Abstract

Volatile Organic compounds (VOCs) are important as they play a major role in the oxidation chemistry of the atmosphere leading to the formation of atmospheric pollutants such as ozone and secondary organic aerosols. Moreover certain VOCs such as benzene and formaldehyde have direct health impacts. In this study, ambient concentrations of VOCs such as methanol, acetone, acetonitrile, isoprene, acetaldehyde, toluene, benzene, sum of xylenes and sum of trimethyl benzenes were measured at ppt level sensitivity for the first time over any Indian site during the monsoon season from June-September 2013 in Mohali (30.6670N; 76.7290E; N.W. IGP). The measured average ± standard deviation for mixing ratios of the compounds for the entire season were: methanol (25.4 ± 11.5 nmol mol-1) > acetone (8.8 ± 7.1 nmol mol-1) > acetaldehyde (6.8 ± 4 nmol mol-1) > toluene (1.8 ± 1.5 nmol mol-1) > benzene (1.6± 3.2 nmol mol-1) > isoprene (1.4 ± 1.0 nmol mol-1) > acetonitrile (1± 0.9 nmol mol-1) > sum of xylenes (0.8 ± 0.8 nmol mol-1) > sum of trimethyl benzenes (0.6 ± 0.5 nmol mol-1) . The average mixing ratios of these VOCs were intercompared with summertime measurements from the same site conducted earlier in the year. The measured average ± standard deviation for mixing ratios during summer 2013 were : methanol (44.9 ± 25.6 nmol mol-1) > acetone (9.3 ± 12.9 nmol mol-1) > acetaldehyde (7.3 ± 3.9 nmol mol-1) > toluene (2.5 ± 2.5 nmol mol-1) > benzene (1.6 ± 1.5 nmol mol-1) > isoprene (1.6 + 0.8 nmol mol-1) > acetonitrile (0.97 ± 0.8 nmol mol-1) > sum of xylenes (1.9 ± 1.8 nmol mol-1) > sum of trimethyl benzenes (0.9 ± 1 nmol mol-1) One of the major factors responsible for the lower mixing ratios during monsoon and the summer season was the enhanced wet scavenging efficiency of VOCs during the monsoon. This was further investigated by elucidating individual factors governing the concentration of the species in monsoon season. In the case of a rain event, soluble species that exist below clouds dissolve into falling raindrops and are removed from the atmosphere depending on the rain event characteristics (rain intensity, raindrop size) and the species' physical and chemical properties. A high sensitivity proton transfer reaction quadrupole mass spectrometer (PTR-QMS), was used to quantify VOCs during periods when it rained and when it was dry. The collective impact of boundary layer dilution, photochemistry and change in emission sources on the ambient

concentrations of the VOCs were delineated using meteorological measurements to obtain the first field dataset derived wet scavenging ratios for the compounds. It was found that the values and trend in wet scavenging ratios for oxygenated VOCs and acetonitrile were: acetonitrile (2.87) > methanol (2.35)> acetone (2.26)> acetaldehyde (1.49) whereas for aromatics VOCs and isoprene it was: benzene (5.75)> toluene (5.73)> sum of xylenes (5.42)> trimethyl benzene (4.22) > isoprene (1.41). These results show that while solubility is a good proxy for parameterizing wet scavenging efficiency in atmospheric chemistry and transport models, simple use of solubility as a proxy would lead to large errors for compounds like methanol and other oxygenated VOCs in the daytime. Instead, the experimentally determined wet scavenging ratios from ambient field studies as showcased here would be a better way forward for parametrizing wet scavenging in atmospheric models.