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# Indian emissions of technology-linked NMVOCs with chemical speciation: An evaluation of the SAPRC99 mechanism with WRF-CAMx simulations

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#### HIGHLIGHTS

• Methodology to map Indian technology-linked NMVOC emissions to published profiles.

- Full speciation into RADM2, SAPRC99, CB-IV reactivity classes.
- $\bullet$  Spatially distributed at 0.25°  $\times$  0.25°, using source-specific proxies.
- Residential and agricultural sectors emit highest reactivity NMVOC species.
- Evaluated for SAPRC99 mechanism.

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#### ABSTRACT

Non-methane volatile organic compounds (NMVOCs) are important precursors to reactions producing tropospheric ozone and secondary organic aerosols. The present work uses a detailed technology-linked NMVOC emission database for India, along with a standard mapping method to measured NMVOC profiles, to develop speciated NMVOC emissions, which are aggregated into multiple chemical mechanisms used in chemical transport models. The fully speciated NMVOC emissions inventory with 423 constituent species, was regrouped into model-ready reactivity classes of the RADM2, SAPRC99 and CB-IV chemical mechanisms, and spatially distributed at  $25 \times 25$  km<sup>2</sup> resolution, using source-specific spatial proxies. Emissions were considered from four major sectors, i.e. industry, transport, agriculture and residential and from non-combustion activities (use of solvents and paints). It was found that residential cooking with biomass fuels, followed by agricultural residue burning in fields and on-road transport, were largest contributors to the highest reactivity group of NMVOC emissions from India. The emissions were evaluated using WRF-CAMx simulations, using the SAPRC99 photochemical mechanism, over India for contrasting months of April, July and October 2010. Modelled columnar abundance of NO<sub>2</sub>. CO and O<sub>3</sub> agreed well with satellite observations both in magnitude and spatial distribution, in the three contrasting months. Evaluation of monthly and spatial differences between model predictions and observations indicates the need for further refinement of the spatial distribution of NO<sub>X</sub> emissions, spatio-temporal distribution of agricultural residue burning emissions.

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#### 1. Introduction

Understanding emissions of non-methane volatile organic compounds (NMVOCs) is important in regard to formation of

ozone, which is identified as a secondary air pollutant, with adverse effects on human health; agricultural productivity and near-term climate change (Shindell et al., 2012). NMVOCs are also precursors to secondary organic aerosols (SOA), an important fraction of particulate matter, which exerts adverse health impacts. In India, in-situ measurements of surface ozone and ozone vertical profiles at various sites (Lal et al., 2000; Naja and Lal, 2002; Naja et al., 2003; Beig et al., 2007; Reddy et al., 2008; Kumar et al., 2010; David and







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Nair, 2011) indicate a seasonal amplitude between 10 and 70 ppbv and a diurnal amplitude between 7 and 35 ppbv at urban and rural areas and 3–7 ppbv in cleaner, marine atmosphere. Limited measurements of SOA as water soluble organic carbon (Kaul et al., 2011; Rastogi et al., 2015), indicate an amplitude from 1 to 90  $\mu$ g m<sup>-3</sup>, with highs attributed to reactive organic gas emissions and atmospheric fog processes. In a recent study by Ojha et al. (2015), it was found that WRF-Chem simulations for ozone over Chennai agreed fairly well with CARIBIC in-situ measurements, except during strong pollution events. Thus, beyond limited observational studies, there are still large gaps in understanding regional ozone and SOA over India.

Early ozone modelling studies over India used offline chemical transport models, with uncoupled chemistry and meteorology (Beig and Brasseur, 2006; Roy et al., 2008; Engardt, 2008). Recent studies which developed and evaluated fully-coupled ozone modelling platforms over India (Kumar et al., 2012a,b; Chatani et al., 2014), found satisfactory agreement with observations, however significant differences (24-39% maximum difference) between measured and model columnar monthly ozone abundances over India, indicating the need to resolve issues impacting model performance on ozone. The need for improvements in NO<sub>X</sub> and CO emission inventories over south Asia was highlighted (Kumar et al., 2012a,b). This was recently addressed through development of new bottom-up CO and NO<sub>X</sub> emission inventories for India (Sadavarte and Venkataraman, 2014; Pandey et al., 2014), and obtaining better agreement with a top-down (Ghude et al., 2013) NO<sub>x</sub> inventory. Sharma et al. (2013) found issues in deterministic prediction of hourly surface ozone concentrations, using the CMAQ model on an urban scale in Delhi, which were improved using a statistical approach. The existing uncertainties in modelled ozone prediction provide motivation for the present study, addressing a systematic development of a fully speciated NMVOC emission inventory for India, as a step toward reducing them.

Speciated NMVOC inventories for Asian countries have been reported (Streets et al., 2003; Wei et al., 2008; Klimont et al., 2002; Li et al., 2014) using profiles from USEPA SPECIATE database (USEPA SPECIATE V.4.3, 2011) and the CORINAIR inventory (EEA, 2000) in conjunction with available measurements of NMVOC profiles, especially for biofuel stoves and open biomass burning. Sharma et al. (2015) developed a speciated NMVOC inventory for India estimating sectoral fuel use, emission factors from the GAINS-ASIA database and speciation profiles from Wei et al. (2008, 2014). This inventory has significant technology divisions, in both industrial process and solvent activities, with a spatially distribution at  $36 \times 36 \text{ km}^2$ . Citing comparativeness between China and India in income levels, product use and legislations on VOCs, Sharma et al. (2015) used source profiles listed Wei et al. (2008), which include measurements from China for some sources and from the USEPA SPECIATE database for others.

The objective in the present work is to use a detailed technology-linked NMVOC emission inventory for India (Sadavarte and Venkataraman, 2014; Pandey et al., 2014), along with a standard mapping method to measured NMVOC profiles, to develop speciated NMVOC emissions, which is aggregated into multiple chemical mechanisms used in chemical transport models. The inventory includes over 113 activities and technologies that emit NMVOCs (Sadavarte and Venkataraman, 2014; Pandey et al., 2014), in industry, transport, residential and agricultural sectors, as well as from non-combustion activities including solvent use and painting operations in the industrial and residential sectors. In the absence of Indian speciated NMVOC profile measurements, both USEPA SPECIATE profiles (USEPA SPECIATE, V.4.3, 2011) and newer NMVOC profile measurements (Wei et al., 2008) were reviewed. Recent information on NMVOC emission trends (Wei et al., 2014) in China, emphasizes the need to assess trends in emissions of different NMVOC species, and total ozone forming potential. While the USEPA SPECIATE profiles were somewhat older, they had a clearer one-to-one correspondence with technologies in the Indian inventory. The need for using an explicit speciation assignment approach for NMVOCs (Li et al., 2014) has been emphasized, to reduce uncertainties. A standard methodology (Carter, 2010) was available for aggregation of SPECIATE compounds to different chemical mechanisms used in photochemistry calculations. This led to the choice of SPECIATE profiles in this study.

The specific objectives of this paper are: (i) to implement a standard mapping methodology between technology/activity based NMVOC emissions and corresponding speciation profiles to develop a speciated NMVOC inventory for India (ii) to aggregate species into reactivity classes of multiple chemical mechanisms using a standard methodology (iii) provide detailed spatial distribution of the emissions at 25 km resolution, using different proxies at the source category level, to obtain a model-ready speciated NMVOC emissions database (iv) to carry out preliminary evaluation for one chemical mechanism using simulations with a chemical transport model (WRF-CAMx) against satellite and in-situ trace gas observations. Since the focus here is on development of a speciated NMVOC inventory and identification of improvements needed in the magnitudes and spatial distribution of sectoral emissions, we limit the modelling evaluation to basic questions about the inventory's ability to simulate ozone totals in months of differing emissions, leaving a full evaluation of an ozone modelling platform fora future study.

#### 2. Methodology

Emissions of NMVOC from five different sectors were estimated for the year 1996–2015 which includes industry, transport, residential, agriculture and informal industry (Sadavarte and Venkataraman, 2014; Pandey et al., 2014), with detailed calculations for 2010, which was the year selected for speciation. Fig. S1 shows a distribution of the annual NMVOC emissions from these sectors by source category and the contributing activities and technologies. Total anthropogenic NMVOC emissions in India in 2010 were10.5 Tg. Sectoral shares of emissions, in order of importance, were from residential (49%), on-road transport (17%), agricultural residue burning in fields (17%) and non-combustion activities in industrial and residential sectors 12%. This is broadly consistent with sectoral NMVOC emissions for India reported in INTEX-B (Zhang et al., 2009; Li et al., 2014), REAS v.2.1 (Kurokawa et al., 2013) inventories and in Sharma et al. (2015).

The transport sector contributes about 1.78 Tg of tail-pipe and 0.10 Tg of evaporative emissions, oil extraction and processing contributes 0.20 Tg, refineries contribute about 0.04 Tg, decorative painting 0.11 Tg and domestic painting 0.13 Tg. Shares of non-combustion emissions are somewhat lower in the present inventory, which needs further inclusion of activities like personal care and adhesive applications. Emissions from informal industries, which include brick production, agricultural products and food processes, amounted to less than 2% of the national total and hence have not been taken into account in this paper. The following sections describe the methodology for speciation of NMVOCs based on the emitting source, followed by regrouping into reactivity classes needed as input to commonly used photochemical mechanisms.

#### 2.1. Speciation methodology for NMVOC emissions

The speciation methodology involves disaggregation of the emissions specific to an activity or technology, into constituent chemical species. Photochemical conversion of NMVOCs to ozone and further to SOA, differ for each constituent species, based on rates of pathways of photochemical oxidation (Carter, 2010; Passant, 2002; Wei et al., 2008). NMVOCs, disaggregated by activity-technology divisions, are speciated using speciation profiles, thereafter collected into reactivity classes, aggregated by source category and gridded using source-specific spatial distribution proxies.

## 2.1.1. Mapping of activities and technologies emitting NMVOCs to speciation profiles

A realistic mapping of actual technologies or activities leading to emission of NMVOCs to measured speciation profiles is needed to obtain accuracy in magnitude and spatial distribution of the emissions. A methodology was adopted for mapping the NMVOC emission activities in India to those with available measured profiles (Fig. 1). The criteria chosen for making the mapping vary with each sector. For industry, comparison is made on the basis of the type of fuel used, its form/state (i.e. solid, liquid or gaseous), composition, calorific value and combustion temperature of the process. Specific fuel consumption (SFC) per unit mass of raw material or per unit of product formed is also used as a basis for comparison where such information is available for the process. For activities/technologies associated with the transport sector, fuel characteristics (Bharat standard vis-à-vis EURO standard, www. cpcb.nic.in; www.ec.europa.eu/environment) and vehicle duty are main parameters while others include engine type, vehicle type and vintage. Relatively less information is available for the residential and agriculture sectors. Hence comparison with available NMVOC measurement profiles is done with the type of operation (biomass fuel cooking, kerosene lighting, agricultural residue burning, tractors, etc.), fuel used and efficiency being the main parameters. In all these cases, 'similarity' is established once 60% or more of the parameters under the framework match. Table 1 lists the combustion activities resulting in NMVOC production and indicate the selected measured profiles. In addition to combustion, solvent use operations in industries, including paint application, polymer production and processing and printing lead to significant emissions of NMVOCs (Klimont et al., 2002), which are listed in Table 2.

#### 2.1.2. Speciation profile data

In the absence of Indian speciated profile measurements, both USEPA SPECIATE profiles (USEPA SPECIATE, V.4.3, 2011) and newer NMVOC profile measurements (Wei et al., 2008, 2014) were reviewed. It was possible to make a one-to-one mapping with the technologies included in the Indian emission inventory (Sadavarte and Venkataraman, 2014; Pandey et al., 2014) and those in the USEPA SPECIATE database, leading to choice of this database. In addition, a specific method of aggregation of NMVOC species calculated from SPECIATE profiles to reactivity classes in different chemical mechanisms was available (Carter, 2010). This allowed use of a standard methodology both for the speciation and aggregation to different chemical mechanisms, thus leading to adoption of the SPECIATE profiles in this work. Additional information sources were used to develop speciation profiles for each activity/ technology taken into consideration. National Atmospheric Emissions Inventory (NAEI) speciation modules for NMVOCs (Passant, 2002) and Andreae and Merlet (2001) for open biomass burning. The USEPA SPECIATE database (Simon et al., 2010) contains a total of 1624 organic gas profiles exist in the updated version of the database. Profiles for most combustion-based and solvent-use activities have been obtained from this database. Chiefly profiles for on-road diesel vehicles, printing and paint application have been used from NAEI modules. The NAEI includes 111 source profiles, with photochemical ozone creating potential (POCP) values (Derwent et al., 1998) specified for every constituting species (Passant, 2002). Where sources do not match exactly, the documented speciation of a similar source is applied exactly, even though this would lead to uncertainties. While an exact match for sources and combustion technologies was found for about 60% of NMVOC annual emissions, similar source speciation was applied to about 40% of NMVOC annual emissions. The importance of the oxygenated VOC or OVOC fraction was pointed out, particularly to emissions from biomass fuel burning and diesel vehicles (Li et al., 2014), wherein this fraction was added to existing NMVOC speciation profiles. While OVOC species such as aldehydes, ketones and alcohols are present in the profiles used in this work, we do not add a specific OVOC fraction to the profiles. For China, more exhaustive speciation of anthropogenic and biogenic NMVOC are available (Wei et al., 2008; Zheng et al., 2009). The lack of availability of Indian speciation profiles, did not permit further customising to reflect local NMVOC speciation characteristics. Field burning of agricultural residues in India, largely involves cereal straws and sugarcane leaves. For these, the speciation profile of Andreae and Merlet, 2001 (Table 1), was used, without modification of the OVOC fraction.

#### 2.1.3. Regrouping into reactivity classes

In this work, speciation resulted in estimated emissions of over four hundred chemical species from the different activitytechnology divisions. However, speciated NMVOCs cannot serve as direct inputs to chemical transport models. Regrouping these species into suitable classes based on their reactivity and chemical similarity (Li et al., 2014; Middleton and Carter, 1990) is needed for model-ready inputs. While detailed treatment of reactions in the atmosphere is desirable for accuracy, availability of computational resources and complexities associated with explicit treatment of individual species poses limitations. Photochemical mechanisms widely used in models apply molecular lumping, based on similar reactivity, to place several chemical molecules into specified reactivity classes. This reduces the numbers of chemical reactions in a photochemical model and saves computational time. The numbers of reactivity classes considered in different chemical mechanisms are 12 in CB-IV (Gery et al., 1989), 19 in RADM2 and 33in SAPRC99 (Stockwell et al., 1990; Carter, 2000). Reactivity classes used in CB-IV are based on molecular lumping and structural lumping of species based on similarities in carbon bonds. Hence, fewer model species are required to represent bond groups. The RADM2 and SAPRC99 mechanisms, on the other hand, involve aggregation of species into model classes in terms of similarities in reactions of entire molecules. This molecular lumping technique necessitates development of a larger number of surrogate species.

In the present study, the chemical constituents of NMVOCs have been lumped into SAPRC99, RADM2 and CBM-IV reactivity classes. For most species, lumping into these classes was done using the speciation assignments available as Excel sheets in the website: http://www.cert.ucr.edu/~carter/emitdb (Carter, 2004). For isomers of a species weight fractions available from measurement profiles have been distributed proportionately into respective reactivity classes. A similar approach has been adopted for ambiguous groups such as C13+ alkanes. A significant proportion of NMVOC emissions constitute unspeciated and unknown or unidentified chemical species. Jathar et al. (2014) have proposed a method by which they were able to group unspeciated compounds from some activities into n-alkane classes most representative of the activity under consideration, in terms of SOA yield. For other activities, these species were distributed in equal proportions into all reactivity classes. Three major groups were constituted, based on reactivity with hydroxyl radical, to facilitate discussion and interpretation.



Fig. 1. Methodology for mapping of NMVOC emitting activity/technology to measured speciation profiles.

The respective rate constants (k<sub>OH</sub>) were  $\sim \geq 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for reactivity Group I,  $\sim 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for reactivity Group II and  $\sim \leq 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for reactivity Group III which includes less reactive compounds. However, reactivity classes, specified in the chemical mechanisms, are retained to prepare model-ready inputs for photochemical modelling.

#### 2.2. Spatial distribution and seasonality

Emissions are spatially distributed at  $0.25^{\circ} \times 0.25^{\circ}$  resolution over India (7–39°N, 67–99°E) into 128 × 128 grid elements in east-

west and north-south directions, per earlier work (Sadavarte and Venkataraman, 2014; Pandey et al., 2014). Briefly, division between rural and urban layers was made explicitly, for residential emissions (Pandey et al., 2014) calculated using district level rural and urban population using different fuel types. On-road gasoline emissions were distributed using urban population density with an assumption of gasoline vehicles use limited to urban population (Pandey and Venkataraman, 2014). On-road diesel emissions were distributed using a detailed shape file with the following shares to the national "golden quadrilateral" (30%), national highways (40%), state highways (20%) and urban grids (10%). The extent of freight transport on different highway corridors is derived from data in the

#### Table 1

Combustion activities leading to NMVOC emissions with corresponding speciation profiles/USEPA SPECIATE database V.4.3, 2011.

Sector	Source category	Activity/technology	Speciate profile	
Industry Thermal power		Pulverised coal boiler (PCB)	External combustion sources- Electric generation	
	LPS (Large point source)	) Cyclone combustor/stoker/Fluidized bed combustor (FCB)/PCB- non	Coal-fired boiler-Industrial	
		thermal power		
		Cement kiln	Cement industry <sup>a</sup>	
		Coke ovens	By-product coke oven stack gas	
		Sinter plant	Iron sintering	
		Blast furnace	Blast furnaces	
		Basic oxygen furnace	Basic oxygen furnace	
		Induction Furnace (IF)/	Secondary metal production- grey iron foundries- pouring	
		Electric Arc Furnace (EAF)	and casting	
		Aluminium smelter	Primary aluminium production	
	Industrial oil & gas	Oil fired boilers- High speed diesel (HSD), Light distillate oil (LDO)	External combustion sources- distillate oil	
		Oil fired boilers-Low sulphur heavy stock (LSHS), Furnace oil (FO)	External combustion sources- residual oil	
		Gas fired boiler	External combustion sources- natural gas	
		Gas turbine/diesel generator	Natural gas turbine	
Transport	On-road gasoline	Passenger 2/4 stroke 2-Wheeler	2-stroke petrol engines <sup>a</sup>	
		Passenger 4 stroke (cars)	Light Duty Gasoline Vehicles - 46 Car Study	
	On-road diesel	Passenger cars (4-Wheeler)	Road transport, diesel, light duty <sup>a</sup>	
		3- wheelers		
		Light duty		
		Heavy duty	Road transport, diesel, heavy duty <sup>a</sup>	
	Railways	Locomotives & workshops	Reciprocating diesel engine	
Shipping		Shipping	Shipping <sup>a</sup>	
	Aviation	Landing/Take-Off (LTO)	Aircraft exhaust- commercial	
Agriculture	e Agricultural residue	Cereal straw burning	Biomass burning <sup>b</sup>	
	burning	Sugarcane burning		
	Diesel use	Tractors	Diesel use: farm equipment	
Residential Biomass fuel burning		Traditional stoves- wood	Residential wood combustion	
		Traditional stoves- dungcakes		
		Traditional stoves- ag residue		
		Traditional stoves- coal		
	Liquid & gaseous fuels	Cooking (LPG & Kerosene)	Domestic combustion of oil <sup>4</sup>	
		Lighting (Kerosene)		

<sup>a</sup> Profile obtained from EEA.

<sup>b</sup> Profile obtained from Andreae and Merlet (2001).

annual reports of the Ministry of the Road Transport and Highways (MoRTH, 2014) and special reports on the freight movement in India, conducted by the Clean Air Asia (Clean Air Asia, 2014). Overall, the golden quadrilateral and the highways link the most active ports and the major urban hubs, therefore accounting for most freight activity and related emissions. For commercial activities including light industries, again urban population density was used for emission distribution.

Temporal distribution of emissions from different sources were accounted in residential water heating/space heating and agriculture residue burning, using a switch turning emissions on when monthly mean temperature (data from the Indian Meteorological Department) below 20 °C occurred at a district level (Pandey et al., 2014). Seasonality in agricultural residue burning was derived from MODIS fire-count data in agricultural land-use areas (Venkataraman et al., 2006), representing a monthly mean spatio-temporal distribution of the mid-2000s. Other emission sources are treated on an annual basis. The monthly emissions of species constituting the thirty-three SAPRC99 reactivity classes were disaggregated into thirteen source categories (Sadavarte and Venkataraman, 2014) and spatially distributed, using the corresponding spatial proxies.

#### 2.3. Evaluation of ozone chemistry using WRF-CAMx simulations

A first level of evaluation of the emission inventory is done in this study, while more detailed evaluation will be undertaken in future work. Simulations over the Indian Subcontinent were carried out using the CAMx version 6.10, to understand transport, reaction and removal of ozone and its precursors over the domain. All the calculations were conducted at  $0.25^{\circ} \times 0.25^{\circ}$  spatial resolution

(~25 km). CAMx is an open-access three-dimensional grid-based Eulerian photochemical model (www.camx.com). The model requires specifications of emissions, meteorology and geographic inputs in suitable formats to generate hourly outputs of ozone concentration fields. The inventories by Sadavarte and Venkataraman (2014) and Pandey and Venkataraman (2014) were used to establish the gridded emissions base for PM, SO<sub>2</sub>, NO<sub>X</sub> and CO species and the NMVOC from this study, at the model grid resolution. Biogenic emissions were obtained from EDGAR global inventory (Olivier et al., 1996). Gas-phase chemistry from the SAPRC99 mechanism was utilized, with initial and boundary conditions from the MOZART-4 offline model (Emmons et al., 2010). This SAPRC99 mechanism is linked to an optional modal and sizesegregated primary and secondary PM treatments to account for the production of sulfate, nitrate, and secondary organic aerosols. WRF 3.5.1, coupled with NCEP reanalysis fields, was utilized to generate hourly meteorological fields of wind vectors, pressure, temperature, humidity, cloud cover, and diffusivity. Dry deposition is treated as a first order removal mechanism in the models lowest layer (designated at 30 m – domain average). Deposition velocity for the gaseous and particulate species, per grid, is determined within the CAMx model for 26 land-use categories. Wet scavenging is activated in the model, within or below a precipitating cloud with appropriate scavenging coefficient assigned for gases and particles.

An attempt was made to capture contrasting emissions, for an evaluation of the inventory. In addition to monthly invariant energy-use emissions, seasonal emissions include burning of biomass in agricultural fields, forests, and for residential water/ space heating (April), an absence of open fires (July) and predominantly agricultural residues (Oct). While these months bear a contrast in chemistry, wet deposition and photochemical activity,

#### Table 2

Solvent-use activities leading to NMVOC emissions with corresponding speciation profiles/USEPA SPECIATE database V.4.3, 2011.

Sector	Source category	Activity/technology		Speciate profile	
Industry	Other industries	Paint application	Vehicle refinishing	Paint: vehicle refinishing <sup>a</sup>	
			Automobile mfg.	Automotive painting: downwind ground-based compositions	
			Other industrial	Paint: general industrial <sup>a</sup>	
		Printing	Packaging	Printing- flexography/non-publication gravure <sup>a</sup>	
			Offset printing	Offset printing	
			Publication	Printing/publication- ink thinning solvents- methyl isobutyl ketone	
			Screen printing	Printing- screen printing <sup>a</sup>	
		Preservation of wood		Wood furniture coating	
		Paint production		Paint & coating mfg.	
		Ink production		Ink manufacture <sup>4</sup>	
		Asphalt blowing		Asphalt roofing	
		Asphalt production			
		Production of tyres		Automobile tire production	
		Carbon black production	on	Chemical mfg: Carbon black production	
		Ethylene		Olefins mfg: ethylene & propylene	
		Propylene			
		LDPE		Plastics bag manufacturing	
		HDPE			
		Polypropylene		Manufacturing- plastics- polypropylene	
		PVC production		Plastics production- VC and copolymers	
		Vinyl chloride			
		PVC processing			
		Storage of organic che	micals	Organic chemical storage	
		Textile production		Textile products- General fabric operations	
		Bread production		Pressurized food products	
		Beer production		Alcohols production	
		Spirits production		Thinning solvents/mineral spirits	
		Rolling mills		Industrial point source- fabricated metal products	
		Synthetic rubber proce	essing	Rubber processes <sup>a</sup>	
		Pulp and paper production		Pulp and paper mills	
	Industrial oil & gas	Fugitive leakage from refinery Extraction and handling		Refinery fugitive emissions	
				Conventional oil & gas extraction	
		Service station- gasoli	ne	Whole gasoline: service station profile	
		Oil & gas production (	LPG)	Oil & gas production- fugitives- unclassified	
		Transport and depot			
RESIDENTIAL	Solvent use	Paint application	Architectural	Architectural coatings- solvent coating and thinning solvent	
			Domestic	Decorative paint <sup>a</sup>	
		Domestic use of solver	nts	Solvent use- domestic solvents	

<sup>a</sup> Profile obtained from EEA.

the present evaluation is limited to understanding the accuracy in magnitude and spatial distribution of emissions estimated here, and in identifying improvements needed in the inventory. Modelled fields of precursor gases, NO<sub>2</sub> and CO (tropospheric column abundance) and of ozone (tropospheric column abundance and surface concentrations) were extracted for evaluation against published ground station measurements and satellite detected trace gas abundance.

#### 2.4. Ground station and satellite data

Evaluation of the speciated NMVOC inventory was done using a comparison of modelled trace gas fields with both ground station measurements and satellite observations. Ozone surface concentrations from published data over several sites in the Indian subcontinent (including Lal et al., 2000; Naja and Lal, 2002; Naja et al., 2003; Ahammad et al., 2006; Beig et al., 2007; Reddy et al., 2008; Kumar et al., 2010; David and Nair, 2011), were compiled for the period 2000–2010. The data come from diverse locations including northern elevated sites (Darjeeling and Nainital), peninsular sites (Ahmedabad, Mt. Abu, Pune) and southern sites (Anantpur, Gadanki, Thumba). Earlier studies have used measured seasonal cycle of ozone. For an initial evaluation of the new NMVOC inventory developed in this work, the months of April, July and October, with contrasting emissions, were considered. While surface measurements do not correspond to the base-year of emissions and year of model simulation, they provide a climatological picture of seasonal ozone surface concentrations at diverse locations during 2000–2010.

This study uses surface concentrations and vertical profiles of ozone retrieved from the Tropospheric Emission Spectrometer (TES) sensor, total column of CO from the Measurement of Pollution in the Troposphere (MOPITT) sensor and tropospheric column NO<sub>2</sub> abundances from the Ozone Monitoring Instrument (OMI) sensor. The OMI is a nadir viewing UV-Visible spectrometer, with a spectral coverage of 264-504 nm, measuring solar radiation back scattered from earth surface and atmosphere (Levelt et al., 2006), providing near global coverage daily. Level 3 monthly gridded datasets at spatial resolution of  $0.25^{\circ} \times 0.25^{\circ}$  are used for the study. About 16,000 data points were available for the months of April, July and October (Fig. S5). Satellite derived CO column abundance are used from the MOPITT, a multi-channel thermal infrared (TIR) and near infrared (NIR) instrument with a ground footprint of  $22 \times 22$  km<sup>2</sup> and swath of 640 km, with global coverage in a threeday period. Total columnar CO from MOPITT is representative of the tropospheric column CO, since the satellite has the maximum sensitivity in this region (Kumar et al., 2012a,b). Monthly gridded total column CO (TIR, version 005) at spatial resolution of  $1^{\circ} \times 1^{\circ}$ for April and July are used, with 1076 and 727 data points available, respectively, for April and July. Retrievals of both tropospheric column ozone and surface ozone concentrations were obtained from the TES, a high spectral resolution infrared Fourier Transform spectrometer on-board Aura satellite (NASA's - Earth Orbiting satellite with an equator over pass time of ~1.45 p.m.). Earth's radiances are measured in the spectral range of  $650-3250 \text{ cm}^{-1}$ , while those in the range 993-1070 cm<sup>-1</sup> are used to retrieve atmospheric ozone (Worden et al., 2004) using an optical estimation method (Rodgers, 2000). The sensor has a footprint of 5.3 km  $\times$  8.3 km in Nadir mode and a vertical resolution of 6–7 km. Version 004 of Level 2 nadir ozone (global survey) data were used. Ozone concentrations from the TES at individual levels, including the surface level (Fig. S6) were used to evaluate modelled surface concentrations and vertical distribution. TES retrievals had fewer data points in April (291 column and 200 surface) compared to those in July (554 columnar and 489 surface), from only 6 days of valid measurements. For the study region, tropospheric column abundance of ozone from the OMI-MLS sensor were also evaluated against those from TES, and found to be in good agreement for the months considered, however, only TES data are reported in the paper.

#### 2.5. Statistical metrics

Three statistical measures have been employed to evaluate model performance: index of agreement (IA), mean normalized bias (MNB) and root mean square error (RMSE) following earlier studies (Sokhi et al., 2006; Tuccella et al., 2012; Grell et al., 2005) to statistically quantify agreement between predicted and observed data. IA evaluates spatial correlation of predicted and observed concentrations. The MNB is a useful tool to measure the relative bias of the model, with positive and negative values indicating over- or under-prediction by the model, respectively. RMSE compensates for opposite signs of residual terms, and is a good measure of accuracy. Mathematical formulations to calculate these metrics have been given (see section S2.0 of Supplementary Information).

#### 3. Results and discussion

#### 3.1. Speciated NMVOC emissions

Total NMVOC emissions for India for 2010 were estimated as 10.5 Tg (Figs. S1 and S2). As discussed in Section 2.1.3, speciated NMVOCs are classified into reactivity classes for three widely used chemical mechanisms including CB-IV (12 classes), RADM2 (19 classes) and SAPRC99 (33 classes). We further group these reactivity classes into three groups, to facilitate interpretation, Group I-III, from highest to lowest reactivity, respectively, based on reaction constant with hydroxyl radical. Fig. 2 shows total national emissions of NMVOCs in terms of Giga-moles of reactivity classes, for each of the three mechanisms considered. The largest emissions, in terms of Gmoly<sup>-1</sup> are for CB-IV speciation, especially for emissions Group III, with the lowest reactivity. This group includes 'PAR' model species, which is a surrogate for single-bonded one-carbon atom and thereby represents most alkyl groups (Gerv et al., 1989). For example, *n*-pentane would be represented as 5 PAR and ethylbenzene as 1 TOL + 1 PAR. Also, the conversion factor used for determination of moles of model species representative of unit mass of actual chemical species is dependent on the mechanism. Hence, a stark contrast in total emissions of CB-IV species is observed, against those from RADM2 and SAPRC99 reactivity classes, which show much lower annual molar emissions of reactive compounds.

The difference in treatment of reactions of model species with oxidants across the mechanisms is expected to translate directly or indirectly into differences in predicted concentration levels for secondary pollutants. From previous studies, it is usually observed that SAPRC mechanism yields higher ozone concentrations as against CB mechanism (Faraji et al., 2008; Pan et al., 2008; Yarwood et al., 2003). It assumes reactions of mono-substituted aromatics



Fig. 2. Annual emissions of lumped reactivity groups corresponding to different chemical mechanisms.

(toluene and ethyl benzene) to be ring-opening, with the formation of highly reactive products. The yield of peroxy radicals are also assumed to be higher, resulting in greater production of ozone relative to that for CB mechanism (Faraji et al., 2008). Further, the production of higher aldehydes, responsible for production of free radicals that result in increased ozone concentrations, is greater (Faraji et al., 2008). The SAPRC99 mechanism was found to compare more favourably with observed ozone trends as against the CB-IV mechanism (Byun, 2002), based on simulations made for the Houston-Galveston metropolitan area from the period August 23 to September 1, 2000 indicative of rapid high ozone episodes. The latter tends to under-predict concentrations, especially under low VOC/NO<sub>X</sub> conditions (Dodge, 2000). RADM2 was seen to predict maximum ozone yields excellently, with values lying within  $\pm 6\%$  of smog chamber experimental results in individual alkane/NO<sub>X</sub> and alkene experiments. However, poor agreement was found with individual aromatic and biogenic VOC experiments (Dodge, 2000). However, the absence of studies over the Indian domain, using different chemical mechanisms, does not permit a considered choice of mechanism in this study. The SAPRC mechanisms was chosen, but different mechanisms cannot be compared directly from differences in lumping techniques and level of complexity of treatment of reactions of individual NMVOCs. Thus, the estimated larger emissions of less reactive species, but smaller emissions of more reactive species, using CB-IV speciation, may or may not predict ozone levels differing from the other two mechanisms, but must be evaluated through simulations. Further, lumping strategies which allow good model performance for ozone prediction, may not always do well for secondary organic aerosol prediction. It was pointed out (Murphy and Pandis, 2009) that a careful allocation of primary organic aerosol volatility is needed, to better simulate gasparticle partitioning and consequent oxidized secondary organic aerosol formation in particle phase. However, such higher order effects are beyond the scope of the present study.

#### 3.2. Sectoral disaggregation into reactivity classes

A complete disaggregation of emissions from sectors into model reactivity classes (Fig. 3) shows panels arranged from left to right in increasing order of number of constituent classes for the mechanisms and therefore complexity in treatment of reaction photochemistry. For each panel, model classes are arranged in the decreasing order of reactivity as Groups I, II and III. India has an agro-based economy with agriculture with nearly 69% of the

population (www.censusindia.gov.in) living in rural India, with wide use of biomass fuels for cooking. Hence, the residential and agricultural sectors emit majority of NMVOCs, with significant contributions from on-road transport. For each reactivity group of speciated NMVOCs, again contributions are highest from residential followed by on-road transport and agriculture sectors. The predominance of residential sector NMVOC emissions is specific to south Asia, as also borne out in other inventories (Zhang et al., 2009; Li et al., 2014). Alkanes contribute to about 23% of NMVOC emissions mainly from transport, residential and industry sectors. Alkenes and alkynes contribute to 31%, primarily from residential, agriculture and transport activities. Aldehydes and ketones form 17%, originating from residential, agriculture and transport sectors, while aromatic compounds contribute to 3% of NMVOC emissions. Toxic compound emissions of 147 Gg of benzene, 100 Gg of toluene and 53 Gg of xylene are estimated for April, July and October.

In terms of emission totals, this study is in broad agreement with recent inventories for India (Li et al., 2014; Sharma et al., 2015). Sectoral shares are somewhat different (Fig. S2), with 50% residential, 17% transport, 18% agriculture and 15% industrial emissions. Industrial emissions are 15:85% respectively from combustion and solvent use activities. Examination of activities and technologies that is responsible for most emissions (Fig. 4), indicates residential wood combustion followed by on-road vehicles and agricultural residue burning are major contributing activities for all three reactivity groups of speciated NMVOCs. Aggregating into RADM2 classes leads to greater Group I classes (highly reactive) and lesser amounts of Group III classes (least reactive) (Fig. 4(a) and (c) respectively). Significant amounts of high reactivity species (Group I classes, largely HC8 lump), come from 'other industries' and residential solid fuel combustion which are somewhat lower for CB-IV and SAPRC99 mechanisms. For CB-IV and SAPRC99 classes, emissions of the corresponding species are distributed mainly across Groups II and III. The relatively large amounts of Group III class emissions in the CB-IV mechanism comes from 'other industries', on-road gasoline vehicles, residential wood combustion and agricultural residues burning (Fig. 4c). This is from the PAR model class, which lumps together single-carbon bond compounds. Compared to Sharma et al. (2015), this work estimates a somewhat larger amount of emissions of aldehydes and ketones. While the profiles used in this work contained these compounds, additional OVOC fractions (Li et al., 2014) were not added to the profiles, which could increase still further the emissions of these reactive compounds. Dissimilarities in amounts of compounds emitted in different model classes cannot be assumed, a priori, to lead to differences in ozone and SOA formation, but need to be explicitly evaluated in simulations using different chemical mechanisms.

#### 3.3. Emissions input to model simulations

Emissions input to the model (Table 3), have seasonality in agricultural residue burning, forest burning and the use of biomass fuels for residential space and water heating leading to larger injection of NO<sub>X</sub>, CO and NMVOCs in April and October, than in July. Sectoral shares of total NMVOC emissions, in April, were residential (40%) followed by agricultural (30%), and transport and industry (15% each) sectors, while in July, in the absence of open burning, shares were residential (~60%) followed by transport (20%) and industry (15%) sectors. In October emission shares were residential (42%), agricultural residue burning (25%), industry (15%) and transport (17%). Reactive NMVOC in Group I (Fig. 3), including olefins and aldehydes, were predominantly emitted from residential and agricultural sector activities. Spatial distributions of NMVOCs were made for SAPRC99 reactivity classes, as described in Section 2.2, based on spatial proxies specific to different source categories. Consistent with sources in Fig. 3, spatial distributions for the highest reactivity group (Group I), for the months of April, July and October 2010 (Fig. 5) show larger emission fluxes of high reactivity NMVOCs in both April and October, in north India (Ganga Plain), from seasonal agricultural field burning emissions superimposed on those from residential activities. Seasonality in emissions from agricultural residue burning in fields is from temporally distributed MODIS active fires in agricultural land-use grids (Venkataraman et al., 2006), while spatial distribution is made at the district level, based on production of cereals and sugarcane, whose residue is burned in fields. Agricultural field burning is also practised in peninsular India, leading to emissions in this region as well (Fig. 5a, c). Emissions from residential cooking and lighting, spatially distributed using district-level user populations of



Fig. 3. Sectoral share of NMVOC emissions, parsed by reactivity class (Gmoly<sup>-1</sup>). Panel (a) CB-IV (b) RADM2 and (c) SAPRC99.



Fig. 4. Activity/technology contributions to annual emissions of NMVOC lumped reactivity groups for different chemical mechanisms. Panels (a), (b) and (c) correspond to reactivity groups I, II and III respectively, from highest to lowest reactivity.

Table 3	
Emissions fluxes input to the model for April, July and October 2010 (Gg $\mathrm{mon}^{-1}$	).

Species	Contribution from the sector						
		Power	Industry	Transport	Residential	Agriculture	Total
NO <sub>X</sub>	Apr	161	132	83	24	151	551
	Jul				22	84	482
	Oct				23	135	534
CO	Apr	53	621	772	2337	1960	5744
	Jul				2183	221	3850
	Oct				2238	1410	5093
NMVOC	Apr	7	135	147	390	309	988
	Jul				364	40	693
	Oct				373	217	879
PM <sub>2.5</sub>	Apr	79	115	22	204	175	596
	Jul				192	24	433
	Oct				196	146	559
BC	Apr	0	16	12	39	19	86
	Jul				37	7	73
	Oct				38	15	82
OC	Apr	1	11	7	74	60	155
	Jul				70	7	97
	Oct				71	50	141
SO <sub>2</sub>	Apr	257	312	5	14	13	601
	Jul				13	2	589
	Oct				14	10	598

different fuels, are high in the Indo-Gangetic plains, from extensive use of firewood and agricultural residues for cooking in biomass stoves. About 20% of NMVOC emissions in the highest reactivity group come from transport sources, largely from gasoline powered vehicles, distributed spatially using layers of urban population density, commercial activity and land-use categories.

#### 3.4. Evaluation of the inventory through WRF-CAMx simulations

Tropospheric chemistry simulations were conducted for April, July and October months of 2010, as months of contrasting emissions, to evaluate trace gas and ozone fields from the model with corresponding satellite observations. Previous studies have emphasized the need for improvements in NO<sub>X</sub> emission inventories over south Asia in order to adequately simulate photochemistry leading to ozone production (Kunhikrishnan et al., 2006; Kumar et al., 2012a,b). As described earlier, these simulations used emission fluxes from a recent multi-pollutant inventory (Sadavarte and Venkataraman, 2014; Pandey et al., 2014) for India, which have been extensively evaluated against published inventories for India. Emissions of  $NO_X$  agreed well both in magnitude (5.6 Tgy<sup>-1</sup>) and spatial distribution with the top-down NO<sub>X</sub> inventory for India (Ghude et al., 2013), with an RMSE between the two inventories of 16  $\text{Gggrid}^{-1}\text{v}^{-1}$  and a high index of agreement of 0.76. Thus, an evaluation of simulated trace gas fields against observations was intended to assess the accuracy of the speciated NMVOC emission magnitudes and spatial and monthly distributions developed in this study.

#### 3.4.1. Evaluation of columnar trace gas abundance

The inventory was evaluated through a comparison of modelled trace gas fields, of NO<sub>2</sub>, CO and O<sub>3</sub>, with those from satellite for the simulation periods of April, July and October 2010, over the Indian domain. As simulations made in this work were for inventory evaluation, rather than model evaluation, satellite products were used as-is, without filtering for cloud interference (e.g. Kumar et al., 2012a,b), and compared with direct model output without application of averaging kernels. Modelled trace gas fields are evaluated using both ground level and satellite observations. The modelled fields capture features in observations, with columnar abundance of NO<sub>2</sub>, CO and O<sub>3</sub> is larger in April and October, than in July (Fig. 6), with broad agreement both in magnitude and spatial distribution. Statistical goodness of fit parameters (defined in supplementary information, Section S2.0), used to evaluate modelled columnar burdens against satellite observations (Table 4) included RMSE, MNB and IA (index of agreement), a measure of agreement between



Fig. 5. Spatial distribution of group I of NMVOC emissions fluxes for (a) April (b) July and (c) October 2010.

spatial distributions of modelled and observational fields.

Modelled tropospheric column CO in October is significantly larger in the model (Fig. 6) than in measurements (MNB = 0.5 and IA of 0.55) (Table 4). This results from an assumed seasonality agricultural residue burning, representative of the mid 2000s, indicating a need to update spatio-temporal distribution in the bottom-up field burning emission used here. While newer wildfire emission products using recent satellite sensors and algorithms (GFED and FINN) indicate ability or better capture small, shortduration agricultural fires, an evaluation of the agricultural fire emissions from India, in these global databases, is needed against bottom-up estimates to reconcile uncertainties in both approaches and to resolve differences. However, agreement is good in April (MNB = -0.1 and high IA = 0.76) and satisfactory in July (MNB of 0.6, IA = 0.7).

Modelled NO<sub>2</sub>, spatial distributions exhibit expected patterns with NO<sub>2</sub> confined closer to NO<sub>X</sub> emission regions, from its higher reactivity, and closely follow the distribution in observations. However, magnitude of modelled NO<sub>2</sub> is larger than observations in all three months (MNB between 0.5 and 1 and IA between 0.46 and

0.64). The peaks around the large coal-fired and gas-fired power plants are evident, followed by the highs over the Indo-Gangetic plain linked to industrial sectors (which include formal manufacturing industries like steel, cement, pharma, fertilizers, and textiles, and informal industries like brick manufacturing). Mean normalized bias showed relatively greater overestimation of column NO<sub>2</sub> in July than in April, compared to OMI retrievals. Spatial distribution plots (Fig. 6, top panel) indicate model overprediction of NO<sub>2</sub> in the Indo-Gangetic plains. This could result from the use of urban population as a spatial proxy for light industry emissions, which results in adding to the high emission flux of NO<sub>X</sub> in Indo-Gangetic plains. This indicates the need for a more accurate method of distributing industrial emissions of NO<sub>X</sub>.

Ozone satellite retrievals had a small number of samples in October, leading to difficulties in quantitative comparison. RMSE and mean normalised bias were fairly well bounded, while IA was satisfactory in April and July. A wider spatial distribution resulted from interplay between rates of atmospheric transport and photochemistry leading, respectively, to decay or production. Some of the disagreement may be related to use of the full atmospheric



Fig. 6. Spatial distribution of tropospheric column (a) CO ( $\times 10^{17}$  molecule/cm<sup>2</sup>) (b) NO<sub>2</sub> ( $\times 10^{15}$  molecule/cm<sup>2</sup>) and (c) ozone ( $\times 10^{17}$  molecule/cm<sup>2</sup>) from satellite data and WRF-CAMx for the months of April, July and October 2010.

#### Table 4

Statistical metrics comparing columnar abundance of CO,  $NO_2$  and  $O_3$  from WRF-CAMx model with satellite observations.

Species	Month	RMSE	MNB <sup>d</sup>	IA	No. of points
СО	April	0.7 <sup>a</sup>	-0.1	0.76	992
	July	0.8 <sup>a</sup>	0.6	0.70	820
	October	0.9 <sup>a</sup>	0.5	0.55	976
NO <sub>2</sub>	April	2.2 <sup>b</sup>	0.5	0.54	16,384
	July	1.9 <sup>b</sup>	1.0	0.46	16,384
	October	1.6 <sup>b</sup>	0.5	0.64	16,384
O <sub>3</sub>	April	0.3 <sup>c</sup>	0.1	0.61	128
	July	0.3 <sup>c</sup>	-0.2	0.51	128
	October	0.4 <sup>c</sup>	-0.1	0.22	97

<sup>a</sup> Unit:  $\times 10^{17}$  molecule cm<sup>-2</sup>.

<sup>b</sup> Unit:  $\times 10^{15}$  molecule cm<sup>-2</sup>.

<sup>c</sup> Unit:  $\times 10^{17}$  molecule cm<sup>-2</sup>.

<sup>d</sup> Unit: fraction.

column, rather than the lower tropospheric (surface to 500 hPa), used in previous studies (Kumar et al., 2012a,b).

## 3.4.2. Evaluation of ozone surface concentrations and vertical distribution

Evaluation of O<sub>3</sub> surface concentrations against in-situ measurements, found satisfactory agreement from comparison of monthly mean surface ozone concentrations with ground-station measurements at eight sites across India (Fig. 7,  $R^2 = 0.56$ ;  $m = 12.53 \pm 0.85$ ). A model over-prediction could be linked to increases in emissions during the 2000–2010 period, with the simulation corresponding to the highest emissions (2010) in the period, but observations being largely from the early part of the decade. April and October ozone surface concentrations (filled and grey symbols, Fig. 7), are higher than corresponding values in July (open symbols, Fig. 7). However, more coherent measurement datasets are needed, along with finer resolution modelling to make quantitative comparisons.

The model does not display much skill, when evaluated against



Fig. 7. Evaluation of WRF-CAMx monthly mean ozone concentration with climatological in-situ measurements during 2000–2010.

TES measurements (Fig. S6). However, it may be noted that the TES measurements are instantaneous ozone surface concentration values. In a given month the TES sensor has only a single overpass at given lat-lon, wherein the measured instantaneous O3 surface concentration is compared with model daytime average concentration the same location. The TES sensor has a small footprint of  $5.4 \text{ km}^2$ , while model values are averaged on a grid of  $25 \times 25 \text{ km}^2$ . Further, Kumar et al. (2012a,b) used TES kernel averaging of WRF-

Chem output before making a direct comparison, however, it was not possible to do this processing in this study. For the purposes of this work, the evaluation against TES surface concentrations, does not provide any insights for inventory improvement. Once again, there is need for a strong regional O3 monitoring network.

An attempt was made to evaluate the modelled O3 vertical distribution. Monthly mean, spatially averaged concentrations at each vertical level from the TES sensor over the modelling domain of  $7^{\circ}$ N to  $39^{\circ}$ N and  $67^{\circ}$ E to  $99^{\circ}$ E were in good agreement with TES observations in April, while somewhat underestimated in July (Fig. S7). Since the underestimation was not significant at the surface, it was felt that this may not be the result of too low NMVOC emissions in July. The underestimation was significant (factor of 1.5–2) between 300 and 500 hPa. The evaluation of vertical distributions, does not provide much insight into the inventory, but is rather a method to evaluate model chemistry and transport processes, therefore, further evaluation was not undertaken.

Modelled NO<sub>2</sub> abundances, larger than in observations, indicate the existence of a NO<sub>X</sub> limited chemistry regime, wherein significant amounts of emitted NO would have reacted to form NO<sub>2</sub> and O<sub>3</sub>, while NMVOCs and CO would remain unreacted. Such indicative inferences need verification through detailed chemistry evaluation with comprehensive measurements of VOC species and O<sub>3</sub>. However, the policy implication is that, expected increases in future industry and transport activity, accompanied by NO<sub>X</sub> emissions, could lead to increases in future ozone concentrations. Thus NMVOC control strategies are needed, particularly in the residential and agricultural sectors, which emit the highest reactivity species. Thus, interventions which substitute biomass cooking stoves and agricultural residue burning, with low-emission technologies and practices, would be important to bound future surface ozone concentrations.

#### 4. Conclusions

The present work uses a detailed technology-linked NMVOC emission database for India, along with a standard mapping method to measured NMVOC profiles, to develop speciated NMVOC emissions, which are aggregated into multiple chemical mechanisms used in chemical transport models. While state-of-the-art Indian NMVOC profiles, are not yet available, the use of an explicit speciation assignment approach, following Li et al. (2014), is a first step to constraining uncertainties in NMVOC emissions. Emissions are included from combustion activities in four sectors (industry, transport, agriculture and residential) and noncombustion activities (solvent extraction units), mapped to NMVOC profiles in the USEPA SPECIATE database, to obtain emissions of over 400 compounds. The speciated NMVOC database was further regrouped into model-ready species classes of RADM2, SAPRC99 and CB-IV gas-phase mechanisms, and spatially distributed at  $0.25^{\circ} \times 0.25^{\circ}$  resolution, using source-specific spatial proxies. Residential wood combustion for cooking and agricultural residue burning in fields, followed by transport activities, were the largest contributors to highly reactive NMVOC species emissions over India. Simulations were made to diagnose shortcomings in the inventory, using the WRF-CAMx model, with the SAPRC99 photochemical mechanism, over India for contrasting months of April, July and October, which have differing emissions. Modelled columnar abundance of NO<sub>2</sub>, CO and O<sub>3</sub> agree well with in-situ and satellite observations, both in magnitude and spatial distribution, on monthly scales. Model over-prediction of NO<sub>2</sub> in the Indo-Gangetic plains, was attributed to the use of urban population as a spatial proxy for light industry emissions, which results in adding to the high emission flux of NO<sub>X</sub> in Indo-Gangetic plains. Thus, further refinement of spatial distribution of NO<sub>X</sub> emissions is needed. Model over-prediction of CO in October, was attributed to a satellite derived spatio-temporal distribution, typical of the mid-2000s, which needs updation. The inventory needs extension to include other anthropogenic sources of NMVOC emissions, including the use of personal products, and biogenic emissions.

Future work is needed to fully evaluate the performance of inventories prepared in this work based on different chemical mechanisms for ozone prediction in India. Overall, the work indicates a  $NO_X$  limited chemistry regime, implying that future increases in industry and transport activity, could drive increases in future ozone concentrations. This emphasizes the need for NMVOC control strategies, particularly in the residential and agricultural sectors, which emit the highest reactivity NMVOC species, to achieve control of ozone, which is both a short-lived climate pollutant and an air pollutant that negatively affects human health and crop production. Finally, future Indian measurements of NMVOC profiles from local sources are needed to improve our understanding of regional air quality and climate change effects from ozone.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.03.037.

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