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Title:	Investigation of Rarely Measured VOCs Emitted from Wheat Residue Fires in the Summer Time Air of N.W. Indo-Gangetic Plain
Authors:	Sohpaul, B. (/jspui/browse?type=author&value=Sohpaul%2C+B.)
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Abstract: Biomass burning is a significant source of reactive and toxic ambient volatile organic compounds. Every year, extensive wheat crop residue burning (> 5500 km²) occurs during the months of April-May in the North West Indo-Gangetic Plain (NW- IGP). The gases and particles emitted from such fires impact atmospheric chemical processes, the biosphere and human health (e.g. benzene, a human carcinogen, is emitted from such fires). Till date, there has been no study in NW-IGP quantifying the contribution of wheat residue burning on the ambient mixing ratios of volatile organic compounds. Here, using a high sensitivity proton-transfer reaction mass spectrometry we have quantified 27 different organic compounds ($n \geq 47504$ in pre-harvest and $n \geq 17260$ in post-harvest for each species), which were likely emitted (at a confidence interval of 99.99 %) from the regional post-harvest wheat residue fires. Out of 27 VOCs, 14 VOCs were reported for the first time over N.W. IGP and those newly reported VOCs are propyne, propene, formamide, formic acid, acrolein, methylketene, acetamide, acetic acid, nitromethane, hydroxyacetone, 2,3-butanedione, 2-furaldehyde, styrene and naphthalene. The measurements were performed at the IISER Mohali Atmospheric Chemistry Facility, a sub-urban site in the NW-IGP from February 2013 – May 2013, spanning both the pre and post wheat harvest periods. The post-harvest period was characterized by significantly high concentrations of acetonitrile (chemical marker for biomass burning), carcinogenic benzenoids, methanol, acetaldehyde, nitromethane, hydroxyacetone and other VOCs. The average mixing ratios (average $\pm 1\sigma$ ambient variability) of acetonitrile (1.35 ± 1.30 ppb) and 2,3-butanedione (2.35 ± 1.08 ppb) in post-harvest period were higher by a factor of 1.8 relative to pre-harvest period. Different VOC/acetonitrile emission ratios and high absolute concentrations during post-harvest period in comparison to pre-harvest period implies altered source signatures in post-harvest period with strong contribution from biomass fires. A new compound, i.e., 2,3-butanedione (most plausible identity for $m/z = 87$) was also detected and reported for the first time in ambient Indian air. It has both primary (wheat residue fires) and secondary sources (oxidation of trimethylbenzenes) and its major fate is photolysis resulting in formation of peroxyacetyl nitrate, an ingredient of urban smog. Major VOC emissions due to the post-harvest fires were constrained and ranked as follows: methanol (5.28 Gg)> acetone (1.53 Gg)> propene (0.75 Gg) > benzene (0.58 Gg). The total average reactive carbon due to all 27 VOCs during pre-harvest and post-harvest period was 259.7 ppbC and 496.6 ppbC, respectively. The total O₃ production potential due to 22 VOCs during post-harvest period was higher by a factor of 1.7 relative to pre-harvest period for both morning (06:00 to 12:00 LT) and afternoon (12:00 to 18:00 LT) times. These results help explain the 19 ppb enhancement in surface ozone concentrations during post-harvest wheat residue fires as reported by Kumar et al. (2016). The four major contributors were isoprene (26–31 %), acetaldehyde (24 %), acrolein (13–14 %) and 2-furaldehyde (7–9 %), which collectively accounted for more than 72 % of the total O₃ formation potential. The order of SOA formation potential for VOCs in pre-harvest period was benzene > toluene > xylenes > naphthalene > trimethylbenzenes > isoprene > styrene, whereas the order in post-harvest period was benzene > toluene > naphthalene > xylenes > trimethylbenzenes > isoprene > styrene. This study provides the first detailed experimental evidence of the large scale perturbation to ambient VOC chemical composition and secondary pollutant formation in the N.W. IGP which strongly impairs the regional air quality.

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