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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Biomass burning emissions disturbances on the isoprene oxidation in a tropical forest" *by* Fernando C. Santos et al.

Anonymous Referee #1

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This manuscript examines the oxidative capacity of the atmosphere above the Amazon Rainforest, focusing in particular on variations with altitude within the boundary layer and cloud layer, and on the perturbations to that oxidative capacity wrought by biomass burning plumes. Working with atmospheric measurements conducted from aircraft during the SAMBBA campaign in the Brazilian Amazon in 2012, the authors use CO as a biomass burning tracer to identify plumes, and further use ratios of ozone and CO enhancement to identify aged and fresh plumes. The authors then use the ratio between concentrations of isoprene's reactive products (MVK + MACR + ISOPOOH, measured by PTR-MS) and isoprene itself (measured by PTR-MS and corrected for furan interference by comparison to WAS-GC-FID), along with an estimation of processing time since isoprene emission to the airmass, to calculate concentrations of

[OH] within that airmass. Fresh plumes are found to have substantially higher product-to-isoprene ratios, and higher estimated OH, than aged plumes or background conditions, demonstrating that biomass burning events can intensify oxidation processes. The authors also highlight variations in altitude: in background air masses, calculated [OH] increased markedly from the surface layer to the cloud layer, while the increase was diminished in aged plumes and in fresh plumes it decreased slightly.

Measurements and models of the oxidative capacity of the remote troposphere, and in particular of OH concentrations in forested regions, have been notoriously difficult and error-prone, but their accurate estimation is crucial to understanding the fates of biogenic emissions in those environments and the roles that such biogenic emissions play in OH titration and/or recycling. New or updated methods to make such estimations, such as the one the authors provide here, are therefore an important research goal for atmospheric chemists. However, as explained in the general comments below, more characterization of the discrepancies with alternate methods and of potential biases and errors in this new method are necessary before it can be broadly applied.

General comments:

1) It would greatly enhance the utility and strength of both the methods and main conclusions - the variation in oxidative capacity of the Amazon boundary layer between pristine, fresh, and aged smoke plume conditions - in this manuscript to include more discussion of potential sources of error and uncertainty, and the spread in the data. In particular, the lack of ranges and error bounds on measurements from this study and on the [OH] numbers reported in Table 4 makes them difficult to interpret, because it is not clear (a) whether these results hold broadly for all plumes under all conditions, and for the background under all conditions, and (b) what the uncertainty is in the estimates. There are a lot of assumptions & steps to get from what you measure (which itself has ranges and uncertainties) to what you infer, and I think it's slightly misleading and less useful to report single numbers as averages in the three conditions. Figure 8 does a good job breaking this down to show variation in the product:isoprene ratio within and

across altitudes under the three conditions, but it would be nice to see that translated to uncertainties in OH, and to see an expansion in the discussion of potential sources of error

2) Kind of as a continuation of the previous comment, it would also benefit this manuscript to have more discussion of the departure of your results from those of Karl et al. (2007) and other studies, and whether or not those discrepancies are expected from the differences in methods used between the studies. It is surprising that such similar methods can give such vastly differing results, and merits further description of why the estimates in Karl et al. were two orders of magnitude higher. There is a section listing results of some previous studies (L 388 - 408), but it does not delve far into why different studies found such different values and what reasons exist to believe certain numbers in place of others. In particular, the background values reported in this study seem substantially lower than recent studies that used similar organic ratios (e.g. Liu et al. 2016) - how can these be reconciled?

3) The use of a single value for the total yield of [MVK + MACR + ISOPOOH] from isoprene (0.55) and for the rate of [MVK + MACR + ISOPOOH] + OH (6.1e-11 cm3 molec-1 s-1) seems potentially problematic. Under the range of conditions reported in this study, the pathways of isoprene oxidation can differ drastically, from an overwhelming fraction of the isoprene-derived peroxy radicals reacting with NO (giving combined MVK + MACR yields ~57%, from the numbers on L 112, and no ISOPOOH) to very low-NO chemistry in which a large fraction isomerizes (forming MVK and MACR in small yields) and the rest reacts with HO2 to form ISOPOOH in very large yields (up to 93%, Liu et al. 2013). Given that the three first-generation products also have very different oxidation rates, as you note in section S2, the rate of product loss can also vary widely depending on the oxidative conditions (particularly the concentrations of NO). For example, the attached figures show the steady-state daytime [ISOPOOH + MVK + MACR] / isoprene ratio, the steady state [ISOPOOH] / [MVK + MACR] ratio, and the steady-state [OH] as a function of [NO] for various isoprene oxidation models

(MCM from Jenkin et al. 2015, Caltech from Wennberg et al. 2018, and GEOS-Chem versions 10 and 11), using the box modeling conditions described in Jenkin et al. 2015. The variations with NO are pronounces.

These variations in yields and rates could be treated in different ways: you could just incorporate them as uncertainties in the model, in which case, they merit much more discussion in this manuscript; or, you could use the measured NO in the air masses sampled to calculate the assumed fractions of MVK, MACR, and ISOPOOH produced from isoprene, and from that to calculate the bulk oxidation rate of these products, using one of the isoprene oxidation models shown in the attached figures. You could also consider bringing temperature into the equation, since all the oxidation rates (and some of the yields) vary with temperature as well.

Content comments:

L 44 - please clarify whether or not this includes methane. L 45 - what is meant by the "balance" of VOC's emitted by anthrop[ogen]ic and biogenic sources? As written, it sounds like the anthropogenic and biogenic sources are in balance with each other, which is presumably not the case; is this meant to imply that sources are balanced with sinks (i.e. oxidation)? L 51 - it is unclear here what is meant by the clause "affect the VOC... process." Does this mean that the Amazon and similar regions have unique oxidative chemistry? The OH radical initiates isoprene oxidation ubiquitously, so I'm not sure how the "OH radical strengthening the process" in the Amazon uniquely affects VOC oxidation. L 89-91 - please include citations for these "significant advances" - as it stands, this sentence is too vague to identify what advances are being referred to. L 91 - what are these two pathways? RO2 and NO? The peroxy radicals produced from isoprene can undergo a number of subsequent reaction pathways, including with NO (e.g. Tuazon et al. 1990), HO2 (e.g. St. Clair et al. 2015), RO2 (e.g. Jenkin et al. 1998), and self-reactions / isomerizations (e.g. Peeters et al. 2009). Therefore it is not just an accurate understanding of two pathways alone that are required! L 111-114 - I see the figure in Jenkin et al. 2015 these are reported from, but it's important that these are also from a specific environment - it is not just the level of NO that matters for these yields (because other pathways can yield MVK and methacrolein, and because concentrations of other reactants can influence the branching between isoprene peroxy radical isomers that react with NO to yield these products). L 152 - ISOPOOH is not isobaric with MVK and MACR - it's a decomposition interference. If it was only calibrated with MVK and MACR, do you have some estimate of how efficient the decomposition of ISOPOOH –> m/z 71 was? L 217-218 - see general comment (3) above about these assumptions regard the oxidation rates and yields of [MVK + MACR + ISOPOOH] L 303 - what is meant by "producing a value around 50% and 14%, respectively"? Are these the measured reductions in isoprene mixing ratios from the BG to the plumes? L 315 - here you say the [MVK+MACR+ISOPOOH]/isoprene ratio is low in fresh plumes, which appears to be corroborated in Figure 7, but on L 320-321 and later you quote high values of the [MVK+MACR+ISOPOOH]/isoprene ratio in fresh plumes, as shown in Figure 8. How do these coincide? L 336 - what is meant by "as in AP levels"? It appears from Table 4 that AP isoprene oxidation is constant with altitude, unlike BG. L 344-345 - how does an increase in photolysis rates increase the [MVK+MACR+ISOPOOH]/isoprene ratio? If it speeds up oxidation in general, it may remove isoprene faster, but if it also increases the photolysis of MVK, MACR, and ISOPOOH (rather than isoprene) it may cause faster removal of the products instead. L 378 - two orders of magnitude is a lot! The values quoted from here down to L 408 span a wide range, and it is therefore not clear whether saying the "OH concentration values presented in this study agree in order of magnitude with more modeled and observed values previously reported" (L 388-389) is a useful metric. See general comments (1) and (2) above. L 404 - Why is the quoted range from Williams et al. (2001) 0.6-1.1 here but 0.7-101 on L 391 above?

Minor copyediting comments:

L 19 - "trace gases measurements" –> "trace gas measurements" L 45 - "anthropic" –> "anthropogenic" L 46 - "sub-products" - does this just mean later-generation products? Or co-products? Unclear. L 186 - "flights" –> "flight" L 203 - "ISOPOHH" –> "ISOPOOH" L 304 - ">1,2000 m" –> ">1,200 m" L 354 - "showed" –> "shown" L 372 - "value" –> "values" L 379 - "tends" –> "tend" L 396 - "from Sacramento region" –> "from the Sacramento region" L 430 - "regarding the isoprene" –> "regarding isoprene" L 431 - "Near fresh and aged smoke" is not needed L 503 - this citation is missing a journal name L 506 - all of the authors are duplicated in the reference for Feiner, et al. L 634 - the URL isn't needed here L 655 - a number of the authors are duplicated in the reference for Stroud, et al. L 666 - does this reference refer to the chapter in "Atmospheric and Aerosol Chemistry"? If so it should include: "In: McNeill V., Ariya P. (eds) Atmospheric and Aerosol Chemistry. Topics in Current Chemistry, vol 339. DOI https://doi.org/10.1007/128_2012_359" L 671 - Whalley's name is duplicated in the reference for Whalley, et al, 2013. Also, given the title, is this just a duplicate of the Whalley, Stone, and Heard reference above? L 685 - this ACPD reference should probably be for the final ACP paper instead

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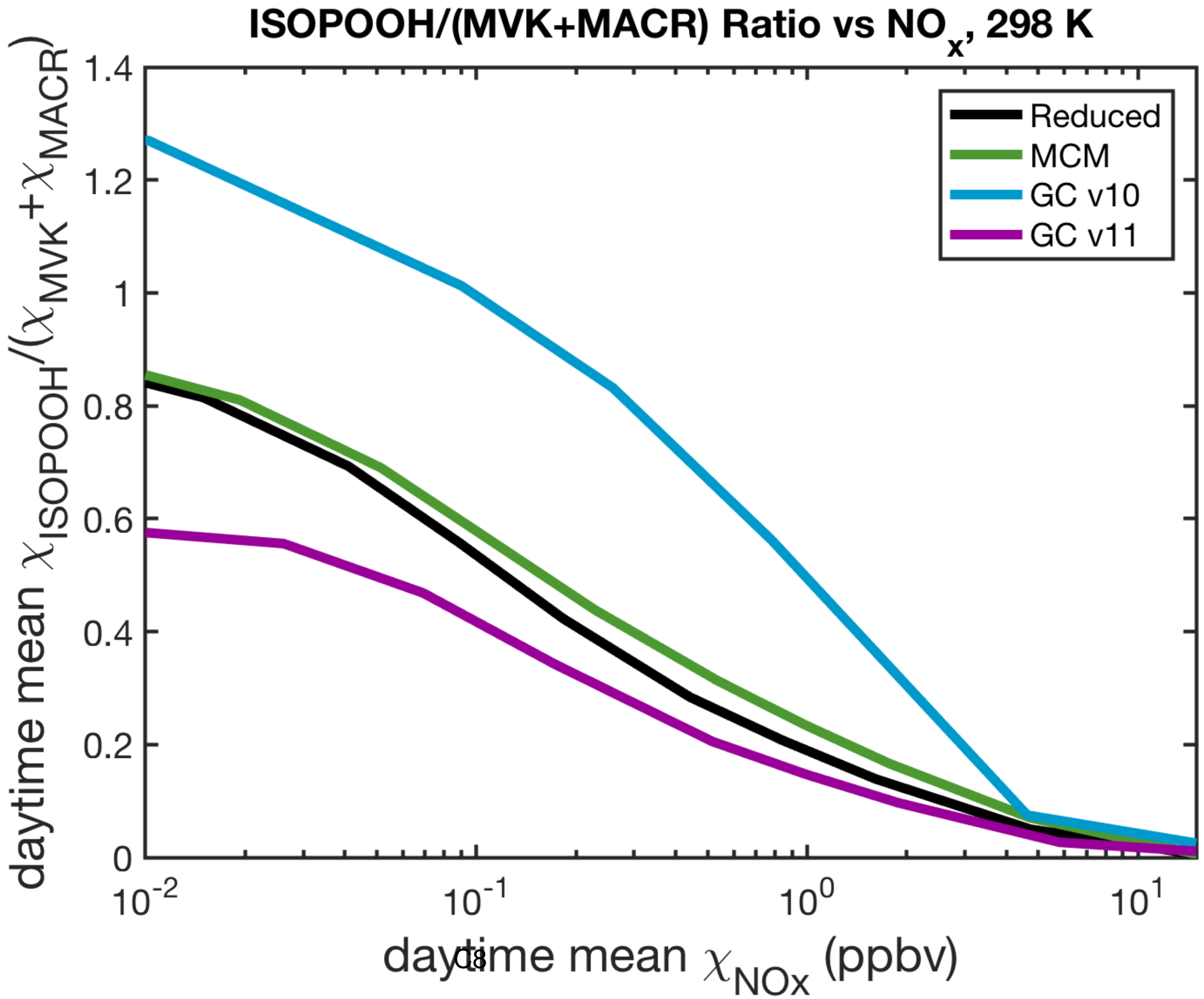
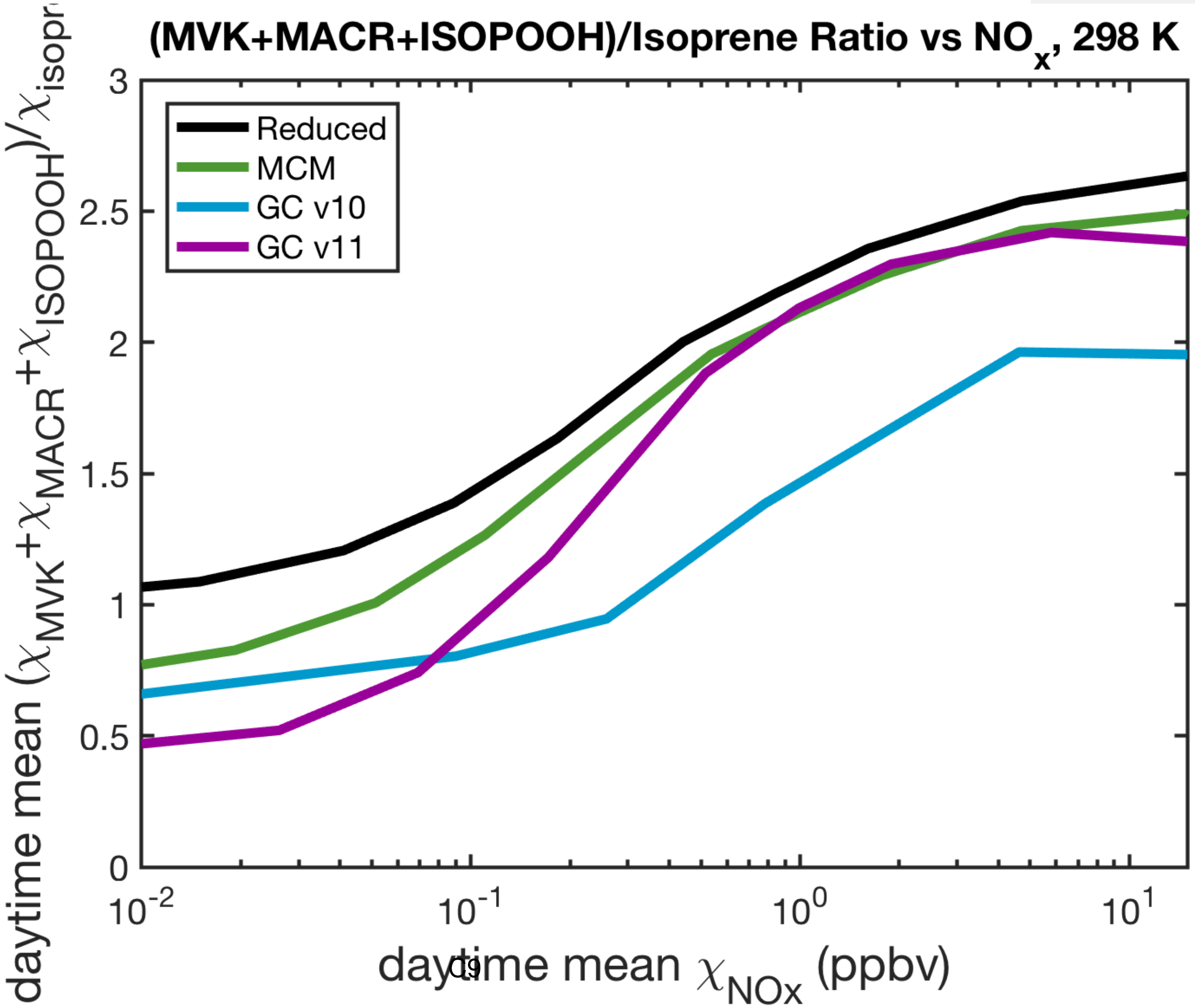
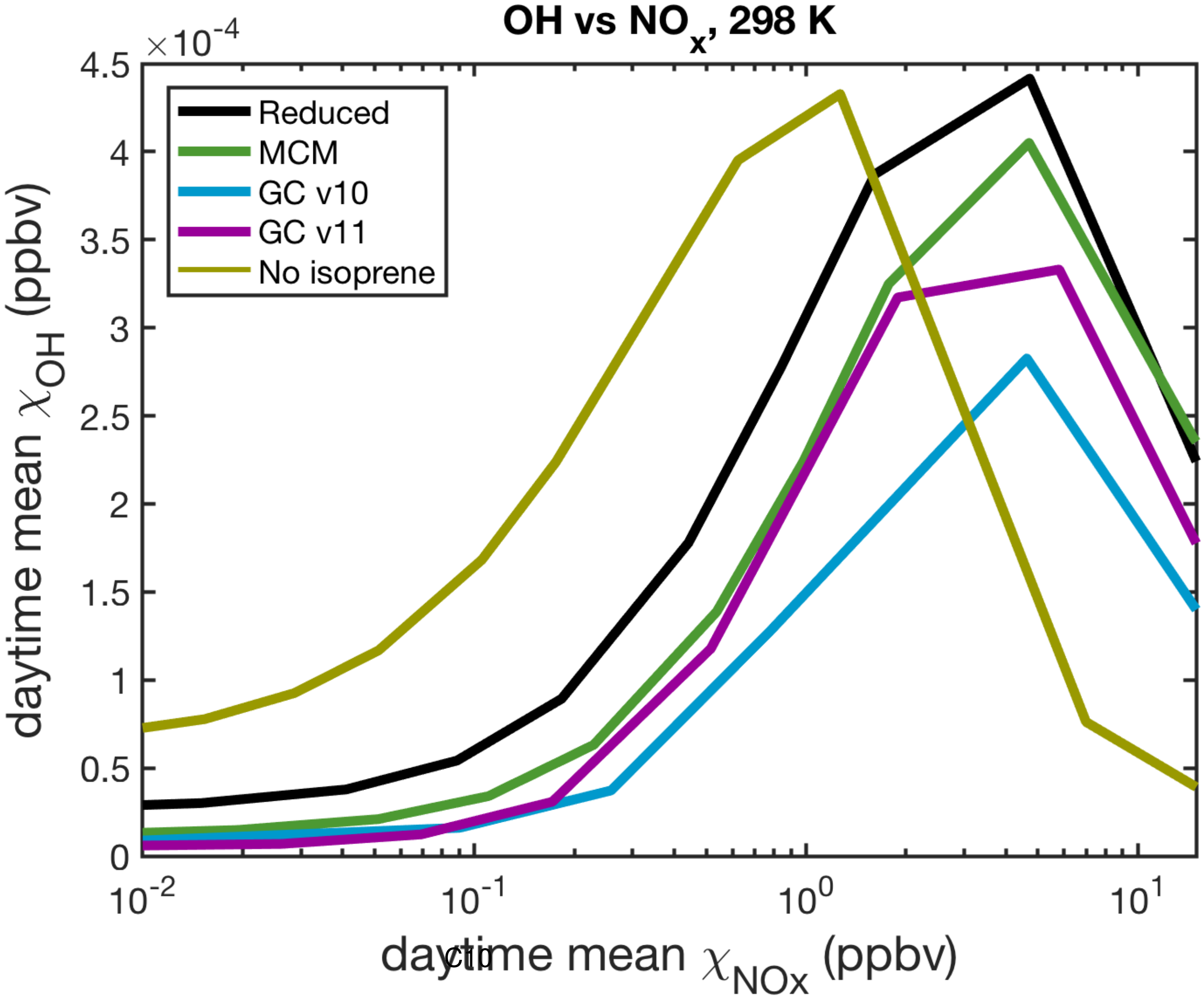

ISOPOOH/(MVK+MACR) Ratio vs NO$_x$, 298 K
daytime mean $\chi_{ISOPOOH}/(\chi_{MVK}+\chi_{MACR})$
daytime mean χ_{NOx} (ppbv)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
10^{-2}
10^{-1}
10^{0}
10^{1}
Reduced
MCM
GC v10
GC v11


(MVK+MACR+ISOPOOH)/Isoprene Ratio vs NO_x, 298 K
Reduced
MCM
GC v10
GC v11
daytime mean $(\chi_{MVK}+\chi_{MACR}+\chi_{ISOPOOH})/\chi_{isopr}$
3
2.5
2
1.5
1
0.5
0
10^{-2}
10^{-1}
10^{0}
10^{1}
daytime mean χ_{NOx} (ppbv)


OH vs NO$_x$, 298 K
$\times 10^{-4}$
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
daytime mean χ_{OH} (ppbv)
Reduced
MCM
GC v10
GC v11
No isoprene
10^{-2}
10^{-1}
10^{0}
10^{1}
daytime mean χ_{NOx} (ppbv)