Title:	Non-methane hydrocarbon (NMHC) fingerprints of major urban and agricultural emission sources for use in source apportionment studies
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Abstract:	In complex atmospheric emission environments such as urban agglomerates, multiple sources control the ambient chemical composition driving air quality and regional climate. In contrast to pristine sites, where reliance on single or a few chemical tracers is often adequate for resolving pollution plumes and source influences, the comprehensive chemical fingerprinting of sources using nonmethane hydrocarbons (NMHCs) and the identification of suitable tracer molecules and emission ratios becomes necessary. Here, we characterise and present chemical fingerprints of some major urban and agricultural emission sources active in South Asia, such as paddy stubble burning, garbage burning, idling vehicular exhaust and evaporative fuel emissions. A total of 121 whole air samples were actively collected from the different emission sources in passivated air sampling steel canisters and then analysed for 49 NMHCs (22 alkanes, 16 aromatics, 10 alkenes and one alkyne) using thermal desorption gas chromatography flame ionisation detection. Several new insights were obtained. Propane was found to be present in paddy stubble fire emissions (8 %), and therefore, for an environment impacted by crop residue fires, the use of propane as a fugitive liquefied petroleum gas (LPG) emission tracer must be done with caution. Propene was found to be ~ 1.6 times greater (by weight) than ethene in smouldering paddy fires. Compositional differences were observed between evaporative emissions of domestic LPG and commercial LPG, which are used in South Asia. While the domestic LPG vapours had more propane (40 ± 6 %) than n-butane (19 ± 2 %), the converse was true for commercial LPG vapours (7 ± 6 % and 37 ± 4 %, respectively). Isoprene was identified as a new tracer for distinguishing paddy stubble and garbage burning in the absence of isoprene emissions at night from biogenic sources. Analyses of source-specific inter-NMHC molar ratios revealed that toluene/benzene ratios can be used to distinguish among paddy stubble fire emissions in the flaming (0.38 ± 0.11) and smouldering stages (1.40 ± 0.10), garbage burning flaming (0.26 ± 0.07) and smouldering emissions (0.59 ± 0.16), and traffic emissions (3.54 ± 0.21), whereas i-pentane = npentane can be used to distinguish biomass burning emissions (0.06 1.46) from the petrol-dominated traffic and fossil fuel emissions (2.83 4.13). i-butane = n-butane ratios were similar (0.20 0.30) for many sources and could be used as a tracer for photochemical ageing. In agreement with previous studies, i-pentane, propane and acetylene were identified as suitable chemical tracers for petrol vehicular and evaporative emissions, LPG evaporative and vehicular emissions and flaming-stage biomass fires, respectively. The secondary pollutant formation potential and human health impact of the sources was also assessed in terms of their hydroxyl radical (OH) reactivity (s-1), ozone formation potential (OFP; gO3/gNMHC) and fractional benzene, toluene, ethylbenzene and xylenes (BTEX) content. Petrol vehicular emissions, paddy stubble fires and garbage fires were found to have a higher pollution potential (at = 95 % confidence interval) relative to the other sources studied in this work. Thus, many results of this study provide a new foundational framework for quantitative source apportionment studies in complex emission environments.
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