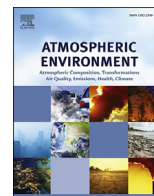




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Variation of the NMVOC speciation in the solvent sector and the sensitivity of modelled tropospheric ozone



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HIGHLIGHTS

- The role of NMVOC speciation for ozone production was tested using a box model.
- There is significant variation in NMVOC speciation for solvent sector emissions.
- Results indicate that speciation could have a significant impact on modelled ozone.
- Choice of chemical mechanism also influenced ozone production.

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ABSTRACT

Non-methane volatile organic compounds (NMVOCs) are detrimental to human health owing to the toxicity of many of the NMVOC species, as well as their role in the formation of secondary air pollutants such as tropospheric ozone (O₃) and secondary organic aerosol. The speciation and amount of NMVOCs emitted into the troposphere are represented in emission inventories (EIs) for input to chemical transport models that predict air pollutant levels. Much of the information in EIs pertaining to speciation of NMVOCs is likely outdated, but before taking on the task of providing an up-to-date and highly speciated EI, a better understanding of the sensitivity of models to the change in NMVOC input would be highly beneficial. According to the EIs, the solvent sector is the most important sector for NMVOC emissions. Here, the sensitivity of modelled tropospheric O₃ to NMVOC emission inventory speciation was investigated by comparing the maximum potential difference in O₃ produced using a variety of reported solvent sector EI speciations in an idealized study using a box model. The sensitivity was tested using three chemical mechanisms that describe O₃ production chemistry, typically employed for different types of modelling scales – point (MCM v3.2), regional (RADM2), and global (MOZART-4). In the box model simulations, a maximum difference of 15 ppbv (ca. 22% of the mean O₃ mixing ratio of 69 ppbv) between the different EI speciations of the solvent sector was calculated. In comparison, for the same EI speciation, but comparing the three different mechanisms, a maximum difference of 6.7 ppbv was observed. Relationships were found between the relative contribution of NMVOC compound classes (alkanes and oxygenated species) in the speciations to the amount of Ox produced in the box model. These results indicate that modelled tropospheric O₃ is sensitive to the speciation of NMVOCs as specified by emission inventories, suggesting that detailed updates to the EI speciation information would be warranted. Furthermore, modelled tropospheric O₃ was also sensitive to the choice of chemical mechanism and further evaluation of both of these sensitivities in more realistic chemical-transport models is needed.

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1. Introduction

Volatile organic compounds (VOCs) have adverse effects on health, both directly through the toxicity of the VOCs themselves

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(Laurent and Hauschild, 2014) and indirectly as a precursor of secondary air pollutants. Tropospheric ozone (O_3) is a secondary air pollutant formed from the degradation of VOCs in the presence of nitrogen oxides (NO_x) and sunlight (Atkinson, 2000). Numerical chemical transport models use emissions of non-methane VOCs (NMVOCs) and NO_x , as well as carbon monoxide and methane, to calculate O_3 concentrations. Anthropogenic NMVOC emissions are allocated in emission inventories (EIs) to sectors by source (e.g. industry, solvent use). The type of NMVOCs emitted varies widely from one source to another, with the sectors determining the source profile or speciation of the NMVOCs applied.

The ozone forming potential of NMVOC species differs substantially (Butler et al., 2011). Accurately representing NMVOCs in emission inventories is therefore crucial to be able to reproduce air quality conditions in models, for understanding atmospheric chemistry and the impact of policy measures. As measurements from China have shown, the variation in VOC speciation can vary significantly in different cities and regions, which is crucial for implementing effective policy measures (Shao et al., 2009; Zheng et al., 2009). The challenge of improving NMVOCs in emission inventories and understanding how accurately these inventories represent real-world conditions is compounded by the lack of (long-term) measurements of NMVOCs compounds, limited efforts on updating emission factors, and the variable reactivity of various NMVOC compounds which makes validation of the emission inventories and the assessment of the capacity of models to capture NMVOCs and accurately represent them difficult. In addition, national reporting typically only includes total NMVOC emissions and no information on speciation. 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.

Despite EIs being critical model input, there are many uncertainties associated with EIs – many of which are not quantified – such as the speciation of NMVOCs and relative contribution of the different sectors to total NMVOC emissions. Significant discrepancies have been documented between the contributions of NMVOC species as represented in EIs and ambient measurements of the NMVOC, with some species being significantly over- or under-represented (Borbon et al., 2013; Coll et al., 2010). The application of protocols developed for a particular country or region (e.g., the US, the UK), which are often adopted in other countries for the development of emission inventories and NMVOC speciation, can also lead to errors and significant differences in NMVOC species between measurements and the emissions estimates (e.g., Chen et al., 2010). EIs also often fail to capture the seasonality in NMVOC emissions (Boynard et al., 2014), for example, because the reporting requires annual total emissions only. In a study comparing emission inventories and datasets for North America and Europe, substantial differences were found for temporal profiles, including the timing of emission release throughout the year and diurnal patterns, noting that owing to possible effects on subsequent atmospheric chemistry further study is warranted (Pouliot et al., 2012).

Furthermore, the current NMVOC speciation applied in many models is based on older data. A global speciation of the NMVOC emissions inventory 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). Similar NMVOC profiles were also used in the RETRO project, during which an update of the speciation information to the year 1995 for source sub-sector contributions was produced, although no new NMVOC split data were generated or used in RETRO beyond this limited sub-sector contribution reassessment (Schultz et al., 2007). The resulting NMVOC

speciation per sector was released with the EDGAR inventory, providing emissions from 1960 to 2000 and has not been updated significantly since then (Olivier et al., 2005). Other NMVOC speciation recommendations exist, for example, the EMEP model has a default speciation by sector divided into 14 species or categories of species (Simpson et al., 2012), which was derived from work by Passant (2002) based on information from the UK. Reported NMVOC speciation has been shown to change over time. The UK National Atmospheric Emission Inventory provides information on the top 50 NMVOCs by mass to the total NMVOC emissions reported. From 1998 to 2008 the species listed have changed, even among the top 10 (Murrells et al., 2010; NETC, 2000). This indicates that speciation information likely requires regular updating.

In addition, the reported emissions often do not agree with attribution to emission sectors based on measurements. For example, a study conducted in Wuppertal, Germany found that while the German Emission Inventory indicated that 51% of the total NMVOC emissions were attributed to solvent use and only 14% to traffic, measurements indicated a maximum contribution of solvent use to approximately 23% of NMVOCs emissions for the area, and a dominating contribution from traffic sources (Niedojadlo et al., 2007). Similarly, a study in Augsburg, Germany found an overestimation of solvents based on a comparison of measurements and emissions data indicating wider applicability of these results (Mannscheck et al., 2002; Slemr et al., 2002). Further studies have also found that especially for urban areas, vehicles are a major and often dominant source of NMVOC emissions (Borbon et al., 2002, 2013; Boynard et al., 2014; Brulfert et al., 2005; Vega et al., 2000; Warneke et al., 2007). While the majority of studies cited were conducted in developed countries, accurate representation of emissions and sectoral attribution is likely to be an even larger issue in developing nations, where on the whole much less reliable information is available.

Improving an EI requires a large amount of effort due to the diverse sources and variety of inputs used in their construction. Before undertaking such a task, it would be valuable to know whether models are sensitive to changing NMVOC input. In other words, is it worth the effort? In particular, how large are the differences in modelled O_3 using different EIs as model input. In this study we address one aspect of NMVOC EI improvement, specifically, speciation, to better understand the sensitivity of modelled O_3 to different NMVOC speciations with a focus on the solvent sector. In current inventories, the solvent sector is in many cases the largest source of NMVOC emissions. For example, according to data presented by the EEA from the national emissions reported to the Convention on Long-range Transboundary Air Pollution (CLRTAP), the sector 'Solvent and product use' contributed ca. 3.4 million kt of emissions and accounted for 43.10% of the total NMVOC emissions in Europe in 2011. This was higher than all other sectors including 'road transport' (14.60%), and 'commercial, institutional and households' (16.70%), the two next largest sectors (EEA, 2013). Similarly, in the UK (one of the countries providing the most detailed NMVOC speciation as part of their EI) in 2008, 'solvent and other product use' accounted for 42% of the total NMVOC emissions, with the next highest contribution originating in the 'extraction and distribution of fossil fuels' (20%), followed by road transport (14%) (Murrells et al., 2010). Although total emissions of NMVOCs have been reported to be declining over the past decades, since a peak ca. 1990, the large fractional contribution of the solvent sector to total NMVOC emissions is in part owing to the much sharper reductions that have been attributed to NMVOC emissions from the road transport sector, ca. –80% between 1990 and 2011, in comparison to ca. –40% reduction for solvents (EEA, 2013). While this study was limited to the solvent sector for the reasons just discussed, there are a variety of other source sectors, including

those outside of urban areas that could significantly affect ozone production, such as the rapidly developing area of oil and natural gas extraction (Thompson et al., 2014). Recent work has shown that emissions from such sources are likely underestimated in current inventories, including much larger than expected observations of alkanes (Gilman et al., 2013; Pétron et al., 2012).

Finally, previous work evaluating the over- or under-estimation of certain hydrocarbon species in the emission inventories used in chemical transport models found that differences in speciation can have a strong incidence on the representation of the air mass reactivity, resulting in an effect on the ozone production and an impact on peak concentrations (Coll et al., 2010). For these reasons, an investigation into the effect of speciation on ozone production was undertaken. Specifically, the maximum potential difference in modelled O₃ produced by various solvent sector EI NMVOC speciations using an idealized box model setup was investigated.

2. Methods

2.1. Solvent sector NMVOC emission inventories

Through a literature survey a variety of source profiles for the solvent sector were identified, with a focus on Europe. The solvent sector EIs represent a range of case studies, including the European average NMVOC speciation (TNO), from the 'TNO-MACC' inventory widely used in chemical-transport modelling (Bultjes et al., 2002), a model specific speciation (EMEP) providing the basis for the EMEP model (Simpson et al., 2012), a general global anthropogenic speciation often used in global models from the IPCC AR3 (IPCC) (Ehhalt et al., 2001), and country specific profiles for Germany (Friedrich et al., 2002), Greece (Sidiropoulos and Tsilingiridis, 2007) and the UK (Goodwin, 2000; Murrells et al., 2010). Two time-points of the Greek and UK profiles are included to represent the evolution of solvent sector NMVOC emissions over time. Table 1 lists all solvent sector EIs compared in this study and the number of different NMVOCs included in the original profile. Although similar numbers of species may be listed in the Table, even similar numbers of species from the same country do not indicate that the same specific species are included within this group.

To provide a visual comparison of the composition of these different solvent sector speciations, the composition of the profiles was translated to a common basis for comparison based on functional group and carbon number. For this some compounds are 'translated' directly as they exist individually, e.g., ethane, propane, whereas others are grouped or 'lumped' into categories, e.g., alcohols, or higher alkanes. This was necessary because the inventories include differing amounts of detail, with some including only 10 species or groups and others 50, and the 10 or 50 species are often not the same 10 or 50 species or groups. The common basis facilitates comparisons. Fig. 1 shows the percent contribution of each compound or category for all the solvent sector speciations considered in this study. It should be noted that this 'translation' of

the solvent sector speciation was not used as input for the box model, but rather to demonstrate and visualize the difference in speciation. For box model input the original speciation was used and then mapped onto the individual chemical mechanisms. The original speciation information is provided in Tables S1a–g in the Supplemental Information (SI).

2.2. Model description

The MECCA box model (Sander et al., 2005) was used as described in Coates and Butler (2015) without any meteorology or transport processes that are included in 3-D models to focus solely on the photochemical gas-phase processes that produce O₃. Model runs were performed using the detailed gas-phase chemistry of the Master Chemical Mechanism (MCM v3.2) (Bloss et al., 2005; Jenkin et al., 1997, 2003; Rickard et al., 2015; Saunders et al., 2003).

Reduced chemical mechanisms are used by 3-D models for reasons of computational efficiency and these reduced chemical mechanisms typically represent NMVOC by aggregating many VOC into a surrogate mechanism species (lumping). Hence, changing the chemical mechanism in a model also changes the NMVOC input. The sensitivity of modelled O₃ mixing ratios was therefore also determined using the MOZART-4 (Emmons et al., 2010) and RADM2 (Stockwell et al., 1990) mechanisms which are typically used for global and regional modelling studies, respectively. Detailed information on the implementation of MOZART-4 and RADM2 into the MECCA box model can be found in Coates and Butler (2015).

2.3. Model setup and simulations

The model was run under equinoctial conditions representative of 34° north (roughly the city of Los Angeles, USA). CO and O₃ were initialized at 200 ppbv and 40 ppbv and then allowed to evolve freely; methane (CH₄) was fixed at 1.8 ppmv. In each model run (one for each speciation tested), NO_x conditions that induced maximum O₃ production were used. This was achieved by emitting the amount of nitric oxide (NO) needed to balance the chemical source of radicals at each time step as described in more detail by Butler et al. (2011). In order to assess whether the different NO sources used in each model run were responsible for the differences in predicted ozone, an additional set of runs was conducted using a 'mean NO source.' For the 'mean NO source' runs, the NO emissions for each time step of the 'tuned NO' runs (one for each speciation tested) was averaged to provide the mean NO emissions for each mechanism.

Model runs were performed using each of the solvent sector EIs of Table 1 using the three gas-phase chemistry schemes (MCM v3.2, MOZART-4 and RADM2). A further set of model runs was performed with each EI after "tagging" each of the chemical mechanisms for the emitted NMVOC. This tagging approach followed Butler et al. (2011) and allowed for attribution of Ox production back to the emitted VOC. As O₃ production is dominated by rapid

Table 1

Solvent sector emission inventories compared in this study. The number of species reflect those originally reported.

Speciation code	Type	# of Species	References
TNO	European average	23	Bultjes et al. (2002)
IPCC	Global	23	Ehhalt et al. (2001)
EMEP	Model specific	14	Simpson et al. (2012)
DE94	Country specific	10	Friedrich et al. (2002)
GR95	Country specific	32	Sidiropoulos and Tsilingiridis (2007)
GR05	Country specific	32	Sidiropoulos and Tsilingiridis (2007)
UK98	Country specific	50	Goodwin (2000)
UK08	Country specific	50	Murrells et al. (2010)

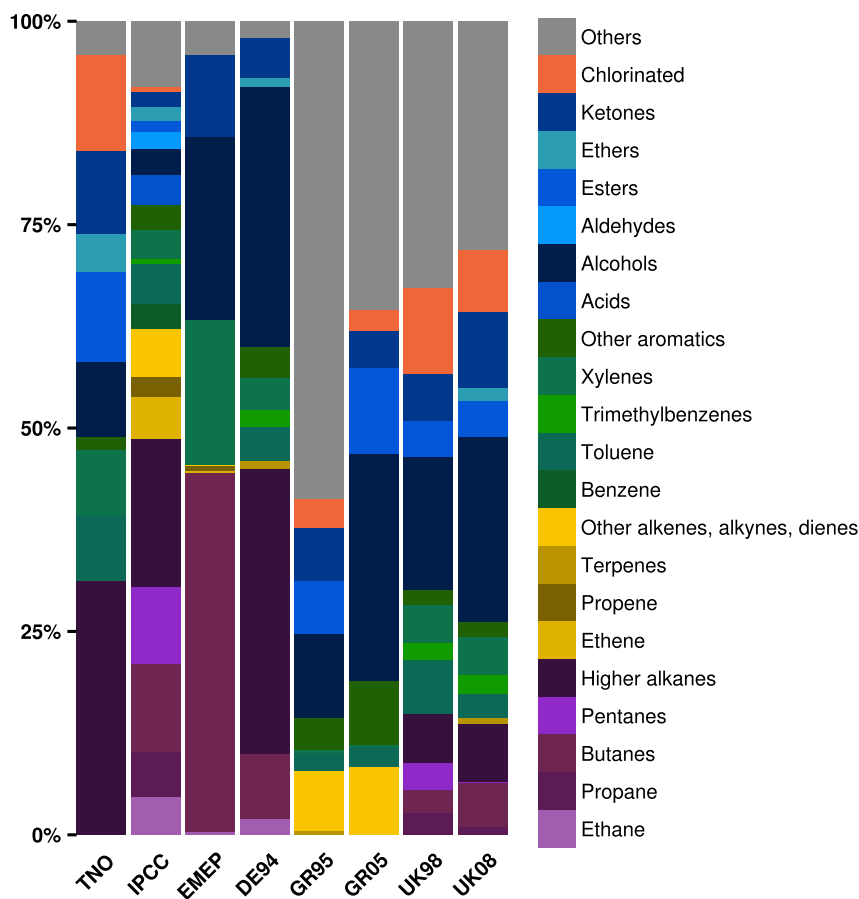


Fig. 1. Solvent sector speciation profiles, as percent contributions by mass, translated to the individual NMVOCs and lumped NMVOC categories used as a common basis for comparison. Similar colors are used to relate compounds by class, e.g., alkanes are grouped and depicted in purples, alkenes and alkynes are grouped and depicted in yellows, etc. See Table 1 for speciation codes and references. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

photochemical cycles, the Ox family was used as a surrogate for O₃ production. For this work, the Ox family was defined as including O₃, NO₂, O, O¹D, NO₃, N₂O₅ and other species that are involved in fast photochemical production and loss cycles with NO₂. This definition of the Ox family implies that Ox production budgets are a measure of the number of NO to NO₂ conversions by peroxy radicals formed during VOC degradation. As all organic peroxy radicals are tagged for the emitted NMVOC, the tag and the reaction rate were used to attribute Ox production back to the emitted VOC. Butler et al. (2011) shows that under the conditions of maximum ozone production as used in this study, the production rate of Ox is closely related to the production rate of ozone, and includes more details of the tagging approach.

2.4. NMVOC initial conditions

This study considered an idealized urban area of 1000 km² with total NMVOC emissions of 1000 tons day⁻¹ (Warneke et al., 2007). As the solvent sector contributed 43% to total NMVOC emissions (EEA, 2013), the total amount of NMVOC emissions in each model run was 430 tons day⁻¹. The total NMVOC emissions were then allocated to the individual NMVOC and groups of NMVOC specified by the EIs in Table 1 that were represented by MCM v3.2 species. Since the MCM is a near explicit mechanism, in many cases lumped species needed to be separated into their individual components for use in this mechanism. For this, an informed allocation was preferred, rather than making different assumptions for different

cases or simply allocating an equal fraction to each species falling under the lumped group. Therefore, Passant (2002) was used to facilitate this allocation, which reports some of the most detailed speciation information available for NMVOC emissions based on detailed profiles from individual activities. The composite profile for Standardized Nomenclature for Air Pollutants (SNAP) category 6 (solvent use sector) with percent contributions from 127 individual NMVOCs specified for SNAP 6 in Passant (2002) was used to provide more explicit speciation information where needed. This is provided in Table S1a. For example, the TNO EI specifies a contribution of 8% from 'xylenes' as a group to the total NMVOC emissions. As the MCM v3.2 represents xylenes not as a group, but as the individual NMVOCs, the relative amounts of the emissions were calculated and attributed to the individual xylene isomers (*m*-, *o*- and *p*-xylene) using the information provided for the solvent sector by Passant (2002) and thereby integrated into the MCM v3.2. The calculation of the attribution of xylenes to individual xylene species is depicted in Table 2. Following the same process, in the case where some NMVOC contribution was attributed to 'others' the NMVOCs listed in the Passant (2002) speciation for solvent use and not already accounted for were used to attribute contributions from the remaining NMVOCs. Finally, in the case of the speciation for Greece, 'white spirit' was included in the speciation profile. Sidiropoulos and Tsilingiridis (2007) also included the composition of white spirit, and therefore the cycloalkanes, paraffins and aromatics represented by the MCMv3.2 having the same carbon numbers as listed by Sidiropoulos and Tsilingiridis (2007) were

Table 2
Example attribution of lumped NMVOC species categories to individual compounds using [Passant \(2002\)](#).

TNO Category	MCM species	Passant % contribution	TNO % contribution	Adjusted % contribution
Xylenes	MXYL (<i>m</i> -xylene)	3.2	7.99	5.33 (= 3.2/4.8 × 8)
	OXYL (<i>o</i> -xylene)	0.8		1.33 (= 0.8/4.8 × 8)
	PXYL (<i>p</i> -xylene)	0.8		1.33 (= 0.8/4.8 × 8)
Total		4.8	7.99	7.99

used to represent NMVOC emissions from white spirit in this study. NMVOC emissions were held constant for the first 6 h of simulations, representing a pulse of NMVOC emissions.

The initial NMVOC emissions and NMVOC species represented by the MCM v3.2 were mapped to the MOZART-4 and RADM2 primary species based on the recommendations from the literature ([Emmons et al., 2010](#); [Stockwell et al., 1990](#)). Then the MCM v3.2 species and respective emissions were aggregated into the MOZART-4 and RADM2 species by weighting the MCM v3.2 emissions by the respective carbon numbers. This approach ensured that the amount of emitted reactive carbon was the same in each model run despite the different chemistry schemes.

Two additional sets of runs were done using each solvent sector speciation with each chemical mechanism to evaluate the magnitude of the effect in increasingly realistic conditions, adding (a) emissions for all other anthropogenic emission sectors, followed by (b) biogenic emissions in addition to the anthropogenic emissions of (a). The remaining anthropogenic emissions contributed an additional 570 tons day⁻¹ to complete the 1000 tons day⁻¹ for the idealized urban area. The relative contributions of each sector were based on the same literature source as the solvent sector contribution ([EEA, 2013](#)), and the speciation used for these emissions was a European average provided by TNO ([Buitjes et al., 2002](#)). For the biogenics run, all anthropogenic emissions were included, plus an additional 440 tons day⁻¹ of biogenic emissions. Specifically 150 tons day⁻¹ of isoprene and 290 tons day⁻¹ of monoterpene emissions were added to the initial emissions pulse. These values were based on the annual total European emissions information used in the EMEP model ([Simpson et al., 2012](#)). The relative contribution of the biogenic (isoprene and monoterpene) emissions to the total anthropogenic NMVOC emissions was calculated and averaged for all of Europe. This average was then related to the hypothetical emissions of 1000 tons day⁻¹ used in the box model, to provide a reasonable estimate for biogenic emissions. These runs were done to provide the context for incrementally including more realistic conditions for the box model and estimate the effect of changing the NMVOC speciation of the solvent sector emissions.

3. Results

3.1. Comparison of solvent sector speciation

[Fig. 1](#) presents the comparison of the solvent sector speciations used in this study, translated to the common basis categories to facilitate the comparison, as described in Section 2.1. There is significant variation across the different speciations for the solvent sector. It should be noted that the IPCC speciation is a general speciation that does not distinguish between sectors and therefore if this profile were used in modelling, the solvent sector speciation would equal that of e.g., road transport or agriculture. Even among certain species categories, there are significant variations. For example, the alkanes in the solvent sector are represented completely as higher alkanes in the TNO inventory, whereas the EMEP model solvent speciation represents the vast majority of the

alkanes as butanes with the exception of a small contribution from ethane. The IPCC and UK representations have the alkanes distributed more explicitly across the 4–5 alkane species and groups. Furthermore, the relative contribution of alkanes to the total also varies significantly. For Greece, alkanes are not included in the solvent sector speciation at all, whereas for a number of the other speciations contributions from alkanes are almost 50% of the total. In addition to the diversity in NMVOC speciation likely resulting from different information sources and spatial differences, the multiple years provided for Greece and the UK show differences in the two profiles for the different years, indicating an evolution or change in NMVOC speciation over time. For both the UK and Greece the later profiles show a larger contribution from alcohols and a slight reduction in chlorinated NMVOCs. And in the case of the UK, while the overall amount attributed to alkanes has remained relatively similar, the speciation within the alkanes shifted, being dominated more by butanes and higher alkanes in 2008 than 1998.

In mapping these NMVOC speciation details onto the different chemical mechanisms significant differences result based on what species are lumped or represented explicitly. As discussed in section 2.4, additional information was used from the detailed speciation provided by [Passant \(2002\)](#) where explicit speciation was needed when only lumped categories were provided by the emission inventory used, as in the case of mapping many of the EI onto the MCM v3.2 mechanism. To compare the input emissions speciation of the different mechanisms, the original input speciation as translated for the mechanisms, was again translated further into the common basis categories, to facilitate comparison, as for [Fig. 1](#). This is shown in [Fig. 2](#), with each group of three comparing the speciation of the same EI, as translated for input into each of the three chemical mechanisms used. (The original speciation information is provided in SI for reference, [Tables S1a–g](#).) As the most explicit mechanism included here the MCM v3.2 retains the highest amount of speciation information, and in some cases greater speciation information than the inventory may initially provide (as suggested by the example of xylenes in section 2.4). For example, the MOZART-4 mechanism allows for input of 21 species or NMVOC categories, while the MCM v3.2 allows for ca. 150. For example, in the case of the EMEP speciation, the original speciation of alkanes provided for the solvent sector in the EMEP model, is 0.4% ethane and 44% *n*-butane. When translated onto the respective mechanisms used here, across all mechanisms the alkanes are represented by a small contribution from ethane, but the rest is then represented as butanes in the MCM v3.2, whereas in MOZART-4 butanes are lumped into the ‘big alkanes’ category, which have a reactivity representative of pentanes for the whole category, and in RADM2, butanes are lumped in the HC3 category, representative of propane. For more details on the mechanisms and their comparison, please see [Coates and Butler \(2015\)](#). This comparison demonstrates that even with the same starting point for input data, significant differences in ozone production may result owing to how these species and their secondary chemistry are represented when translated to different chemical mechanisms.

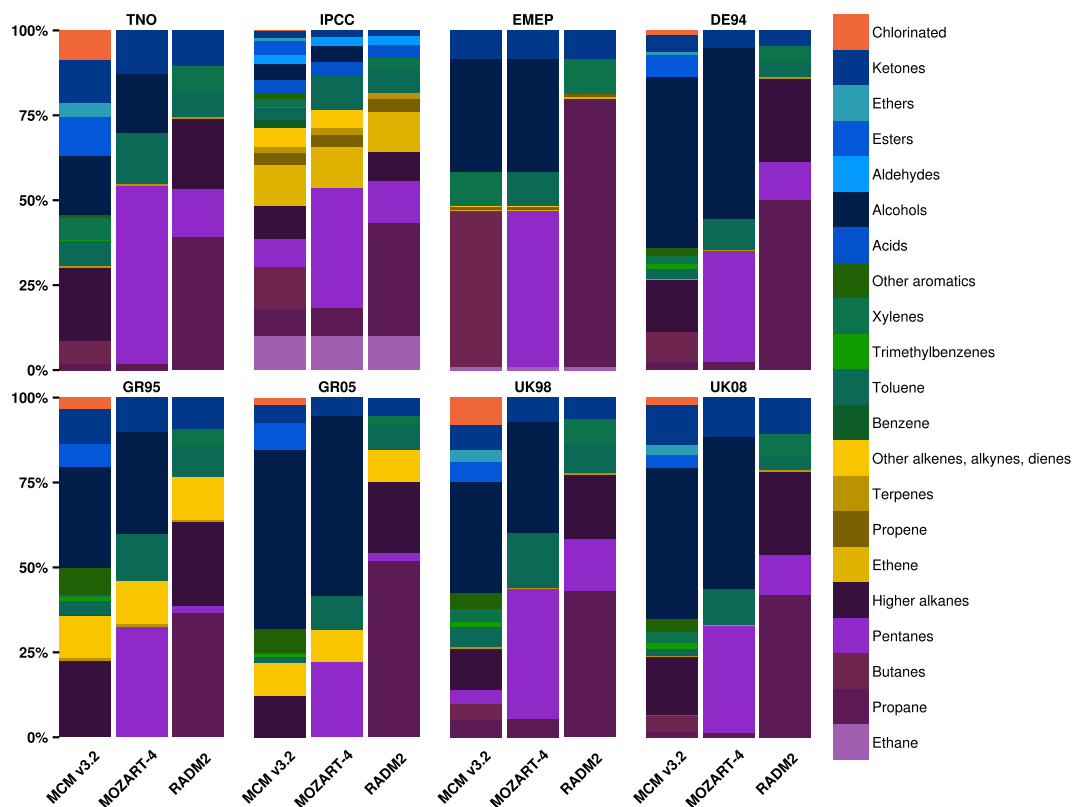


Fig. 2. Solvent sector speciation profiles, as percent contributions by mass, illustrating the differences owing to representation in the different chemical mechanisms, the MCM v3.2, MOZART-4, and RADM2. As in Fig. 1, the profiles were translated to the individual NMVOCs and NMVOC categories that were used as a common basis for comparison. Speciation profiles are grouped by emission inventory, with each group of three stacked bars representing one of the chemical mechanisms used in the box model.

3.2. Sensitivity of O_3 and Ox production budgets

3.2.1. O_3 time series from the eight solvent sector speciations

The sensitivity of modelled O_3 to the NMVOC speciation specified by the EIs listed in Table 1 is shown in Fig. 3 for each chemical mechanism. The top plot in the figure compares the time series of the O_3 mixing ratios obtained in each model run with tuned NO

emissions for each speciation, grouped by mechanism. To quantify the differences in the amount of ozone produced by the different speciations, the maximum difference between the speciations at every model time step (20 min) was calculated. The mean and standard deviation of the maximum differences were then calculated for each day and the entire time period. These values indicate the effect that speciation has on ozone levels within one

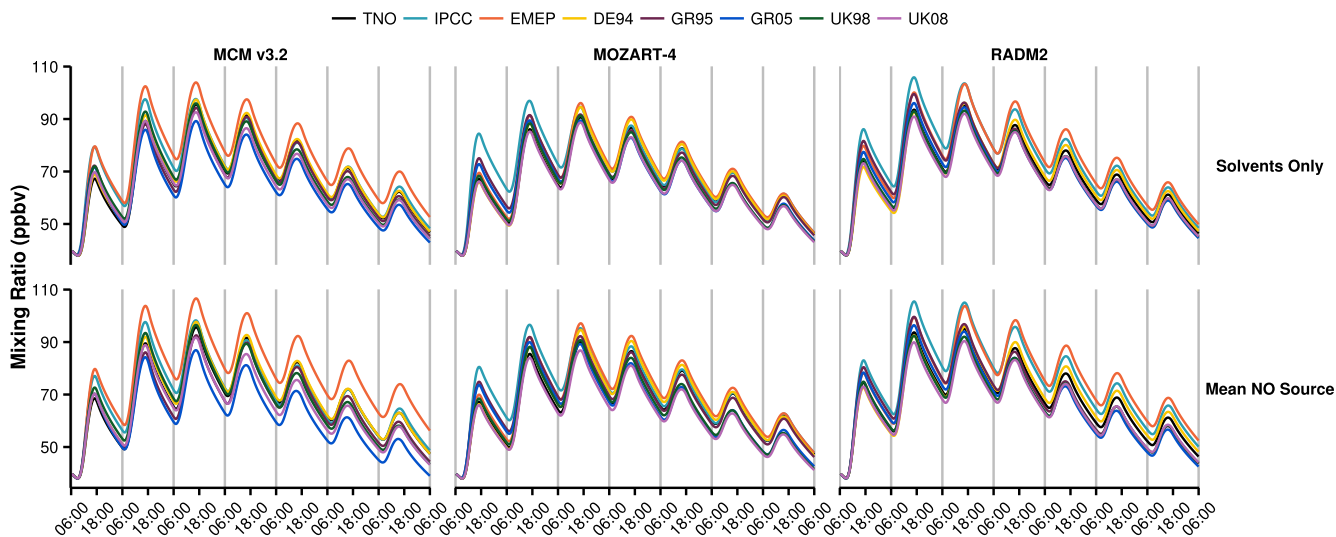


Fig. 3. O_3 mixing ratios produced during the box model run with (top) tuned NO emissions and (bottom) mean NO emissions. The only variation among the runs for each mechanism was the solvent sector speciation and for the tuned NO runs the NO emissions tuned for maximum O_3 production, while for the mean NO runs the same time series of NO emissions was used. The labels reflect the solvent sector speciation EI.

mechanism and are presented in Table 3. The mean maximum difference over the entire simulation (all days) ranged from 7.7 to 12 ppbv O₃ for the three different chemical mechanisms, which is about 11–17% of the mean modelled O₃ mixing ratio. The largest standard deviation in the maximum difference over the entire run (3.7 ppbv O₃) was found for the MOZART-4 mechanism, although this was similar for the MCM v3.2 (2.7 ppbv) and RADM2 (3.5 ppbv). The largest difference in the amount of ozone produced by the different speciations was on the first day for the MOZART-4 runs, but on the second day for the MCM v3.2 and RADM2, with differences decreasing towards the end of the seven days for all mechanisms. In all cases, the standard deviation for the individual days was largest on the first day.

The highest and lowest maxima in O₃ can also be compared, which we did for the second day of the run. In this case, the difference between the highest and lowest maxima of the second day O₃ mixing ratios were 17 ppbv for the MCM v3.2, 12 ppbv in MOZART-4 and 17 ppbv for RADM2. This statistic shows somewhat larger differences relative to the mean maximum difference across the individual time points. In general, the IPCC and EMEP speciations produced the largest O₃ mixing ratios for each chemical mechanism across the 7 days of the run, and in many cases are separated from the group of speciations producing a more similar amount of ozone for one or more days over the course of the run – in some cases for the entire duration of the run.

The results for the ‘mean NO’ runs were found to be similar to the results of the ‘tuned NO’ runs, but amplified, as shown in Fig. 3 (bottom) and Table 3. For the ‘mean NO’ runs the differences in the amount of ozone produced was greater between the different speciations than for the ‘tuned NO’ runs. This results from some speciations producing less ozone, while others produced similar amounts as in the tuned NO runs. Despite the increased differences in ozone mixing ratios, those speciations that produced the most ozone under ‘tuned NO’ conditions also produced the most ozone in the ‘mean NO’ runs and similarly for those speciations that produced lower amounts of ozone.

As an extra sensitivity study to the conditions in the study design, an additional run was done where the square size of the city was increased by a factor of 10, from 1000 sq. km to 10,000 sq. km which is still very much on the order of large cities. This resulted in roughly a factor of 10 decrease in the mean maximum difference observed across the 7 day run, ranging from an average mean maximum difference for all days of 0.9 ± 0.3 to 1.9 ± 0.4 ppbv across the three mechanisms. Interestingly however, the mean modelled ozone mixing ratio only decreased by about half, so the relative contribution of the mean maximum difference observed ranged from ca. 1.5–5.7% of the mean ozone mixing ratios. These results are summarized in Table S2. While the larger area means a smaller effect, this study was set up as an idealized test case. Furthermore,

this study investigates the differences in speciation profiles for only one sector, and from a region of the world where the sector attribution and general data quality are likely more reliable than in many other regions, therefore the results discussed here are likely conservative estimates if all sectors were to be considered and/or data from other regions.

3.2.2. O₃ mixing ratio differences owing to mechanisms

To provide a frame of reference, the amount of ozone produced by the 8 solvent sector speciations was also compared within the three mechanisms used in this study. These results are shown in Fig. 4 and summarized in Table 4. While the differences produced by mechanism choice are significant, the variation tended to be smaller in comparison to the differences observed owing to the different speciations within one mechanism. The largest mean maximum difference among the mechanisms over the model run was found for the EMEP speciation (6.7 ppbv for tuned NO runs and 8.2 ppbv for the mean NO runs). The smallest mean maximum differences were 2.1 ppbv and 3.3 ppbv for the tuned NO and mean NO runs, respectively. As was the case for the differences owing to speciation, the ‘mean NO’ runs in comparison to the ‘tuned NO’ runs led to an amplification of the differences observed but followed the same general pattern (Table 4). These results are in line with those from a much more extensive mechanism comparison study, where an 8 ppbv difference in O₃ mixing ratio was observed on the first day among 8 mechanisms (Coates and Butler, 2015).

3.2.3. Attribution of ozone production to individual NMVOCs

In order to understand the differences in modelled O₃ resulting from the different solvent sector speciations, we show both the first day and cumulative (all 7 days) Ox production budgets from the same model run allocated to the TNO EI categories for comparison in Fig. 5 (absolute amounts) and Fig. 6 (relative contribution, without CO and methane for better comparison of the NMVOC species). This allocation is possible using the tagging approach which was previously used in Butler et al. (2011) to allocate Ox production to emitted NMVOC over Los Angeles and Beijing and in Coates and Butler (2015) to compare the Ox produced over Los Angeles by several chemical mechanisms, including MOZART-4 and RADM2, to MCM v3.2.

These figures show that the importance of the different NMVOC classes for Ox production depends on whether a model run of one day or multiple days is considered. On the first day the more reactive species such as alkenes and aromatics produced the most Ox. Whereas at the end of the seven days, alkanes had the largest impact on cumulative Ox production – over half of the total Ox production budget from NMVOCs. The first day vs seven day Ox production could be considered illustrative of the role these species play in urban vs background ozone formation, respectively.

Table 3

Mean and standard deviation of the maximum difference in ozone produced by the different solvent sector speciations (solvent sector emissions only) for the tuned NO and mean NO model runs. The mean ozone mixing ratio across for the entire run is also included. Each day defined as 6am–6am.

	Tuned NO			Mean NO		
	MCM	MOZART	RADM2	MCM	MOZART	RADM2
Day 1	8.5 ± 4.1	12 ± 6.3	11 ± 5.8	7.5 ± 4.3	9.6 ± 5.4	14 ± 7.9
Day 2	15 ± 2.5	11 ± 1.8	15 ± 1.5	17 ± 3.6	12 ± 0.81	21 ± 2.6
Day 3	14 ± 0.63	6.8 ± 0.81	13 ± 0.92	18 ± 1.2	9.3 ± 0.70	18 ± 1.2
Day 4	12 ± 0.77	6.8 ± 0.85	12 ± 0.99	18 ± 1.6	9.9 ± 1.1	15 ± 0.89
Day 5	12 ± 1.1	6.5 ± 0.56	11 ± 0.84	19 ± 1.9	9.9 ± 0.80	14 ± 1.2
Day 6	12 ± 1.1	5.6 ± 0.45	8.6 ± 0.74	20 ± 1.8	9.0 ± 0.54	13 ± 0.84
Day 7	11 ± 0.94	4.4 ± 0.39	6.4 ± 0.62	19 ± 1.5	7.5 ± 0.42	11 ± 0.63
All days	12 ± 2.7	7.7 ± 3.7	11 ± 3.5	17 ± 4.6	9.5 ± 2.4	15 ± 4.5
Mean O ₃ all days	69	67	67	68	67	67

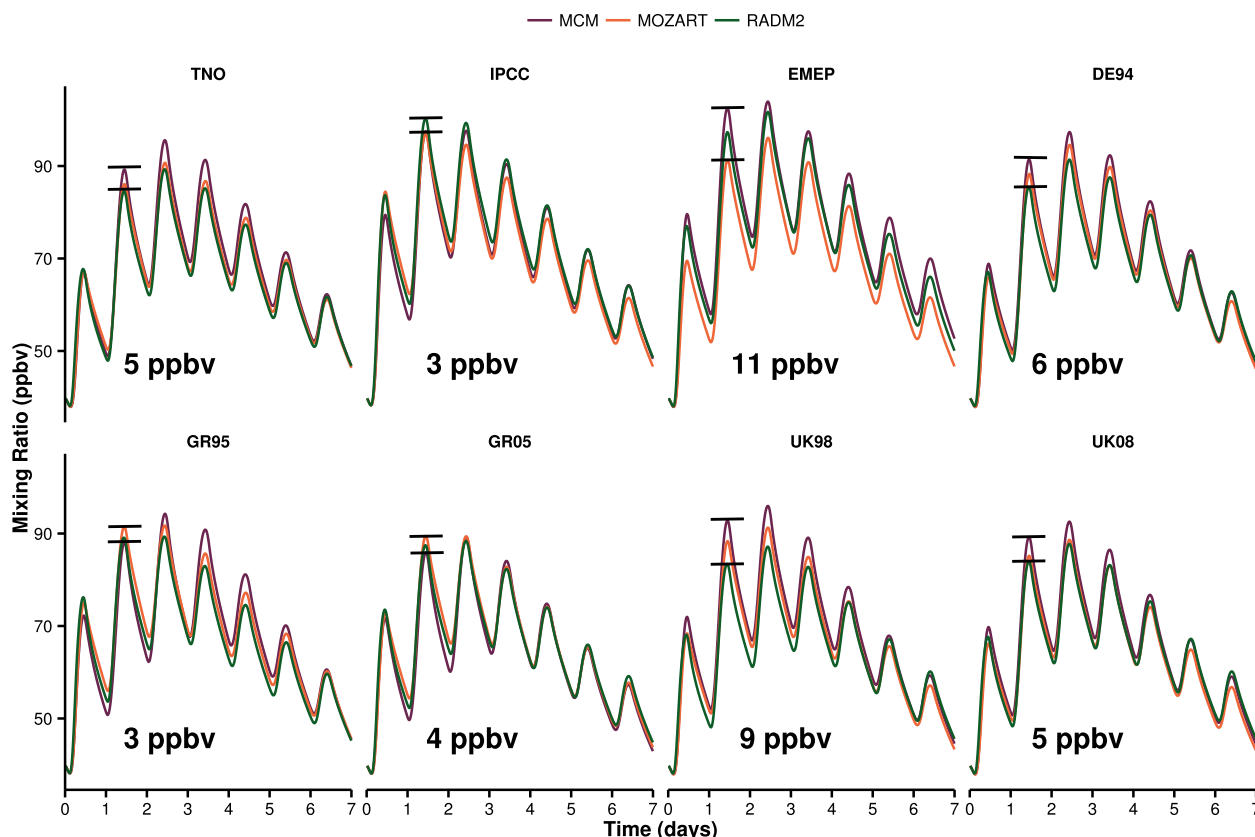


Fig. 4. As for Fig. 3, but grouped by solvent sector speciation, so as to compare the differences among mechanisms.

Table 4

Mean and standard deviation of the maximum difference in ozone produced by the same solvent sector speciation, implemented into the 3 different mechanisms.

	TNO	IPCC	EMEP	DE94	GR95	GR05	UK98	UK08
Tuned NO	3.0 ± 1.6	3.2 ± 1.2	6.7 ± 1.9	2.9 ± 1.4	3.9 ± 1.9	2.1 ± 1.7	4.2 ± 2.3	2.8 ± 1.1
Mean NO	3.3 ± 1.6	4.6 ± 1.9	8.2 ± 2.0	4.4 ± 2.9	5.4 ± 3.1	3.7 ± 2.0	5.3 ± 2.6	4.7 ± 2.1

3.2.4. Correlations between NMVOC compound class and Ox production

Section 3.2.3 showed that alkanes had the largest contribution to Ox production after seven days, whereas aromatics and alkenes have a larger contribution to Ox production in the first day. In this section, we further analyze the impact of the different compound types on Ox production by correlating the total amount of the different compound class of emissions specified in each EI with the total Ox produced during the first day and at the end of the model runs. This correlation between total Ox production at the end of the model run and the percent of total emissions that compound class represents is shown in Fig. 7 (first day results are not shown). The Pearson correlation coefficients in Fig. 7 show that EI speciation profiles specifying more alkane emissions were positively correlated with Ox production for the 7 day run, with *r* values ranging from 0.76 to 0.87 for the three chemical mechanisms. In particular, the IPCC and EMEP EI speciation profiles specify larger alkane emissions than any other EI speciation profile and in turn have the largest Ox production, as was also reflected in their O₃ mixing ratios at the top of the group in Fig. 3 for each mechanism. Correlation results for the first day Ox production and alkanes, still showed a positive relationship, although the correlations were less strong, with *r* values of 0.63 (MCM v3.2), 0.54 (MOZART-4), and 0.23 (RADM2). Given the lower reactivity and greater contributions of

alkanes to Ox production on the longer timescale, these results are in line with those from section 3.2.3.

The inverse is true for solvent sector EI speciation profiles that specify a larger contribution from oxygenated NMVOC groups, such as those for Greece, the UK, or Germany, which led to lower Ox production after seven days than EIs with lesser contributions from oxygenated species. The negative correlation ranged from −0.60 to −0.82, depending on the mechanism. These results were very similar to the first day Ox correlations, with *r* values ranging from −0.61 to −0.78. For aromatic species there was no consistent correlation across the mechanisms for the first day Ox or the seven day Ox, and the Pearson correlation coefficients were quite low, indicating no strong correlation between the contribution of aromatic species to the total emissions and the total Ox production. Because not all speciations include alkenes, this correlation analysis was not carried out for alkenes.

3.3. Larger context

To consider conditions approaching more realistic conditions for the box model evaluation of the effect of NMVOC solvent sector speciation, two additional runs were done where (a) emissions for all other non-solvent anthropogenic emission sectors were added, and (b) biogenic emissions were added in addition to the other

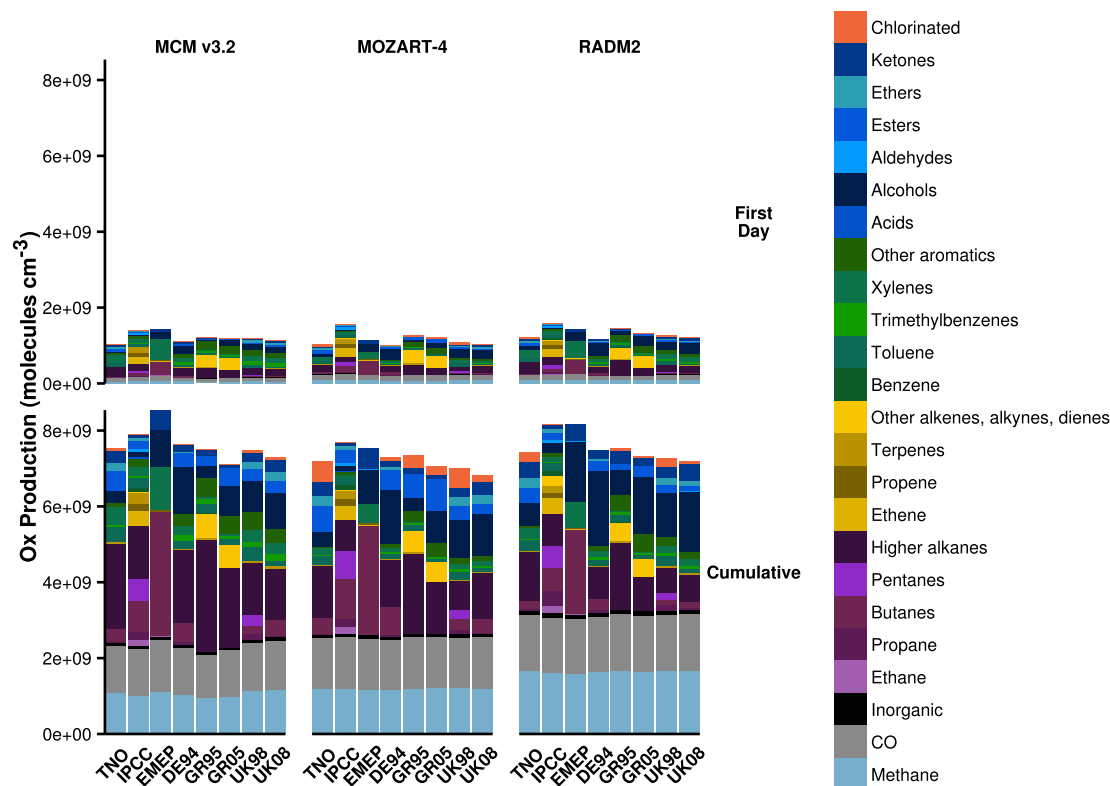


Fig. 5. The total amount of Ox produced during (top) the first day and (bottom) over entire cumulative 7-days included in the model run allocated to the NMVOC species or groups. Translated to the common basis categories for comparison.

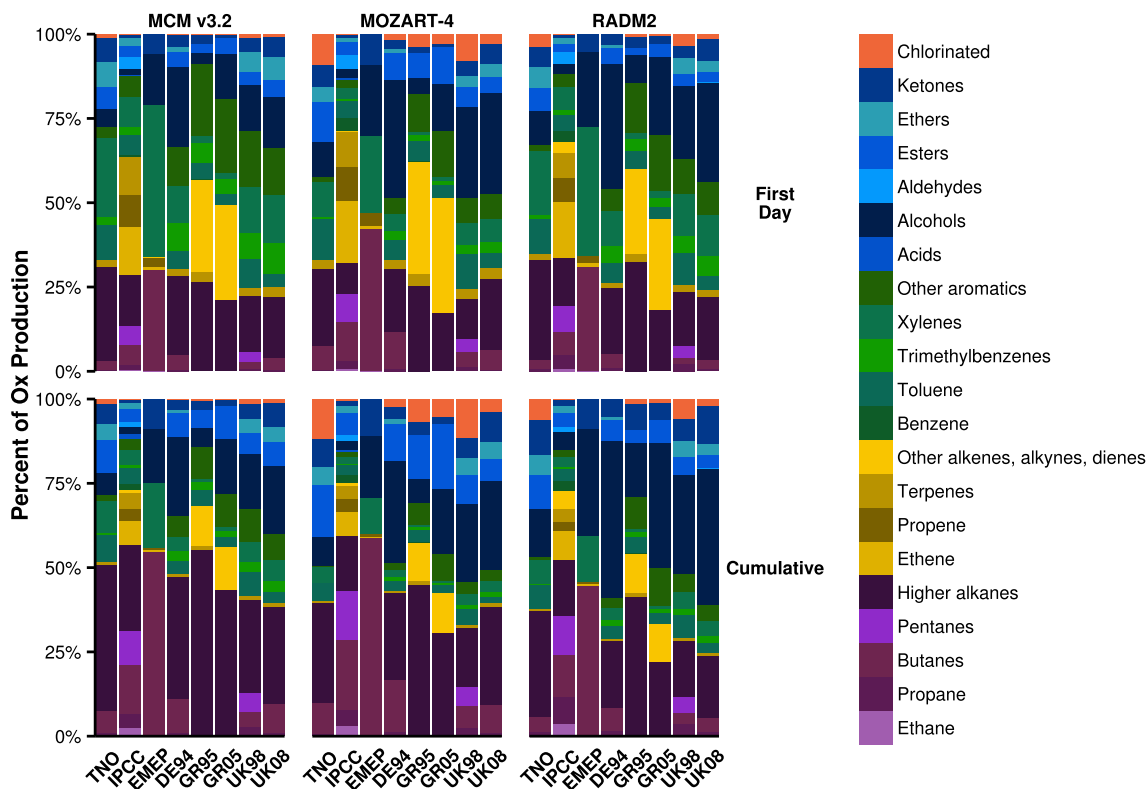


Fig. 6. As Fig. 5 but as percent contributions by mass. Carbon monoxide, methane, and inorganic species were not included in the percent contribution allocations so as to better compare the NMVOC contributions.

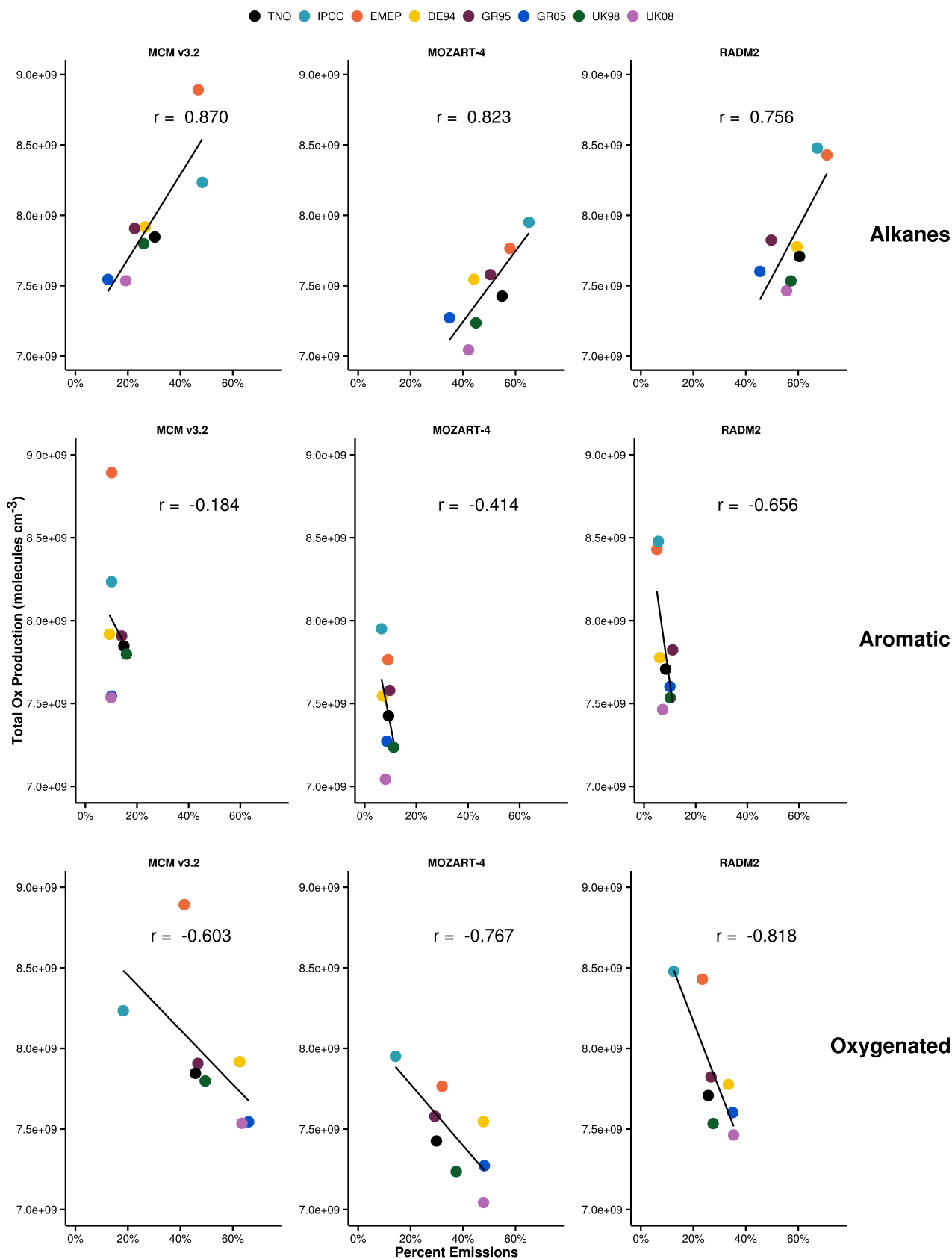


Fig. 7. Correlation of total Ox production (cumulative, 7-day) to the fraction of (top) alkanes, (middle) aromatic, and (bottom) oxygenated NMVOC emissions specified by each EI, presented by mechanism. The Pearson correlation coefficient, r , is given.

anthropogenic emission section emissions of (a). In both cases, the additional emissions were the same across all runs in terms of amount of NMVOC emissions added and speciation attributed. The only parameter varied between the runs was, as previously, the solvent sector speciation. As would be expected, the overall amount of ozone produced increased because of the tuned NO source and increase in NMVOC emissions, but the maximum difference in O₃ owing to the different solvent sector speciations decreased. Specifically, for the added anthropogenic emissions, the maximum difference in O₃ produced over the course of the entire run was 9.2, 6.2, and 7.9 ppbv for the MCM v3.2, MOZART-4, and RADM2, respectively. This implies a reduction of the impact by about ~20–30% (compare Table 5 with Table 3). In the case of the additional anthropogenic emissions plus the biogenic emissions, the maximum difference for the entire run decreased further in the case of the MCM v3.2 and MOZART-4, but remained similar for RADM2. The maximum differences calculated were not significantly different from run (a), in that the maximum differences in O₃ were within the standard deviation among the speciations between the two runs. These statistics are summarized in Table 5. The patterns in the amount of O₃ produced for the different speciations, even with the added emissions, remained the same as those in Fig. 3.

4. Discussion

While there are no studies that evaluate the role of NMVOC speciation on ozone production in the way that it is done in this study, the studies by Coll et al. (2010) and Chen et al. (2010) have significant similarities. Coll et al. (2010) evaluated the ESCOMPTE EI for the Marseille, France area in comparison to measurements for over- or under-estimation of specific hydrocarbons, followed by a model study using a regional chemical-transport model, CHIMERE, to evaluate the degree of sensitivity of the model to the emission profile inputs. The model was run a number of times with perturbations of the non-methane hydrocarbon (NMHC) profile based on the range of uncertainties from the measurement-EI evaluation. Similarly to this study, the variation was in the speciation only and the total mass of NMVOC emissions remained constant. They found that the biases in the inventory could result in differences of 2–10 ppbv in peak O₃ over the study area (Coll et al., 2010), which are quite similar to the effect quantified in the box model runs that included anthropogenic emissions from all sectors and biogenic emissions.

Chen et al. (2010) implemented a sub-mechanism in a regional chemical-transport model that allowed for tracking of all of the photochemical assessment monitoring stations (PAMS) species, which are the suite of NMVOCs measured at US EPA monitoring sites; monitoring of the suite of PAMS species has been adopted by some other countries, e.g., Taiwan. Applied to a case study in Taiwan, emissions of individual species were able to be corrected based on measurement information, with correction factors of 0.06–34, based on calculated correlations of observation and model simulations for each species. The conclusion of the study was that the detailed speciation of the VOCs in EI needs evaluation,

and that improved speciation information can improve the accurate representation of NMVOCs in models (Chen et al., 2010). While the effect on ozone production was not evaluated as part of that study, a follow-up study did evaluate the effect of improved NMVOC emissions on not only the NMVOCs themselves, but also ozone (Chen et al., 2014). In this case, the total amount of emissions were not kept constant, but increased by ca. 25%, most of which was concentrated in the alkyne and alkane NMVOC species, followed by a lesser increase in the alkene and aromatic species. These changes resulted in a change in the average ozone of 2.9 ppb, and a significant improvement in the model simulations (Chen et al., 2014). These results from Chen et al. (Chen et al., 2010, 2014) and Coll et al. (2010) indicate that, as also observed in the box modelling conducted in this study, NMVOC speciation does have an impact on the modelled ozone concentrations. In such modelling studies, the impact will also depend on whether the area of study is mainly a VOC-limited or NO_x-limited ozone regime.

The majority of studies that evaluated EI have done so by comparing with measurements, and/or continue on to assess the NMVOC speciation using ozone formation potentials (OFPs) to suggest target sectors for ozone mitigation action. Such work highlights the differences in NMVOC speciation identified by measurements and source apportionment in comparison to EIs, as outlined in the introduction. These differences and the use of OFPs to inform mitigation actions emphasize the importance of accurate NMVOC speciation in EIs. The Ox production attribution results for the first day from this study (Section 3.2.3) parallel the use of OFPs. For example, Li et al. (2014) compared modelled O₃ produced from different EIs used over East Asia focusing on the representation of individual NMVOC between the EIs. They calculated the ozone formation potential of individual VOCs by multiplying the fractional contributions of the VOC emissions from its source by the Maximum Incremental Reactivity (MIR) of the VOC. MIR values were calculated in Carter (1994) using model runs of one day. This method emphasized the impact of reactive VOC which produce maximum O₃ on the first day at the expense of less-reactive VOC such as alkanes that produce maximum O₃ after the first day. These results are consistent with our first day Ox production budgets (Figs. 5 and 6), however when considering multi-day model runs, less reactive species, such as alkanes, have a higher potential to produce O₃ (Butler et al., 2011; Coates and Butler, 2015) which is also seen in Figs. 5 and 6. This large contribution of alkanes to Ox production during multi-day model runs is also seen in Butler et al. (2011) and Coates and Butler (2015).

Considering the correlation results presented in Fig. 7, when comparing the solvent sector speciations for the two different years each for Greece and the UK, the more recent EI speciations both specify a larger contribution from oxygenated NMVOC and lower contributions from alkanes than the earlier versions of the inventories. This demonstrates that the speciation of the NMVOC emissions change over time, as would be expected given changes in processes, activities, and technology. This demonstrates a need for updating not only the total NMVOC emissions as is done more frequently through yearly reporting, but also the NMVOC speciation in inventories.

A number of studies have evaluated NMVOCs based on methods similar to the first day ozone production potential used in this study, such as OFP or OH reactivity methods. Such methods estimating ozone production potential are often linked to source information and the relative contributions of sources to ozone production to inform mitigation options. For example, in the speciated NMVOC emissions for Asia developed by Li et al. (2014), of the 700 individual NMVOCs evaluated, 30 species with the highest OFPs were considered in greater detail. Of these species, 5 were oxygenated NMVOCs, while only 2 alkanes made the list,

Table 5

Mean and standard deviation of the maximum difference in ozone produced by the different solvent sector speciations over the course of the entire 7 day run including the larger context of all other anthropogenic emissions and these plus biogenic emissions.

	MCM	MOZART	RADM2
+ Anthro emiss	9.2 ± 2.1	6.2 ± 3.4	7.9 ± 1.8
+ Anthro & bio emiss	8.7 ± 2.6	5.0 ± 2.2	8.0 ± 2.1

noting that emphasis was placed on the OVOCs and alkenes because of their high contributions to the OFPs, in comparison to their contribution to mass of emissions, which was found to be quite low. Different profiles (speciation) were also evaluated and they found differences in OFP of up to a factor of 3 owing to the different profiles. This emphasizes the sensitivity of OFP to the profiles (speciation) information used (Li et al., 2014). Similarly, Gilman et al. (2009) evaluated measurements of NMVOCs in the Houston and Gavelston Bay area using OH reactivity, which is another way of estimating OFP. Their results attributed the greatest reactivity (ozone formatting potential) to oxygenated VOCs and alkenes, with increases in the OH reactivity in the area attributed to heavy influence from industrial emissions.

These different methods of assessing contribution to O₃ production would likely result in different recommendations as to which sources to focus O₃ mitigation actions on, as alkane dominated sources would not be targeted if first-day OFP methods were used in the assessment. That said, from the mitigation perspective, none of these methods includes consideration of the differences in human toxicology of the NMVOC species, either, instead focusing only on O₃ production. In a study that did consider both aspects, they found that the species contributing significantly to ozone production are often not the same as those with the highest toxicity (Laurent and Hauschild, 2014). Finally, the more reactive species will tend to be more relevant for ozone formation in e.g. urban areas, closer to the emission sources, whereas the less reactive species, such as alkanes, will react on longer timescales more relevant for background conditions.

5. Conclusions

These results show that NMVOC speciation can have a significant effect on the amount of ozone produced in an idealized system, such as a box model. While not directly representative of the real world situation, such a system is a valuable tool to study and understand sensitivities and (inter-) dependencies of a complex atmospheric chemical nature. Significant differences in modelled O₃ were obtained using detailed gas-phase chemistry (MCM v3.2) and simplified chemical mechanisms (MOZART-4 and RADM2). While Ox production is typically dominated by alkenes and aromatics in the first 24 h of the box model runs, after seven days, alkanes had the largest contribution to the total Ox production budget. Furthermore, correlations between the contribution of NMVOC compound classes to the overall NMVOC emissions and the amount of Ox produced were found to be positively correlated to alkanes and negatively correlated to oxygenated species, with no clear relationship observed for aromatics. The correlation between Ox production and amount of alkanes was less for the first day Ox than for the entire 7 days, which would be expected given their lower reactivities. These results indicate that representation of the speciation of NMVOCs in emission inventories will influence the modelled amount of ozone produced, especially when considering that these species are often lumped into compound groups. Therefore, an over- or under-representation of a certain class of compound could result in significant differences in the amount of ozone produced, over the shorter and longer term. While various ozone formation potential factors provide effective estimates as to which species are most crucial to reduce when considered over the short term (1 day), such a study also shows that some of the slower reacting NMVOCs are also important to target if ozone reductions are desired, with implications for which sources and sectors are to be considered and prioritized. This study was not designed to evaluate which solvent sector speciation is most 'correct', and therefore no recommendations are given as to which speciation should be used. An evaluation of activity data, composition of

emissions, and comparison with measurements, among other factors would be needed to evaluate the emission inventories to understand which might be the best representation of reality.

One aspect not considered here was the role of NMVOCs in secondary organic aerosol (SOA) formation. In addition to the role as ozone precursors, NMVOCs are also critical precursors to SOA (Hallquist et al., 2009; Jimenez et al., 2009). NMVOC speciation information also plays an important role for understanding and modelling SOA formation, as certain classes of VOCs have been identified as more likely to lead to SOA formation owing to reactivity characteristics and subsequent oxidation products (Hallquist et al., 2009). For example, a study of NMVOC in Santiago de Chile evaluated NMVOC for their role in ozone formation, but also SOA, and found that SOA formation was strongly linked to traffic emissions, and more specifically aromatic compounds (Rappenglück et al., 2005). This aspect should be included in the evaluation of future studies, as it also has a policy relevance related to informing mitigation measures.

This study was an idealized, simplified, first evaluation of the possible effect of NMVOC speciation in emission inventories and the possible consequences for modelled ozone predictions. The simple and transparent approach of the box model studies reported here help put the impact of various parameters in perspective. The maximum impact of the speciation profile on O₃ mixing ratios ranged from 7.7 to 17 ppbv; this was about 10–25% of the average O₃ mixing ratios in the box model runs. The choice of mechanism had about half that impact (3–12%). Both the speciation and the choice of chemical mechanism have an effect on the modelled O₃ concentrations. Given the results of this study where the maximum potential difference in modelled ozone was assessed, further work is recommended to conduct a similar study to evaluate the role of NMVOC speciation under more realistic conditions in a regional and/or global chemical-transport model. Such a study has been initiated by the authors. The result of this study has, and further evaluation will have implications for the necessity of updated NMVOC speciation in emission inventories, as well as the amount of detail appropriate to provide regarding speciation, which could lead to improved capacity of models to capture ambient concentrations of ozone. Current efforts to address the improvement or updating of speciation of NMVOCs in emission inventories and for use in modelling could benefit significantly from regulatory authorities including speciation information along with the emissions reporting, which is currently not the case for the vast majority of countries.

Finally, the combination of a couple of factors could lead to significant changes in the overall NMVOC speciation representation for total NMVOCs in EI. Specifically, the disagreement between the measurements and reported (EI) data as to the contribution of different sectors to NMVOC emissions, as outlined in the introduction and the radically different NMVOC speciation profiles between e.g. the solvent use and road transport sectors. Furthermore, the differences assessed here were based on data from Europe. In regions where data is much sparser and/or less reliable, such as developing nations, the differences are likely to be greater and therefore the results here are likely a conservative estimate in terms of overall ozone impacts. Given the result of this study, which shows significant differences in the amount of O₃ produced for the various speciation profiles available for within one sector, a much greater difference in speciation owing to large shifts in the contributions of different sectors to NMVOC emissions could result in even greater differences in the speciation of NMVOC emissions and thereby atmospheric reactivity, chemistry, and ambient concentrations of O₃, and possibly other species, as they are represented and assessed in models.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.03.057>.

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