than during summer or in the afternoon have been selected (Aronian et al., 1989; Vega et al., 2000). In the CMB calculation, ambient measurement data and source profiles are necessary for input data. VOCs emitted into the atmosphere undergo loss processes such as chemical reactions. The degree of loss of VOCs varies depending on its reactivity and the abundance of radicals in the atmosphere. For example, propylene is highly reactive, and its chemical degradation on its way from the source to the receptor may significantly alter the measured VOC composition. As a consequence, fitting the VOC source profile to the measured VOC data may cause a significant error in the CMB calculation unless the loss effect is taken into account.

In this study, we considered the photochemical loss of VOCs in the estimation of source strengths to investigate how significantly chemical loss affects the CMB calculation. In addition, ozone formation potential (OFP) and toxicity of major VOC sources were addressed.

2. Experimental method

2.1. Input data for CMB calculation

The CMB model requires two data sets for estimating source contribution estimates: (1) ambient measurement data and (2) source profiles. The geographical location of the sampling site is shown in Fig. 1. In brief, the sampling location is located in central Seoul, surrounded by residential and commercial areas and approximately 300 m from major roads. In addition, no significant local emission sources were found near the sampling location, suggesting that the sampling location in this study is adequate for representing the mixture of various VOC emission sources. VOC concentrations were measured from 8 through 13 September 1998. On each sampling day, three 2-h-integrated canister samples were collected in the morning (from 07:00 a.m. to 09:00 a.m.), afternoon (02:00 p.m. to 04:00 p.m.), and evening (06:00 p.m. to 08:00 p.m.), respectively. A total of 18 samples were collected during the study period. Thirty-three species were used for fitting compounds. The time-based concentrations of measured VOCs are shown in Fig. 2.

The source profiles used in this study were measured in Seoul in 2000 (Na et al., 2004). The prototype of source profiles is presented in Table 1. The source profiles used for the modified CMB modeling are reconstructed according to reaction loss by OH radical and ambient temperature. They include vehicle exhaust from a traffic tunnel (combination of gasoline-, diesel-, and butane-powered vehicle and motorcycles), composite gasoline evaporation (gasoline evaporation arising from filling up the tank plus whole gasoline evaporation caused by spills), solvent use (paints and thinners), liquefied petroleum gas (LPG), and liquefied natural gas (LNG). Since the CMB model is often unable to tell gasoline evaporation and whole liquid gasoline evaporation apart due to co-linearity, these two source profiles are combined.

The selection of source types for receptor modeling is based on the emission inventory estimated in 1997 by the Ministry of Environment (MOE, 2000)