

Open fires perturb atmospheric chemistry through direct emissions as well as photo-chemical transformation of precursor emissions to secondary gases and aerosol particles resulting in strong air quality and climate feedbacks. Further they can serve as both sources and sinks of ambient hydroxyl (OH) radicals, which control the oxidizing efficiency of the atmosphere and are responsible for removal of major climate active gases and pollutants. Similar to several regions of the world, the Indo-Gangetic Plain (IGP) is impacted by large scale open burning as a result of post harvest fires, periodic clearing of landfills through controlled burning and small diffused open fires lit for waste disposal and heating in winter. Research on this topic in this demographically important region of the world has however been limited to bulk analyses of aerosols, measurement of long-lived greenhouse gases including ozone and few light hydrocarbons (C₂-C₄ compounds), without adequate knowledge about all relevant volatile organic compounds (VOCs) and a process based mechanistic understanding of the total ambient chemical reactivity introduced due to such fires. This thesis work first delineates the seasonality, diurnal variability, reactivity and ozone production potential of a suite of twenty three ambient volatile organic compounds, carbon monoxide and nitrogen oxides through high temporal resolution in-situ measurements made every minute from August 2011-September 2013 using proton transfer reaction mass spectrometry. The role of meteorological and chemical drivers of key VOCs such as isoprene and acetaldehyde, and high ozone concentrations during summer and autumn seasons are then investigated in detail. It is shown that crop residue fires in the summer season drive a 29% enhancement of ambient ozone concentrations when highest daily ozone concentrations of the year are observed. Further, the 8 h national ambient ozone standard was exceeded 62% of the time over the 451 days study period. To assess what fraction of the compounds emitted from the fires are unknown and/or missing, I further carried out the first ambient field experiment of its kind worldwide to assess the reactivity and VOC budget of fire plumes through direct measurements of the total OH reactivity and all major OH reactants. For this purpose I had to develop and validate a new analytical technique christened VOC-OHM that could enable rapid sequential measurements of OH reactivity and VOCs using a single proton transfer reaction mass spectrometer (PTR-MS). Using direct OH reactivity measurements and supporting measurements of a suite of 42 gases present at ppt-ppb levels, I found that while the chemical composition of air could be almost fully explained by the measured and modelled photo-oxidation products during pre-harvest summertime conditions (missing fraction was 5%), there was a surprising 40 % increase in the missing OH reactivity due to presence of new/unmeasured compounds in the summertime post-harvest periods influenced by large scale open crop residue biomass fires. The large increase was accompanied by a greater than two-fold increase in total OH reactivity from 28 s⁻¹ to 64 s⁻¹ and correlated with rapid photochemical formation of rare compounds. Many of these compounds are missing from state of the art atmospheric chemistry models and the results of my thesis will help improve understanding of air quality and atmospheric chemistry in biomass fire impacted atmospheric environments worldwide.