Speciation of 49 C2-C10 NMHCs during the post-harvest paddy residue fire emission period in the N.W. Indo Gangetic Plain using Thermal Desorption Gas Chromatography Flame Ionization Detection (TD-GC-FID)

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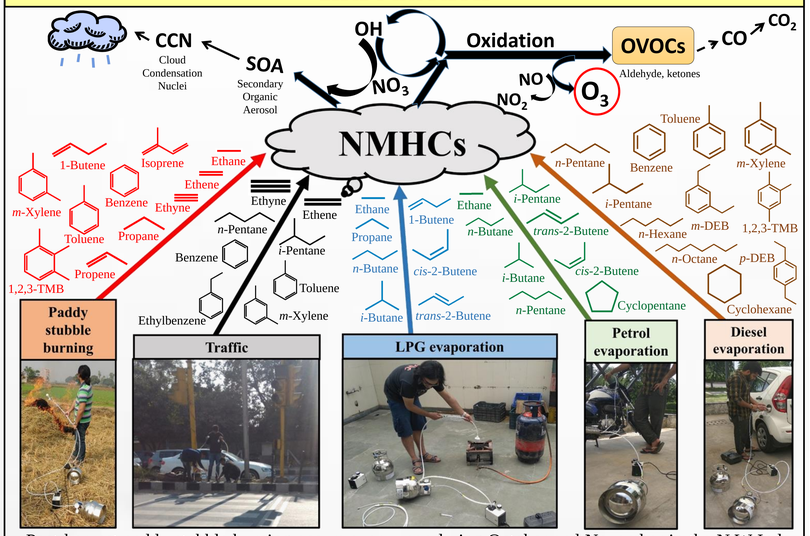
Introduction



Post-harvest paddy stubble burning occurs every year during October and November in the N.W Indo Gangetic Plain (NW-IGP) where 13-14 Tg of paddy residue is burnt in open over a large area > 12600 km^2 (90% area of Punjab & 32% area of Haryana are under combine harvesters[1]). This activity emits a large number of gaseous and particulate pollutants into the air and causes severe deterioration in regional air quality. Therefore, comprehensive quantification of the speciation and sources of NMHCs through "chemical fingerprinting" as well as ambient measurements are necessary for quantifying emissions from the fires and characterizing the reactant mixture responsible for the air pollution.

Materials and Methods

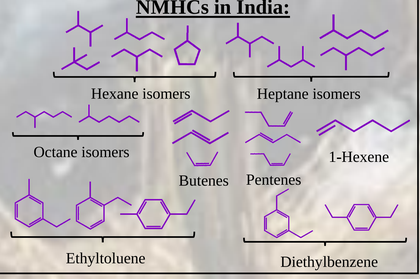
Site Description

The measurements were performed at IISER Mohali Atmospheric Chemistry Measurement Facility. The site is a regionally representative suburban location in the NW-IGP.[2,3] Ambient measurements were performed over a period of two weeks from 10-24 Nov, 2016. Whole air samples from specific sources (paddy stubble fires, traffic and fuel evaporation) were collected in Mohali, Chandigarh and adjacent villages.

Measurement details

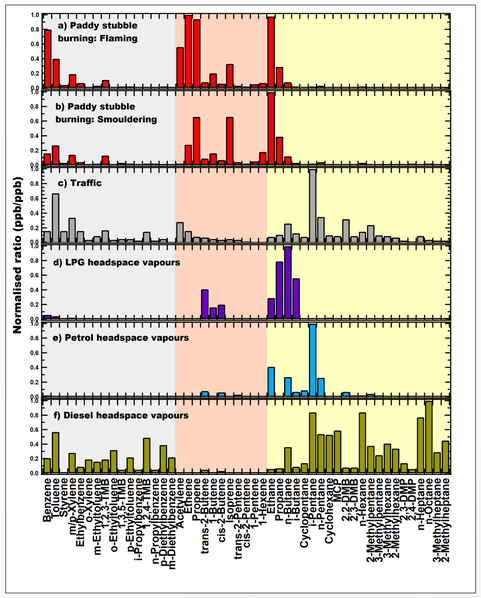
- NMHCs were measured using TD-GC-FID: Gas Chromatograph columns equipped with two Flame Ionization detectors (GC-FID, 7890B Agilent Technologies, USA) and a thermal desorption unit (Unity 2 and CIA Advantage-HL, Markes International, UK) optimized for quantification of 49 C2-C10 NMHCs. Detection limit : 2-104 ppt, overall measurement uncertainty <15%.
- CO_2 and CH_4 : Cavity Ring Down Spectrometer (Model G2508, Piccaro, USA), overall measurement uncertainty <4%.[4]
- CO: Non dispersive infrared (NDIR) filter correlation spectrometer (Thermo Fisher Scientific, Model 48i), overall measurement uncertainty <6%.[1,4]
- Offline samples were collected in commercially available 6L passivated SilcoCan air sampling steel canister (Restek, USA) that were preconditioned as per EPA TO15 method.

First time measurements of following NMHCs in India:



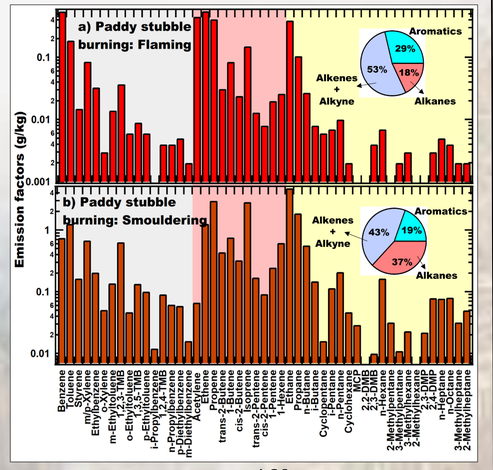
Results and Discussion

"Chemical fingerprinting" of emission sources



- *i*-Pentane : traffic/fossil fuel tracer; Acetylene : general combustion tracer
- Propane was found to be one of the major emissions from the paddy stubble fires and hence not an ideal LPG emission tracer in such a complex emission environment.

Emission factors of NMHCs (g/kg) from paddy stubble fires

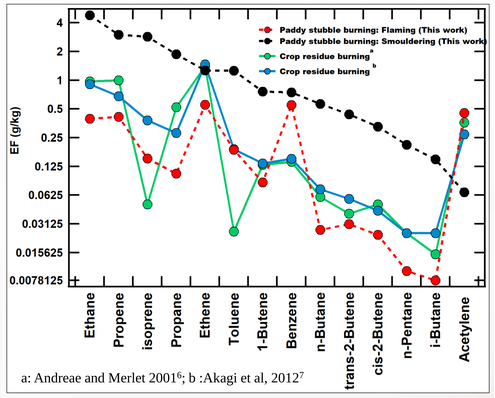


$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}$$

MCE ≥ 0.95 : Flaming fire;
MCE = 0.8-0.82 : Smouldering fire [5,7]

- Emission factors were calculated by carbon mass balance method[5]:

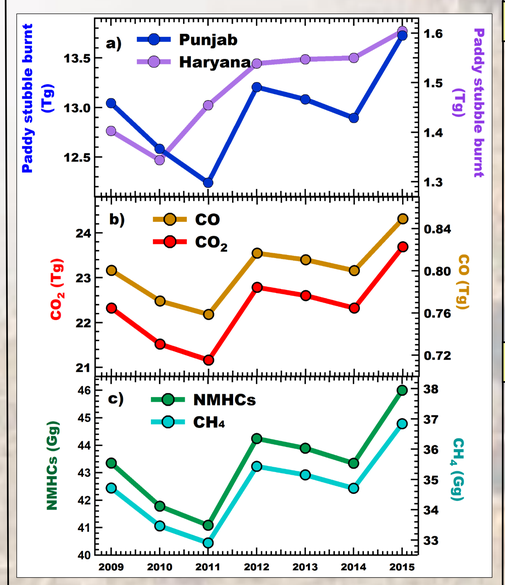
$$EF\left(\frac{g}{kg}\right) = F_c \times 1000\left(\frac{g}{kg}\right) \times \frac{MM_x}{MM_c} \times \frac{C_x}{C_{total}}$$



a: Andreae and Merlet 2001[6]; b :Akagi et al, 2012[7]

The EFs obtained here for flaming fires agree well with the EFs reported in literature and used in emission inventories, however smouldering EFs are much higher.

Quantification of emissions from paddy stubble burning in NW-IGP

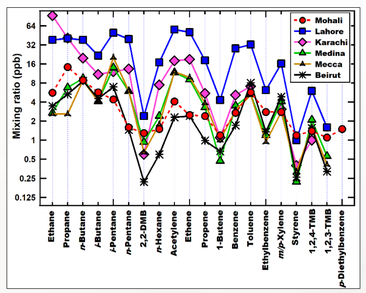


- Emissions of trace gases over Punjab and Haryana (NW-IGP) were estimated from paddy stubble fires under flaming conditions[8,9]:

Total Emissions = Σ(A x B x C x D x E x EF$_i$)

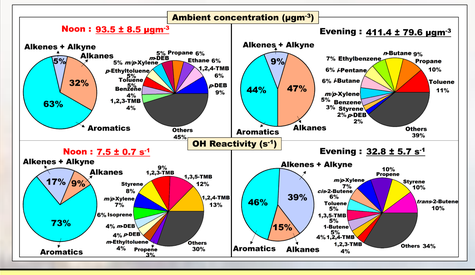
where, A: annual crop production (kg) for 2009-2015 [10],
B: Residue to crop ratio (1.50) [1],
C: Dry matter fraction of crop (0.86) [8,9],
D: Fraction of crop residue burnt (0.9 for Punjab and 0.32 for Haryana) [1]
E: Fraction actually oxidized (0.9) [8,9]
EF$_i$: Emission factor for air pollutant (this work)

- Smouldering EFs point to even higher emissions.



Ambient air speciation

- Comprehensive quantification of 49 C2-C10 NMHCs using TD-GC-FID in ambient air.
- Average mixing ratios of five most abundant NMHCs : Propane (14.3 ppb) > *n*-Butane (8.9 ppb) > Toluene (5.7 ppb) > *i*-Butane (5.7 ppb) > Ethane (5.6 ppb).
- Average mixing ratios of C2-C5 alkanes were lower than the reported levels in Lahore[12] and Karachi[13]



- Aromatics were the largest contributor to the observed mass concentration (40-60%) and OH reactivity (40-70%).
- Anthropogenic source of post-harvest paddy stubble burning was identified as major source of NMHCs in this environment during post monsoon.

Conclusion

- Chemical fingerprinting of the sources reveal distinct emission profiles. *i*-Pentane and Acetylene were identified as traffic/fossil fuel and combustion tracers respectively, while Diesel evaporative emissions were identified as the sources of Diethylbenzenes. Propane being one of the major emission from the paddy stubble fires was not an ideal LPG emission tracer.
- Emission factors for 49 NMHCs from paddy stubble fires were calculated and smouldering stage EFs were found to be upto 20 times higher than flaming stage EFs .
- Emissions of CO_2, CO, CH_4 and NMHCs over Punjab and Haryana (NW-IGP) from paddy stubble fires were quantified to be 24 Tg, 0.85 Tg, 46 Tg and 37 Gg respectively, which suggests that large amount of reactive carbon is available for photochemical oxidation and the large fraction of aromatics emphasizes the air toxicity and a major contributor to the poor air quality.
- First ever comprehensive quantification of 49 C2-C10 NMHCs using TD-GC-FID in ambient air over India during November identified paddy stubble burning as major source of NMHCs in this atmospheric environment.

References

1. Liu, T.; Marlier, M. E.; Karambelas, A.; Jain, M.; Singh, S.; Singh, M. K.; Gautam, R.; DeFries, R. S., Missing emissions from post-monsoon agricultural fires in northwestern India: regional limitations of MODIS burned area and active fire products. *EarthArXiv. March* **2018,** *21*.
2. Sinha, V.; Kumar, V.; Sarkar, C., Chemical composition of pre-monsoon air in the Indo-Gangetic Plain measured using a new air quality facility and PTR-MS: high surface ozone and strong influence of biomass burning. *Atmospheric Chemistry and Physics* **2014,** *14*, (12), 5921-5941.
3. Pawar, H.; Garg, S.; Kumar, V.; Sachan, H.; Arya, R.; Sarkar, C.; Chandra, B.; Sinha, B., Quantifying the contribution of long-range transport to particulate matter (PM) mass loadings at a suburban site in the north-western Indo-Gangetic Plain (NW-IGP). *Atmospheric Chemistry and Physics* **2015,** *15*, (16), 9501-9520.
4. Chandra, B.; Sinha, V.; Hakkim, H.; Sinha, B., Storage stability studies and field application of low cost glass flasks for analyses of thirteen ambient VOCs using proton transfer reaction mass spectrometry. *International Journal of Mass Spectrometry* **2017,** *419*, 11-19.
5. R.J. Yokelson, J.G. Goode, D.E. Ward, R.A. Susott, R.E. Babbitt, D.D. Wade, I. Bertschi, D.W.T. Griffith, W.M. Hao, Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy, *J. Geophys. Res. Atmos.* 104, **1999**, 30109–30125.
6. Andreae, M. O.; Merlet, P., Emission of trace gases and aerosols from biomass burning. *Global biogeochemical cycles* **2001,** *15*, (4), 955-966.
7. Akagi, S. K.; Yokelson, R. J.; Wiedinmyer, C.; Alvarado, M. J.; Reid, J. S.; Karl, T.; Crounse, J. D.; Wennberg, P. O., Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos. Chem. Phys.* **2011,** *11*, (9), 4039-4072.
8. Revised IPCC Guidelines for National Greenhouse Gas Inventories: Reference Manual; The Intergovernmental Panel on Climate Change (IPCC),**1996**; https://www.ipcc-nggip.iges.or.jp/public/gl/invs6c.html.
9. IPCC Guidelines for National Greenhouse Gas Inventories: General Guidance and Reporting; Intergovernmental Panel on Climate Change (IPCC),**2006**; https://www.ipcc-nggip.iges.or.jp/public/2006gl/vol1.html.
10. AGRICULTURE - Statistical Year Book India; Directorate of Economics and Statistics, Department of Agriculture and Cooperation (DAC), Ministry of Agriculture, Government of India,**2017**; http://mospi.nic.in/statistical-year-book-india/2017/177.
11. Aggarwal, P., *Land use analysis and planning for sustainable food security: with an illustration for the state of Haryana, India*. IRRI: 2001.
12. Barletta, B.; Simpson, I. J.; Blake, N. J.; Meinardi, S.; Emmons, L. K.; Aburizaiza, O. S.; Siddique, A.; Zeb, J.; Liya, E. Y.; Khwaja, H. A., Characterization of carbon monoxide, methane and nonmethane hydrocarbons in emerging cities of Saudi Arabia and Pakistan and in Singapore. *Journal of Atmospheric Chemistry* **2017,** *74*, (1), 87-113.
13. Barletta, B.; Meinardi, S.; Simpson, I. J.; Khwaja, H. A.; Blake, D. R.; Rowland, F. S., Mixing ratios of volatile organic compounds (VOCs) in the atmosphere of Karachi, Pakistan. *Atmospheric Environment* **2002,** *36*, (21), 3429-3443.
14. Salameh, T.; Sauvage, S.; Afif, C.; Borbon, A.; Léonardis, T.; Brioude, J.; Waked, A.; Locoge, N., Exploring the seasonal NMHC distribution in an urban area of the Middle East during ECOCEM campaigns: Very high loadings dominated by local emissions and dynamics, *Environ. Chem.* **2015**, 12, 316–328

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