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Interactive comment on "Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem" *by* S. Archer-Nicholls et al

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Whilst disappointed that the second referee was unable to provide a review, we are grateful to the first referee and editor for their comments, which have provoked significant further investigation of our developments. In particular we are grateful that the referee found the material that we have presented to be original and worthy of publication.

We do, however have one important point of dispute with the referee. The title of our manuscript is "Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem". The aims and scope section of the

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home page of GMD includes a statement that “development and technical papers, describing development such as new parameterisations or technical aspects of running models...” are one of the “manuscript types considered for peer-reviewed publication”. Such papers might be contrasted with those that assess the performance of complex models or describe methods of assessing model performance. To state that evaluation of the new scheme against observations is absolutely mandatory in the current paper is overly prescriptive of the requirements on a manuscript and has certainly not been uniformly applied to previous GMD manuscripts.

There are very good reasons for choosing the approach we have taken with this manuscript. The most important of these is the sheer scale of the model development and evaluation process. We are incorporating schemes in the model that predict trace atmospheric constituents, the most important of which are extremely difficult to measure. The measurement techniques are state-of-the-science and field deployment is extremely challenging. Data to test the model scheme with appropriate observations is unavailable in many regards. Since the publication of the GMDD manuscript, we have submitted an extensive comparison of the predictions of the model against airborne measurements of key constituents in the nighttime chemistry project RONOCO (Lowe et al., 2014). Combining that body of work with this one would make the resulting manuscript at best unwieldy, at worst unreadable. We have scoped further evaluation possibilities in our reply to Question 5. We trust that these measures address the referee’s requirement for model–measurement comparison related to the gaseous oxidation and N_2O_5 heterogeneous chemistry schemes.

So far as the primary marine organic scheme is concerned, there are simply no measurements for its evaluation. There are no routine or geographically distributed measurements with which to compare that can distinguish marine organic components from any other. In particular, the AMS technique that has been widely adopted for online continuous measurements of organic aerosol components is insensitive to refractory components such as the seasalt matrix with which primary marine organics will be mixed. However, the routines for prediction of this marine organic fraction have been developed and included in the model. We are reporting this process. Many scientists, including our group, will be interested in the ability to make predictions of the loadings, distributions and impacts. Is the referee suggesting that it is not appropriate to include such developments until it's possible to validate them with measurements? If so, we strongly disagree. The primary marine organic particulate emission scheme couples and relates directly to the sectional MOSAIC treatment of aerosol in WRF-Chem and hence fits within the scope of the current manuscript, "Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem". Recommendation for its removal is in contradiction to the referee's statement that "I have no objections against the content of the paper at all".

To address the specific remarks of the referee:

1) Title of the paper: Be more specific about the scientific topic of the paper or about the implemented mechanism. The additions to WRF-Chem have been implemented in order to achieve some scientific goal. This should also be reflected in the title. On the other hand, it is not necessary to mention the version of WRF-Chem already in the title.

After careful consideration, we feel that we cannot comply with this request and have not changed the title. First, the request is based on the assumption that the developments were motivated by a common scientific goal. Second, it would make the title unwieldy (e.g. inclusion of the CRIv2-R5 chemical mechanism, heterogeneous N_2O_5 uptake and primary marine organic aerosol emissions in version 3.5.1 of the online regional model, WRF-Chem). The common thread in the developments is not a specific scientific topic, but that they all relate to representations in the chemical modules that should allow more faithful simulation of processes that contribute to atmospheric composition. As such they will benefit multiple purposes and scientific goals as outlined in the relevant sections of the manuscript.

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As requested by the editor, and to comply with GMD-specific requirements, we have kept the version number in the title.

2) Abstract: Why do the improvements you made make WRF-Chem 'more suitable' for the mentioned purposes?

Prior to our development, WRF-Chem did not include heterogeneous uptake of the main reservoir of the main nighttime oxidant. Therefore our developments make WRF-Chem more suitable for studying nighttime chemistry. Neither did WRF-Chem carry a gas phase degradation mechanism as explicit as CRIv2-R5, nor one traceable to the near-explicit MCM prior to our work. Therefore, inclusion of CRIv2-R5 makes WRF-Chem more suitable for more explicit representation of VOC degradation. WRF-Chem previously did not represent primary marine organic components. Its inclusion therefore makes the model more suitable for studying the primary marine contribution of organic components. These are all stated explicitly in the abstract, so we are unsure what the referee is asking. However, we recognise that the abstract could be interpreted as though the nighttime chemistry was a main, if not sole focus. We have therefore reordered the wording of the abstract to make it clear that the developments go beyond nighttime processes to provide a more useful suite of coupled developments:

“We have made a number of developments to the Weather, Research and Forecasting model coupled with Chemistry (WRF-Chem), with the aim of improving model prediction of trace atmospheric gas-phase chemical and aerosol composition; and of interactions between air quality and weather. A reduced form of the Common Reactive Intermediates gas-phase chemical mechanism (CRIv2-R5) has been added, using the Kinetic Pre-Processor (KPP) interface, to enable more explicit simulation of VOC degradation. N2O5 heterogeneous chemistry has been added to the existing sectional MOSAIC aerosol module, and coupled to both the CRIv2-R5 and existing CBM-Z gas-phase schemes. Modifications have also been made to the sea-spray aerosol emission representation, allowing the inclusion of primary organic material in sea-spray aerosol.

We have worked on the European domain, with a particular focus on making the model suitable for the study of nighttime chemistry and oxidation by the nitrate radical in the UK atmosphere. Driven by appropriate emissions, wind fields and chemical boundary conditions, implementation of the different developments are illustrated, using a modified version of WRF-Chem 3.4.1, in order to demonstrate the impact that these changes have in the North-West European domain. These developments are publicly available in WRF-Chem from version 3.5.1 onwards."

3) Introduction: The first three paragraphs (until '... solved separately') are true, but there is no relationship to the content of the paper. I suggest removing these paragraphs.

We provide the first three paragraphs as an introduction for WRF-Chem, laying the groundwork for why we need such models. Complete removal of these paragraphs would rely on all readers knowing what WRF-Chem is and what it is used for. To avoid making the paper less accessible to the general reader, we have retained some of the general introduction but abbreviated the text to:

"Coupled simulations of atmospheric dynamics, pollutant transport, chemical transformation and mixed-phase processes are challenging because of the complexities of the interactions and feedbacks between these processes. Historically, these systems have been researched in isolation, leading to the development and use of offline chemical transport models (CTMs) that are driven by atmospheric fields calculated by a previously run meteorological model. CTMs can investigate chemical processes under various prevailing meteorological conditions, but not the influence of atmospheric composition on meteorology. This limitation has driven the development of online coupled models (Baklanov et al., 2011).

WRF-Chem is such a fully coupled, "online" regional model with integrated meteorological, gas-phase chemistry and aerosol components (Grell et al., 2005). WRF-Chem is built around the Advanced Research WRF (ARW) core, which handles the meteorology, physics and transport components of the model (Skamarock et al., 2005). Transport of chemical species is calculated using the same prognostic equations, timestep, physical parameterisations and coordinate system used for conserved variables in the ARW core model."

4) Marine Organic Aerosol: This issue must be either related more closely to the main topic of the paper. Alternatively, the subject of the marine aerosol could be removed from this paper and be addressed in another short paper in more detail.

See reply to general remarks. This statement is predicated on an incorrect assumption that the common thread of the paper is a specific scientific topic. The common thread, as stated in the response to specific point 1, is that they all relate to representations in the chemical modules that should allow more faithful simulation of processes that contribute to atmospheric composition. All code is provided freely as part of the v3.5.1 WRF-Chem distribution and all details are provided in the paper for any reader to directly reproduce our results. We are using this parameterisation in ongoing work and intend to publish more extensive results in the fullness of time. Its inclusion in the current manuscript provides a referenced description for any other users should they wish to avail themselves of the capability. We believe that milking publications from small developments such as the primary marine source function inclusion would not be in the interests of GMD or the scientific community.

5) Analysis of model results: Please add some comparison with observations

As noted above in the general remark, this request has been covered in some detail by Lowe et al. (2014). However, this evaluation and comparison only covers the nighttime chemistry developments in the model; suitable measurements were not made in RONOCO to evaluate the gas phase chemistry (CRIv2-R5) scheme (particularly daytime photochemistry) and the primary marine organic scheme. We have searched extensively for datasets to evaluate both schemes at scales appropriate for the WRF-Chem simulations, in order to investigate a standalone evaluation study. Given the results of the comparison between CBM-Z and CRIv2-R5 already presented in the manuscript, none exist that would be sensitive to the differences between the schemes and that could comprehensively test the gas phase chemistry. The vast majority of the species in both mechanisms are not routinely measured with useful geographical coverage (indeed the VOC and OVOC surrogates in both schemes are unmeasurable). OH, HO_2 and RO_2 radicals are seldom available outside intensive measurement periods and never with substantial geographical coverage. Surface level measurements of NO, NO_2 and O_3 are particularly poor comparators for disentangling chemical differences, the nitrogen oxides very largely reflecting the emissions and photostationary state; O_3 being strongly buffered. The need for a comparison of the performance of all chemical scheme options and linkages in WRF-Chem has been discussed within the WRF Atmospheric Chemistry development Working Group 11 and will likely result in a substantial community effort to conduct this evaluation. However, such a comparison has yet to be carried out. A pre-emptive extensive unilateral comparison of just two of the options is not an efficient approach.

That said, we have previously participated in a UK Defra modelling intercomparison exercise with a prototype of the model version reported in this manuscript. However, the lack of uniformity in specification of domains, boundary conditions, meteorological drivers and emissions methodology renders this approach unsuitable for immediate duplication. However, in order to respond as positively as possible to the referee's request we have made a comparison of the CBM-Z and CRI simulated ozone and NOx for 4 Defra rural background measurement locations as shown in Figures 1-3 below. Measurement stations were chosen to give as broad coverage of the UK as possible within the limitations of the station distribution and data availability during the period of our model study. The study period (July 2010) is representative of a range of British summer conditions: broadly zonal airflow in the start of the campaign brought clean air across from the Atlantic; around the 20th July a high pressure system brought air from continental Europe across the UK, resulting in elevated pollution conditions; following this a series of frontal systems based over the UK, washing out the pollution and bringing cleaner air from the Atlantic again (see Morgan et al, 2014, and Lowe et al, 2014, for more details).

Both oxidation schemes carry the latest kinetic recommendations for the relevant reactions and as can be seen, make near identical predictions of all species at the measurement locations, reflecting their near identical photostationary response to the identical emissions, radiation and meteorology. The comparisons with the measurements are not so close (and hence cannot be used to evaluate the chemical schemes). This leads to one of three conclusions: either both gas phase chemical schemes suffer the same problems or the problems are unrelated to the chemical schemes and concern problems elsewhere in the model or with the measurements. In the former case, we can only point to the extensive box modelling studies evaluating both CBM-Z and CRI. Furthermore, it is extremely unlikely that there are big surprises in rates of reaction playing a role in the calculation of the photostationary state. The latter cases are clearly out of scope of the paper, since we are not evaluating emissions, meteorology, boundary conditions or radiation schemes within WRF-Chem, nor pollutant measurements in the Defra network.

We do not believe that these comparisons with the DEFRA measurements contribute any further insights on the main focus of this paper. These initial comparisons open the door to a more comprehensive evaluation of this and other regional model frameworks that should include all processes that can contribute to the apparent disparity. But such an evaluation is outside the scope of our manuscript, which reports the development of the gaseous degradation mechanism. If the editor believes that the inclusion of this study in the paper would be desirable then we will include it, otherwise we would prefer to leave it out.

6) First line of 4.1: Please specify 'very well'.

The CRIv2 scheme has been compared against the MCM v3.1 scheme in box-model studies across a range of VOC/NOx ratios: generally the predicted ozone from the two schemes was found to agree within (roughly) 2–4% (Jenkin et al, 2008). The, further reduced, CRIv2-R5 scheme was compared against the CRIv2 scheme in Watson et al (2008): for ozone the divergence between schemes was generally less than 1%, and for NOx of between 1–4% (dependent on the VOC/NOx ratio). Discussing in detail the chain of validation from MCM v3.1 through to CRIv2-R5 would take more explanation than is appropriate for this paper. So we suggest adding this estimate of fit after the phrase "very well":

"(predicted ozone concentrations generally deviate by less than 5% across a wide range of VOC:NOx ratios)"

and adding the Watson et al (2008) reference to the end of this sentence too.

7) P. 893, line 20,21: 'This added NO_3 *is likely due to the faster rate of ...'*

We have run the test suggested by the reviewer (see Figure 4). This shows that the faster rate does not increase the NO3 mixing ratio sufficient to match the NO_3 mixing ratios in the CRI scheme.

After some more investigation, we believe that the higher NO3 mixing ratios (at 300 metres above ground level) in CRIv2-R5 are, most probably, related to the higher NO2 mixing ratios at these altitudes in this scheme during the night.

The higher mixing ratios of NO_2 at night using CRIv2-R5, away from pollution sources, are most probably related to the greater formation of PAN (and similar compounds) that occurs during the day using CRIv2-R5 rather than CBM-Z; which then thermally decompose through the night, maintaining NO_2 mixing ratios (see panels A B in Figure 5, below). Another factor in this story could also be the different manners in which these two schemes treat the decomposition of organic nitrates (ONIT), which form significant reservoirs for NO2 in both schemes, but have significantly higher mixing ratios in CBM-Z (see panel C in Figure 5). In CRIv2-R5 (following the MCM methodology) ONIT compounds reaction with OH to directly produce NO_2:

$$[\mathrm{ONIT-compound}] + \mathrm{OH} => [\mathrm{VOC}] + \mathrm{NO_2} \quad (1)$$

In CBM-Z this same reaction produces nitratoalkyl peroxy radicals (NAP):

$$\mathrm{ONIT} + \mathrm{OH} => \mathrm{NAP} \quad (2)$$

These radicals can then take part in several different reactions:

$$\mathrm{NAP} + \mathrm{NO} => \mathrm{NO_2} + \mathrm{NAO} \quad (3)$$
$$\mathrm{NAP} + \mathrm{HO_2} => \mathrm{ONIT} \quad (4)$$
$$\mathrm{NAP} + \mathrm{RO_2} => \mathrm{NAO} + \mathrm{RO} \quad (5)$$

NAO then thermally decomposes to 50% NO2 and 50% ONIT. The practical impact of these extra reactions is to slow the destruction of ONIT, allowing for more build up of these species in the CBM-Z simulation.

During the development of both the MCM and CBM-Z the authors of these schemes acknowledged that there is little experimental evidence for the reactions involving NAP (Zaveri Peters, 1999; Saunders et al, 2003). In developing CBM-Z the choice was made to follow a theoretical reaction scheme suggested by Atkinson (1990); whilst during the development of the MCM the decision was made to keep this process as simple as possible and assume that the [ONIT]+OH reaction simply releases NOx. Whilst both approaches are valid, given the current scientific knowledge, it appears that the choice of which approach to use could have significant impacts on the long-range transport of NOx.

However, untangling the exact causes of the higher NO_3 mixing ratios in CRIv2-R5 compared with CBM-Z would require an in-depth analysis of the implications of these choices for the processing of PAN, ONIT and NOx. This analysis would require chemical tendency information for each of the relevant species. Whilst we have made some, limited, off-line analysis of these tendencies for OH and NO3, proper analysis would require on-line calculation of all tendencies for all chemical species, something which is not yet available in WRF-Chem, but which has been identified by the WP11 working group as a high priority development that needs to be carried out. Additionally, such as study, as well as being very difficult without the ready availability of chemical tendency information, is outside of the scope of this paper. Instead, if the editor agrees, we propose to just remove our incorrect suggestion that the reviewer identified (and the sentence following it) from the paper.

8) Page 895, lines 10 - 15: These pieces of text just summarize common knowledge and obvious features. Looking into regional effects and discussion of a model evaluation against measurements could add to a in depth discussion of the impact of the new implementations on the model results.

We concede that most readers will know that OH and NO_3 are the dominant daytime and nighttime oxidants, so we have cut the superfluous text. It is less well known that nighttime OH oxidation is comparable to NO_3. This is retained, but rephrased thus:

“NO_3 oxidation of VOCs is important during the night, but it should be noted that the OH oxidation of VOCs is still non-negligible during this period; indeed the rates for this are comparable to those for NO_3 driven oxidation.”

See our reply to the general remarks and question 5 as to evaluations against measurements. NO_3 comparisons are the subject of our ACPD paper, but OH measurements are unavailable for regional model evaluation.

9) Figure 3: It is hard to recognize anything on these stamp-like figures, unless they are enlarged to 200

This might be perceived as a limitation of the GMDD format, though we consider it an advantage; the layout of these figures is suited to an A4 page if printed. Since GMD is predominantly an online journal and pdf is a vector format, we have endeavoured to take appropriate advantage of the available technology. This allows straightforward enlargement to 200% (or even 1000% for single panels) on a reasonable screen. We have tried to arrange the panels so that those best for comparison can be viewed together under enlargement. We could split the panels for a print version, but it could lead to the criticism of too many figures in the online version when they can be clustered as we have done. We will be happy to respond to editorial guidance on this matter.

10) Figures 8 and 9: The quality of these figures is very poor. A height scale is missing and opacity does not show. I suggest replacing the VAPOR figures.

Illustrating the spatial distribution of chemical species across a 3-D domain is a difficult task. We have chosen to use these 3-D plots, as imperfect as they are, to give an accessible, qualitative, illustration to how the distributions of NO_3 and sea-salt aerosol change between the scenarios across the whole domain. We acknowledge that it is difficult to gain exact, quantitative, differences from these plots – but this is not what they are intended for (to do this would require a series of 2-D horizontal and vertical slices through the domain, which would still be, differently, spatially limited).

However, much of the information in Figure 8 is carried in Figure 4, so we have replaced Figure 8 with an animation in the supplementary material showing the change in NO_3 through time (in the same style as Fig 8, but also with an added altitude axis). The information in Figure 9 is not carried elsewhere in the manuscript, and so is retained. However, we have added a vertical axis to the VAPOR plots in Figure 9, and also created an animation of this Figure too (which will be in the supplementary material). We feel these changes better convey the temporal, as well spatial, variability observed in the model and uses the multimedia format of the GMD journal to full effect.

References (extra to those already in the GMDD paper):

Atkinson, R: Gas-phase tropospheric chemistry of organic compounds: A review, Atmos. Environ., 24A, 1-41, 1990

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Defra Automatic Urban and Rural Network: http://uk-air.defra.gov.uk/networks/network-info?view=aurn

Lowe, D., Archer-Nicholls, S., Morgan, W., Allan, J., Utembe, S., Ouyang, B., Aruffo, E., Le Breton, M., Zaveri, R. A., Di Carlo, P., Percival, C., Coe, H., Jones, R., and McFiggans, G.: WRF-Chem model predictions of the regional impacts of N2O5 heterogeneous processes on nighttime chemistry over North-Western Europe, Atmos. Chem. Phys. Discuss., 14, 20883-20943, doi:10.5194/acpd-14-20883-2014, 2014

Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N2O5 uptake: airborne regional measurements in North-Western Europe, Atmos. Chem. Phys. Discuss., 14, 19673–19718, doi:10.5194/acpd-14-19673-2014, 2014

Interactive comment on Geosci. Model Dev. Discuss., 7, 871, 2014.

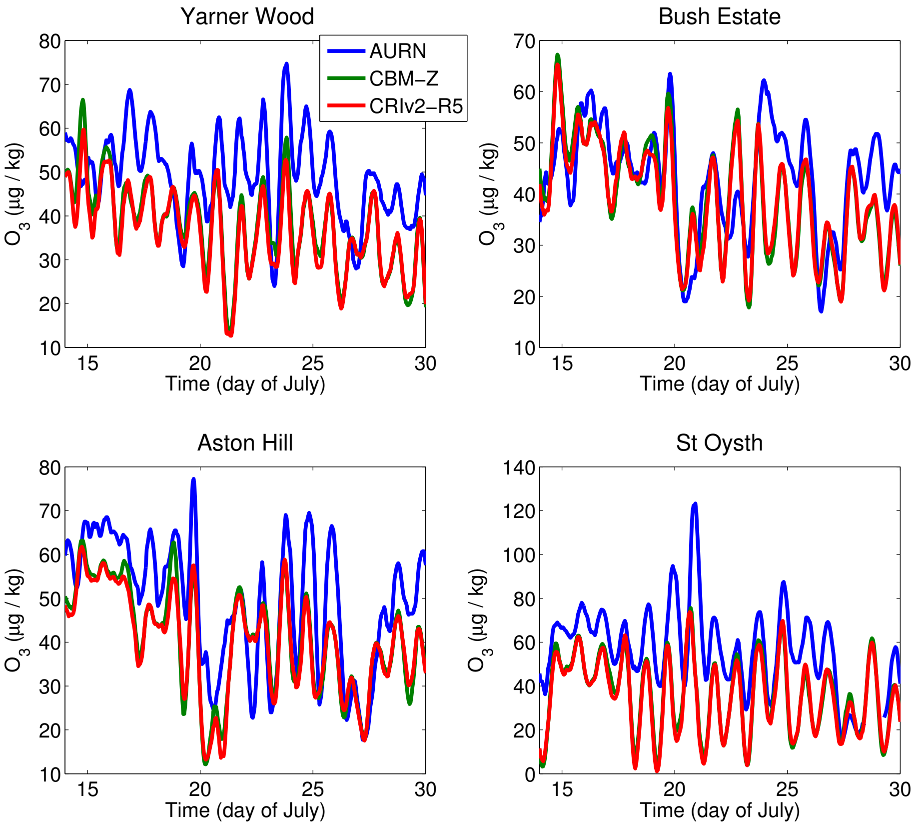

Fig. 1. Comparison of 8-hour running means of “background rural” ozone measurements (blue lines) and model data (green line for CBM-Z simulation; red line for CRIv2-R5 simulation) taken at Yarner Wood (50.60

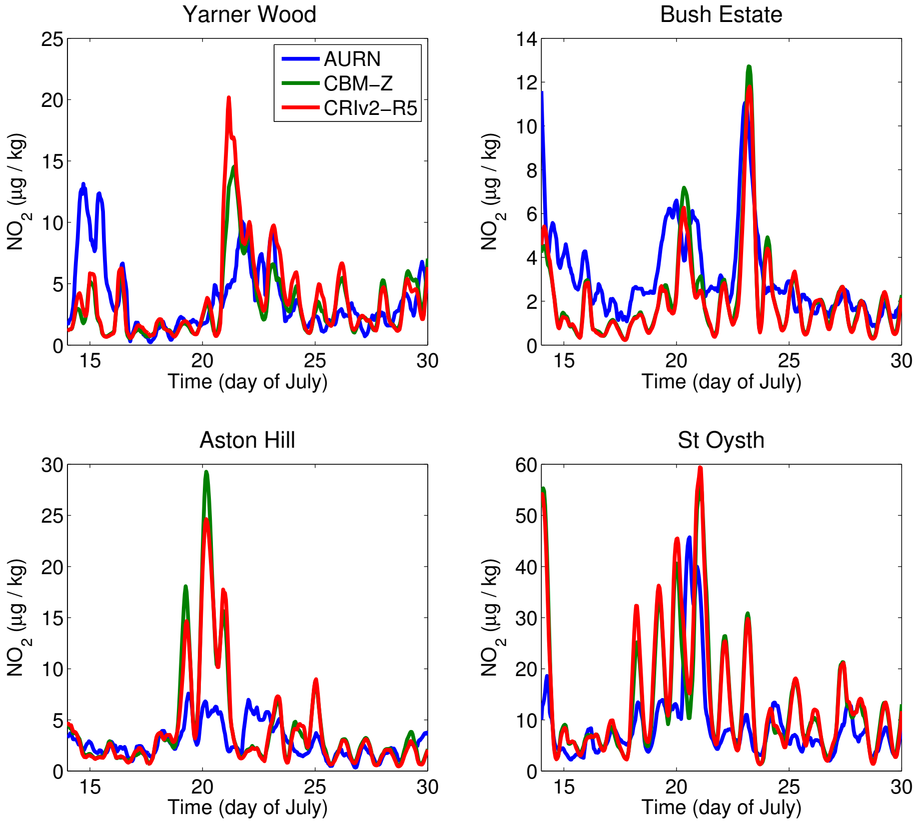

Fig. 2. Comparison of 8-hour running means of modeled and measured NOÂň2 at the same locations as in Figure 2.

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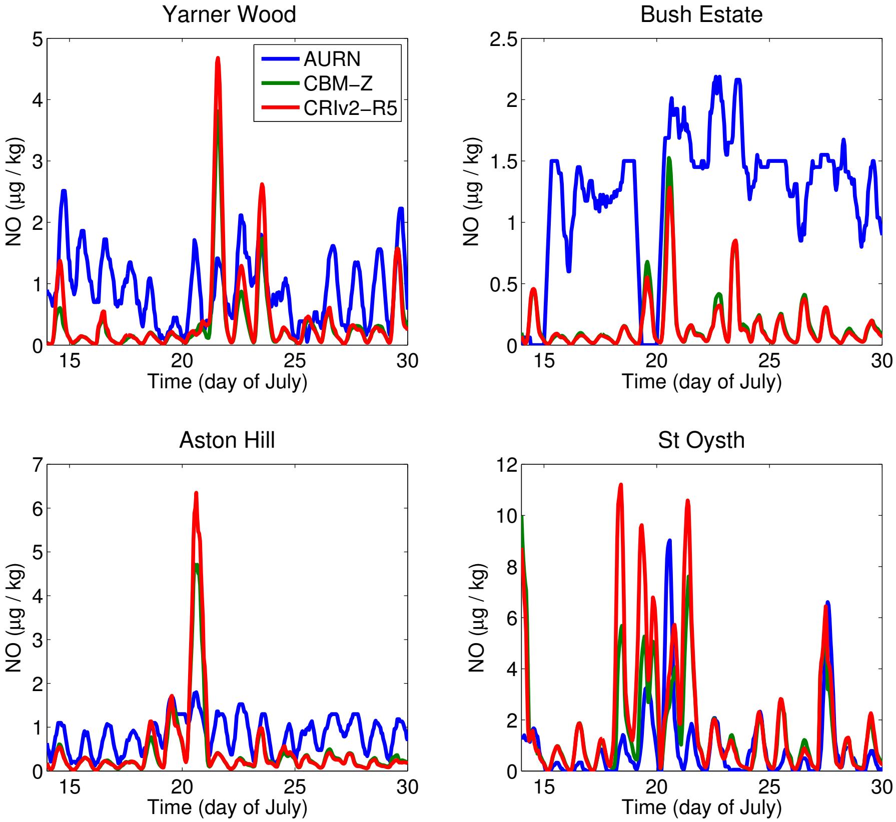

Fig. 3. Comparison of 8-hour running means of modeled and measured NOÂň at the same locations as for Figure 2.

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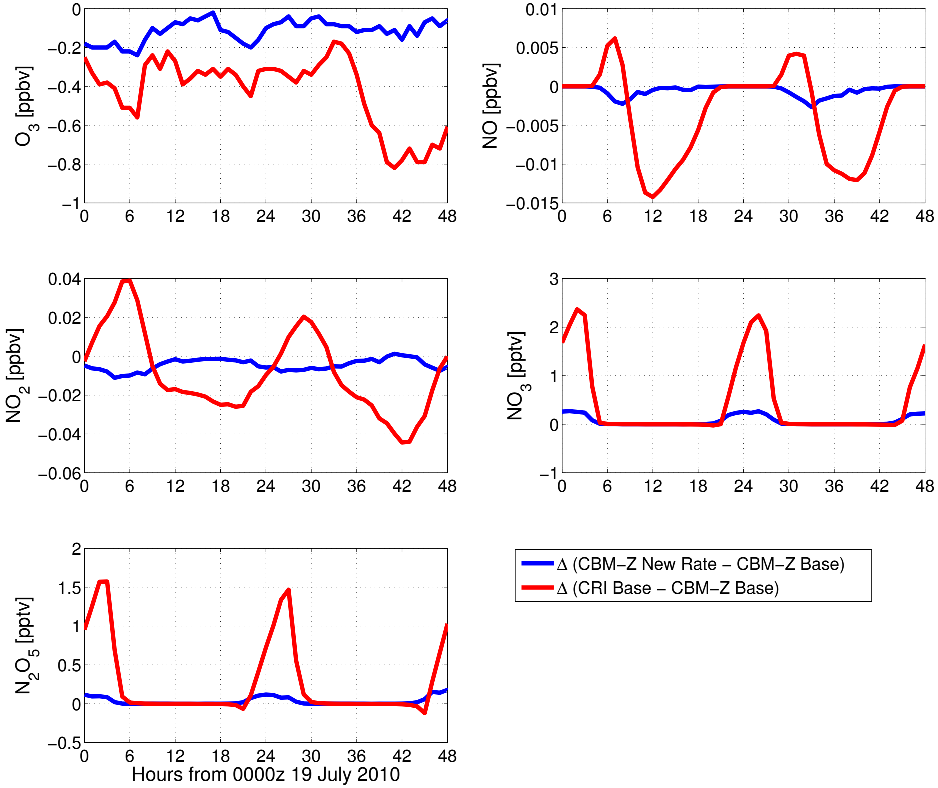

Fig. 4. Comparison of the domain-averaged (interpolated to 300 metres above ground level) mixing ratios of O3, NO, NO2, NO3, and N2O5. The red line is the CRIv2R5 median value minus the original CBM-Z median

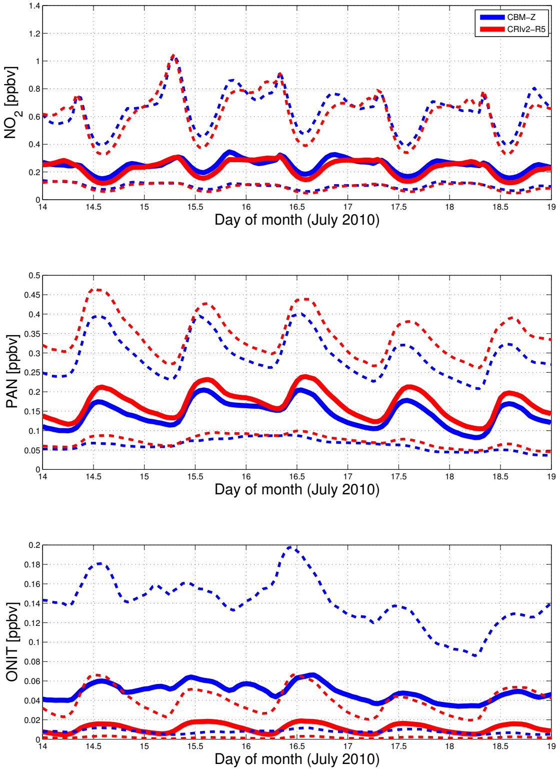

Fig. 5. Mixing ratios of NO2 (panel A), “PAN” (B), and “ONIT” (C) interpolated at 300 metres above ground level, across the whole model domain, for the CBM-Z (blue lines) and CRIv2-R5 (red lines) simulations.

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