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


RESEARCH ARTICLE

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Comparing Urban Anthropogenic NMVOC Measurements With Representation in Emission Inventories—A Global Perspective

Key Points:

- Representation of non-methane volatile organic compounds (NMVOCs) in global emission inventories is poor. It is better in regional inventories but still needs improvement
- Measurements of oxygenated NMVOCs are lacking in existing data and limit the scope of the evaluation of emission inventories
- NMVOC measurements are most available in North America and Asia and should be expanded to provide more data for Africa, South America

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Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Emission inventories are a critical basis for air quality and climate modeling, as well as policy decisions. Non-methane volatile organic compounds (NMVOCs) are key precursor compounds in ozone and secondary organic aerosol formation. Accurately representing NMVOCs in emission inventories is crucial for understanding atmospheric chemistry, the impact of policy measures, and climate projections. Improving NMVOC representation in emission inventories is fraught with challenges, ranging from the lack of (long-term) NMVOC measurements, limited efforts in updating emission factors, to the diversity of NMVOC species reactivity. Here we take an initial step to evaluate the representation of urban NMVOC speciation in an emission inventory (EDGARv4.3.2 and EDGARv6.1) at the global level. To compare the urban measurements of NMVOCs to the emission inventory estimates, ratios of individual NMVOCs to acetylene are used. Owing to limitations in measurement data and grouping of NMVOCs in emission inventories, the comparison includes only a limited number of alkanes, alkenes, and aromatics. Results show little to no agreement between the ratios in the observations and those in the global emission inventory for the species compared (r^2 0.01–0.20). This could be related to incorrect speciation profiles and/or spatial allocation of NMVOCs to urban areas. Regional emission inventories show better agreement among the ratios (r^2 0.43–0.70). The inclusion of oxygenated species in NMVOC measurements, as well as greater global coverage of measurements could improve representation of NMVOC species in emission inventories, and a mosaic of regional inventories may be a better approach.

Plain Language Summary Accurate representation of non-methane volatile organic compounds in emission inventories is critical for understanding atmospheric chemistry, as input for air quality and climate models, and quantifying the impact of policy. The area is however under researched. This study brings together available measurements of non-methane volatile organic compounds from urban areas and uses them to evaluate their representation in emission inventories. The findings show that for those species evaluated, there is poor agreement between the measurements and emission inventories. Recommendations for future research and improvement include more measurements of non-methane volatile organic compounds, including oxygenated species, and over a greater geographical area.

1. Introduction

Emissions inventories are a critical input to air quality and climate modeling. Accurate emission inventories are a necessary foundation for any modeling activity, when aiming to simulate past, current, or future atmospheric conditions and processes, from the local to the global scale. Non-methane volatile organic compounds (NMVOCs) are key precursor compounds in ozone and secondary organic aerosol formation (de Gouw et al., 2005; Seinfeld, 2016). Accurately representing NMVOCs in emission inventories is needed to simulate air quality in models, and for understanding atmospheric chemistry, the impact of policy measures, and climate

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projections. While emissions of NO_2 —another important O_3 precursor—has received substantial assessment not only through ground-based observations but also via satellite information (e.g., de Foy et al., 2015, 2016; Goldberg et al., 2019), this is not possible in the same way for NMVOCs. The challenge of improving NMVOCs in emission inventories and understanding how accurately these inventories represent real-world conditions is compounded by sparsity of high-quality measurements of NMVOCs around the globe, limited efforts on updating emission factors, and the variable reactivity of NMVOCs. This in turn makes validation of emission inventories, and the assessment of models to simulate NMVOCs and accurately represent them difficult. Another complication is that emission inventories generally report NMVOCs as a single lumped value in kg/yr, any further speciation needs to come from applying speciation profiles that may be old or originally from other regions. Further complicating this issue is a lack of understanding of the relative importance as to whether total NMVOC emissions or NMVOC speciation is more, less, or equally important, including the relative importance of the changes in speciation and total emissions over time. In this work, we focus on evaluating the representation of anthropogenic NMVOC speciation in emission inventories comparing urban areas across the globe. We do not include biogenic NMVOCs or address any secondary products in the analysis.

The current NMVOC speciation applied in many models is outdated. Previously, the Netherlands Organization for Applied Scientific Research (TNO) provided a global speciation of the NMVOC emissions inventory that was developed in the 1990s and made available in 1996 for the base year 1990 in the framework of the EDGAR project (Olivier et al., 2001). The same basic information by source sector was used to provide an NMVOC speciation to be used in models within the RETRO project (Schultz et al., 2007). This included an update of the lumped speciation information to 1995 source sub-sector contributions. No new NMVOC split data were generated or used in RETRO beyond this sub-sector contribution reassessment. The resulting NMVOC split per sector was released with the EDGAR version 3.0 inventory. The NMVOC speciation was not updated significantly until very recently. A new NMVOC speciation developed by Huang et al. (2017) was included in the latest release of EDGARv4.3.2. Other NMVOC speciation recommendations exist as well. For example, the European Monitoring and Evaluation Program (EMEP) model has a default NMVOC speciation by sector divided into 14 species/categories of species (Simpson et al., 2012), which was derived from work by Passant (2002) based on detailed information from the UK. At this point, however, most global models are still using the NMVOC speciation from the REanalysis of the Tropospheric chemical composition (RETRO) emission inventory in one form or another. Unfortunately, most of the information as to what the speciation is based on and how it was derived is not easily accessible, and a lack of knowledge with respect to NMVOC reactivity and/or relative importance of species, leads to inconsistent grouping (or “lumping”) of NMVOCs to fit in model mechanisms. These inconsistencies in how emission inventory speciation information is mapped onto chemical mechanisms can lead to inaccuracies and/or introduce unpredictable uncertainties (Li et al., 2014; Zhao et al., 2017). Furthermore, studies that compare measurements of NMVOCs to emission inventories have found that there are significant errors in the speciation, with some species being significantly under- or over-represented (e.g., Borbon et al., 2013; Boynard et al., 2014; Coll et al., 2010; Dominutti et al., 2019; Dominutti et al., 2020; Warneke et al., 2007). NMVOC profiles may well be region specific and using them outside of their domain can be problematic. For example, the application of US-developed emission factors and speciation profiles, which are often adopted in countries outside of the US for the development of emission inventories and NMVOC speciation, can lead to errors and significant differences in NMVOC species between measurements and the emissions estimates (e.g., Chen et al., 2010).

Since the EDGAR/RETRO NMVOC speciation profiles were developed around 1995, the NMVOC speciation of various emission source sectors have changed owing to changes in regulation, fuel quality, use patterns, and general development of goods and technology. In-situ observations also illustrate the change over time of the composition of VOC sources, or source strengths, as an indication of changes in the speciation of VOC sources as a response to emission controls or changing activities, as well as the seasonality in emissions. Boynard et al. (2014) showed that emission ratios of VOCs changed by up to a factor of seven between summer and winter, which is a result of regulatory directives, such as a change in fuel formulation in the road transport sector (Gentner et al., 2009). Gasoline fuel has also been reformulated over time to reduce aromaticity, and the blend with ethanol increased (Dunmore et al., 2016; Kirchstetter et al., 1999a, 1999b). As demonstrated by the example of the solvent sector in von Schneidmesser et al. (2016), there is significant diversity in NMVOC speciation, including spatial differences and evolution over time. A box model evaluation of these differences in NMVOC speciation indicated a large effect on ozone production (von Schneidmesser et al., 2016). More recently, McDonald et al. (2018) showed that as transportation emissions decrease the use of volatile chemical products (also known as the solvent

sector), which includes for example, pesticides, coatings, personal care products, has increased substantially in relative importance with current inventories underestimating their contribution. Mo et al. (2021) illustrated rapid growth in solvent use in China owing to industrialization. This has implications of modeling ozone and secondary organic aerosol in urban cores (Coggon et al., 2021; Kim et al., 2022; Qin et al., 2021; Seltzer et al., 2021), and resulting impacts on human health (Nault et al., 2021). Overall, both emissions from transport and solvents are important sources of NMVOCs in urban areas, but the relative importance of their contributions to the individual NMVOCs and total NMVOC emissions is still an issue where the observations and emission inventories often show disagreements (e.g., Gaimoz et al., 2011; McDonald et al., 2018; Niedojadlo et al., 2007).

The scope of the current work is focused on anthropogenic NMVOC emissions and urban areas. Many urban areas tend to be VOC-limited in the context of O₃ production (e.g., Karl et al., 2018; Sicard et al., 2020), and it is therefore critical to accurately capture NMVOC emissions in urban areas if mitigation measures are to be effective. Common relationships among NMVOCs across urban areas globally have previously indicated similarity in the dominant emission source for certain NMVOCs, and the importance of motor vehicles (Borbon et al., 2018; Parrish et al., 2009; Salameh et al., 2017; Thera et al., 2019; von Schneidmesser et al., 2010). Furthermore, the use of NMVOC measurements in urban areas has been used to provide a check on the primary emissions for NMVOCs in reported inventories, as in Warneke et al. (2007), Borbon et al. (2013), and McDonald et al. (2018). These studies typically compare measured atmospheric enhancement ratios of individual NMVOCs to carbon monoxide (CO) or acetylene to parallel ratios in emission inventories (EI). In many cases these studies have shown significant measurement-inventory discrepancies by factors of two or more for individual species (Borbon et al., 2013; Dominutti et al., 2020; Thera et al., 2019; Warneke et al., 2007). Alternatively, eddy covariance techniques can be used to quantify NMVOC fluxes to also provide a constraint on emissions, as shown in Karl et al. (2018), where they identified a large amount of oxygenated NMVOCs from urban emission sources that was not captured in primary emission estimates. Unfortunately, measurements alone cannot be used to directly change the NMVOC profiles as they give partial information on the mixed atmosphere, not individual emission sources. Such discrepancies have implications for air quality modeling and the accurate simulation and prediction of not only NMVOCs but also other species such as ozone or secondary organic aerosol.

This study is an effort of the Global Emissions Initiative (GEIA, <http://www.geiacenter.org/>) Working Group on NMVOCs and brings together available measurements of NMVOCs from urban areas in conjunction with a global emission inventory to provide a synthesis of such comparisons against the same baseline—the global inventory—that covers all areas. Comparisons to both EDGARv4.3.2 (Huang et al., 2017) and EDGARv6.1 (JRC, 2022) are made. The comparison to the later version (EDGARv6.1) is shown in the main text and is what is referred to with the “global EI” or EDGAR unless specified otherwise; all other plots are available in the Supporting Information. We also compare the measurement data to regional inventories constructed in different regions of the globe to draw additional insights and provide recommendations for future development of global NMVOC inventories. Comparison to other global inventories such as the Hemispheric Transport of Air Pollution (HTAP) inventory (Janssens-Maenhout et al., 2015) or the Community Emissions Data System (CEDS) inventory (Hoesly et al., 2018) are not included in this analysis. HTAP was not included because it does not provide NMVOC speciation information (Janssens-Maenhout et al., 2015). CEDS was not included for reasons of scope, because of strong similarities between EDGAR and CEDS with respect to NMVOC distribution and speciation. For example, the data from the EDGAR inventory were used in CEDS for default non-combustion data sources where national inventory data were not available, such as for solvent use in the case of NMVOCs; the proxy data for gridding were also primarily from EDGAR (Hoesly et al., 2018).

2. Methods

We utilize the VOC to acetylene ratios of NMVOCs in urban areas to evaluate emission inventories with both global and regional coverage and assembled a set of speciated NMVOC measurement data from urban areas around the globe. A conceptual overview of the process is provided in Figure S1 in Supporting Information S1 and described in detail in the text of this section.

We used the VOC/acetylene ratio rather than VOC/CO ratio as our metric for comparison with EIs due to the former being more widely available than the latter. We also compiled a list of NMVOCs that were routinely measured across cities and over time. The NMVOCs considered include ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, ethene, propene, ethyne, benzene, toluene, *o*-xylene, and *m* + *p*-xylene. The cross-listing of

Table 1
NMVOCs Included in the Study Oriented to the NMVOC Species and Species Groups Included in the EDGAR Inventory

EDGAR code	EDGAR specie(s)	Measured specie(s)
voc1	Alkanols	–
voc2	Ethane	Ethane
voc3	Propane	Propane
voc4	Butanes	<i>n</i> -Butane, <i>i</i> -Butane
voc5	Pentanes	<i>i</i> -Pentane, <i>n</i> -Pentane
voc6	Hexanes and higher	–
voc7	Ethene	Ethene
voc8	Propene	Propene
voc9	Acetylene	Acetylene
voc10	Isoprenes	–
voc11	Monoterpenes	–
voc12	Other alk(adi)enes/alkynes	–
voc13	Benzene	Benzene
voc14	Toluene	Toluene
voc15	Xylenes	<i>o</i> -Xylene, <i>m</i> + <i>p</i> -Xylene
voc16	Trimethylbenzenes	–
voc17	Other aromatics	–
voc18	Esters	–
voc19	Ethers	–
voc20	Chlorinated hydrocarbons	–
voc21	Methanal	–
voc22	Other alkanals	–
voc23	Alkanones	–
voc24	Acids	–
voc25	Other	–

Note. For those species or groups that have no corresponding measured specie(s), no comparison could be made.

“species” in the EDGAR inventory with ambient measurements is provided in Table 1. Unfortunately, an insufficient number of studies included oxygenated species or others beyond those listed here to provide a meaningful comparison. Only more recently have oxygenated VOCs been more routinely measured and used to assess urban emission inventories (Coggon et al., 2021; Gkatzelis et al., 2021; Karl et al., 2018; McDonald et al., 2018). Furthermore, grouped species classes, as included in the EI, do not allow for a meaningful comparison either. The comparison is therefore limited to species that are both measured and represented in the EI as individual species or species with minimal grouping, primarily a select number of alkanes, alkenes, and aromatic compounds (see Table 1). We recognize the limited number of species in the EI comparison as a limitation of this study and recommend a need for more routine measurements of oxygenated VOCs in future monitoring networks and field campaign efforts.

2.1. NMVOC Data

Figure 1 shows the urban locations of the NMVOC measurement data included in this study. Table S1 in Supporting Information S1 contains a more detailed list including the location latitude and longitude, dates, and sources (citations) of the 80+ locations for the measurement data. We tried to rely on the peer-reviewed literature as much as possible. Data were identified through a literature search (prior to 2019) and via the GEIA network. The data include measurements from short-term field campaigns as well as longer-term routine monitoring. Measurement techniques include both online and offline measurements, such as proton transfer reaction-mass spectrometry (PTRMS), whole air canister samples analyzed by gas chromatography, and online gas chromatography with flame ionization detection. For further details, the reader is referred to Table S1 in Supporting Information S1 and the associated citations. As the figure and table make clear, there is substantially more data available for the United States and Asia relative to all other regions. The paucity of data in Europe is surprising with only three sites available. An explanation could be that monitoring of NMVOCs in the 1990s and 2000s was often a national agency task in Europe without the prerequisite to publish the data in peer-reviewed papers. In that case, more data may well be available but would have to be retrieved from gray literature and reporting in different languages. This is out of scope for the current review. A complete table of the reported or calculated ratios for the measurement data

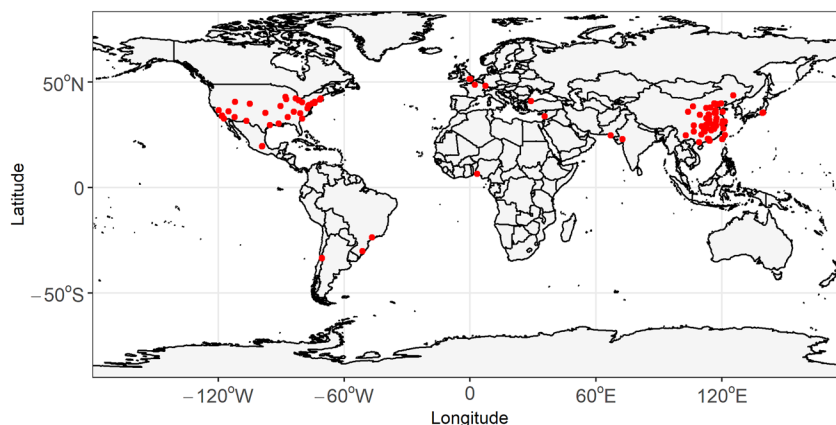


Figure 1. Locations of NMVOC measurement data used in the study from 1996 to 2015.

used is provided in Table S2 in Supporting Information S1. We also recognize the sparsity of NMVOC measurements in various regions of the globe as a limitation of this study, and recommend increased coverage of NMVOC measurements, such as in South America, Africa, and Europe, as well as East/South Asia.

2.2. Ratios

We calculated ratios between individual NMVOCs to acetylene for both measurements and emission inventory data to facilitate comparison, following previous work (Borbon et al., 2013; Warneke et al., 2007). While ratios to CO have also been used in the past (Hassler et al., 2016; von Schneidemesser et al., 2010), the datasets available for use are much more limited, owing to the requirement that CO is measured in parallel to the NMVOC measurements. CO and acetylene have been used as they are tracers of combustion sources, specifically vehicle exhaust in urban areas, and are relatively inert (Warneke et al., 2007), but may have substantial secondary sources in some regions (Simon et al., 2018). For comparison with the EI data, the year and month of the measurement data were matched to the year and month of the EI data, as EDGAR provides monthly data from 1970 to 2012 (EDGARv4.3.2) and 1970–2018 (EDGARv6.1). The temporal matching is done to capture seasonal differences, as well as the evolution of emission sources over time. A number of assumptions were made for the sake of simplification in the first step, including an assumption that urban measurements represent relatively fresh emissions. For this reason, we used ratios that were estimated using the photochemical age method, as well as simple ratios using linear regression fits from data in urban areas, where a photochemical age estimate was not available, as well as ratios that we calculated based on reported (hourly) VOC data. Possible nighttime ratios are used because under these conditions photochemistry is limited. The data therefore include ratios that were reported as ratios in the published literature, as well as ratios that we calculated based on published mixing ratio data. More detail on the photochemical age method can be found in Borbon et al. (2013) and references therein. Briefly, this method accounts for the photochemical processing of air masses based on hydrocarbon ratios that are then extrapolated to zero photochemical age for the estimation of emission ratios. We did a comparison of ratios calculated from ambient observations and ratios based on the photochemical age method and found that for most species the ambient ratio were within 25% of the photochemical age method (Section S2 and Figure S2 in Supporting Information S1). Furthermore, previous studies have shown good agreement between the photochemical age and simple linear regression ratios of nighttime data (Borbon et al., 2013; Parrish et al., 2009; Salameh et al., 2017; von Schneidemesser et al., 2010), as well as daily (24 h) and nighttime ratios (Dominutti et al., 2020) (see also Figure S3 in Supporting Information S1 for a comparison from one site included in this work).

The ratios from the EI reflect the ratios present in the emission inventory grid cells above the urban areas, matching the coordinates to where the measurements were made. Different numbers of grid cells were extracted from EDGAR v4.3.2, including 1 cell that overlapped the measurement site as well as 9 and 25 cells that overlap and surround the measurement site. Each grid cell is $0.1^\circ \times 0.1^\circ$ spatial resolution. While all were evaluated, no substantial differences were observed for the number of cells extracted (data not shown) and therefore the nine-cell extraction is presented in the rest of the paper. This is likely related to the fact that the relative presence of urban VOC sources are distributed with proxies, that is, population, so that they are similar across the extent of an urban area. This is also consistent with previous work, in which the ratios between emissions of different species were found to be relatively independent of domain size (Borbon et al., 2013). The global EDGAR inventory was chosen as the basis for comparison to provide a consistent baseline across all observational sites. Sectoral attribution of emissions for individual VOCs is shown at the level of national totals rather than extracted cells. However, a comparison of the total NMVOC emissions at national level to the nine-cell extractions for the VOCs evaluated showed largely linear relationships with r^2 values of 0.6 and higher (see Section S3, Figures S4–S6 in Supporting Information S1). This indicates that national total emissions are largely downscaled to urban regions, reflecting that the spatial distribution of anthropogenic emissions largely follows the spatial distribution of the human population. Finally, the most relevant source sectors for urban areas are likely mobile sources, residential combustion and solvents, as many energy and industrial sources are often located outside of urban areas, and we therefore focus on those here. The details of which sub-sectors fall under each overarching category are provided in Table S3 in Supporting Information S1. Mobile sources include not only on-road transportation, but also off-road engines, such as rail and ships.

2.3. Regional Emission Inventories

UK: For comparison to observational data in London, England, data from the UK National Atmospheric Emission Inventory (UK NAEI) was used (e.g., Murrells et al., 2010a; <https://naei.beis.gov.uk/>). Total NMVOC emissions

are provided for the UK. NMVOC speciation was retrieved from the annual “UK Emissions of Air Pollutants 1970 to 2005” reports. NMVOC speciation was provided for the top 50 NMVOCs in these reports for both total NMVOC emissions and by sector for the years 2000 through 2009, as well as some earlier years, however these are not included in the data used here (e.g. Murrells et al., 2010a, 2010b). For comparing the UK NAEI to observations, the yearly average ratios were used to correspond to the speciation data which was available only by year. While observational ratios were included for London through 2012 for the comparison with EDGAR, the comparison to the NAEI only went through 2009 owing to the availability of the speciation information for the inventory. The sectoral distribution at national level for total NMVOCs was retrieved from <https://naei.beis.gov.uk/data/data-selector-results?q=155503> (accessed date 3.3.22) for 2012 (UKNAEI, 2012). The year 2012 was chosen because both monitoring and campaign data exist for London during that time.

US: The anthropogenic VOC emissions for the US are from recent studies for Los Angeles (McDonald et al., 2018) and New York City (Coggon et al., 2021). Briefly, mobile source emissions are constructed using a fuel-based approach, and volatile chemical product (VCP) emissions from a mass balance of the petrochemical industry are described in detail in McDonald et al. (2018). Speciation profiles are based on literature values for road transportation (Gentner et al., 2012, 2013), and surveys of consumer products and architectural coatings by the California Air Resources Board (CARB, 2018, 2019). Other non-mobile and non-VCP emission sources are taken from the US Environmental Protection Agency's National Emissions Inventory (NEI) and speciated utilizing the Speciate database (USEPA, 2014). The Los Angeles inventory is constructed for 2010 and New York inventory for 2018.

China: The speciated VOC emissions for Beijing are estimated following the bottom-up framework of the Multi-resolution Emission Inventory for China (MEIC, available at <http://www.meicmodel.org>; Li et al., 2014, 2019). The total VOC emissions were calculated based on a technology-based methodology, as detailed described in a series of papers (Li et al., 2014, 2019; Zheng et al., 2018). Specifically, an accurate speciation framework of VOC to individual species for each source category were developed by Li et al. (2014), which reduced the uncertainties of inaccurate mapping processes. A composite profile database was established by integrating the local measured profiles and supplementing with SPECIATE v4.5 (available at <https://www.epa.gov/air-emissions-modeling/speciate-version-45-through-40>, last access: 21 April 2018) database for absent sources (Li et al., 2019). MEIC emissions with detailed speciation information for Beijing are developed for 2011 and the same as those used in the SOA modelling and human health assessment of Nault et al. (2021).

3. Results and Discussion

3.1. Comparing Observationally Derived Emission Ratios to Those in Emission Inventories

3.1.1. Global Emission Inventory Comparison

Figure 2 shows the comparison of VOC to acetylene ratios for measurements and EI data from 80+ urban areas in 14 countries, presented by geographical region [Figure 2 (EDGARv6.1), Figure S7 in Supporting Information S1 (EDGARv4.3.2)]. Ratios from all nine VOC species from Table 1 are plotted for both the EI (y-axis) and observations (x-axis) as individual markers. The comparison includes all anthropogenic NMVOC emissions and is not limited to specific source sectors from the inventory. We perform a simple linear regression calculated in log space to first get a bulk analysis of how similar/dissimilar the EI and observed VOC to acetylene ratios are. The number of EI versus observation matches and the coefficient of determination is shown in each panel. To first order, Figure 2 shows a large amount of scatter and no discernible agreement between the observations and the global EI ($R^2 = 0.01\text{--}0.20$), both for individual continents (North America, Europe, and Asia) and across the globe. Next, we focus on key elements that can affect the EI and observed comparisons, including NMVOC speciation and trends.

Figure 3 allows for a more differentiated look at where some of this variability is coming from with respect to NMVOC species. Both the EDGAR EI and observations of VOC to acetylene ratios are plotted as box plots (25th to 75th percentile) along with the geometric mean. There are some systematic differences for compound classes, with the ratios for alkenes being consistently higher in EDGAR than in the observations across North America, Europe, and Asia (+15% to +250%). For aromatics, the emission inventory ratios are significantly higher than the observational ratios for North America (+210%), while for Europe and Asia the gap is not as large (−41% and +82%, respectively). The largest differences (greater than a factor of 2) are observed for North America, especially for alkenes and aromatics. Some factors that may account for the variability in the differences seen for

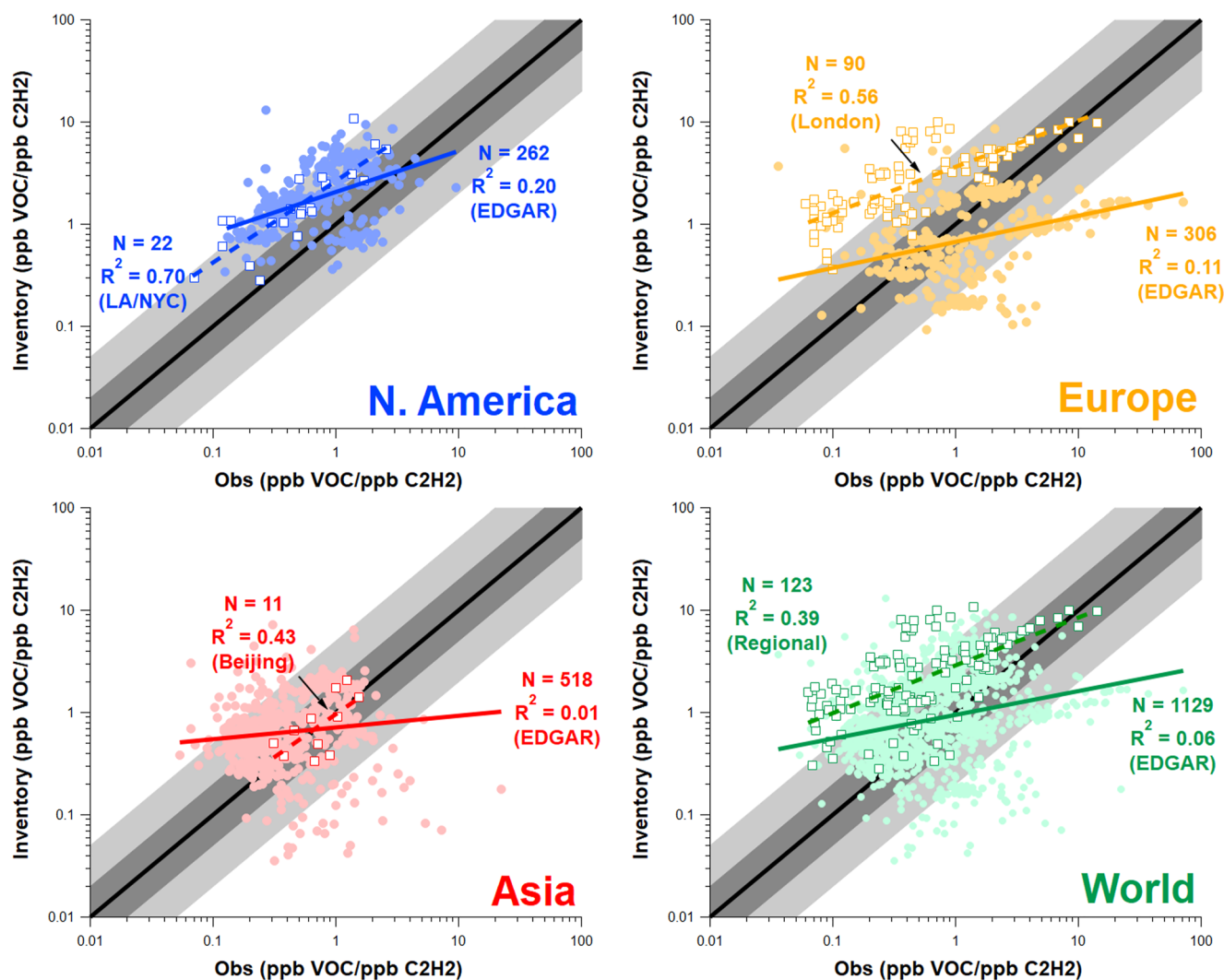


Figure 2. Comparison of individual VOC/acetylene ratios in observations (x-axis) and EDGARv6.1 emissions inventory (y-axis) grouped by global region. Each marker represents an individual VOC at a given location and year that has been matched with emission inventories. Filled circles represent the comparison of the global emission inventory (EDGAR) versus observations. The solid lines are a linear regression of the global inventory versus observations estimated in log space. Open squares and dashed lines are the same for regional inventories (see main text).

the observational and inventory ratios for aromatics, may be due to differences in dominant fuel used in transport (e.g., gasoline vs. diesel), efforts to remove aromatics from fuels, and efforts to reduce fuel evaporation at gas stations. The larger difference in the US may be a reflection of for example, the reformulation and efforts to remove aromatics from fuels and/or solvent-borne formulations of coatings that have been phased out in the US (Kirchstetter et al., 1999a; Stockwell et al., 2021), which may not be fully accounted for in the EDGAR EI. The differences between observations and EI showed some improvements for Europe and for aromatics in North America when comparing EDGARv4.3.2 (Figure S8 in Supporting Information S1) and EDGARv6.1 (Figure 3). This is a reflection of updates to the spatial distribution of emission, as well as technology updates for the road transport sector that were carried out in the later version of EDGAR (Crippa et al., 2021; JRC, 2022; Oreggioni et al., 2022). It should also be noted that total NMVOC emissions are quite uncertain for certain sectors and in general compared to some of the other pollutants reported in EI. While this figure provides information on the species with the greatest disagreements, future work should look more closely at the similarities and differences in the speciation profiles used for each continent. It may be that the profiles could be more similar in reality than reflected in EDGAR, or in some cases where specific fuels are used, such as ethanol in Brazil, that stark differences are a reality and result in even larger differences in the speciation profiles. Regionally, the overall mismatch is smallest for Europe, and largest for North America (Figure 3). More specifically, for Europe, the agreement

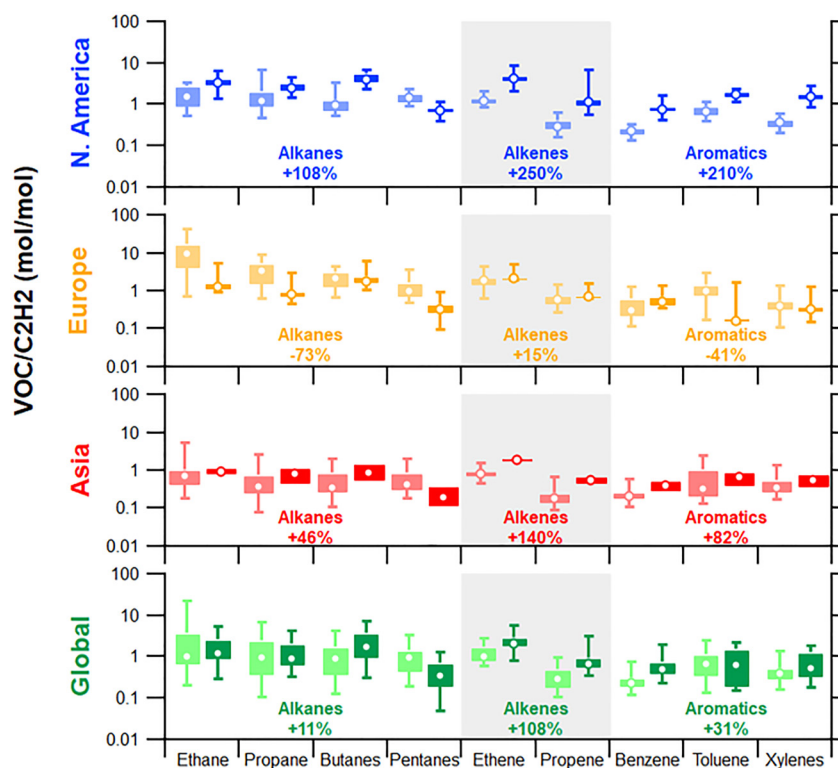


Figure 3. VOC to acetylene ratios for observations (lighter shade) and global EDGARv6.1 emission inventory data (darker shade) for North America (top row), Europe (second row), Asia (third row), and Global (bottom row). Circles represent the geometric mean, and boxes represent the 25th to 75th percentile. The whiskers represent the 2.5 and 97.5 percentiles (95% confidence interval). Relative differences in the inventory versus the observations are denoted in each panel calculated on the geometric mean. Gray shading is present to indicate the different compound class sections of the plot.

for the two alkene species is relatively good, while the alkanes and aromatics are under-estimated. For North America these species are significantly overestimated by more than 200%. Although these comparisons are also dependent on how well acetylene is represented in the inventory, the large gap between especially Europe and North America suggest something more fundamental is likely not being captured in the representation of these continents in the EDGAR NMVOC inventory. This would require a deeper analysis into region-specific technologies and associated emission factors.

3.1.2. Regional Emission Inventory Comparison

While the focus in this work was the comparison using a global inventory that allows for a consistent baseline across regions, previous work has generally compared emission ratios using regional and/or national inventories. Figure 2 includes the observational ratios in comparison to both the global EI ratios from EDGAR, as well as ratios from regional EI. Monitoring data from two sites in London, England (Marylebone Road, roadside station, 2000–2009 and Eltham, urban background station, 2004–2009) are compared to the UK NAEI data; measurements from New York (2018) and Los Angeles, USA (2010) are compared to the urban EIs from Coggon et al. (2021) and McDonald et al. (2018), respectively; measurements from China (2010) are compared to the Multi-resolution Emission Inventory for China (MEIC) (http://meicmodel.org/?page_id=125&lang=en). These comparisons show an improved agreement over the comparison to the ratios from the global inventories, with r^2 values ranging from 0.43 to 0.70. This is consistent with previous work comparing data from Los Angeles, USA and Paris, France, to regional inventories that showed some consistency between inventories and observations, with many of the compounds agreeing within a factor of two (Borbon et al., 2013). It should be noted, however, that for the North American and European comparison to the regional inventory, the r^2 is improved, but also shows an over-estimation of the ratios in the inventory compared to the observations.

Possible reasons for improved agreement may be that regional inventories provide higher spatial resolution relating to source contributions and/or more localized emissions information including the use of country-specific

emission factors. The speciation data applied may also be more representative, although the spatial resolution of the speciation information tends to be more coarse than total emissions information (e.g., speciation at national level vs. total emissions by sector at $1 \text{ km} \times 1 \text{ km}$ resolution). For example, the UK NAEI gets its speciation information from detailed work by Passant specific to the UK (Passant, 2002). By comparison, the EDGAR inventory NMVOC speciation for Europe is based on the Institute of Energy Economics and Rational Energy Use database, as well as information from the EMEP/EEA guidebook for road transport (Huang et al., 2017 and references therein). In many cases, however, the speciation information applied is not based on region specific data (e.g., Chen et al., 2010). For example, given the lack of data for Africa, the EDGAR inventory relies on data from the US SPECIATE database, which is a common practice for regions where such data is not available (Huang et al., 2017). The challenge of understanding source sector contributions and measuring sufficient speciated VOCs to address source sectors, such as solvents, exists in both regional and global inventories. Previous work in Europe from a decade or more ago compared measurements in urban areas with regional inventories in France, Germany, and Switzerland (Gaimoz et al., 2011; Lanz et al., 2008; Niedojadlo et al., 2007; Theloke & Friedrich, 2007). All study results suggested a mismatch between the emissions attributed to traffic and solvent sectors, with the regional inventories attributing much larger contributions to solvents than measurements would suggest. The highest discrepancies have been observed in some of the previous studies for the solvent related species (Gaimoz et al., 2011; Theloke & Friedrich, 2007). As shown in more recent work, these contributions are also changing over time (e.g., McDonald et al., 2018), but many of the challenges remain. Specifically, that as noted, the solvent sector is a diffuse source associated with high uncertainties both in terms of what solvents are used as well as where these are emitted, and, as in this study, the NMVOC measurements limit the comparison by not capturing the species critical for understanding this contribution. For example, the top five species in terms of mass emissions in the UK NAEI (2009) for solvents were ethanol, methanol, butane, acetone, and trichloroethene, whereas for road transport they were toluene, *i*-pentane, acetylene, butane, and benzene. While those NMVOCs with the greatest mass emissions for road transport are included here, to adequately capture the solvent sector emissions we would need more data on oxygenated species. It will be difficult and time consuming to disentangle all possible causes for the observed mismatch between the regional and global inventories, but the measurement-based comparison clearly shows more consistency of observational data with regional inventories. This is not unexpected, and it may have implications for global atmospheric chemistry modeling. One way of addressing this in the short term is to build mosaic inventories such as done under HTAP (Janssens-Maenhout et al., 2015) or CEDS (Hoesly et al., 2018), and advise modelers to use such a mosaic inventory next to a consistent global inventory as a sensitivity test for their system. Unfortunately, the current HTAPv3 mosaic inventory does not include speciated NMVOC emissions (https://edgar.jrc.ec.europa.eu/dataset_htap_v3).

3.2. The Role of Source Sectors

Figure 4 shows the dominant source sectors in the inventories for the US, UK, and China. While yearly emissions information is provided in EDGAR and in the UK NAEI (2012 was selected because of the availability of measurement data), the years for the US and China reflect the time for which the regional emission inventories were reported. As noted in the methods section, the source sector contributions from the extracted cells over the urban centers generally showed a linear relationship to the source sector contributions at the national level (Section S3, Figures S4–S6 in Supporting Information S1) and the national level data are used for comparison. Previous work comparing VOC ratios in urban areas demonstrated substantial similarity across urban areas in different regions and attributed this in large part to the predominance of vehicle emissions for the compounds investigated (Parrish et al., 2009; von Schneidemesser et al., 2010). It is, however, not only a matter of speciation, but also total emissions. While solvent sector emissions are becoming more important over time (McDonald et al., 2018), the data included here spans over a decade, with much of the data from the 2000s. In that sense, part of the poor agreement between the inventories and the observations may be owing to the specific VOCs included in the comparison. In EDGAR, the contribution of the source sectors shows significant differences across the regions, especially for solvents (21%–38%). Interestingly, the regional inventories show greater similarities in the relative contribution of the source sectors to overall emissions across the three countries, such as for mobile sources (13%–20%) and solvents (37%–42%). In almost all cases, mobile sources have a smaller contribution than the solvent sector.

Many of the VOCs that dominate solvent sector emissions are not those included in this study because observations of these species are lacking, nor does the data from recent years necessarily always reflect this change in importance. In order to further consider this issue, we did a comparison of the observational ratios to source

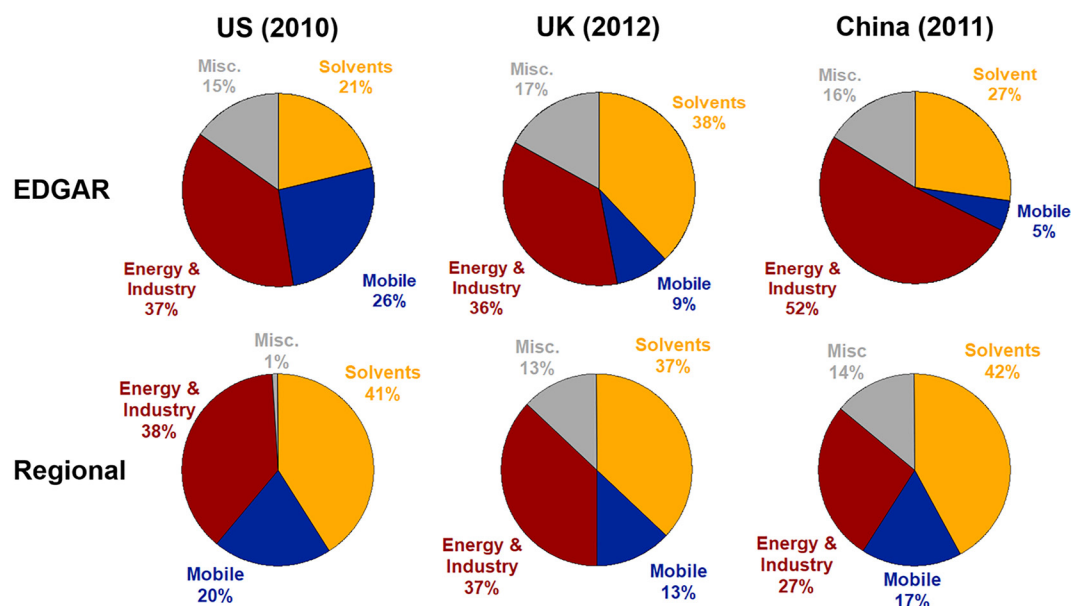


Figure 4. Source sector contributions in terms of VOC mass for the US, UK, and China in the global EDGARv6.1 inventory (top row) and the regionally specific inventories (bottom row). For the specific grouping of source sectors into broad comparable categories, see Table S3 in Supporting Information S1.

sector ratios from EDGAR (rather than total NMVOC ratios). The comparison to the residential, mobile, and solvent sectors all showed a large amount of scatter and no discernible agreement (all $r^2 \leq 0.05$) (Figures S9–S11 in Supporting Information S1). This may be an indication that the observations reflect the aggregate of total emissions and cannot be used for such a sector specific comparison.

Finally, differences in the relative contribution from source sectors and the associated speciation (NMVOC composition) has implications for atmospheric processes as the overall composition will influence the local ozone formation potential and total reactivity. Greater attention should be given to estimating mass VOC emission rates for key sectors, including solvents, energy (including infrastructure/leaks), and transportation.

3.3. Trends in Emission Inventory and Measurement Ratios

One hypothesis for some of the scatter may be the wide spread of time that the data covers (1996–2014). Figure 5 shows the changes over time in the global average of the ratios in the observations and inventory for all locations (Table S1 in Supporting Information S1) included in the study. The data were binned to 4-year intervals (1998–2014), and a global mean value and associated 95% confidence interval were calculated and evaluated with a simple linear regression for a qualitative understanding of differences in long-term trends. All species exhibit a greater than 5% per year difference between the global EDGAR inventory and the observations, with the exception of pentanes. When compounded over a 15-year period, this rate of change results in a factor of ~ 2 difference in the trend.

To provide a complete interpretation of these causes of the changes we would need far more complete measurements of NMVOC species in urban areas, accompanied by updated speciation profiles for the sources, over the course of the ca. 20–25 years than is available. That said, there are several possibilities for these changes. Emissions and concentrations of acetylene (denominator in the ratios) will likely have changed over time. However, if the changes in acetylene were the factor dominating these changes, the trends in the inventory and observations would likely be more similar in their direction, which is not what is shown in Figure 5. The changes are likely a combination of factors, among which changing acetylene is one. The changes on the inventory side are likely owing to changes in source sector strengths as the speciation profiles used have not changed substantially. That the trends in inventory and observations are generally in contradiction suggests real-world speciation may have changed over time and is not represented in the time series of the global inventory. However, in compiling the update to speciation profiles, the profiles are, out of necessity, based largely on existing profiles from established

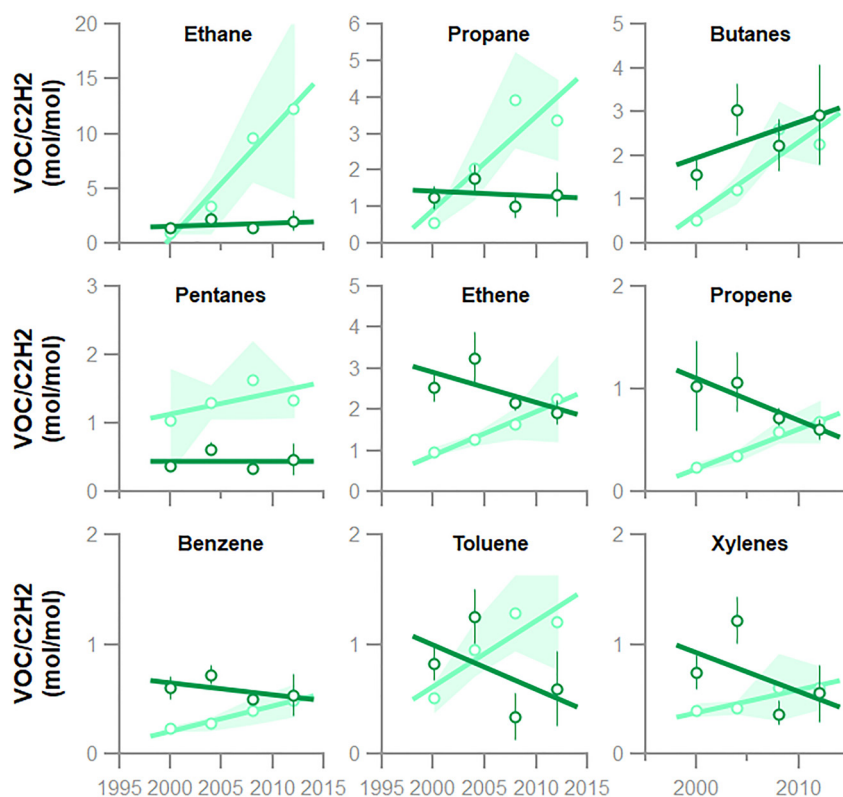


Figure 5. Long-term trend in VOC to acetylene ratio for observations (light green) and global EDGARv6.1 inventory (dark green) averaged globally for all sites included in this study. A complete site list is provided in Table S1 in Supporting Information S1. Data are binned in 4-year increments (1998–2014) before linear regressions are performed (solid lines) on the observations and inventory. Open dots are the mean, error bars, and shading indicate the 95% confidence intervals. All bins have at least 15 data points.

databases and publications, which are geographically limited and not updated regularly owing to the amount of effort associated to such a task (Huang et al., 2017).

Changes in speciation profiles are also compounded with changes in the relative strength of sources for the various NMVOCs, adding complexity to their representation in inventories over time. For example, ethane emissions are dominated by natural gas supply infrastructure (Peischl et al., 2013), while ethene, propene (and acetylene) originate from tailpipe exhaust (Coggon et al., 2021). The growth in ethane/ C_2H_2 ratio is likely due to growing sources of leaks of natural gas pipelines that have been under accounted for in emission inventories (Plant et al., 2019). Propane and butanes are common propellants in chemical products, and their increasing trend relative to acetylene in the observations could arise from a shift from mobile to solvent-dominated emissions. Similarly, aromatics, such as toluene, are from transportation (Gkatzelis et al., 2021) but are also found in solvent-borne coatings (Mo et al., 2021; Stockwell et al., 2021), and ratios relative to acetylene could increase from increasing relative contributions from solvents. Increasing ratios in ethene and propene could arise from a shift of mobile source to refinery and petrochemical facility emissions that can be located in major metropolitan regions and are enhanced in light alkene emissions (Johansson et al., 2014). Further research into the changes in these sources in urban environments would add to our understanding of NMVOC emissions and improve their representation. For example, the growth of ethane/acetylene in the observations suggests more research in fugitive leaks in cities could be helpful (Plant et al., 2019).

4. Summary and Further Work

This work aims to shed light on the issue of NMVOC speciation in EI and how this can lead to improvements and further research efforts in this area. Initial comparisons have shown large differences in the agreement/disagreement between the ratios in the global, and to a more limited extent regional, emission inventories compared

to those in the measurements that vary depending on the specific NMVOC. The comparison shows that regional inventories have a significantly better correlation between inventory and observational species ratios. This suggests that their source sector contributions in combination with NMVOC profiles are more realistic. Global datasets are essential for global assessments and as a data resource for regions where no local information is available. Therefore, further work is needed how this regional information can be used or integrated in global datasets to improve their quality and representation.

There are a number of challenges associated with such comparisons: the spatial and temporal resolution of such inventories is often rather coarse (0.1° and monthly for EDGAR v4.3.2) or for some other inventories, just select year(s) that may not match the time period of the measurements. The observational data come from ambient measurements in urban areas, which are not necessarily spatially representative, and therefore not a perfect match. Furthermore, spatial proxies used to distribute emissions, as well as atmospheric chemistry processes can add a confounding factor (as discussed in the context of the different types of ratios used for the observations). However, there are also benefits in that the use of a global EI allows for comparability across different urban regions globally, as well as a possible check via inter-comparison on the reported inventory data that is otherwise often lacking. Further work, evaluating the influence of different denominators, such as benzene or CO, for the VOC ratios could provide additional insights. It is worth noting however, that previous work has found improved agreement when using ratios to acetylene relative to ratios to CO when both were evaluated (Borbon et al., 2013). The results are consistent across studies that evaluated ratios for similar locations (Borbon et al., 2013; Dominutti et al., 2020; Warneke et al., 2007). This may be owing to the compounded uncertainty when EI for different types of species, for example, VOC and CO, are used and that CO is only combustion source related. Going forward, considering alternative options for the denominator in such an analysis may be needed as both acetylene and CO are tracers linked to combustion emissions from vehicles in urban areas, and a tracer related to volatile chemical products (solvents) may be better suited as this source increases in importance.

Several recommendations can be made based on this work, beyond the recognition of the clear need for additional research on VOCs and their representation in emissions inventories. As is true for many atmospheric composition observation datasets, the coverage over the globe is unbalanced with too few observations in the tropics and southern hemisphere. Most of the data compiled here were available for North America and Asia (largely China). Even in Europe the datasets were limited. It should also be noted that there are some measurement campaigns that include detailed measurements of NMVOCs, including in some regions that are poorly represented in this work, but could not be included because of for example, a lack of acetylene measurements or are as yet unpublished (e.g., Dominutti et al., 2019, 2023). Longer-term or more routine measurements of VOCs would be useful, as would the inclusion of a greater number of species, specifically oxygenated VOCs, as well as measurements of total reactivity. The aspect of reactivity and how much of the total reactivity is captured by the measured NMVOCs and ozone formation potential are particularly relevant from a mitigation perspective, as demonstrated in previous work (e.g. (Simpson et al., 2020; von Schneidemesser et al., 2011; Whalley et al., 2016), but were out of scope for this paper. From the emission inventory side, our results indicate that a mosaic approach based on regional inventories may improve representation for NMVOCs given the difficulty and complexity involved in keeping speciation profiles and sectoral emission trends that are often region-specific up to date. Such efforts would help to improve our understanding of NMVOCs in terms of their representation in emissions inventories, but also for their overall role in the atmosphere.

Data Availability Statement

Data used in this study are provided in Supporting Information S1 and is made available on Zenodo (<https://zenodo.org/record/7796264>; <https://doi.org/10.5281/zenodo.7796264>). Specifically, the reference for each data location included is in Table S1 in Supporting Information S1. Further associated data (not used in the analysis, but gathered, e.g., further NMVOC species) can be provided upon request.

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