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Distributions of C_2–C_5 NMHCs and related trace gases at a tropical urban site in India

L.K. Sahu*, S. Lal

Physical Research Laboratory (PRL), Navrangpura, Ahmedabad 380 009, India

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Abstract

Simultaneous surface measurements of C_2–C_5 non-methane hydrocarbons (NMHCs), O_3, CO and CH_4 were made during the year 2002 at a tropical urban site, Ahmedabad. This is the first time that NMHCs levels have been characterized in detail in India. The diurnal distributions of these species show pronounced variations in the winter months and less during the summer months. The seasonal variations of all these species show substantially higher levels during the winter and lowest during the summer season. The strength (winter to summer ratios) of seasonal variations in NMHCs are observed to be higher than other reported measurements elsewhere. The seasonal changes in transport patterns, boundary layer height and OH concentrations, all contribute in the seasonal variations of these trace gases. The correlation studies of various NMHCs and CO indicate dominant role of local emissions in the observed distributions of trace gases. The natural gas emission and leakage of liquid petroleum gas contribute to elevated levels of ethane and propane. While emissions from vehicular exhaust are found to be dominant sources of ethene, propene and acetylene. The higher C_2H_2/CO ratio of about 6.4 pptv/ppbv indicates influences of fresh emissions at Ahmedabad.

Keywords: NMHCs; Ozone; Seasonal variations; Pollution; Vehicular exhaust

1. Introduction

Non-methane hydrocarbons (NMHCs) play an important role in the chemistry of the troposphere as precursors of O_3 and peroxyacetylnitrate (PAN). Many model studies have indicated that ground level O_3 concentrations, especially peak levels, in rural and semi-rural areas are sensitive to change in anthropogenic emissions of NMHCs, CO and nitrogen oxides (NO_x) (Jacob et al., 1993; Solomon et al., 2000). There is a lack of study related to the tropospheric chemistry in the tropical region. This is the region of large biogenic and pyrogenic emissions of trace gases, including NMHCs, which react with high OH concentration and thus make it the most active photochemical region of the atmosphere (Andreae and Crutzen, 1997). Emissions of atmospheric pollutants are increasing in the Asian region (Streets and Waldhoff, 2000; Akimoto, 2003). Due to these increases in pollutant levels, tropospheric O_3 levels may increase significantly in future in this part of the world (Hauglustaine et al., 1998; Lelieveld et al., 2001). Estimations made using the chemical transport model (NASS/GISS) show that on increasing the anthropogenic emissions (by two

*Corresponding author. Fax: +91 79 26314659.
E-mail address: lokesh@prl.res.in (L.K. Sahu).

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and four times), O_3 production efficiency is maximum over the Indian region followed by Japan and China, which is explained on the basis of increase in OH and peroxy radicals (Berntsen et al., 1996). Various investigations of NMHCs have been attempted to obtain their characteristic variations in urban sites of Asia (Rao et al., 1997; Morikawa et al., 1998; Sharma et al., 2000; Barletta et al., 2002; Yang et al., 2005). But complete seasonal distributions of even light NMHCs in tropical urban regions have been rarely reported.

Over the Indian region, only limited simultaneous measurements of O_3 and some of its precursors (CO, CH_4 and NO_x) are available (Lal et al., 2000; Naja and Lal, 2002). However, till recent years there have been no systematic simultaneous measurements of surface O_3 and NMHCs over this region. Recognizing the importance of such studies, simultaneous measurements of NMHCs along with O_3, CO and CH_4 have been made at Ahmedabad. Results of this study are being discussed in this paper.

2. Description of the site, general meteorology and experiments

The observational site, Physical Research Laboratory (PRL), is situated at the western edge of Ahmedabad (23°N, 72.6°E, 49 m asl) city. It is an urbanized city having a thermal power station and numerous industries in east and north outskirts. However, the measurement site is 10–15 km away from highly polluted regions of the city. A layout of Ahmedabad city describing locations of the observational site and industrial areas are given in Lal et al. (1998). The population of Ahmedabad is about 5.5 million and currently total number of vehicles is about 1.8 million. Major vehicles for transportation in this city are buses, cars, two- and three-wheelers (motorbikes, scooters and auto-rickshaws). Due to rapidly increasing number of vehicles (about 10% per year), the transport-related activities are the major contributors of various pollutants.

From early May to September/October each year when the inter-tropical convergence zone (ITCZ) moves northward across India, marine air masses from the Arabian Sea and the Indian Ocean or the so-called southwest monsoon (summer monsoon) dominates at Ahmedabad. The long-range transport of continental air masses from the northwest part of the Asian continent starts to prevail over India when ITCZ moves back southward in September and October. These months are regarded as transition period of the monsoon when the exchange of marine and continental air masses can be observed. In the winter and spring seasons, this place gets mostly westerly and northwesterly winds.

Online measurements of C_2–C_5 NMHCs were started in September 2001 at Ahmedabad; however, full year data for 2002 are being discussed here. The measured NMHCs are ethane (C_2H_6), propane (C_3H_8), butanes (C_4H_{10}), pentanes (C_5H_{12}), ethene (C_2H_4), propene (C_3H_6) and acetylene (C_2H_2). Simultaneous measurements of CO and CH_4 were also performed. Air samples for these measurements were drawn from the terrace of the laboratory building through an stainless steel (SS) tube ($\frac{1}{4}$-in diameter OD) directly into the injection systems of the respective gas chromatographs (GCs). Measurements of CO, CH_4 and NMHCs were made continuously for 72 h (3 days) with about 1-h interval during all the months of the year 2002. The gas chromatographic techniques with flame ionization detector (FID) have been used for the analyses of NMHCs, CH_4 and CO.

The experimental system consists of a Hewlett-Packard 5890 series II GC with a FID for NMHCs analyses. The column was a 50 m × 0.32 mm porous layer open tubular (PLOT) column of KCl/Al_2O_3 stationary phase. High purity helium (He) was used as carrier gas. The air samples of 300–500 ml were preconcentrated using a cryo-trapping procedure. The column oven temperature was ramped from 0 to 200 °C in three steps to separate C_2–C_5 NMHCs. Analyses of CO and CH_4 were performed by another GC (Varian Vista 6000, USA). For the separation CO and CH_4, a molecular sieve-packed SS column of length 5 m was employed. He gas was used as carrier gas. Since FID does not response to CO directly, measurements were made by converting it into CH_4 using a methanizer (Ni catalyst heated at 325 °C). For this analysis column temperature was kept constant at 75 °C. Air samples were introduced directly into a sample loop of ~3 ml and subsequently injected into the GC column by a eight port switching valve (VICI, USA).

Reproducibility in NMHCs analyses ranged from 3% to 10%. In general, lower molecular weight NMHCs showed better reproducibility. Calibrations of all C_2–C_5 NMHCs were performed using Scott, USA supplied calibration mixture. We have also calibrated these NMHCs using two different