

1) whether the model predicts nitrate qualitatively consistent with observations, e.g., in the model, how much daytime nitrate production vs how much nighttime production, and is the relative importance the same as observations?

2) in the Tucson validation case, how is nitrate concentration in the model compared to the observations? the model reproduced the observed $\delta^{15}\text{N}$ very well, indicating nitrate in the city (observations) were mainly from local conversion of NO_x to nitrate. It would be simply pull out the model predicted nitrate mass (seasonal pattern if it is difficult to convert the modeled nitrate production to air concentration and compare with the observations directly) and compare with observations. In other words, if the model can't produce the mass right (it is often the case even for a chemical transport model), something strange may happen and need to be clarified.

Thank you for the comment. Some of these concerns were addresses in early versions but were deleted to limit manuscript length, but can be added back with elimination of the case studies. The reviewer is asking two questions that are important and subtly different. The first is whether the mechanism (model) is accurately capturing photochemistry. The mechanism itself has been reviewed and validated by numerous studies over the past 20 years so we will not address that here. However, did our modification alter the validity of the mechanism? To test this, we ran the 24 test cases studies described in Stockwell et al 1997, without our addition of aerosol reaction or O_3 deposition, and compared O_3 predicted by RACM and iRACM and they matched identically. Thus our addition of 96 isotopologue reactions is not impacting the oxidation chemistry of RACM. We added the below text and a new Supplementary material figure.

P. 7 text added

We also tested whether the addition of ^{15}N isotopologues had any effect on the RACM's predictions of trace gases over time. Plots of mixing ratios of trace gases such as HNO_3 and O_3 predicted by RACM versus those iRACM run under the same conditions (see Stockwell's 24 simulation tests) yield a slope of 1 with an $R^2 > 0.99$, which expected since the addition of ^{15}N compounds is only about 0.3 % of total NO_x and thus should not differ from the RACM predictions.

The second reviewer comment hints at something often ignored when using 0-D box models and that is whether the model can predict real world trace gas concentrations? Since RACM and other mechanisms are usually validated by chamber studies where emission, deposition and dilution are often not relevant (chemistry in an inert box) they can be a challenge to use when comparing to real world trace gas concentrations. This is important since the NO_y $\delta^{15}\text{N}$ is reflecting different isotope fractionations in different oxidation pathways. We spent a spend time examining this at the beginning of the study when simulations would produce O_3 mixing ratios that were unreasonable based on observations, which in turn amplified oxidation state of the model. We address this with the added text and a new figure in Supplement, which is also used to assess the accuracy of the Tucson simulations.

P 16.

2.4.4 Addition of O₃ deposition to i_NRACM

Photochemical mechanisms such as RACM are validated by comparing model predictions with observed trace gas concentration evolution in chambers studies, which has its limitations. For example, Stockwell et. al. compared RACM, RADM2, and SPARC mechanisms ability to predict trace gases concentrations (e.g. O₃, NO₂, toluene) with those observed in chamber experiments (see Stockwell et. al., Fig 3-9) and achieve good agreement between the model and experiments. These experiment-model comparisons essentially validate the rate constant assumptions in the chemical mechanism. Box models are, however, limited in their ability to predict real world concentrations because many do not account for pollutant deposition (dry or wet) since these are handled when the mechanism is incorporated into 1, 2 and 3D transport models. Similarly, dilution by of trace gases due to vertical (or horizontal) transport is typically not incorporated into 0-box models. This can lead to the buildup (or depletion) of key oxidants, particularly O₃ (see Fig. 6 in Stockwell et.al.). This in turn will significantly alter NO_x oxidation pathways, and since the δ⁵N in i_NRACM is effectively a function on changing oxidation pathways, this would impact i_NRACM ability to accurately predict the observations of δ⁵N in the real world. In order to eliminate this bias, we added a O₃ deposition reaction and adjusted the rate until O₃ mixing ratios were in line with typical suburban mixing ratios (20-30 ppb) and exhibited a typical O₃ diurnal mixing ratio variation, low nighttime/high midday, that are observed in most environments (Fig S2). This results in simulated daytime maximum OH concentrations on the order of ~ 8 x 10⁶ molecules cm⁻³ and daytime average of ~ 2 x 10⁶ molecules cm⁻³ (Fig S2) that are typical of overserved concentrations in urban and suburban environments (see refs. in the review by Monks, 2005). This gives us confidence that i_NRACM is accurately capturing boundary layer photochemistry and can be used to predict δ⁵N in NO_y compounds.

As to the reviewers question about day/night HNO₃ production we added the following.

P. 27

Analysis of hourly HNO₃ production (in June) revealed that ~80% of HNO₃ is produced in the daytime, mainly by the NO₂ + OH reaction and 20% is produced during the night (N₂O₅ heterogenous hydrolysis). The model reproduces O₃ and NO_x concentrations rather accurately (Fig S2) but HNO₃ concentrations that are about 10 times the PM NO₃⁻ concentration. This is not surprising because the 0-D models do not account for HNO₃ deposition, its dilution as it mixes into to the top of the boundary layer, or partitioning between aerosol and the gas phase. Indeed, seasonal differences in boundary layer height alone can dilute by a factor of 5 or higher [Riha, 2013].