Sensitivity of Modelled Tropospheric Ozone to VOC Emission Inventories

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Abstract

Volatile organic compounds (VOCs) are detrimental to human health both directly and indirectly, through their role in the formation of secondary air pollutants such as tropospheric ozone (O_3). The identity and amounts of VOCs emitted into the troposphere are represented in emission inventories (EIs) for input to chemical transport models that predict air pollutant levels. These EIs are outdated but before taking on the task of providing an up-to-date and highly speciated EI, the sensitivity of models to the change in VOC input needs to be addressed. We determine the sensitivity of modelled tropospheric O_3 to VOC emission inventories by comparing the maximum potential difference in O_3 levels using various solvent sector EIs in an idealised

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study using a boxmodel. We further test this sensitivity using three chemical mechanisms that describe O_3 production chemistry at different scales – point (MCM v3.2), regional (RADM2) and global (MOZART-4). Under the conditions of our study, we find a maximum difference of 17 ppbv between different EIs of the solvent sector, reproduced by each chemical mechanism. At the end of the seven-day model runs, alkanes have the largest contribution (up to 40%) to O_3 production and the amount of total alkane emissions specified by the solvent sector emission inventories is directly related to the amount of O_3 produced. These results indicate that modelled tropospheric O_3 is sensitive to the distribution of VOCs specified by emission inventories and that the maximum amount of O_x produced from an updated emission inventory depends on the amount of alkane emissions specified.

1   Introduction

Volatile organic compounds (VOCs) have an adverse effect on health, both directly and indirectly as a precursor of secondary air pollutants (Laurent and Hauschild, 2014). Tropospheric ozone (O_3) is one such secondary air pollutant formed from the degradation of VOC in the presence of nitrogen oxides (NO_x) and sunlight (Atkinson, 2000). Numerical chemical transport models use emissions of NMVOCs (non-methane VOCs) and NO_x to predict O_3 concentrations.

Emission Inventories (EIs) allocate anthropogenic NMVOC emissions into sectors by source (e.g. industry, solvent use), these sectors are further sub-divided into individual NMVOC and groups of NMVOC with relative contributions to total sector emissions. Modelling studies may use EIs to determine the NMVOC species represented by the model and the amounts of emitted NMVOC. Despite EIs being widely used as model input, there are many uncertainties with EIs, such as discrepancies between the contributions of NMVOC specified by an EI and ambient measurements of the NMVOC

(Borbon et al., 2013), also EIs fail to capture the change in NMVOC emissions over time (Boynard et al., 2014).

Li et al. (2014) have compared the modelled tropospheric O_3 produced from different EIs used over east Asia using multiple chemical mechanisms. They calculate the ozone formation potential of individual NMVOC and determine that highly reactive VOC, such as ethene and reactive aromatic VOC, have the largest impact on tropospheric O_3 production.

Improving an EI requires a large amount of effort due to the diverse sources and variety of inputs. Before undertaking such a task, it is valuable to know whether models are sensitive to changing NMVOC input. In particular, how large are the differences in modelled O_3 using different EIs as model input.

In this study, we address the sensitivity of modelled O_3 to different EIs of the solvent sector; we consider the solvent sector as this has the largest contribution to NMVOC emissions (EEA, 2011) and EIs for this sector specify differing NMVOC and relative contributions. We calculate the maximum potential difference in modelled O_3 produced by various solvent sector EIs using an idealised boxmodel setup.

2 Materials and Methods

2.1 Solvent Sector NMVOC Emission Inventories

Solvent sector EIs were chosen to represent a range of case studies, including the european average NMVOC speciation (TNO), a model specific speciation (EMEP), a general anthropogenic speciation (IPCC) and country specific profiles for Germany, Greece and the UK. Two time-points of the Greek and UK profiles are included to represent the evolution of solvent sector NMVOC emissions over time. Table 2.1 lists all these solvent sector EIs compared in

Table 1: The solvent sector emission inventories compared in this study.

Speciation	Comment	Reference
TNO	European average	Builtjes et al. (2002)
IPCC	Model Specific	Ehhalt et al. (2001)
EMEP	Model Specific	Simpson et al. (2012)
DE94	Country Specific	Friedrich et al. (2002)
GR95	Country Specific	Sidiropoulos and Tsilingiridis (2007)
GR05	Country Specific	Sidiropoulos and Tsilingiridis (2007)
UK98	Country Specific	Goodwin (2000)
UK08	Country Specific	Murrells et al. (2010)

this study.

2.2 Model Description

We use the MECCA boxmodel (Sander et al., 2005) 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 O_3. Model runs were performed using the detailed gas-phase chemistry of the Master Chemical Mechanism (MCM v3.2) (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2015).

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. We also determined the sensitivity of modelled O_3 mixing ratios using the MOZART-4 (Emmons et al., 2010) and RADM2 (Stockwell et al., 1990) mechanisms which are used for global and regional modelling studies, respectively. Coates and Butler (2015) describes

the implementation of MOZART-4 and RADM2 into the MECCA boxmodel.

2.3 Model Setup and Simulations

The model is run under equinoctical conditions representative of 34 degrees North (roughly the city of Los Angeles, USA). CO and O_3 were initialised at 200 ppbv and 40 ppbv and then allowed to evolve freely, methane (CH_4) was fixed at 1.8 ppmv. In each model run, we used NO_x conditions that induce maximum O_3 production by emitting the amount of NO needed to balance the chemical source of radicals at each time step.

Model runs were performed using each of the solvent sector EIs of Table 2.1 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 Coates and Butler (2015) and allows attribution of O_x production back to the emitted VOC. As O_3 production is dominated by rapid photochemical cycles, the O_x family is used as a surrogate for O_3 production. We define the O_x family to include O_3, NO_2, O, O^1D, NO_3, N_2O_5 and other species that are involved in fast photochemical production and loss cycles with NO_2.

2.4 NMVOC Initial Conditions

This study considered an idealised urban area of 1000 km^2 with total NMVOC emissions of 1000 tons day^{-1} (Warneke et al., 2007). As the solvent sector contributes 43% to total NMVOC emissions (EEA, 2011), 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 2.1 that

116 are represented by MCM v3.2 species. When an EI specified a group of
117 NMVOC then Passant (2002) was used to determine the individual NMVOC
118 and contributions of the specified group. For example, the TNO EI specifies
119 a contribution of 8% from xylenes; the contributions of the individual xylene
120 isomers are listed in Passant (2002) and used to calculate the emissions of
121 m-, o- and p-xylene in the TNO model run with MCM v3.2 chemistry. The
122 NMVOC emissions were held constant until noon of first day.

123 The initial NMVOC emissions and NMVOC species represented by the
124 MCM v3.2 were mapped to the MOZART-4 and RADM2 primary species
125 based on the recommendations from the respective literature (Emmons et al.,
126 2010; Stockwell et al., 1990). The MCM v3.2 species and respective emissions
127 were aggregated into the MOZART-4 and RADM2 species by weighting
128 the MCM v3.2 emissions by the respective carbon numbers. This approach
129 ensured that the amount of emitted reactive carbon was same in each model
130 run with the different chemistry schemes.

131 3   Results and Discussion

132 3.1   Sensitivity of O_3 and O_x Production Budgets

133 The sensitivity of modelled O_3 to the NMVOC specified by the EIs listed in
134 Table 2.1 with each chemical mechanism is shown in Fig. 1 by comparing
135 the time series of the O_3 mixing ratios obtained in each model run. The
136 differences between the highest and lowest maxima of the second day O_3
137 mixing ratios are 17 ppbv using MCM v3.2, 12 ppbv in MOZART-4 and
138 17 ppbv with RADM2. In general, the model specific EIs (IPCC and EMEP)
139 produce the largest O_3 mixing ratios in each chemical mechanism.

140 The time series of O_3 mixing ratios obtained with the different EIs have

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Figure 1: Differences in the time series of O_3 mixing ratios for each solvent sector EI using each chemical mechanism.
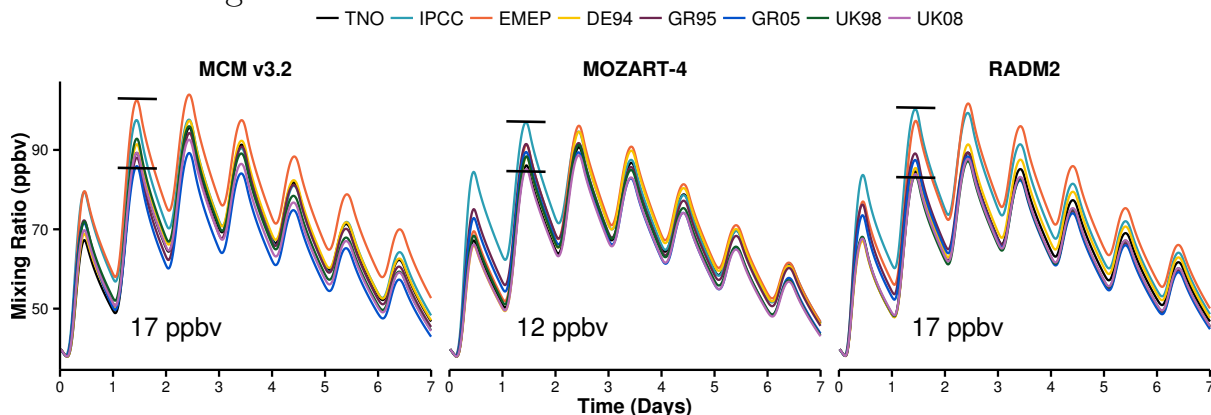
₁₄₁ a different spread in the reduced chemical mechanisms (MOZART-4 and

₁₄₂ RADM2) than the more detailed MCM v3.2. Using MOZART-4, the time

₁₄₃ series of O_3 mixing ratios have a lower spread than the MCM v3.2 runs.

₁₄₄ With RADM2, most speciations produce similar time series of O_3 mixing

₁₄₅ ratios except for EMEP and IPCC which are higher than the rest. These

₁₄₆ different spreads are due to the effect of lumping the emitted NMVOC from

₁₄₇ the MCM v3.2 into the mechanism species specified by MOZART-4 and

₁₄₈ RADM2. For example, the TNO solvent sector emissions are represented

₁₄₉ using 58 MCM v3.2 species but only 8 are required by MOZART-4 and 7 by

₁₅₀ RADM2.

₁₅₁ In order to understand the differences in modelled O_3 seen in Fig. 1, we

₁₅₂ show the first day and cumulative O_x production budgets allocated to the

₁₅₃ NMVOC groups specified by the EIs (Fig. 2). This allocation is possible using

₁₅₄ the tagging approach which was previously used in Butler et al. (2011) to

₁₅₅ allocate O_x production to emitted NMVOC over Los Angeles and Beijing and

₁₅₆ in Coates and Butler (2015) to compare the O_x produced over Los Angeles

₁₅₇ by several chemical mechanisms, including MOZART-4 and RADM2, to

₁₅₈ MCM v3.2.

₁₅₉ Figure 2 shows that O_x production is influenced by different groups

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Figure 2: The first day and cumulative O_x production budgets at the end of the model run allocated to the groups specified by the EIs, showing which emitted NMVOC groups contribute the most to O_x production.
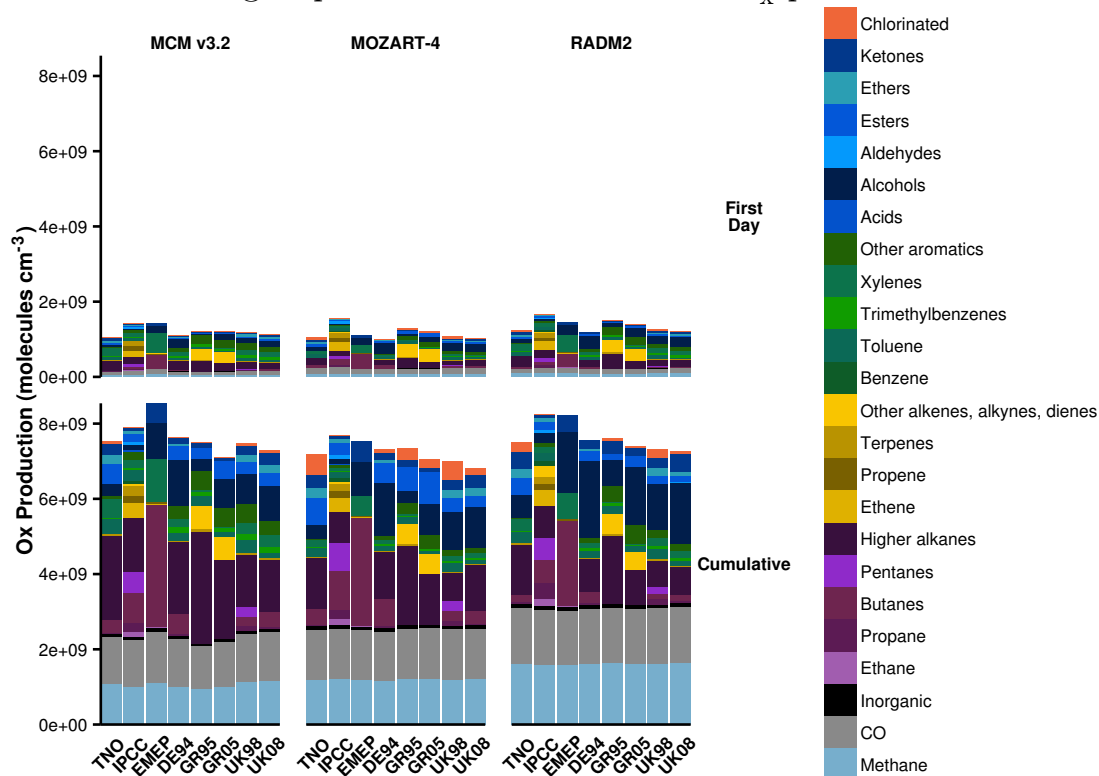
depending on the whether a model run of one day or multiple days is considered. On the first day the more reactive species such as alkenes (ethene, propene, terpenes and other alkenes) and many aromatics (xylenes, trimethylbenzenes) that produce the most O_x. Whereas at the end of seven days, alkanes (ethane, propane, butane, pentanes and higher alkanes) have the largest impact on cumulative O_x production (up to 40% of the total O_x production budget). This large contribution of alkanes to O_x production during multi-day model runs is also seen in Butler et al. (2011) and Coates and Butler (2015).

Li et al. (2014) compared modelled O_3 produced from different EIs used over East Asia focusing on the representation of individual NMVOC between the EIs. They calculate the ozone formation potential (OFP) of individual VOC 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 which emphasises the impact of reactive VOC which produce maximum O_3 on the first day at the expense of less-reactive VOC such as alkanes that produce maximum O_3 after the first day. These results are consistent with our first day O_x production budgets (Fig. 2), however when considering multi-day model runs, alkanes have a higher potential to produce O_3 (Butler et al., 2011; Coates and Butler, 2015) which is also seen in Fig. 2.

The cumulative O_x production from the different EIs between the chemical mechanisms (Fig. 2) show similar results to Coates and Butler (2015). Namely, that alkenes (ethene, propene, other alkenes, terpenes) produce similar amounts of O_x between mechanisms while the O_x produced from aromatics (benzene, toluene, xylenes, trimethylbenzenes and other aromatics) and alkanes (ethane, propane, butanes, pentanes and higher alkanes) is generally lower in the simplified chemical mechanisms (MOZART-4 and RADM2) than the MCM v3.2.

3.2 Alkanes and Ox Production

Section 3.1 showed that alkanes have the largest contribution to O_x production after seven days. In this section, we further analyse the impact of alkanes on O_x production by correlating the total amount of alkane emissions specified in each EI with the total O_x produced in the model runs. This correlation between total O_x production at the end of the model run and the percent of total alkane emissions is shown in Fig. 3. The Pearson correlation coefficients in Fig. 3 show that EIs specifying more alkane emissions produce more O_x. In particular, the model specific EIs (IPCC and EMEP) EIs specify larger alkane emissions than any other EI and in turn have the largest O_3 mixing ratios in Fig. 1.

Figure 3: Correlation of total O_x production at the end of the model run to the fraction of alkanes emissions specified by each EI. The Pearson correlation coefficient, r, is also shown.
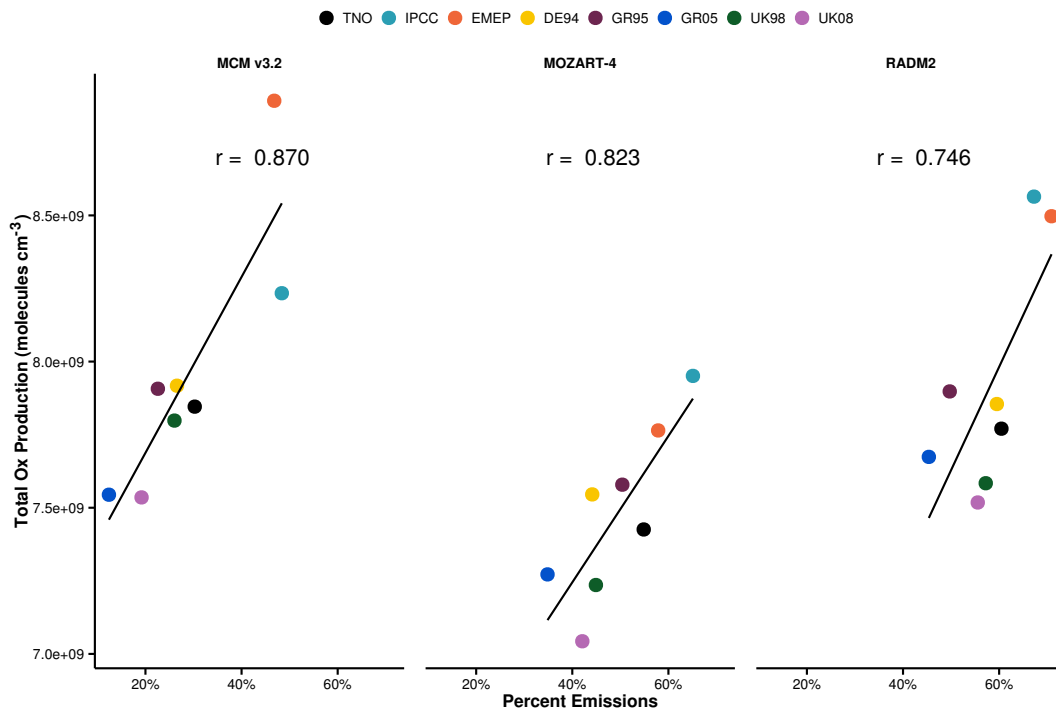
Solvent sector EIs that are based on ambient measurements specify a larger contribution from oxygenated NMVOC groups leading to lower O_x production than EIs with larger alkane contributions. Moreover, the more recent EIs for Greece and the UK specify a larger contribution from oxygenated NMVOC than the earlier version, and thus have lower contributions from alkanes. These results indicate that solvent sector emissions are trending towards larger emissions from oxygenated NMVOC and that the EIs specified by the IPCC and EMEP models are out of date.

4   Conclusions

Our modelling study suggests that the choice of emission inventory speciation influences modelled tropospheric O_3 mixing ratios. Similar differences in modelled O_3 are obtained using detailed gas-phase chemistry (MCM v3.2) and

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simplified chemical mechanisms (MOZART-4 and RADM2). We have shown that after model runs of seven days, alkanes have the largest contribution to the O_x production budget. Furthermore, the amount of O_x produced is directly related to the amount of alkane emissions specified by the EI.

Emission inventories that are used specifically for model inputs (IPCC and EMEP) need to be updated to reflect EIs based on ambient measurements which indicate lower emissions from alkanes. We have determined the maximum potential difference of modelled O_3 between solvent sector EIs and chemical mechanisms using a boxmodel and NO_x conditions that produce maximum O_3. These differences in O_3 may be reduced in a 3-D model due to effects of transport and dilution and should be determined in future work.

Acknowledgements

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