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Title: Overview of VOC emissions and chemistry from PTR-TOF-MS measurements during the SusKat-

ABC campaign: high acetaldehyde, isoprene and isocyanic acid in wintertime air of the

Kathmandu Valley

Authors: Sarkar, C. (/jspui/browse?type=author&value=Sarkar%2C+C.)

Sinha, V. (/jspui/browse?type=author&value=Sinha%2C+V.)

Kumar, Vinod (/jspui/browse?type=author&value=Kumar%2C+Vinod)

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Abstract:

The Kathmandu Valley in Nepal suffers from severe wintertime air pollution. Volatile organic compounds (VOCs) are key constituents of air pollution, though their specific role in the valley is poorly understood due to insufficient data. During the SusKat-ABC (Sustainable Atmosphere for the Kathmandu Valley-Atmospheric Brown Clouds) field campaign conducted in Nepal in the winter of 2012-2013, a comprehensive study was carried out to characterise the chemical composition of ambient Kathmandu air, including the determination of speciated VOCs, by deploying a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS) - the first such deployment in South Asia. In the study, 71 ion peaks (for which measured ambient concentrations exceeded the 2σ detection limit) were detected in the PTR-TOF-MS mass scan data, highlighting the chemical complexity of ambient air in the valley. Of the 71 species, 37 were found to have campaign average concentrations greater than 200 ppt and were identified based on their spectral characteristics, ambient diel profiles and correlation with specific emission tracers as a result of the high mass resolution (m/ Δ m > 4200) and temporal resolution (1 min) of the PTR-TOF-MS. The concentration ranking in the average VOC mixing ratios during our wintertime deployment was acetaldehyde (8.8 ppb) > methanol (7.4 ppb) > acetone + propanal (4.2 ppb) > benzene (2.7 ppb) > toluene (1.5 ppb) > isoprene (1.1 ppb) > acetonitrile (1.1 ppb) > C8-aromatics $(\hat{g}1/4\ 1\ ppb) > furan (\hat{g}1/4\ 0.5\ ppb) > C9-aromatics (0.4\ ppb)$. Distinct diel profiles were observed for the nominal isobaric compounds isoprene (m/z=69.070) and furan (m/z=69.033). Comparison with wintertime measurements from several locations elsewhere in the world showed mixing ratios of acetaldehyde (~9 ppb), acetonitrile (~1 ppb) and isoprene (~1 ppb) to be among the highest reported to date. Two "new" ambient compounds, namely formamide (m/z=46.029) and acetamide (m/z=60.051), which can photochemically produce isocyanic acid in the atmosphere, are reported in this study along with nitromethane (a tracer for diesel exhaust), which has only recently been detected in ambient studies. Two distinct periods were selected during the campaign for detailed analysis: the first was associated with high wintertime emissions of biogenic isoprene and the second with elevated levels of ambient acetonitrile, benzene and isocyanic acid from biomass burning activities. Emissions from biomass burning and biomass co-fired brick kilns were found to be the dominant sources for compounds such as propyne, propene, benzene and propanenitrile, which correlated strongly with acetonitrile (r2 > 0.7), a chemical tracer for biomass burning. The calculated total VOC OH reactivity was dominated by acetaldehyde (24.0 %), isoprene (20.2 %) and propene (18.7 %), while oxygenated VOCs and isoprene collectively contributed to more than 68 % of the total ozone production potential. Based on known secondary organic aerosol (SOA) yields and measured ambient concentrations in the Kathmandu Valley, the relative SOA production potential of VOCs were benzene > naphthalene > toluene > xylenes > monoterpenes > trimethylbenzenes > styrene > isoprene. The first ambient measurements from any site in South Asia of compounds with significant health effects such as isocyanic acid, formamide, acetamide, naphthalene and nitromethane have been reported in this study. Our results suggest that mitigation of intense wintertime biomass burning activities, in particular point sources such biomass co-fired brick kilns, would be important to reduce the emission and formation of toxic VOCs (such as benzene and isocyanic acid) in the Kathmandu Valley.

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