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Geoscientific Model Development Discussions

Interactive comment on "i_NRACM: Incorporating ^{15}N into the Regional Atmospheric Chemistry Mechanism (RACM) for assessing the role photochemistry plays in controlling the isotopic composition of NO_x, NO_y, and atmospheric nitrate." *by* Greg Michalski et al.

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We would like to thank the two reviewers for their thoughtful and constructive comments and appolgize for the delayed response. We struggled for some time with how to shorten the manuscript (reviewer 1) while at the same time answering questions raised by reviewer. It is always a trade-off between clarity and brevity. We were following

Stockwell's original RACM paper format (model, mechanisms, test cases) to have a mirror comparison. We then realized that realized that 3.3 section is not absolutely relevant since there is no observational data to evaluate of each the test cases and that section 3.3 would be better as a stand-alone paper. There we can dig deeper into the issue brought up by the reviewers and include other effects (sunlight, emissions). Also it would allow us to make predictions that could be tested by observations, it is too bad we didn't think of that earlier! Therefore, we have cut 3.3 (8 pages), sections 2.4.4 and other text and reduced paper's length by 9 pages. This also resolves the many issues of the below by both reviewers. Thank the reviewers for guiding us to this change of course. Below we address the other reviewer's concerns.

The manuscript is overlong and could stand another read-through focused on eliminating redundant text and moving details to the SI. Section 2.4 for example, could be moved. I think upgrading section 2.4.4 out of section 2.4 is warranted. This section could also describe the Tuscon case.

No one knows about this article length better than the authors! See first paragraph

Figures 1, 4, 5 can be moved to the SI. A table is needed in the main text to summarize the scenarios in sections 3.1 and 3.2. It is too difficult to track what reactions are included or excluded from the different cases and quite frustrating to interpret axes like Fig. 12 where two different cases are subtracted. Fig 12 and Fig. 14 require y-axis labels.

See reply to comment 1.

Another suggestion includes moving sections 3.3.1-3.3.4 to the SI and instead using an abbreviated table to report the initial conditions and emissions of each scenario, with only the most important compounds from Table S8 (e.g. NO, NO2, HNO3, PAN, (and isotopes) and total VOC). See reply to comment 1

Regarding the case in section 3.4, I agree with the other anonymous reviewer that 48

hours may be problematic as it appears to be within the dynamic phase of the 5-day simulation examples in section 3.3. It would be prudent to run the model out to 5 days or longer to get a sense for the steady-state that will be reached. The samples are 24 hour PM collections. We based our 48 hour simulation based on an estimated lifetime of the airmass at the collections. At an average wind speed of 2 m/s and a 20 km diameter of the city (and urban island in the middle of the desert), air mass lifetimes are on the order of 3-4 hours. 48 is well beyond that accounting for possible stagnant air. The unfortunate limitation of the box model is that at true equilibrium, the HNO3 ïĄď15N will simply equal the NOx ïĄď15N. These are other issues we will address in the follow up paper.

How were the emissions for the Tuscon case applied? What temporal assumptions were made? What is the sensitivity to this? We assume constant monthly annual emissions throughout the year and day. This is the advantage of the Tucson site is the lack of industry and significant vegetation and that the emissions are essentially constant (mainly vehicles), we show this in a new supplement figure from a student thesis. Hourly emissions are another matter, but this is irrelevant given the sampling time of NO3- to which we are comparing (24 hr). The Stockwell model is not easily amendable to hourly changes in emissions. The second paper will give us the opportunity to explore this effect.

How are the assumptions with respect to the heterogenous reaction of N2O5 impacting the results in Fig. 19? This is small, the we have added another supplement showing daily PM mass for the year, which is 40 ug/m3 +/- 10 ug. Since the N2O5 fraction (10 %) is small to begin with and the N2O5 fractionation is not widely different than OH pathway the variation from N2O5 is small. Another issue we will explore in the follow up paper.

What is the expected impact from developments to this part of the mechanism in the future? We have embellished on this in the conclusion section

Are there significant concentrations of 15NH4 and 15NH3 in the atmosphere? If so, can this impact the measured δ15N data for PM2.5 and PM10?

The analysis technique for determining the ïĄď15N of NO3- is specific to NO3- only (and NO2-) My major concerns/comments are as follows: 1. Most of the reaction rate constants of the N-15 substituted molecules in the model were estimated by multiplying the general chemical reaction rate constant by the fractionation factor. This technologically is not a big issue, however, in some specific reactions, I think the authors oversimplified the treatments. Especially, for the case of OH + NO2aÌĂHNO3 reaction. The authors considered this is an EIE instead of KIE, as it is a third body reaction that contains two steps: firstly formed an activated *HNO3, and which can be deactivated to HNO3 or decompose to NO2 and OH. The authors stated the first step, OH + NO2 <-> *HNO3 is the dominant isotope step and that induces a large fractionation factor. But I don't quite get the point: if this is a EIE process, then during the lifetime of *HNO3 to HNO3, would an isotope equilibrium between NO2 and *HNO3 be able to fully established? The author should compare the rate of *HNO3 decomposition, and its rate of collision with M to form HNO3, if the decomposition rate is orders of magnitude larger than the collision rate to form HNO3, then the assumption of OH+NO2aÌĂHNO3 is an EIE with alpha of 40 permil is valid. Otherwise, the isotope effect caused by this reaction need to be reevaluated, as well as the entire model results as currently in the model this reaction accounts a large fraction of the overall isotope difference from NOx to HNO3. We agree that the NO2 + OH fractionation factor is uncertain. We can estimate this based on approximate lifetime of the activated complex and the reaction rate. The bimolecular collisional rate constant for NO2 + OH $\rightarrow$NO2OH* is $\sim$ is of 2 x 10-10 compared to the recently updated measured high pressure rate constant 6.3 x 10-11. This means formation and decomposition of the activated complex is 3 times faster than HNO3 production sufficient time for equilibrium of N isotopologues since they only require a single collision and separation to achieve equilibrium (unlike O atoms). Conceptually one can think of an ensemble of 1 x 106 NO2 molecules, with natural abundance isotopologues = air N2. The two isotopolugues collide with OH kf at

approximately the same rate, and disassociate kr by of calculated factor of 1.04 (0.96) then the activated complex ensemble will have isotopically equilibrated by this single cycle. We will explore this effect, and all sensitivity to all fractionation factors, in detail in the subsequent paper 2. The treatment of N2O5 hydrolysis: The model doesn't contain aerosol chemistry but considering the importance of N2O5 hydrolysis in nighttime HNO3 production, this has to be involved in the model. The authors treated this as a first order reaction to go directly as k*[N2O5] aÌĂ 2HNO3. This is a common method, but in order to get it right (so the isotopes are correct), the authors at least need to compare the production of HNO3 from this parametrized first-order reaction is realistic, i.e., it will dominate nighttime HNO3 production and account for a large fraction of total nitrate production in the system. This is because N2O5 hydrolysis is a dominant HNO3 production pathway, contributing to $\sim$ 40 % of total HNO3 budget which comparable with the OH + NO2 pathway in the daytime (Alexander et al., 2019 ACP). Unfortunately, from the limited figures in SI, it appears the nighttime HNO3 production is often flattened in the four simulation cases. If this is true, then the parametrization of the N2O5 reaction in the model is probably wrong. P.s., this is one of the reasons that I think more illustrating data/figure needs to be provided. To evaluate the isotope behaves in the model, the chemistry has to be first correctly simulated. So the authors need to first show the day and night HNO3 production and discuss whether the production close enough to the observations. As noted in the text the first order absolute rate constants are based on the current literature values, which are a function of aerosol surface area. Our plausible range of first order rate constants is based on these experiment/observational studies, therefore they cannot be "wrong" in the model unless the body of peer review literature is incorrect. Figure 13. Our kN2O5 = 1.0 s-1 is simalr to others such as Yvon et al. (1996, kN2O5 = 1.0 s-1), Riemer et al. (kN2O5 = 0.9 s-1). It is difficult to access the effect in simulations because much is happening, this was the point of figures 13 and 14. 3. Mass balance. As a box model, it is a closed system, so mass, as well as isotopes has to be conserved. Otherwise there might be something wrong with the model setup. So I think the authors should show a mass balance figure,

with the time evaluation of total N, as well as total N-15 in the model. This is important to evaluate the overall model performance. We agree but the figure would simply be a straight line of zero so aa figure would not be enlightening. We have added "These simulations were also used to test whether iNRACM achieve N isotope mass balance via S15N/S14N where the sums are the ending abundances of all N compounds. This resulted in d15N = 0 for all simulations." to page 8

4. I am curious why the model predict a large seasonal variations in d15N of HNO3 for the case of Tucson city, but in the four case simulations (i.e., urban, rural, forest and marine) there were minimum diurnal cycle in d15N of HNO3 especially in the last few days of the simulations. This is strange, as explained by the authors, the relative importance of NO isotope exchange versus Leighton cycle and OH reaction determined the seasonal cycle, but at the same time, won't be the shift of this relative importance from day to night larger than that in the seasonal scale? So why the modeled diurnal cycle is so small compared to the modeled seasonal cycle? In addition, the authors state the Tucson case d15N HNO3 was reported as 48 hours simulation result, I wondered what it will look like if for 4 or 5 days simulation, which is the typical lifetime of atmospheric nitrate. In other words, why picked 48 hours? Two things are happening during these simulations. The first is near instantaneous isotope fractionation during the photochemistry and the second is isotope mass balance. Similar to the simulations, the real world atmosphere will reflect these two competing processes. At the beginning of the simulations the isotopic change in secondary N compounds (NOy except NOx) is large because there is no initial concentration of these compounds and their resulting ïĄď15N is entirely due to the isotope fractionation factors. As the simulation progresses those NOy compounds that are stable and build up, HNO3 in particular will always approach the ïĄď15N of the NO emission by mass balance, ie by the end of the five day simulation 99% of the emitted NO has been converted to HNO3 and thus must approximately have the same ïĄď15N as the NO because is a closed system. In the real world the system is open, either due to deposition (wet/dry removal of HNO3) or advective transport. Our 48 hour choice was based on the size of the

city and a low average windspeed which would replace the regional air mass at least every 48 hours. A 5 day simulation is imposing a stagnant 5 day air mass over the city, which is unrealistic. The model highlight the importance of atmospheric lifetimes in controlling ïĄď15N of NOy. At very short lifetimes (post rainy day) the ïĄď15N should partition strongly, but with long lifetimes the values are controlled by mass balance, in particular long lived reservoirs like HNO3 or PAN. The annual trend is driven by hours of daylight. Something we will explore in detail in subsequent paper. 5. During the day time, the model result indicates that NO-NO2 isotope exchange is very small compared to the Leighton cycle and the OH reaction. I just wanted to see more data to prove this, i.e., can the authors compare the rate of exchange versus the reaction rates of the Leighton cycle and OH reaction during the daytime? The daytime results show NOx exchange lite is similar to or less than Leighton, but is condition dependent. Both these lifetimes are on the order of 100 sec during peak sunlight and moderate NOx mixing rations (few 10s ppb). The lifetime of NO2 with respect to OH + NO2 is several hours at peak sunlight. The question is the exchange relative to Leighton which will be a function of NOx mixing ratio and changing j coefficients. Evaluating this is the purpose of figure 8 (in original). Those show at high NOx exchange is still dominant even during the daytime (8a), but Leighton becomes dominant at low NOx during day, and slowly achieve equilibrium at night (8c) At steady state -NO2/dt = NO2/dt = 1/jNO2 = 1/(.001s) = 100 s -dNO2/dt = HNO3/dt = 1/k[OH] = 1/(6.3*10-11)(2.5 x106) = 6350 s 6. The last, I suggest to authors to add another case simulation, that in the middle of 5 day simulation, varying the d15N of emitted NO from 0 to, e.g., 10 permil, and see how the isotopes of NOy in the system vary. This will be interesting as in real environment, NOx emitted from different sources and its isotope vary all the time. This would be interesting, but we avoid this simulation for two reasons. The first is that the entire objective of the paper is to show potential ïĄď15N changes in the absence of any ïĄď15N "sources effect". This objective is laid out on page 4, lines 34-42. Adding source variation would add layers of complexity and add confusion. Second the emissions in this box model are at a fixed rate (and ratio) and would re-

quire reprogramming the model to change on a $\frac{1}{2}$ hour basis (time step) and there is not much current evidence on how these ratio emissions would values change hourly in the real world. This paper we explicitly say that this is only evaluating the photochemical effect on ïĄď15N . We have new papers in review that address the source effect, and another that will assess source (and mixing) and chemistry combined. The following are some general comments: 1. P6, line 38-39, this approach has also been mentioned by Bao et al. 2015 (https://doi.org/10.1016/j.gca.2015.07.038) and He et al. 2020 (https://bg.copernicus.org/preprints/bg-2020-120/). The quantum approach goes all the way back to Urey, Mayer, and Biegelisen! and is common knowledge in the field 2. Section 2.3.1, for the sensitivity tests in this and other similar sections, it is unclear how many chemistry are involved. For example, in figure 2, was nighttime chemistry involved? If yes, why d15N of HNO3 stays the same at night but when d15N of NO2 is very low? We are not fully understanding the reviewer's question. In every sensitivity test all N reactions are replicated and all a=1 except for one reaction. This is repeated for each N reaction. For each of those 96 simulations we test if NOx, HONO, or HNO3 ïĄď15N changes by 1 permil or more. Fig 1 (1) shows a non-sensative reaction (NO3 + NO) and Fig. 2 shows a sensitive reaction (NO2→NO + O). How ïĄď15N is partitioned the way they do is a complex function initial concentrations, emission rates, simulation length, isotope mass balance. . .etc. These are discussed in the subsequent sections. 3. Section 2.3.1, the second paragraph, the discussion on daytime NO3 and NO2O5, I think this can be made less complicated to just show the mass of these molecules during the daytime, their negligible mass during daytime is the reason of their negligible isotope effects. We agree that NO3, N2O5 is low at night, but this is not the intent of the section. The intent was to show that "sensitive/nonsensative" classification of the reactions was only valid using the NOx, HNO3, HONO as the test molecules. The intent of this section is to show that reactions producing/consuming NO3 and N2O5 could impact their ïĄď15N values (ie. NO3 photolysis) but not necessarily the NOx,HNO3, and HONO. This effect would be independent of their concentration. The point being that IF you wanted to model NO3 ïĄď15N then one would need the more exotic frac-

tionation factors, but not for the main compounds. 4. Section 3.14, what is eplison-48? If you meant the NO2 + Oh reaction, won't it be e-39? Yes, this was a typo! 5. Section 3.3.5, line 35: .d15N(NO-NO2) = + 20 ‰ but From Figure 15, I didn't see this 20 per mil difference in early nighttime of 1/2 and 6/2; 6. Same section, line 37: Shouldn't be Jan. 2 and Jun 2? 7. Same section, last sentence: "conditions it requires about 6 hours for NOx to achieve full isotopic equilibrium", I doubt this. First, Walters et al. paper in GRL 2016 actually shows the exchange is fast. In addition, in this simulations, it seems the d15N difference between NO and NO2 reach the maximum by late night, but this could be a result of mass balance, i.e., when almost all NO is converted to NO2, and d15N of NO2 approaches to zero (the starting value), and by mass balance NO will be very negative. It will be much more helpful to understand this if the fraction of NO overnight can be plotted. This issue also exists for all other case simulations. In addition, the model has continued NO emissions with d15N of zero (not a completely closed system), how does this continued add-up of NO affect the isotopes of the system? 8. P28, Line 35-36: can you pull out the rate of isotope exchange between NO and NO2, as well as the rate of photolysis and Leighton cycle at daytime and night? it is surprising that at daytime isotope exchange appears to be negligible. 9. P29, Line 11-12, what is SI Fig. X? and there is no OH figure in SI. These are all explainable, and will be addressed per comment reply 1.

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