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RTEII: A new high-resolution (0.1° × 0.1°) road transport emission inventory for India of 74 speciated NMVOCs, CO, NO_x, NH_3, CH_4, CO_2, $PM_{2.5}$ reveals massive overestimation of NO_x and CO and missing nitromethane emissions by existing inventories

Haseeb Hakkim, Ashish Kumar, Saurabh Annadate, Baerbel Sinha, Vinayak Sinha *

Department of Earth and Environmental Sciences, Indian Institute of Science Education and Research Mohali, Sector 81, SAS Nagar, Manauli PO, Mohali, Punjab, 140306, India

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A B S T R A C T

21 of 30 most polluted cities for particulate matter ($PM_{2.5}$) are in India, yet the distribution, identity and emissions of volatile organic compounds (VOCs) from traffic, which are $PM_{2.5}$ and ozone precursors, remain unknown. Here, we measured emission factors (EFs) of 74 VOCs from a range of Indian vehicle-technology and fuel types. When combined with 0.1 ° × 0.1 ° spatially resolved activity data for the year 2015, toluene (137 ± 39 Gg yr^1), isopentane (111 ± 38 $Ggyr^{-1}$), and acetaldehyde (41 ± 6 $Ggyr^{-1}$) were top 3-VOC emissions. Petrol-2-wheelers and LPG-3-wheelers emitted the highest VOCs (EFs> 50 gVOC/L) and had highest secondary pollutant formation potential, so their replacement with electric vehicles would improve air quality. EDGARv4.3.2 and REASv.2.1 emission inventories overestimated total road sector emitted VOCs due to obsolete EFs and activity data, in particular over-estimating ethene, propene, ethyl benzene, 2,2- dimethyl butane, CO, NO_x while significantly under-estimating acetaldehyde. Nitromethane emissions were missing from previous inventories and with isocyanic acid and benzene contributed significantly to toxic emissions (summed total ~41 ± 4 $Ggyr^{-1}$). Knowledge of key VOCs emitted from the world's third largest road-network provides critical new data for mitigating secondary pollutant formation over India and will enable more accurate modelling of atmospheric composition over South Asia.

1. Introduction

India has witnessed rapid growth and diversification in its transportation sector in the past decade. With the third largest road network in the world, traffic emissions have long been recognized as a major pollution source for Indian cities, 21 of which are amongst the world's top 30 most polluted cities for particulate matter ($PM_{2.5}$) (IQAir, 2019) and also experience high ozone pollution. While it has been shown that more than 50% of the fine-mode PM_1 is made of secondary aerosol originating from gas phase precursors including volatile organic compounds (VOCs) in several Indian cities (Gani et al., 2019; Gawhane et al., 2017; Ojha et al., 2020), no information exists concerning the identity, emissions and distribution of VOCs emitted from the road transport sector over India. Emission inventories used by global and regional chemical transport models to account for traffic emissions over India such as Emission Database for Global Atmospheric Research, EDGARv4.3.2 (Huang et al., 2017) and Regional Emission inventory in Asia, REASv2.1 (Kurokawa et al., 2013) rely on outdated emission factors of two decades or older vehicles and have not been updated for new emission control technology, use of fuel portfolio and fleet composition. Just to highlight, emission standards for new vehicles were made Bharat stage-3 (equivalent to Euro-3) compliant by April 2010 all over India and sales of highly polluting 2-stroke engine-2-wheelers were completely stopped after 2000 by legislation. Rapid changes in transport sector emissions therefore necessitate updating of emission inventories (Reyna et al., 2015) so that air quality and chemical transport models are able to forecast atmospheric composition and air quality accurately over the region. The Indian transport sector is known to be a significant contributor to the total country-wide emissions of nitrogen oxides (NO_x; 25–55%; 4–5 Tg yr^{-1}) (Huang et al., 2017; Kurokawa et al., 2013; Li

* Corresponding author.
E-mail address: vsinha@iisermohali.ac.in (V. Sinha).

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et al., 2017). Increasing air pollution over India due to both ozone and secondary organic aerosol (Gani et al., 2019; V Kumar et al., 2016), for which NO_x and VOCs act as precursors, render the road transport, a key sector for reduction of healthcare costs estimated to be 3% of the Indian GDP due to air pollution alone (World Bank, 2016).

A key limitation of current emission inventories reporting VOCs from the transport sector is that they provide only a lumped representation of volatile organic compounds present in the vehicular exhaust emissions and are therefore poorly constrained in terms of identity of VOCs (Huang et al., 2017; Kurokawa et al., 2013; Q Zhang et al., 2009). Lack of such information presents a critical knowledge-gap for deciding which VOCs are important to monitor and regulate from traffic emissions. The maximum speciation or number of individual VOCs reported by any existing inventory for the road transport sector in India is only 12 (Sharma et al., 2015). VOCs differ considerably in their chemical reactivity and ozone and SOA formation potentials (Carter, 1994; Derwent et al., 2010). Oxygenated VOCs like acetaldehyde are particularly reactive and can fuel ozone formation regionally but also form peroxy acetyl nitrates, which are lachrymators and transfer reactive nitrogen from the urban to the remote troposphere and also act as a source of HO_x (OH and HO_2) radicals. With global models unable to reproduce acetaldehyde in urban outflow (Millet et al., 2010), there remain open questions about missing urban VOC sources and their strengths. Aromatics like toluene and xylenes have high secondary organic aerosol formation yields. Hence it is crucial to identify the individual VOCs responsible for detrimental impacts on atmospheric composition and air quality from the road-transport sector and map their distribution and emissions over the Indian region.

Here, we first measured emission factors (EFs) for 74 speciated VOCs, methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) using a suite of analytical techniques like thermal desorption-gas chromatography-flame ionization detection, proton transfer reaction mass spectrometry and cavity ring down spectroscopy. These were measured for major fuel and vehicle categories prevalent over India. In order to determine trade-offs of fuel and vehicle choices for emissions and air quality, we then assessed the ozone and secondary organic aerosol formation potential of emitted VOCs from these major vehicle and fuel categories. By combining the EFs with high resolution activity data, we then calculated gridded emissions over the Indian region at a spatial resolution of $0.1^\circ \times 0.1^\circ$ for the year 2015. Comparisons with existing emission inventories to identify significant changes and new results relative to the data in the existing emission inventories for VOCs and major criteria air pollutants were further carried out for highlighting the novelty of this study.

2. Materials and methods

2.1. Emission factor measurements

Tailpipe-emissions from 72 vehicles were sampled, spanning a range of size, age, engine technology and fuels including petrol (23), diesel (33), liquefied petroleum gas (LPG, 9) and compressed natural gas (CNG, 7). Table S1 lists the details. Sampling was carried out in Chandigarh and Mohali (30.660–30.750°N, 76.700–76.840°E) between March-2017 and October-2018. Vehicles were chosen for sampling based on common and popular vehicle models in India. Tailpipe-emissions were collected after the engine had warmed up during idling stage when emissions are unlikely to be underestimated (Brodrick et al., 2002; Deng et al., 2020; Rahman et al., 2013). Gas samples were collected in 6 L passivated SilcoCan steel canisters (Restek, USA) using a Teflon VOC pump at a flow rate of 5500 ml min^{-1} (Model - N 86 KT.45.18; KNF pump) and pressurized up to 30 psi as per previously validated and reported protocol (A Kumar et al., 2020). The analyses were completed within 72 h of collection at the IISER Mohali Central Atmospheric Chemistry Facility in India (Chandra et al., 2017; Sinha et al., 2014). A thermal desorption gas chromatograph flame ionization detector (Model7890 B, Agilent Technologies, Santa Clara, CA, US) and high-sensitivity proton transfer reaction mass spectrometer (HS Model 11-07HS-088, Ionicon Analytik Gesellschaft, Austria) were used for quantification of the non-methane VOCs (details in text S1, S2 of supplement and Figure S1). Carbon dioxide (CO_2) and methane (CH_4) were measured using a cavity ring down spectrometer (Model G2508, Picarro, Santa Clara, CA, USA as detailed in text S3) and carbon monoxide (CO) was measured using a nondispersive infrared (NDIR) filter correlation spectrometer (Thermo Fisher Scientific, Model No. 48i). Instruments and the list of compounds measured in the exhaust emissions are listed in Table S2. Further details pertaining to calibrations are available in Table S3, Table S4 and elsewhere (Chandra et al., 2017; V Kumar et al., 2018). The total measurement uncertainty was lower than 16% for 60 VOCs whereas 14 VOCs had an uncertainty lower than 40%. The measurement uncertainty for CO_2, CH_4 and CO was less than 6%.

Emission factors of 74 NMVOCs, CO, CO_2 and CH_4 were calculated using the carbon mass balance (CMB) method (Keita et al., 2018; Yokelson et al., 1999) as given below:

$$EF_x\left(gL^{-1}\right) = F_c \times 1000\left(gkg^{-1}\right)\frac{MM_X\left(g\ mol^{-1}\right)}{MM_C\left(g\ mol^{-1}\right)}\frac{C_X}{C_{total}}d\left(kgL^{-1}\right) \tag{1}$$

$$C_X = \frac{[X]}{[CO_2]} \tag{2}$$

$$C_{total} = \sum_Y\left(nC_Y\frac{[Y]}{[CO_2]}\right) \tag{3}$$

wherein EF_x is the emission factor of X, F_c is mass fraction of carbon in the fuel (0.87 for diesel, 0.82 for petrol, LPG and 0.74 for CNG (EPA, 2015; Gentner et al., 2012; S Zhang et al., 2014). MM_X is molar mass, MM_C is 12.01 g mol^{-1}, C_X is number of moles of X and C_{total} is the total moles of carbon emitted. C_X and C_{total} were calculated using equations (2) and (3) respectively. $[X]$ and $[CO_2]$ are measured concentrations of X and CO_2, Y represents carbon containing compounds including CO_2, CH_4 and CO, nC_Y is number of carbon atoms for the corresponding compound Y and $[Y]$ is measured concentration in exhaust emissions. The fuel consumption for petrol and diesel is reported in litre whereas it is in kg in the case of CNG and LPG. Therefore EFs reported for all the vehicle types were converted from gkg^{-1} to gL^{-1} by multiplying with fuel density, d (0.85: diesel; 0.74: petrol; 0.51: LPG; 0.76: CNG at 288.15 K; 1 atm) (Kamyotra et al., 2010) for consistency and comparison purpose. Fuel specific emission factors and standard error of the measured compounds averaged over different vehicle categories are reported in Table S5. For species that were not measured, we used emission factors from the peer-reviewed literature (Table S5, rows 78–84).

2.2. Activity data

The UN-Adjusted Population density for the year 2015 (CESIN, 2015) was derived from the database of the Centre for International Earth Science Information Network in the frame of the Gridded Population of the World project using procedure described in Balk et al. (2006). The national highway road network in India (1, 32,500 km) was digitized from the official map obtained from National Highways Authority of India (MoSP, 2020) using ArcGIS version 10.2 (ESRI Inc., Redlands, CA, USA). The digitized map consists of a vector database in which each road segment is composed of a series of geospatial points that has a defined location (latitude, longitude) on the base map.

2.3. Fuel consumption

All-India state-wise fuel consumption data for the year 2015–16 was taken from the national fuel consumption statistics report of the Ministry of Petroleum and Natural Gas, Government of India (MNPG, 2016). This report is compiled annually based on the sales figures submitted by different oil marketing companies and retail outlets on a state-wise basis. The fraction of fuel consumed by different vehicle categories within the transport sector (Table S6) was obtained from an all-India survey conducted by Petroleum Planning and Analysis Cell, Ministry of Petroleum and Natural Gas (Nielson, 2013). The survey covered over 2000 retail outlets spread across 150 districts located all over India constituting 85% of the total sale of fuels to derive the fraction of different consuming vehicle categories. The fuel consumption data was then disaggregated on a gridded map of India at a resolution of 0.1 ° × 0.1 ° using population density and road network density (Table S7) as proxies as per previously reported methods (Kuenen et al., 2014; Trombetti et al., 2018). This was done after accounting for the availability of each fuel type via retail network in each grid area.

2.4. Compilation of emission inventory and further calculations

Figure S2 provides a schematic of the method. The total annual emission from road transport sector (E) in metric tonnes per year (t yr^{-1}), of X, for the year 2015 was calculated using equation (4).

$$\text{Total Emission}, \ E_X = \sum_i^N E_{petrol} + \sum_i^N E_{diesel} + \sum_i^N E_{LPG} + \sum_i^N E_{CNG} \tag{4}$$

where E_X stands for the total annual emission of pollutant X, *i* stands for the *i*th number of grid and *N* stands for the total number of grids in the map of India corresponding to 3,287,240 km^2. The contribution from each fuel category was estimated using following methodology as described for the petrol fuelled vehicles:

$$\sum_i^N E_{petrol} = \sum_i^N E_{2w} + \sum_i^N E_{4w} \tag{5}$$

E_{petrol} = Total emission of pollutant m due to petrol exhaust.
E_{2W} = Total emission of pollutant m due to petrol 2-wheelers.
E_{4W} = Total emission of pollutant m due to petrol 4-wheelers.

Petrol 3-wheelers contribute to only 2.34% of the total petrol consumption by the road transport sector (Nielson, 2013). They are being phased out rapidly as several auto drivers have shifted to CNG due to their inherently superior fuel efficiency and augmented infrastructure for CNG refilling (Goyal, 2003; Kathuria, 2004). Therefore we neglected them in our calculations.

$$\sum_i^N E_{2w} = EF_{m,\ 2W} \times \left(\sum_i^N F_{PD,\ 2W} + \sum_i^N F_{RD,\ 2W} \right) \tag{6}$$

$F_{PD,2W}$ = Total fuel consumed by petrol 2-wheelers distributed based on population density
$F_{RD,2W}$ = Total fuel consumed by petrol 2-wheelers distributed based on based upon road network density
$EF_{m,2W}$ = Emission factor of pollutant m in exhaust of petrol 2-wheelers.

$$\sum_i^N F_{PD,\ 2w} = \sum_i^N P_i \times \sum_i^N C_{i,\ 2w} \tag{7}$$

P_i = Population density of *i*th grid.
$C_{i,2W}$ = Per capita fuel consumption for petrol 2-wheelers in the *i*th grid.

$$TF_{PD,2W} = TF_{petrol} \times f \times \alpha_{2W} \times \delta_{2w} \tag{8}$$

$TF_{PD,\ 2W}$ = Total consumption of petrol 2-wheelers in a given state to be distributed based upon population density.
TF_{petrol} = Total consumption of petrol in a given state.
f = Fraction of fuel consumed by the road transport sector (f = 0.99 for petrol, 0.74 for diesel, 0.01 for LPG and 1 for CNG) (Table S6).
α_{2w} = Fraction of petrol consumed by 2-wheelers. The value of α vary from state to state and it ranges from 0.41 to 0.82 for 2-wheelers and 0.14–0.58 for 4-wheelers (α_{4W}) (Table S6).
δ_{2W} = Fraction of fuel consumed by petrol 2-wheelers to be distributed based upon population density (Table S7).

$$C_{2w} = \frac{TF_{PD,2W}}{P} \tag{9}$$

P = Total population of the state.

The *f* and α value for petrol, diesel and LPG were obtained from an in-depth all India survey conducted by the Petroleum Planning and Analysis Cell (PPAC) division of Ministry of Petroleum and Natural Gas, GOI (Nielson, 2013) and that of CNG was obtained from MNPG (2016). For a particular vehicle category, the total fuel consumption in a given state ($TF_{PD,\ 2W}$) is then divided by the total population of the state to calculate the per capita fuel consumption, C_{2W} (equation (9)). Within a state the value of C_{2W} for a particular vehicle category remains constant and only varies between different states.

Similarly

$$\sum_i^N F_{RD,\ 2W} = \sum_i^N b_i \times \sum_i^N G_{i,2W} \tag{10}$$

b_i = No of spatially referenced road network GIS data points passing the grid i.
$G_{i,2W}$ = Fuel consumption due to an individual road network GIS data point in a given state.

For b > 0, equation (10) and thereafter are applied and for b = 0 (i.e., no road network points in grid i, the fuel consumption in a grid is completely attributed to population density (F_{PD}) as per equation (6).

$$TF_{RD,2W} = TF_{petrol} f \times \alpha_{2W} \Upsilon_{2w} \tag{11}$$

$$\sum_i^N G_{i,2W} = \frac{TF_{RD,2W}}{B} \tag{12}$$

Υ_{2W} = Fraction of fuel consumed by petrol 2-wheelers based upon road network density (Table S7).
$TF_{RD,\ 2W}$ = Total consumption of petrol 2-wheelers in a given state based upon road network density
B = Total no of spatially referenced road network GIS data points in the given state.

A grid wise digitized map of the national highway road network in India was developed using ArcGIS version 10.2 (ESRI Inc., Redlands, CA, USA). The spatial accuracy of the road network GIS data points were evaluated by georeferencing a National Highway map obatined from National Highways Authority of India on to the digital map.

The emission from petrol 4-wheelers were then calculated using equations 13–19:

$$\sum_i^N E_{4w} = EF_{m,\ 4w} \times \left(\sum_i^N F_{PD,4w} + \sum_i^N F_{RD,\ 4w} \right) \tag{13}$$

$$\sum_i^N F_{PD,\ 4w} = \times \sum_i^N P_i \times \sum_i^N C_{i,\ 4w} \tag{14}$$

$$TF_{PD,4w} = TF_{petrol} \times f \times \alpha_{4w} \times \delta_{4w} \tag{15}$$

$$C_{LDV} = \frac{TF_{PD,4w}}{P} \quad (16)$$

$$\sum_i^N F_{RD,\ 4w} = \sum_i^N b \times \sum_i^N G_{i,4w} \quad (17)$$

$$TF_{RD,4w} = TF_{petrol} \times f \times \alpha_{4w} \times \Upsilon_{4w} \quad (18)$$

$$\sum_i^N G_{i,4w} = \frac{TF_{RD,4w}}{B} \quad (19)$$

Similar methodology as explained above was used for calculating emissions due to diesel fuelled, LPG fuelled and CNG fuelled vehicles (equations (20)–(22) respectively):

$$\sum_i^N E_{diesel} = \sum_i^N E_{3W} + \sum_i^N E_{4w} + \sum_i^N E_{HDV} \quad (20)$$

$$\sum_i^N E_{LPG} = EF_{m,\ LPG} \times \left(\sum_i^N F_{PD,\ LPG} + \sum_i^N F_{RD,\ LPG} \right) \quad (21)$$

$$\sum_i^N E_{CNG} = EF_{m,\ CNG} \times \left(\sum_i^N F_{PD,\ CNG} + \sum_i^N F_{RD,\ CNG} \right) \quad (22)$$

Detailed method to determine contributions from each fuel category using example calculation is explained in supplement (Text S4; Table S8, Table S9). The overall uncertainty in emissions from each vehicle category calculated by propagating the standard error of the mean of emission factor and the error in fuel consumption data, was 24–49% for VOCs, 10–11% for CO_2, 13–85% for CH_4 and 18–44% for CO.

CO_2 equivalent emissions were calculated using relative Global Warming Potentials (GWP_{100}) (Myhre et al., 2011) per equation (23).

$$Total\ CO_2eq = (28 \times [CH_4]) + [CO_2] \quad (23)$$

where $[CH_4]$ and $[CO_2]$ are the total annual emission of methane and carbon dioxide respectively for each fuel type.

2.5. Calculation of OH reactivity and secondary pollutant formation potentials

Using rate constants for the reaction of VOCs with the hydroxyl radical (McGillen et al., 2020), maximum incremental reactivity method (Carter, 1994) and SOA yields of 38 VOCs compiled from the literature (Table S10) and measured concentrations, the OH reactivity, ozone formation potential (OFP) and SOA production factor (PF) for fuel and vehicle categories were determined using equation (24) (V Kumar and Sinha, 2014), 25 and 26 respectively.

$$\text{Total OH reactivity } (s^{-1}) = \sum_i [NMVOC_i] \times k_{OH+NMVOCi} \quad (24)$$

where $k_{OH+NMVOCi}$ is the rate constant for reaction of $NMVOC_i$ with OH and $[NMVOC_i]$ is measured concentration in tailpipe-exhaust emissions.

$$OFP = \sum_i EF_i \times MIR_i \quad (25)$$

where EF_i is the emission factor and MIR_i is the ozone formation coefficient for VOC species i in the maximum increment reactions of ozone (Carter, 1994, 2009).

$$PF_{SOA} = \sum_i EF_i \times Y_i \quad (26)$$

where PF_{SOA} is the secondary organic aerosol production factor, EFi is the emission factor and Y_i are the yield of VOC species i to form SOA (Table S10).

3. Results and discussion

3.1. Emission factor measurements

Fig. 1 summarizes measured EFs (gNMVOC emitted/L of fuel consumed) of different fuel and vehicle categories alongwith the 5 major VOCs' contributions. EFs of liquefied petroleum gas (LPG) 3-wheelers and petrol 2-wheelers were significantly higher (>50 g L^{-1}) than the other vehicle and fuel categories (<10 g L^{-1}). LPG, widely regarded a cleaner fuel due to its lower direct emissions of CO_2, NO_x, and particular matter (Ristovski et al., 2005) nevertheless had the highest total NMVOC emission factor (62.3 ± 18.2 g L^{-1}). A large fraction of lower alkanes such as *n*-butane (22%) and *i*-butane (14%) were present in exhaust emissions indicating poor burn efficiencies. Toxic aromatic VOCs were found in low amounts (<1%), but reactive alkenes (43%; k_{OH}: 1.0–10.0 $\times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) such as trans-2-butene and propene were high. LPG as a fuel is almost exclusively used by 3-wheelers which operate in stop-and-go commuting mode in many Indian cities.

Petrol 2-wheelers (52.0 ± 15.4 g L^{-1}) had second highest EFs. Aromatic compounds such as toluene, ethylbenzene, xylenes, and carcinogenic benzene (collectively >30%) were among highest emitted VOCs. Optimization of combustion conditions and post-emission control in 2-wheeler engines is more challenging than in 4-wheeler engines (Liu et al., 2008; Platt et al., 2014). CNG vehicles, which were reported to have shown 50% reduction in NO_x and virtually negligible particulate matter in the exhaust emissions (Goyal, 2003), appear to be a better alternative as NMVOC EFs were lower (9.3 ± 4.4 g L^{-1}). Petrol 4-wheelers on the other hand equipped with better Bharat Stage-III (equivalent to Euro-III) or higher-grade catalytic converters had the lowest NMVOC EFs (1.3 ± 0.5 g L^{-1}). The increased contribution of OVOCs (45–50%) and reduced contribution of aromatic VOCs (11–17%) and alkanes (5–6%) to the emitted NMVOCs distinguished petrol and diesel exhaust emissions, though both emitted significant acetaldehyde. All diesel vehicle categories were significant emitters of acetaldehyde and nitromethane. Benzene, ethene and acetone, too, were emitted in significant amounts by diesel engines. Particularly nitromethane and benzene, which are both carcinogens, poses direct health risks (ICE, 2016; WHO, 2019). Exposure effects of nitromethane include eye, nasal and throat irritation, damage to central nervous system, lungs, and liver (DHHS, 1997; Espenship et al., 2019).

3.2. Impact of fuel types and vehicle classes on ozone and SOA formation potential

Fig. 2 shows the comparison of percentage contribution of different chemical classes of NMVOCs to mass concentrations, OH reactivity (s^{-1}), ozone formation potential (OFP) (gO_3 L^{-1} fuel burnt), and secondary organic aerosol production factor (PF) (gSOA L^{-1} fuel burnt). Air quality impacts arise from both direct emissions and the potential of these emissions to form pollutants like ozone and secondary organic aerosols (Figure S3). Given that a significant fraction of $PM_{2.5}$ in megacities like Delhi comprise of secondary organic aerosol (Gani et al., 2019), we analysed the fuel types for their OH reactivity, ozone and SOA formation potentials (Fig. 2). LPG fuelled vehicles had the highest values followed by petrol, diesel and CNG. The total OH reactivity was driven by reactive alkenes (38–92%) and OVOCs (1–46%) across all fuel and vehicle types. Isomers of butene (*trans*-2-butene, *cis*-2-butene and 1-butene) contributed 71% of the total OH reactivity calculated for LPG vehicles, while ethene (39%) and propene (11%) were major contributors in CNG and petrol exhaust respectively (Figure S4). Acetaldehyde was the highest contributing VOC from diesel exhaust with 21% followed by propene (15%) and monoterpenes (14%). Although alkanes were the largest emissions by mass in petrol, LPG and CNG exhaust emissions, it was not reflected in an equally large share of total OH reactivity or OFP due to their slower reaction rate with OH radical. Some studies have suggested that conversion from petrol to LPG fuelled

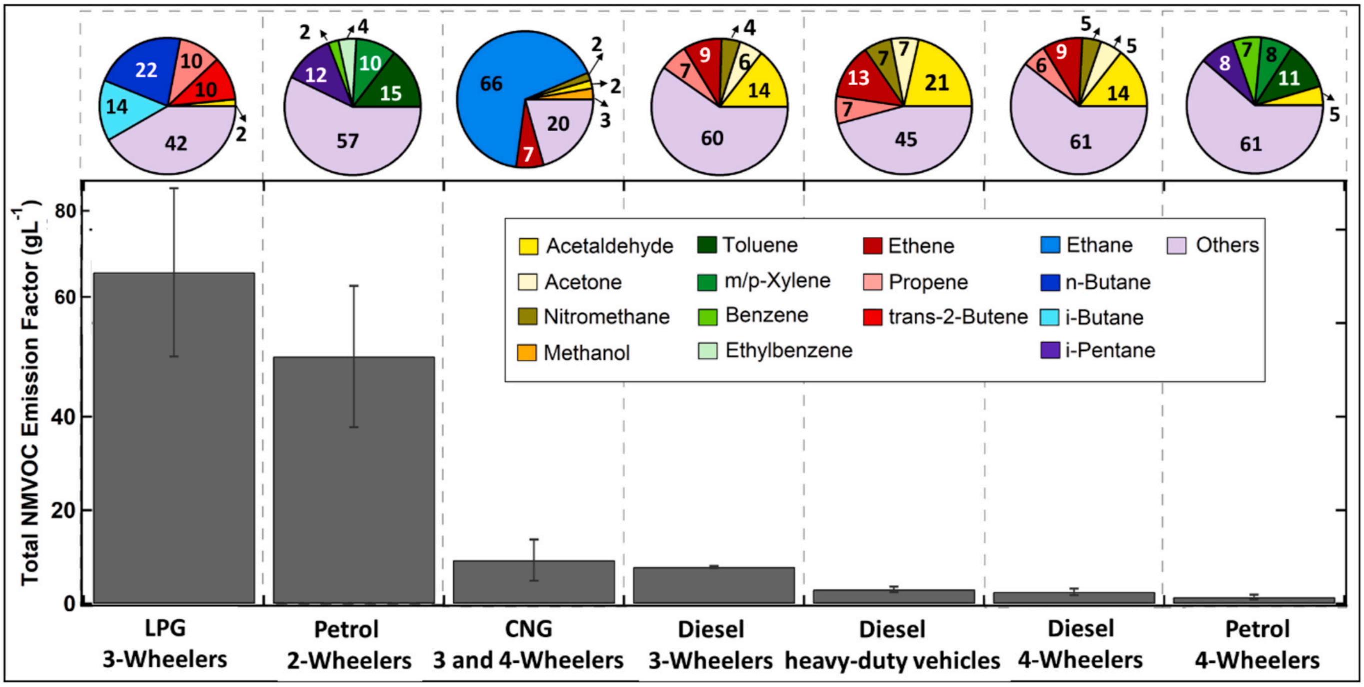

Fig. 1. Non-methane volatile organic compound emission factors (grams of NMVOC emitted per litre of fuel consumed) determined for different fuel and vehicle categories with contributions of the major 5 VOCs (selected based on their emission strength and reactivity) in percentage shown in the pie-charts. Error bars represent the standard error of averaged emission factor.

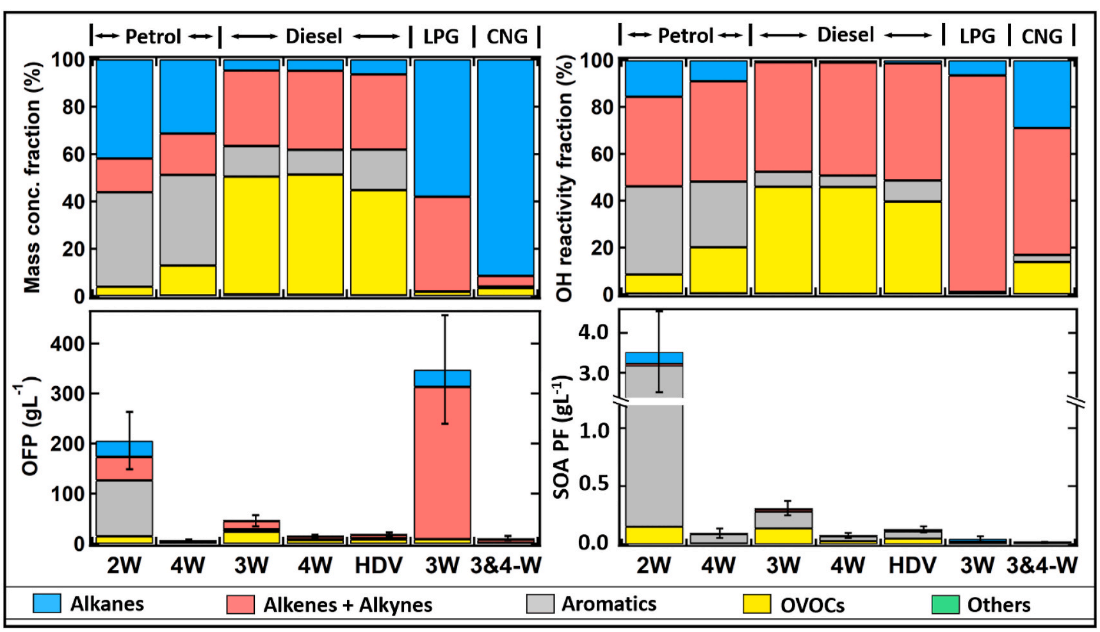

Fig. 2. Comparison of percentage contribution of different chemical classes of NMVOCs to mass concentrations, OH reactivity (s^{-1}), ozone formation potential (OFP) (gO3 L^{-1} fuel burnt), and secondary organic aerosol production factor (PF) (gSOA L^{-1} fuel burnt). Error bars represent the standard error in total OFP and PF.

vehicles can considerably reduce the emission of ozone precursors in exhaust emissions (Barletta et al., 2008; Chang et al., 2001). The OFP value for LPG fuelled vehicles (348 ± 109 g L^{-1}) observed in our study was nearly 3 times higher than that of petrol (128 ± 40 g L^{-1}) and 16 times higher than that of diesel (22 ± 4 g L^{-1}) fuelled vehicles. The bulk emission of alkenes and alkyne such as isomers of butene, propene and propyne present in the LPG exhaust accounted for the largest share of total OFP (~63%). The OFP values for total NMVOCs in the CNG exhausts were much lower (11 ± 4), indicating that using CNG may effectively reduce O_3 formation due to vehicle emissions in urban areas and hence for ozone pollution abatement represents a smarter choice. Among the other fuel types, aromatic VOCs (40–54% in petrol) and OVOCs (49–53% in diesel) were major contributors to OFP.

The vehicular exhaust emissions contribute to $PM_{2.5}$ through both primary organic aerosol (POA) and SOA precursors (Derwent et al., 2010; Jathar et al., 2013). While diesel heavy duty vehicles (HDV) are known to significantly emit POA (Schauer et al., 1999), there is disagreement in the literature about relative contributions of different vehicle classes (Gentner et al., 2017). Some studies (Deng et al., 2017; Gentner et al., 2017; Gordon et al., 2014) report diesel exhausts to be more efficient in forming SOA than petrol exhausts while others (Bahreini et al., 2012; Nordin et al., 2013; Platt et al., 2013) suggest that petrol exhausts can exceed diesel emissions in forming SOA. We found the average SOA formation potential to be highest for petrol (2.19 ± 0.72 g L^{-1}) followed by diesel (0.13 ± 0.03), LPG (0.05 ± 0.02 g L^{-1}) and CNG (0.02 ± 0.004 g L^{-1}) exhaust emissions. This is mainly due to petrol 2-wheelers, which have the highest contribution to SOA production (3.53 ± 1.0 g L^{-1}), a value ~10 times that of diesel 3-wheelers. Benzene, toluene, ethylbenzene and isomers of xylene (BTEX), contributed highest to the total SOA production among aromatics from petrol 2-wheeler (~75%) and from diesel 3-wheeler (~30%) exhaust emissions. For petrol 4-wheelers, the average SOA production factor (PF) (0.095 ± 004 g L^{-1}) was marginally higher than previous reported ranges (0.004–0.07 g L^{-1}) (Liu et al., 2008; Nordin et al., 2013) whereas, diesel vehicle exhaust PFs (0.08 ± 0.02 g L^{-1}) were within reported ranges (0.04–1.5 g L^{-1}) (Chirico et al., 2010; Deng et al., 2017).

The highest SOA production factors for petrol 2-wheelers and diesel 3-wheelers, which together comprise ~25% of the total Indian fuel consumption (Nielson, 2013) suggests a larger contribution to ambient particulate pollution (~65 Gg yr^{-1}; Table S11) than has been hitherto recognized. Current emission control regulatory decisions for PM control rely on primary emissions and focus on diesel HDVs, which consumes 36% of the on-road fuel consumption (Nielson, 2013). Several Indian cities including Delhi are regulating the HDV entry by allowing entry at night (10 p.m.–5 a.m.) (Gulia et al., 2018), while 2 and 3-wheelers are ignored. However, large differences in SOA formation potential of petrol 2-wheelers over diesel HDVs (0.13 ± 0.03) by 27 times suggest both POA and SOA should be considered. While the recent upgrade in emission standard (BS IV to BS VI) would require nearly all diesel engines to use diesel particulate filters to further reduce primary emissions of PM, petrol 2-wheelers would still be an issue.

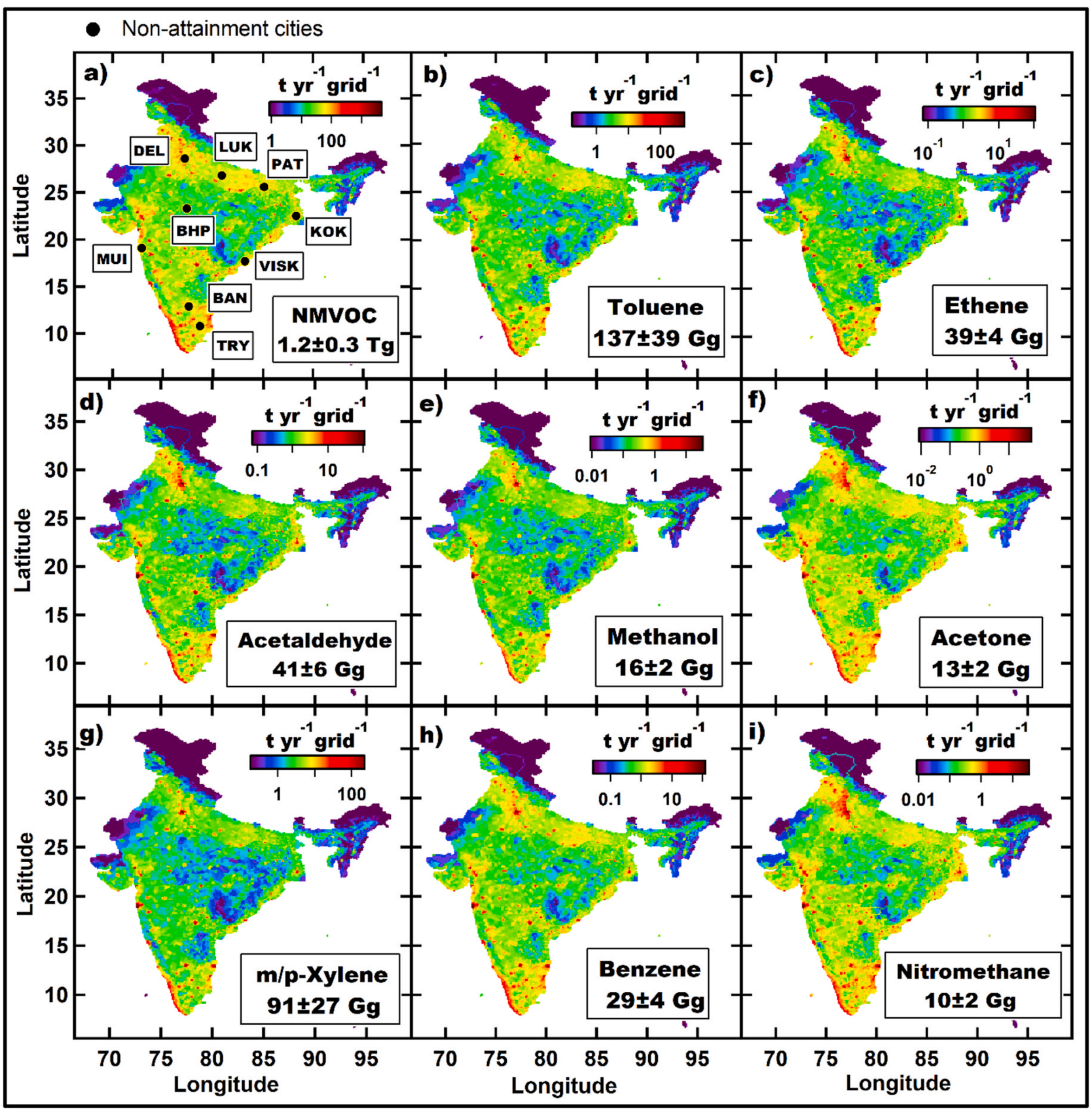

Fig. 3. Annual emissions of total NMVOC and selected VOC species from road transport sector in India for the year 2015–16. Markers indicate the location of major polluted cities identified by central pollution control board of India (CPCB) in which the prescribed national ambient air quality standard (NAAQS) limits are often violated (non-attainment cities). DEL – Delhi, LUK – Lucknow, PAT – PATNA, BHP – Bhopal, MUI – Mumbai, KOK – Kolkata, BAN – Bengaluru, VISK – Visakhapatnam, TRY – Trichy.

3.3. Gridded 0.1-degree x 0.1-degree distribution of traffic emitted NMVOCs over India

Fig. 3 shows the spatial distribution of the total NMVOC emissions and selected VOCs over India emitted from traffic in 2015. VOCs were selected keeping in mind their atmospheric chemistry and air quality relevance. Also marked are 9 “non-attainment” cities with high $PM_{2.5}$, many of which are among the world’s most polluted cities (IQAir, 2019), namely Delhi, Lucknow, Patna, Bhopal, Mumbai, Kolkata, Bengaluru, Visakhapatnam and Trichy. The total annual NMVOC emissions were 1.2 ± 0.3 $Tgyr^{-1}$. The overall spatial emission pattern of NMVOC emissions are highest in congested urban areas and metropolitan cities where 31% of the total population in India resides (ORGI, 2011). This is expected as urban suburban driving constitute most of the passenger transport which is dominated by high NMVOC emitters such as 2-wheelers and 3-wheelers. In fact, rural areas in which 4-wheeler

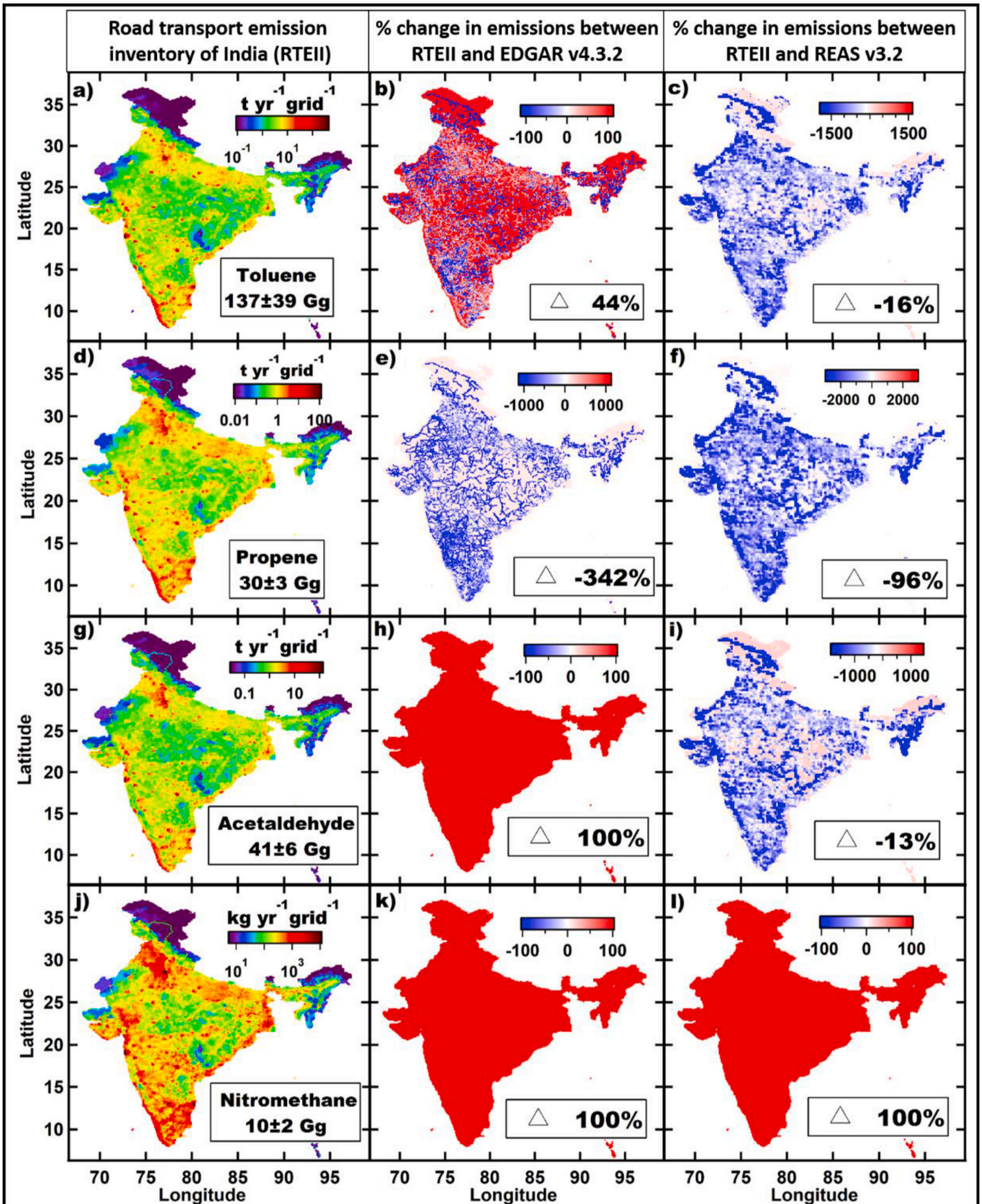

Fig. 4. Annual gridded emissions (0.1 ° × 0.1 °) of toluene, propene, acetaldehyde and nitromethane in the Road Transport Emission Inventory of India (RTEII). And percentage differences relative to EDGAR v4.5 (second column) and REAS v3.2 (third column) emission inventories for the year 2015 over India.

ownership is lower also frequently experience exceedance of $PM_{2.5}$ (Ravishankara et al., 2020). The emissions scale with urban growth and population redistribution rates from rural to urban areas. Exacerbating congestion in traffic, insufficient parking space, narrow village roads and inadequate public transport system render 2-wheelers, a convenient but polluting choice across India.

Owing to their low mileage (<4 kmL^{-1}), high fuel consumption (~36% of the total) and efficient engines which allows relatively more complete burning of fuel, diesel HDVs were responsible for the largest share of CO_2eq emissions (40%). Majority of these emissions (55%) came from road network of inter-city routes and highways which freight goods by the diesel heavy-duty trucks. Maharashtra with a share of ~14% of India's total GDP (MoSP, 2020) is the leading state in fuel consumption and total annual emission for all the vehicle categories under consideration, thus illustrating the impact of economic growth and development on road transport sector emission and the need for decoupling the two through prioritization of cleaner technologies.

Among all the fuel types, petrol powered vehicles have the highest relative contribution to the NMVOC emission with ~80% (0.93 ± 0.3 $Tgyr^{-1}$), followed by diesel 16% (0.19 ± 0.03 $Tgyr^{-1}$), LPG 2% (20.6 ± 0.01 $Ggyr^{-1}$) and CNG 1% (15.6 ± 0.1 $Ggyr^{-1}$) (Figure S4). Although diesel is the most consumed fuel on a national scale, petrol vehicular emissions contributed ~4 times higher than diesel vehicle emissions to the total NMVOC emissions. In addition to that, 94% of the total annual emission of BTEX, one of the most toxic constituents of NMVOCs, were also contributed by 2-wheelers. Given the fact that 78% of all registered vehicle in India are petrol powered 2-wheelers (MoRTH, 2018), they are the major source of pollutant emissions followed by diesel HDVs (8%). The total emissions of CO_2 and CH_4 in terms of CO_2-equivalent emissions amounted to 230.9 ± 28.8 $Tgyr^{-1}$.

3.4. Comparison with existing emission inventories for road transport sector emissions over India

Fig. 4 shows the distribution of the annual gridded emissions (0.1 ° × 0.1 °) of toluene, propene, acetaldehyde and nitromethane in the Road

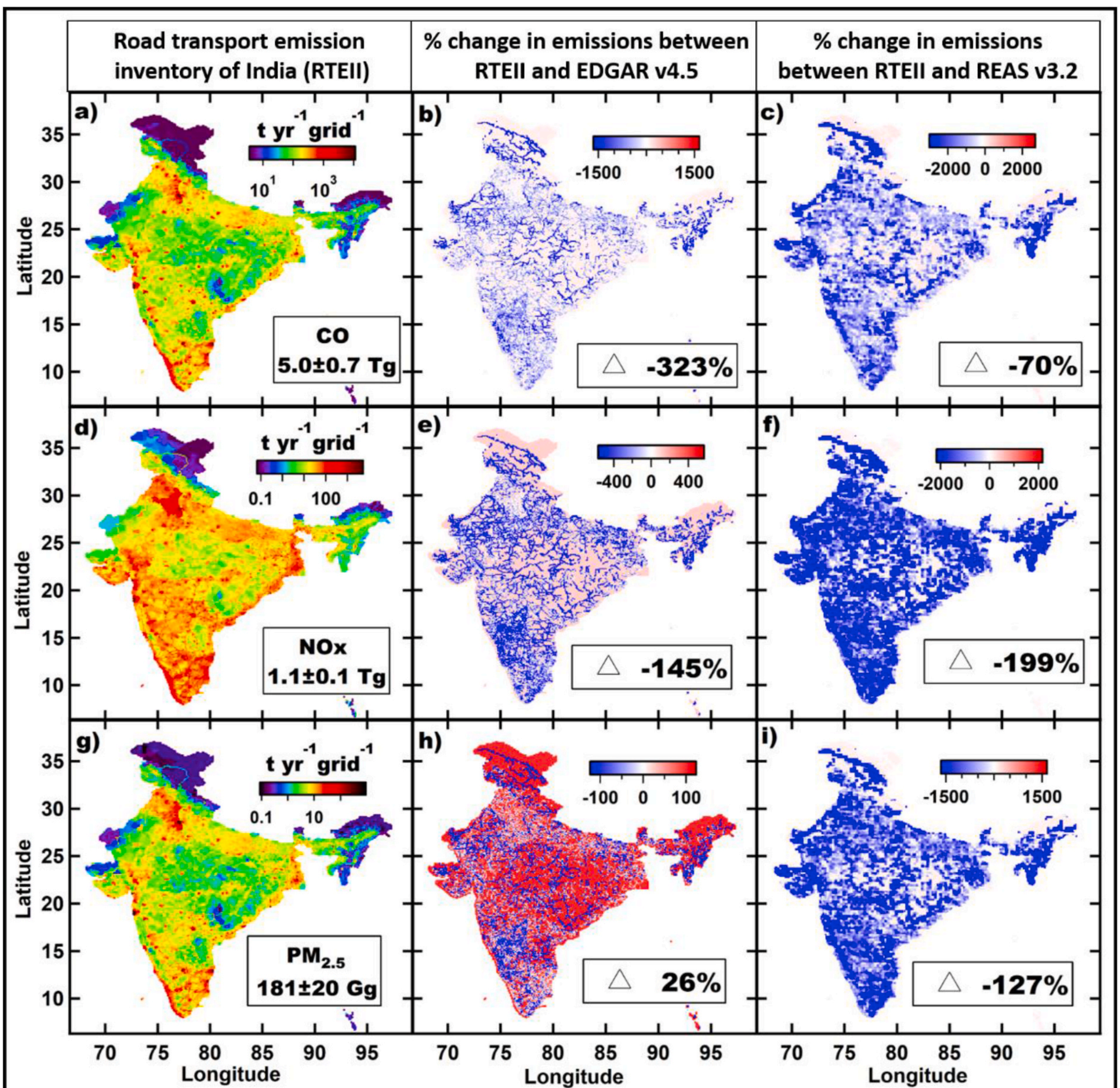

Fig. 5. Annual gridded emissions (0.1 ° × 0.1 °) of the criteria air pollutants carbon monoxide (CO), particulate matter ($PM_{2.5}$) and nitrogen oxides (NOx) in the Road Transport Emission Inventory of India (RTEII). And percentage differences relative to EDGAR v4.5 (second column) and REAS v3.2 (third column) emission inventories for the year 2015 over India.

Transport Emission Inventory of India (RTEII) compiled in this study with percentage differences relative to EDGAR v4.5 (second column) and REAS v3.2 (third column) emission inventories (all for the same year 2015) over India. EDGARv4.3.2 (Crippa et al., 2020; https://edgar.jrc.ec.europa.eu/) and REASv3.2 (Kurokawa et al., 2013; https://www.nies.go.jp/REAS/index.html) emission inventories for the year 2015, were employed for the comparisons. For EDGAR v4.3.2, individual NMVOC annual emissions for the year 2015 were calculated by scaling the emissions reported in 2012 using the growth rate equation derived from the 1970–2012 data. Toluene, acetaldehyde and propene were chosen as they are among the top 10 highest emitted VOCs from traffic sector and differed markedly in magnitude relative to the existing emission inventories. Nitromethane was chosen as it is absent in REAS v3.2 and EDGARv4.3.2 but at the same time is of concern due to the health risks posed by inhalation of nitromethane. Fig. 5 similarly shows the annual gridded emissions ($0.1 \times 0.1^{\circ}$) and differences for the air quality relevant criteria air pollutants: carbon monoxide (CO), particulate matter ($PM_{2.5}$) and nitrogen oxides (NO_x). In general, REASv3.2 tended to overestimate the road transport sector emissions over India significantly for all VOCs and the criteria air pollutants by a magnitude ranging from 12 to 350% (see also Table S13). This is likely due to the use of obsolete emission factors and fleet activity that do not account for the updates in the vehicle technology and fuel portfolio that took place since it was first compiled. EDGARv4.3.2 performed better but still significantly overestimated propene emissions (by 342%) and benzene (by 234%; Figure S5), a species which is widely regulated due to its human carcinogenicity and criteria pollutants such as CO (323%; Fig. 5b), NO_x (145%; Fig. 5e), while underestimating toluene (44%; Fig. 4b) and xylenes (15%), top 2 species with maximum SOA formation potential, as well as $PM_{2.5}$ (26%; Fig. 5h).

Previous studies have stated that EDGAR systematically allocates a much lower fraction of emissions to urban areas as the emissions from on-road transport sector are distributed based on road types and vehicle categories and not considering the population density (Trombetti et al., 2018). Considering the fact that more than half of the households in urban and developed rural areas in India owns a two-wheeler (ICE, 2016), the largest contributor to pollutant traffic emission in India, a spatial distribution of emissions based only on the road network can be inaccurate. Our new inventory attributes a greater share of the emissions to densely populated urban centres in comparison to EDGARv4.3.2, which is consistent with recent source apportionment studies that EDGAR underestimates transport emissions in urban environments in Nepal and north-west India (Pallavi et al., 2019; Sarkar et al., 2017). Although oxygenated VOCs such as acetaldehyde and acetone have been reported in previous investigations of diesel exhaust (Kado et al., 2005; Nelson et al., 2008; Schauer et al., 1999; Yao et al., 2015) we were surprised to note that acetaldehyde was the fourth highest emitted VOC from traffic emissions over India. Remarkably it was almost 2 orders of magnitude greater than the aldehyde emissions currently represented in the EDGARv4.3.2. The missing traffic source of acetaldehyde discovered in this study may help partially explain why global chemical transport models tend to underestimate acetaldehyde in urban outflow relative to observations (Millet et al., 2010).

Nitromethane is a carcinogen (ICE, 2016), and was completely unaccounted for by both EDGARv4.3.2 and REAS3.2 emission inventories. In the troposphere, the lifetime of nitromethane ranges from 30 min to 10 h (Taylor et al., 1980), with photodissociation being the primary removal pathway. Thus, it can play a significant role in rapid ozone formation chemistry as a source of reactive nitrogen within the troposphere, in addition to its health effects. Therefore, traffic emissions need to be considered as a major source for oxygenated VOCs such as acetaldehyde and nitromethane for improved understanding of air pollution and its impact on human health and air quality in both urban and rural regions. Overall, the total annual NMVOC emissions reported in both EDGARv4.3.2 (2.4 $Tgyr^{-1}$) and REASv3.2 (2.8 $Tgyr^{-1}$) were twice as high as our new inventory (1.2 ± 0.3 $Tgyr^{-1}$) (see also Table S13). Total CO_2 emissions in our study (227 ± 28 $Tgyr^{-1}$) were close to both REASv3.2 and EDGARv4.3.2 with 10% difference in emissions while methane emissions were calculated to be 120% higher than the estimate by EDGARv4.3.2 (Table S12). This is likely due to recent additions to the CNG powered vehicle fleet over India.

We now discuss the merits and limitations of our work relative to other emission inventories and also the choice for choosing 2015 as well as its contemporary relevance. 2015 is the year for which the most recent data on asset ownership of households over India was available due to the national health survey study report. On comparing the state level asset ownership (percentage of households owning a certain type of vehicle) and wealth distribution (percentage of households in the highest and second highest income quintile) from the national health survey with the state level per capita fuel sales to 2-wheelers and 4-wheelers, we found that for petrol the state wise per capita fuel sales can be explained by asset ownership using a simple multilinear regression. This finding prompted us to distribute emissions based on per capita petrol sales to certain vehicle classes and population density rather than road network and vehicle registration data. It is clear that most movements of petrol fuelled vehicles are related to people living in certain places going to work (which in rural India includes going to fields and orchards), schools or to local businesses. For capturing emissions accurately vehicle registry data has also been employed in many previous studies. However, in our experience this is of limited use over India because all types of vehicles can be registered as two wheelers (which have lower road tax) and that includes state-wide bus service fleets and HDVs. In addition, not all vehicles plying in rural or even small towns of India are actually registered in that place/state. Household surveys on asset ownership and fuel sale surveys at petrol pumps, on the other hand, more accurately account for occurrence and mobility of vehicles provide a good proxy for actual emission activity in India. While emission factors were measured from vehicles plying over two Indian cities, it should be noted the sample set comprised of the vehicles and fuel types that are representative of most popular models sold and operated all over India. As noted already in the methods section, the EFs measured in our work from these vehicles are unlikely to be underestimated (Brodrick et al., 2002; Deng et al., 2020; Rahman et al., 2013) when we consider variability due to environmental factors, vehicle speed and service time, as they were collected in idling stage. This is a limitation. However, given that even emissions calculated using these EFs are significantly lower for a large suite of VOCs and criteria air pollutants, our work suggests that the extent of overestimation in the existing emission inventories far exceeds the effect of any variability in emission factors due to other factors.

4. Conclusion

This work provides the first detailed chemically speciated (74 VOCs) and high spatially resolved ($0.1^{\circ} \times 0.1^{\circ}$) national emission inventory for road-traffic sector emissions over India. The spatial resolution is better than REAS and MIX Asia ($0.25^{\circ} \times 0.25^{\circ}$) and at par with the EDGARv4.3.2 emission inventory. Use of measured EFs and updated fuel and fleet activity data provides a significant advancement over previous emission quantifications from the road sector over India. LPG and CNG fuelled vehicles which were not in vogue decades ago are now better accounted for by the new emission inventory. The new emission inventory will lead to improved atmospheric chemistry and air quality modelling over the Indian region which has the world's third largest road network. For example, the general tendency of chemical transport models to overestimate surface ozone over India (e.g. Karambelas, 2018; David et al., 2019) relative to observations may in fact be due to existing emission inventories such as EDGARv4.3.2 and REASv3.2 significantly overestimating ozone precursors like CO and NO_x. Toluene, acetaldehyde, 2,2-dimethylbutane and ethylbenzene are among the top traffic emissions which are markedly different relative to existing inventories (ranging from factor of 2–25). VOC emissions of acetaldehyde and nitromethane (collectively 51 ± 6 Gg yr^{-1}) were found to be very significant and absent in some previous emission inventories. Both compounds can influence tropospheric oxidation chemistry through peroxyacetyl nitrate (PAN) formed by the photo-oxidation of acetaldehyde (Fischer et al., 2014), and photo-dissociation of nitromethane which produces methyl radicals and NO_2 (Taylor et al., 1980). The highest polluting vehicles were found to be LPG 3-wheelers and petrol 2-wheelers. Replacement of these by cost effective, electric-powered alternatives, which has already commenced in certain Indian megacities can bring substantial improvements in regional air quality. Insights from this study can also aid in reducing toxic and reactive primary and secondary pollutants arising from traffic emissions through targeted policies and prioritizing what VOCs should be monitored by air pollution control agencies within the country to regulate and reduce exposure in urban agglomerates through setting up of national VOC monitoring networks.

CRediT authorship contribution statement

Haseeb Hakkim: Data curation, Formal analysis, Investigation, Writing – original draft. **Ashish Kumar:** Data curation. **Saurabh Annadate:** Data curation. **Baerbel Sinha:** Conceptualization, Methodology, Funding acquisition, Project administration. **Vinayak Sinha:** Conceptualization, Methodology, Writing – review & editing, Data curation, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aeaoa.2021.100118.

Author contribution

Haseeb Hakkim: writing- original draft preparation, analyses of dataset, first interpretation and data curation. Ashish Kumar: data curation, analyses of dataset. Saurabh Annadate: data curation. Baerbel Sinha: conceptualization, methodology. Vinayak Sinha: conceptualization, methodology, writing, data curation, funding, supervision.

Data availability

Gridded emissions in gy^{-1} can be downloaded from Mendeley data with free standard user login: https://data.mendeley.com/datasets/n6dby9gynn/draft?a=afae596d-bd9d-4e1c-aff3-eb2d41ca17d1.

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