Role of Volatile Organic Compounds and Trace Gases in the Chemistry of Rural Atmosphere

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PREFACE

*Volatile Organic Compounds (VOCs) measurements in tropical rural environments are very sparse and in urgent demand to better understand their role in tropospheric chemical processing. They serve as precursors for tropospheric ozone (O_3) and Secondary Organic Aerosol (SOA) formation, which are the direct indicators of the oxidative capacity specific to a given chemical environment. Many factors influence the oxidative capacity and it differs between urban and rural atmospheres. The present study investigates the oxidative capacity of the less explored tropical rural atmosphere Gadanki in southern peninsular India using VOC measurements and OH loss rates. The importance of VOC measurements emphasizing the tropospheric chemistry in the rural atmosphere has been discussed in **Chapter 1**. Continuous diel VOC measurements have been carried out using the GC-FID technique. The experiments conducted during this thesis have been elaborated in **Chapter 2**, including the details of the measurement site, surface meteorology, and instrumentation to measure VOCs and Trace Gases. The seasonal and diurnal variability of measured VOCs and source apportionment of the VOCs are explained in **Chapter 3**. A total of 31 potential ozone precursor VOCs have been measured. There is a strong seasonal and diurnal variability among the VOC composition. The day time peak and elevated concentration of biogenic VOCs are the distinct feature of rural atmosphere. The source apportionment using Positive Matrix Factorisation (PMF) analysis resulted in four potential emission source factors: biogenic, biomass burning, fossil fuel, and natural gas emissions. Further using the measured VOC data, the potentials for O_3 (OFP) and SOA formation (SOAP) along with the source contribution have been estimated in **Chapter 4**. The aromatic VOCs exhibit the highest OFP as compared to alkanes and alkenes. The increased presence of biogenic VOCs, likely due to increased vegetation cover, could account for the elevated OFP during post monsoon season. The long-chain alkanes show the highest SOAP as compared to alkenes and aromatic VOCs. The summer season has the highest SOAP,* *owing to the enhanced concentrations and photochemistry initiated by OH radicals. Within the sources, biomass-burning VOCs make a substantial contribution to both OFP and SOAP, distinguishing the rural atmosphere from its urban counterpart. Several factors influence the ozone formation, which include precursor concentrations, meteorological conditions, and transport. However, OFP and PEC do not involve these factors while assessing ozone formation. To overcome this limitation, ozone isopleths are used to study VOC /NO_X sensitivity. In* ***Chapter 5****, the site Gadanki has been identified as a NO_x-limited regime, using the ozone production regime indicator (Θ) value. Subsequently, efforts have been made to understand the role of VOC and NO_x concentrations, along with meteorological conditions and transport, in quantifying the seasonal variation of ozone formation in terms of VOC/NO_x sensitivity using Ozone Isopleth Plotting Package (OZIPR) model. The VOC cross-over points obtained from the ozone isopleth diagrams using the OZIPR model have shown a significant correlation between OFP and PEC values, supporting the variability in ozone formation in most of the seasons at the observational site. Additionally, the highest ozone concentration measured in the summer season is also well reproduced by the VOC cross-over correlations with the OFP and PEC values. The* ***Chapter 6*** *summarises the thesis by emphasizing the findings which are specific to rural chemical environment. The* ***Chapter 7*** *highlights the future scope of the work accompanied with more measurements and modelling techniques.*