

Volatile organic compounds and their measurements in the troposphere

L. K. Sahu*

Volatile organic compounds (VOCs) are ubiquitous atmospheric constituents of both anthropogenic and natural origin. VOCs are important precursors of tropospheric ozone (O_3), and can impact air quality and global climate. Most of primary VOCs and their oxidized products makeup a major fraction of secondary pollutants in urbanized regions. Due to fast reaction rates mainly with the hydroxyl radical (OH), the VOCs control the oxidizing capacity of the troposphere. Measurements of VOCs are important to study the photochemical transformation, both qualitatively and quantitatively. Many aspects of VOCs in the atmosphere remain poorly understood – these include the detection and quantification of by-products of VOCs, their oxidation reactions and their role in oxidant and secondary aerosol formation. In the photochemistry of tropical troposphere, VOCs play a key role due to high abundance of water vapour (H_2O) and intense solar radiation flux. Measurements of these species are rare over the Indian subcontinent and surrounding marine regions. Traditionally, gas chromatography-based methods have been used for the detection of VOCs. Recently, the fast time response and sensitive techniques like proton-transfer reaction mass spectrometer are the emerging tools to detect trace levels of various VOCs in the atmosphere.

Keywords: Atmosphere, measurement techniques, photochemical transformation, volatile organic compounds.

AIR pollution caused by anthropogenic emission of various gaseous and particulate species poses an increasingly serious concern for human health, agriculture (crop yield) and global climate. Among the gaseous constituents, the volatile organic compounds (VOCs) are key components in both polluted and remote regions of the troposphere. VOCs are defined as organic species which have high vapour pressure in the earth's atmosphere¹. VOCs may include a wide range of pollutants, such as non-methane hydrocarbons (NMHCs), carbonyl compounds and organic compounds containing halogens, sulphur or nitrogen². The oxygenated volatile organic compounds (OVOCs), including the functional groups of alcohols, aldehydes, ketones, carboxylic acids and esters are an important subcategory of VOCs. Primarily, VOCs are released into the atmosphere by both anthropogenic and natural processes. The emissions related to the presence or activities of humans are also known as anthropogenic emissions. On the other hand, the biogenic emissions are caused by living organisms or biological processes necessary for the maintenance of life cycles. The major anthropogenic sources include motor-vehicle evaporative and exhaust emission, industries, biomass and biofuel burning, use of chemical solvents, etc. In Asia, anthropogenic

emissions of VOCs are the largest from the residential combustion of coal and biofuels (~34%), and from transportation (~27%). Significant contributions to the global inventory of VOCs are also due to the emissions from biomass burning and wild/forest fires. Emissions of VOCs from biogenic sources, also known as biogenic volatile organic compounds (BVOCs), are the largest contributor to global VOCs. The dominant sources of biogenic emissions are global vegetation and oceans. In tropical photochemistry, BVOCs are estimated to have a disproportionately large impact compared to higher latitudes.

Global emissions of BVOCs are estimated to be about 1150 teragrams of carbon per year ($TgC\ year^{-1}$, 1 teragram = 10^{12} g), which exceeds those of their anthropogenic counterparts by about a factor of 10. Typically, BVOCs have much shorter atmospheric lifetimes than anthropogenic VOCs due to faster reaction rates with OH. In the forested/vegetated areas, isoprene and monoterpenes (α -pinene and β -pinene) are the dominant VOCs which are reactive compared to lighter hydrocarbons³. Among the most abundant BVOCs emitted from vegetation, isoprene and monoterpenes contribute 44% and 11% respectively, to the global budget of biogenic emission. Emissions of BVOCs are influenced by meteorological parameters like solar radiation and temperature. The land-use changes and deforestation can alter the BVOC emissions and also the composition.

L. K. Sahu is in the Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India. *e-mail: lokesh@prl.res.in

than oxides of nitrogen, and can be transported over cleaner region and also to the upper troposphere. Subsequently, PAN-type species, also known as reservoir compounds, release NO_x due to thermal and chemical decomposition. PAN and similar species are formed mostly due to the photo-oxidation of higher-order hydrocarbons. In the planetary boundary layer (PBL) NO_3 can react rapidly with several organic compounds, in particular with monoterpenes and isoprene⁴. Understanding the roles of various precursors of O_3 and modelling them accurately to derive the impact of emission abatements is important for policy makers.

The rate of photochemical production of O_3 in the PBL of urbanized/polluted regions not only depends on the ambient levels of VOCs and NO_x , but also on their ratio (VOC/NO_x)⁵. Because of this complexity (or nonlinearity) in the chemistry and the roles of various meteorological parameters, the quantitative links of emissions of VOCs and NO_x to the concentrations of O_3 and major photochemical oxidants at a particular location and time are not straightforward. The databases of VOC emissions used in atmospheric chemistry or transport models have large uncertainties. Therefore, the predictions of O_3 photochemistry involve model studies dealing with many nonlinear reactions and meteorological inputs and hence the results are expected to be highly uncertain. Another approach, used for specific regions, is to generate O_3 isopleth data. The isopleth represents photochemical formation rate of O_3 as a function of the average emission rates of VOCs and NO_x . Ideally, O_3 isopleth diagrams can be produced by chamber experiments. However, ambient monitoring data have also been used in the empirical kinetic modelling approach (EKMA) developed by the US EPA (Environmental Protection Agency), which relates hourly peak in O_3 with the average of precursor (VOCs and NO_x) concentrations. From several EKMA studies, it has been established that the VOC and NO_x precursors yield a peak O_3 when the VOC/NO_x ratio is between 7 and 10.

Based on photochemical models and empirical parameterizations, generally the decreasing NO_x can lead to an increase in O_3 at high NO_x/VOC ratios. Under this condition, the photochemistry leading to the net production of O_3 falls in a stage known as VOC-limited regime. The O_3 photochemistry in a high VOC/NO_x regime is known as NO_x -limited. VOCs– NO_x sensitivity of O_3 production varies with the time of the day, from event to event and by locations within the same region. The abatement strategies become complicated when photochemical regimes can change from NO_x -sensitive to VOCs-sensitive at a given location. In an urban/polluted region, the prevailing regime can be subjected to the photochemical lifetimes of various VOCs, NO_x and the dilution due to the meteorological conditions. The number of grams of O_3 produced in air per gram of total VOC (TVOC) is defined as specific reactivity. Estimation of the specific reactivity for a given category of source

requires knowledge of the speciated VOCs and their concentrations as well as how much each contributes to the photochemical production of O_3 . A major problem to the study of O_3 – NO_x –VOC sensitivity has been the lack of evidence based on direct measurements rather than model calculations. VOCs are also classified in terms of their ability to form ozone, since compounds which are oxidized quickly lead to substantial O_3 formation close to the source, whereas those which are oxidized more slowly will lead to O_3 formation away from the source. More reactive compounds such as alkenes will contribute most to ozone formation near the point of emission. As time goes by, less reactive compounds such as the alkanes will become more important in producing O_3 . High concentrations of reactive VOCs, such as olefins and aromatics, can be responsible for O_3 and SOA formation.

Indirectly, VOCs play an important role in the earth's radiation budget as large fractions of atmospheric aerosols (scattering type) are derived from organic matter with various volatilities. In the polluted environment, the dominant fraction of organic aerosols (OA) is secondary. In the atmosphere, it is formed from gas-phase species. Recent studies have indicated that SOA formation in polluted air is much more efficient than expected from the measured VOCs and yields determined in the laboratory⁶.

Many halogenated VOCs get photolyzed or react with OH in the troposphere leading to the release of halogen radicals. The source of halogenated VOCs is related to several natural and anthropogenic processes, including the emissions from terrestrial plants, fungi, ocean, biomass burning, fossil-fuel combustion, etc. Methyl chloride (CH_3Cl) is one of the important halogenated VOCs emitted by biomass burning, forest fire and terrestrial vegetation. As shown in Table 1, CH_3Cl is relatively less reactive compared to various NMHCs and can reach the stratosphere and make important contribution to organic chlorine.

Estimation of photochemical 'age' of air mass

In addition to studying the photochemical processes, the measurements of primary VOCs having different lifetimes

Table 1. Reaction rate constants (k) of some VOCs for the reaction with OH radical^{4,13}

| Species | OH rate constant (k) at 298 K ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) | Major sources |
|------------------------|---|------------------------|
| Ethane | 0.257×10^{-12} | Anthropogenic |
| Propane | 1.15×10^{-12} | Anthropogenic |
| <i>n</i> -Butane | 2.54×10^{-12} | Anthropogenic |
| Ethene | 8.52×10^{-12} | Anthropogenic/biogenic |
| Propene | 26.3×10^{-12} | Anthropogenic/biogenic |
| Benzene | 1.23×10^{-12} | Anthropogenic |
| Isoprene | 101×10^{-12} | Biogenic |
| α -Pinene | 53.7×10^{-12} | Biogenic |
| β -Pinene | 78.9×10^{-12} | Biogenic |
| CH_3Cl | 3.6×10^{-14} | Natural/anthropogenic |

can be used to estimate the photochemical age of air mass⁷. If two species, for example, VOC1 and VOC2, have common sources but different reactions rates with OH radicals, then the photochemical age (Δt) of an air parcel can be calculated from the following equation.

$$\Delta t = \frac{1}{(k_{\text{VOC1}} - k_{\text{VOC2}})[\text{OH}]}$$

$$\times [\ln(\text{VOC1}/\text{VOC2})_{t=0} - \ln(\text{VOC1}/\text{VOC2})_t],$$

where $(\text{VOC1})/(\text{VOC2})_t$ is the ratio of the mixing ratios measured at time t , and $(\text{VOC1})/(\text{VOC2})_{t=0}$ is the average emission ratio from the major emission sources. $[\text{OH}]$ is the average concentration of OH radicals. And k_{VOC1} and k_{VOC2} are the reaction rate coefficients for the reactions of OH with VOC1 and VOC2 respectively. If only the OH chemistry is important in the decay of a primary VOC, then the photochemical equation can be written as:

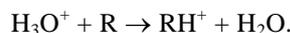
$$\ln \frac{[\text{VOC}]_{t=0}}{[\text{VOC}]_t} = k_{\text{OH}}[\text{OH}] \times t,$$

where $[\text{VOC}]_{t=0}$ and $[\text{VOC}]_t$ are the mixing ratios at any initial time ($t = 0$) and at a later time (t) respectively. In this equation, the slope as a function of the time t and the reaction rate constant k_{OH} allow the estimate of the mean OH concentration $[\text{OH}]$ over the studied period t . The concentration of OH during the day can be estimated from the variation in concentration ratios of aromatic species (like ethyl benzene, toluene, *o*-xylene and *m* + *p*-xylene) to benzene. Aromatics are most preferred for this type of calculation because they have similar lifetimes and sources to benzene and decay almost by reaction with the OH radicals. A model simulation neglecting the emissions of OVOC leads to unrealistically low O_3 mixing ratios compared to the field measurements in the biomass-burning plumes. Therefore, the simultaneous observations of various VOCs, NO_x and meteorological parameters can be helpful for photochemical simulation studies in the boundary layer of polluted regions. In the tropical regions, strong convective storms can transport many reactive VOCs to the middle/upper troposphere in only a few to several hours.

Measurement methods of VOCs in ambient air

Several techniques, such as gas chromatograph (GC) coupled with flame ionization detector (FID) and mass spectrometer (MS) have been used for the analysis of VOCs. Due to technical limitations, many VOCs which play an important role cannot be detected using GC-based techniques. Recently, the proton-transfer reaction mass spectrometry (PTR-MS) technique has been used for the detection of a wider spectrum of VOCs in air (Figure 2)⁸.

In the PTR-MS protonated water (H_3O^+) is used as a source of proton as most of the inorganic constituents of air possess proton affinities lower than that of H_2O , whereas for most organic constituents the opposite is true. The fundamental processes can be described by following reaction.



The fragments of inorganic species can be discarded, which helps identify the desired organic species. In the PTR-MS system, the combination of reaction kinetics and mass spectrometry allows the identification and quantification of individual VOCs on a relatively short timescale. Using the reaction kinetic data and draft-tube parameters, the mixing ratio (MIR) of any VOCs can be calculated as here. If RH^+ (representing an ionized VOC) is the only ionized product and with a condition satisfying $[\text{H}_3\text{O}^+] \gg [\text{RH}^+]$,

$$[\text{MIR}]_R \times kt = [\text{RH}^+]/[\text{H}_3\text{O}^+],$$

where k and t are the proton rate transfer coefficient and reaction time respectively. If both k and t are known, then the measured ratio of $[\text{RH}^+]/[\text{H}_3\text{O}^+]$ detected by the MS allows the determination of absolute concentration of RH (or VOCs). The real-time detection and quantification of these trace-level constituents require no pre-concentration prior to the measurements⁹. Because of the fast response time (1s) and low detection limit (10–100 pptv), the PTR-MS system can be used in a variety of platforms (ground-based, airborne, ship-borne, etc.).

Summary

The recent change in air composition is connected with growing industrialization and urbanization, developing megacities and increasing traffic. Human activities have resulted in changing emissions of many primary trace

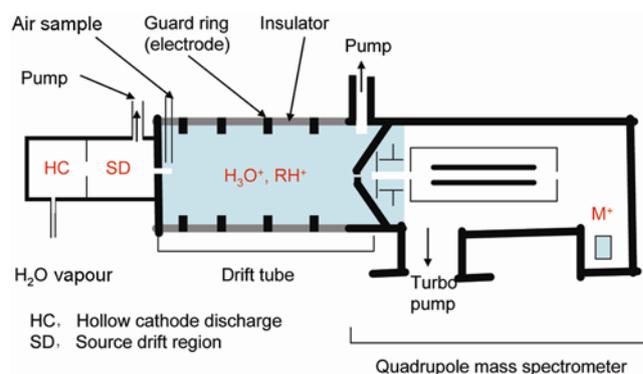


Figure 2. Schematic representation of a proton-transfer reaction mass spectrometer (adapted from Blake *et al.*⁸).

gases, including VOCs and GHGs. The increasing emissions of these species due to human activities have implication to direct or indirect climate change, which in turn can influence the natural emission processes of VOCs and other species. India is a large subcontinent and has vast geographical and climatological variability, where measurements of VOCs are limited^{10–12}. To understand the inhomogeneity in emissions of VOCs, not only in the magnitude of emissions but sector-wise contributions, requires observations of VOCs with a representative spatio-temporal resolution. Individuals or a group can contribute little; there is a need of coordinated efforts for studies of VOCs. Multiplatform observations involving aircraft, ship and ground stations are the key to understanding the environmental and climatic importance of VOCs. There is a growing demand for VOCs inventory data for India by global modellers. Due to tremendous technological progress in VOCs detection and quantification using GC and PTR-MS, measurements of VOCs from local to regional scales can be accomplished. The observations of VOCs along with other species like NO_x will be important to understand the photochemistry leading to formation of O₃ and SOA at urban, rural and remote (both marine and terrestrial) locations.

1. Goldstein, A. H. and Galbally, I. E., Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.*, 2007, **41**, 1514–1521.
2. Derwent, R. G., Volatile organic compounds in atmosphere. *Environ. Sci. Technol.*, 1995, **4**, 1–15.
3. Guenther, A., Are plant emissions green? *Nature*, 2008, **452**, 701–702.
4. Atkinson, R. *et al.*, Evaluated kinetic and photochemical data for atmospheric chemistry. Organic species: Supplement VII. *J. Phys. Chem. Ref. Data*, 1997, **28**, 191–393.
5. Finlayson-Pitts, B. J. and Pitts Jr, J. N., Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. *Science*, 1997, **276**, 1045–1052.
6. de Gouw, J. A. *et al.*, Organic aerosol formation downwind from the deepwater horizon oil spill. *Science*, 2011, **331**, 1295–1299.
7. Greenberg, J. P., Helmig, D. and Zimmerman, P. R., Seasonal measurements of nonmethane hydrocarbons and carbon monoxide at the Mauna Loa Observatory during the Mauna Loa Observatory Photochemistry Experiment 2. *J. Geophys. Res. D*, 1996, **101**, 14581–14598.
8. Blake, R. S., Monks, P. S. and Ellis, A. M., Proton-transfer reaction mass spectrometry. *Chem. Rev.*, 2009, **109**, 861–896.
9. de Gouw, J., Warneke, C., Karl, T., Eerdeken, G., van der Veen, C. and Fall, R., Measurement of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrom. Rev.*, 2007, **26**, 223–257.
10. Sahu, L. K., Lal, S. and Venkataramani, S., Impact of monsoon circulations on oceanic emissions of light alkenes over Bay of Bengal. *Global Biogeochem. Cycles*, 2010, **24**, GB4028, doi:10.1029/2009GB003766.
11. Sahu, L. K. and Lal, S., Distributions of C₂–C₅ NMHCs and related trace gases at a tropical urban site in India. *Atmos. Environ.*, 2006, **40**, 880–889.
12. Sahu, L. K. and Lal, S., Characterization of C₂–C₄ NMHCs distributions at a high altitude tropical site in India. *J. Atmos. Chem.*, 2006, **54**, 161–175.
13. Seinfeld, J. H. and Pandis, S. N., *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley, New York, 1998, pp. 1297–1308.

ACKNOWLEDGEMENT. I thank Shyam Lal, S. Venkataramani, Varun Sheel and Y. B. Acharya for their suggestions.

Received 10 October 2011; revised accepted 17 April 2012