Atmospheric Research 164–165 (2015) 84–94

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

High time and mass resolved PTR-TOF-MS measurements of VOCs at an urban site of India during winter: Role of anthropogenic, biomass burning, biogenic and photochemical sources

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A R T I C L E I N F O

Article history:
Received 9 January 2015
Received in revised form 29 April 2015
Accepted 30 April 2015
Available online 7 May 2015

Keywords:
VOCs
Biogenic
India
Traffic
Photochemical
PTR-TOF-MS

A B S T R A C T

This study is based on the high mass and time-resolved measurements of seven VOCs using a PTR-TOF-MS instrument at an urban site of India during winter 2013. Daily levels of OVOCs and aromatics were in the ranges of 3.5–37 ppbv and 0.85–23 ppbv, respectively with OVOCs accounted for up to 80% of total measured VOCs. The impact of long-range transport from the polluted Indo-Gangetic Plain and clean Thar desert was observed during the episodes of high and low VOCs, respectively. VOCs exhibited strong diurnal variations with peaks during morning and evening hours and lowest in the afternoon. Relatively elevated aromatics during evening hours coincided with the lowest-OVOCs indicating influence of fresh vehicular emissions. Emission ratios of isoprene and OVOCs with respect to benzene followed the diurnal cycles of temperature and solar flux indicating role of biogenic and photochemical processes, respectively. Correlation study of VOCs with benzene suggests major contribution from anthropogenic and also from biogenic and secondary sources to some extent. The higher emission ratios of Δmethanol/Δacetonitrile correspond to the episodes of long-range transport from biomass burning sources located in the Indo-Gangetic Plain (IGP). In addition to the pattern of emission, the diurnal and day-to-day variations of VOCs were influenced by the local meteorological conditions and depth of planetary boundary layer (PBL).

1. Introduction

Volatile organic compounds (VOCs) play an important role in the chemistry of the troposphere and may impact air quality and environment (Velasco et al., 2007; Goldstein and Galbally, 2007). Atmospheric VOCs represent a large variety of species such as non-methane hydrocarbons (NMHCs), carbonyl compounds and organic compounds containing elements of halogen, sulfur, nitrogen, etc. Oxygenated volatile organic compounds (OVOCs) make an important subgroup of VOCs consisting of aliphatic alcohols, aldehydes, ketones and organic acids (Król et al., 2010). The chemical removal of VOCs includes the reactions with OH, O_3 and nitrate radical (NO_3) (Atkinson and Arey, 2003). In the lower atmosphere, the nonlinear reactions between VOCs and NOx ($=NO + NO_2$) in the presence of sunlight can lead to the formation of ozone (O_3) and secondary organic aerosols (SOA) in polluted regions (Finlayson-Pitts and Pitts, 1997; Duan et al., 2008; Suthawaree et al., 2012). Ozone and SOA are key atmospheric components which can adversely impact human health, air quality and crop yields (Krupa et al., 2001; van Zelm et al., 2008). In addition, both O_3 and SOA are radiatively active constituents of the troposphere and can contribute to the climate change (IPCC, 2007). The long-term exposure to the elevated levels of certain VOCs can be potentially harmful to human health (Sahu, 2012; Pandey and Sahu, 2014). VOCs are emitted into the atmosphere from a variety of both natural and anthropogenic sources. The global emission budget of VOCs has been estimated to be in the range of 1200–1350 Tg C yr^{-1} (Goldstein and Galbally, 2007). The major anthropogenic sources include emissions from solvent use (paints, adhesives, printing), road transport (combustion of fossil fuels), extraction and distribution of fossil fuels, etc. (Wang and Zhao, 2008). Emission from biomass burning sources could contribute as large as 500 Tg C yr^{-1} to the global budget of VOCs (Yokelson et al., 2008). In the study region, the transport from biomass burning sources mainly from the open burning of agricultural-waste can also be an important source of VOCs. The post-harvest agricultural-waste burning in Asia varies with the region and harvesting practice (Pandey and Sahu, 2014; Tang et al., 2013; Zhao et al., 2015).

India has a large geographical and climatological diversity where both natural and anthropogenic emission sources of VOCs coexist. India is one of the fastest growing countries in Asia and experiencing serious air pollution due to rapid urbanization and ever increasing number of motor vehicles (Pucher et al., 2007). There has been a growing

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http://dx.doi.org/10.1016/j.atmosres.2015.04.021
0169-8095/

demand of VOCs inventory data for Indian region by the global modeling community (Srivastava and Majumdar, 2010). Thus far, the measurement based studies of VOCs have been reported to be extremely rare in this part of the world (Sahu and Lal, 2006a,b; Sahu et al., 2010; Lal et al., 2008, 2012; Sinha et al., 2014). The present study is based on ambient measurements of VOCs using continuous operation of a novel PTR-TOF-MS instrument at an urban site (23°N, 72.6°E, 49 m asl) of Ahmedabad, India during the winter period of year 2013. Thus far, the previous studies over the western region of India have been focused mainly to investigate the importance of anthropogenic emission and local meteorology. The primary objective of this study is to investigate the role of anthropogenic, biomass burning, biogenic and photochemical sources in the diurnal and day-to-day variations of VOCs. We have also used other supporting data such as back trajectory, and meteorological fire count data. The characteristics of diurnal variation of VOCs have been discussed in view of the short-term changes in local meteorology and strength of local emissions.

2. Materials and methods

2.1. Performance of PTR-TOF-MS system

The proton transfer reaction-mass spectrometry (PTR-MS) technique has been used for real time measurements of VOCs (Lindinger et al., 1998; de Gouw and Warneke, 2007; Blake et al., 2009). In this study, the measurements of ambient VOCs were performed using the PTR-TOF-MS 8000 instrument (Ionicon Analytik GmbH Innsbruck, Austria) between 27 November and 31 December 2013 (see Fig. 1). Ambient air was drawn using an external pump at a flow rate of about 20 l min^{-1} through a 2.5 m long PFA Teflon tube placed outside the laboratory which is located in the 5th floor of the main building. A sub-stream of air off the main sample line was connected to the PTR-TOF-MS. Ambient air was introduced into the reaction drift tube via 1.5 m long heated (at 60 °C) PEEK tubing with a flow rate of about 60 ml min^{-1}. The key operating parameters viz. pressure, temperature and voltage in the drift were held at 2.3 mbar, 50 °C and 600 V, respectively. This set of parameters corresponds to an E/N ratio of about 130 Td (where E = electric field strength, N = gas number density, 1 Td = 10^{-17} V cm^2). The PTR-TOF-MS was operated using protonated water (H_3O^+) as the reagent ion and the mass spectra up to 280 m/z were recorded. The data was acquired using the TOF-Daq software (version 1.2.93, Tofwerk AG, Switzerland). A thorough and detailed description of the PTR-TOF-MS instrument, method to calculate the mixing ratio of VOCs and data acquisition are presented elsewhere (Jordan et al., 2009; Graus et al., 2010).

The background (zero) and calibration of the PTR-TOF-MS were performed using a gas calibration unit (GCU) (GCU-advanced v2.0, Ionicon Analytik). The inlet of the PTR-TOF-MS was directly connected to the GCU outlet via a Teflon® PFA fitting. The background signals were quantified by introducing VOC-free gas (zero-air) generated by Supelpure HC filter (Supelco, USA) and a heated VOC scrubber catalyst at 350 °C. The PTR-TOF-MS system was calibrated using a dynamic dilution. To generate various calibration steps (multi-point), the standard gas flow was adjusted using a mass flow controller (MFC) to provide variable quantities of standard gas into the dilution gas flow. The standard mixture (L5388, Ionicon Analytik GmbH Innsbruck, Austria) containing about 1 ppmv ± 5% of each VOC compound has been used for the calibration of PTR-TOF-MS data. The background (zero) and multi-point calibration of the PTR-TOF-MS were performed on 27 Nov and 02, 14, 28 Dec, 2013. The count rate of H_3O^+ (m/z = 19.0178) ions was deduced from $H_3^{18}O^+$ (m/z = 21.0221) signal by using a known natural isotopic ratio (499:1) of $^{16}O/^{18}O$. The calibration factors (ncps ppbv^{-1}) for VOCs were derived from the relation between the normalized sensitivity and known volume mixing ratio introduced in the PTR-TOF-MS (see Table 1). The overall uncertainties were in the range of 8.3–13.1% which include propagation of errors in the flow rate of GCU, RH of zero air and calibration mixture. The spectra were stored every 30 s in the compressed HDF5 format. However, depending on the type analysis and also on the time resolution of meteorological data, the VOC data averaged for different time intervals of 5 min, 10 min, 1 h, 1 day, etc. have been used in the present study.

2.2. Study site

The measurement site, Physical Research Laboratory (PRL), is situated in the western zone of Ahmedabad City (Fig. 1). It is the fifth largest city and seventh-largest metropolitan area of India with a population of over 6.5 million. The increasing emission from the transportation sector is one of the major causes of rising levels of air pollutants in the city. In winter season, the prevailing winds from the northwest–northeast (NW–NE) sector can transport the dry and polluted air from the Indo-Gangetic Plain (IGP) and surrounding continental regions (Srivastava et al., 2010). As shown in Fig. 2, the time series of meteorological parameters viz. wind speed, relative humidity (RH), pressure, temperature and solar flux show significant variations during the study period. The mean ± standard deviation values of temperature, RH, wind speed and pressure were 22.4 ± 2 °C, 46 ± 6%, 2 ± 0.5 ms^{-1} and 1005 ± 1.7 hPa, respectively during the study period. The isentropic back trajectories were calculated using the Japanese 25-year ReAnalysis (JRA-25, 6 h, 1.25° × 1.25°) data (Onogi et al., 2007; Sahu et al., 2014). The 7 day back trajectories were calculated at an altitude of 50 m over Ahmedabad. The fire count (hotspot) data detected by the satellite-based Moderate Resolution Imaging SpectroRadiometer (MODIS) instruments have been used to investigate the spatiotemporal variation of open biomass burning (Giglio et al., 2003).

3. Results and discussion

3.1. Times series of VOCs and effect of long-range transport

As shown in Fig. 2, the time series of VOCs show a large range of variations. An episode of elevated VOCs during 05–22 December, 2013 coincided with lower wind speeds due to prevailing low pressure conditions. During this period, the mean mixing ratios of methanol, acetone and acetaldehyde were 26 ± 4 ppbv, 6.7 ± 1 ppbv and 6.3 ± 1.0 ppbv, respectively (Table 2). The daily means of primary VOCs such as acetonitrile, isoprene, benzene and toluene were 0.94 ± 0.16 ppbv, 1.95 ± 0.38 ppbv, 3.14 ± 0.65 pbbv and 9.6 ± 2.5 ppbv, respectively. Analysis of back trajectories during 05–22 December indicated the transport of pollutants from the NE direction (see Fig. 3a). However, the origin of some trajectories can be traced over the IGP including regions of Pakistan. Therefore, particularly during 05–22 December, the transport of air from the biomass burning sources located in the western IGP including Punjab province could have influenced the measurements of VOCs at Ahmedabad. It is well known that the IGP is one of the most polluted regions in the world in terms of gas and aerosol loading (Lal et al., 2012). The higher mixing ratios of acetonitrile during 05–22 December suggest the long-range transport of VOCs from the active biomass burning regions of north India. In India, crop waste open burning shows strong spatial and temporal variations. During October to December period, the open burning of paddy crop waste (straw) over Indo-Gangetic plain (IGP) is dominant land clearing process. The agriculture wastes burning in the states of Punjab, Haryana and western Uttar Pradesh are potential contributor of biomass burning emissions.

The observations of lower VOCs during 23–31 December coincided with the period of relatively high wind speeds. As shown in Fig. 3b, the back trajectories indicate the transport of air masses mostly from the NW–NE sector originated or passed over the Thar desert of Rajasthan. This region is sparsely populated where emissions of VOCs from both anthropogenic and biomass burning sources are much less than those in the IGP (Yadav et al., 2014). The ambient pressure along the