Measurements of reactive Volatile Organic Compounds (VOCs) and their emissions in agricultural and urban atmospheric environments of the Indo-Gangetic Plain (IGP)

A thesis

submitted by

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Declaration

I hereby declare that this thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy is without any unauthorised external assistance and used only sources acknowledged in the work. All textual passages which are appropriated verbatim or paraphrased from published and unpublished texts as well as all information obtained from oral sources are duly indicated and listed in accordance with bibliographical rules. In carrying out this research, I complied with the rules of standard scientific practice as formulated in the statutes of the Indian Institute of Science Education and Research, Mohali. This document has not been submitted for qualifications to any other institution.

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In my capacity as the supervisor of the candidate's thesis work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Vinayak Sinha
(Supervisor)

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List of Publications

1. **Chandra, B.P.**, Sinha, V., Hakkim, H. and Sinha, B., Storage stability studies and field application of low cost glass flasks for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry, *International Journal of Mass Spectrometry*, 419, 11-19, 2017.
2. **Chandra, B. P.,** and Sinha, V., Contribution of post-harvest agricultural paddy residue fires in the N.W. Indo-Gangetic Plain to ambient carcinogenic benzenoids, toxic isocyanic acid and carbon monoxide, *Environment International*, 88, 187-197 2016.
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4. Kumar, V., **Chandra, B. P.,** and Sinha, V.: Large unexplained suite of chemically reactive compounds present in ambient air due to biomass fires, *Scientific Reports*, 8, 626, 2018.
5. Garg, S., **Chandra, B. P.,** Sinha, V., Sarda-Esteve, R., Gros, V., and Sinha, B., Limitation of the Use of the Absorption Angstrom Exponent for Source Apportionment of Equivalent Black Carbon: a Case Study from the North West Indo-Gangetic Plain, Environmental Science and Technology, 50(2), 814–824, 2016.
6. Ghude, S. D., Bhat, G. S., Prabhakaran, T., Jenamani, R. K., Chate, D. M., Safai, P. D., Karipot, A. K., Konwar M., Pithani, P., Sinha, V., Rao, P. S. P., Dixit, S. A., Tiwari, S., Todekar, K., Varpe, S., Srivastava, A. K., Bisht, D. S., Murugavel, P., Ali, K., Mina, U., Dharua, M., Jaya Rao, Y., Padmakumari, B., Hazra, A., Nigam, N., Shende, U., Lal, D. M., **Chandra, B. P.**, Mishra, A. K., Kumar, A., Hakkim, H., Pawar, H., Acharja, P., Kulkarni, R., Subharthi, C., Balaji, B., Varghese, M., Bera, S. and Rajeevan, M., Winter fog experiment over the Indo-Gangetic plains of India, *Current Science*, 112, 4, 2017.
7. Pawar, H., Garg, S., Kumar, V., Sachan, H., Arya, R., Sarkar, C., **Chandra, B. P.** and Sinha, B., Quantifying the contribution of long-range transport to Particulate Matter (PM) mass loadings at a suburban site in the North-Western Indo Gangetic Plain (IGP), *Atmos. Chem. Phys.,* 15, 9501-9520, 2015.
8. Sinha, B., Sangwan, K. S., Maurya, Y., Kumar, V., Sarkar, C., **Chandra, B. P.** and Sinha, V., Assessment of crop yield losses in Punjab and Haryana using two years of continuous in-situ ozone measurements, *Atmos. Chem. Phys.*, 15, 9555-9576, 2015.

Synopsis

Volatile Organic Compounds (VOCs) are ubiquitous atmospheric constituents possessing both natural and anthropogenic sources. They play a critical role in formation of tropospheric ozone (O_3) and secondary organic aerosol (SOA). Both O_3 and SOA are important from the standpoint of air quality and climate due to their impacts on crop productivity, human health and the radiative forcing of the atmosphere. Through photochemical reactions, VOCs also strongly influence ambient hydroxyl and hydroperoxy radical (collectively called HOx) budgets which control the removal rates of gaseous pollutants, including greenhouse gases such as methane from the atmosphere. In addition, chronic exposure to certain VOCs is associated with direct health risks (e.g. benzene is a human carcinogen). These effects of VOCs are manifested even at atmospheric concentration levels as low as parts per trillion (ppt) and parts per billion (ppb). Speciation of VOCs present in ambient air and understanding the role played by them in key atmospheric processes is, therefore of, great research importance and relevance in understudied regions of the world such as South Asia. Ambient measurements of VOCs are associated with several analytical challenges such as sample integrity being compromised during collection and storage and precision of VOC measurements due to their low concentrations at which these compounds are typically present in ambient atmospheric environments. Over the Indian subcontinent there is a large VOC data gap due to a paucity of spatially and temporally resolved in-situ measurements. In my thesis work, to address some of this missing knowledge and data gap, I have investigated the emissions and tropospheric chemistry of VOCs from agricultural and urban sources in north-west India through ambient measurements performed at Mohali and Delhi and enabled by application of innovative low cost whole air samplers designed and validated by me in my thesis work.

Chapter 1: Introduction

In the first chapter I present an overview of the importance of VOCs in the atmosphere accompanied by a literature review of the current state of knowledge with respect to the emissions and tropospheric chemistry of VOCs over the Indian subcontinent. This is followed by the motivation for my thesis work which was prompted by the following five major questions as listed below:

1) How much do emissions from open paddy residue fires in the northwest Indo-Gangetic Plain (N.W. IGP) contribute to the enhanced ambient concentrations of VOCs such as carcinogenic benzenoids, carbon monoxide, and toxic isocyanic acid?

2) What is the enhanced cancer risk due to the exposure to benzene emissions from paddy residue fires in the N.W IGP?

3) How can one enable ambient VOC speciation studies using low-cost whole air glass flask samplers and offline proton transfer reaction mass spectrometry without compromising the analytical aspects such as sample integrity and precision of VOC measurements?

4) What is the typical VOC and greenhouse gas speciation at a traffic thoroughfare in Delhi during winter?

5) Was the odd-even traffic rule restriction implemented in Delhi during winter 2016 (1-15 January 2016) effective in reducing primary traffic emissions of VOCs and greenhouse gases?

Chapter 2: Measurements of VOCs by proton transfer mass spectrometry (PTR-MS)

This chapter describes the instrumental technique, namely proton transfer reaction mass spectrometry, which has been employed extensively for VOC measurements reported in my thesis work. Quantification of VOCs (typically ppt-ppb range) in ambient air which is a complex mixture is a challenging task as the chemical composition of ambient air varies rapidly in response to emission and meteorological changes. The presence of more abundant gases such as water vapour, carbon dioxide, methane and oxygen may also cause interferences. Traditionally, techniques such as gas chromatography (GC) equipped with flame ionization /mass spectrometry/photo ionization detectors (GC-FID/GC-MS/GC-PID), have been used for measuring VOCs in ambient air. Today, using the gas chromatographic technique, a suite of VOCs can be measured at concentrations as low as 0.1 ppt. Despite these advantages, the chromatography based methods are slower than online mass spectrometric analyses in terms of temporal resolution and several measurement artefacts can arise during collection, storage and pre-concentration. Pre-concentration process and separation of constituents of a gas mixture on the capillary column limits the time resolution and hence this technique is not suitable to study the process on a time scale of few minutes or less. In particular several oxygenated VOCs such as acetaldehyde, methanol and acetone and short-lived reactive VOCs cannot be reliably quantified using most conventional gas chromatographic methods due to storage artefacts in canisters/adsorption tubes and chromatographic interferences. Hence, in the past few decades, highly mass and time resolved mass spectrometric techniques which are faster than chromatographic techniques have emerged for the quantification of VOCs. In this regard, high sensitivity proton transfer reaction mass spectrometry (PTR-MS) based on the soft chemical ionization technique is one of the most advanced and sensitive techniques currently available to detect VOCs at trace concentrations of few ppt in the ambient air in real time (few seconds time resolution) over an appropriate mass range for ambient VOCs (21- 200 amu). Using this technique, real time quantification of VOC is possible in a rapidly changing atmosphere so that information about specific emission activity can be deduced accurately from the highly time resolved measurements.

Within the instrument, analyte VOC molecules with a proton affinity (P.A.) greater than that of water vapour (691.2 kJ mol^{-1}) are chemically ionized with the reagent hydronium ions (H_3O^+) and form protonated molecular ions (with m/z = molecular ion + 1) of VOC, and these products are then separated in the mass analyzer before detection using secondary electron multipliers or channeltrons. The major advantage of this type of ionization is that all major constituents of ambient air such as nitrogen (78%), oxygen (21%), water vapour, argon, carbon dioxide, methane have proton affnities lower than that of water vapour (165.2 kcal mol^{-1}) and hence they do not cause interferences in the detection. In particular, due to very high sensitivity there is no need for pre-concentration or storage of sample for achieving ppt detection limit. Further, the soft ionization method ensures negligible/less fragmentation of product ion. In this chapter I discuss and describe these important measurement aspects of PTR-Q-MS which uses a quadrupole as mass analyzer which I employed in my thesis work for ambient VOC measurements.

Chapter 3: Contribution of post-harvest agricultural paddy residue fires in the N.W. Indo-Gangetic Plain to ambient carcinogenic benzenoids, toxic isocyanic acid and carbon monoxide

In this chapter I investigated how the post-harvest agricultural paddy residue fires in the N.W. Indo-Gangetic Plain influenced ambient concentration enhancements of benzenoids, isocyanic acid and carbon monoxide using three years (2012-2014) of continuous online in-situ measurements during the pre-paddy harvest and post-paddy harvest periods after taking into account variability in meteorological conditions. Fetch region was similar for both periods. Using MODIS satellite fire count data over this region and chemical tracers for the post-harvest biomass burning activity, I demonstrated that the open paddy residue fires are the major driver for the regional-scale ambient enhancements of these compounds in the post-paddy harvest season. The average concentrations of acetonitrile (1.62 ± 0.18 ppb), benzene (2.51 ± 0.28 ppb), toluene (3.72 ± 0.41 ppb), C8-aromatics (2.88 ± 0.30 ppb), C9-aromatics (1.55 ± 0.19 ppb) and CO (552 ± 113 ppb) in the post-paddy harvest periods were about 1.3-2.1 times larger relative to the pre-harvest concentrations for all these compounds. For isocyanic acid, a compound with both primary and secondary sources, the concentration in the post-paddy harvest period was 0.97 ± 0.17 ppb. The annual average concentrations of benzene, a class A carcinogen, exceeded the annual exposure limit of 1.6 ppb at NTP mandated by the National Ambient Air Quality Standard of India (NAAQS). I show that mitigating the post-harvest paddy residue fires can lower the annual average concentration of benzene and ensure compliance with the NAAQS at sites few kilometers downwind of the burning fields. Calculations of excessive lifetime cancer risk due to benzene amount to 25 and 10 per million inhabitants for children and adults, respectively, exceeding the United States Environmental Protection Agency (USEPA) threshold of 1 per million inhabitants. Annual exposure to isocyanic acid was close to 1 ppb, the concentration considered to be sufficient to enhance risks for cardiovascular diseases and cataracts. This study makes a case for urgent mitigation of post-harvest paddy residue fires as the unknown synergistic effect of multi-pollutant exposure due to emissions from this anthropogenic source may be posing grave health risks to the population of the N.W. IGP.

Chapter 4: Storage stability studies and field application of low cost glass flasks for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry

In this chapter I present the validation and application of a novel method for ambient VOC speciation and emission factor studies using low cost (< 100 USD) whole air glass flask samplers and proton transfer reaction mass spectrometry. The objective of this study was to enable acquisition of VOC data from multiple sites and/or remote sites where online measurements of the mass spectrometer remains unfeasible. Quantification of ambient whole air samples which contain reactive and short-lived VOCs such as acetaldehyde, isoprene, dimethyl sulphide and trimethyl benzenes at ppt-ppb concentrations is analytically challenging and generally accomplished using online proton transfer reaction mass spectrometry. Current analytical methods suggested by agencies such as the USEPA recommend collection of whole air samples in stainless steel canisters with passivated surfaces for the determination of VOCs but their high costs (>1000 USD per canister) are deterrents to large scale usage and deployment in ambient studies. Consequently there is paucity of VOC data in vast regions of the world. Experiments to assess the stability during storage of thirteen VOCs, many of which are very reactive, using low cost glass flask samplers showed that acetaldehyde, acetonitrile, acetone, dimethyl sulphide, methyl vinyl and methyl ethyl ketones, benzene, xylenes, trimethyl benzenes and monoterpenes can be quantified reproducibly within the respective precision error (e.g. 40% at 100 ppt α-pinene and 3 % at 13 ppb acetaldehyde) between collection and storage (at > 95% confidence), for samples analyzed within 10 days of collection. For toluene and isoprene, similar results were obtained until day 9 and 1, respectively and at confidence >70%, over the 10 day period. A storage artefact was observed for methanol resulting in higher analytical uncertainty of upto 40%. After validation, I applied the method for measuring toluene/benzene emission ratios and aromatic VOCs in traffic plumes, and determining VOC emission factors (gVOC/kg fuel) from an agricultural wheat straw fire in India. The results of this study demonstrate that use of the low cost glass flask samplers described herein can significantly improve acquisition of spatially and temporally resolved datasets for atmospheric chemistry and air quality studies at sites where online deployment of instruments remains unfeasible and thus now many more regions of India can be become accessible for such studies.

Chapter 5: Odd-even traffic rule implementation during winter 2016 in Delhi did not reduce traffic emissions of VOCs, carbon dioxide, methane and carbon monoxide

In this chapter, I investigated the impact of the odd-even traffic rule implemented in Delhi during the winter 2016 (1-15 January 2016) on primary traffic emissions.

I measured thirteen unique and strong VOC chemical tracers including toluene, sum of xylenes and ethylbenzene isomers which are excellent tracers of auto-mobile exhaust emissions, along with carbon monoxide, carbon dioxide and methane at a strategic arterial road (28.57°N, 77.11°E, 220 a.m.s.l) in Delhi. All the collected samples were analysed at the IISER Mohali atmospheric chemistry facility within 5 days of collection. Whole air ambient samples (n=27) were collected in the morning (07:00-08:00 IST), afternoon (13:30-14:30 IST) and night (19:00-20:00 IST) during periods when odd-even rule was active (OA) (1, 2, 4, 11, 12 and 13 January 2016) and inactive (OI) (31 December 2015 and 20-21 January 2016), respectively and analyzed at the IISER Mohali atmospheric chemistry facility. The average mass concentration ranking and the toluene/benzene (T/B) ratios were characteristic of primary traffic emissions in both OA and OI samples, with the largest fraction comprising of aromatic compounds (55-70% of total). Statistical tests (Mann-Whitney U) showed likely increase ($p \leq 0.16$; OA> OI) in median concentrations for 13 of 16 measured gases during morning and afternoon periods, whereas no significant difference was observed for evening samples (sampling hour: 19:00-20:00 I.S.T).

This suggests that many four-wheeler users chose to commute earlier, to overcome the 8:00 AM-8:00 PM restrictions and/or there was an increase in the number of exempted public transport vehicles. Thus, the odd-even rule did not result in anticipated traffic emission reductions in January 2016, likely due to the changed temporal and fleet emission behavior triggered in response to the regulation. Based on the key observations of this study, it would be advisable to deploy online VOC measurements of the kind reported in this study at multiple strategic sites for future assessment studies. This would enable one to address the current uncertainties with respect to quantitative source apportionment of air pollutants in Delhi and helps in formulating air pollution mitigation strategies for multiple urban sources rather than just traffic emissions.

Contents

Chapter 1

Introduction

1.1 Structure of Earth’s atmosphere

The atmosphere that surrounds the earth is vital for many forms of life including human beings. In terms of its composition, nitrogen (N_2) and oxygen (O_2) account for 78% and 21% respectively, with remainder made up of water vapour (H_2O), argon (Ar), carbon dioxide (CO_2), neon (Ne), helium (He), methane (CH_4), nitrous oxide (N_2O), ozone (O_3) and volatile organic compounds (VOCs) (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000).

Earth's atmosphere consists of four different primarily layers namely troposphere, stratosphere, mesosphere and thermosphere. These are characterized by distinct temperature and pressure regimes which vary with altitude. The troposphere is the lower part of the atmosphere that extends from the Earth's surface to an average altitude of 10-18 km depending on the latitude and season. This layer is characterized by rapid vertical mixing and decrease in temperature with altitude due to adiabatic cooling with convection. Temperature in the troposphere ranges from 217 to 288 K and pressure ranges from 75 to 1013 hPa (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000). Even though it is the thinnest layer compared to other layers of atmosphere, about 80% of the atmospheric mass (> 90% of all air molecules) is contained in it. Moreover, several life-sustaining processes such as hydrological and biogeochemical cycles are associated with this part of the atmosphere.

Stratosphere generally extends from 20 km up to 50 km and is associated with slow vertical mixing, although the starting altitude is strongly dependent in latitude and season. For example in the poles the stratosphere starts already at about 10 km altitude. Temperature and pressure in the stratosphere ranges from 217 K to 271 K and 55 hPa to 0.8 hPa, respectively (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000). In this layer, the Sun’s ultraviolet radiation (UV) (240-290 nm) is absorbed by the stratospheric ozone leading to increase in temperature with altitude. In this way stratospheric ozone shields the Earth’s surface from most of the harmful ultraviolet radiation of the Sun and hence it known as the `good ozone'. Whereas, tropospheric ozone is known as `bad ozone’, whenever it is present in excess of few tens of ppb (e.g. > 40 ppb) it is known to have negative impact on crop productivity, air quality and human health (IPCC, 2013; Haggen-Smit., 1952; Giles., 2005; Ashworth et al., 2015; Sinha et al., 2015).

Above the stratosphere is the mesosphere, which can extend from 50 km upto 90 km. In the mesosphere, the temperature once again decreases with increasing altitude. In this layer, temperature ranges from 271 K to 210 K (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000). The air pressure at the bottom of the layer is well below the 1% of the pressure at sea level and continues dropping as you go higher. Thermosphere is present above the mesosphere, extends from 90 km up to 500 km and the temperature in the thermosphere ranges from 700 K to 2300 K or higher (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000).

Even though, nitrogen and oxygen together make up almost 99% of atmospheric volume, it is the trace gases such as volatile organic compounds (VOCs) in the atmosphere, which exists at mixing ratios of parts per trillion (ppt) to parts per billion (ppb), that drive the exciting chemistry of the lower atmosphere playing key roles in air quality and climate (Goldstein and Galbally, 2007; Lewis et al., 2000). In the following sections (1.2 and 1.3), I described the origin and fate of VOCs in the atmosphere and their impacts on the tropospheric chemistry.

1.2 Sources and sinks of volatile organic compounds (VOCs) in the atmosphere

Volatile Organic Compounds (VOCs) are defined as carbon containing compounds which possess high vapour pressure (> 10 Pa at 20ºC) and low boiling point (< 260ºC) at standard atmospheric pressure (101.3 kPa) (Koppmann, 2007). VOCs include saturated and unsaturated hydrocarbons, aromatics, oxygenated species such as alcohols, aldehydes, ketones, esters, acids, nitrogen containing species such as nitriles, amines, amides, halocarbons and organosulphur compounds, excluding carbon monoxide (CO) and carbon dioxide (CO_2) and carbonates (Koppmann, 2007; Goldstein and Galbally, 2007).

VOCs play vital role in atmospheric chemistry from the regional to the global level. Other than methane and formaldehyde not much was known about VOCs in the earth’s atmosphere before 1950. Thereafter, the key role of VOCs in atmospheric chemistry was recognized from the air pollution episodes such as London and Los Angeles smog. In the recent Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2013), the summary for policy makers clearly identifies VOCs as climate forcing agents and the estimated VOC global radiative forcing (radiative forcing is defined as resulting flux imbalance in the radiative budget for the Earth system caused by total extra amount of an atmospheric constituent added to the atmosphere since 1750 (pre-industrial time)) to be +0.05 to +0.15 W m^{-2}. Moreover, in this report the level of current scientific understanding of VOC impacts on climate change has been described only as “medium” while the level of scientific understanding of the impact of aerosols on climate is now considered to be high. Therefore scientific studies related to VOCs are a priority area of research.

Figure 1.1 shows an illustrative picture depicting the sources, sinks and fate of VOCs emitted into the atmosphere. VOCs have diverse direct and indirect sources (Hewitt, 1999; Goldstein and Galbally, 2007; Lewis et al., 2000; Koppmann, 2007). Direct sources of VOC include biogenic, biomass burning and anthropogenic sources. Biogenic sources consists of processes associated with growth, sustenance and decay of living organisms (plants, animals and microorganisms). Globally, the biogenic source is the largest direct source of VOCs, with total emissions estimated to be 815-1530 Tg y^{-1} (Guenther et al., 1995; Warneck and Williams, 2012). The second largest source of VOCs is biomass burning, with total emissions estimated to be 400-740 Tg y^{-1} (Akagi et al., 2011). Anthropogenic activity is an important source of VOC, with the total emissions estimated to be 71-175 Tg y^{-1} (Warneck and Williams, 2012). Anthropogenic sources include emissions from fossil fuel extraction and refining, incomplete combustion of fossil fuel by automotive transport and power generators, evaporation of solvents used in domestic and industrial operations and emissions from landfill sites (Hewitt, 1999; Lewis et al., 2000; Koppmann, 2007). Indirect sources include formation of VOCs in the atmosphere from precursor molecules through oxidation and/or photolysis (Singh, 2004; Atkinson and Arey, 2003).

VOCs emitted in the lower atmosphere undergo transport and mixing in the planetary boundary layer, and are subjected to photochemical oxidation along with the other removal mechanisms such as surface deposition (vegetation/aerosol) or washout in rain water (wet deposition) (Koppmann, 2007; Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000). Reactions with the hydroxyl radical (OH) during the daytime represent the dominant sink for most of the VOCs (Lelieveld et al., 2016). Oceans also acts as sink for some of the short chain VOCs such as methanol. Reactions with ozone, photolysis and reactions with nitrate radical (NO_3) during nighttime also act as sinks of VOCs (Atkinson and Arey, 2003; Warneke et al., 2004). For a given VOC its atmospheric lifetime is estimated using the overall removal rate which includes reaction with radical species, photolysis, and deposition. Atmospheric lifetime of VOCs vary from minutes to several years (Atkinson and Arey, 2003), depending on its properties.

Table 1.1 lists some major atmospheric VOCs relevant to this thesis and their major sources and sinks along with global budgets and tropospheric lifetimes (at 298 K) (Source References: Millet et al., 2008; Warneck and Williams., 2012; Singh, 2004; Marandino et al., 2005; Jardine et al., 2015; Henze et al., 2008; Atkinson and Arey, 2003; Roberts et al., 2014). Reaction with the hydroxyl (OH) radical is the major removal process for most of these VOCs during the daytime in the troposphere. Hence, I have estimated their typical atmospheric chemical lifetimes at 298 K for OH radical reactions with 12-h daytime [OH] concentration to be 2×10^6 molecules cm^{-3} (Atkinson and Arey, 2003).

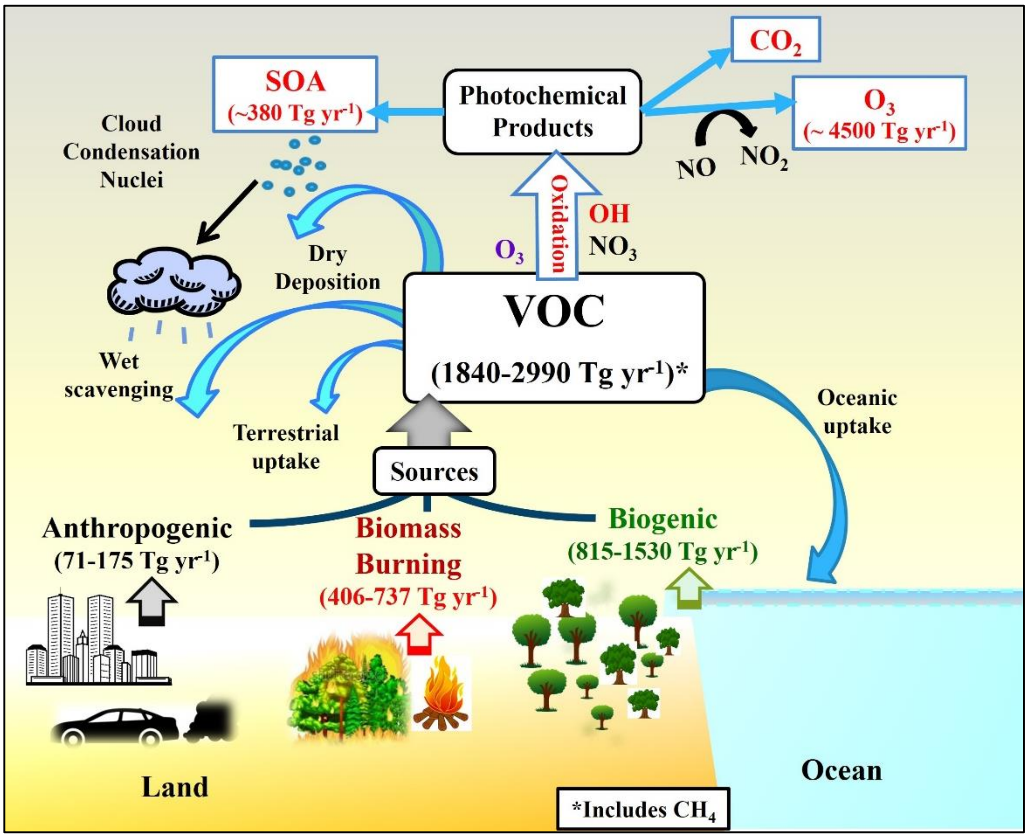


Figure 1.1. Illustrative cartoon of the origin and fate of VOC emissions in the troposphere

Table 1.1. Major sources, sinks and global budgets of some important VOCs in the troposphere and their estimated atmospheric chemical lifetime

VOCs (chemical formula)	Major sources (Tg y^{-1})	Major sinks (Tg y^{-1})	atmospheric chemical lifetime @
Methanol (CH_3OH)[1]	Terrestrial plant growth (80), plant decay (23), biomass burning (12), atmospheric production (35), urban sources (5), oceans and biogenic (85)	Gas phase oxidation by OH (88), dry deposition in land (40), wet deposition (13), uptake by oceans (101)	~ 12 days
Acetonitrile (CH_3CN)[2]	Biomass burning (1.2)	Reaction with OH (0.3), uptake by oceans (1.2)	~ 7 months
Acetaldehyde (CH_3CHO)[1]	Hydrocarbon oxidation (128), vegetation (23), ocean emissions (57), biomass burning (3), anthropogenic emissions (2)	Reaction with OH (188), photolysis (22), dry and wet deposition (3)	~ 8.8 hours

Acetone (CH_3COCH_3)[3]	Hydrocarbon oxidation (20-36), vegetation (25-75), ocean emissions (0-15), biomass burning (7-11), anthropogenic emissions (2)	Photolysis (14-30), reaction with OH (11-25), wet and dry deposition (46-96)	~ 68 days
Dimethylsufide (CH_3SCH_3)[4]	Ocean emissions (50), soils and vegetation (1)	Reaction with OH and NO_3	~ 2 days
Isoprene (C_5H_8)[2]	Emissions from deciduous trees (570)	Reaction with OH	~ 1.4 hours
Benzene (C_6H_6)[2]	Industrial and fossil fuel (1.5), biofuel (2), biomass burning (2.7)	Reaction with OH	~ 9.5 days
Toluene (C_7H_8)[2]	Industrial and fossil fuel (4.7), biofuel (1.1), biomass burning (1.8)	Reaction with OH	~ 2.1 days
Xylene isomers (C_8H_{10})[5,*]	Industrial and fossil fuel (3.5), biofuel (0.5), biomass burning (0.7)	Reaction with OH	~ 5-10 hours
Monoterpene isomers $(C_{10}H_{16})$[6]	Emissions from coniferous and deciduous trees (140)	Reaction with OH and O_3	~ 2-5 hours
Isocyanic acid (HCNO)[7]	Biomass combustion, photo-oxidation of amines and amides, diesel engines	Wet and dry deposition, photolysis, reaction with OH	-

[1]Millet et al., 2008, [2]Warneck and Williams., 2012, [3]Singh., 2004 and Marandino et al., 2005, [4] Jardine et al., 2015,[5]Henze et al., 2008, [6]Atkinson and Arey 2003, [6]Roberts et al., 2014

* Units of xylene emissions reported in the table is TgC y^{-1}.

[@] Atmospheric chemical lifetime are estimated at 298 K for OH radical reactions with 12-h daytime [OH] = 2×10^6 molecules cm^{-3} (Atkinson and Arey, 2003)

In the next section, I elucidate the importance of VOC in tropospheric chemistry through photochemical reactions with hydroxyl radicals (OH) and nitrogen oxides.

1.3 Impact of volatile organic compounds (VOCs) on tropospheric chemistry

The impact of VOCs on tropospheric chemistry stems from the role played by VOCs in controlling the budget of hydroxyl radicals and driving ozone and secondary organic aerosol formation in the troposphere.

1.3.1 Role of volatile organic compounds (VOCs) in tropospheric ozone formation

Tropospheric ozone is an important greenhouse gas which contributes to global warming (IPCC, 2013). Since 1750, changes in tropospheric ozone account for about 17% of the total anthropogenic radiative forcing of 2.29 W m^{-2}. It plays a key role in atmospheric chemical processes. However, whenever it is present in excessive amount in lower troposphere (> 40 ppb), it is known to have adverse effects on air quality, human health and crop productivity (Haggen-Smit., 1952; Giles., 2005; Ashworth et al., 2015; Sinha et al., 2015; Jerrett et al., 2009). Photolysis (< 420 nm) of NO_2 is the pathway through which the ozone is formed in the troposphere during day time (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000; Jacob, 1999). NO_2 undergoes photo dissociation to form an NO and an oxygen atom (O^3P) in its triplet state. Rapidly, this oxygen (O^3P) atom reacts with molecular oxygen (O_2) in the presence of a third body (usually N_2 and O_2) to form ozone (O_3). Third reaction partner absorbs the excess vibrational energy and stabilizes the produced O_3 molecule. Thereafter, the formed O_3 molecule reacts rapidly with NO to reform NO_2 and O_2. The net result of these reactions as represented by reactions [R1] to [R3] and constitutes a null cycle with no net production of O_3. This photostationary state between O_3-NO-NO_2 is formed during the daytime on a time scale of few hundred seconds (Mannschreck et al., 2004).

$$\mathrm{NO_2} + h\nu \xrightarrow[\ ]{\substack{J_{NO2} \\ (\lambda < 420nm)}} \mathrm{NO} + \mathrm{O(^3P)} \qquad [\mathrm{R1}]$$

$$\mathrm{O(^3P)} + \mathrm{O_2} + \mathrm{M} \xrightarrow{\substack{\mathrm{k_{298}} = (5.6-6)\times10^{-34} \\ (\mathrm{cm^6 molecule^{-2} s^{-1}})}} \mathrm{O_3} + \mathrm{M} \qquad [\mathrm{R2}]$$

$$\mathrm{NO} + \mathrm{O_3} \xrightarrow{\substack{\mathrm{k_{298}} = 1.8\times10^{-14} \\ (\mathrm{cm^3 molecule^{-1} s^{-1}})}} \mathrm{O_2} + \mathrm{NO_2} \qquad [\mathrm{R3}]$$

Here, in the reaction [R2], M represents third body (usually N_2 and O_2). Rate constants of reaction [R2] and [R3] are shown for temperature of 298K (Atkinson et al., 2004; Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000).

In presence of VOC, formation of ozone occurs outside the photo-stationary state (PSS). This is due to occurrence of chemical pathways other than reaction between O_3 and NO that converts the NO to NO_2. Other major pathways that oxidize NO to NO_2 are the reactions of NO with peroxy radicals ($PO_2 = RO_2 + HO_2$), which are formed as a result of oxidation of VOCs (represented as RH) or CO with hydroxyl radicals in the daytime as represented by the reactions [R4] and [R5] (Seinfeld and Pandis, 2006; Jacob, 1999).

$$\mathrm{RH} + \mathrm{OH} \xrightarrow{\mathrm{O_2}} \mathrm{RO_2} + \mathrm{H_2O} \qquad [\mathrm{R4}]$$

$$\mathrm{CO + OH \xrightarrow{O_2} CO_2 + O_2H} \qquad [R5]$$

Formed peroxy radical perturbs the photo-stationary state by oxidizing the NO to NO_2 which on photolysis produces O_3 molecule.

$$\mathrm{RO_2 + NO \longrightarrow RO + NO_2} \quad [R6]$$

Alkoxy radical formed via reaction [R6] can react with O_2, or can isomerize or thermally decompose to give lower carbonyl compounds and hydroperoxy (HO_2) radical which can react with NO to produce hydroxyl radical (OH) and another molecule of NO_2.

$$\mathrm{RO + O_2 \longrightarrow R^1CHO + HO_2} \quad [R7]$$

$$\mathrm{HO_2 + NO \xrightarrow[\ ]{\substack{k_{298}=8.1\times10^{-12}\\(cm^3molecule^{-1}s^{-1})}} HO + NO_2} \qquad [R8]$$

In general, upon oxidation, one molecule of VOC can produce a minimum two molecules NO_2 which on photolysis can lead to the formation of two molecules of O_3 outside the photo-stationary state in the troposphere. However, depending on VOC structure, several molecules of NO_2 can be formed which can undergo photo-dissociation to produce several O_3 molecules outside the photo-stationary state. Thus, VOCs tend to fuel the formation of ozone in the troposphere. Among all the reactions from [R4] to [R8], reaction [R4] is generally the slowest and rate determining step for the production of O_3 from VOCs in the lower atmosphere. This shows the importance of VOC-OH reactivity for tropospheric ozone formation.

Depending on the environment, the reaction chain of O_3 production can be terminated by loss of HO_x radicals either through reaction pathway [R9] or [R10]. In a pristine environment where VOC concentrations are high (or low NOx), the major chain termination pathway is through the reaction [R9] and under these conditions O_3 production linearly depends on NOx concentration as shown in the equation 2 (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000; Jacob, 1999).

$$\mathrm{HO_2 + HO_2 \xrightarrow{\substack{k_{298}= 1.6\times10^{-12}\\(cm^3molecule^{-1}s^{-1})}} H_2O_2 + O_2} \quad [R9]$$

$$P_{O_3} = 2k_{R8}\left(\frac{P_{HO_x}}{k_{R9}}\right)^{\frac{1}{2}} \times [NO] \qquad [2]$$

In a polluted environment where NO_x concentration are high, the major chain termination pathway is through the reaction [R10] and under such conditions O_3 production inversely depends on NOx concentration and limited by VOC concentration as shown in the equation 3 (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts, 2000; Jacob, 1999).

$$\mathrm{OH + NO_2 + M \xrightarrow{\substack{k_{298,(M=N2)}= 3.3\times10^{-30}\\(cm^6molecule^{-2}s^{-1})}} HNO_3 + M} \quad [R10]$$

$$P_{O_3} = 2k_{R4}\frac{P_{HO_x}}{k_{R10}} \times \frac{[RH]}{[NO_2] \times [M]} \qquad [3]$$

Where, P_{O3} is the maximum ozone production, P_{HOx} represents HO_x ($OH + HO_2$) production rate and [NO], [RH], [NO_2] and [M] are the concentrations of NO, VOCs, NO_2 and the reaction partner (N_2 or O_2), respectively. Reaction rate constant of [R9] and [R10] are estimated at 298K (Atkinson et al., 2004).

Tropospheric O_3 is also the primary source for the production of hydroxyl radicals (OH), the main atmospheric oxidant which controls the abundance and distribution of many atmospheric constituents including greenhouse gases such as methane and VOCs as described earlier using the reactions [R4] to [R10].

In the lower atmosphere, photolysis of ozone due to solar ultra violet radiation ($\lambda < 340$nm) followed by reaction of some of the excited oxygen atoms (O^1D) with water vapour results in primary production of hydroxyl radicals (OH). This reaction pathway is represented by the reactions [R11] and [R12]. Reaction rate constant of [R12] is estimated at the temperature 298K (Atkinson et al., 2004).

$$O_3 + h\nu \xrightarrow{(\lambda < 340nm)} O_2 + O(^1D) \qquad [R11]$$

$$O(^1D) + H_2O \xrightarrow[]{\substack{k_{298} = 2.2\times10^{-10} \\ (cm^3 molecule^{-1} s^{-1})}} 2OH \quad [R12]$$

1.3.2 Contribution of volatile organic compounds (VOCs) to secondary organic aerosol (SOA) ozone formation

Secondary organic aerosol (SOA) plays an important role for the Earth's climate due to their optical and radiative properties by absorbing and scattering solar radiation (IPCC, 2013). Further they can also act as cloud condensation nuclei (CCN) and thus affect the cloud cycle (Rosenfeld et al., 2008). SOA is produced from the atmospheric oxidation of VOCs released into the atmosphere from various anthropogenic and biogenic sources. Globally, SOA formation from the biogenic VOC emissions is estimated to be 20-380 Tg y^{-1} (IPCC, 2013). Flux estimates for the anthropogenic and biomass burning of organic aerosol are estimated to be 4-27 TgC y^{-1} and 17-34 TgC y^{-1}, respectively (Hallquist et al., 2009).

During the initial oxidation by OH radical, VOCs form products that have higher solubility and lower volatility than the parent VOCs. These oxidation products consist of minimum one oxygen containing functional group such as alcohol (-OH), aldehyde (-C(=O)H), ketone (-C(=O)-), carboxylic acid (-C(=O)OH), percarboxylic acid (-C(=O)OOH), hydroperoxide (-OOH), nitrate (-ONO_2) and peroxyacylnitrate (-C(=O)$OONO_2$) (Hallquist et al., 2009). These products on further oxidation yield multifunctional oxygenated organic compounds with even lower volatility which are even more hydrophilic in nature. These oxidation products can readily partition into the aerosol phase, leading to the SOA formation.

Ozonolysis of biogenic VOCs such as monoterpenes and sesquiterpenes is another important pathway through which SOA can be formed in the troposphere (Mellouki, 2014; Iinuma et al., 2013). Several laboratory and field measurements show that SOA yields of VOC have strong dependence on NO_x levels (Ng et al., 2007; Kroll et al., 2006).

1.4 Current scenario on characterization of VOCs over Indian subcontinent

Most of the previous trace gas studies from the Indian sub-continent have been focused on characterizing the emissions of primary air pollutants such as carbon monoxide, sulfur dioxide, ozone and nitrogen oxides, greenhouse gases, black carbon and particulate matter (PM_{10}, $PM_{2.5}$) (Kulshrestha et al., 1997; Lal et al., 2000; Gadi et al., 2003; Ahammed et al., 2006; Venkataraman et al., 2006; Sahai et al., 2007; Ghude et al., 2008 and Lal et al., 2008). Over the Indian subcontinent only few studies have been conducted thus far to understand the emissions and chemistry of VOCs. Most of these VOC studies have been carried out using slow offline techniques, and have focused on urban sites in Delhi, Mumbai and Kolkata primarily influenced by traffic and industrial sources (Srivastava et al., 2004; Srivastava et al., 2005a, b and c; Dutta et al., 2009; Majumdar et al., 2011). Measurements of non-methane hydrocarbons (C_2-C_5 NMHCs) using Gas Chromatography-Flame Ionization Detector (GC-FID) were carried out at Delhi, Mumbai, Kolkata, Ahmedabad, Kanpur, Hissar and at a high altitude site in Nainital in central Himalayas (Srivastava et al., 2005a; Mohan et al., 1997; Mallik et al., 2014; Sahu and Lal, 2006; Lal et al., 2012 and Sarangi et al., 2016). These early studies frequently showed appreciable contribution from fossil fuel usage and other anthropogenic sources. In 2011, measurements of VOCs using proton transfer reaction mass spectrometry commenced for the first time at any Indian site and the first measurements of VOCs such as isoprene and acetaldehyde in ambient Indian air became available (Sinha et al., 2014; Sarkar et al., 2013; Kumar et al., 2016; Chandra and Sinha, 2016). Prior to these measurements, the INDOEX campaign has provided evidence of high VOC concentrations in the outflow of air masses from the Indian subcontinent by deploying the PTR-MS technique (Lelieveld et al., 2001; Sprung et al., 2001). Due to the inadequate understanding of VOC concentrations and distributions over India, there continues to be a large data gap from this region pertaining to their emission strengths and hence effects on air quality and atmospheric chemistry.

1.5 Motivation and thesis outline

Rapid increases in population, urbanization and industrialization over the Indian sub-continent have changed the land use land cover and strengthened the impact of anthropogenic emissions. As a consequence, myriad urban and rural emission sources of VOCs have escalated, affecting both air quality and climate at urban, regional and even at continental scales. On the other hand as discussed in Section 1.4, it is clear that there is inadequate data of VOCs available over the Indian sub-continent as well as lack of understanding of how regional large scale activities such as agricultural burning impact VOC emissions and atmospheric chemistry over the region.

Open crop residue burning is an important anthropogenic activity that happens extensively in the northwest Indo-Gangetic Plain (N.W. IGP), the bread basket of South Asia. A previous study from our group by Sarkar et al. (2013) showed a threefold enhancement in ambient levels of carcinogenic benzenoids and acetonitrile in air masses affected by the paddy residue fires. However, no long term in-situ field studies have been reported from the region so far, focusing on the emissions of health relevant VOCs from this activity.

Techniques such as proton transfer reaction mass spectrometry (PTR-QMS), gas chromatography (GC) and fourier-transform infrared spectrometry (FTIR) are employed for VOC measurements in ambient air. However, deployment of these instruments in the field is hampered by logistical issues such as power and safety. Even if deployment were possible, it may be desirable to obtain measurements from multiple sites instead of just a single site. Keeping in mind the above background, affordable offline VOC samplers are needed for improving the existing spatial and temporal VOC data coverage and deriving source speciation profiles.

Thus through this thesis, I would like to address the following questions;

1) How much do emissions from open paddy residue fires in the northwest Indo-Gangetic Plain (N.W. IGP) contribute to the enhanced ambient concentrations of VOCs of carcinogenic benzenoids, carbon monoxide, and toxic isocyanic acid?

2) What is the enhanced cancer risk due to the exposure to benzene emissions from paddy residue fires in the N.W IGP?

3) How can one enable ambient VOC speciation studies using low-cost whole air glass flask samplers and offline proton transfer reaction mass spectrometry without comprising on analytical aspects such as sample integrity and precision of VOC measurements?

4) What is the typical VOC and greenhouse gas speciation at a traffic thoroughfare in Delhi during winter?

5) Was the odd-even traffic rule restriction implemented in Delhi during winter 2016 (1-15 January 2016) effective in reducing primary traffic emissions of VOCs and greenhouse gases?

The first and second question is addressed in Chapter 3 of this thesis wherein the contribution of open paddy fires during the post-harvest period to the enhanced ambient concentrations of carcinogenic benzenoids and toxic isocyanic acid are assessed using three years of long term in-situ measurements (2012-2014) in addition to assessing the human health risk as a consequence of exposure to carcinogenic benzene emissions from open paddy fires. The third question is addressed in Chapter 4, wherein I have discussed the validation and application of a novel method for ambient VOC speciation studies using low-cost whole air glass flask samplers and offline proton transfer reaction mass spectrometry that can help reduce the paucity of VOC datasets. The fourth and fifth questions have been addressed in Chapter 5 where I have presented the speciation of VOCs at a traffic thoroughfare in Delhi and assessed the impact of the odd-even traffic rule (implemented in Delhi during 1-15 January 2016) on primary traffic emissions using measurements of 13 VOCs, carbon monoxide, carbon dioxide and methane.

Chapter 2

Measurement of VOCs using proton transfer mass spectrometry (PTR-MS)

The precision and accuracy of what we can measure governs our understanding of atmospheric chemistry. Quantification of VOCs (typically ppt-ppb range) in complex ambient air mixture is a challenging task as its chemical composition changes in response to emissions and meteorological changes. Over the past two decades, several measurement techniques have been developed and deployed to quantify ambient VOC mole fractions which has significantly improved our understanding of VOC emissions, chemical processing, transport, and loss mechanisms (Goldstein and Galbally, 2007; Koppmann, 2007; Jones et al., 2014). These techniques range from in-situ through ground-based sampling to global mapping techniques such as satellites (Warneke et al., 2004; Ras et al., 2009; Aragón et al., 2000; Blake et al., 2009; Kumar and Víden, 2007; Pérez Ballesta et al., 2016; Kim et al., 2012). Each of these techniques has both advantages and disadvantages. For example, high frequency measurements (seconds to minutes) are required for the quantification of fluxes, whereas for understanding the long term trends could be achieved by performing the less frequent measurements (daily, weekly or monthly). For in-situ measurements of VOC, gas chromatography (GC) based techniques are commonly used (Christian et al., 2004; Jones et al., 2014). In this technique, air samples collected in either canister or on adsorption tubes has to be pre-concentrated due to low concentrations involved (ppt-ppb). Using this technique a suite of VOCs can be measured at concentrations as low as 0.1 ppt (Christian et al., 2004; Jones et al., 2014). Despite these advantages, several measurement artefacts can arise during collection, storage and pre-concentration. Moreover, highly reactive oxygenated VOCs such as methanol, acetone and acetaldehyde cannot be accurately quantified using this technique due to storage artefacts in canisters/adsorption tubes. Another major disadvantage is with respect to its time resolution. Pre-concentration process and separation of constituents of a gas mixture on the capillary column limits the time resolution and hence this technique is not suitable to study the process on a time scale of few minutes or less. Hence, in the past few decades, highly mass and time resolved mass spectrometric techniques which are faster than chromatographic techniques have emerged for the quantification of VOCs (Lindinger et al., 1998; Lindinger et al., 2001; de Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017). However, the usage of electron impact ionization mass spectrometry for the VOC measurements in the ambient air is limited due to contributions from inorganic constituents of Earth's atmosphere such N_2, O_2 and CO_2 to the lower end of the mass spectrum and extensive fragmentation. Mass spectrometric methods based on soft chemical ionization technique are better suited for the ambient studies of VOCs. Measurement of VOCs reported in this thesis were performed using proton transfer reaction mass spectrometry, which relies on soft chemical ionization. Over the past decade, this technique has been widely used for numerous ambient VOC studies and provided new insights pertaining to ambient VOC emissions and chemistry in varied ecosystems (Lindinger et al., 1998; Lindinger et al., 2001; Hewitt et al., 2003; Hansel et al., 1999; de Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017). Using this technique, real time quantification of VOC is possible in a rapidly changing atmosphere so that information about specific emission activity can be deduced accurately from the highly time resolved measurements. Details pertaining to this mass spectrometry technique are described in subsequent sections.

2.1 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

A high-sensitivity proton transfer reaction quadrupole mass spectrometer (HS Model 11-07HS-088; Ionicon Analytik Gesellschaft, Austria) was used to carry out the VOC measurements reported in this work. This technique was developed by Professor Werner Lindinger and co-workers at the University of Innsbruck in Austria in 1995 (Lindinger et al., 1998; Lindinger et al., 2001). It is a soft chemical ionization (no/low fragmentation of product ion) mass spectrometric technique, wherein analyte VOC molecules with a proton affinity (P.A.) greater than that of water vapour (691.2 kJ mol^{-1}) are chemically ionized with the reagent hydronium ions (H_3O^+) and form protonated molecular ions (with m/z = molecular ion + 1) of VOC and these product ions are then separated in the mass analyzer before detection using secondary electron multipliers or channeltrons. The reaction between VOCs and the reagent hydronium ion (H_3O^+) can be expressed as,

$$\mathrm{VOC} + \mathrm{H_3\,O^+} \rightarrow \mathrm{VOCH^+} + \mathrm{H_2\,O} \quad [\mathrm{R13}]$$

Table 2.1 lists proton affinities (P.A) of VOCs reported in this work. As major atmospheric gases such as nitrogen (493.7 kJ mol^{-1}), oxygen (420.9 kJ mol^{-1}), carbon dioxide (540,6 kJ mol^{-1}), carbon monoxide (624.3 kJ mol^{-1}), nitrous oxide (571.1 kJ mol^{-1}) and and methane (543.5 kJ mol^{-1}) have proton affnities lower than water vapour (691.2 kJ mol^{-1}), they do not cause interferences in the detection of these trace level VOCs. (Warneke et al., 2004; Warneke et al., 2003; de Gouw and Warneke, 2007; Blake et al., 2009; Yuan et al., 2017)

Table 2.1. Proton affinities (P.A) of VOCs reported in this work (taken from compilation of proton affnity list provided by Ionicon Analytik GmbH, Innsbruck, Austria)

Compound	Proton affinity (kJ mol^{-1})
Methanol	754.4
Acetonitrile	779.1
Isocyanic acid	753.1
Acetaldehyde	769.0
Acetone	812.1
Dimethylsulfide	830.9
Isoprene	832.2
Furan	796.6
Methyl ethyl ketone	827.6
Methyl vinyl ketone	832.6
Benzene	748.9
Toluene	782.4
p-Xylene	795.0
1,2,4 Trimethylbenzene	836.4

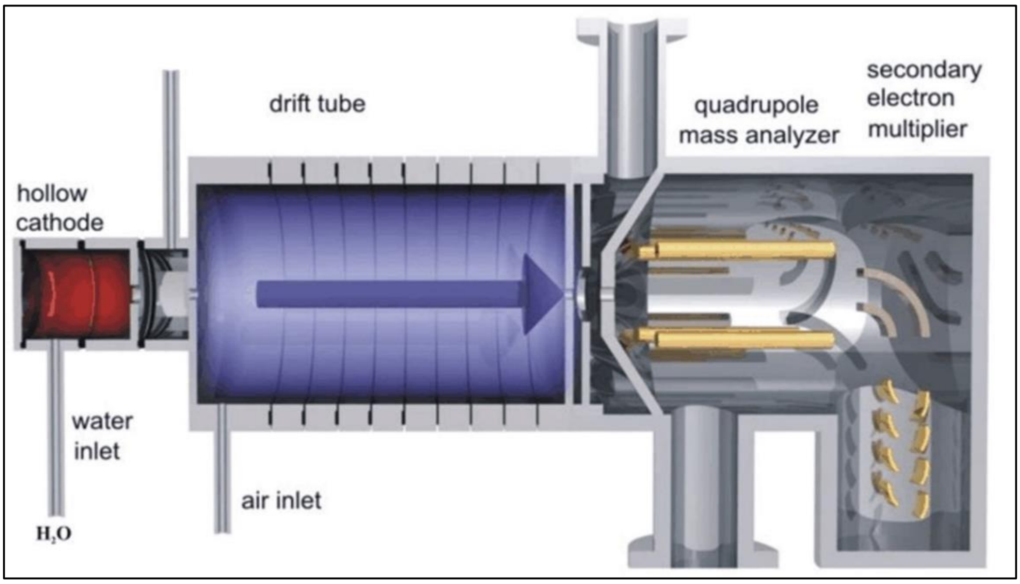


Figure 2.1. Schematic diagram of the proton transfer reaction mass spectrometer (PTR-MS) instrument (Source: Ionicon analytik GmbH, Innsbruck, Austria)

The instrument consists of four major parts:

a) Ion source
b) Drift tube
c) Mass analyzer
d) Detector

Descriptions of each component in the proton transfer reaction mass spectrometer are provided below:

2.1.1 Ion source

It produces a pure stream of reagent H_3O^+ ions (> 95 %) by plasma discharge of ultrapure water vapor in a hollow-cathode tube. It is further divided in two chambers: in the first chamber, the following reactions take place (Lindinger et al., 1998; Lindinger et al., 2001).

$$\mathrm{e^- + H_2O \rightarrow H_2O^+ + 2e^-} \qquad [R14]$$

$$\mathrm{e^- + H_2O \rightarrow H_2{}^+ + O + 2e^-} \; [R15]$$

$$\mathrm{e^- + H_2O \rightarrow O^+ + H_2 + 2e^-} \quad [R16]$$

$$\mathrm{e^- + H_2O \rightarrow H^+ + OH + 2e^-} \quad [R17]$$

The ions produced from the aforementioned reactions enter into the second chamber and finally hydronium ion forms through the following ion-molecule reactions.

$$\mathrm{O^+ + H_2O \rightarrow H_2O^+ + O} \qquad [R18]$$

$$\mathrm{H_2{}^+ + H_2O \rightarrow H_2O^+ + H_2} \quad [R19]$$

$$\mathrm{H^+ + H_2O \rightarrow H_2O^+ + H} \qquad [R20]$$

$$\mathrm{H_2O^+ + H_2O \rightarrow H_3O^+ + OH} \quad [R21]$$

The presence of unreacted water vapour in the ion source can leads to the formation of cluster ions of the type $H_3O^+(H_2O)_n$ via the following process

$$\mathrm{H_3O^+(H_2O)_{n-1} + H_2O + M \rightarrow H_3O^+(H_2O)_n + M} \quad [R22]$$

Where M is a third body. Water vapour in the analyte gas can also lead to the formation of $H_3O^+(H_2O)_n$. The key point to note that water clusters possess higher proton affinity than the bare water molecules (P.A of H_3O^+: 691.1 kJ mol^{-1}). As more water molecules are added, the proton affinity of the water cluster increases (P.A of $H_3O^+(H_2O)$: 808 kJ mol^{-1}) (de Gouw and Warneke, 2007; Blake et al., 2009). Hence, most of the VOCs whose proton affinity lies between H_3O^+ and H_3O^+ (H_2O), therefore accept a proton from H_3O^+ but not from $H_3O^+(H_2O)$ (de Gouw and Warneke, 2007; Blake et al., 2009). Proportion of these water cluster relative to H_3O^+ were minimized by operating the PTR-MS at the optimum reduced electric field (E/N) of ~135 Td (see later in Section 2.1.2). In this thesis work, I have monitored the first (H_3O^+ (H_2O)) and second water clusters (H_3O^+ $(H_2O)_2$) ion signals at m/z signals 37 and 55, respectively and their percentage with respect to the primary reagent ion (H_3O^+) were always less than 7% and 2%, respectively. Calibration experiments have shown that normalizing the measured ion signals to both m/z 19 and m/z 37 for our instrumental settings of ∼135 Td yielded a rather constant sensitivity beyond 25% RH for all the compounds reported in the thesis (Sinha et al., 2014). This is consistent with previous studies (de Gouw et al., 2007) where at such E/N ratios in the drift tube, the influence of humidity changes became less significant.

Impurity ions such as NO^+ and O_2^+ are also produced in the ion source by other unwanted reactions due to presence of traces of air (N_2 and O_2). However for the PTR-MS system used in this thesis work, the impurity ion signals due to NO^+ and O_2^+ were always less than 1 % and 4 % of the primary ion signal, respectively. The flow of water vapor entering into ion source was maintained between 3 and 5 sccm. For the first and second chamber voltages were set to 80-120V and 60-100V, respectively.

2.1.2 Drift tube

Drift tube is a reaction chamber in which soft chemical ionization of analyte VOCs takes place. It consists of a number of stainless steel rings separated by Teflon rings, which seal the vacuum and isolate the drift rings electrically. These rings are connected through a resistor network, which divides the overall applied drift tube voltage into a homogeneously increasing voltage and establishes a homogeneous electric field inside the reaction chamber. Reagent hydronium ions (H_3O^+) from ions source enter the drift tube through a Venturi-type inlet. Due to an applied electric field hydronium ions (H_3O^+) ions move towards the detection part, while the ions undergo collisions with the analyte VOC gas molecules. During the collisions proton transfer reactions take place between VOCs that possess a proton affinity greater than that of water vapour. The inherent energy transfer during the ionization process of proton transfer is only in the order of 0-2 eV which is much less than energy transfer (~70 eV) during electron impact ionization process. Hence, the fragmentation is largely suppressed, which leads to easily interpretable mass spectra of VOCs (molecular weight +1). Once, the VOC (R) molecule is ionized, it is immediately extracted by the applied electric field towards the detector and it cannot undergo any further reactions. From the number of collisions the resulting number of protonated VOC molecular ions ($[RH^+]$) can be expressed as follows (Lindinger et al., 1998; Lindinger et al., 2001; de Gouw and Warneke., 2007),

$$[\mathrm{RH}^+] = [\mathrm{H}_3\,\mathrm{O}^+]_0 \left(1 - \mathrm{e}^{-\mathrm{k}[\mathrm{R}]\mathrm{t}}\right) \qquad (2.1)$$

where, [R] is the concentration of the VOC, $[H_3O^+]_0$ is the concentration of reagent ions injected from the ion source, k is the collision rate coefficient for the proton transfer reaction (typical value 10^{-9} cm^3 s^{-1}) and t is the time available for the reaction in the drift tube (9.3 cm).

It is assumed that the only loss of reagent ions occurs through proton transfer reactions with VOCs. As only a small fraction of H_3O^+ ions react in the drift tube under typical instrumental conditions, Equation (2.1) can be reasonably approximated as,

$$[RH^+] = [H_3\,O^+]_0\,[R]kt \qquad (2.2)$$

The above assumption remains valid unless the concentration of VOC (>10 ppm) is much higher and the number of primary reagent ions is significantly depleted in the ionization process. Re-arrangement of Equation (2.2) provides the number density of VOC injected inside the drift tube according to the following Equation (2.3).

$$[R] = \frac{[RH^+]}{[H_3\,O^+]} \times \frac{1}{kt} \qquad (2.3)$$

Where, $[RH^+]$ and $[H_3O^+]$ are the product and primary ion signal detected by the detector.

Using, drift tube pressure and temperature, reaction rate constant (k) of proton transfer from hydronium ion to a VOC and reaction time (t) the number density of the VOC [R] can be converted into the mixing ratio and is typically expressed in parts-per-billion by volume (ppb), as follows:

$$R_{ppbV} = \frac{[R] \times 10^9}{[air]} \qquad (2.4)$$

Where, [air] is the number density of air molecules in the drift tube. The factor 10^9 converts the concentration to ppb.

$$[air] = \frac{273.15}{T_{drift}[K]} \times \frac{6.023 \times 10^{23}\mathrm{cm}^{-3}}{22400} \times \frac{p_{drift}\,[mbar]}{1013mbar} \qquad (2.5)$$

Reaction time (t) is given by,

$$t = \frac{L^2}{\mu U} = \frac{L^2 \times 273.15 \times p_{drift}}{T_{drift} \times 1013 \times \mu_o \times U} \qquad (2.6)$$

Where, L is the length of the drift tube (cm) , U is the voltage across the drift tube (V) p_{drift} and T_{drift} are drift tube pressure (mbar) and temperature (K), respectively and μ_o is the reduced mobility of the H_3O^+ (2.76 $cm^2\,V^{-1}\,S^{-1}$).

After substituting Equations (2.3), (2.5) and (2.6) in the Equation (2.4), the final Equation (2.7) for calculating the mixing ratio of VOC is given by

$$[R_{ppbV}] = \frac{[RH^+] \times 10^9 \times \mu_o \times 22400 \times 1013^2 \times {T_{drift}}^2 \times Tr_{[H_3\,O^+]}}{K \times L^2 \times [H_3\,O^+] \times {p_{drift}}^2 \times 6.023 \times 10^{23} \times 273.15^2 \times Tr_{[RH^+]}} \qquad (2.7)$$

Where, $Tr_{[RH+]}$ and $Tr_{[H3O+]}$ are transmission efficiency of product ion and primary ion respectively.

In addition to the reaction [R13], analyte VOC molecules ions $[RH^+]$ and primary reagent ions $[H_3O^+]$ can form the cluster with water molecule as,

$$H_3\,O^+ + nH_2\,O \rightarrow H_3\,O^+(H_2\,O)_n \quad [R23]$$

$$RH^+ + H_3\,O^+(H_2\,O)_n \rightarrow RH\,(H_3\,O^+) + H_2\,O\ [R24]$$

These cluster ions will complicate the interpretation of mass spectra. Cluster ion formation can be reduced by increasing the kinetic energy of the reagent ions. Mobility of the ion depends on the electric field and pressure in the drift tube. The drift tube velocity is a parameter of E/N ratio called reduced electric field and it is shown in the following Equation (2.8) (de Gouw and Warneke, 2007; Blake et al., 2009).

$$V_d = \mu_o N_o \times \frac{E}{N} \quad (2.8)$$

Where, μ_0 is the reduced mobility of the ion in the vacuum, N_0 is the number density at standard temperature (T_0 = 273.15 K) and pressure (P_0 = 1 atm), E is the applied electric field (U/L; U is drift tube voltage (V) and L is the length of the drift tube) and N is the number density of the gas in the drift tube at applied temperature and pressure. E/N ratio is expressed in Townsend unit (1 Td = 10^{-17} V cm^2). During the process of optimizing reduced electric field, ‘E/N” ratio was varied between 80-145 Td by varying the drift tube voltage between 400-650V at a constant drift tube temperature and pressure of 60oC and 2.2 mbar, respectively. Below 130 Td of reduced electric field the percentage of first water cluster ions was always above 10% relative to H_3O^+, which has increased the undesirable ligand switching reactions between analyte molecule and $H_3O^+(H_2O)$ as represented in above reaction R24 and caused complications in mass spectral analysis. Whereas, increase in reduced electric field above 140 Td has reduced ion clustering within the drift tube but it lead to more fragmentation and some of product ion have minor losses in the drift tube. Hence, in this thesis work PTR-MS is operated at an optimum reduced electric field of ~ 135 Townsend at which the interference due to the formation of cluster ions and fragmentation is reasonable (Sinha et al., 2014; Kumar et al., 2016; Chandra and Sinha, 2016).

2.1.3 Mass analyzer

In this thesis work, PTR-MS technique equipped with the quadrupole is used for the analysis of VOCs. A quadrupole consists of four parallel cylindrical metal rods. Their typical radius is 10-20 mm radius and length is 20 cm. Among these four rods, pair of opposing rods are electrically connected to a balanced voltage source having a radio frequency component super imposed on a constant potential. Only ions of a certain mass-to-charge ratio will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods. Figure 2.2 shows schematic of the quadrupole.

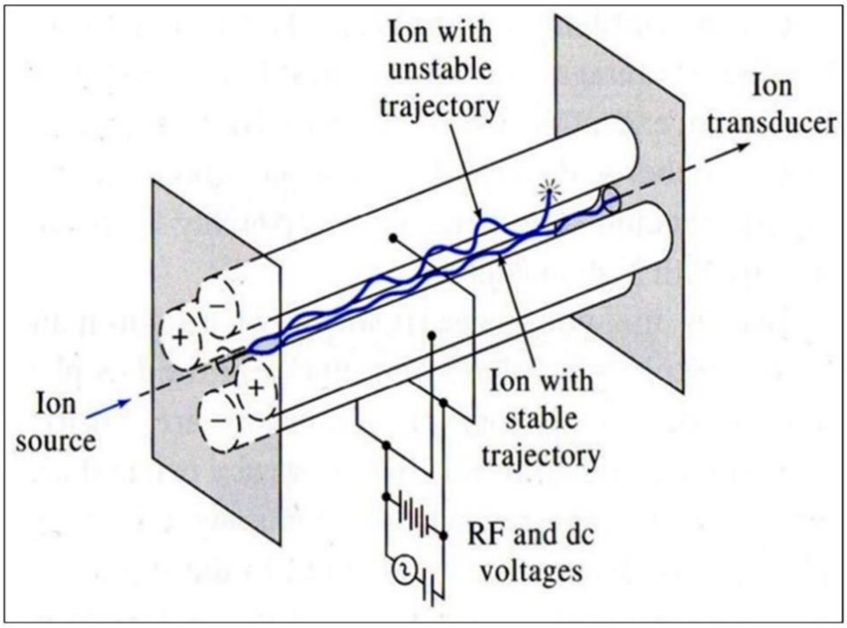


Figure 2.2. Schematic of a quadrupole analyzer (Source: Skoog,D., et al., Principles of Instrumental Analysis, 2007, Reproduced with kind permission from Thomson Brooks/Cole., Belmont, CA)

This is explained by using Mathieu's differential equation of motion (Hoffmann and Stroobant, 2007). Voltages of all the rods have DC component (U or –U) along with the RF component of voltage with frequency ω (= 2πν, ν is the RF field frequency) and amplitude V. Ions travelling along the z-axis are influenced by the total electric field originating from the applied potentials ($ø_0$) on the rods:

$$-ø_o = -(\mathrm{U} - \cos\omega t) \text{ and } ø_o = +(\mathrm{U} - \cos\omega t) \quad (2.9)$$

The ions accelerated along the z-axis are also submitted to accelerations along
x and y as a result of forces induced by the electric fields. From Newton’s second law:

$$\mathrm{F} = \mathrm{ma} = \mathrm{q}\vec{E}$$

$$\mathrm{F_x} = \mathrm{m}\frac{\mathrm{d^2x}}{\mathrm{d^2t}} = -\mathrm{ze}\frac{\delta ø}{\delta \mathrm{x}} \quad (2.10)$$

$$\mathrm{F_y} = \mathrm{m}\frac{\mathrm{d^2y}}{\mathrm{d^2t}} = -\mathrm{ze}\frac{\delta ø}{\delta \mathrm{y}} \quad (2.11)$$

With a hyperboloidal interior surface, ø is a function of $ø_0$

$$ø_{\mathrm{x,y}} = ø_o \frac{(x^2 - y^2)}{{r_o}^2} = (\mathrm{U} - \cos\omega t)\frac{(x^2 - y^2)}{{r_o}^2} \quad (2.12)$$

Up on differentiation and rearranging the Equations (2.10) and (2.11), the following are the equations of motion:

$$\frac{\mathrm{d^2x}}{\mathrm{d^2t}} + \frac{2ze}{m{r_o}^2}(\mathrm{U} - \cos\omega t)\mathrm{x} = 0 \quad (2.13)$$

$$\frac{d^2y}{d^2t} - \frac{2ze}{mr_o{}^2}(U - \cos\omega t)y = 0 \quad (2.14)$$

For a given quadrupole, r_0 and $\omega = 2\pi v$ is constant. U and V are the variables. For an ion of any mass, x and y can be determined during a time span as a function of U and V. As long as the values of x and y remain less than r_0, the ion will be able to pass through the quadropole without touching the rods. Otherwise, the ion discharges itself against a rod and is not detected.

The mass resolution of quadrupole is ∼1 amu over the whole mass range and the response time can be as low as 50 ms. The PTR-QMS can be operated in two different modes - a) selective ion detection mode and b) mass scan mode. In this thesis work, a dwell time of 200 ms was set for measuring the primary reagent ion (H_3O^+) while for the other masses dwell time ≥ 200 ms was used. As mass scan mode operates over the whole mass range, the time taken to finish a cycle of measurement is longer in duration relative to the selective ion detection mode. Operating the PTR-QMS in a mass scan mode permits possibilities for identifying new compounds.

2.1.4 Detector

Secondary electron multiplier (SEM) is the most widely used detector in mass spectrometry. It comprises of a conversion dynode, a series of further dynodes and a collector. The typical operating pressure for the detection region is 10^{-5} mbar. In order to increase detection efficiency, ions are first accelerated to high velocity using a conversion dynode at high potential (±3 to ±30 kV). Any positive or negative ion striking the conversion dynode causes the emission of secondary particles (positive or negatively charged ions). The first dynode converts these secondary particles/ions to electrons. These electrons are then amplified by a cascade effect in the electron multiplier to produce a current. The electron multipliers may be of either the discrete dynode or the continuous dynode type.

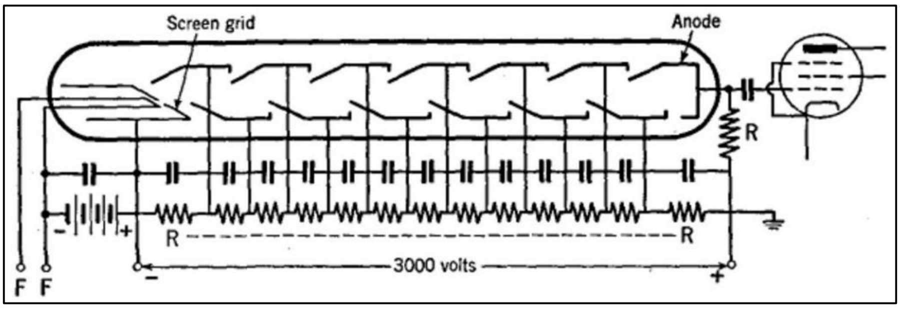


Figure 2.3. Schematic of secondary electron multiplier. (Source: Skoog,D., et al., Principles of Instrumental Analysis, 2007, Reproduced with kind permission from Thomson Brooks/Cole., Belmont, CA)

The PTR-QMS used in this thesis for the VOC quantification contains a Balzers SEM which is a discrete dynode. In this, dynodes are held at decreasing negative potentials (−1 to −5 kV) by a chain of resistors and the output of the multiplier remains at ground potential. Figure 2.3 shows the schematic of electron multiplier. Secondary electrons emitted from the surface of first dynode by the striking secondary particles generated from the conversion dynode are accelerated to the next dynode as it is held at a lower potential. Secondary electrons strike the second dynode causing the emission of more electrons and this process continues as the secondary electrons move towards the ground potential. Thus a cascade flow of electrons provides an electric current at the end of the electron multiplier that is then increased by conventional electronic amplification. Generally, Balzers SEM is operated between 1400 V and 3500 V.

The measured m/z ion signals ($I(RH^+)$) in counts per second (cps) are then converted to normalized counts per second (ncps) with respect to sum of primary ion (H_3O^+) signal ($I(H_3O^+)$) and first water cluster ($(H_2O)H_3O^+$) signal ($I(H_3O^+(H_2O))$ at a drift tube pressure (P_{drift}) of 2 mbar and drift tube temperature (T_{drift}) of 60ºC using the following normalization Equation (2.15) (Sinha et al., 2009; Tani et al., 2004)

$$\mathrm{ncps} = \frac{\mathrm{I(RH^+)} \times 10^6}{\mathrm{I(H_3O^+)} + \mathrm{I(H_3O^+(H_2O)}} \times \frac{2}{\mathrm{p_{drift}}} \times \frac{\mathrm{T_{drift}}}{298.15} \quad (2.15)$$

The normalized signals (normalized counts per second or ncps) are then converted to ppb using the sensitivity factors derived from the calibration experiments. The atmospheric abundance of all the calibrated VOCs that are reported in this thesis work were varied between 0.5 and 20 ppbv, for more than 97% of the data set. Hence, calibrations in this study were performed in the range of 0.5-20 ppb using a pre-mixed VOC gas standard (Apel–Riemer Environmental,Inc., Colorado, USA) containing methanol, acetonitrile, acetone, acetaldehyde, dimethylsulphide, isoprene, benzene, toluene, p-xylene, 1,2,4- trimethylbenzene and α-pinene at circa 500 ppb at different relative humidity (0 - 90% RH). The gas standard was dynamically diluted with VOC free-zero air generated using a Gas Calibraton Unit (GCU-s v2.1, Ionimed Analytik, Innsbruck, Austria). The flows of both the standard gas and zero air mass flow controllers are also measured independently before and after the calibration experiments using a NIST calibrated flow meter (BIOS Drycal definer 220).

Examples of the calibration results performed on the 10 October 2015 at 70 % RH that show sensitivity and linearity ($r^2 = 0.99$ in each case) of selected VOCs such as methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulfide, isoprene, benzene and toluene are shown in the Figure 2.4(a-h). Y-axis represents the measured normalized counts per second at the corresponding m/z channels and X-axis represents the introduced concentration of gas standard. The slope of the calibration plot (ncps ppb^{-1}) represents the sensitivity of PTR-MS instrument at m/z corresponding to the measured VOCs. The horizontal error bars represent the root mean square propagation of errors due to error in gas standard (stated accuracy better than 5 %) and 2% each error for the two mass flow controllers used during calibration. The vertical error bars represent 2σ instrumental precision error while sampling the standard gas at each dilution point. An example for the real time PTR-MS spectrum in the mass range between 31 and 210 amu obtained from the ambient air measured at IISER Mohali Atmospheric facility at 00:01 LT on 13.12.2013.

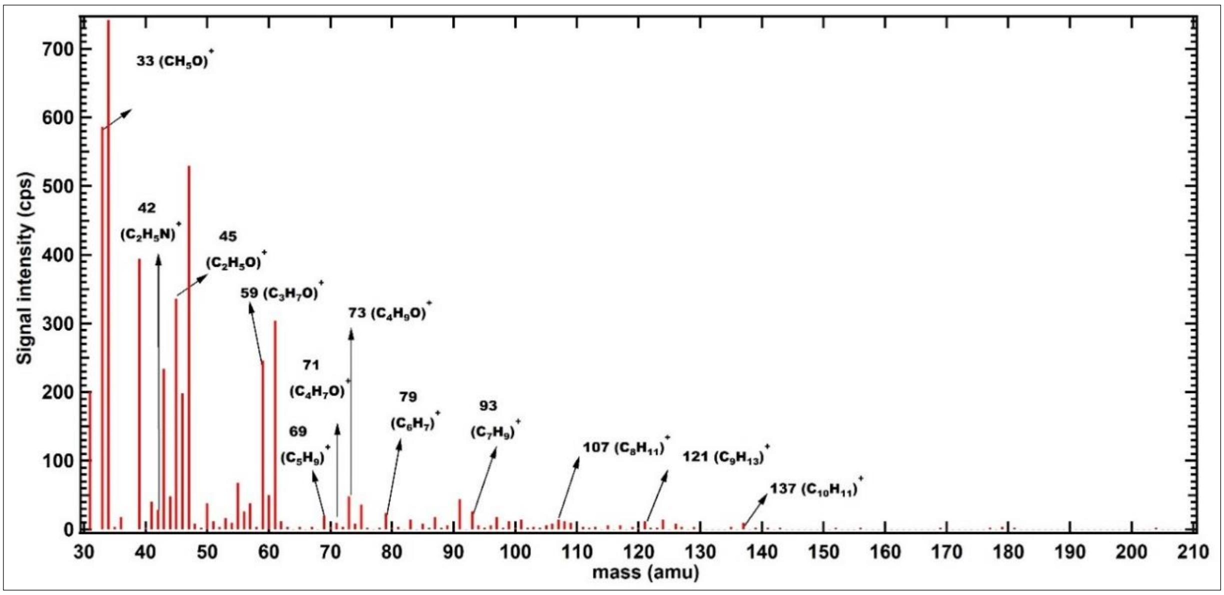


Figure 2.4. PTR-MS spectrum (mass range: 31-210 amu) obtained from the ambient air measured at IISER Mohali Atmospheric facility at 00:01 LT on 13.12.2013

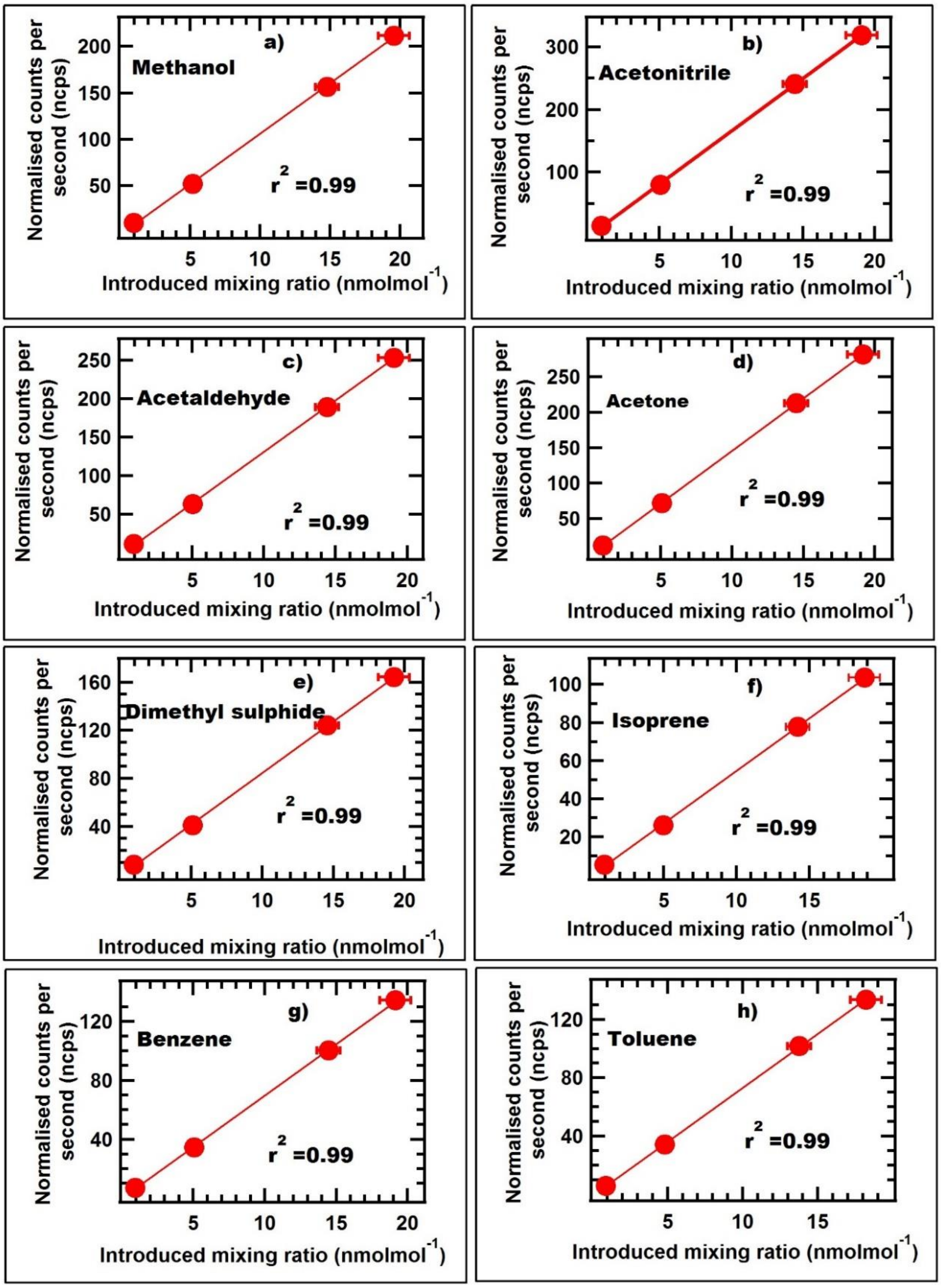


Figure 2.5. Sensitivity and linearity of selected VOCs a) methanol, b) acetonitrile, c) acetaldehyde, d) acetone, e) dimethyl sulphide, f) isoprene, g) benzene and h) toluene in the calibration experiment performed on 10 October 2015 at 70 % RH.

Application and validation studies of proton transfer reaction mass spectrometry technique to assess the reliability of attributing VOCs to specific m/z ratios have been carried extensively in urban, forested and rural regions of the world by inter comparing with other more specific analytical techniques (e.g., GC-FID) and has been described in two comprehensive reviews by de Gouw and Warneke (2007) and Blake et al., (2009). These studies showed that for PTR-QMS, VOCs such as methanol, acetonitrile, acetaldehyde, acetone, dimethylsulfide, isoprene, methyl vinyl ketone, methyl ethyl ketone, benzene, toluene, sum of C8-aromatics, sum of C9-aromatics and monoterpenes are the major contributors at m/z ratios 33, 42, 45, 59, 69, 71,73,79, 93, 107, 121 and 131 respectively (de Gouw and Warneke, 2007). Both propanal and glyoxal are also detected at m/z 59 using a PTR-QMS. However, the contribution of these species range from 0% - 10% and hence acetone is the major contributor species at m/z 59. In the biomass burning plumes and urban areas, detection of isoprene at m/z ratio 69 can have contribution due to presence of furan at the same nominal mass (Christian et al., 2004). The measurement of methyl ethyl ketone using a PTR-QMS can have interference from third water cluster $(H_3O)^+(H_2O)_3$. In this study, PTR-MS is operated at an E/N ratio of ~135 Townsend, at which the formation of $(H_3O)^+(H_2O)_3$ is negligible. Trimethylbenzene, ethyl toluene and propyl benzene can have very small interferences due to $C^{35}C^{37}Cl^{+\ 2}$ ions from CCl_4 (´Spanel and Smith., 1999). However this interference should be a constant offset as the variability of CCl_4 is extremely low in the atmosphere. About 0.078 % of the O_2^+ is known to be detected at the m/z 33 due to ^{17}O isotopic contribution. Hence the signal for methanol is corrected for 0.078% of O_2^+ landing at m/z 33 as were other isotopologue signals. For monoterpenes, calibrations at the instrumental settings employed in the study clearly showed that 38% of the total molecular ion signal was detected at m/ z = 137 and 62 % at m/z = 81, consistent with fragmentation patterns reported previously by Tani et al. (2004) for similar reaction conditions in the drift tube.

Chapter 3

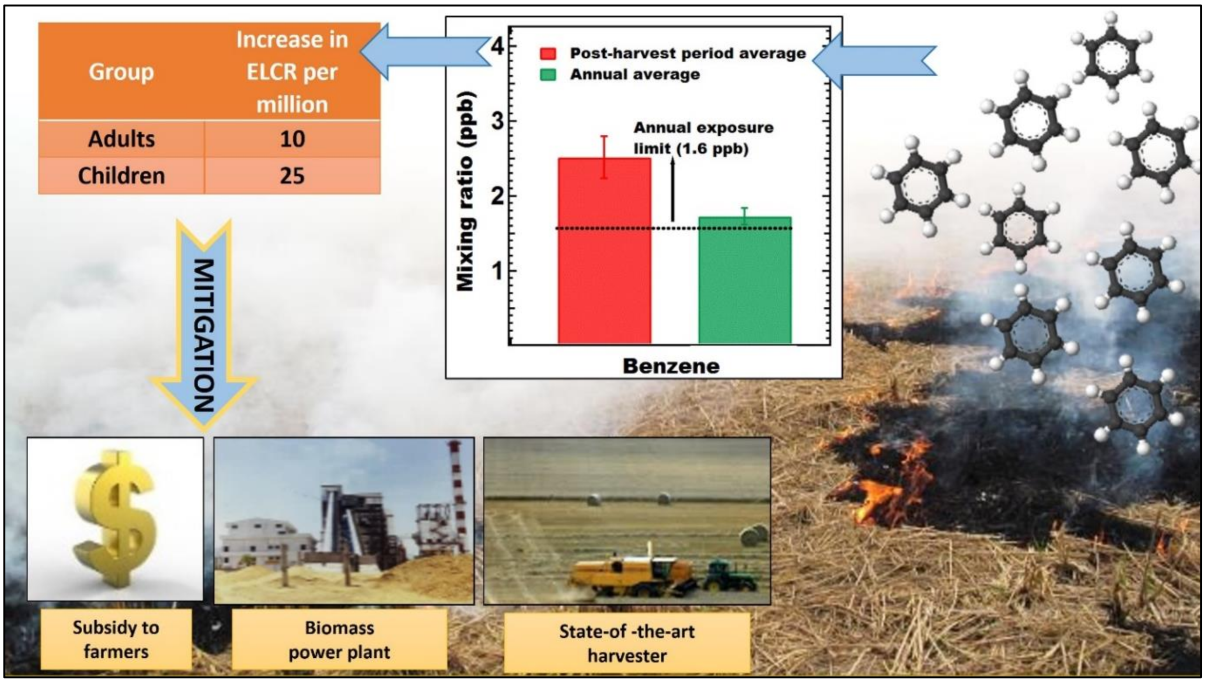
Contribution of post-harvest agricultural paddy residue fires in the N.W. Indo-Gangetic Plain to ambient carcinogenic benzenoids, toxic isocyanic acid and carbon monoxide

Abstract*

In the North West Indo-Gangetic Plain (N. W. IGP), large scale post-harvest paddy residue fires occur every year during the months of October-November. This anthropogenic perturbation causes contamination of the atmospheric environment with adverse impacts on regional air quality posing health risks for the population exposed to high concentrations of carcinogens such as benzene and toxic VOCs such as isocyanic acid. These gases and carbon monoxide are known to be emitted from biomass fires along with acetonitrile. Yet no long-term in-situ measurements quantifying the impact of this activity have been carried out in the N.W. IGP. Using high quality continuous online in-situ measurements of these gases at a strategic downwind site over a three year period from 2012-2014, I demonstrate the strong impact of this anthropogenic emission activity on ambient concentrations of these gases. In contrast to the pre paddy harvest period, excellent correlation of benzenoids, isocyanic acid and CO with acetonitrile (a biomass burning chemical tracer); ($r \geq 0.82$) and distinct VOC/acetonitrile emission ratios were observed for the post-paddy harvest period which was also characterized by high ambient concentrations of these species . The average concentrations of acetonitrile (1.62 ± 0.18 ppb), benzene (2.51 ± 0.28 ppb), toluene (3.72 ± 0.41 ppb), C8-aromatics (2.88 ± 0.30 ppb), C9-aromatics (1.55 ± 0.19 ppb) and CO (552 ± 113 ppb) in the post-paddy harvest periods were about 1.5 times higher than the annual average concentrations. For isocyanic acid, a compound with both primary and secondary sources, the concentration in the post-paddy harvest period was 0.97 ± 0.17 ppb. The annual average concentrations of benzene, a class A carcinogen, exceeded the annual exposure limit of 1.6 ppb at NTP mandated by the National Ambient Air Quality Standard of India (NAAQS).

Note:** Results presented in this chapter have already been published as first author and follow as "Chandra, B. P.,** and Sinha, V., Contribution of post-harvest agricultural paddy residue fires in the N.W. Indo-Gangetic Plain to ambient carcinogenic benzenoids, toxic isocyanic acid and carbon monoxide, Environment International, 88, 187-197 2016*."

I show that mitigating the post-harvest paddy residue fires can lower the annual average concentration of benzene and ensure compliance with the NAAQS. Calculations of excessive lifetime cancer risk due to benzene amount to 25 and 10 per million inhabitants for children and adults, respectively, exceeding the USEPA threshold of 1 per million inhabitants. Annual exposure to isocyanic acid was close to 1 ppb, the concentration considered to be sufficient to enhance risks for cardiovascular diseases and cataracts. This study makes a case for urgent mitigation of post-harvest paddy residue fires as the unknown synergistic effect of multi-pollutant exposure due to emissions from this anthropogenic source may be posing grave health risks to the population of the N.W. IGP.



Group	Increase in ELCR per million
Adults	10
Children	25

Figure 3.1. Graphical abstract showing excessive lifetime cancer risk due to benzene emissions from open paddy residue burning and mitigation strategies.

3.1 Introduction

Concern regarding exposure to ambient Volatile Organic Compounds (VOCs) detrimental to human health has been increasing worldwide (Dodson et al., 2007; Lim et al., 2012; Du et al., 2014). Isocyanic acid is a VOC with serious demonstrated health impacts on humans (Roberts et al., 2011, Wang et al., 2007). Due to analytical constraints however, ambient isocyanic acid has only been quantified at seven sites worldwide (Boulder, Colorado (Roberts et al., 2011); Los Angeles, California (Roberts et al., 2011); Toronto, Ontario (Wentzell et al., 2013); Fort Collins, Colorado (Roberts et al., 2014); Calgary, Alberta (Woodward-Massey et al., 2014);La

Jolla, California (Zhao et al., 2014) and in Kathmandu, Nepal (Sarkar et al., 2015)). Being a highly soluble gas at physiological pH (Roberts et al., 2011), it can dissociate to produce toxic levels of cyanate ion (NCO^-) in the blood stream. Inhalation of isocyanic acid at ambient concentrations above 1ppb can result in cyanate ion (NCO^-) concentrations high enough (Roberts et al., 2011) to produce significant health effects in humans such as atherosclerosis, cataracts and rheumatoid arthritis due to protein damage (Wang et al., 2007). The mechanism is thought to be an in-vivo carbamylation reaction of isocyanic acid (HNCO) and its conjugate anion (NCO^-) with protein molecules, which leads to post-translational protein modification (Stark et al., 1960) and triggers the inflammatory response typical of smoke-related health effects (Wang et al., 2007). Based on the sparsely available measured dataset , the known sources of this compound to the atmosphere are biomass burning fires (Roberts et al., 2010; Veres et al., 2010), photo-oxidation of amines and amides with ambient hydroxyl radicals (Barnes et al., 2010; Lee and Wexler, 2013; Borduas et al., 2014), diesel exhaust (Kröcher et al., 2005; Wentzell et al., 2013) and light duty gasoline vehicles (Brady et al., 2014). A small contribution to the global budget is made by tobacco smoke as well (Baker and Bishop, 2004;Hansson et al., 2004). The present global budget (1.5 Tg a^{-1}) does not incorporate secondary photochemical sources (Young et al., 2012), and it is imperative to assess the importance of this source in varied ecosystems and environments.

Benzenoids are a class of organic compounds possessing a six-carbon aromatic ring, which act as environmental contaminants at concentrations even as low as few ppb. Of these, benzene the simplest and most well-regulated is classified by the United States Environmental Protection Agency (US EPA) as a group “A” human carcinogen (Rushton and Romaniuk, 1997; Khalade et al., 2010; Li et al., 2014). Various studies have attributed enhanced risks for leukemia, blood bone marrow disease, vertigo, drowsiness, headache, nausea, aplastic anaemia, pancytopenia and myelodysplastic syndrome cytopenia to benzene exposure (Duarte-Davidson et al., 2001). Acknowledging the harmful effects due to inhalation of ambient benzene, several agencies (e.g. World Health Organization (WHO), United States Environmental Protection Agency (USEPA), European Environmental Agency (EEA), Ministry of Environment and Forests (MOEF), India) have implemented air quality standards for benzene to regulate the annual exposure of populations to ambient benzene. For example, the National Air Quality Standards (NAAQS) of India (NAAQS, 2009) issued by Ministry of Environment, Forest and Climate Change (MOEF),India, stipulate that annually averaged ambient benzene concentrations at a site should not exceed 1.6 ppb at Normal Temperature and Pressure (NTP). Besides benzene, several other benzenoid compounds can adversely affect human health. Exposure to high concentrations (above100 ppm) of toluene for about six hours can cause eye irritation, nasal irritation, headaches, dizziness, kidney damage, and impair thinking ability (The Agency for Toxic Substances and Disease Registry (ATSDR, 2000). Toluene exposure can also exacerbate hearing loss in a noisy environment (Chang et al., 2006). Acute exposure to xylenes can cause neurological and respiratory health problems in humans (ATSDR, 2007). Currently, benzenoids other than benzene are classified as group “D” carcinogens by the US EPA. In ambient air, benzenoid compounds also play a significant role in formation of secondary pollutants such as fine mode particulate matter (PM_1), in the form of secondary organic aerosol particularly “brown carbon” phenolic derivatives which are the major contributors to urban smog and have serious health effects (Henze et al., 2008; Misztal et al., 2015).

Large scale agricultural burning of paddy residue is an activity that takes place every year during the post-paddy harvest paddy seasons of October and November, in the N.W Indo-Gangetic Plain (IGP).This practice gained popularity after introduction of the mechanized “combine harvester” technology in 1986, which removes grains from standing paddy crops, but leaves the paddy residue (as straw) scattered on the field. The most frequent and cheapest disposal practice is to set fire to the paddy residue, which results in large scale emissions of a multitude of gas and aerosol species. Estimates of the area burnt during the paddy residue burning activity in the state of Punjab in India (N.W. IGP, where 80% of the land use is agricultural), alone amounted to 12,685 sq. km in 2005 (Badarinath et al., 2006), while the total amount of crop residue burnt annually in India is estimated to be 289 Tg (Venkataraman et al., 2006). Previous modeling and experimental studies from the IGP have only examined the impact of this activity in the context of climate active greenhouse gases and primary air pollutants such as carbon monoxide, nitrogen oxides and black carbon (Venkataraman et al., 2006; Sahai et al., 2007), but no long-term field observations have examined the emissions of benzenoids and isocyanic acid, which can also be emitted from these open fires. Several studies involving laboratory test fires have demonstrated that benzenoids and isocyanic acid are emitted in significant concentrations during combustion or pyrolysis of biomass (Andreae and Merlet, 2001; Burling et al., 2010; Roberts et al., 2010; Veres et al., 2010; Warneke et al., 2011; Stockwell et al., 2015). A recent study by our group (Sarkar et al., 2013), documented three-fold enhancements in ambient benzenoids (with concentrations as high as 16 ppb for benzene and 13-40 ppb for other benzenoids) in paddy residue fire emission plumes during a single night in November, 2012.

The objective of this study is to assess enhancements in ambient concentrations of benzenoids and isocyanic acid during the pre-paddy harvest and post-paddy harvest seasons using three years (2012-2014) of continuous online in-situ measurements at the IISER Mohali atmospheric chemistry facility, a representative suburban site in the N.W.IGP (Sinha et al., 2014; Pawar et al., 2015). Factors considered in the analyses are: 1) the diel and day to day variability in ambient chemical concentrations, 2) region specific satellite-derived fire activity data, 3) inter-annual variability of meteorological factors during the pre and post-paddy harvest seasons, 4) correlation with the biomass burning chemical tracer acetonitrile and 5) analysis of the chemical emission ratios of benzenoids and isocyanic acid to acetonitrile during the pre and post-paddy harvest seasons. Finally, a first order cancer risk assessment due to the post-paddy harvest fire emissions of benzene has also been undertaken.

3.2 Experimental

3.2.1 Site description

The measurements reported in this work were performed at the IISER Mohali atmospheric chemistry facility (30.679°N, 76.729°E; 310 m a.s.l.), which is a regionally representative suburban site (Sinha et al., 2014; Pawar et al., 2015) located in the N.W. Indo Gangetic Plain. A blue triangle in Figure 3.2 (a) and (b) marks the location of the site. A detailed description of the site including technical details pertaining to sampling inlets, instrumentation and surrounding land use are available elsewhere (Sinha et al., 2014; Pawar et al., 2015). Hence, only details relevant for the present analyses are presented here.

The black square boxes in Figure 3.2 (a) and (b), enclose the major agricultural regions in the N.W. IGP between 28°N to33°N and 72°E to 79°E and include the Indian states of Punjab, Haryana, and parts of Himachal Pradesh, Uttarakhand, Uttar Pradesh as well as the province of Punjab in Pakistan.

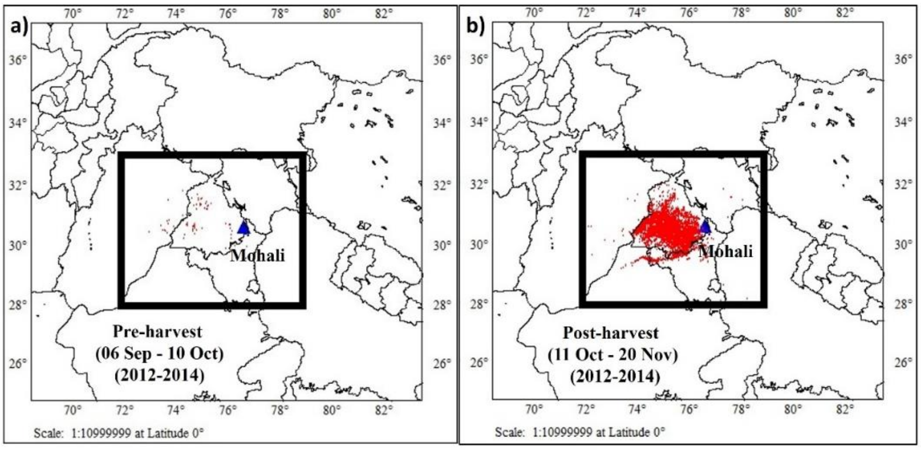


Figure 3.2. Total number of fire counts detected (at ≥ 80% confidence interval) in all the three years (2012-2014) by MODIS satellite in the north west Indo-Gangetic Plain (black square box)

during **(a)** pre-paddy harvest period (06 September- 10 October) and **(b)** post-paddy harvest period (11 October- 20 November). Blue triangle shows the location of the measurement site (30.667^{o}N, 76.729^{o}E, 310 m a.s.l.).

3.2.2 Criteria for selection of pre and post-paddy harvest paddy season durations and prevalent meteorology

The time periods of the pre and post-paddy harvest seasons in 2012, 2013 and 2014 were determined based on the following three criteria: 1) remotely sensed regional fire activity data, 2) consistency of fetch region and meteorological conditions, 3) information relayed by the local population and farmers. Satellite fire counts data over the region (red dots in black square box of Figure 3.2) were detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) installed on two sun-synchronous polar orbiting satellites called Aqua and Terra (MODIS: NASA/University of Maryland, 2002, MODIS Hotspot/Active Fire Detections Dataset, http://maps.geog.umd.edu). A detailed 72 hour back trajectory cluster analysis for the measurement site has already shown that the the wind flow was predominantly northwesterly in the post-monsoon season (Pawar et al., 2015). At the site, the period before 06 September may technically also be considered to be part of the pre-harvest season, but the occurrence of frequent monsoonal rains and variable wind flows (e.g. southeasterly and southwesterly (Pawar et al., 2015)) rendered it unsuitable for our analysis, which requires that a contrast in the chemical composition between the pre and post-paddy harvest periods is not driven by meteorological factors. From 06 September till 10 October, the wind flow was predominantly northwesterly in 2012, 2013 and 2014 (Pawar et al., 2015). The paddy crops in the region mature at slightly different times in individual agircultural fields over 9-10 weeks between 11 October and 20 November. Once the paddy grain has been harvested using the combine harvester, the loose paddy straw which remains on the field is set on fire. Generally, no additive fuels are required as the straw combusts readily. The start and end of this activity can be qualitatively inferred from the daily satellite fire counts data which was one of the criteria used for selecting the pre and post-paddy harvest durations. The other major criteria was that the wind flow should be predominantly from the agricultural land use areas northwest of the site (Sinha et al., 2014) during both the pre and post-paddy harvest periods.

Figure 3.3 summarizes the number of daily fire counts detected using MODIS (at greater than 80% confidence interval) from 06 September to 10 October (hereafter termed the pre-paddy harvest season and shaded light yellow in Figure 3.3) and from 11 October to 20 November (hereafter termed the post- paddy harvest season and shaded pale brown in Figure 3.3). These were detected over the region spanning 28°N -33°N and 72°E -79°E (black boxes in Figure 3.2 (a) and (b)) during the years 2012, 2013 and 2014. The total number of open fires detected during the post-paddy harvest season in the years 2012, 2013 and 2014 were 1838, 1808 and 2342 respectively, whereas during all the pre-paddy harvest seasons from 2012 to 2014, the total number of fire counts were always below 50. While one can argue about the exact start date by 1-2 days for the post-paddy harvest paddy periods in individual years, I chose 11 October to be the start date after consideration of the data over the three year period. Further, to illustrate the spatial extent of the open fires, the total number of fire counts detected in all the pre and post-paddy harvest periods during 2012-2014 are shown as red dots in Figure 3.2 (a) and (b). Note that to minimize false fire positives (Hantson et al., 2013), only fire counts detected at a confidence interval ≥80% were considered for analyses presented in this work.

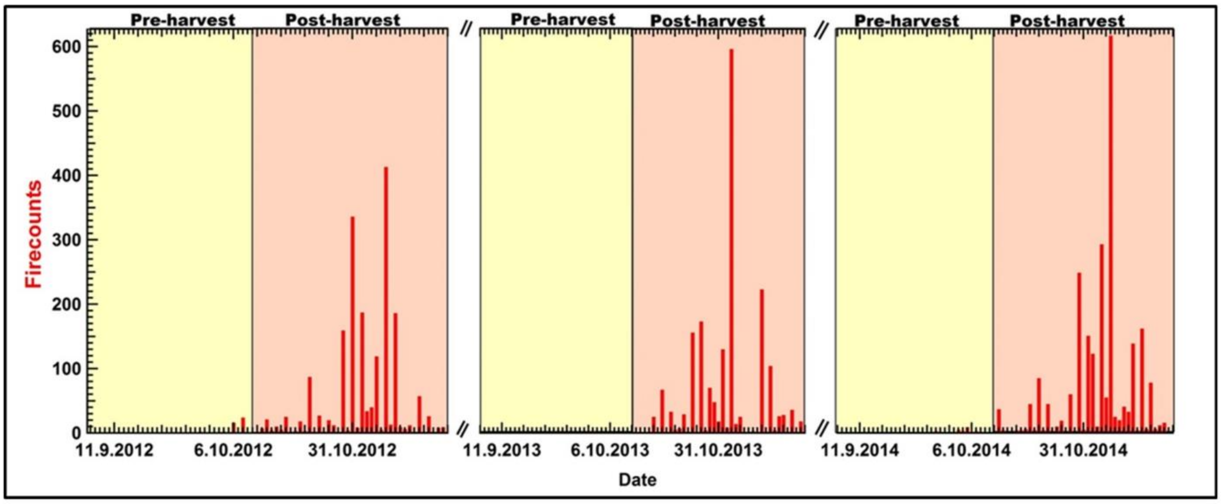


Figure 3.3. Daily fire counts detected by MODIS satellite at confidence interval ≥ 80% over the northwest Indo-Gangetic Plain (28°N to 33°N and 72°E to79°E) during the pre-paddy harvest (06 September- 10 October) and post-paddy harvest paddy season (11 October- 20 November) in 2012, 2013 and 2014.

Wind speed, wind direction, ambient temperature and relative humidity are measured routinely (Sinha et al., 2014) at the facility using meteorological sensors (Met One Instruments Inc., Rowlett, Texas, USA) at a temporal resolution of 1 minute. The range of meteorological parameters such as ambient temperature, relative humidity, wind speed and wind direction were comparable for all the pre-paddy harvest (06 September - 10 October) and post-paddy harvest periods (11 October- 20 November) for the years 2012, 2013 and 2014 and are listed in Table

3.1. In both periods, for all the years (2012- 2014), the average wind speed was 3 - 4 ms^{-1} with a predominantly northwestern fetch region. In the pre and post-paddy harvest of 2014, wind sensor data was not available. This similarity in meteorology and fetch region between pre and post-paddy harvest seasons provides confidence for examining the influence of emission activity on ambient chemical concentration enhancements.

To ensure better statistical confidence in the analyses (see Section 3.3.2 – 3.3.5), data acquired in the respective pre and post-paddy harvest periods of all three years were merged to derive composite pre and post-paddy harvest datasets.

Table 3.1. Comparison of three years (2012-2014) average ambient temperature, relative humidity, wind speed and wind direction during the pre-harvest and post-harvest periods. The number in parentheses corresponds to the ±1σ ambient variability.

Year	2012	2013	2014
Season	Pre-harvest (06 September -10 October)		
Ambient temperature (°C)	27.5 (3.0)	27.6 (3.1)	27.9 (2.9)
Relative humidity (%)	68.7 (15.0)	70.4 (11.3)	73.3 (13.5)
Wind speed (ms^{-1})	4.3 (2.6)	3.8 (2.6)	-
Wind direction (median)	North west	North west	North west
Season	Post-paddy harvest (11 October-20November)		
Ambient temperature (°C)	22.0 (4.3)	22.1 (4.8)	22.4 (4.4)
Relative humidity (%)	52.7 (14.2)	55.3 (16.4)	57.1 (16.4)
Wind speed (ms^{-1})	3.7 (2.3)	3.8 (2.5)	-
Wind direction (median)	North west	North west	North west

3.2.3 Measurements of benzenoids, isocyanic acid and carbon monoxide

VOCs were measured using a commercial high sensitivity proton transfer reaction mass spectrometer (PTR-MS; HS Model11-07HS-088; Ionicon Analytik Gesellschaft, Austria) equipped with a quadrupole mass analyzer. A full characterization of this instrument including protocols for humidity dependent calibrations and instrumental background checks at respective m/z channels has been provided previously (Sinha et al., 2014). Acetonitrile (C_2H_3N; M.W.:41 g /mol), a chemical marker compound for air masses influenced by biomass burning emissions

(Holzinger et al., 1999; Holzinger et al.,2001; de Gouw and Warneke (2007)) was detected at its protonated organic ion m/z = 42 Th. Benzene (C_6H_6; M.W.:78 g /mol), toluene (C_7H_8; M.W.:92 g /mol), C8-aromatics (sum of all the isomers of xylene and ethyl benzene; C_8H_{10}; M.W.:106 g /mol) and C9-aromatics (sum of all the isomers of trimethylbenzene; C_9H_{12}; M.W.:120 g /mol) were detected at their respective protonated organic ions (MH^+): m/z 79, m/z 93, m/z 107 and m/z 121, after soft chemical ionization with hydronium ions, the chemical reagent ions in the PTR-MS technique. Two reviews, de Gouw and Warneke (2007) and Blake et al. (2009) have extensively discussed and demonstrated the validity of these mass identifications and accuracy of this approach for online measurements of these compounds in a variety of ecosystems and ambient plumes. The detection of isocyanic acid in the atmosphere is a more recent achievement first reported from fire plumes in Colorado at concentrations as low as 200 ppt by deploying a negative-ion proton transfer reaction mass spectrometer (Roberts et al., 2011). Subsequently, Gylestam et al. (2011), Warneke et al. (2011), Jankowski et al. (2014) and Borduas et al. (2014) have shown that isocyanic acid (proton affinity: 753.1 kJ mol^{-1}) can be detected using proton-transfer reaction mass spectrometry that employs hydronium ions as reagent ions. Our group recently performed ambient measurements in Kathmandu using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS) (Sarkar et al., 2015) which had a mass resolution sufficient to measure the exact monoisotopic protonated organic ion of isocyanic acid ($HCNOH^+$; m/z 44.014 Th). We provide the mass scan acquired using the PTR-TOF-MS as Figure 3.4 clearly shows that the most dominant peak at nominal m/z 44 arises from isocyanic acid. Hence, the signal detected at m/z 44 was attributed to isocyanic acid. Calibration experiments by dynamic dilution of VOC gas standards with VOC free zero air and instrumental background checks at different m/z channels were performed as detailed in Sinha et al. (2014). The sensitivity (ncps/ppb) and measurement uncertainties for acetonitrile and aromatics were determined from these calibration experiments following the protocol described in our previous studies (Kumar and Sinha, 2014; Sinha et al., 2014). For isocyanic acid, the sensitivity factor was determined using quadratic fits derived from a plot of the sensitivity factors of the calibrated compounds (ncps/ppb versus m/z) as described in the work of Warneke et al. (2011).

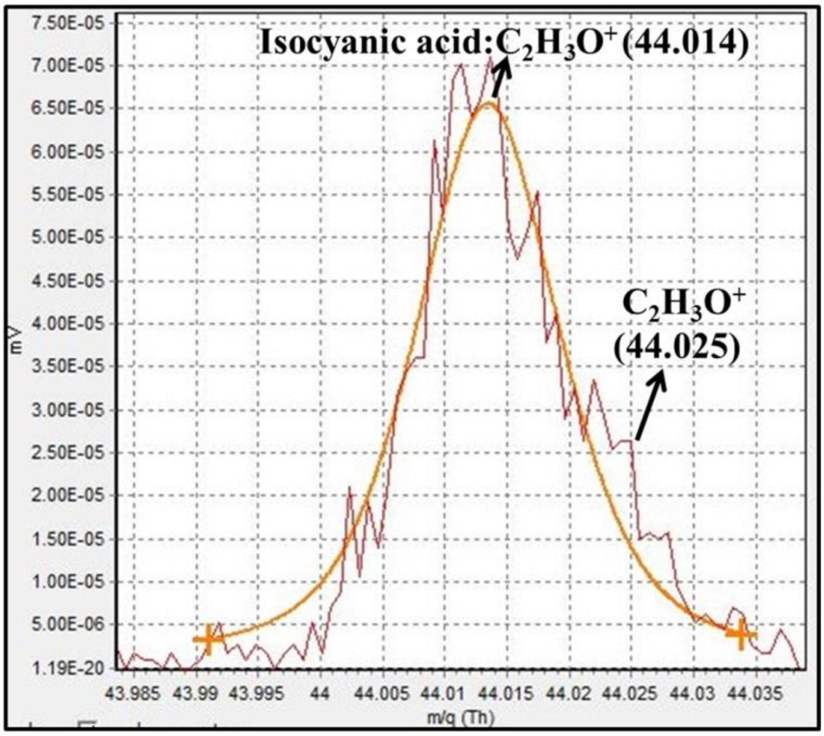


Figure 3.4. Expanded mass spectrum of (30 second average) isocyanic acid (m/z 44.014 Th) obtained at 09:24 LT on 13 January 2013 using PTR-TOF-MS in Kathmandu valley shows the dominant peak at nominal m/z 44 arises from isocyanic acid (source: supplement of Sarkar et al., 2015)

In any long-term deployment, changes in instrumental settings and mechanical wear and tear can affect the instrument sensitivity. In order to ensure that measurements made at different times could be related to ambient variability and not such instrumental changes, calibrations were performed at regular intervals from 2012 to 2014. Figure 3.5 shows the timeline of the sensitivity factors for all the calibrated compounds reported in this work, and it can be seen that no drastic changes in the sensitivities occurred. The instrument was operated at an (electric field by number density) E/N ratio of ~135 Td. Calibration experiments and ambient measurements were performed under identical instrumental parameters. VOCs were measured with a dwell time of 1s in the selected ion- monitoring mode from 24 August 2011 to 01 October 2013 and in mass scan mode (mass range: 21-210 a.m.u) from 02 October 2013 to 31 December 2014.

The total uncertainties for the ambient measurements reported in this work are as follows: benzene and toluene measurements (<15%), acetonitrile, C8 and C9 aromatics (< 25% for each compound). The uncertainty for isocyanic acid was estimated to be less than 50% based on the error of the quadratic fits. The limit of detection defined as twice the standard deviation of the instrumental signal while sampling VOC free air into the instrument, varied between 0.03-0.10 ppb for the benzenoids and acetonitrile to less than 0.08 ppb for isocyanic acid.

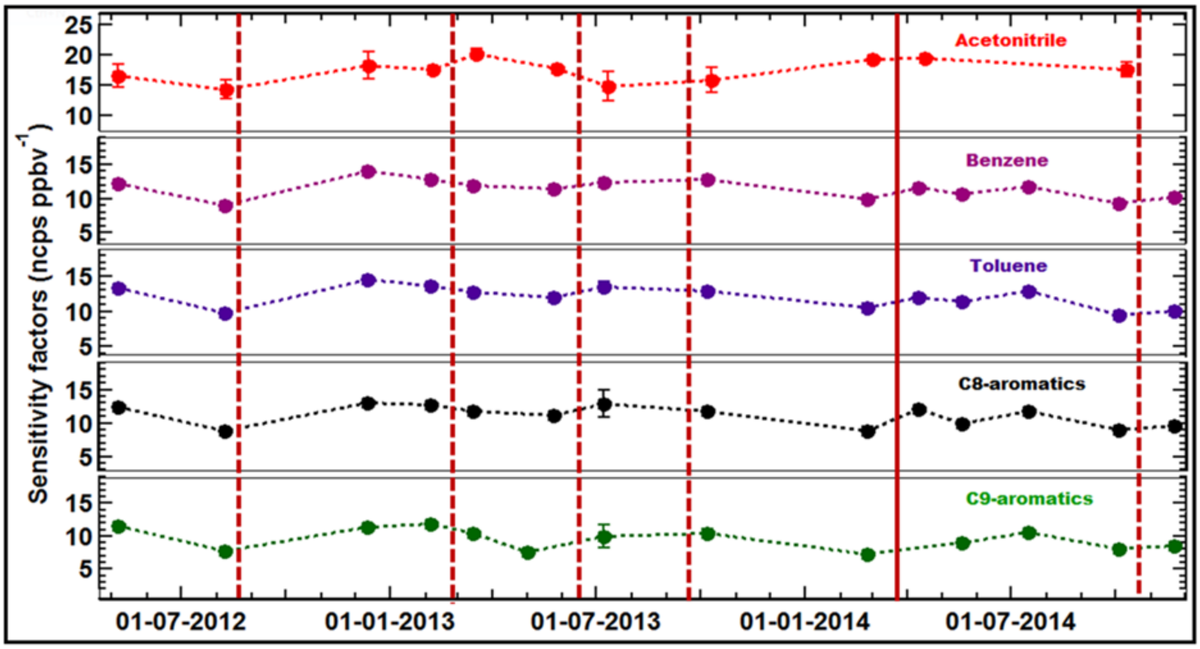


Figure 3.5. Trend in sensitivities of acetonitrile, benzene, toluene, C8-aromatics (xylene at m/z107) and C9-aromatics (trimethyl benzene at m/z 121) during PTR-MS calibration experiments conducted over the study period. Vertical bars at each point correspond to the 1σ error. Dotted brown vertical lines show the timings at which the detector (secondary electron multiplier) voltages were changed and the dark brown vertical line shows when the detector was replaced.

Carbon monoxide (CO) was measured using non-dispersive infrared (NDIR) filter correlation spectroscopy (Thermo Fisher Scientific, Model No. 48i). The full description and characterization of the instrument in terms of linearity and accuracy is available elsewhere (Sinha et al., 2014). Calibrations were performed once a month over a dynamic range of 100-1500 ppb while zero drifts were corrected on a daily basis. The linearity over the dynamic range was excellent (r^2=0.99). Calibration factors (0.99 ± 0.07) for CO were stable throughout the study period (refer Table S1). During the three years, the total uncertainty of CO measurements was always below 6% whereas the limit of detection varied between 8- 13 ppb CO.

Table 3.2. Summary of the CO calibration experiments

Date of Calibration Experiment	Calibration factor	Limit of detection (ppb)*	Uncertainty (%)#
08-11-2012	1.14	10.0	5. 9
02-09-2013	0.95	9.6	5.9
04-10-2013	1.03	8.2	5.9
26-11-2013	0.93	12.2	6.1
08-09-2014	0.91	8.6	6.1
14-10-2014	0.98	14.0	5.8
17-11-2014	1.02	12.2	6.1

*defined as 2σ of measured signal while measuring CO free zero air

#root mean square propagation of 5% accuracy error inherent in the CO gas standard, the 2σ instrumental precision error while sampling 500 ppb of CO and flow uncertainty of 2% for each mass flow controller used during dynamic dilution

The inlets of both the instruments were co-located at a height of 20 m above the ground and in line Teflon particle filters were used to protect the sampling inlets from floating dust and debris (pictorial representation is available in Fig. 5 of Sinha et al. (2014)). Total inlet and sampling residence times were always less than 40 s for both instruments.

Using the high time resolution VOCs measurements (1 minute temporal resolution: from August 2011 to October1, 2013, 4 minute temporal resolution: from October 2, 2013 onwards) and CO (1 minute temporal resolution throughout), we calculated: i) 24 hour average concentrations of the gases (or daily averages) as reported in Section 3.3.1 ii) Composite of three years' pre and post-paddy harvest hourly averages as reported in Section 3.3.2 and 3.3.3. iii) Annual average concentrations for each year as reported and discussed in Section 3.3.4 and 3.3.5.

3.3 Results and discussion

3.3.1 Analyses of the time series of VOCs and CO during pre and post-paddy harvest periods

Figure 3.6 shows the time series of the ambient concentrations (as daily means; solid lines) for acetonitrile (top panel), benzene (second panel), toluene (third panel), sum of C8-aromatics (fourth panel), sum of C9-aromatics (fifth panel), isocyanic acid (sixth panel) and CO (last panel) during the pre-paddy harvest (06 September - 10 October) and post-paddy harvest (11October – 20 November) periods in 2012, 2013 and 2014. The shaded regions (in corresponding colours) represent the ambient variability as 25 th and 75 th percentiles (inter-quartile range). It is evident from the time series that the daily average concentrations for all the benzenoids, isocyanic acid and CO were generally higher in the post-paddy harvest seasons relative to the pre-paddy harvest seasons. In particular, elevated concentrations of acetonitrile (a specific chemical marker for biomass burning (Holzinger et al., 1999; Holzinger et al., 2001; de Gouw and Warneke (2007)) on several days in all the three years (> 2 ppb) during the post-paddy harvest period are indicative of enhanced biomass burning activity, consistent with the paddy residue fires being active. In addition, the concentrations of the benzenoids, isocyanic acid and CO (a tracer for inefficient combustion) tended to correlate with enhancements in acetonitrile during the post-paddy harvest period, consistent with their co-emission from the fires (Warneke et al., 2011; Stockwell et al., 2015).

The daily average concentrations of acetonitrile, benzene, toluene, C8-aromatics, C9-aromatics, isocyanic acid and CO were higher in the post-harvest periods relative to the pre-harvest periods by factors of 1.5, 1.9, 1.8, 2.1, 1.8, 1.3 and 1.5, respectively. The data breaks in Figure 3.6 occur during early to mid-September each year (which mark the end of the 2-3 months long monsoon season at the site), when ambient air is very humid. Continuous measurements with the PTR-MS during prolonged periods of high humidity create frequent inlet blockage problems due to sticky aerosol particles, resulting in instrument downtime for the ambient VOC measurements. As part of our quality assurance for the measurements in such challenging conditions, we need to purge the inlet lines with dry zero air for long periods and also clean the ion source of the mass spectrometer frequently. Isocyanic acid was monitored for only part of the pre-harvest period in 2013 due to an operator oversight.

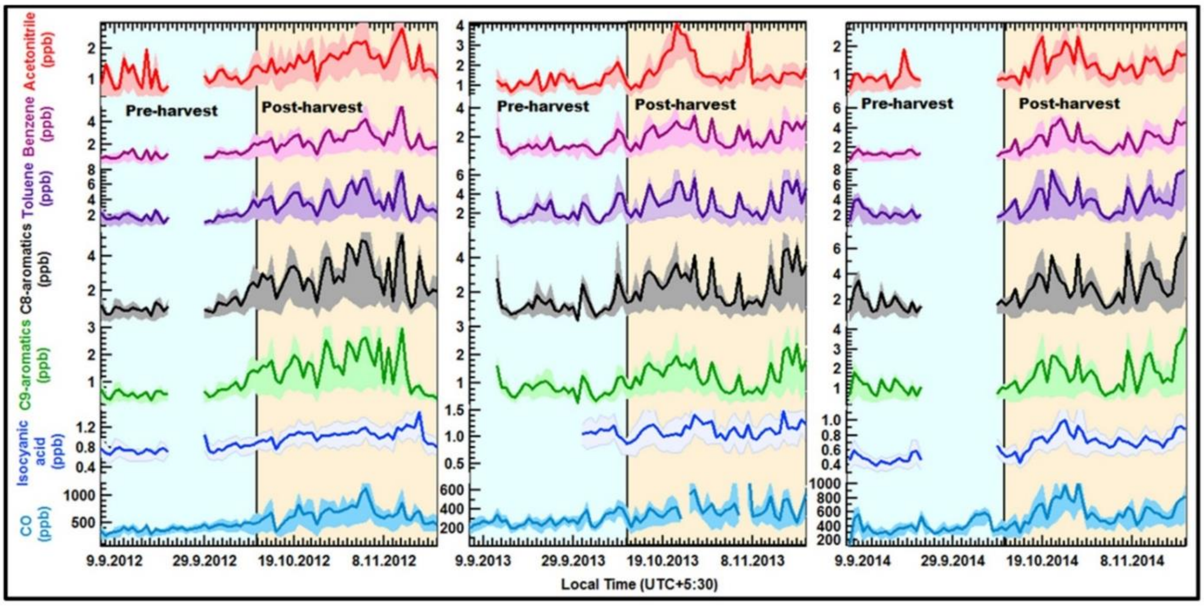


Figure 3.6. Time series of daily average concentrations of acetonitrile (top panel), benzene (second panel), toluene (third panel), C8-aromatics (fourth panel), C9-aromatics (fifth panel), isocyanic acid (sixth panel) and CO (last panel) in pre-paddy harvest (06 September- 10 October; shown in pale blue region) and post-paddy harvest paddy periods (11 October- 20 November; shown in pale brown region) during 2012, 2013 and 2014. Solid lines represent the daily means while the shaded coloured regions represent the daily ambient variability as the 25th and 75th percentiles.

Pair wise comparisons using “Tukey’s studentised” Honestly Significant Difference (HSD) test (Sheskin, 2011) were performed to ascertain statistical difference if any, for the pre and post - harvest data of each year for all the reported species. The results are summarized in Table 3.3. In all the three years, that is 2012, 2013, and 2014, a p-value of 0.000008 was obtained for each pair of the pre and post- harvest benzene, toluene, C8 and C9 aromatics, acetonitrile and CO data pointing to a highly significant difference at a confidence interval > 99.999% (or 4 σ confidence interval).The distribution of isocyanic acid datasets during pre and post-harvest seasons of 2012 and 2014 were also different at a confidence interval > 99.999% (or 4 σ confidence interval). In 2013, pre-harvest data of isocyanic acid was significantly different from values for post-harvest season at a confidence interval of > 95.45% or 2 σ (p-value: 0.005).

Table 3.3. Summary of Honestly Significant Difference (HSD) test performed for the pre and post-paddy harvest data set of each year for all the reported species

	p-values		
Compounds	2012	2013	2014
Acetonitrile	0.000008	0.000008	0.000008
Benzene	0.000008	0.000008	0.000008
Toluene	0.000008	0.000008	0.000008
C8-aromatics	0.000008	0.000008	0.000008
C9-aromatics	0.000008	0.000008	0.000008
Isocyanic acid	0.000008	0.005	0.000008
CO	0.000008	0.000008	0.000008

3.3.2 Analysis of diel concentrations profiles of VOCs and CO during the pre and post-paddy harvest periods

Our field surveys and information shared by the rural population revealed that the paddy residue is generally set on fire in the late afternoon /evening hours when meteorological conditions are calm (to minimize the risk of the fire becoming uncontrollable) and it is easier to avoid checks by law enforcement officials (legally it is forbidden to burn the paddy residue (Kumar et al., 2015)). In the next section, I examine the average hourly diel concentration profiles for benzenoids, isocyanic acid and CO to ascertain whether a diel time dependence exists for the paddy residue burning activity.

Figure 3.7 (a-g) shows the diel box and whisker plot for concentration profiles of acetonitrile, benzene, toluene, C8-aromatics (sum of xylene and ethylbenzene), C9-aromatics (sum of trimethylbenzene isomers), isocyanic acid and CO derived from the composite three year dataset (2012, 2013 and 2014), during the pre-paddy harvest (shown in blue colour; $n \geq 54{,}006$ for each species where n= number of measurements) and post-paddy harvest periods (shown in red colour; $n \geq 83{,}296$ for each species). The horizontal axis represents the start time of the corresponding hourly bin. The line connects the average hourly concentrations, the median is presented by a cross, while the width of the box encompasses the interquartile range (25th and 75th percentiles) with whiskers showing the10th and 90th percentile.

It can be seen that the average mixing ratios of acetonitrile (a chemical tracer for biomass burning) were twice as high during the evening hours (19:00-21:00; Local Time) in the post-paddy harvest period relative to the pre- paddy harvest period (3 ppb Vs 1.5 ppb) and continued to be significantly higher until midnight, with values typically exceeding the interquartile variability observed during corresponding pre-paddy harvest period. The increase in acetonitrile mixing ratios commenced around 15:00 hours, when the boundary layer height was not expected to decrease, due to the thermal heating of surface air, clearly indicating the role of a strong emission source. Note the timing of increase at 15:00 hours, was consistent with the information provided by the local population about the typical timing for when paddy residue was set on fire. From midnight until sunrise the concentration profiles of acetonitrile during both the pre-paddy harvest and post-paddy harvest periods hovered around 1.5 ppb, and were comparable considering the overall inter-quartile variability for these hours during both periods. After sunrise the concentrations tended to decrease due to the dilution effect exerted by a growing daytime boundary layer. Note due to the low chemical reactivity of acetonitrile with atmospheric oxidants (atmospheric lifetime is ~ 9 months (Warneck and Williams, 2012)), chemical loss would not contribute much to the observed diel decrease. Around 14:00 hours, the minima of the diel concentrations were attained but note that even during the period of the diel minima, average concentrations observed during the post-harvest periods exceeded those observed during the pre-harvest period by several hundred ppt. Thus, the diel profile of acetonitrile in the post-paddy harvest period clearly captured the regional ambient concentration enhancements and correlated with the timings of when most fires are lighted to burn the paddy residue. The afternoon to nighttime increase (15:00 till midnight) observed in acetonitrile, during the post-paddy harvest periods, also occurred in the diel profiles of the benzenoids (benzene, toluene, C8 and C9 aromatics) and CO. There is some emission activity involving use of biofuels such as wood in the morning hours at the site which contributes to the slight morning time increases for all these species at the site, and has already been discussed in Sinha et al. (2014). Interestingly, by afternoon (11:00 to 16:00 L.T), the average mixing ratios of the more reactive benzenoids like toluene (atmospheric lifetime of ~2 days (Atkinson, 2000)), C8 and C9-aromatics (atmospheric lifetime of few hours during the day time (Atkinson, 2000)) reached similar concentrations in both pre and post-paddy harvest periods. In contrast, the levels of longer lived tracers such as benzene (a long-lived benzenoid with residence time of ~10 days in troposphere, (Atkinson, 2000; Warneck and Williams, 2012)) and CO (inefficient combustion tracer, residence time of ~ 2 months (Warneck and Williams, 2012)), were somewhat higher during the post-paddy harvest period, indicating an increase in the regional background concentrations for the longer live species due to the paddy fires. As the fetch region is comparable for the pre-harvest and post-harvest season and the source signature in the post-harvest season is markedly different due to the strong emissions from paddy residue fires, it is along expected lines that the regional background concentrations increase for the longer lived species markedly due to the larger accumulation tendency of these compounds. This is further confirmed by the distinct emission ratios signatures observed for individual compounds with respect to the biomass burning tracer "acetonitrile" in Section 3.3.3. The diel profile of isocyanic acid suggests a strong photochemical source with clear diurnal variation during both the pre and post-paddy harvest periods and average concentrations above 1 ppb (reckoned to be the toxic threshold concentration (Wang et al., 2007)) for 15 out of 24 hours during the post-harvest period. Also note the presence of the secondary peak between 17:00 to 20:00 hours during the post-paddy harvest period in the diel profile of isocyanic acid, which was completely absent in the pre-paddy harvest period, and points to a primary emission source for the compound from the paddy residue fires. As reported in previous studies (Roberts et al., 2011; Roberts et al., 2014), isocyanic acid has both primary and secondary sources in the atmosphere. While primary emission occurs from biomass fires (Roberts et al., 2010), it can also be formed photochemically through hydroxyl radical-initiated reactions of amines and amides during the daytime (Sarkar et al., 2015; Barnes et al., 2010; Borduas et al., 2014; Roberts et al., 2014).

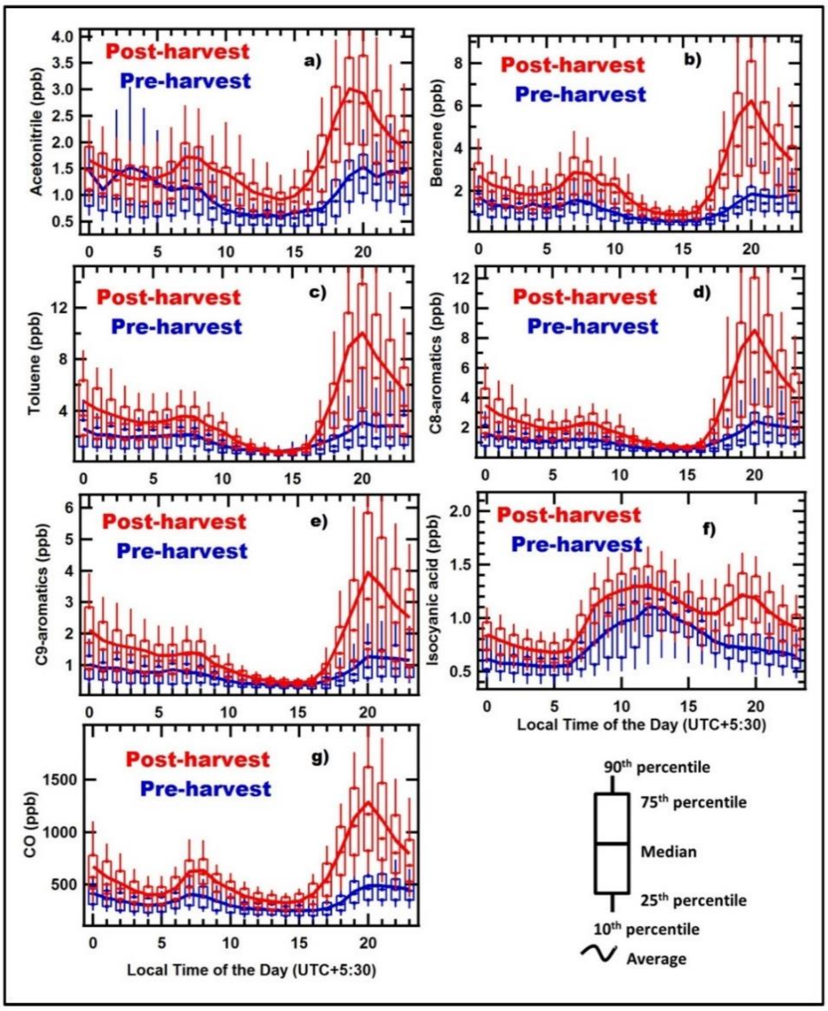


Figure 3.7. Diel box and whisker profiles of (a) acetonitrile, (b) benzene, (c) toluene, (d) C8-aromatics (sum of xylene and ethyl benzene) (e) C9-aromatics (sum of trimethylbenzene), (f)

isocyanic acid and (g) carbon monoxide derived from the three year dataset (2012, 2013,2014). Measurement statistics: During pre- paddy harvest period ($n \geq 54006$ measurements for each species) & during post-paddy harvest period ($n \geq 83296$ measurements for each species).

3.3.3 Analysis of VOC / acetonitrile (chemical marker for biomass burning) emission ratios during the pre-paddy harvest and post-paddy harvest periods

In this section, I further examine the chemical source signatures of individual compounds during the pre and post-paddy harvest periods using VOC/acetonitrile emission ratios Figure 3.8 (a-f). summarizes the correlations of benzene, toluene, C8-aromatics (sum of xylene and ethylbenzene), C9-aromatics (sum of trimethylbenzene), isocyanic acid and CO with acetonitrile (the chemical marker compound for biomass burning). To avoid complications due to photochemical formation /loss of compounds, only the night time concentrations were considered. The blue (pre paddy harvest) and red (post paddy harvest) dots in the plots are the hourly averaged chemical concentrations for each hour of the night time (between18:00 to 06:00 L.T; 12 points), derived using three years (2012 -2014) of in-situ measurements during the pre and post-paddy harvest periods, respectively. The slope of these linear regression fits ($r^2 \geq 0.88$ in all cases except for C-9 aromatics where $r^2 = 0.67$) yields an emission ratio of VOCs and CO to acetonitrile (as ppb of species/ppb of acetonitrile). The high absolute concentrations and very high correlations observed for all compounds with acetonitrile during the post-paddy harvest periods ($r \geq 0.93$ in all cases except for C-9 aromatics where $r = 0.82$) and the absence/weak correlation during the pre-paddy harvest periods for the same compounds ($r \leq 0.60$ in all cases except benzene for which $r = 0.7$ only) highlight that during the period influenced by paddy residue fires, the source signature of these compounds is vastly different and is dominated by the biomass combustion source. p-value of 0.000008 was obtained for each pair of pre and post-harvest night time data for all reported species pointing to a highly significant difference at a confidence interval > 99.999% (or 4 σ confidence interval. The post-paddy harvest emission ratios of benzenoids (benzene, toluene, C8 and C9 aromatics) to acetonitrile and ratio of CO to acetonitile are generally twice the pre-paddy harvest period emission ratios. For isocyanic acid, the r value changes from – 0.08 (pre-paddy harvest) to 0.99 (post-paddy harvest), and is similarly accompanied by significant increase in absolute concentrations. The primary emission sources of CO that were active in the vicinity of the measurement site throughout the year were traffic, garbage fires, and biofuel burning for cooking purpose (Garg et al., 2015). Additional emissions in the polluted summer and polluted post monsoon seasons occurred due to crop residue fires and in winter due to open burning of combustible material for domestic heating (Garg et al., 2015). It has already been shown from the previous study from our group (Kumar et al., 2016) that the absolute ambient concentrations of CO at our measurement site during the post-harvest period were higher by a factor of 1.3-3 times compared to remaining seasons due to the impact of open crop residue fires. Furthermore, the correlation of CO with the acetonitrile (a compound that is emitted strongly only from biomass combustion and not traffic sources) in other seasons was weaker ($r \leq 0.60$ in all seasons except crop fire influenced periods in summer and post monsoon for which $r \geq 0.7$). Thus, different emission ratios, excellent correlation with acetonitrile and high absolute concentrations in the post-paddy harvest period unequivocally shows that the contributions from the open paddy residue fires during the post-paddy harvest period dominate the regional enhancement of carcinogenic benzenoids, carbon monoxide as well as toxic isocyanic acid.

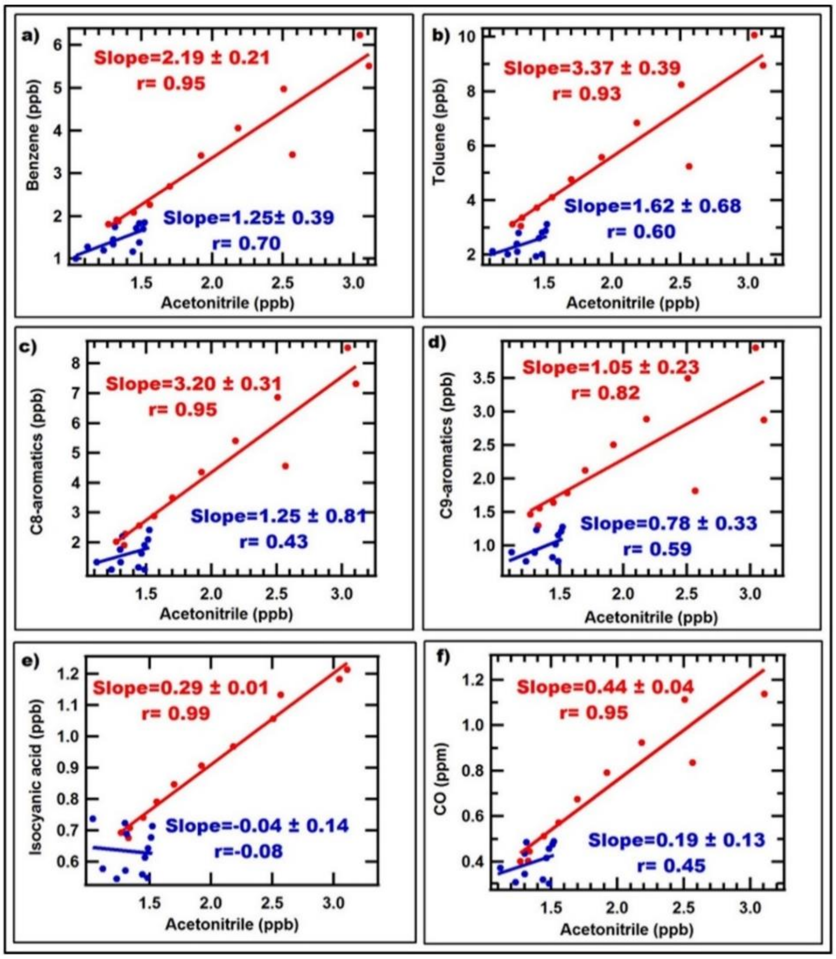


Figure 3.8. Correlation plots for (a) benzene (b) toluene (c) C8-aromatics (d) C9-aromatics (e) isocyanic acid (f) carbon monoxide with acetonitrile (biomass burning tracer) during the pre-

harvest (blue markers) and post-paddy harvest periods (red markers). Data points in these plots are night time hourly average concentrations (18:00 to 06:00 L.T) derived from the three year (2012-2014) pre and post-paddy harvest period composite dataset. Solid lines are the linear regression fits through these data points.

3.3.4 Comparisons of post-paddy harvest period concentrations with the annually averaged mixing ratios of VOCs and CO

In order to compare the contribution of the post-paddy harvest period concentrations to the annual average concentrations and a hypothetical world where the post-paddy harvest period concentrations are substituted by the pre-paddy harvest concentrations, in Figure 3.9 (a) and (b) a summary is provided in the form of red, green and blue histograms. The red bars represent the average concentration during three years' of the post-paddy harvest periods with vertical bars reflecting the standard deviation (ambient variability) associated with three years averages of post-paddy harvest (derived from n ≥ 83,293 measurements for each compound), green bars represent the three years' annual average (derived from n ≥ 797,268 measurements for each compound) with vertical bars reflecting the standard deviation (ambient variability) associated with three annual averages. Hypothetical annual average for each individual year is calculated using Equation (3.1). Blue bars represent the three years' of calculated hypothetical annual averages with vertical bars reflecting the standard deviation (inter-annual variability) based on three hypothetical annual averages.

$$\mathrm{H_a} = \frac{\mathrm{A} \times 365 - \mathrm{B} \times 41 + \mathrm{C} \times 41}{365} \qquad (3.1)$$

Where, A is the annual average concentration of each individual year (2012–2014), B and C are the average concentrations of each individual year's post-paddy harvest and pre-paddy harvest periods, respectively. In all three cases (red, green and blue), the entire three year dataset for respective periods was employed. The average concentrations of acetonitrile (1.62 ± 0.18 ppb), benzene (2.51 ± 0.28 ppb), toluene (3.72 ± 0.41 ppb), C8-aromatics (2.88 ± 0.30 ppb), C9-aromatics (1.55 ± 0.19 ppb) and CO (552 ± 113 ppb) in the post-paddy harvest periods were about 1.5 times higher than the annual average concentrations. For isocyanic acid, a compound with both primary and secondary sources, the concentration in the post-paddy harvest period (0.97 ± 0.17 ppb) increased by only by 0.03 ppb in comparison to the annual average concentration. Note however, both 0.97 and 0.94 ppb are quite close to the 1 ppb threshold that is considered to be harmful. The higher concentrations observed during the post-paddy harvest periods that last 41 days in a year, clearly contribute adversely to the annual average concentrations of benzenoid compounds by increasing the exposure risk. In particular, the average concentration of benzene during the post-paddy harvest season is about 40% higher than the annual ambient air quality standard of 1.6 ppb at NTP. The observed annual average concentration of benzene (1.73 ± 0.11 ppb) violated the annual exposure limit (~1.6 ppb) stipulated by the national pollution control agency of India. Mitigation of benzene emissions during the post-paddy harvest period could therefore lower the annual concentrations of benzene, a carcinogen by ~0.13 ppb and ensure compliance with the National Ambient Air Quality Standard of India for benzene (1.6 ppb at NTP).

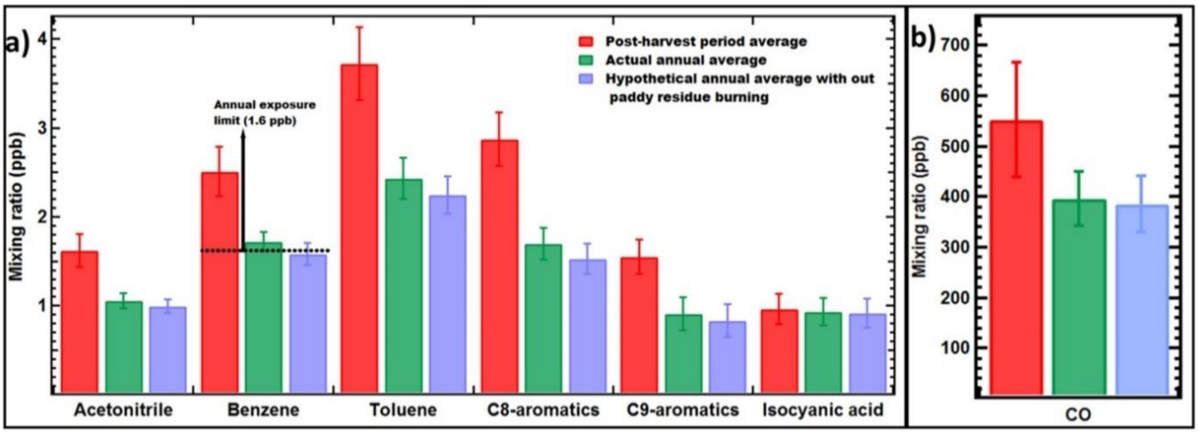


Figure 3.9. Comparison of average ambient mixing ratios during the post-paddy harvest periods (red histogram), annual average (green histogram) and hypothetical annual average if paddy residue burning were to be absent (blue histogram) from 2012 to2014 for (a) VOCs (acetonitrile, benzene, toluene, C8 and C9-aromatics and isocyanic acid) and (b) carbon monoxide. Vertical bars on red and green histograms reflects the standard deviation of three year's post-harvest and annual avearge respectively. Vertical bars on blue histogram reflects the standard deviation of three hypothetiacal annual averages. Black dotted lines shows the annual exposure limit for benzene.

The annual average concentration of benzene, toluene C8 and C9 aromatics reported in this work derived from three years of long term in-situ measurements performed at a regionally representative sub-urban site in the N.W. IGP is the first ambient data set from India so far. Therefore, in order to assess how the annual averaged levels of the measured species compare with annual average concentrations reported in some other sites in the world, I have summarised the annually averaged mixing ratios (ppb) of aromatic VOCs at several sites in the world in

Table 3.4. It can be seen that the annual averages for benzene (1.72 ± 0.11 ppb), toluene (2.43 ± 0.23 ppb), C8-aromatics (1.69 ± 0.18 ppb) observed in the present study at a sub-urban site are 3 to15 times higher than the annual average concentrations reported at suburban sites in New Jersey, U.S.A; Jeddah, Saudi Arabia; Welgegund, South Africa and Donon, France but comparable to the annual concentrations at urban sites such as University College, London and Lille, France.

Table 3.4. Annually averaged mixing ratios (ppb) of aromatic VOCs at several sites in the world

Location	Benzene	Toluene	C8-aromatics#	C9-aromatics*	References
Mohali, India	1.72 (0.11)	2.43 (0.23)	1.69 (0.17)	0.91(0.19)	This work
Turnersville, New Jersey (U.S.A)	0.43	0.85	0.16	-	Pankow et al. (2003)
Jeddah, Saudi Arabia	0.41	1.4	2.99	-	Alghamdi et al. (2014)
University College, London	1.87	3.62	3.67	-	Derwent et al. (2000)
Lille, France	2.43	5.12	4.36	-	Borbon et al. (2002)
Welgegund, South Africa	0.29	0.89	1.41	-	Jaars et al. (2014)
Donon, France	0.16 (0.13)	0.16 (0.16)	0.13 (0.13)	0.06 (0.04)	Sauvage et al. (2009)

Number in parentheses represents the variability as ±1σ.

#Sum of xylene and ethylbenzene. *Sum of trimethylbenzene isomers

3.3.5 Health risk assessment and implication for policy and research

In the this section I discuss the health risks associated with exposure to benzene and isocyanic acid, the two compounds which pose the gravest risk for inhabitants of the N.W.IGP among all the compounds measured and reported in this work.. Here, an attempt is made to estimate the increased cancer risk due to post-paddy harvest fire emissions of benzene (Li et al., 2009) . Increased cancer risk was determined for adults and children (≤ 6years) in Punjab and Haryana, India, which have large densely populated agricultural regions, using Equation (3.2), (3.3)and (3.4) (Betha and Balasubramanian, 2014; Du et al., 2014) as outlined below:

$$\Delta \text{ Risk} = \text{ELCR}_{\text{scenario}-1} - \text{ELCR}_{\text{scenario}-2} \tag{3.2}$$

$$\text{ELCR} = (\text{CDI}_{\text{benzene}} \times \text{CPF}_{\text{benzene}}) \tag{3.3}$$

$$\text{CDI}_{\text{benzene}} = \frac{\text{IR} \times \text{EF} \times \text{ED} \times 90\%}{\text{BM} \times \text{AT}} \times \text{E}_{\text{benzene}} \tag{3.4}$$

Where, ELCR is the excessive lifetime cancer risk due to the intake of benzene for two scenarios (scenario 1 and scenario 2) that consider different exposure concentrations. In scenario-1, the exposure concentrations are the measured annual average concentrations of benzene (from 2012 to 2014) whereas, in scenario-2 exposure concentrations are the hypothetical annual averages of benzene (H_a) obtained by using Equation 1, which represents a world in which the influence of post-harvest paddy residue fires is absent.

$CPF_{benzene}$ is the inhalation Cancer Potency Factor for benzene (value: 0.1 kg mg^{-1} day; Office of Environmental Health Hazard Assessment (OEHHA, 2011)).

$CDI_{benzene}$ is the daily inhalation intake of benzene (mg $kg^{-1}day^{-1}$) determined by using equation 4; IR is the typical inhalation rate assumed to be 20 $m^3day^{-1}$for adults and 10 m^3day^{-1} for children (Gurjar and Mohan, 2003; Betha and Balasubramanian, 2014); EF is the exposure frequency, taken as 365 days yr^{-1} to the ambient annual average concentrations as per scenario 1 and 2 (that is,with and without post harvest paddy residue fires); ED is the exposure duration considered to be 6 years for children and 70 years for adults, assuming that they are exposed to these concentrations throughout their life time (Gurjar and Mohan, 2003; Betha and Balasubramanian, 2014); BM is the average body mass typically assumed to be 70 kg for adults and 15 kg for children (Gurjar and Mohan, 2003; Betha and Balasubramanian, 2014); AT is the average lifetime considered to be 70 years × 365 days for adults and 6 years × 365 days for children; and 90% is the absorption factor of VOCs in humans (Li et al., 2009; Du et al., 2014); $E_{benzene}$ is the average exposure concentration of benzene (mg m^{-3}) in scenario-1 and 2.

Excessive life time cancer risk when the influence of paddy residue fires is absent is 141 per million adults and 330 per million children. Moreover, calculations of the increased excessive lifetime cancer risks due to the influence of the post-paddy harvest fires, reveal that 10 per million adults and 25 per million children will experience increased risks. The cancer risk in children is higher than the adults owing to their low body weight, resulting in higher intake of toxins. For both adults and children, the calculated cancer risks exceed the acceptable USEPA benchmark of one per million (10^{-6}). Considering the entire population of Punjab and Haryana together (Census, 2011), the projected increase in additional cancer cases is 468 for 46.8 millions adults and 155 for 6.2 million children.

The inhalation exposure to toxic doses of isocyanic acid during the post paddy harvest period (0.97 ± 0.17 ppb) and annually (0.94 ± 0.15 ppb) at concentrations close to 1 ppb, can result in cyanate ion (NCO^-) concentrations in human blood after dissociation at physiological pH. The resulting bioaccumulation due to potential residence time of few months (Borduas et al. 2015) can cause protein carbamylation reactions within the human body and enhance health risks for contracting cardiovascular and cataract problems (Roberts et al., 2011; Wang et al., 2007). Regulatory guidelines are not yet in place for this emerging air contaminant, and future epidemiological studies need to quantify the health risk effects due to chronic exposure to ambient isocyanic acid at such high concentrations.

I would like to draw attention to certain aspects of our work to put our results and analyzes in correct perspective. First, the site of our measurements is several kilometers downwind of the agricultural fields which acted as major point sources of the benzenoids and isocyanic acid. As discussed while analyzing nigh time plumes when paddy fires were active in the region (Sarkar et al. 2013), the concentrations closer to the agricultural fields where the burning occurs, would be much higher as subsequent transport of plumes accompanied by mixing with background air would result in dilution. Thus, calculations in this study likely underestimate the cancer risk for the agricultural regions where the burning activity occurs. Hence, there is an urgent need to map the spatio-temporal distribution of health relevant VOCs at sites in closer proximity to the agricultural fields and rural sites to get a more accurate assessment of the exposure. This should be made a priority area for future research. In future, seasonal and inter-annual variations of these pollutants over the N.W.IGP will be studied to augment the current understanding of emission sources and chemical processes. This will assist in designing the better mitigation strategies to curb the emissions over this region.

3.4 Conclusions

This is the first ever study to report long term in-situ measurements of acetonitrile, benzene, toluene, C8 and C9 aromatics along with toxic isocyanic acid from the N.W. IGP, a molecule which has only recently been measured in ambient air studies. Using MODIS satellite fire count data over this region, the day to day variability in ambient concentrations of the VOCs and CO and the correlation and emission ratios of benzenoids and isocyanic acid with acetonitrile (chemical tracer of biomass burning), I demonstrated that the open paddy residue fires are a dominant source in the post-paddy harvest season and responsible for regionally enhanced ambient concentrations. The annual exposure concentration to benzene, a human carcinogen exceeded the National Ambient Air Quality Standard (NAAQS: 1.6 ppb) stipulated by the regulatory authority in India, namely the Ministry of Environment, Forest and Climate Change (MOEF), India and both annually averaged and average post-paddy harvest period ambient concentrations of isocyanic acid (~0.9 ppb) were close to a toxic threshold of 1 ppb. I showed that by mitigating paddy residue fire related emissions, the ambient concentration of benzene can be brought into compliance with the NAAQS. An exposure risk assessment analysis was also carried out to quantify the potential increase in cancer related cases due the post-paddy harvest fire emissions of benzene. These results suggest there is a significant increase in the cancer risk to adults as well as children of 10 and 25 per million inhabitants, respectively, which exceeds the USEPA regulatory threshold of 1 per million inhabitants.

In this study, only the health risks of benzene and isocyanic have been elucidated, but the open fires co-emit black carbon and other gas phase air toxins so that the the actual health risk arising from the exposure is likely to be even higher, than what has been reported here due to synergistic effects (Logue et al., 2010). It would be advisable to carry out studies related to the synergistic effects of exposure to multiple pollutants in future. Therefore, development of economically viable solutions and their enforcement/implementation are necessary to mitigate open paddy residue burning. A recent summary (IGBP, 2014) has proposed that providing farmers with incentives for alternate usages of the paddy residue and strategies to convince farmers to switch to better harvesting technology, which removes and bundles up the paddy residue in addition to the grains could help, as it would reduce the cost of manual labour required to collect the paddy residue into bundles. In absence of a market for paddy residue, promoting the use of the “happy seeder” machine that sows through the residue and leaves it on the field as mulch has also been suggested as a mitigation alternative. It is hoped that this work will provide a strong scientific case for undertaking effective mitigation efforts.

Chapter 4

Storage stability studies and field application of low cost glass flasks for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry

Abstract*

Ambient volatile organic compounds play a key role in atmospheric chemistry and air pollution studies due to their chemical reactivity and in several instances high toxicity. Quantification of ambient whole air samples which contain reactive and short-lived VOCs such as acetaldehyde, isoprene, dimethylsulphide and trimethylbenzenes at ppt-ppb concentrations is analytically challenging and generally accomplished using online proton transfer reaction mass spectrometry. Deployment of online instrumentation is still not feasible in several regions of the world due to practical constraints (power, safety issues). Consequently there is paucity of VOC data in vast regions of the world. I present here, the validation and application of a novel method for ambient VOC speciation and emission factor studies using low cost (< 100 USD) whole air glass flask samplers and offline proton transfer reaction mass spectrometry that can help reduce the paucity of VOC datasets. Experiments to assess the stability during storage of thirteen VOCs, many of which are very reactive, showed that acetaldehyde, acetonitrile, acetone, dimethylsulphide, methyl vinyl and methyl ethyl ketones, benzene, xylenes, trimethylbenzenes and monoterpenes can be quantified reproducibly within the respective precision error (e.g. 40% at 100ppt α-pinene and 3 % at 13ppb acetaldehyde) between collection and storage (at > 95% confidence), for samples analyzed within 10 days of collection. For toluene and isoprene, similar results were obtained until day 9 and 1, respectively and at confidence >70%, over the 10 day period. A storage artefact was observed for methanol resulting in higher analytical uncertainty of upto 40%. I applied the method for measuring toluene/benzene emission ratios and aromatic VOCs in traffic plumes, and determining VOC emission factors (gVOC/kg fuel) from an agricultural wheat straw fire in India.

***Note:** Results presented in this chapter have already been published as first author and follow as "*Chandra, B.P., Sinha, V., Hakkim, H. and Sinha, B., Storage stability studies and field application of low cost glass flasks for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry, International Journal of Mass Spectrometry, 419, 11-19, 2017*."

The results of this study demonstrate that use of the low cost glass flask samplers described herein can significantly improve acquisition of spatially and temporally resolved datasets for atmospheric chemistry and air quality studies at sites where online deployment of instruments remains unfeasible.

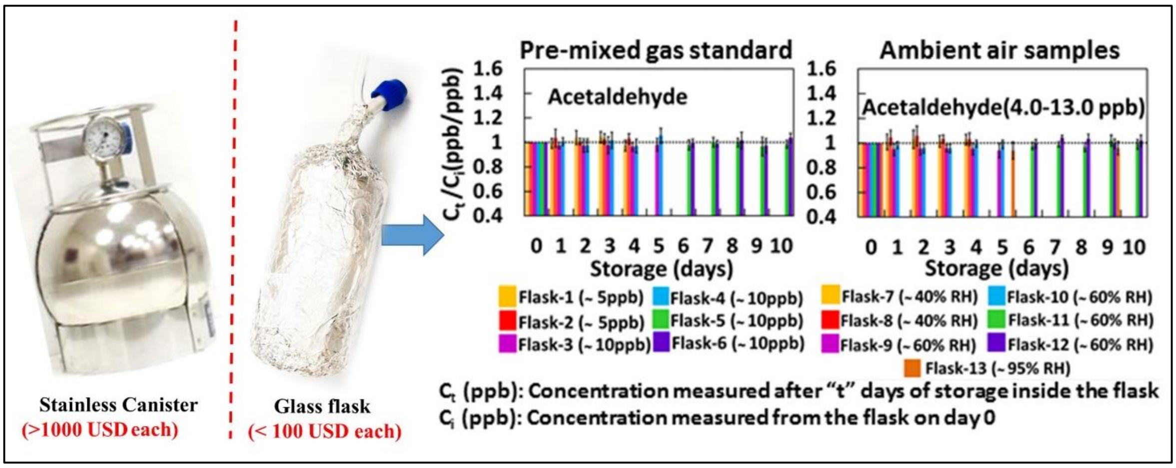


Figure 4.1. Graphical abstract showing the importance and applicability of whole air glass flask samplers

4.1. Introduction

Volatile organic compounds (VOCs) are emitted from a wide variety of natural and anthropogenic sources into the atmosphere (Atkinson and Arey, 2003; de Gouw and Warneke, 2007; Williams and Koppmann, 2007; Gómez et al., 2004; Domeño et al., 2004; Sartin et al., 2001). They play a key role in tropospheric chemistry due to their reactivity (Atkinson, 2000;Goldstein and Galbally, 2007). VOCs such as methanol, acetonitrile, acetaldehyde, acetone, methyl vinyl ketone (MVK), methyl ethyl ketone (MEK), dimethylsulfide (DMS), isoprene, benzene, toluene, C8-aromatics (e.g. xylene isomers and ethylbenzene), C9-aromatics (e.g. trimethylbenzene isomers and propylbenzene) and monoterpenes are among the most important VOCs present in ambient air and have been detected at numerous sites around the world (Atkinson, 2000; Warneck and Williams, 2012; de Gouw and Warneke, 2007).

Methanol, acetaldehyde, acetone, MVK and MEK possess both photochemical and primary emission sources (Mellouki et al., 2015) and influence atmospheric radical budgets. Biogenic emissions of isoprene (440-660 TgC y^{-1}) and monoterpenes (117 TgC y^{-1}) (Guenther et al., 2006;Guenther et al., 1995) contribute 40-50% of the total annual global VOC budget of 1300 TgC y^{-1} (Hallquist et al., 2009; Goldstein and Galbally, 2007). Aromatic compounds such as benzene, toluene, xylene, ethylbenzene, trimethylbenzene and propylbenzene are amongst the most important reactive ambient air toxics in urban environments (2010;http://www.who.int/indoorair/publications/9789289002134/en/). These compounds which are emitted mainly by traffic, industrial sources and biomass combustion strongly fuel the formation of ozone and secondary organic aerosol (Henze et al., 2008;Misztal et al., 2015). Acetonitrile, is useful as a chemical marker for identifying biomass fire plumes (Andreae and Merlet, 2001; de Gouw and Warneke, 2007; Holzinger et al., 1999; de Gouw et al., 2003; Chandra and Sinha, 2016). Phytoplankton emit dimethyl sulphide (Watts, 2000) and recent studies have also reported its emission from soil, leaf litter, and biomass burning (Sarkar et al., 2016;Williams and Koppmann, 2007;Kesselmeier and Hubert, 2002;Jardine et al., 2015). Despite the importance of the aforementioned thirteen VOCs in varied atmospheric environments (de Gouw and Warneke, 2007; Atkinson, 2000; Warneck and Williams, 2012; Kumar and Sinha, 2014; Sarkar et al., 2016; Chandra and Sinha, 2016) ambient in-situ measurements of these compounds are globally very sparse. Proton transfer reaction mass spectrometry has been widely employed for measuring these VOCs in ambient air during field deployments (de Gouw and Warneke, 2007), though gas chromatography (GC) equipped with flame ionization /mass spectrometry/photo ionization detectors (GC-FID/GC-MS/GC-PID), and fourier-transform infrared spectroscopy (FTIR) (Ras et al., 2009; Aragón et al., 2000; Blake et al., 2009) have also been used to quantify a subset of these ambient VOCs. However, on-site field deployment of such instruments is not always feasible because of logistical and safety issues. Thus, VOC emission inventories even from densely populated regions such as South Asia are poorly constrained due to paucity of spatially and temporally resolved VOC datasets, source specific VOC speciation profiles and emission factor measurements. This in turn limits the accuracy and performance of air pollution and chemistry transport models used for predicting air quality and climate.

With regard to quantification of methanol, acetonitrile, acetaldehyde, acetone, DMS, isoprene, MVK, MEK, benzene, toluene, C8-aromatics, C9-aromatics and monoterpenes most existing offline samplers based on solid adsorbents and whole air Tedlar samplers experience interferences due to reported changes in sample integrity that can occur at the collection, transfer and analysis stages (Ras et al., 2009; Aragón et al., 2000). Hence, for reactive VOCs, the United States Environmental Protection Agency (USEPA) recommends collection of whole air samples in stainless steel canisters with passivated surfaces for the determination of VOCs but their high costs (>1000 USD per canister) are deterrents to large scale usage and deployment. Alternatively, Pollmann et al. (Pollmann et al., 2008) demonstrated use of low cost glass flask samplers for sampling and storage of C2-C7 alkanes, benzene and toluene in glass flasks. Several recent studies have further investigated the storage stability and demonstrated improved application of diffusive VOC samplers and Tedlar bags for selected VOCs (Pérez Ballesta et al., 2016; Kim et al., 2012). However, to date there has been no systematic study investigating the potential use of low cost glass flasks (price range < 100 USD each) for sampling and offline measurements of methanol, acetonitrile, acetaldehyde, acetone, DMS, isoprene, MVK, MEK, benzene, toluene and the sum of C8-aromatics, C9-aromatics and monoterpenes using proton transfer reaction mass spectrometry.

Here, I first undertake comprehensive validation experiments of a self-developed method and protocol for offline collection of whole air VOC samples in re-useable low cost glass flask samplers. I assess the stability of the thirteen VOCs namely methanol, acetonitrile, acetaldehyde, acetone, DMS, isoprene, MVK, MEK, benzene, toluene, the sum of C8-aromatics, C9-aromatics and monoterpenes during storage inside the glass flasks over a 10 day period for various (n=6) premixed gas standard mixtures at different concentrations and humidity and for ambient air samples (n=7). After the validation experiments, I employed the samplers in the field for (i) measurement of toluene/benzene ratios and aromatic VOCs in traffic plumes (a well constrained emission source) and (ii) determining emission factors (gVOC emitted/kg fuel burnt) of the thirteen VOCs in a flaming stage agricultural wheat straw fire plume.

4.2. Experimental section

4.2.1 Description of glass flask sampler and practical considerations

Figure 4.2(a) shows a picture of the sampling setup including the 2 L custom-made borosilicate glass flask equipped with a 10 mm Teflon bore and screw cock (Vensil Glass Works Limited, Bangalore, India), Teflon tubing (9.5 mm o.d.), and a Teflon VOC pump (Model - N 86 KT.45.18; KNF pump) equipped with a pressure control valve. One port of the pump is connected to the Teflon inlet which has an inline Teflon membrane filter (Pore size 0.45µm) while the other port is connected to the glass flask. The air is sampled actively. Based on a few experiments which resulted in breakage of the flask due to overpressure, metal sheaths were used only during the time of filling the glass flasks upto ~ 2 bar in order to ensure protection from any accidental implosion/breakage of the glass flask. After the sample was collected, the metal sheath was removed and the glass flasks were stored at room temperature in the dark during transportation by covering the flasks with aluminum foil to avoid unwanted photo-induced chemical reactions due to stray radiation, until analyses at the IISER Mohali Atmospheric Chemistry Facility. All sampling involving the gas standard mixtures were conducted at room temperature whereas ambient samples were collected under ambient conditions. All the measurement analyses were performed at room temperature (~ 25°C).

The following cleaning and conditioning protocols were followed prior to collection of ambient whole air samples: (i) The flasks were conditioned in an oven (Model -1210D/8; Jain Scientific Glass works, India) for 8 hours at 180^{o}C after being thoroughly rinsed with chromic acid de-ionized water to remove sticky organic material, (ii) thereafter, the flasks were filled with VOC free zero air (~2 bar) produced using a Gas Calibration Unit (GCU-A, Ionimed Analytik) (Kumar and Sinha, 2014) and evacuated (~300 mbar) atleast thrice to remove any potential residual effects (iii) the flasks were wrapped with aluminium foil. All tubing, pump fittings and mass flow controllers were also purged with zero air to remove potential memory effects due to previous samples.

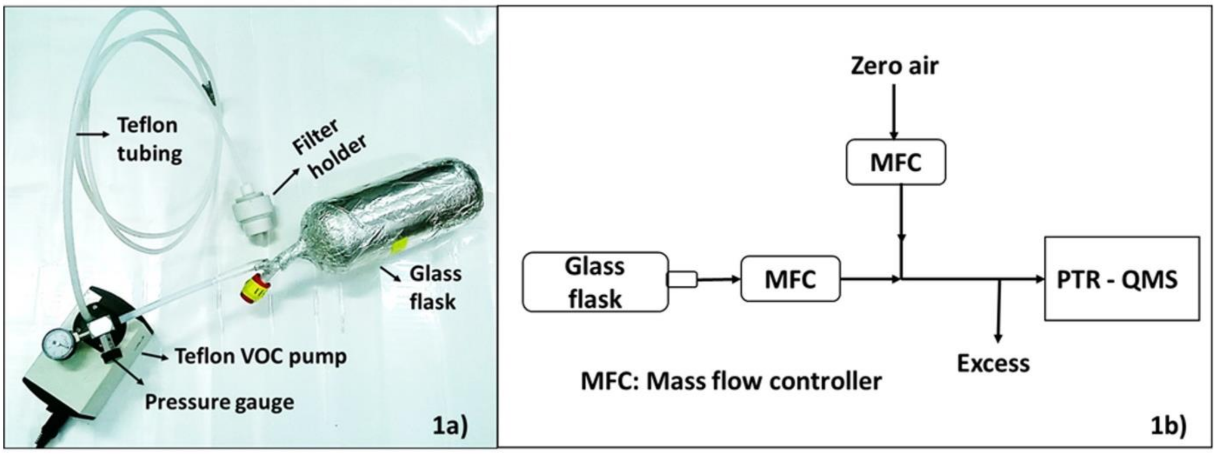


Figure 4.2 (a). Picture of the whole air sample collection setup along with customised borosilicate glass flask; (b) Flow schematic used for analysing VOCs from whole air samples collected in glass flask using the PTR-QMS instrument.

4.2.2 Analysis of VOCs sampled in the glass flask using proton transfer reaction quadrupole mass spectrometry (PTR-QMS)

Methanol, acetonitrile, acetone, acetaldehyde, DMS, isoprene, MVK, MEK, benzene, toluene, the sum of C8–aromatics, C9–aromatics and monoterpenes, present in air samples collected in the glass flasks, were measured using a high sensitivity proton transfer reaction quadrupole mass spectrometer (PTR-QMS; HS Model11-07HS-088; Ionicon Analytik Gesellschaft, Austria) that has been previously characterized in detail (Chandra and Sinha, 2016;Sinha et al., 2014;Kumar and Sinha, 2014). Use of the PTR-QMS technique for measurements of these

VOCs has been extensively validated in diverse atmospheric environments as reviewed previously (de Gouw and Warneke, 2007; Blake et al., 2009). Briefly, analyte VOC molecules with a proton affinity greater than water (691.2 KJ/mol) undergo soft-chemical ionisation with the reagent hydronium ions within a drift tube to form protonated molecular organic ions (typically with product ion of (m/z) = molecular ion + 1). For some analyte molecules such as alpha pinene, fragmentation can occur, but knowledge of the fragmentation pattern and ions still enables accurate quantification (de Gouw and Warneke, 2007). The product ions are then separated using a quadrupole mass analyzer and detected using a secondary electron multiplier. Figure 4.2(b) shows the flow schematic employed for measuring the VOCs. Sample flow from the glass flask (~100 ml/min) was regulated using a mass flow controller (MFC: EL-FLOW; Bronkhorst high-tech; stated uncertainty 2%). The flows of mass flow controllers are also measured independently before and after the experiments using a NIST calibrated flow meter (BIOS Drycal definer 220). For the samples collected near the point sources containing VOCs at high concentrations (> 30 ppb), the samples were diluted using VOC free-zero air. VOCs were measured with a dwell time of 1s in ion-selective monitoring mode at each m/z channel. The total time required for acquiring the 10 measurement cycles was around 3 minutes. Calibration experiments to determine compound specific sensitivities (ncps/ppb) were performed by dynamic dilution of VOC gas standards (Apel–Riemer Environmental,Inc., Colorado, USA; containing the gases reported in this work at circa 500 ppb). Analytical detail of the PTR-MS instrument used in this work and its operating conditions are available in Sinha et al. (2014) and Chandra and Sinha (2016). Instrument background checks were performed regularly and uncertainties were determined as described in our previous works (Sinha et al., 2014; Chandra and Sinha, 2016; Kumar and Sinha, 2014). The isotopic contribution of O_2^+ ions at m/z 33 channel have been accounted by subtracting the m/z 32 signal contributing to the m/z 33 signal (i.e., m/z 32×0.00078) as described in detail previously (Sinha et al., 2014). Instrumental backgrounds at relevant m/z ion channels were < 80 ppt for all ions, except methanol (m/z 33), acetaldehyde (m/z 45) and acetone (m/z 59) for which it was < 0.4 ppb. The total measurement uncertainty using the PTR-QMS instrument was less than 15 % for benzene, toluene, acetonitrile, acetone, acetaldehyde and MVK never exceeded ~25% for the other VOCs reported in this work.

4.2.3 Supporting measurements of carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4)

In order to determine emission factors (gVOC emitted/kg fuel burnt) (Yokelson et al., 1999) from wheat straw fires for VOCs reported in this study, CO, CO_2 and CH_4 were also measured in the air samples. These gases are stable inside glass flasks for periods of even up to a year (Pollmann et al., 2008) CO was quantified using non-dispersive infrared (NDIR) filter correlation spectroscopy (Thermo Fisher Scientific, Model No. 48i) as described in our previous works (Chandra and Sinha, 2016; Sinha et al., 2014). Samples collected from point sources containing high concentrations of CO were diluted with zero air before analysis. The total uncertainty for CO measurements was less than 6% and the limit of detection varied between 5–11 ppb.

CO_2 and CH_4 were measured using a high precision Cavity Ring Down Spectroscopy (CRDS) analyzer (Model G2508, Picarro, Santa Clara, USA). Within the instrument, light from a tuneable semiconductor diode is passed through a high precision wavelength monitor to a finesse optical cavity with high reflectivity (>99.995%) mirrors. Light circulates in the cavity traversing path lengths of 20 km or more. The ring down time of the cavity with and without absorption due to the target gas is calculated and compared continuously to obtain the concentration (Crosson, 2008). The temperature and pressure of the cavity is regulated at 45°C and 140 Torr (with variations of less than 20mK and 0.1 Torr, respectively), resulting in highly stable spectroscopic features. CO_2 and CH_4 were quantified at wavelengths of 1.603 µm and 1.659 µm respectively (Crosson, 2008). The measurements were performed at a frequency of 1Hz. Calibrations for CO_2 and CH_4 were performed by dynamic dilution of a gas standard mixture (Phoenix Gases Ltd., Navi Mumbai, India; traceable to NIST, USA containing CO_2 at 1998±39 ppm and CH_4 at 9.2±0.2 ppm in Nitrogen). The instrument also quantifies the water vapour concentrations in the sampled air. For all the samples analyzed in this work, the water vapour concentrations were <1%. Thus, the experimentally derived water vapour correction algorithm provided by the manufacturer was sufficient to correct for the dilution and broadening effect on CO_2 and CH_4 measurements due to presence of water vapour (Crosson, 2008; Rella et al., 2013; Chen et al., 2010). The dry mixing ratios so obtained were used for further analyses. The overall uncertainty for measurements of CO_2 and CH_4, calculated using the root mean square propagation of individual uncertainties: e.g. accuracy error of gas standard (2%), 2σ instrumental precision error (0.1% for CO_2 and 0.3% for CH_4), flow reproducibility (2%), for each MFC, was < 4 % in each case. The limit of detection was better than 0.5 ppm and 1.5 ppb, for CO_2 and CH_4, respectively.

4.3. Results and discussion

4.3.1 Validation experiments for assessing stability of VOCs inside the glass flasks over a 10 period

In order to assess the stability of methanol, acetonitrile, acetaldehyde, acetone, DMS, isoprene, MVK, MEK, benzene, toluene, sum of C8–aromatics, sum of C9–aromatics and monoterpenes inside the glass flasks over a period of 10 days I conducted experiments with (i) gas mixtures containing these compounds at approximately 5 ppb and 10 ppb (total: 6 flasks) and (ii) with ambient air samples containing the thirteen compounds (total: 7 flasks). These are described below.

4.3.1.1 Experiments with gas mixtures containing the thirteen compounds

Using the active sampling procedure described in Section 4.2.1, the glass flasks (2L volume) were filled up to 2 bar pressure using a Teflon VOC sampling pump at room temperature. While two flasks (hereafter termed flask 1 and 2) were filled using a gas stream containing the thirteen compounds at circa 5 ppb and 70% RH, four flasks (hereafter termed flask 3, 4, 5 and 6) were filled using a gas stream containing ~ 10 ppb of the compounds at 70 % RH. The gas stream mixtures of ~5 ppb and 10 ppb concentration were generated by dynamic dilution of a VOC gas standard (Apel–Riemer Environmental,Inc., Colorado, USA), which contained methanol, acetonitrile, acetone, acetaldehyde, DMS, isoprene, MVK, MEK, benzene, toluene, p-xylene, 1,2,4- trimethylbenzene and α-pinene, each at ~ 500 ppb. Dynamic dilution using VOC free zero air at 70% RH was accomplished using a Gas Calibration Unit (GCU-A, Ionimed Analytik) (Kumar and Sinha, 2014). The flasks were stored in a dark container at room temperature (~ 25°C) whenever they were not being analyzed for VOCs using the PTR-QMS instrument. The flasks were analysed for ~3 minutes with the PTR-QMS instrument (suction flow of instrument <100 ml/min). The use of MFCs ensured a regulated stable flow into the instrument but required an over pressure at the MFC entrance port.

Analyses of flasks 1 and 2 were performed on the day the two flasks were filled (termed day 0) and on days 1, 2, 3 and 4 every 24 h. To assess the stability of VOCs for up to 10 days, four flasks (hereafter termed flasks 3, 4, 5 and 6) were filled with ~10 ppb of the VOCs at 70% RH using the same gas stream mixture. Flasks 3 and 4 were analyzed on days 0, 1, 2, 3, 4 and 5 whereas flasks 5 and 6 were analyzed on days 0, 6, 7, 8, 9 and 10, enabling storage and analyzes to be performed over a 10 day period. The choice for a 10 day study period was based on the rationale that 10 days would be adequate for transportation of air samples from remote locations to an instrumental facility containing a PTR-QMS instrument. I decided to use flasks of 2L volume (which could be sampled a maximum of 6 times) rather than larger volume flasks, as it presented an optimum from the point of view of logistics related to transportation and packing. Figure 4.3 summarizes the results of the above experiments for acetonitrile, acetone, acetaldehyde, dimethylsulphide, isoprene, methyl vinyl ketone, methyl ethyl ketone, benzene, toluene, p-xylene,1,2,4-trimethylbenzene and α-pinene for flasks 1 and 2 (duplicates containing ~5 ppb of each VOC at 70% RH over a 4 day period) and flasks 3,4,5 and 6 (replicates containing ~10ppb of each VOC at 70% RH over a 10 day period). The vertical axes show the ratio C_t / C_i (ppb/ppb), where C_t is the VOC's concentration in the flask after "t" days ($t \leq 10$) of storage and C_i is the VOC concentration measured from the same flask on the day it was filled (day 0). Vertical error bars in each histogram in Figure 4.3 represents the 1σ PTR-QMS instrumental precision error while measuring the VOCs. Note that in all the six flasks, the ratio of "C_t / C_i (ppb/ppb) for all 12 VOCs shown in Figure 4.3 was always within the 1σ precision error varying between 0.9-1.1. Therefore, all the 12 VOCs shown in Fig. 2 were stable over the period of 10 days. For methanol (the only VOC from among the 13 VOCs studied in this work not shown in Figure 4.3), I observed an initial increase upto day 6, which levelled off by day 7 (shown in Figure 4.6(a)). The maximum observed increase in the concentration of methanol over the 10 day period among all 6 flasks was below 40% relative to the initially measured concentration on day 0 (C_i (ppb)).

Also, ratio between the initially measured VOC concentrations (C_i (ppb)) from the glass flask using the PTR-QMS instrument to the theoretically determined reference concentrations (C_r (ppb)) of each VOC (determined by dynamic dilution using zero air of the VOC gas standard), was determined and results are shown in Figure 4.4. The ratio of "C_i / C_r (ppb/ppb) for all 13 VOCs shown in Figure 4.4 was always within the 1σ precision error and varied between 0.9-1.1. Therefore, condensation and/or memory effects due to usage of a Teflon VOC pump, control valve and mass flow controller, do not seem to cause any loss or artefacts during sampling.

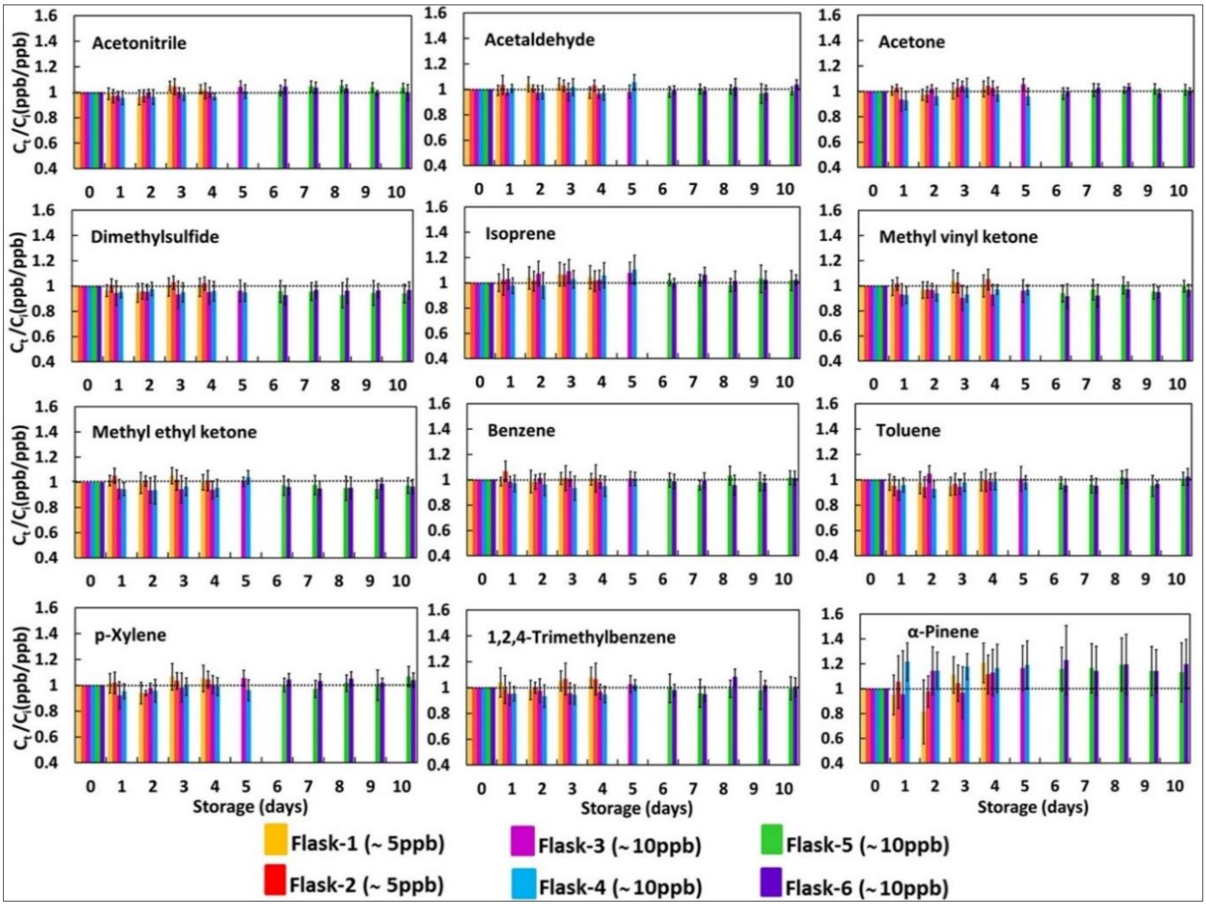


Figure 4.3. VOC stability in the glass flasks containing pre-mixed gas standards stored at 70% RH and analyzed over a 10 day storage period: Histogram values in each VOC panel correspond to the ratio of VOC concentration measured after "t" days of storage (C_t (ppb)) to the initially measured concentration of VOC from the flask on day 0 (C_i (ppb)). Error bars on each histogram represent the precision error. Dotted black lines in each VOC panel show the 1:1 ratio (C_t/ C_i (ppb/ppb) whereas coloured legends denote the VOC concentrations and flask numbers, respectively.

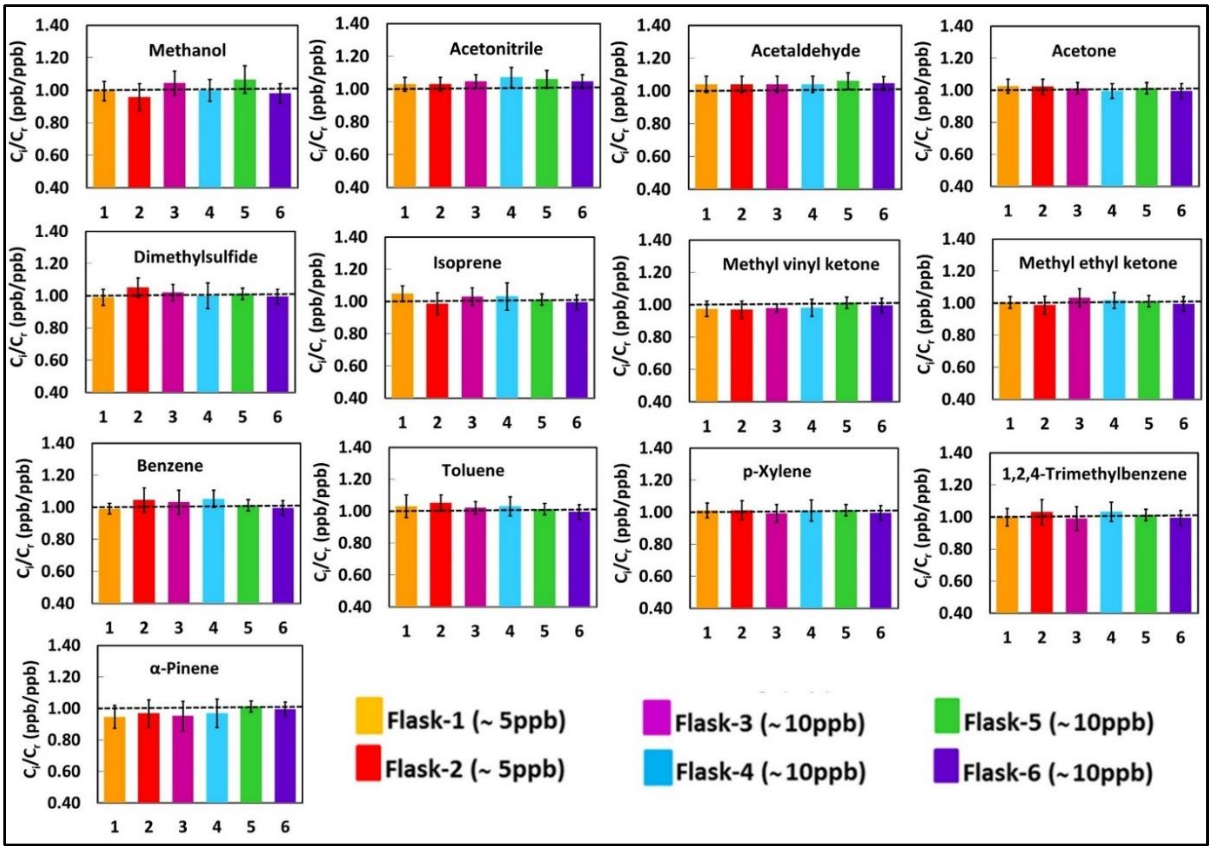


Figure 4.4. VOC stability in the glass flasks containing pre-mixed gas standards stored at 70% RH and analyzed on the same day of filling day 0. Histogram values in each VOC panel correspond initially measured concentration of VOC from the flask on day 0 (C_i (ppb)) using the PTR-QMS instrument to the theoretically determined reference concentration (C_r(ppb)) of each VOC (determined by dynamic dilution using zero air of the VOC gas standard). Error bars on each histogram represent the precision error. Dotted black lines in each VOC panel show the 1:1 ratio (C_i/ C_r (ppb/ppb) whereas coloured legends denote the VOC concentrations and flask numbers, respectively.

4.3.1.2 Experiments with ambient air samples collected and stored in the glass flasks

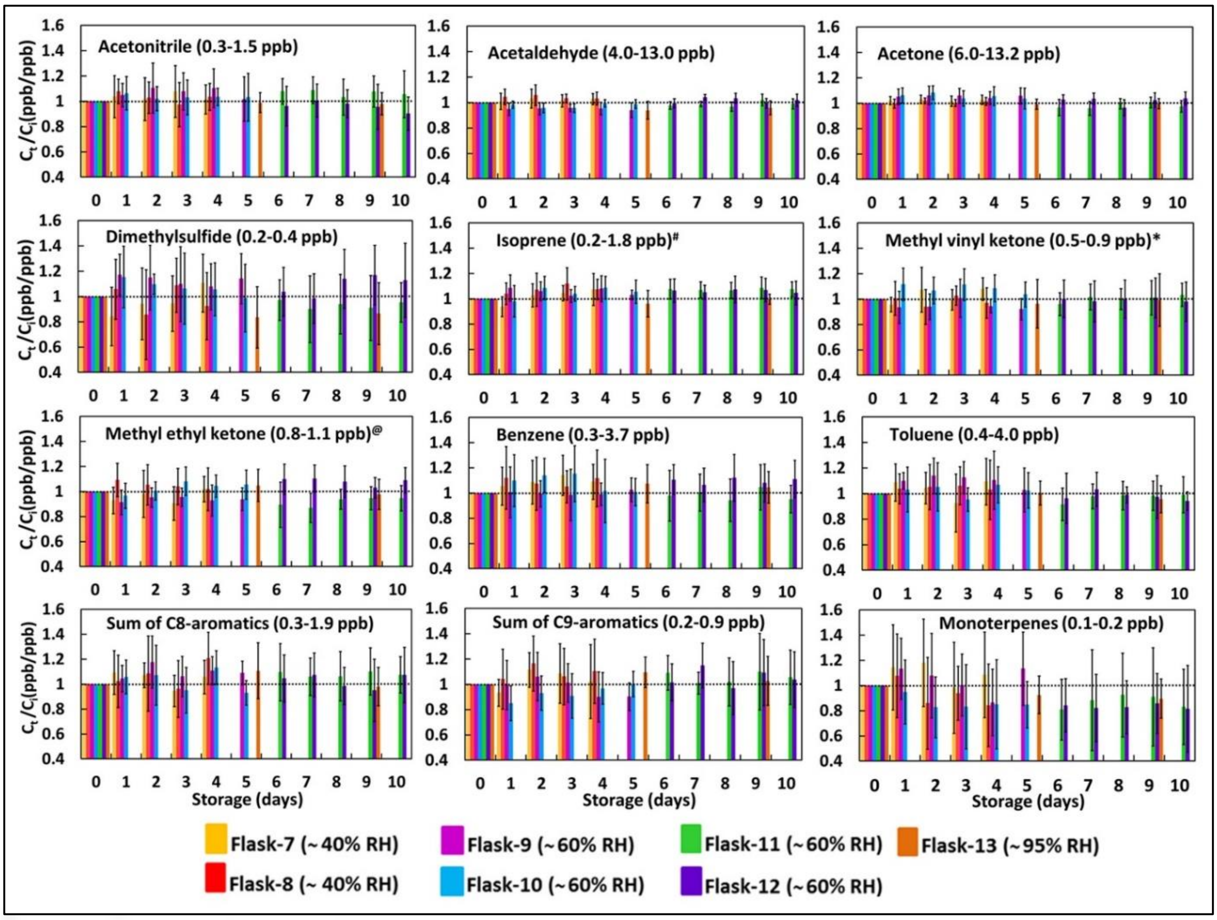
In a second series of experiments, I assessed the stability of these VOCs in ambient air samples that were collected and stored in the glass flasks over a 10 day period. Using the active sampling procedure described in Section 4.2.1, the pre-treated glass flasks were filled upto 2 bar pressure using a Teflon VOC sampling pump at ambient temperature. The ambient air samples were collected on the roof top of the IISER Mohali Atmospheric Chemistry Facility in the northwest

Indo-Gangetic Plain (30.667º N, 76.729º E, 310 m a.s.l.), a site and facility already described in detail in our previous works (Sinha et al., 2014; Pawar et al., 2015; Sarkar et al., 2013).

In the first set of experiments, two flasks (flasks 7 and 8) were filled with ambient air in the afternoon on October 2, 2015 between 14:30-14:45 local time (L.T.) when ambient RH was 40% and ambient ozone was 70 ppb. In the second set of experiments, ambient air was sampled into four flasks (hereafter termed flasks 9, 10, 11 and 12) in the afternoon on August 28, 2016 between 12:35-12:50 L.T. when ambient RH was 60% and ozone was 60 ppb. Finally in the third experiment one flask (hereafter termed flask 13) was filled with ambient air in the morning under foggy conditions (ambient RH 95%) on January 23, 2016 between 7:50-7:55 L.T. The ambient air samples in flasks 7 and 8 were stored over a 4 day period and analysed for VOCs on days 0, 1, 2, 3 and 4 at 24 h intervals. The ambient air samples in flasks 9 and 10 were stored over a 5 day period and analysed on days 0, 1, 2, 3, 4 and 5 at 24 h intervals, whereas the ambient samples in flasks 11 and 12 were stored for 10 days, and analyzed for VOCs on days 0, 6, 7, 8, 9 and 10. Flask 13 which was collected at high ambient RH of 95% was stored over a 9 day period, and analyzed for VOCs on days 0, 5 and 9. These three sets of experiments were helpful in determining the stability of the VOCs in the presence of other ambient air chemical constituents inside the flask.

Figure 4.5 summarises the results observed for the ambient air samples in flasks 7, 8, 9, 10, 11, 12 and 13 in a manner analogous to Figure 4.3, where C_t is the VOC's concentration in the flask after "t" days ($t \leq 10$) of storage and C_i is the VOC concentration measured from the same flask on day 0. The range for the day 0 ambient mixing ratios (that is measured C_i values) from the flasks for each compound during the three experiments is shown in individual VOC panels of Figure 4.5. In the ambient flask samples, measurements attributed to isoprene, MVK and MEK by the PTR-QMS instrument represent upper limits for the concentrations of these compounds due to minor potential isobaric contributions from other compounds (de Gouw and Warneke, 2007). The results showed that even for the air samples with complex chemical composition in the northwest IGP (Sinha et al., 2014), the stability of the 12 VOCs in ambient air samples was comparable to simpler mixtures containing only these compounds (Section 4.3.1.1). The ratios of "C_t/C_i (ppb/ppb)" for each of the 12 compounds varied between 0.9-1.1 over a period of 10 days and were always within the respective 1σ precision error of the instrumental analyses. It may be noted that the precision error of the PTR-QMS instrument is variable and is higher in percentage terms at low concentration measurements due to less favourable Signal/Noise ratio (e.g. 2.3% for 15.3 ppb methanol and 44 % for 0.18 ppb alpha-pinene). For methanol, again an initial increase was observed as in the case of samples consisting of simpler gas mixtures prepared using gas standards of the compounds (shown in Figure 4.6 (b)), with the maximum increase being less than 40% relative to the initial concentration during successive analyses from all the flasks. It is unclear as to what causes initial methanol increase in both ambient and gas standard mixtures inside the glass flasks, though there is indication of an RH dependence with samples collected at high RH faring better. Both methanol and water vapour are “sticky” molecules and the artefact appears to be related to wall effects. It may be possible to improve the analyses of methanol by collecting samples under high humidity, however this requires further work to unravel the possible mechanism causing the artefact. In any case our results suggest that grab sampling of methanol can carried out meaningfully, despite a higher uncertainty of upto 40%.

Note that, flasks 7 and 8 contained ozone at a concentration of ~70 ppb which was co-sampled along with VOCs in the ambient air. It did not seem to have any significant effect on the stability of 13 VOCs studied in this work over a 10 day period. This is likely due to the destruction of ozone through surface reactions with the inner walls of the sampler and/or auto-oxidation reactions being faster than reactions of ozone with these VOCs. These effects have been observed and reported in several previous studies pertaining to VOC sampling using glass flasks and canisters (Pollmann et al., 2008; Palluau et al., 2007; Harper 2000). Pollmann et al. (2008) did not observe any significant decrease of isoprene in the glass flask as a function of increasing co-sampled ozone. A study by Palluau et al. (2007) reported that co-sampling of ozone did not have any significant effect on unsaturated VOCs as it was likely destroyed in surface reactions with inner walls of the silica-coated canister inner walls. Harper (2000) also stated that co-sampling ozone into canisters is not a problem since it would get consumed rapidly through auto-oxidation reactions on the surface walls of the sampler. Our results also suggest that sampling and stability of the 13 VOCs reported in this work are highly unlikely to be affected by the ozonolysis reactions due to a combination of factors already discussed and reported in the previous studies (Pollmann et al., 2008; Palluau et al., 2007; Harper 2000).



#Isobaric contribution of furan to the isoprene measurements at nominal m/z =69.

*Isobaric contribution of methacrolein and crotonaldehyde to the methyl vinyl ketone measurements at nominal m/z =71

@ Isobaric contribution of methylglyoxal and butanal to the methyl ethyl ketone measurements at nominal m/z =73

Figure 4.5. VOC stability in the glass flasks containing ambient air samples (at 40%, 60% and 95% ambient RH) analyzed over a 10 day storage period: Histogram values in each VOC panel (number in parentheses shows range of ambient VOC concentrations for all the ambient flask samples (n=7) on day 0) correspond to the ratio of VOC concentration measured after "t" days of storage (C_t (ppb)) to the initially measured concentration of VOC from the flask on day 0 (C_i (ppb)). Error bars on each histogram represent the precision error. Dotted black lines in each VOC panel show the 1:1 ratio (C_t/ C_i (ppb/ppb) whereas coloured legends provide information on the flask number and RH.

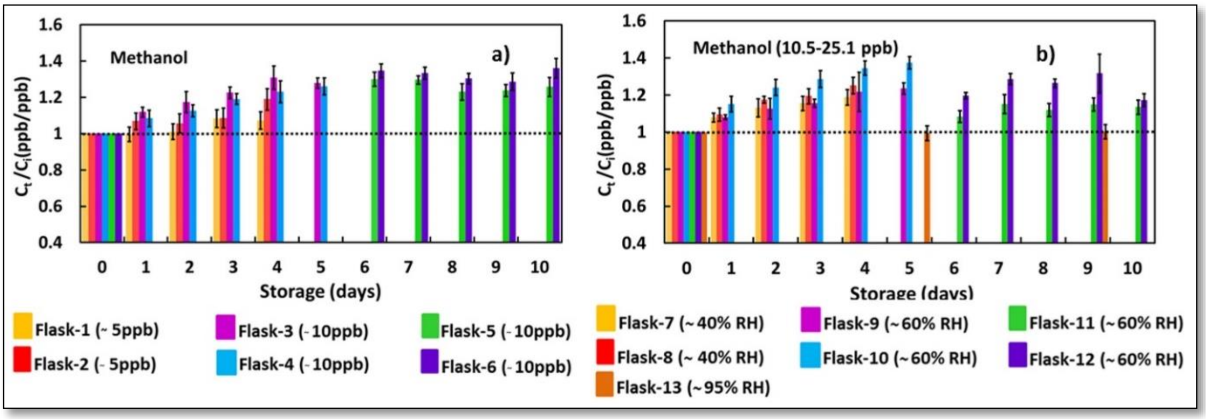


Figure 4.6. (a) Stability of methanol in the glass flasks stored at 70% RH analyzed over a 10 day storage period. (b) Stability of methanol in the glass flasks analyzed over a 10 day storage period filled with ambient air samples at 40%, 60% and 95% ambient RH. Histogram values in each VOC panel correspond to the ratio of VOC concentration measured after "t" days of storage (C_t (ppb)) to the initially measured concentration of VOC from the flask on day 0 (C_i (ppb)). Error bars on each histogram represent the precision error. Dotted black lines in each methanol panel show the 1:1 ratio (C_t/ C_i (ppb/ppb). Coloured legends provide information on VOC concentrations and flask numbers in Figure 4.6 (a) and the flask number and RH in Figure 4.6 (b) respectively. Number in the parentheses in Figure 4.6 (b) shows range of ambient methanol concentrations for all the ambient flask samples (n=7) on day 0.

In order to ascertain statistical difference if any pertaining to stability of the 12 VOCs during storage, paired t-test was employed for each VOC using the concentration values measured after "t" days (C_t) of storage in the flask and the initial concentration on day 0 (C_i). This test was performed by combining the data from all the 13 flask experiments. Based on the t-tests it could be concluded with more than 95% confidence that there was no difference in the VOC concentrations measured from the flask on day 0 and on each of the subsequent days for a period of upto 10 days for acetonitrile, acetone, DMS, MVK, MEK, benzene, sum of the C8 and C9 aromatics and monoterpenes. There was no difference with a confidence level of 95% till day 9 for toluene and day 1 for isoprene, respectively and overall no difference at a confidence level >70% for both toluene and isoprene. The results of the paired t-test are listed in Table 4.1. Therefore, the experiments and the statistical tests demonstrate that the whole air sample collection methodology presented in this work is suitable for characterising these 12 VOCs in ambient air reproducibly within the respective precision errors, if analyzed within 10 days of sample collection in the flask. For methanol, considering the similar behaviour observed for both the complex ambient air mixtures and the simpler gas mixture of thirteen compounds, the method could still be useful but with much higher uncertainty of 40% due to an as yet unknown storage artefact.

Table 4.1. Summary of paired t-test results performed for the concentration measured after "t" days of storage and initial concentration measured on day 0 using combined data set of pre-mixed standards and ambient air samples for all the reported VOCs, reporting the probability of a change in the mean concentration within the flask as "very unlikely" (V.U; p (same mean) >0.95), "unlikely" (U; p (same mean) >0.7) and "very likely" (V.L; p (same mean) <0.05).

Compound	Day 1/Day0	Day 2/Day0	Day 3/Day0	Day 4/Day0	Day 5/Day0	Day 6/Day0	Day 7/Day0	Day 8/Day0	Day 9/Day0	Day10/Day0
Methanol	V.L	V.L	V.L	V.L	V.L	V.L	V.L	V.L	V.L	V.L
Acetonitrile	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Acetaldehyde	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Acetone	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Dimethylsulfide	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Isoprene	V.U	U	U	U	U	U	U	U	U	U
Methyl vinyl ketone	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Methyl ethyl ketone	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Benzene	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Toluene	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	U
p-xylene	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
1,2,4 - Trimethylbenzene	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U
Monoterpenes	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U	V.U

4.3.2 Application of the glass flask samplers for characterisation of VOCs in ambient air at a traffic thoroughfare and in the plume of an agricultural wheat straw fire

After the validation experiments described above, I applied the glass flask samplers at Tribune Chowk (30.704º N, 76.789º E, 330 m a.s.l.), Chandigarh, a busy traffic thoroughfare which connects Chandigarh to the capital of India, New Delhi, and experiences average traffic flow of circa 5000 passenger cars per hour (Sood et al., 2014). I chose such an area source for the first field application of the glass flasks because benzene, toluene and xylene emission ratio signatures from traffic sources are better constrained than most other urban sources and have been reported in the peer reviewed literature from numerous sites. The ambient air sample was collected in a flask about 0.5 m above the ground at 15:00 I.S.T. on March 22, 2015. Figure 4.7 (a) shows the photograph taken during sampling at Tribune Chowk, Chandigarh. Vehicles plying through the site are typically a mixed fleet of diesel, petrol/gasoline and Liquefied Petroleum Gas (LPG) powered vehicles.

In the second experiment, ambient air samples in a flaming stage agricultural wheat straw fire plume were collected in a glass flask at an agricultural field in Raipur Khurad, Mohali (30.652º N, 76.709º E, 305 m a.s.l.) on May 2, 2015 between 17:30-18:00 local time. Figure 4.7 (b) shows the photograph taken during sampling from the wheat residue burning plume in flaming stage. Prior to the lighting of the wheat straw fires, ambient air samples were also collected in another glass flask from the same agricultural field, after ensuring there were no active nearby fires. This enabled us to calculate excess mixing ratios of VOCs (Andreae and Merlet, 2001; Akagi et al., 2011; Kudo et al., 2014) for this source.

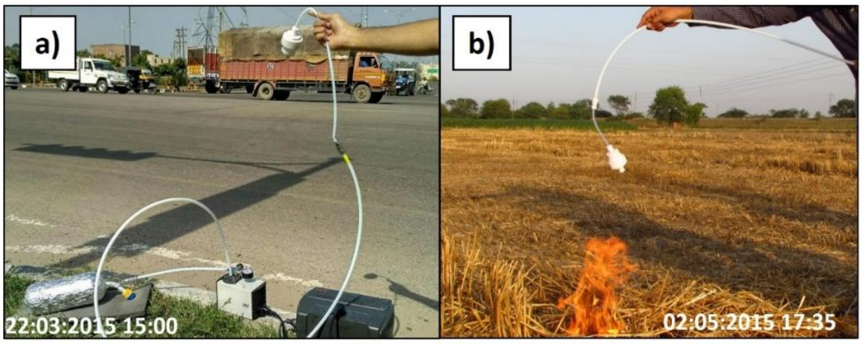


Figure 4.7. (a) Photograph taken during the whole air sample collection in the glass flask at Tribune Chowk, Chandigarh on 22.03.2015 at 15:00 local time. (b) Photograph taken during

the whole air sample collection in the glass flask from wheat residue burning plume in flaming stage at an agricultural field in Raipur Khurad, Mohali, Punjab on 02.05.2015 at 17:35 local time.

All the whole air samples collected in the glass flasks as mentioned above were transported and analysed within 5 hours of sample collection at the IISER Mohali Atmospheric Chemistry Facility for the thirteen VOCs in ion selective mode with a dwell time of 1s per m/z using the PTR-QMS instrument. Keeping in mind the expected high VOC concentrations (>30 ppb) in the plumes of the wheat straw fires, I diluted the sample flow exiting the glass flask as shown in Figure 4.2(b) with VOC free-zero air by a factor of ~ 6. The non-fire influenced ambient sample from the agricultural field and the traffic thoroughfare sample were analysed without dilution. For the agricultural wheat straw fires, analyses for carbon monoxide, carbon dioxide and methane were also performed from the same glass flasks using the CRDS GHG analyzer described in Section 4.2.3.

4.3.3 Comparison of benzene, toluene and sum of C8-aromatics road side concentrations with traffic source sampling studies elsewhere

Benzene, toluene, and sum of C8-aromatics (ethyl benzene and xylene isomers) are among the most abundant aromatic VOCs present in auto-mobile exhaust (Singh et al., 1985; Jobson et al., 2005; Henze et al., 2008). Table 4.2 shows the concentrations of benzene, toluene and sum of C8-aromatics as well as the ratio of toluene/benzene measured at the traffic thoroughfare in Chandigarh and from traffic sites in other cities. While direct comparison of the absolute VOC concentrations in the different studies should be treated with caution as traffic density, type of fuels, and meteorological conditions can induce variability, nonetheless emission ratios and observed concentration ranges should be similar for sites where the mixing ratios of aromatic compounds is controlled primarily by traffic emissions. The observed concentrations of benzene (21.5 ± 0.9 ppb), toluene (58.1 ± 1.7 ppb) and sum of the C8 aromatics (69.5 ± 1.5 ppb) appeared to be reasonable and in the concentration range reported at high traffic density sites in cities of developing countries such as Karachi (M.A. Jinnah Road), Pakistan (Barletta et al., 2002) and Cairo (Ramis), Egypt (Khoder, 2007) and near a road in New Delhi (AIIMS), India (Hoque et al., 2008), considering the ambient variability reported in those studies. The toluene/benzene (T/B) emission ratios of 2.7 ± 0.2 obtained for our grab sample was within the range of reported T/B ratios for traffic plumes in different cities such as Birmingham, UK (Kim et al., 2001);

Karachi, Pakistan (Barletta et al., 2002); Cairo, Egypt (Khoder, 2007); New Delhi, India (Hoque et al., 2008); tail pipe emissions of vehicular exhaust in Netherlands (2.7) (Guicherit, 1997); a tunnel study in Hong Kong (2.26 ± 0.86) (Ho et al., 2009) and for urban traffic in Paris (3.15 ± 0.25) (Vardoulakis et al., 2002). Thus, the results obtained by using the glass flask samplers in this work appear to generally agree with those reported in the peer reviewed literature from locations similar to our site.

Table 4.2. Concentrations (ppb) of benzene, toluene and sum of C8-aromatics and the ratio of toluene to benzene measured at traffic thoroughfare, Chandigarh compared to traffic related sites in other cities

Location	Benzene	Toluene	Sum of C8-aromatics[#]	Toluene /benzene
Birmingham, UK[a]	14.6 (6.6)	27.0 (12.5)	15.1 (5.7)	1.8 (1.2)
Hongkong, China[b]	8.3 (10.4)	20.5 (19.8)	4.5 (5.4)	3.3
Karachi, Pakistan[c]	19.7 (18.0)	44.0 (41)	46.0 (31.2)	2.3
Cairo, Egypt[d]	28.1 (3.3)	58.2 (9.5)	61.0 (6.2)	2.5
New Delhi, India[e]	34.5 (16.6)	50.8 (21.3)	35.8 (35.7)	1.5-2.2
Chandigarh, India[f]	21.5 (0.9)	58.1 (1.7)	69.9 (1.5)	2.7 (0.2)

Number in parentheses represents the variability as standard deviation. [#] Sum of ethyl benzene and structural isomers of xylene

[a] Kim et al. (2001) (Measurements reported in μgm^{-3} are converted to ppb at reported temperature and pressure), [b] Chan et al. (2002) (Measurements reported in μgm^{-3} are converted to ppb at normal temperature and pressure), [c] Barletta et al. (2002), [d] Khoder (2007), [e] Hoque et al. (2008), [f] This Study (Number in the parentheses in the current study represents the measurement uncertainty as standard deviation)

4.3.4 VOC emission factors from the wheat straw fire plume and comparison with controlled laboratory fire experiments and field measurements

Previous laboratory and field measurements (Yokelson et al., 1999; Akagi et al., 2011; Stockwell et al., 2015; Yokelson et al., 2013; Inomata et al., 2015; Xinghua et al., 2009; Kudo et al., 2014), have shown that the VOC emission factors (g of VOC emitted per kg of fuel burnt) from biomass fires depends on the combustion efficiency of the fire. Hence we determined the modified combustion efficiency (MCE) using CO and CO_2 measurements in our grab sample using Equation (4.1) (Akagi et al., 2011; Yokelson et al., 1999).

$$\mathrm{MCE} = \frac{\Delta \mathrm{CO_2}}{(\Delta \mathrm{CO_2} + \Delta \mathrm{CO})} \quad (4.1)$$

Where in, $\triangle CO_2$ and $\triangle CO$ is the difference between concentrations measured in the plume and the background air (i.e. ambient air before the fire was lit). The value of MCE for the fire plume sample was 0.99 which corresponds to flaming combustion (Akagi et al., 2011; Stockwell et al., 2015).

Table 4.3 summarizes the results of the VOC emission factors (EF, g/kg) for each of the thirteen VOCs, which was determined for the grab sample, using a carbon mass balance method proposed in previous works and represented by Equation (4.2) (Yokelson et al., 1999;Yokelson et al., 2013).

$$\mathrm{EF_X}\left(\frac{\mathrm{g}}{\mathrm{kg}}\right) = \mathrm{F_c} \times 1000\ \left(\frac{\mathrm{g}}{\mathrm{kg}}\right) \times \frac{\mathrm{MM_X(g)}}{\mathrm{MM_C(g)}} \times \frac{\mathrm{C_X}}{\mathrm{C_{total}}} \quad (4.2)$$

Where F_c is the mass fraction of carbon in the fuel taken as 0.5 for the present case (Inomata et al., 2015; Akagi et al., 2011; Stockwell et al., 2015), MM_X is the molar mass of the compound X, MM_C is the molar mass of carbon (12.01 $\mathrm{gmol^{-1}}$), C_X is the number of emitted moles of X and C_{total} is the total number of moles of carbon emitted. C_X and C_{total} were calculated using Equation (4.3) and (4.4) respectively (Yokelson et al., 1999; Akagi et al., 2011; Andreae and Merlet, 2001).

$$\mathrm{C_X} = \frac{\mathrm{X_{(p)}} - \mathrm{X_{(b)}}}{\mathrm{CO_{2(p)}} - \mathrm{CO_{2(b)}}} \quad (4.3)$$

$$\mathrm{C_{total}} = \sum \left(\mathrm{nC_Y} \times \frac{\mathrm{Y_{(p)}} - \mathrm{Y_{(b)}}}{\mathrm{CO_{2(p)}} - \mathrm{CO_{2(b)}}}\right) \quad (4.4)$$

Where $X_{(p)}$, and $CO_{2(p)}$ are the measured concentrations of compounds X and CO_2 in the fire plume and $X_{(b)}$ and $CO_{2(b)}$ are the measured concentrations of compounds X and CO_2 in background air (before the burning started), respectively. Y represents carbon containing compounds including CO_2, CH_4 and CO, nC_Y is the number of carbon atoms for the corresponding compound Y, and $Y_{(p)}$ and $Y_{(b)}$ are the measured plume and background air concentrations.

The emission factors for methanol, acetonitrile, acetaldehyde, acetone, DMS, isoprene + furan, MVK, MEK, benzene, toluene, sum of C8-aromatics, sum of C9-aromatics and monoterpenes were: 0.20 (± 0.13), 0.02 (± 0.01), 0.17 (± 0.11), 0.07 (± 0.04), 0.01 (± 0.01), 0.09 (±0.01), 0.04 (± 0.03), 0.05 (± 0.04), 0.05 (± 0.03), 0.03 (± 0.02), 0.02 (± 0.01), 0.01 (± 0.004) 0.002 (±0.001) g/kg, respectively. Numbers in the parentheses represent the total uncertainty calculated using the root mean square error propagation of the individual uncertainties. In Table 4.3 I also compared emission factors for each of the 13 VOCs with values reported in previous wheat straw fire emission studies comprising of controlled laboratory fire experiments conducted by Inomata et al. (2015) and Stockwell et al. (2015) and field measurements reported in the work of Kudo et al. (2014) and Xinghua et al. (2009), For the comparison I only considered the fires which had MCE corresponding to flaming combustion. Note that the emission factors for methanol, acetonitrile, acetaldehyde, acetone, isoprene/furan, MVK and MEK obtained for our grab sample were comparable to emission factors reported in the previous studies (Stockwell et al., 2015; Kudo et al., 2014; Inomata et al., 2015). Emission factors of aromatics reported in our study were 2-9 times lower than the values reported in these studies, which could be due to variability in the chemical composition of the wheat straw. Based on the sampling of a single fire, it would be improper to conclude that wheat straw fires in the agricultural fields of northwest India are associated with lower emission factors for aromatics. Nevertheless, the first field applications of the glass flasks demonstrate the suitability of the samplers for use in ambient VOC speciation and emission factor studies and can help improve VOC speciation and emission factor data from pyrogenic sources in regions where deployment of online instrumentation such as proton transfer reaction mass spectrometers is infeasible due to practical constraints.

Table 4.3. Emission factors (g/kg) of thirteen VOCs from grab sample of the wheat straw fire plume compared to emissions factors reported in previous studies

Emission factor (g/kg)	This work Wheat straw[a]	Literature Wheat straw[b]	Literature Wheat straw[c]	Literature Wheat straw[d]	Literature Wheat straw[e]
MCE	0.99	0.97	0.99	0.95	
Methanol	0.20 (0.13)	0.30 (0.30)		0.48 (0.23)	
Acetonitrile	0.02 (0.01)	0.06 (0.05)	0.01	0.05 (0.02)	
Acetaldehyde	0.17 (0.11)	0.30 (0.20)	0.19	0.60 (0.32)	
Acetone	0.07 (0.04)^	0.20 (0.10)^	0.24	0.21 (0.10)	
Dimethylsulfide	0.01 (0.01)				
Isoprene	0.09 (0.06)[#]	0.08 (0.07)[#]	0.08	0.14 (0.05)	0.05 (0.02)
Methyl vinyl ketone	0.04 (0.03)[*]	0.11 (0.08)[*]	0.06	0.14 (0.07)	
Methyl ethyl ketone	0.05 (0.04)[@]	0.16 (0.10)[@]	0.05	0.15 (0.05)	
Benzene	0.05 (0.03)	0.25 (0.10)	0.09 (0.02)	0.14 (0.04)	0.31 (0.08)
Toluene	0.03 (0.02)	0.11 (0.01)	0.16 (0.04)	0.08 (0.04)	0.14 (0.06)
Sum of C8-aromatics	0.02 (0.01)	0.05	0.18 (0.05)	0.05 (0.01)	0.09 (0.05)
Sum of C9-aromatics	0.01 (0.004)	0.02	0.03 (0.02)	0.02 (0.01)	0.06 (0.04)
Monoterpenes	0.002 (0.001)			0.02 (0.01)	

The values in parentheses are the range of data (+/- errors)., [a]Number in the parentheses in the current study represents the measurement uncertainty as standard deviation, [b]Inomata et al. (2015), [c]Kudo et al. (2014), [d]Stockwell et al. (2015), [e]Xinghua et al. (2009), ^ Emission factor of acetone + propanal, [#]Emission factor of isoprene + furan, [*]Emission factor of methyl vinyl ketone + methacrolein, [@]Emission factor of methyl ethyl ketone + methylglyoxal + butanal

4.4 Conclusion

In conclusion, this study has validated and demonstrated the suitability of low cost glass flask samplers for use in ambient VOC speciation and emission factor studies to carry out measurements of acetonitrile, acetaldehyde, acetone, DMS, isoprene, MVK, MEK, benzene, toluene, sum of C8-aromatic, sum of C9-aromatics and monoterpenes, using laboratory and ambient field experiments. Experiments and statistical tests to assess stability of VOCs during storage showed that acetonitrile, acetone, dimethyl sulphide, methyl vinyl and methyl ethyl ketones, benzene, xylenes, trimethylbenzenes and monoterpenes can be quantified reproducibly within the respective precision errors between collection and storage (at > 95% confidence), for samples analyzed within 10 days of collection. For toluene and isoprene, similar results were obtained until day 9 and 1, respectively and at confidence >70%, over the 10 day period. Results from two ambient field tests appeared reasonable. Hence, the use of the low cost VOC glass flask samplers affords the opportunity to significantly advance understanding regarding the spatial and temporal distributions of these ambient VOCs as well as determination of their emission factors in field studies. This will help improve regional VOC emission inventories and can extend the possibilities for generic VOC head space sampling studies in food flavour, process monitoring and breath gas analyses investigations, which are currently dependent on availability of online instrumentation.

Chapter 5

Odd-even traffic rule implementation during winter 2016 in Delhi did not reduce traffic emissions of VOCs, carbon dioxide, methane and carbon monoxide

Abstract*

I investigated the impact of the odd-even traffic rule (implemented in Delhi during 1-15 January 2016) on primary traffic emissions using measurements of thirteen VOCs, carbon monoxide, carbon dioxide and methane at a strategic arterial road in Delhi (28.57°N, 77.11°E, 220 a.m.s.l). Whole air samples (n=27) were collected during odd-even rule active (OA) and inactive (OI) days and analyzed at the IISER Mohali atmospheric chemistry facility. The average mass concentration ranking and the toluene/benzene (T/B) ratios were characteristic of primary traffic emissions in both OA and OI samples, with the largest fraction comprising of aromatic compounds (55-70% of total). Statistical tests showed likely increase ($p \leq 0.16$; OA> OI) in median concentrations of 13 of 16 measured gases during morning and afternoon periods (sampling hours: 07:00-08:00 and 13:30-14:30 I.S.T.), whereas no significant difference was observed for evening samples (sampling hour: 19:00-20:00 I.S.T). This suggests that many four-wheeler users chose to commute earlier, to beat the 8:00 AM-8:00 PM restrictions and/or there was an increase in the number of exempted public transport vehicles. Thus, the odd-even rule did not result in anticipated traffic emission reductions in January 2016, likely due to the changed temporal and fleet emission behavior triggered in response to the regulation.

***Note:** Results presented in this chapter have already been published as first author and follow as "*Chandra, B.P., Sinha, V, H. Hakkim, H., Kumar, A., Pawar, H., A. Mishra, A. K., Sharma, G., Pallavi., Garg,S., Ghude, S. D., Chate, D. M., Pithani,P., Kulkarni,R., Jenamani, R. K and Rajeevan, M., Odd-even traffic rule implementation during winter 2016 in Delhi did not reduce traffic emissions of VOCs, carbon dioxide, methane and carbon monoxide, Current Science (in press).*

5.1 Introduction

Delhi is the world's second most populous megacity containing 25 million inhabitants (United Nations, 2014). Rapid urbanization and increased use of motorized vehicles are among the major factors attributed for its increasing air pollution (Nagpure et al., 2014; Guttikunda and Calori, 2013; Sindhwani and Goyal, 2014).

Delhi has the highest number of personal vehicles in India, with a total registered fleet of 2.9 million cars/jeeps and 6.1 million two-wheeler motor vehicles which alone contributed to 93% of total registered vehicles (circa 9.7 million), as on March 31, 2016 (DES, 2016). From 2011 onwards, every year on an average about 150,000 cars/jeeps and 300,000 two-wheelers were registered (DES, 2016). Concurrently, in recent times Delhi has experienced several air pollution episodes in which criteria air pollutants exceeded both Indian regulatory and World Health Organization (WHO) standards for considerable periods (WHO, 2016). In the past decade, significant initiatives such as conversion of 3-wheelers and the bus fleet from petrol and diesel to compressed natural gas (CNG), construction of a 180 km metro rail system and fly-overs improved the air quality of Delhi (Goel and Guttikunda, 2015; Beig et al., 2013), but the benefits were rapidly lost with the overall increase in number of vehicles and other urban emission sources.

Inspired by various road-use rationing schemes implemented in megacities such as Mexico city (Davis et al., 2008), Beijing (Tan et al., 2016) and Sao Paulo (Mahendra, 2008), as a measure against the severe wintertime air pollution in 2016, the State Government of Delhi implemented the odd-even rule on a trial basis for a period of 15 days from 1 to 15 January 2016. The rule (Sipilä et al., 2010) entailed, that during the 15 day trial period, only odd license-plate private four wheelers/cars could ply between 08:00 and 20:00 hours local time on odd days and only even license-plate numbered private four wheelers/cars could ply on even days. It is worth noting that public transport buses, two wheelers, trucks, CNG operated passenger cars and three wheelers were exempted from the rule. All schools in Delhi were closed during the period, with school buses enlisted for enhancing the exempted public transport fleet. The rule was also not applicable on Sundays.

Using the data obtained from the Central Pollution Control Board (CPCB) monitoring stations in Delhi, some studies (Goyal and Gandhi, 2016; Singhania et al., 2016; Pavani and Aryasri, 2016) investigated the impact of this rule on ambient concentrations of nitrogen oxides (NO_x), sulphur dioxide (SO_2), ozone (O_3) and particulate matter (PM_{10} and $PM_{2.5}$). However, as none of these air pollutants are unique and strong chemical tracers for traffic emissions, and the ambient chemical composition at monitoring stations were controlled by mixed emission sources, rather than primary traffic emissions, the question of whether traffic emissions had reduced as a result of the odd-even rule could not be addressed conclusively. In fact, contradictory surmises (Goyal and Gandhi, 2016; Singhania et al., 2016; Pavani and Aryasri, 2016) were presented concerning the impact of the odd-even rule on reduction of traffic emissions and air pollution within Delhi.

Volatile organic compounds (VOCs) are better suited as chemical tracers compared to criteria air pollutants such as sulphur dioxide (SO_2), ozone (O_3) and particulate matter (PM_{10} and $PM_{2.5}$), for constraining a variety of emission sources due to their shorter chemical lifetimes and better specificity as tracers of different types of emission activity and processes. Thus, VOCs such as toluene, sum of xylenes and ethylbenzene isomers are excellent tracers of auto-mobile exhaust emissions (Henze et al., 2008; Singh et al., 1985) and have been used as traffic emission tracers in numerous cities (Parrish et al., 2009; Baker et al., 2008). Additionally, these VOCs play a significant role in the formation of fine mode aerosol particles (PM_1) through photochemical reactions involving ambient hydroxyl radicals, and can have serious health effects, when present at concentrations exceeding several tens of ppb (Li et al., 2009). Acetonitrile is a good tracer of biomass burning plumes (Holzinger et al., 1999), oxygenated VOCs such as acetaldehyde, acetone, methyl vinyl ketone (MVK) and methyl ethyl ketone (MEK) have strong photochemical sources (Mellouki et al., 2015) while daytime isoprene is a good tracer for biogenic emissions (Guenther et al., 2006). Note that all the non-aromatic VOCs (except methane) are present in lower concentrations relative to aromatic compounds in vehicular tail pipe exhaust emissions (Borbon et al., 2001; Holzinger et al., 2001; Ban-Weiss et al., 2008).

The objective of this study was to assess the impact of the odd-even rule implemented in Delhi during January 2016 on primary traffic emissions. Whole air samples were collected in pre-treated glass flasks at the Indian Oil Corporation Limited (IOCL) arterial road so as to sample primary traffic emissions during odd-even rule active (OA) and inactive (OI) periods. A total of twenty seven ambient whole air samples were collected in the morning (07:00-08:00 IST), afternoon (13:30-14:30 IST) and night (19:00- 20:00 IST) during periods when odd-even rule was active (1, 2, 4, 11, 12 and 13 January 2016) and inactive (31 December 2015 and 20-21 January 2016), respectively. Thirteen volatile organic compounds including toluene and carbon dioxide, methane and carbon monoxide were analyzed in the whole air samples at the IISER Mohali atmospheric chemistry facility (Sinha et al., 2014; Sarkar et al., 2013). Data for odd-even active and inactive periods were subjected to the Mann-Whitney U test for assessing statistically significant differences, if any. Moreover, the total VOC, carbon monoxide, methane and carbon dioxide mass concentrations and observed ambient variability were used to assess variance in the traffic emission intensity between the odd-even active and inactive periods.

5.2 Experimental

5.2.1 Site description and meteorology

All the whole air samples were collected in specially conditioned glass flasks at the Indian Oil Corporation Limited (IOCL) arterial road (28.57°N, 77.11°E, 220 a.m.s.l). This road is a strategic arterial road which connects the residential colonies of Dwarka, the commercial and business centres of the Sadar Bazar in central Delhi, the sub-urban residential colonies of Palam in south west Delhi and the New Delhi international airport. A mixed fleet of 35,000 to 40,000 diesel, petrol and gasoline powered vehicles have been reported to ply through this road during peak traffic hours (Basu, 23 February 2013, New Delhi). Figure 5.1 (a) and 5.1 (b) show the location of the site on the map of Delhi (plotted using Pan Map GIS software). The red marker depicts the sampling site whereas the yellow and green markers show central Delhi and Dwarka, respectively. The land use in the vicinity of the measurement site is shown in Figure 5.1 (b), as a zoomed Google Earth image obtained on 14 September 2015;13:55 Indian Standard Time (IST). As can be seen there are no large industrial point sources in the vicinity. Hence, the site presented a suitable option for investigating the impact of the odd-even rule on primary traffic emissions.

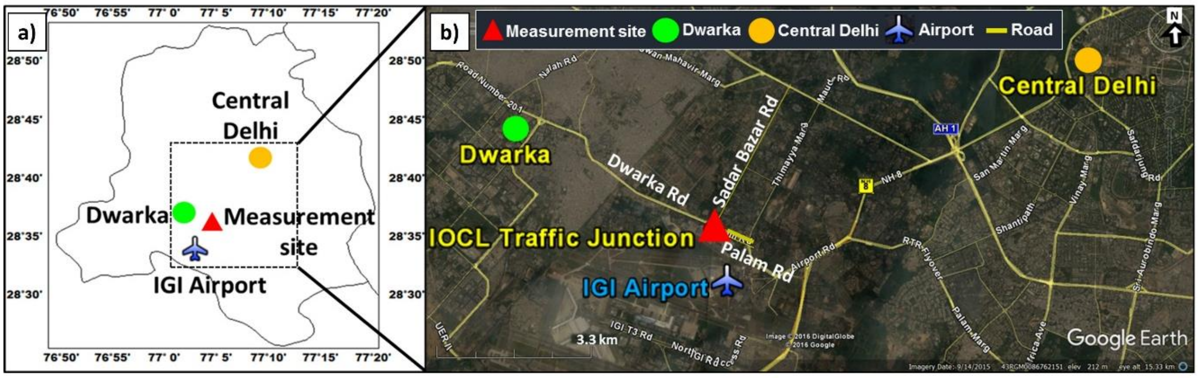


Figure 5.1. a) Map of the Delhi showing sampling location (red marker), airport (blue marker), Dwarka (green marker) and Central Delhi (yellow marker). b) Google Earth image (obtained on 14 September 2015 13:55 IST) showing zoomed view of the land use in the vicinity of the measurement site (IOCL traffic junction, Dwarka road, New Delhi).

Measurements of meteorological parameters were available at 10 m above the ground from a tower at the Indira Gandhi International airport (Ghude et al., 2017) which was 1.7 km away from our sampling site. Table 5.1 summarizes the average ambient temperature (ºC) and relative humidity (%) measured during the respective morning, afternoon and night sampling hours during both the odd-even rule active (OA) and inactive (OI) periods. Higher afternoon (by 30%) and nighttime (by 25%) average ambient temperatures were observed during odd even active (OA) relative to odod-even inactive (OI) periods. This suggests a higher mixed layer depth and stronger dilution effect at the sampling site, when the odd-even rule was in place.

Table 5.1. Average ± 1σ ambient variability of ambient temperature and relative humidity during the periods when odd rule was active (OA) (1, 2, 4, 11, 12 and 13 January 2016) and inactive (OI) 31 December 2015, 20 and 21 January 2016).

Met parameters	Morning (7:00-8:00 IST)		Afternoon (13:30-14:30 IST)		Night (19:00-20:00 IST)	
	Active (OA)	Inactive (OI)	Active (OA)	Inactive (IA)	Active (OA)	Inactive (IA)
Temperature (ºC)	12.6 ± 1.2	9.8 ± 1.1	22.2 ± 1.1	16.7 ± 4.5	18.1 ± 1.3	14.5 ± 3.9
Relative humidity (%)	72.4 ± 5.3	78.9 ± 4.9	36.2 ± 6.3	46.3 ± 17.4	54.6 ± 10.7	57.3 ± 16.4

5.2.2 Sampling and analyses of VOCs using PTR-MS, GHGs using CRDS and CO using a non-dispersive filter correlation IR spectrometer at the IISER Mohali atmospheric chemistry facility

A total of twenty seven ambient whole air samples were collected in the morning (7:00-8:00 IST), afternoon (13:30-14:30 IST) and night (19:00- 20:00 IST) during periods when the odd-even rule was active (1, 2, 4, 11, 12 and 13 January 2016) and inactive (31 December 2015 and 20-21 January 2016), respectively. Care was taken to ensure that the sampling was not biased by singular vehicles and direct tail pipe emissions. This was done by sampling at a height of 1.5 m above the road on the divider and at a spot where vehicles were not allowed to stop at all.

The sample collection time was about 2 minutes and in our experience during this time, at least 15-20 vehicles passed by the collection point. Thus, the samples we collected represent the emission signature of at least 15-20 vehicles and would not be biased by emission signatures of just one or two vehicles.

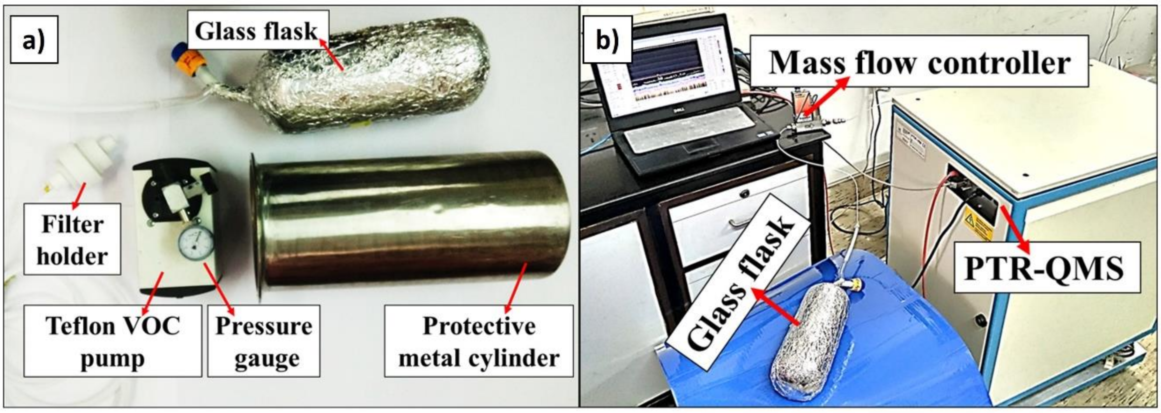


Figure 5.2. a) Picture of the equipment employed for the whole air sample collection using custom-made borosilicate glass flask. b) Picture of VOC analysis set up for measuring VOCs from collected whole air samples in the glass flask using PTR-QMS.

Figure 5.2 (a) shows a picture of the equipment employed for whole air sample collection, namely a 2L customized borosilicate glass flask (Vensil Glass Works Limited, Bangalore, India), Teflon sample inlet tubing (9.5 mm o.d.) with inline Teflon filter holder, and a Teflon VOC pump (Model - N 86 104 KT.45.18; KNF pump), equipped with a pressure control valve. Prior to the collection of ambient whole air samples on-site, the glass flasks were cleansed and conditioned using the following protocol: (1) the flasks were cleaned with chromic acid to remove sticky organic material and rinsed with de-ionized water, (2) the flasks were then heated in an oven (Model -1210D/8; Jain Scientific Glass works, India) for 8 hours at 180^{o}C, (3) thereafter, the flasks were filled with VOC free zero air (~2 bar) produced using a Gas Calibration Unit (GCU-A, Ionimed Analytik) (Kumar and Sinha, 2014) and evacuatedand refilled (~300 mbar) atleast thrice, to remove potential residual effects, (4) finally the flasks were sheathed with aluminium foil to shield them from ambient radiation. The application of glass flasks for whole air grab sampling of VOCs including storage stability of C2-C7 hydrocarbons, benzene and toluene has previously been validated (Pollmann et al., 2008; Chandra et al., 2017).

During sample collection, the air was sampled actively into the pre-treated glass flask using the Teflon VOC sampling pump and the glass flasks were pressurized only up to 2 bar. The sampling inlet was protected from floating dust and ambient particles using a Teflon membrane filter (pore size 0.45µm). Once the desired pressure was reached, the Teflon screw on the flask was closed and the flask was stored in a dark container, until analysis within 5 days of sample collection at the IISER Mohali Atmospheric Chemistry Facility. A detailed technical description of this unique facility in India has been provided in previous works from our research group (Sinha et al., 2014; Sarkar et al., 2013; Chandra and Sinha, 2016). Hence, only a brief description is provided here.

Figure 5.2 (b) shows the analysis set up for VOC measurements from the glass flask using a high sensitivity Proton Transfer Reaction Quadrupole Mass Spectrometer (PTR-QMS; HS Model11-07HS-088; Ionicon Analytik Gesellschaft, Austria). Within the PTR-QMS, analyte molecules undergo very soft chemical ionization with hydronium ions $(H_3O)^+$, which are the primary reagent ions, and the protonated ions are separated using a quadrupole mass analyzer and detected using a secondary electron multiplier (Sarkar et al., 2013; Sinha et al., 2014). Each VOC was measured with a dwell time of 1s in selected ion-monitoring mode. The thirteen VOCs namely: methanol, acetonitrile, acetaldehyde, acetone, dimethyl sulphide (DMS), isoprene, methyl vinyl ketone (MVK), methyl ethyl ketone (MEK), benzene, toluene, sum of xylene and ethylbenzene isomers, sum of trimethylbenzene and propylbenzene isomers and the monoterpenes were detected at their respective protonated organic ions (MH^+): m/z 33, m/z 42, m/z 45, m/z 59, m/z 63, m/z 71, m/z 73, m/z 79, m/z 93, m/z 107, m/z 121 and m/z 137, respectively. These VOCs identifications are in keeping with extensive validation experiments performed in a variety of ecosystems and have been reviewed in detail previously (de Gouw and Warneke, 2007; Blake et al., 2009). Due to isobaric contributions of furan to the signal at m/z 69 and potential minor isobaric contributions to MVK and MEK, our measurements represent an upper limit for isoprene, MVK and MEK concentrations (Sinha et al., 2014; de Gouw and Warneke, 2007). The sample flow (~100 ml/min) from the glass flask was regulated using a mass flow controller (MFC: EL-FLOW; Bronkhorst high-tech; stated uncertainty 2%). Calibration experiments were performed on 2 December 2015 and 15 January 2016 to determine sensitivities, by dynamic dilution of a custom-ordered VOC gas standard (Apel-Riemer Environmental, Inc., Colorado, USA). The sensitivity factors (ncps/ppb) and measurement uncertainties for the aforementioned 13 VOCs were determined, according to the protocols detailed in our previous works (Kumar and Sinha 2014; Sinha et al., 2014; Chandra and Sinha, 2016). All mixing ratios so obtained were converted to the mass concentrations using the measured ambient temperatures and pressures relevant for the sample. The total measurement uncertainties were as follows: methanol, acetonitrile, acetaldehyde, acetone, benzene and toluene (< 15%) , acetonitrile, DMS, isoprene, MEK and MVK (< 20%) and for sum of xylenes and ethylbenzene isomers, sum of trimethylbenzenes and propylbenzene isomers and monoterpenes (< 25%). The limit of detection (2 σ noise while sampling VOC free air) ranged between 0.03–0.15 μg m^{-3} and was never an issue for any of the ambient air samples from Delhi. Carbon dioxide (CO_2) and methane (CH_4) were measured using a Cavity Ring Down Spectrometer (CRDS) (Model G2508, Picarro, Santa Clara, USA) whereas carbon monoxide (CO) was measured using a non-dispersive infrared (NDIR) filter correlation spectrometer (Thermo Fisher Scientific, Model No. 48i), as described in our previous work(Sarkar et al., 2013;Sinha et al., 2014). Calibration experiments were performed for the CRDS instrument by dynamic dilution of a gas standard mixture of CO_2 and CH_4 (Phoenix Gases Ltd., Navi Mumbai, India; traceable to NIST, USA) on 19 December 2015 and for the CO analyzer on 12 December 2015 and 19 January 2016 by dynamic dilution of a gas standard (Chemtron Science Laboratories Pvt. Ltd., Mumbai), respectively. The total uncertainty for the CO measurements was always below 6% and for the measurements of CO_2 and CH_4 was < 4 % in each case. The limit of detection for CO_2, CH_4 and CO was below 0.5 μg m^{-3}, 0.2 μg m^{-3} and 12 μg m^{-3}, respectively. Concentrations of CO_2 and CH_4 reported in this study were corrected for the dilution and broadening effect due to presence of water vapour (Rella et al., 2013).

5.3 Results and discussion

Figure 5.3 presents a summary of the average VOC fractional contributions to the total measured VOC mass concentration (μg m^{-3}) for the morning (7:00-8:00 IST), afternoon (13:30-14:30 IST) and nighttime (19:00-20:00 IST) during both the odd-even rule active (OA) and inactive (OI) periods. Also shown as red, blue and black histograms are the average measured mass concentrations (μg m^{-3}) of CO_2, CH_4 and CO, respectively. Vertical bars on the histograms represent the 1σ measurement uncertainty.

The average mass concentration ranking of measured species was characteristic of traffic plumes (Ho et al., 2009; Baudic et al., 2016; Barletta et al., 2002), the same in all the collected samples (n=27) are as follows: CO_2 (OA_{avg}= 997.8 mg m^{-3}; OI_{avg}= 930.7 mg m^{-3}) > CO (OA_{avg}= 3.9 mg m^{-3}; OI_{avg}= 4.2 mg m^{-3}) > CH_4 (OA_{avg}= 2.7 mg m^{-3}; OI_{avg}= 2.2 mg m^{-3}) > toluene (OA_{avg}= 90.7 μg m^{-3}; OI_{avg}= 71.3 μg m^{-3})> sum of xylenes and ethylbenzene isomers (OA_{avg}= 77.6 μg m^{-3}; OI_{avg}= 61.6 μg m^{-3}) > sum of trimethylbenzenes and propylbenzene isomers (OA_{avg}= 45.5 μg m^{-3}; OI_{avg}= 36.3 μg m^{-3}) > methanol (OA_{avg}= 56.3 μg m^{-3}; OI_{avg}= 40.1 μg m^{-3}) > benzene (OA_{avg}= 40.0 μg m^{-3}; OI_{avg}= 34.3 μg m^{-3}) > acetone (OA_{avg}= 30.4 μg m^{-3}; OI_{avg}= 22.6 μg m^{-3} > acetaldehyde (OA_{avg}= 30.4 μg m^{-3}; OI_{avg}= 22.6 μg m^{-3}) > sum of isoprene and furan (OA_{avg}= 16.7 μg m^{-3}; OI_{avg}= 12.0 μg m^{-3}) > methyl ethyl ketone (OA_{avg}= 9.8 μg m^{-3}; OI_{avg}= 6.2 μg m^{-3}) > methyl vinyl ketone (OA_{avg}= 7.9 μg m^{-3}; OI_{avg}= 5.6 μg m^{-3}) > acetonitrile (OA_{avg}= 4.0 μg m^{-}

^{3}; OI_{avg}= 3.0 µg m^{-3}) > monoterpenes (OA_{avg}= 2.5 µg m^{-3}; OI_{avg}= 1.7 µg m^{-3}) > dimethyl sulphide (OA_{avg}= 1.2 µg m^{-3}; OI_{avg}= 1.1 µg m^{-3}).

The total fraction of measured aromatic mass concentrations (105.0-351.6 µg m^{-3}; sum of benzene, toluene, sum of xylenes and ethylbenzene isomers and sum of trimethylbenzenes and propylbenzene isomers) accounted for 55-70% of the total measured VOC mass concentrations in all samples. It is worth mentioning that in ambient surface air at sites where the chemical composition is not controlled by primary traffic emissions, the sum of oxygenated VOCs such as methanol, acetaldehyde, acetone, methyl vinyl ketone, methyl ethyl ketone typically exceeds the sum of the concentrations of aromatic compounds such as benzene, toluene, sum of xylenes and ethylbenzene isomers and sum of trimethylbenzenes and propylbenzene isomers as reported in previous studies (Sinha et al., 2014; Sarkar et al., 2016). Toluene and alkyl benzenes are major constituents of auto-mobile exhaust (Henze et al., 2008; Singh et al., 1985), in part because of the use of such compounds and their derivatives as additives that improve the fuel octane rating and anti-knock properties.

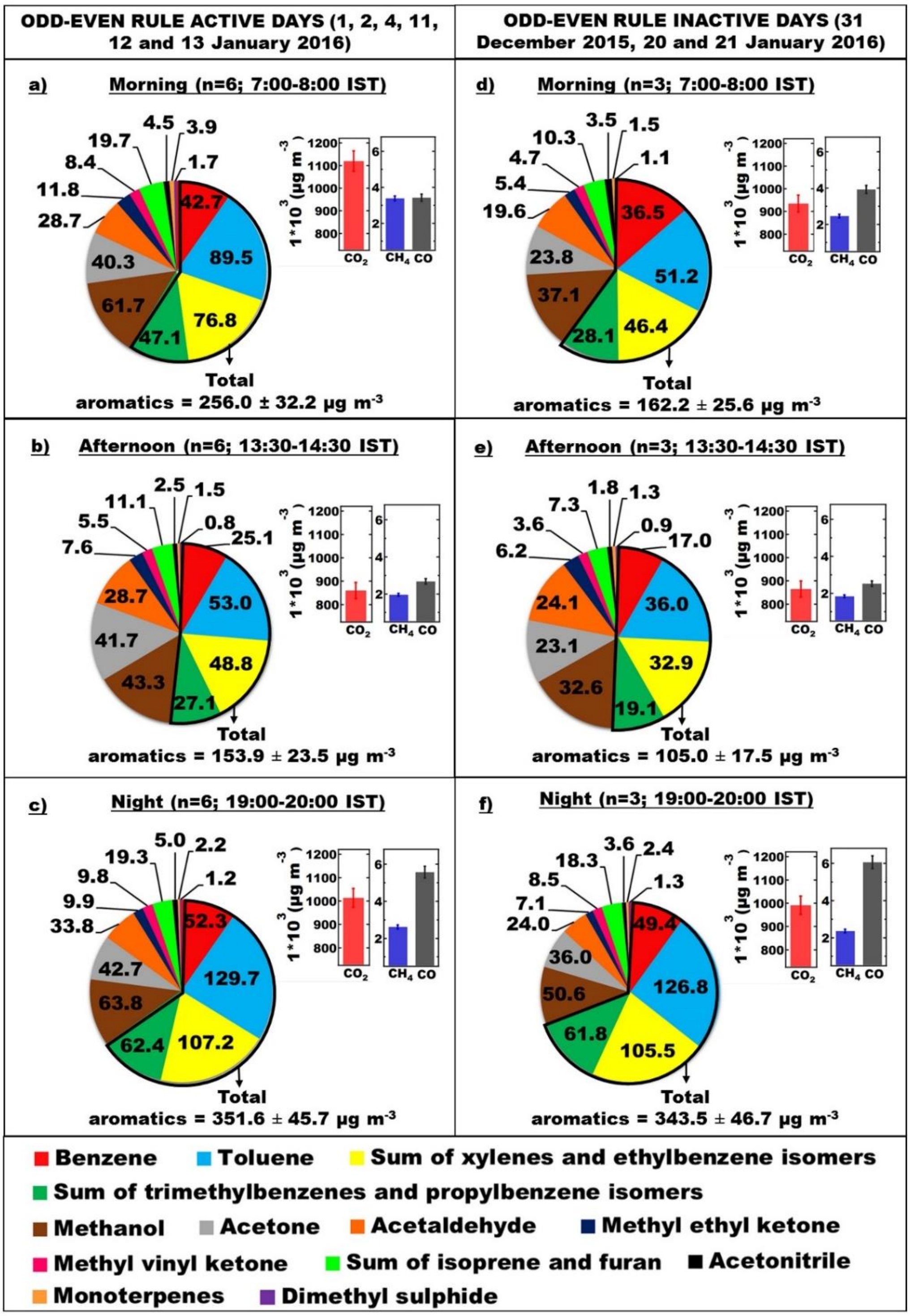


Figure 5.3. Pie charts (a-f) show VOC speciation during odd-even rule active days and odd-even rule inactive days derived from the measurements (n) at IOCL traffic thorough fare, New Delhi. Each fraction in each pie chart represents their respective averaged measured VOC mass concentration (µg m^{-3}). Highlighted fraction of each pie chart with the black line shows the total fraction of measured aromatic mass concentrations in the total measured VOC mass concentration in µg m^{-3} ± 1 standard deviation (total measurement uncertainty). Inserted red, blue and black histograms in each pie chart (a-f) are the averaged measured mass concentration

of carbon dioxide, methane and carbon monoxide respectively. Vertical bars on each histogram represents the total measurement uncertainty as standard deviation.

Table 5.2. Comparison of average benzene, toluene and sum of xylene and ethyl benzene isomers concentrations (μg m^{-3}) and the average ratio of toluene to benzene measured at sampling site (28.57°N, 77.11°E, 220 a.m.s.l) with road-side measurements at selected sites elsewhere in the world.

Location	Benzene (B)	Toluene (T)	Sum of xylenes and ethylbenzene isomers	Average T/B ratio
Birmingham, UK[a]	49.6	108.1	69.5	2.2
Algiers, Algeria[b]	27.1	39.2	33.1	1.5
Kolkata, India[c]	30.8	52.1	48.5	1.7
Delhi (Connaught Place), India[d]	97	180	144	1.9
Delhi (Okhla), India[d]	89	204	118	2.3
Delhi (AIIMS), India[d]	110	191	155	1.7
Delhi (IOCL traffic junction), India[e]	38.1	84.3	72.3	2.2

[a]Kim et al., (2001), [b]Kerbachi et al., (2006), [c]Som et al., (2007), [d]Hoque et al., (2008), [e]This study

Table 5.2 shows a comparison of the average concentrations (μg m^{-3}) acquired in the present study for benzene, toluene and the sum of xylenes and ethylbenzene isomers and their concentration ranking (toluene > sum of xylenes and ethylbenzene isomers > benzene) with traffic sites in UK (Kim et al., 2001) , Algeria (Kerbachi et al., 2006) and previous traffic emission studies in Kolkata (Som et al., 2012) and Delhi (Hoque et al., 2008). Direct comparison of the absolute VOC concentration values in different studies should be treated with caution as the type of fuel, traffic density and meteorological conditions can induce large variability, but toluene (T) to benzene (B) (T/B) concentration ratios are better indicators for characterizing traffic plume signatures. Note that the (T/B) concentration ratios greater than 1 are characteristic of traffic emission ratios, and considering ambient variability of individual datasets (T/B=2.7 ± 0.2 during OA and T/B= 2.1 ± 0.8 during OI), comparable to the T/B ratios reported from traffic plumes in Birmingham, UK (2.2) (Kim et al., 2001); Algiers, Algeria (1.5) (Kerbachi et al., 2006); Kolkatta (1.7) (Som et al., 2012); Connaught Place, Delhi (1.9) (Hoque et al., 2008); Okhla, Delhi (2.3) (Hoque et al., 2008); and AIIMS, Delhi (1.7) (Hoque et al., 2008).

The average morning mass concentrations in samples collected between 7 - 8 AM local time for all measured VOCs during the odd-even rule active periods (OA) was 436.6 ± 161.5 µg m^{-3} out of which aromatic compounds contributed 256.0 ± 32.2 µg m^{-3} (note numbers are: average ± 1 σ ambient variability). These are 1.6 times higher than the average of all measured VOCs during the odd-even rule inactive periods of 269.2 ± 124.3) µg m^{-3}. This suggests that a large number of personal vehicle users may have opted to commute before the traffic restrictions were put in place (odd-even rule enforcement timings were 8 AM - 8 PM). In the afternoon, during the odd-even rule active period, the measured average total mass concentrations of VOCs was 256.0 ± 32.2 µg m^{-3} while that of the total aromatic compounds was 153.9 ± 23.5 µg m^{-3}, which is about 1.4 times higher compared to corresponding odd-even inactive rule period values. Note that this is despite the odd-even rule active period being characterized by warmer afternoons and hence potentially higher mixed depth layer and dilution ($T_{avg,OA}$= 22.2 °C vs $T_{avg,IA}$ = 16.7 °C). Given the fact that during OA periods there was an overall increase reported in the number of vehicles that were exempt from the rule such as motorized two-wheelers (12%), three wheelers (12%), taxis (22%) and buses (138%) (Goyal and Gandhi, 2016), and the fact that two wheelers have higher emissions per unit than cars fitted with latest emission control technology (Sindhwani and Goyal, 2014; Goyal et al., 2013) the combination can explain the observed data. In the night-time, average measured mass concentrations of VOCs were comparable within the 1σ ambient variability range.

I further employed robust statistics (Mann-Whitney U) (Sheskin, 2011) to test for statistically significant differences if any at critical significance of 0.2, for the median concentrations of the measured VOCs and trace gases in samples collected during the odd-even rule active and inactive periods. The results are as under:

i) Median concentrations for morning samples were significantly higher (Confidence interval ≥84% or $p \leq 0.16$) during the odd-even rule active periods for all compounds except benzene, CO and acetonitrile. It is worth mentioning that neither benzene nor CO nor acetonitrile have traffic as their dominant source.

ii) Median concentrations for afternoon samples were also significantly higher (Confidence interval >90% or $p < 0.1$) during the odd-even rule active periods for all compounds except methane, methanol and dimethyl sulphide.

iii) Median concentrations for nighttime samples did not have statistically significant differences between OA and OI periods.

In view of the obtained experimental data and the statistical test results, I therefore conclude that the odd-even rule policy measure did not result in reduction of primary traffic emissions. Instead, it appears that there was an overall increase in traffic emissions, likely due to the changed temporal and fleet emission behavior triggered in response to the rule. We think two factors combined together can help explain the higher traffic emissions observed during the period when the odd-even rule was enforced. The first is that a large number of personal vehicle users appear to have opted to commute before the traffic restrictions were put in place (odd-even rule enforcement timings were 8 AM - 8 PM). Secondly, there was an overall increase reported in the number of vehicles that were exempt from the rule such as motorized two-wheelers, three wheelers, taxis and buses by 12-138 % (Goyal and Gandhi, 2016). The emissions from the increased fleet of exempt vehicles therefore appear to have offset the reduction of emissions accomplished by controlling personal four wheeler vehicles/cars. Study of tailpipe emission from different vehicular types by our group (Ashish et al., in prep.) show that total VOC emission especially aromatics from the two wheelers are about 300 times higher than the CNG fuelled 3 wheelers, taxis and buses. Also, note that the most of school buses which were used for public transportation during this OA period run on gasoline or diesel. Hence, the increment in 2 wheelers is significant enough to account for the higher VOC concentration observed during the OA period compared to IA period. Another point worth considering is that the odd-even rule may have resulted in traffic decongestion during peak hours which may certainly have benefitted commuters. However, with regard to this point, I submit that enhanced traffic emissions during times of the day when the dilution effect due to the atmospheric boundary layer is low (e.g. early morning before 8 AM and at night after sunset) could lead to higher peak concentrations of several health relevant carcinogenic VOCs such as benzene.

While several important insights have been gained by this study, as part of the future assessment studies, it would be advisable to design experiments deploying online measurements of the VOCs reported in this study at multiple strategic sites. Further, combining measurements of tail pipe emissions from key major vehicle types plying the roads along with information about the number and type of vehicles (e.g. through webcam recording at sampling point), would help provide more detailed information concerning the major emitters. Such an experimental design would also help address current uncertainties with regard to quantitative source apportionment of air pollutants in Delhi, similar to the manner demonstrated recently for the Kathmandu Valley (Sarkar et al., 2017) and enable air pollution mitigation efforts for multiple urban sources rather than just traffic emissions.

5.4 Conclusion

In conclusion, this study carried out using the measurements of thirteen unique and strong VOC chemical tracers including toluene, sum of xylenes and ethylbenzene isomers which are excellent tracers of auto-mobile exhaust emissions, along with carbon monoxide, carbon dioxide and methane at a strategic arterial road in Delhi shows that the odd-even rule implemented by Delhi state government on experimental basis did not result in reduction of primary traffic emissions. Moreover, statistical tests (Mann-Whitney U) showed likely increase in median concentrations of thirteen out of sixteen measured gases during odd-even rule active morning and afternoon periods at a confident interval ≥84% or $p \leq 0.16$, whereas no significant difference was observed for evening samples. This study reveals that the odd-even rule policy measure did not result in reduction of primary traffic emissions of VOCs and greenhouse gases. Instead there was an overall increase in traffic emissions, likely due to the changed temporal and fleet emission behavior triggered in response to the rule. Specifically, many private vehicle users affected by the restriction chose to commute to office before 8 A.M.to beat the rule, and the increase in the overall number of exempted vehicles on the road (e.g. public transport buses, two wheelers) overwhelmed whatever decrease in emissions was accomplished by restricting the private vehicles. Based on the key insights gained from this study, as part of the future experimental design it would be advisable to deploy online VOC measurements of the kind reported here at multiple strategic sites, combining measurements of tail pipe emissions from key major vehicle types plying the roads along with information about the number and type of vehicles (e.g. through webcam recording at sampling point). This would help address current uncertainties associated with respect to the quantitative source apportionment of air pollutants in Delhi, similar to the manner demonstrated recently for the Kathmandu Valley and enable to formulate better air pollution mitigation efforts for multiple urban sources rather than just traffic emissions.

Chapter 6

Conclusions: Summary and outlook

Every year during the post-paddy harvest paddy seasons of October and November, in the northwest Indo-Gangetic Plain (IGP) large scale agricultural burning of paddy residue takes place which results in large scale emissions of a multitude of gas and aerosol species. In the first study, using three years (2012-2014) of continuous online in-situ measurements performed during the pre and post paddy harvest seasons at a representative suburban site in the N.W.IGP, I demonstrated that open paddy residue fires are the major driver for the regional-scale ambient enhancements of isocyanic acid, benzenoids and carbon monoxide in the post-paddy harvest seasons. This study reports the first ever long term in-situ measurements of acetonitrile, benzene, toluene, C8 and C9 aromatics along with toxic isocyanic acid from the N.W. IGP, a molecule which has only recently been measured in ambient air studies. Factors considered in this analysis were: 1) satellite remote sensing data of fire counts, 2) the day to day and diel variability in ambient concentrations of benzenoids, isocyanic acid and CO and 3) correlation and emission ratios of benzenoids, isocyanic acid and CO with acetonitrile (a chemical maker compound for tracing biomass fires) and 4) measurements made at the area source. The daily average concentrations of acetonitrile, benzene, toluene, C8-aromatics, C9-aromatics, isocyanic acid and CO were higher in the post-harvest periods relative to the pre-harvest periods by factors of 1.5, 1.9, 1.8, 2.1, 1.8, 1.3 and 1.5, respectively. The annual exposure concentration to benzene, a human carcinogen exceeded the National Ambient Air Quality Standard (NAAQS: 1.6 ppb) stipulated by the Ministry of Environment, Forest and Climate Change (MOEF), India. I show that by mitigating paddy residue fire related emissions, the ambient concentration of benzene can be brought into compliance with the NAAQS. Cancer risk assessment due to the post-paddy harvest fire emissions of benzene reveal that there is a significant increase in the cancer risk to adults as well as children of 10 and 25 per million inhabitants, respectively, which exceeds the USEPA regulatory threshold of 1 per million inhabitants. Further, both annually averaged and average post-paddy harvest period ambient concentrations of isocyanic acid were close to 1 ppb, the concentration considered to be sufficient to enhance risks for cardiovascular diseases and cataracts through in-vivo protein de-carbamylation reactions in the human body. Note that the measurement site reported in this study is several kilometers downwind of the agricultural fields and therefore this study likely underestimates the cancer risk for the agricultural regions where the burning activity occurs. This study makes a case for urgent mitigation of post-harvest paddy residue fires as the unknown synergistic effect of multi-pollutant exposure due to emissions from this anthropogenic source may be posing grave health risks to the population of the N.W. IGP.

In the next study, to provide a solution for reducing the paucity of VOC datasets in remote and logistically challenging regions of the world where deployment of online instrumentation is not feasible due to practical constraints (power, safety issues), I developed an analytical method and protocol for offline collection of whole air VOC samples in re-useable low cost glass flask samplers (< 100 USD) which can then be analyzed without compromising sample integrity using proton transfer mass spectrometry. I assessed the stability of several VOCs, many of which are reactive and unstable in common samplers such as Tedlar bags. The thirteen VOCs namely methanol, acetaldehyde, acetone, dimethyl sulphide, methyl vinyl and methyl ethyl ketones, isoprene, toluene, benzene, acetonitrile, xylenes, trimethylbenzenes and monoterpenes were studied during storage inside the glass flasks over a 10 day period using both premixed gas standards at varied concentrations and in ambient air samples containing ozone and variable water vapour. Stability tests showed that 12 of the 13 VOCs can be quantified reproducibly within the respective precision errors between collection and storage (at > 70% confidence), if samples are analyzed within 10 days of collection. A storage artefact was observed for methanol resulting in higher analytical uncertainty of upto 40%. After the validation experiments, I employed the samplers in the field for (i) measurement of toluene/benzene ratios and aromatic VOCs in traffic plumes (a well constrained emission source) and (ii) determining emission factors (gVOC emitted/kg fuel burnt) of the thirteen VOCs in a flaming stage agricultural wheat straw fire plume in Punjab. Results from two ambient field tests appeared reasonable. Thus, these glass flask samplers can be used as a substitute for the more costly stainless canisters passivated with proprietary coatings and which cost upwards of 1300 USD a piece.

Finally, I assessed the impact of the odd-even rule implemented by Delhi state government for 15 days (1-15 January 2016) during the winter 2016 on experimental basis on primary traffic emissions. During this field experiment, I measured thirteen VOC chemical tracers including toluene, sum of xylenes and ethylbenzene isomers which are excellent tracers of auto-mobile exhaust emissions, along with CO, CO2 and CH4 at a strategic arterial road in Delhi during the odd-even active (OA: 1, 2, 4, 11, 12 and 13 January 2016) and inactive (OI: 31 December 2015 and 20-21 January 2016) periods. A total of twenty seven ambient whole air samples were collected in the morning (07:00-08:00 IST), afternoon (13:30-14:30 IST) and night (19:00-20:00 IST) were analysed at the IISER Mohali atmospheric chemistry facility within 5 days of collection. In all the samples the average mass concentration ranking and the toluene/benzene (T/B) ratios were characteristic of primary traffic emissions in both OA (T/B=2.7 ± 0.2) and OI (T/B= 2.1 ± 0.8) samples, with the largest fraction comprising of aromatic compounds (55-70%

of total). Statistical tests (Mann-Whitney U) showed likely increase in median concentrations of 13 out of 16 measured gases during odd-even rule active morning and afternoon periods at a confident interval ≥84% or $p \leq 0.16$, whereas no significant difference was observed for evening samples. This study reveals that the odd-even rule policy measure did not result in reduction of primary traffic emissions of VOCs and greenhouse gases. Instead there was an overall increase in traffic emissions, likely due to the changed temporal and fleet emission behavior triggered in response to the rule. Specifically, many personal four-wheeler users chose to commute early in the morning, to beat the 8:00 AM-8:00 PM restrictions, and overall increase reported in the number of vehicles that were exempt from the rule such as motorized two-wheelers, three wheelers, taxis and buses by 12-138% overwhelmed whatever decrease in emissions was accomplished by restricting the private four wheeler vehicles.

Based on key findings obtained from the study on impact of post-harvest agricultural paddy residue fires emissions in the northwest IGP presented in this thesis, future efforts should focus on the development of economically viable solutions and their enforcement/implementation to mitigate open paddy residue burning. It emphasis the need for mapping the spatio-temporal distribution of health relevant VOCs at sites in closer proximity to the agricultural fields and rural sites to get a more accurate assessment and need for future epidemiological studies to quantify the health risk effects due to chronic exposure to toxic isocyanic acid at such ambient high concentrations.

The use low cost glass flasks that were presented in this thesis work for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry affords the opportunity to significantly advance understanding regarding the spatial and temporal distributions of these ambient VOCs as well as determination of their emission factors in field studies. This will help improve regional VOC emission inventories and can extend the possibilities for generic VOC head space sampling studies in food flavour, process monitoring and breath gas analyses investigations, which are currently dependent on availability of online instrumentation

Further, based on the valuable insights gained from the odd-even case study findings presented in this thesis, as part of the future experimental design it would be advisable to deploy online VOC measurements of the kind reported here at multiple strategic sites, combining measurements of tail pipe emissions from key major vehicle types plying the roads along with information about the number and type of vehicles (e.g. through webcam recording at sampling point). This would help address current uncertainties associated with respect to the quantitative source apportionment of air pollutants in Delhi, similar to the manner demonstrated recently for the Kathmandu Valley (Sarkar et al., 2017) and enable to formulate better air pollution mitigation efforts for multiple urban sources rather than just traffic emissions.

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