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Investigating the behaviour of the CRI-MECH gas-phase chemistry scheme on a regional scale for different seasons using the WRF-Chem model



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ABSTRACT

The behaviour of the CRI-MECH chemistry scheme was investigated over North-West Europe for the first week of each month for the year of 2015 using the mesoscale non-hydrostatic 3-D meteorological model, WRF-Chem. The model simulations of the distribution of important trace gas species (e.g. ozone, CO, NO, NO₂ and SO₂) were compared with ground-based measurements of selected rural and urban areas in UK. The model validation using the UK Defra Automatic Urban and Rural Network (AURN) measured data from sites across the UK showed a reasonable agreement between model-measurement for ozone ($R = 0.45$ for rural sites and $R = 0.34$ for urban sites), for NO₂ ($R = 0.65$ for rural sites and $R = 0.45$ for urban sites) and for NO ($R = 0.35$ for rural sites and $R = 0.22$ for urban sites). However, a poor correlation between model-measurement is found for CO ($R = 0.15$ for urban sites) and for SO₂ ($R = 0.1$ for rural sites and $R = 0.27$ for urban sites). Further investigations showed a poorer performance of the model ozone, CO, NO and NO₂ during summer and autumn months compared with winter months. The differences in model performance were most noticeable for ozone with the other species having more variance between sites and months. The possible causes for the deviations between the modelled and the measured data are discussed.

1. Introduction

Carbon monoxide (CO), volatile organic compounds (VOCs) and nitrogen oxides (NO_x = NO + NO₂) are important as a result of their ability to facilitate the formation of ozone in the troposphere (e.g. Jenkin and Clemmitshaw, 2000; Jonson et al., 2006). Ozone is both a powerful oxidant and a potent Greenhouse gas that is made in situ in both the Troposphere and Stratosphere. Thus, any model chemistry scheme must be sufficiently complex to accurately model ozone. All of these compounds are known to have detrimental health effects upon inhalation (Pénard-Morand and Annesi-Maesano, 2004; WHO, 2003) and so their formation, transport and removal needs to be well modelled. Sulfuric acid (H₂SO₄) and nitric acid (HNO₃) originating from SO₂ and NO_x, respectively are secondary sources of particulate matter whose concentrations are influenced by tropospheric chemistry (Meng et al., 1997). Although direct emissions dominate for many of these species, tropospheric chemistry plays an important role, particularly when considering the long-range transport away from the emission sources to cleaner regions. The chemistry of clean and polluted air is drastically different and can control whether a species is formed or

depleted. Therefore, it is important to study the spatial and temporal variation of trace species and their impacts on the air quality regionally and globally.

Policymakers require measurements across a range of sites (clean to polluted) to inform and effect policy to combat problems such as poor air quality, climate change and ecosystem degradation. However, ambient air measurements are limited in terms of spatiality giving a snapshot of the atmosphere at a given space and time. An alternative approach using an atmospheric computer model, which is a mathematical representation of dynamical, physical, chemical and radiative processes in the atmosphere, can give a necessary framework for integrating our understanding of atmospheric processes with ambient measurements. WRF-Chem is a coupled Eulerian 3-D regional atmospheric model that has been proven to be appropriate for studying the 3-D distribution of chemicals throughout the troposphere (Kumar et al., 2012; Al Razi and Hiroshi, 2012; Ghude et al., 2013; Zhong et al., 2016). Meteorology and chemistry play important, interconnected, roles in determining the composition of the atmosphere. For example, the physical parameters can influence the chemistry as temperature and pressure affect rates of gas-phase reactions. Meteorological events like

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rain and wind also affect what chemistry takes place as they affect transport and loss rates through deposition. Likewise, the atmospheric composition can affect other parameters. For example, it has been shown that biomass burning, industrial and urban air pollution can suppress precipitation (Rosenfeld, 2000; Warner, 1968). The reduction of precipitation occurs as a result of an increase in the availability of cloud condensation nuclei (CCN) in the polluted column promoting the formation of more, smaller, water droplets within the clouds, preventing the growth of droplets large enough to fall as rain. Sulphate aerosols initiated by oxidation of sulfur compounds can play an important role in radiative cooling both directly and indirectly. They scatter back incoming solar radiation and affect cloud lifetime and radiative properties (Brasseur and Roeckner, 2005) and so there are key feedback effects on atmospheric composition via the chemical transformation of species in the atmosphere.

The representation of chemistry in a model (e.g. CRI-v2R5, Jenkin et al., 2008) is very important to reproduce ozone globally and regionally. Recently, Criegee intermediates have been proposed to play a significant role in atmospheric sulphate and nitrate chemistry by forming sulfuric acid and nitrate radical (Khan et al., 2018), but the Criegee chemistry is currently absent in the CRI scheme of the model. Thus, for SO₂ (and NO₂, to a lesser degree), more complex chemistry including Criegee chemistry in the current CRI scheme may be required. However, it will be useful to investigate how the current CRI scheme is replicating atmospheric composition before adding Criegee chemistry to the scheme.

A few studies have employed the WRF-Chem regional model with different chemistry schemes MOZART-4 (Emmons et al., 2010), CBM-Z (Zaveri and Peters, 1999), RACM (Stockwell et al., 1997), RADM2 (Stockwell et al., 1990) and SAPRC99 (Carter, 2000) to simulate the temporal and spatial distribution of trace gases in the troposphere. The two most commonly used chemical mechanisms, RADM2 and CBM-Z integrated with WRF-Chem over the European domain have previously been used to simulate the gaseous species in a number of studies (Tuccella et al., 2012; Ritter et al., 2013; Hodnebrog et al., 2012). Comparison studies of the two schemes suggested that the CBM-Z scheme is more accurate than the RADM2 scheme in terms of reconstructing the gaseous species (Balzarini et al., 2015; Knote et al., 2015; Karlický et al., 2017).

The CRI-MECH chemical scheme (Jenkin et al., 2008; Watson et al., 2008; Utembe et al., 2010, 2011) is significantly more detailed than these chemistry schemes and has been successfully used in a global chemical transport model, STOCHEM. The evaluation of the trace species after implementing the scheme in STOCHEM model has been shown in our recent publications (Utembe et al., 2010, 2011; Khan et al., 2015a, 2015b, 2015c). The CRI-MECH chemistry scheme has previously been successfully incorporated into the WRF-Chem regional model to investigate the improvement of the prediction of trace gas species and aerosol composition over North-West Europe (Archer-Nicholls et al., 2014; Lowe et al., 2015). In the study of Archer-Nicholls et al. (2014), they used two chemical schemes, CRI-MECH and CBM-Z to simulate the distribution of gas species over North-West Europe during July 2010 and compared the model predictions of ozone, NO and NO₂ using both schemes, with the measurement data for four selected Defra Automatic Urban and Rural Network (AURN) measurement sites. Running the WRF-Chem model after incorporation of CRI-MECH chemistry scheme over mainland Europe and a comparison with CBM-Z gave very similar ozone and NO₂ levels and VOC:NOx ratios with slightly higher maximum ozone and less daytime NO in CRI-MECH. Overall the similarity between model predictions using these chemical schemes is very close, much closer than the fit between model and measurement suggesting the acceptability of CRI-MECH over other chemical schemes in terms of the simulating of the important gaseous species (Archer-Nicholls et al., 2014). In the study, we extend the work of Archer-Nicholls et al. (2014), to look at the behaviour of CRI-MECH for ozone, NO, NO₂, CO and SO₂ for different seasons by conducting

Table 1
WRF-Chem parameterizations used for this study.

Process	WRF-Chem option
Microphysics	Purdue Lin scheme (Lin et al., 1983)
Long-wave radiation	RRTMG scheme (Mlawer et al., 1997)
Short-wave radiation	Goddard scheme (Chou and Suarez, 1994)
Surface layer	Monin-obukhov similarity scheme (Monin and Obukhov, 1954)
Land-surface model	Noah Land-surface model (Chen and Dudhia, 2001)
Chemical boundary layer	MOZART global model (Emmons et al., 2010)
Cumulus parameterization	Grell 3D ensemble scheme (Grell and Dévényi, 2002)
Photolysis scheme	Fast-J (Wild et al., 2000)
Gas-phase mechanism	CRI-MECH (Jenkin et al., 2008; Watson et al., 2008)
Biogenic emissions	MEGAN (Guenther et al., 2006)
Anthropogenic emissions	TNO and NAEI (Pouliot et al., 2012; Kuenen et al., 2014)
Aerosol module	MOSAIC (Zaveri et al., 2008)

twelve week-long simulations, one at the start of each month of 2015, over North-West Europe. The model ozone, CO, NOx and SO₂ data is then evaluated against AURN UK measured data from 17 measurement sites.

2. Methods

2.1. WRF-Chem model

WRF-Chem is a mesoscale non-hydrostatic 3-D meteorological model that has fully coupled “online” chemistry. WRF-Chem has modules that describe a wide range of physical and chemical processes such as, transportation, radiation, photolysis, deposition, emission and chemical transformation (Grell et al., 2005). The meteorological, physical and chemical parameterizations used for this study are summarised in Table 1. The model domain has a 15 km horizontal resolution, with 134 (E–W) by 146 (N–S) grid cells covering North-West Europe, and 41 vertical levels with enhanced resolution within the planetary boundary layer (Archer-Nicholls et al., 2014). Meteorology is driven using ECMWF ERA-Interim reanalysis data (Dee et al., 2011), with a 6 hourly time resolution, and surface data extracted on a N256 gaussian grid, while volume data was extracted at a lower resolution on a N128 gaussian grid. Chemical boundary conditions are taken from the MOZART global model (Emmons et al., 2010). Biogenic emissions were calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) system (<https://www2.acom.ucar.edu/modeling/model-emissions-gases-and-aerosols-nature-megan>). This global model calculates emissions from terrestrial ecosystems with a resolution of 1 km × 1 km and is driven by vegetation, weather and atmospheric composition. The inventory accounts for all known natural emission processes which are believed to be of atmospheric significance. There are currently approximately 150 species accounted for, grouped into 20 categories depending on emission variation with meteorological conditions (Guenther et al., 2012). Anthropogenic emissions of NOx, CO, CH₄, SO₂, NH₃, NMVOCs, PM_{2.5} and PM₁₀ were obtained using a combination of the UK National Atmospheric Emissions Inventory (NAEI) for UK and the Netherlands Organisation for Applied Scientific Research's emission inventory (TNO-MACC-III) (Pouliot et al., 2012; Kuenen et al., 2014) for Europe. Emissions were primarily taken from NAEI data and TNO data only used for species unavailable in NAEI data. TNO data used in this study is for the year 2011 and has a resolution of 0.125 degrees longitude by 0.0625 degrees latitude. Data was obtained from a variety of sources though most of the data were obtained from countries' own reporting of their emissions inventories. Where data are not available other sources like the GAINS model, the EDGAR inventory or bottom-up calculations were used. Inconsistencies were also avoided by not using reported data that varies widely among different countries

emissions reports. For example, emissions from shipping are estimated by TNO rather than taken from inconsistent data which may cause double counting of, or holes in, the data. Most western European countries provide good emission reports and so emissions data taken from TNO should be of good accuracy. The NAEI data used in this study are for the year 2015 and has a resolution of 1 km by 1 km. Data are disaggregated into 11 UNECE source sectors: combustion in energy production and transfer, combustion in commercial institutions, residential and agricultural sectors, combustion in industry, production processes, extraction or distribution of fossil fuels, solvent use, road transport and other transport which are combined with emission factors to estimate emissions. Data were then verified and checked to ensure anomalous results and errors were corrected. Emissions data from NAEI and TNO is the most complete and accurate data available for UK regional modeling. The emissions were scaled by monthly, day of the week and hourly scaling factors according to Simpson et al. (2012) and then distributed to the model grid using the scripts developed by Hodnebrog et al. (2012).

The gas-phase scheme used in this study was the CRI-MECH scheme, containing 233 species and 637 reactions. The Kinetic Pre-Processor (KPP) interface in WRF-Chem was used to add this scheme and CRI-MECH provides a more accurate representation of atmospheric chemistry especially regarding reactions of organic compounds. The dry deposition is treated using the Wesely model (Wesely, 1989; Erisman et al., 1994) and the wet deposition is treated using the equilibrium approach based on Henry's law constants considering the transfer of species into cloud droplets and ultimately into rain droplets (Neu and Prather, 2012). Partitioning to the condensed-phase is treated dynamically within the MOSAIC aerosol module, driven by the MESA-MTEM multi-component equilibrium solver (Zaveri et al., 2008). Simulations were performed for the first seven days of every month in 2015, in order to examine the model performance for different seasons. For each simulation the first day was treated as the spin-up period, and not used in the following comparisons, while for the other 6 days the model was sampled every 3 h. The simulations in this study are intended to be indicative of the general trends in model performance through the sampled year. However, due to the shortness of the simulated periods, it is quite possible that there will be meteorological conditions which have been missed, or are over-represented, in these simulations, which could influence the comparisons that follow.

2.2. Measured data: validation and ratification

To validate the model, we used measurement data from the Department for Environment, Food and Rural Affairs (DEFRA) Automatic Urban and Rural Network (AURN) (<http://uk-air.defra.gov.uk/>) collected during 2015. The network gathers high resolution hourly concentration data of chemical species (e.g. CO, ozone, NO, NO₂ and SO₂). Ozone is measured by UV photometry, NO and NO₂ by chemiluminescence, SO₂ by UV fluorescence and CO by IR adsorption (AEA, 2009). All analysers used at monitoring sites reached a minimum MCERTS performance standard (<http://www.csagroupuk.org/services/mcerts/mcerts-product-certification/mcerts-certified-products>), certified by the Environment Agency and gas analysers, UK. The measurement data from the monitoring sites are subject to DEFRA's air quality data validation and ratification process (https://uk-air.defra.gov.uk/assets/documents/Data_Validation_and_Ratification_Process_Apr_2017.pdf). The uncertainty (expressed at a 95% confidence level) of the measurement datasets for all species and sites was around 15% (AEA, 2009).

2.3. Measurement site selection

A total of 17 measurement sites with two different environment types (e.g. urban and rural) are chosen for this study (Table 2). Urban sites are defined as highly or completely built-up areas where

surrounding buildings must have at least two floors. The urban area must not be mixed with non-urbanised areas, excluding parks. Sites are often in residential or commercial zones and away from high traffic areas. However, rural sites are at least “20 km from agglomerations and more than 5 km away from other built-up areas, industrial installations or motorways or major roads”. The sampling point is generally a few metres above the ground and situated away from pollution sources. The majority of urban, and all rural sites, used in the study were classified as background sites. Measurements at background sites are not dominated by any one single source, whether that be a street, industrial site or other source. The species concentrations at background sites are a combined concentration of all sources upwind of the site. Although all sources, including traffic, cities, industrial sites and major roads, are integrated at background sites, rural background sites are still at least 5 km away from built-up or industrial areas. Background stations are representative of a few square kilometres, the largest area of the three sub-classifications, which is smaller than the grid size used by the model (15 km × 15 km). Therefore, when comparing measured and modelled concentrations at these sites it was necessary to consider these factors in any conclusions made. Industrial stations are positioned in the nearest residential area downwind of an industrial area. Species concentrations at industrial sites are dominated by the emissions of the industrial area and the sites are representative of a 250 m – 1 km square area. Traffic sites measure species' concentrations that are dominated by emissions of traffic from roads or motorways. The samplings are from near the road side but away from major junctions and sites are representative of at least 100 m of road. The purpose of traffic and industrial sites is for measuring emissions from their respective sources rather than a more general measurement of the air quality of the surrounding area. Because of the smaller areas for which they are representative, traffic and industrial sites are not as suitable for comparisons with regional models with the grid resolution used here, and so were only used when background sites were not available.

3. Results and discussion

We ran WRF-Chem with the CRI-MECH chemistry scheme over North-West Europe for the first week of each month for the year of 2015. The behaviour of CRI-MECH in simulating ozone, NO, NO₂, CO, SO₂ for different seasons e.g. Summer (June–July–August), Autumn (September–October–November), Winter (December–January–February) and Spring (March–April–May), is investigated. We compare the diurnal and seasonal trends of modelled and observed ozone, NO, NO₂, CO and SO₂ mixing ratios. The spatial variability of simulated and observed mixing ratios are shown in Fig. 1, Fig. 3, Fig. 6, Fig. 8 and Fig. 10; while the detailed analysis of correlation between model-measurement, model biases, and errors, for each of the species are shown in Fig. 2, Fig 5, Fig. 7, Fig. 9 and Fig. 11.

3.1. Ozone

The model-measurement diurnal and seasonal comparison plots for rural and urban sites (Fig. 1) show that the model matched changes in the measured ozone mixing ratios; with observed peaks and troughs at nearly similar times and with similar relative magnitudes. However, the model underestimated ozone mixing ratios by between 5 and 20 ppbv. Similar types of diurnal and seasonal variation were found by Balzarini et al. (2015) and Ritter et al. (2013), who used WRF-Chem with CBM-Z chemical scheme for simulating ozone over European and Swiss domains, respectively. At urban sites in this study, longer timescale trends in ozone mixing ratios were often less well-matched, and sometimes the deviation from measured data was so large that significant changes were not captured by the model (see Supplementary Fig. S1). This is reflected in the average diurnal cycle, with large underpredictions during midday to afternoon.

For both rural and urban sites, the summer and autumn months

Table 2
Types and location of different measurement sites used for model-measurement comparison.

Site name	Site type	Location	Latitude	Longitude	Species measured
Aston Hill	Rural background	North Wales	52.50	-3.03	O ₃ , NO ₂ , NO
Belfast centre	Urban background	Northern Ireland	54.60	-5.93	CO
Birmingham Tyburn	Urban background	Central England	52.51	-1.83	O ₃ , NO ₂ , NO, SO ₂
Cardiff centre	Urban background	South Wales	51.48	-3.18	CO
Charlton mackrell	Rural background	South West England	51.06	-2.68	O ₃
Edinburgh saint leonards	Urban background	South East Scotland	55.95	-3.18	CO
Harwell	Rural background	South East England	51.57	-1.33	O ₃ , NO ₂ , NO, SO ₂
Leeds centre	Urban background	North England	53.80	-1.54	CO
London marylebone road	Urban traffic	South East England	51.52	-0.15	CO, SO ₂
London North Kensington	Urban background	South East England	51.52	-0.21	CO
Manchester Piccadilly	Urban background	North England	53.48	-2.24	O ₃ , NO ₂ , NO
Narberth	Rural background	South Wales	51.78	-4.69	O ₃ , NO ₂ , NO, SO ₂
Port Talbot Margam	Urban industrial	South Wales	51.58	-3.77	CO
Rochester stoke	Rural background	South East England	51.46	0.63	O ₃ , NO ₂ , NO
Sheffield tinsley	Urban background	North England	53.41	-1.40	NO ₂ , NO
St. Osyth	Rural background	South East England	51.78	1.05	O ₃
Strathvaich	Rural background	North Scotland	57.73	-4.78	O ₃

tended to show larger deviations between the modelled and the measured data than that in the winter and spring months (see Fig. 1). Large deviations occurred more often during the summer months and for many sites had an overall poorer prediction of the trend in ozone mixing ratios during the summer months (see Supplementary Fig. S1). Archer-Nicholls et al. (2014) simulated ozone and other species (e.g. NO, NO₂, OH, NO₃) using WRF-chem model coupled with two different chemical schemes, CRI-MECH and CBM-Z during July 2010 and found very similar model ozone values from the two chemical schemes. So other than the errors in chemistry, the uncertainties in the emissions of precursors (e.g. NO_x, VOCs) and of the meteorological fields could be the possible sources of the errors in predicted ozone. The overprediction of NO (shown in a later section) especially in summer time can enhance the titration of ozone leading to lower model ozone in rural and urban areas. The impact of maximum daily temperature on ozone peaks is significant, particularly during the summer in central, southeast and northwest Europe (Hodnebrog et al., 2012; Otero et al., 2016), but there is a significant bias in maximum temperature during summer (up to ~5 K in Europe) (Brunner et al., 2015; Skjøth et al., 2015; Mooney et al., 2013) due to the unusually large error in the synoptic component in WRF-Chem (Solazzo et al., 2017) which might account for some of the differences between modelled and measured ozone in the study.

Lingard et al. (2013) reported that WRF-Chem model results were only representative of regional synoptic conditions at the location of Defra AURN UK monitoring sites and they were poor at replicating local meteorological conditions. These could explain the increase in imbalances between model-measured ozone during the summer months and from midday to afternoon. Further investigation into meteorological errors would be necessary to isolate the causes for the apparent seasonal variation of the model-measurement deviation.

The average correlation coefficient for ozone is 0.4, with a clear distinction between rural ($R = 0.45$) and urban ($R = 0.34$) sites. There is a strong seasonal dependence with better correlation during the spring and winter months than in the summer and autumn months (Fig. 2). These changes in correlation are consistent between the rural and urban sites. The RMS error values for both urban and rural sites showed an increase in deviation during the summer and autumn months which is consistent with the correlation coefficient analysis which showed the lowest correlation in the same months.

3.2. NO₂

The model NO₂ mixing ratios are, in general, lower at urban sites, and greater at rural sites, than the measurements, but the diurnal and

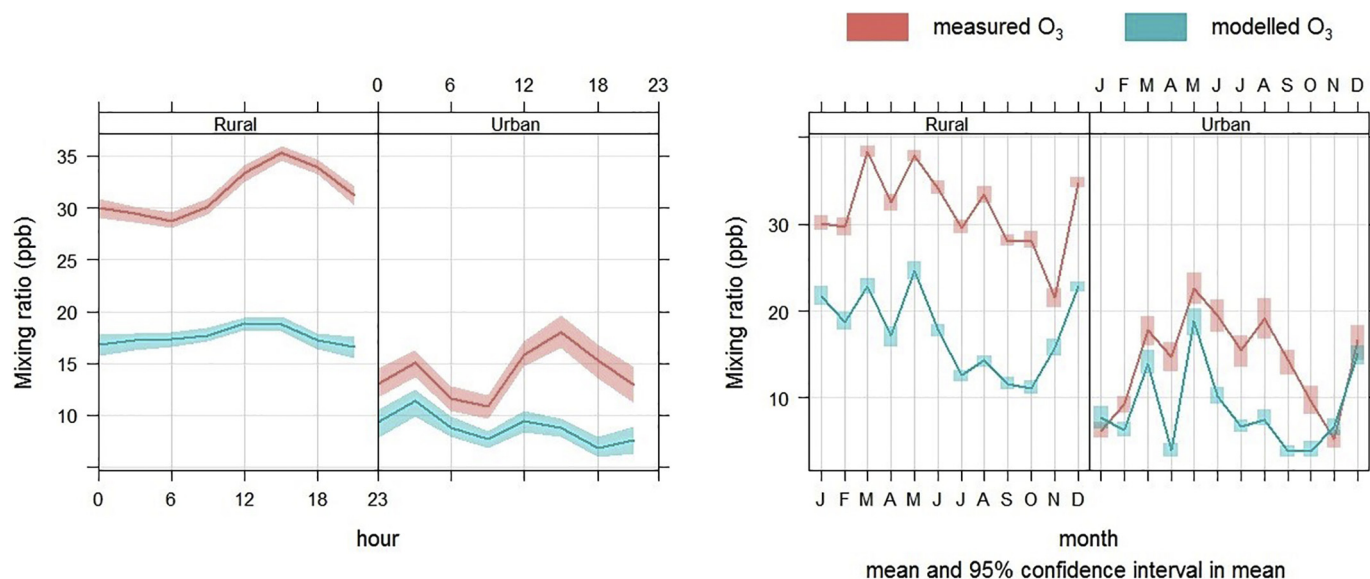


Fig. 1. The average diurnal and monthly measured and modelled ozone mixing ratios at rural and urban sites for 2015.

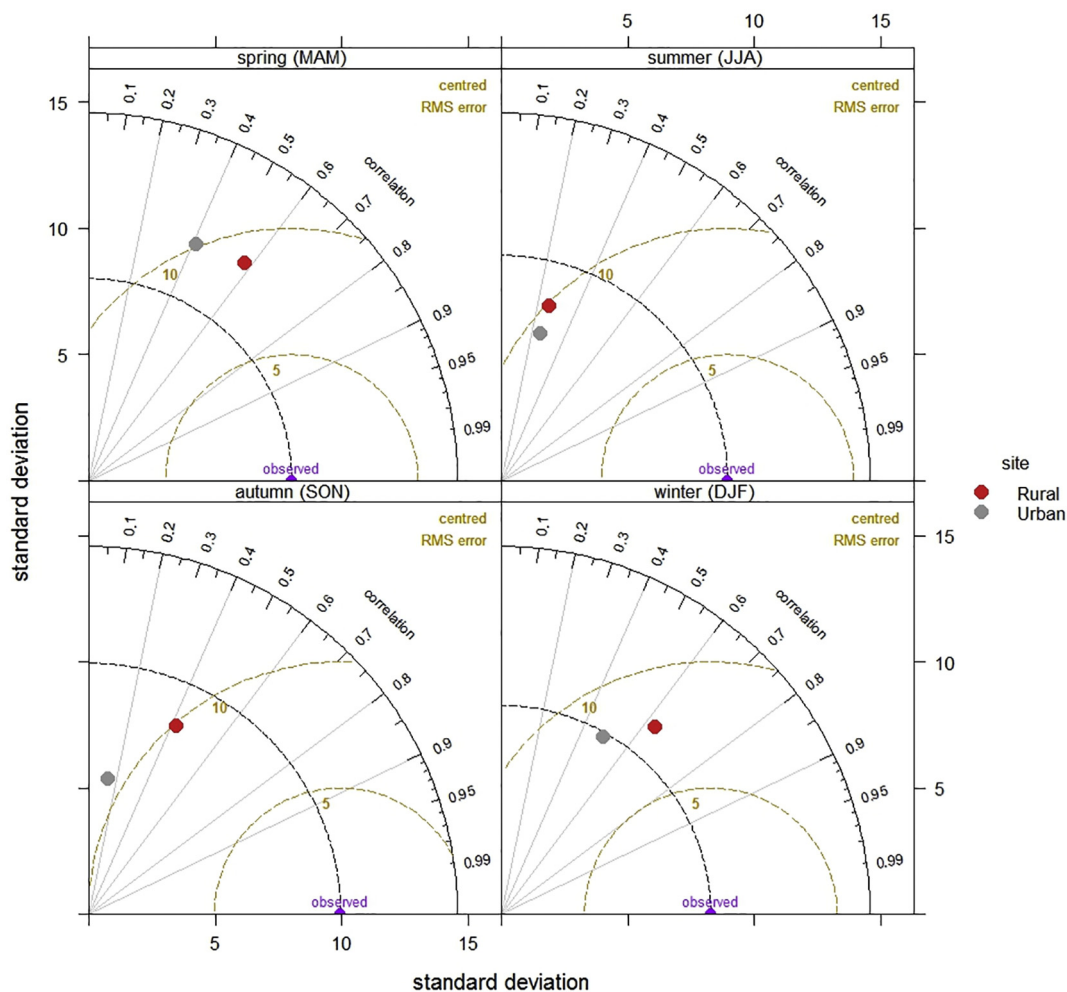


Fig. 2. The average standard deviation, correlation coefficient and RMS error between measured and modelled ozone mixing ratios for each season of 2015 at urban and rural sites.

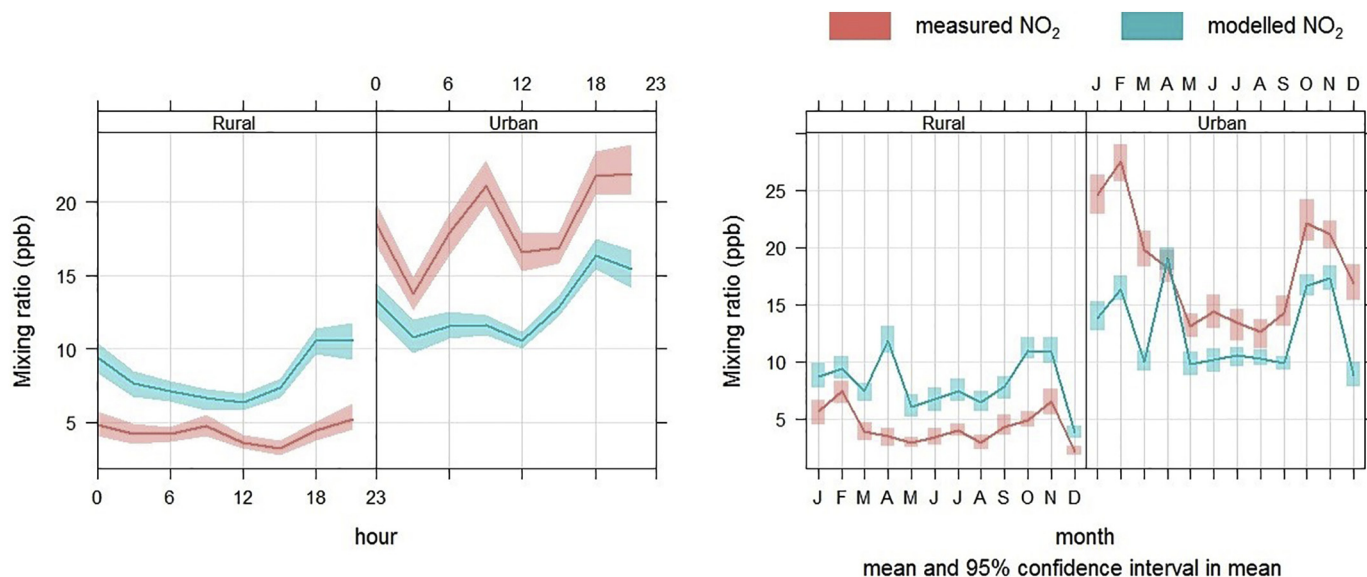


Fig. 3. The average diurnal and monthly measured and modelled NO₂ mixing ratios at rural and urban sites for 2015.

seasonal trends are reasonably well-matched for all sites (see Supplementary Fig. S2). For urban sites, the model performed well during summer months, but there is a general increase in deviations between the model and the measurement during winter months (Fig. 3). Solazzo et al. (2017), Ritter et al. (2013), Balzarini et al. (2015) and Karlický et al. (2017) have also noted an increase in deviations between model-measurement data during the winter months when using of WRF-Chem with RADM2 and CBM-Z chemical schemes. The main difference between the datasets at urban sites is that the model does not capture the magnitude of the measured peak mixing ratios at 9 am local time. Although the model usually predicts the timing of these peaks well, which are associated with morning rush-hour traffic, most often the increase in modelled levels is smaller than the corresponding increase in measured levels. The model uses NO_x and VOC emissions into a grid of 15 km × 15 km resolution neglecting the processing which will occur as those point emissions mix into the whole grid cell, therefore it is not surprising that peaks are lower than measured. In addition, the underprediction of the early morning NO₂ peak could be a result of the underestimation of anthropogenic direct emissions of NO₂. The anthropogenic emissions used in WRF-Chem model revealed that on-land peak emissions were underestimated in the emission map especially in polluted environments (Archer-Nicholls et al., 2014). Using a fixed fraction of NO₂ from NO_x in the emission map cannot represent the actual emission diurnal cycle in urban areas for extreme cases (e.g. higher traffic density, different drive patterns causing higher traffic flows outside of normal rush-hours, industrial activity etc.), which may contribute to the model-measurement differences for polluted background environments.

Moreover, the difference in sites (e.g. local-scale features) may be important for the large deviation between model-measurement during pollution events. There are large differences between the sites even if they are classified as the same type (see Supplementary Fig. S2). For example, some are coastal urban sites whilst others are inland, and some are relatively close to high emission areas whilst some are very far from the emission sources. The resolution of the model used in this study made its performance worse at certain sites if emission sites were

nearby. For example, Rochester Stoke is positioned directly east of London on the coast and there is a westerly wind on all days. The overpredicted NO₂ mixing ratios at Rochester Stoke during spring and summer months could be due to high NO_x mixing ratios in the air from London blowing over the site (Fig. 4).

The correlation coefficient values obtained for NO₂ are found to be higher than that found for ozone, though with a significant difference between rural and urban sites. The average R for all sites is 0.56 with the average value at rural sites equalling 0.65 and at urban sites equalling 0.45 (see Fig. 5). The abundances of NO₂ at rural sites are dominated by NO₂ transport from high concentration areas. However, rural sites are in NO_x sensitive regimes and its concentration will be heavily controlled by chemistry. Therefore, higher R values are indicative of an accurate treatment of NO₂ in rural regions by the model. It is probable that the model grid is too coarse over the urban regions, and the processing of emissions over the sub-grid distances between source and measurement site is not being captured in these simulations.

The correlation coefficient of NO₂ for rural sites is found to be consistent between seasons for both urban and rural areas (Fig. 5). There is no significant seasonal variation in the RMS errors noticed for both urban and rural sites. The concentrations of NO₂ predicted by the model is strongly influenced by chemistry, thus an error in either NO₂ or ozone concentrations would be expected to cause a subsequent error in the other. Further investigation (e.g. updating the seasonal scaling factors of the anthropogenic emissions) is needed to further explore the exact causes and possible consequences of the seasonal variation of the model-measurement agreement.

3.3. NO

NO concentrations are poorly predicted by the model (see supplementary Fig. S3). NO is very reactive and short-lived, thus the error in modelled NO associated with uncertainties in emissions, transport and vertical mixing traveling distance, is likely to be more significant than other air pollutants. At urban sites, the model is underpredicting peak mixing ratios and at rural sites spikes in NO concentrations are consistently overestimated (see Fig. 6). The overlaid NO concentrations at rural background sites, for example Rochester Stoke (see supplementary Fig. S3) showed a good temporal correlation between measured and modelled data, peaks occurred at the same time and overall had the same shape. The ratio of NO to total NO_x is similar for all sites in the model, but not in the measurements, which could be main reason for the over-prediction of modelled NO in rural sites. This deviation from the model-measurement agreement suggests that the model is not just overestimating NO but also not reproducing the photostationary state between ozone, NO and NO₂.

There is a spike in NO concentration during day time and this is matched by the model. Even though spikes occurred at slightly different times and have different relative heights and shapes, there is some correlation between the measured data and the model's predictions. During the winter months, the model underpredicted NO concentrations largely at urban sites as shown in Fig. 6. Similar to NO₂ and ozone, the trends for NO are fairly accurate over times scales of one day, though many changes are still missed by the model, and the overall shape of peaks are not as accurate as some rural sites (see Supplementary Fig. S3).

The monitoring sites with emission sites nearby can be affected by local-scale effects more when observing NO and coarse models (15–50 km grid spacing) show a significant mismatch between model prediction and point site measurements. The homogeneous emissions within relatively large model grid cells cannot give an accurate representation of the sub-grid processing of very heterogeneous sources in urban areas. Solazzo et al. (2017) also found similar impacts of sub-grid processes on NO predictions using the WRF-Chem model with RADM2 chemical scheme, at a grid resolution of 23 km. Even though background sites are representative of several km² around the site, this is

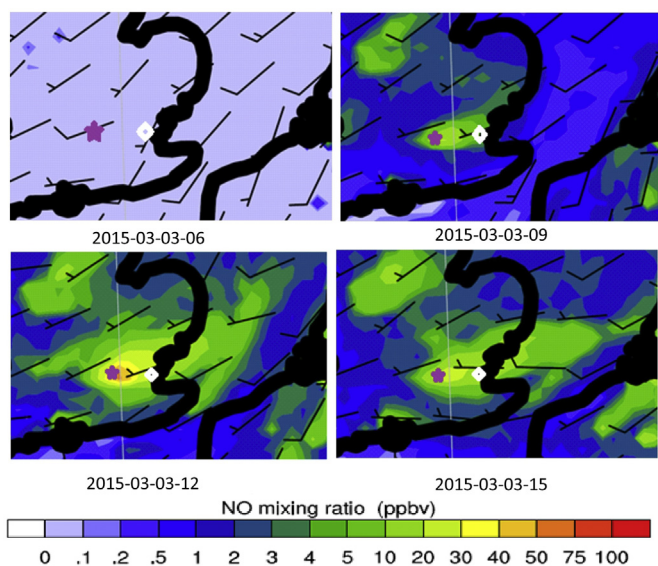


Fig. 4. The NO mixing ratios over the south east of England over a 9 h period during March. Wind barbs show high concentrations of NO being emitted from London and blown east. Note: the map includes the south east of England and part of Belgium and France, the black thick lines are the boundary of the UK (left) and the Europe (right), the brown star represents the position of London and white diamond represents Rochester Stoke site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

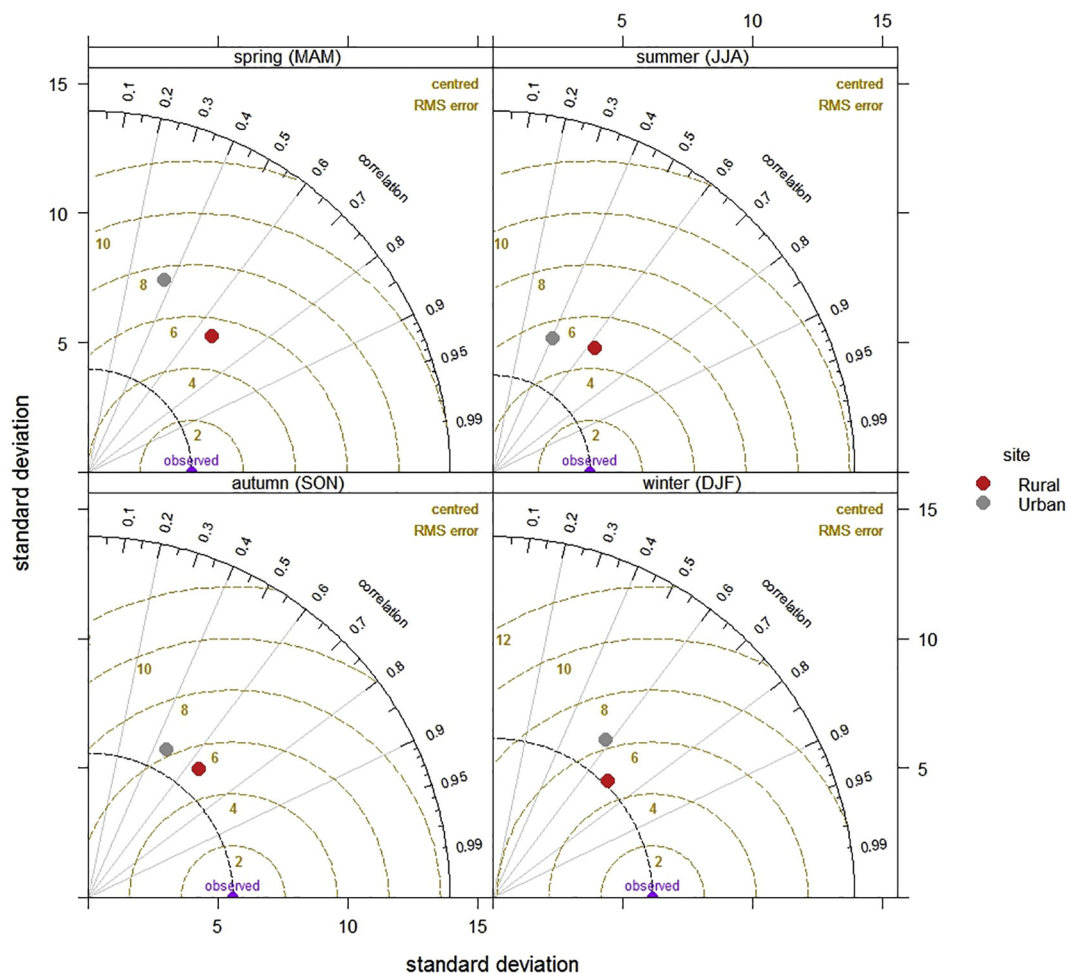


Fig. 5. The average standard deviation, correlation coefficient and RMS error between measured and modelled NO₂ mixing ratios for each season of 2015 at urban and rural sites.

still far smaller than the 15 km grid resolution used in the study. This might be the case at the Rochester Stoke site which is within 15 km of the city Southend and at the Harwell site which is also relatively close to London city. With the sites analysed here, whether the interaction

between the positioning of sites and smearing of emissions across model grids is an important factor cannot be stated confidently, and analysis of further measurement sites with high resolution model needs to be performed.

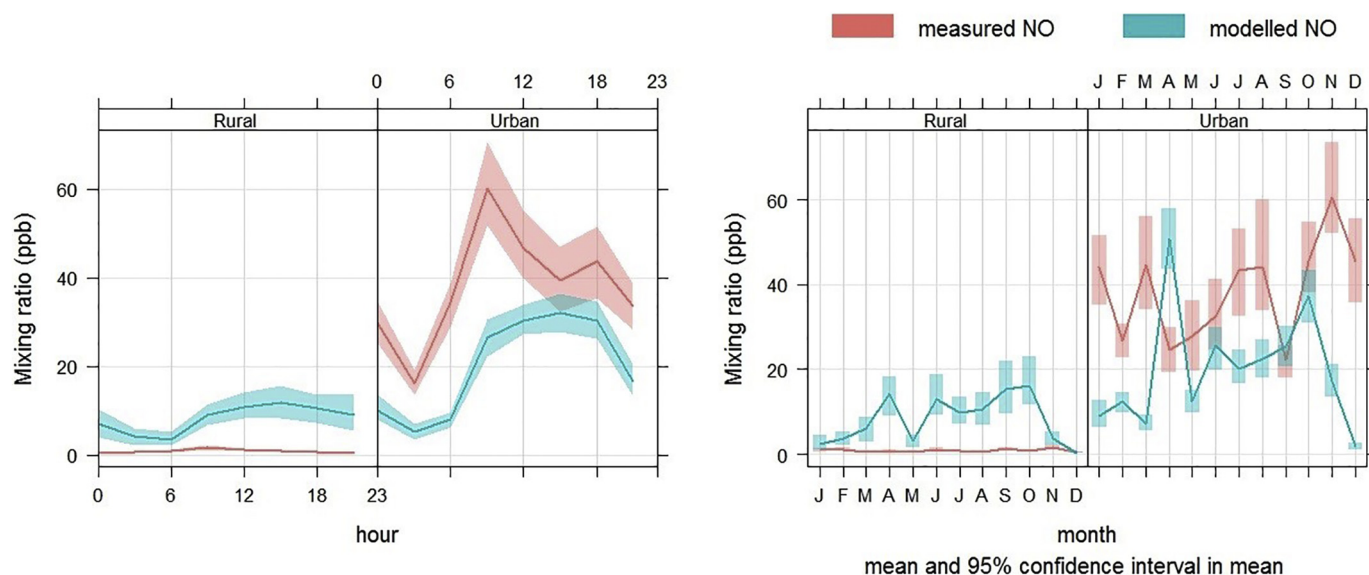


Fig. 6. The average diurnal and monthly measured and modelled NO mixing ratios at rural and urban sites for 2015.

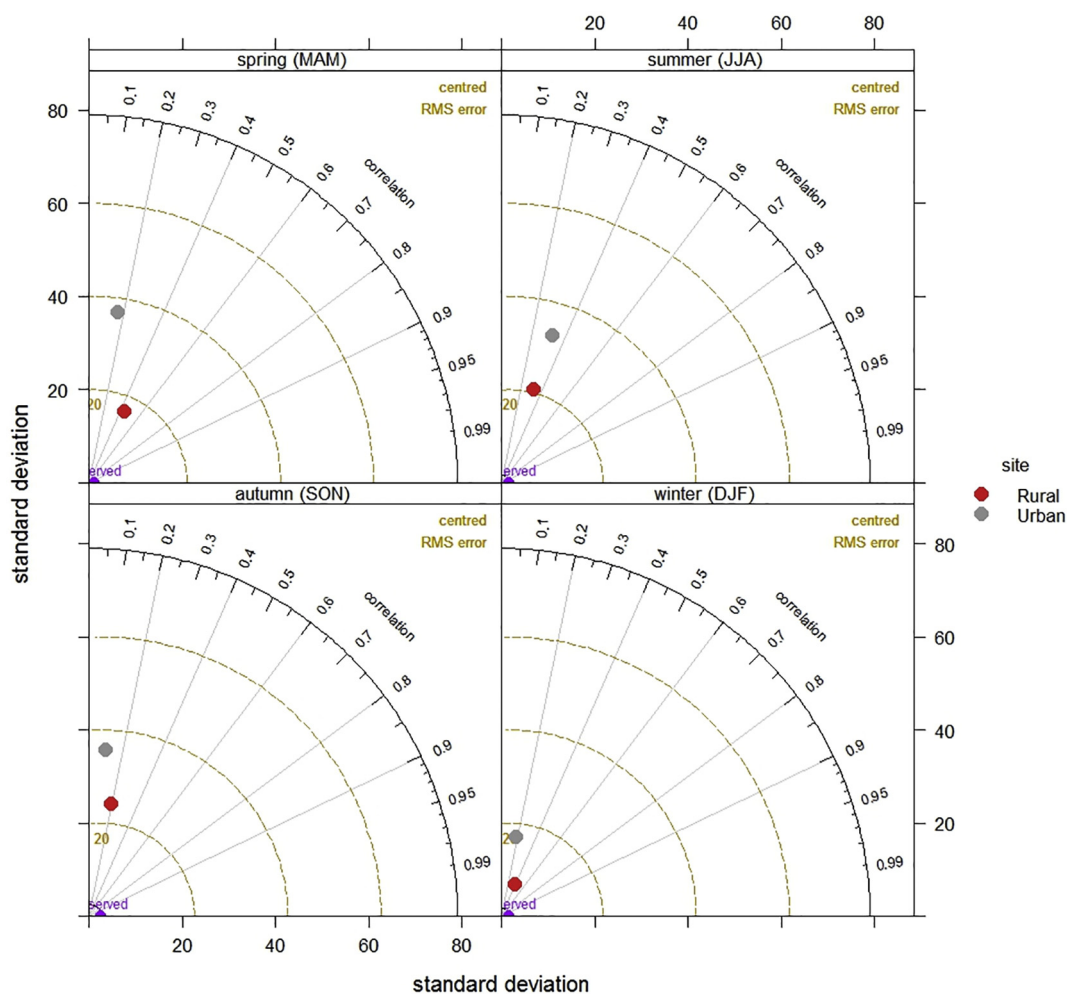


Fig. 7. The average standard deviation, correlation coefficient and RMS error between measured and modelled NO mixing ratios for each season of 2015 at urban and rural sites.

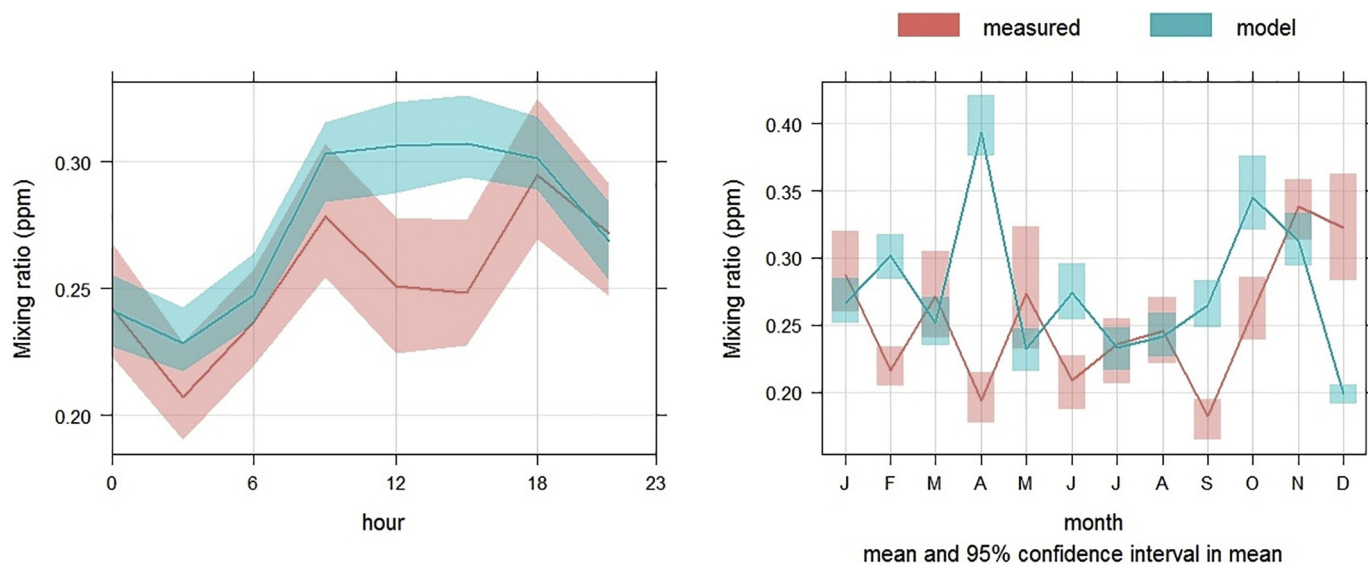


Fig. 8. The average diurnal and monthly measured and modelled CO mixing ratios at urban sites for 2015.

The average correlation coefficient for the rural sites is found to be smaller than that for ozone or NO₂ with a value of 0.35; but at urban sites the average R is far poorer with a value of 0.22, suggesting that the model is unable to capture the more complex emission profiles present

at the urban sites, leading to many mismatched peaks (see supplementary Fig. S3). A weak seasonal dependence with comparatively improved correlation during summer months than the other months for both urban and rural sites (Fig. 7). As NO is closely linked to NO₂ and

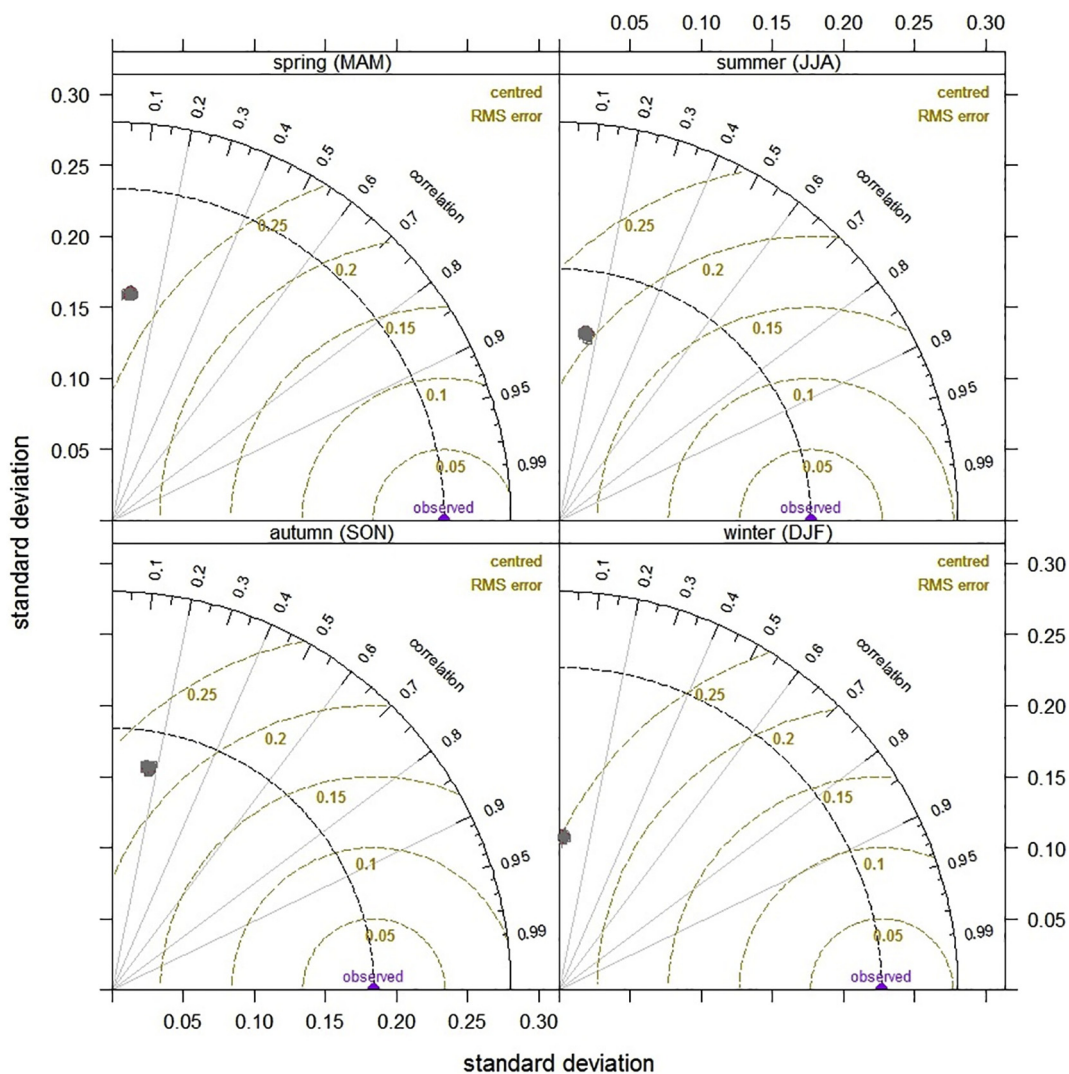


Fig. 9. The average standard deviation, correlation coefficient and RMS error between measured and modelled CO mixing ratios for each season of 2015 at urban sites.

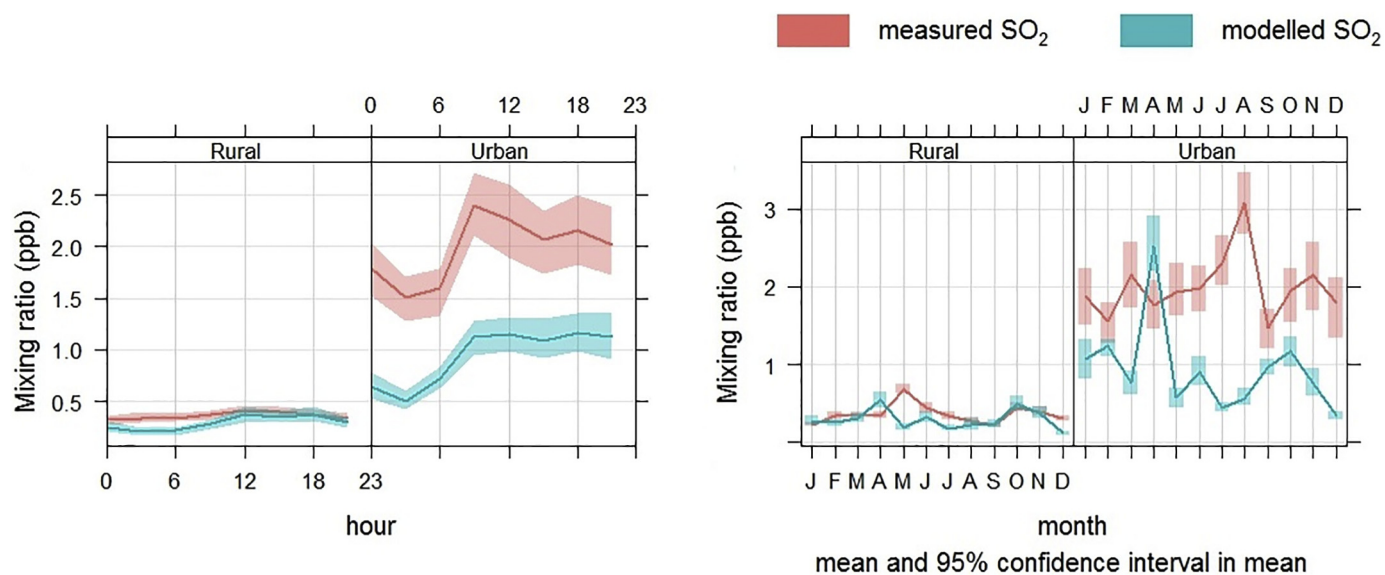


Fig. 10. The average diurnal and monthly measured and modelled SO₂ mixing ratios at rural and urban sites for 2015.

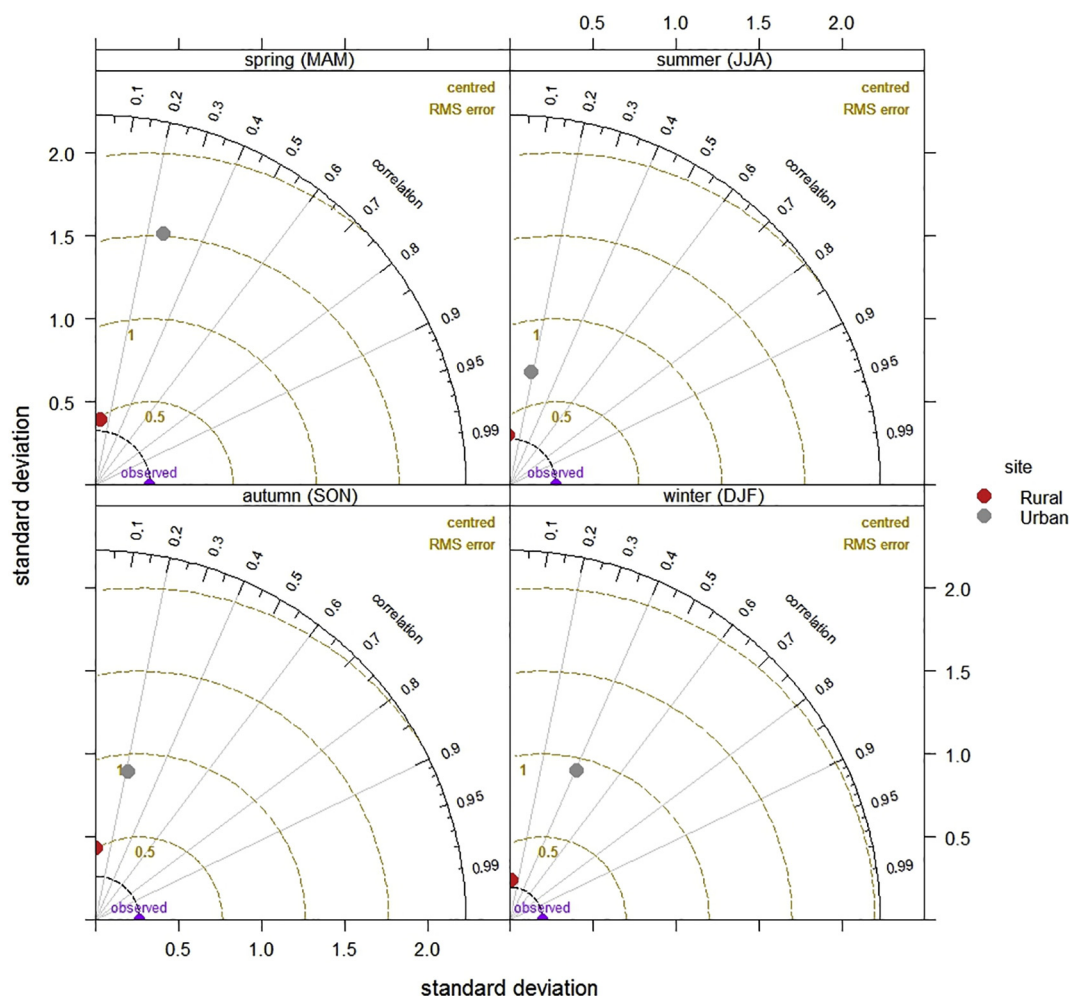


Fig. 11. The average standard deviation, correlation coefficient and RMS error between measured and modelled SO_2 mixing ratios for each season of 2015 at urban and rural sites.

ozone through tropospheric chemistry no insights are gained into a possible cause. Any factor affecting any of the three species will lead to an indirect change on the other two so any of the possible causes mentioned before could still be the reason for a seasonal variation. Future development of the the emissions of NO_x will consider sub-grid processing before injecting into a grid of $15 \text{ km} \times 15 \text{ km}$ which would be invaluable to improve model representation of the species. Compared with ozone and NO_2 , the RMS errors for NO are very large. Like NO_2 the large over/underestimations of the model caused higher deviation values, and these are far larger for NO due to the far greater overestimations. If many of the errors seen in the ozone and NO_2 data are caused by inaccurate NO values this may also explain the relative values of the RMS errors, with the subsequent errors being smaller than the initial error of inaccurate NO mixing ratios.

3.4. CO

The matching of peaks between the modelled and the measured diurnal CO data at the urban sites are comparatively good during night-time. A larger deviation between model-measurement is found during daytime (9 am to 5 pm local time). Although seasonal changes are predicted reasonably by the model, monthly changes are not as regularly predicted as they are for NO_2 and ozone. However, when peak matching did occur, it was of a similar accuracy to the data at urban sites for NO_2 and ozone.

The CO data is a good example of the limitations of comparing a

model of this resolution ($15 \text{ km} \times 15 \text{ km}$) with measurements from an urban site. For most of the months (e.g. summer, autumn and spring) there is very little difference between the measured and the modelled data, but for April there is a significant overestimation, and for December there is a significant underestimation of model CO. CO is a primary pollutant, its error is affected by the diurnal dynamics of the Planetary Boundary Layer (PBL) height, which is most problematic in winter and at night-time, when the modelled PBL has the tendency to become too stable too early, anticipating the evening transition (Pleim et al., 2016). Previous studies (Inness et al., 2013; Giordano et al., 2015) have showed that the domain boundary conditions have no significant contribution to the bias of CO within the model domain. Underestimates in CO emissions within the TNO inventory, especially during winter (Giordano et al., 2015), could be the main driver for model bias in CO. We used fixed temporal emission profiles, but emissions from residential heating are highly dependent on air-temperature and could diverge greatly from these standard emission profiles during periods of unusual weather conditions. These effects could have had an impact on the overprediction during April and underprediction during December, of CO mixing ratios.

The average correlation coefficient for CO is found to be 0.15 which is much smaller than the values found for NO_2 and ozone at urban sites. As CO has a relatively constant concentration in the atmosphere it may be expected that the R values would be higher than that found for the other species. However, no rural sites had CO data so only urban sites were used. Thus, the model performed less well for CO in the turbulent,

emission heavy environment of urban areas. The RMS errors for CO are reasonably high considering the high concentrations and long lifetime of the species in the atmosphere (Fig. 9). Compared with the values for NO₂ at urban sites, CO performs in a similar fashion but with more variation, likely due to the differences between sites (e.g. mixture of urban and industrial) used in the analysis.

3.5. SO₂

Out of all the species looked at, the model predictions for SO₂ were the worst when compared with measured data (see Fig. 10). SO₂ is a major emissions species and so the urban sites showed strong daily increases for most months, but the model was unable to accurately represent the changes seen in SO₂ concentration (Fig. 10). Urban sites are only representative of a few hundred metres of road that is dominated by emissions so the model's performance at these sites is not a good representation of its handling of SO₂.

At rural sites, SO₂ were well predicted in some months, with similar accuracy to the rural sites of the other species (See Fig. 10). The model predicted peaks in the mixing ratios that are not in the measured data and failed to predict many of the peaks that did occur (e.g. Harwell site; Fig. S5). The overall week-long trends are much poorer than for data at rural sites for the other species. For the periods January – April, the model performed the best, with more incorrect peaks occurring during the other months. However, as just two sites are used, whether this was a continuation of the seasonal variation seen for the other species or just variance cannot be known, no strong conclusions could be made on the performance of the model for SO₂ on a regional scale. Although the deviation and RMS errors for rural sites is much smaller than that for urban sites (see Fig. 11), the correlation values for rural sites ($R \sim 0.1$) for all seasons are very small compared with that for urban sites ($R = 0.27$) suggesting poor model performance for rural sites, which is opposite of the performance showed for other species. The other chemical schemes used for WRF-Chem model simulation over European domain also gave poor model-measurement agreement with a Normalized Mean Bias (NMB) of -41.64% (CBM-Z) and -45.62% (RADM2) (Balzarini et al., 2015). The biases for rural sites are found to be 2-fold lower than that in urban sites in this study, which is consistent with the Karlický et al. (2017) study. The underestimation of modelled SO₂ may be not only due to biases in meteorological variables, e.g. surface wind speed (Brunner et al., 2015) but also due to underprediction of emission sources and/or the chemistry scheme complexity.

4. Conclusion

WRF-Chem, using the CRI-MECH chemistry scheme, performed reasonably well on a regional scale when predicting ozone ($R = 0.4$), NO ($R = 0.3$) and NO₂ ($R = 0.6$) concentrations, as validated with the Defra Automatic Urban and Rural Network (AURN) measured data. The modelled seasonal and diurnal variations in NO_x and ozone concentration match the measured variations in rural sites. At urban sites the model tended to perform less well, but for ozone, NO₂ and CO both seasonal and daily trends are reasonably well matched between the measured and the modelled data. However, for CO, the sites showed large variance, and for several sites the model performed as well as it did for NO₂ and ozone at urban sites. For NO, trends are well predicted at rural sites, though this was very site dependent. At urban sites, trends are far more poorly predicted than for ozone, NO₂ and CO with the shape and timing of changes often being inaccurate. Averaging measurement data from multiple sites around an urban region could give more representative measurement data for that region, which might reduce the discrepancies between model and measurement. SO₂ concentrations are poorly predicted, and shorter timescale trends are also poor especially in rural sites. SO₂ is the worst performing species in the model validation, likely due to either underprediction of emission

sources or the chemistry scheme complexity. For most of the species compared, the correlation coefficient values showed a seasonal variation, with poorer performance of the model for both rural and urban sites during the summer and early autumn months. For all species, a lack of urban sites hindered confident evaluation over whether the seasonal variation seen at rural sites was also present at urban ones. Moreover, only one week of data for each month was modelled. Without more data, both from the number of measurement sites analysed and time period modelled, the possibility that any seasonal differences were just due to random variance is significant.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosres.2019.06.021>.

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