Volatile organic compounds (VOCs) play a key role in atmospheric chemistry and air pollution due to their chemical reactivity and in several instances high toxicity (e.g. benzene is a human carcinogen). Measurements of VOCs are associated with several analytical challenges due to the low ambient concentrations (ppt – ppb) and variability of the sample matrix. In recent times, several urban and rural emission sources of VOCs such as agricultural crop residue burning and urban traffic emissions have intensified over the Indo-Gangetic Plain (IGP), affecting both air quality and climate at rural, urban and regional scales. Speciation of VOCs present in ambient air of this understudied region and understanding the role played by them in key atmospheric processes is thus of critical importance. To address these issues, I have investigated the emissions and chemistry of VOCs from agricultural and urban sources in north-west India through ambient measurements performed at Mohali and Delhi. I have also designed and validated an innovative low cost whole air glass flask sampler for offline VOC measurements. 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 the 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 season. 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). For all these compounds, average concentration enhanements in the post-paddy harvest periods were 1.3-2.1 times greater relative to the pre-harvest concentrations. I showed that by mitigating paddy residue fire generated emissions, the ambient concentration of benzene can be brought into compliance with the National Ambient Air Quality Standard of benzene (annual average: 1.6 ppb) at sites few kilometres downwind of the burning fields. Cancer risk assessment due to the post-paddy harvest fire emissions of benzene showed 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, annual exposure to isocyanic acid, a toxic gas similar to methyl isocyanate (the gas responsible for the Bhopal gas tragedy), was 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. 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. After the validation, I applied this method for measuring toluene/benzene emission ratios and aromatic VOCs in ambient traffic plumes, and for determining VOC emission factors (gVOC/kg fuel) from an agricultural wheat straw fire in Punjab. Such samplers can therefore 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 in Delhi during January 2016 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) and inactive (OI) periods. The average mass concentration ranking and the toluene/benzene 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 out of 16 measured gases during morning and afternoon periods, whereas no significant difference was observed for evening samples. This studt shows conclusively, 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 the restriction chose to drive 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.