

Morin et al provide a detailed investigation of the diurnal variability of $\Delta^{17}\text{O}$ of short-lived nitrogen and oxygen containing molecules in the atmosphere utilizing a photochemical box model. The paper is generally well-written – though I have detailed some grammatical and wording issues below. The goal of the paper is to study the impact of previous simplifying assumptions, such as that used in Alexander et al. (2009), on the calculated $\Delta^{17}\text{O}$ of atmospheric nitrate. Such a study is useful using a box-modeling framework, as detailed sensitivity studies can be carried out. I recommend publication after some issues have been addressed.

My main issue with the paper has to do with your recommendation for global modelers. Your recommendation to global modelers could be more broadly applicable and therefore useful. For example, you suggest assigning a value of $\Delta^{17}\text{O}$ for the N_2O_5 and NO_3+H pathway of 33 and 40‰ respectively, but this value is dependent upon the choice of $\Delta^{17}\text{O}(\text{O}_3^*)$ and α ($\Delta^{17}\text{O}(\text{NO}_2)$). $\Delta^{17}\text{O}(\text{NO}_2)$ varies strongly with latitude, so assuming a constant value for $\Delta^{17}\text{O}(\text{nitrate})$ produced by a particular pathway would not work well in a global model. I know from Alexander et al (2009) that $\Delta^{17}\text{O}(\text{NO}_2)$ (or α) varies strongly with latitude using the PSS assumption. Does $\Delta^{17}\text{O}(\text{NO}_2)$ (or α) also vary strongly with time and space at dusk? You could probably test this in your model to see how broadly applicable your recommendations (40‰ and 33‰) are. If possible, it would be much better give your recommendation as a formula with $\Delta^{17}\text{O}(\text{O}_3^*)$ and α as variables. Also, can you provide some error bars associated with the statement that Alexander et al, 2009 is biased low by 1‰ for the NO_2+OH pathway. I would think this could vary over space and time.

Your other recommendation for using a larger integration period (6:00 – 18:00) is not quite as straightforward as you make it sound. When dusk and dawn occur varies a lot in space and time, so choosing one time period would incorporate darkness into some locations (leading to an overestimate of $\Delta^{17}\text{O}(\text{NO}_2)$), while in other locations it would not be significantly difference from what Alexander et al. (2009) did (leading to an underestimate). I haven't yet figured out a way to get around this easily in GEOS-Chem, but your suggestion is not particularly helpful in this regard.

That said, I tried out your recommendation as follows. I changed my assumed $\Delta^{17}\text{O}(\text{O}_3^*)$ from 48‰ to 42‰, so that direct comparison with your recommendation would be meaningful. I then separately assumed that nitrate produced via the N_2O_5 pathway is always equal to 33‰, NO_3+H is always equal to 40‰, and I added 1‰ to my calculations of the $\Delta^{17}\text{O}(\text{nitrate})$ value for the NO_2+OH pathway. I then compared the Alexander et al (2009) calculations (assuming $\Delta^{17}\text{O}(\text{O}_3^*) = 42‰$) with your recommendations. The difference between $\Delta^{17}\text{O}(\text{nitrate})$ from the NO_2+OH pathway is -1‰ everywhere (expressed as Alexander et al, 2009 method – Morin et al., 2011 recommendations). The same comparison for the N_2O_5 hydrolysis and NO_3+H pathways is shown in Figure 1 (only one plot is shown because the results are identical for both pathways). Figure 1 shows the mean summer (JJA) and winter (DJF) difference between calculated $\Delta^{17}\text{O}(\text{nitrate})$ (for nitrate formed only via the N_2O_5 hydrolysis or NO_3+H pathways) at the surface from Alexander et al (2009) compared to your suggestion (expressed as Alexander – Morin). The difference ranges from 2‰ to -12‰ for both

reactions. The Alexander et al method is lower (by up to 12‰) in low latitude forested regions because of the nighttime source of RO₂ (from reactions of O₃ with alkenes) leading to low A_{night} values. Differences elsewhere are small. The maximum overestimate (<2‰) is consistent with your results (Table 5). Figure 2 shows the same difference taking all 3 of your recommendations together for total nitrate (range of -3.6 to 0.5‰ difference). The largest discrepancy between the two approaches again occurs in forested regions. Elsewhere the difference is generally $\leq 1\%$, in part due to the compensating effects of your recommendations. I'm not sure that your box model simulations take this additional source of RO₂ (O₃ + alkenes) into account. You could probably do a sensitivity study to examine this specific case. Although nighttime production rates of RO₂ are uncertain, this does illustrate that you cannot assume that one value (+1‰, 33‰, or 40‰) is appropriate everywhere. I think your sensitivity studies are useful for exploring the bias of the Alexander et al, 2009 paper for any given scenario, but may not be broadly applicable across the globe. Unless you can express your recommendations in the form of an equation with α and $\Delta^{17}\text{O}(\text{O}_3^*)$ as variables, perhaps you should leave out your general recommendation.

It would also be useful to state the relative importance of each nitrate formation pathway. For example, the largest discrepancy between your detailed calculations and the PSS assumption occurs for the N₂O₅ hydrolysis and NO₃+H pathways (according to Figure 5). What is the relative importance of these 2 pathways for total nitrate? According to Alexander et al (2009), globally (annual mean) the NO₂+OH pathway dominates (76%), but the N₂O₅ hydrolysis pathway can dominate (up to 74%) over high northern latitudes over continents and over the Arctic. The NO₃+H pathway is relatively minor (4% globally, annual mean).

I somewhat agree with the first reviewer that there are a lot of tables that could be replaced with some figures, but the advantage of tables is that it is possible to get actual numbers. Although we don't know what the isotopic transfer function is for the NO₂+O₃ reaction, in the absence of better information I think it's justified to use the same transfer function as for the NO+O₃ reaction as there is no reason to think that it would be any different.

I dislike the constant referral to "case 1", "case 2", etc. I am constantly flipping back and forth trying to remember what these are. If you could put some information about each "case" within the text, e.g. replace "case 2" with "case 2 (explicit NO_x)", that would be helpful. Also, refer to the specific reaction formula rather than giving an obscure reaction number that forces the reader to flip through numerous tables trying to figure out what reaction you are talking about.

Grammatical issues:

Plurality is used inappropriately throughout the paper.

Page 30407 line 11: reaction should be reactions

Page 30407 line 12: reaction should be reactions

Page 30409 line 17: model should be models

Page 30410 line 1: reaction should be reactions
Page 30410 line 2: induce should be induces
Page 30411 line 6: model should be models
Page 30412 line 10: channels should be channel
Page 30413 line 12: metrics should be metric
Page 30416 line 20: reaction should be reactions
Page 30427 line 16: metrics should be metric
Page 30429 line 20: tenth should be tenths

Other grammatical or wording issues:

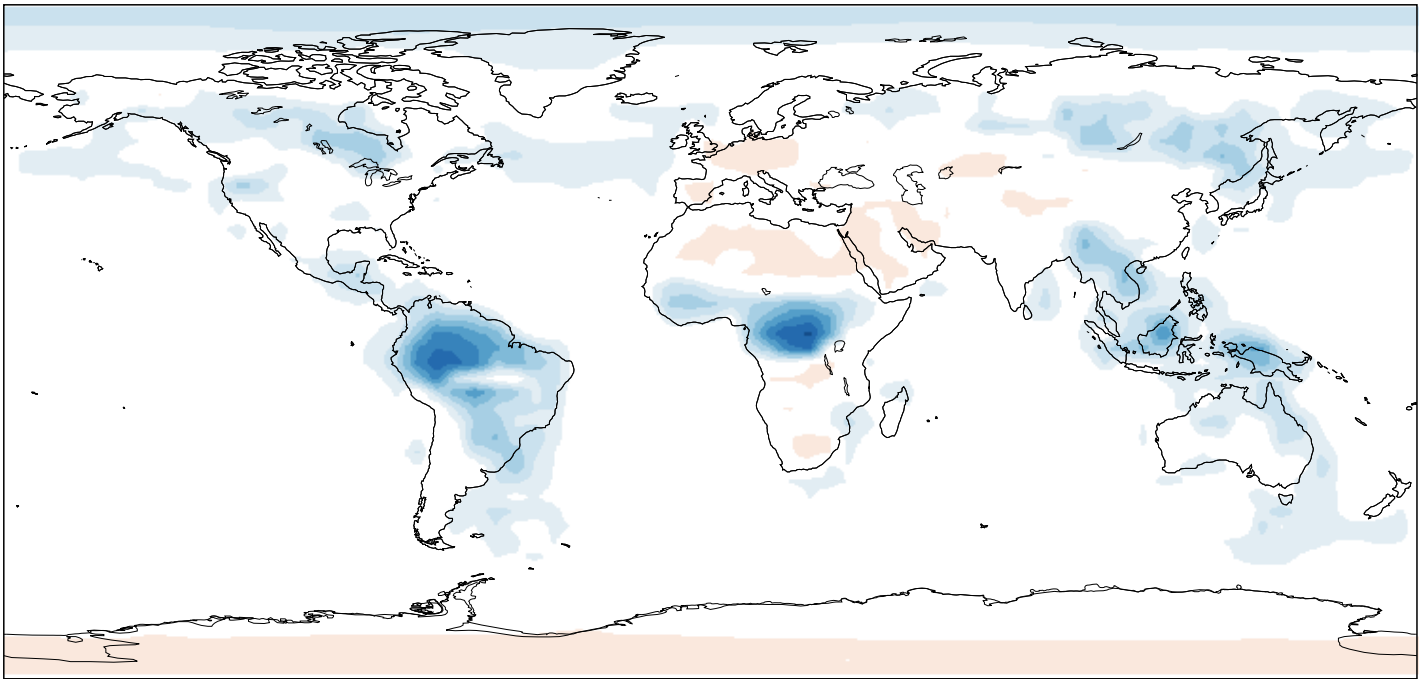
Page 30414 line ? (beginning of section 2.4.2): oxydant should be oxidant
Page 30415 lines 2-7: This is a confusing and awkward sentence. I'm not sure what you're trying to say here.
Page 30416 line 11: Replace "In" with "Due to"
Page 30416 line 12: replace "restrain to using" with "use"
Page 30418 line 19: replace "G2110" with " $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ "
Page 30422 line 1: either describe the "simple parameterization" or provide a reference
Page 30422 lines 6-9: It is not entirely clear what you are doing here. Of course 36 hours is between 24 and 60 hours, but aren't you looking at the diurnal variability? This sentence makes it sound like you are looking at one snapshot in the model (36 hours after initialization), and it is not clear to me what and why you are doing anything at 36 hours.
Page 30422 line 17: Should the "," between " HO_x " and " NO_x " be replaced with "and"?
Page 30423 line 1: explicitly define NO_y
Page 30424 title of section 4.1.2: "peroxide" should be "peroxide"
Page 30425 line 4: "excepted" should be "except for"
Page 30426 line 12: insert "the" between "is" and "dominant"
Page 30427 line 8: "terms if" should be "terms of"
Page 30430 line 2: Change "the impact is non-existing for" to "there is no impact on"
Page 30430 line 3: Put a "." After " H_2O_2 ". Then begin next sentence with "It is more visible"
Page 30430 line 14: "GEOS-CHEM" should be "GEOS-Chem"
Page 30431 line 6: "GEOS-CHEM" should be "GEOS-Chem"
Page 30431 line 7: change "than in Alexander" to "to Alexander"
Page 30431 line 17: "testes" should be "tested"

Remove the following sentence.

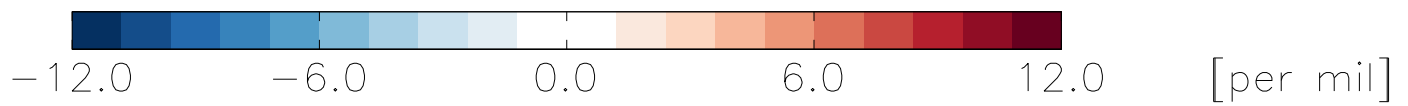
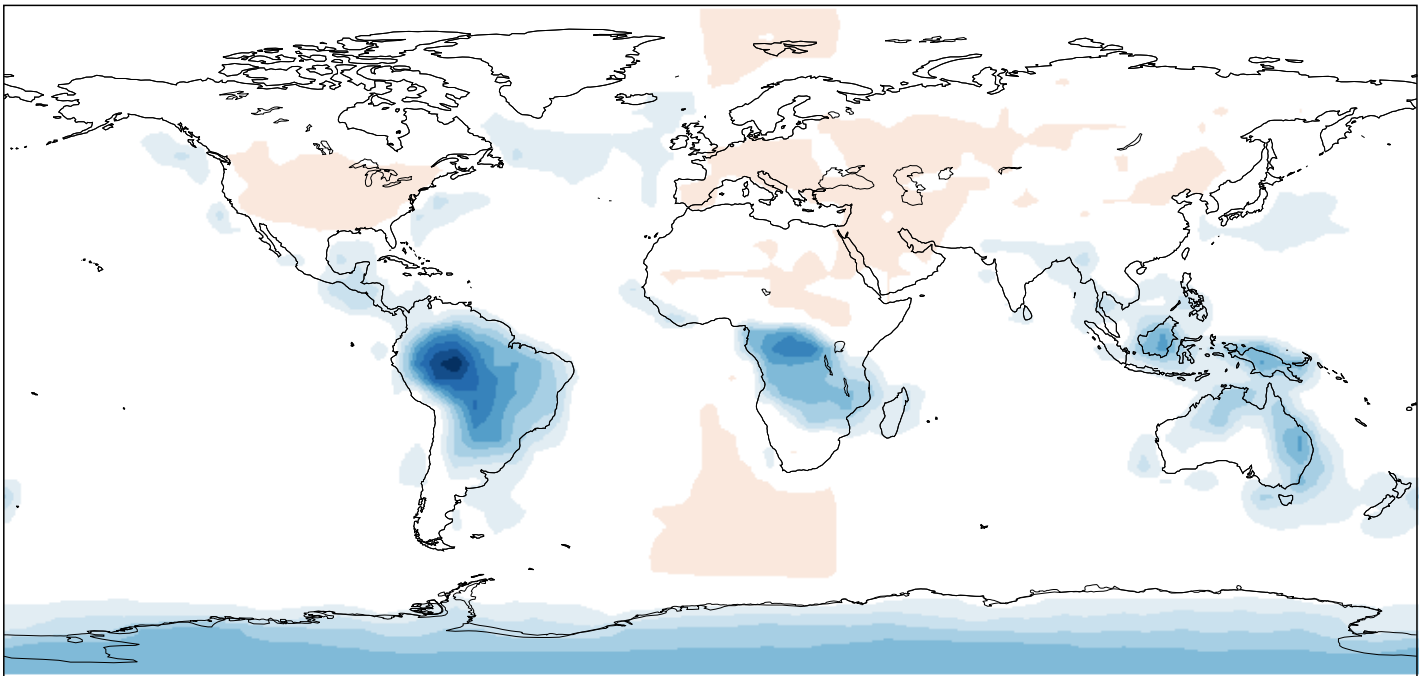
"First of all, general equations are derived from text-book physical principles." Of course they are, so this sentence provides no useful information. This statement sounds personal to me.

Table 5. Indicate ‰ units.

N_2O_5 or $\text{NO}_3 + \text{H}$ only $\Delta^{17}\text{O}(\text{nitrate})$ (JJA)

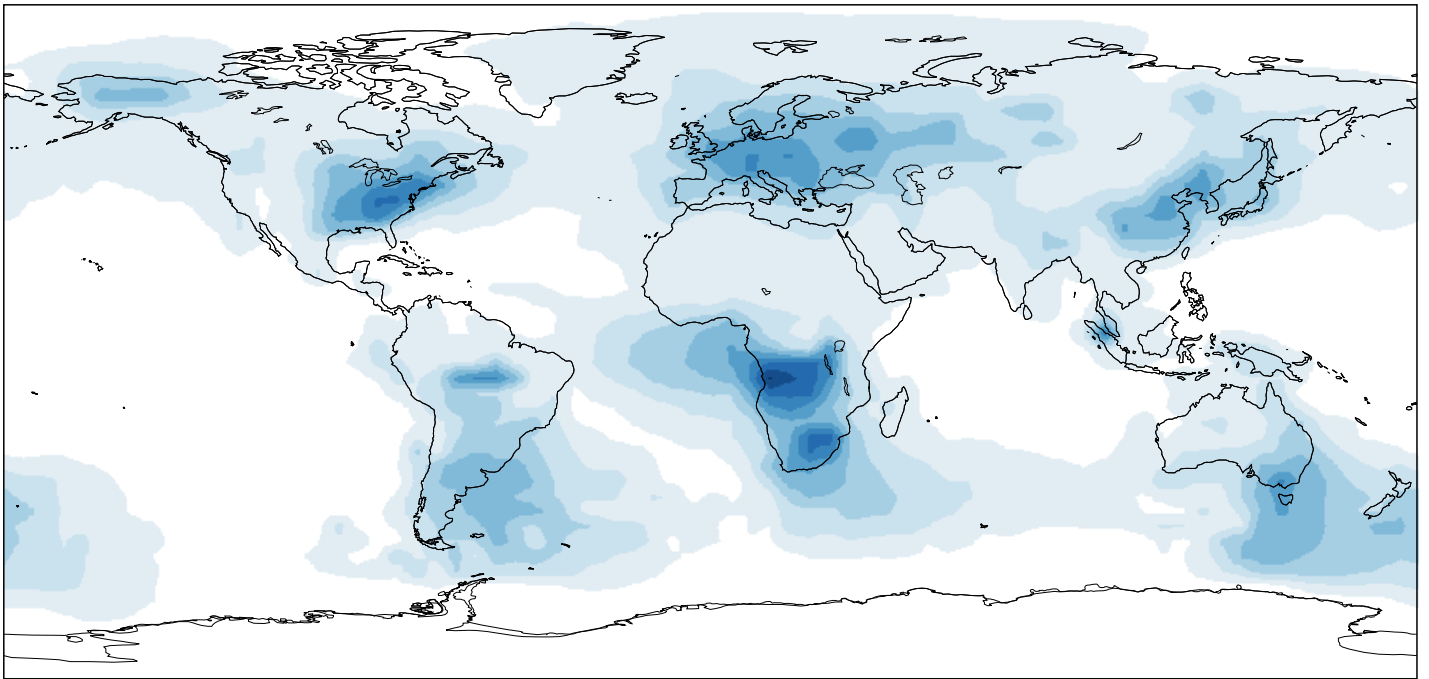


$\Delta^{17}\text{O}(\text{nitrate})$ (DJF)



Total nitrate

$\Delta^{17}\text{O}(\text{nitrate})$ (JJA)



$\Delta^{17}\text{O}(\text{nitrate})$ (DJF)

