

Interactive comment on “A kinetic chemistry tagging technique and its application to modelling the stable isotopic composition of atmospheric trace gases” by S. Gromov et al.

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General comments

We are thankful to the referees for the constructive comments that let us to improve the manuscript leading to the revised version. We acknowledge the great attention paid to the complex layout and computations by the Referee #1. Since the major suggestions of both Referees are congruous, we summarise all replies in the current comment.

In addition, we have slightly revised the structure of the document. The details of the tagging configuration file are moved to the supplemental material. Appendix C has been replaced by the clarification of the isotope transfer formulation (see below). A few definitions in the isotope notation and terms and respective references in Appendix B have been corrected. The English grammar will be improved in the revised version of the manuscript. Please note that the formulae numbering has changed. Below we proceed with the comments on the suggestions made by the Referees (denoted as *R#1* and *R#2*, respectively).

R#1: Section 3 should start with the examples. When introducing the equations in the subsequent sections, the examples would be of great help, if the variables (incl. their values) are directly linked to the example.

As it was suggested by both referees, we have extended the sections with the relevant examples to the chemical and mathematical formulations, where it is applicable. Thus, the extended examples from Sect. 3.6 were used.

R#1: A table of the used variables including the description and units would be helpful.

The used variables are listed in the appendix A, Table A1, including the units. Thus, this comment is not entirely clear to us. Nevertheless, we point the reader to this table in the text of the revised manuscript in the introduction.

R#1: Could you say something about the solution of the tagging ODE: Stability, Attractivity? I.e. Do you always get the same equilibrium solution independent from the initial condition?

Unfortunately, there is no room in the paper for the discussion of the numerical specificities, e.g. tagging ODE solvers' asymptotical properties and stability criteria. We mention that the solvers incorporate schemes capable to handle stiff systems that are custom in kinetic chemistry calculations. This means that each solver employed for the tagging integration ensures that the solution is asymptotically stable. Ordinarily, different solving methods lead to slightly different equilibrium solutions for tagging, i.e. *classes fractions*, depending on the precision chosen. That is similar to what one discovers simulating the *species concentrations* in regular chemistry with different solvers. The regular chemistry (hence, the approximated reaction rates as well) is calculated by KPP with the Rosenbrock solvers that have excellent stability properties (Sandu, 2006). Due to the formulation, the tagging integration intrinsically produces (again, within the given precision) the same total concentrations as in the regular mechanism. We find also, that errors in simulated *class fractions* due to the tagging integration itself are negligibly small compared to those introduced by the rates approximation in Eq.(10). Hence, only the regular mechanism integration time step τ is decisive for the tagging precision.

R#1: Some clarifying statement would be helpful: this tagging is a diagnostic in a sense that it helps to diagnose the regular chemistry. However, the method itself is based on prognostic equations.

We agree with this elucidation; the corresponding statement is added to the end of Sect. 2.4.

R#2: I think the discussion of tags and tracers should distinguish these by saying that what you call 'tracers' should not affect the chemistry, as they are subsets of species that are solved in the mechanism. Where as isotopic compounds are a part of the complete mechanism.

This comment is not completely clear to us, as it appears that we are using not the same terminology as the Referee #2 with respect to the term "tracer". Regarding a "tracer", we imply a more conceptual, or informational definition (Jöckel et al., 2008) of a set of properties for a single species, either measurable in reality or not. For example, a tracer is defined by its data contents (i.e., its abundance) plus additional meta-information like for instance the measuring units (of its abundance), the molar mass, a switch, if the tracer should be transported by large-scale advection, etc. The information of the species concentration (in the correct measuring unit) is used for the chemistry calculations, the molar mass, in contrast, not, however. The tagging is a similar concept within the chemical kinetics: we apply imaginary "tags" to the tracers, separating them according to the isotopic substitution, and the ratios of the rare to abundant isotopes go into the calculations. Thus the "tag" is only an informational property (meta-information), while the concentrations of the classes distinguished by tags are solved for in the mechanism. The latter, in particular, can be the concentrations of the different isotopic compounds.

Nevertheless, we are confused with the terms in the statement "what you call 'tracers' should not affect the chemistry, as they are subsets of species that are solved in the mechanism". We guess, if the tracers are the subsets of species that are solved in the chemical mechanism, in our terminology it should read "what you call 'tagged tracers' **should** affect the chemistry, as they are subsets of 'regular tracers' solved in the mechanism", which then is correct.

Finally, to avoid any confusion we refrain from using the example comparing tags with tracers in the revised version of the manuscript, as it is apparently misleading due to the not well-established terminology.

Specific comments

R#1: page 214 line 16 The specific weight (or I assume molecular mass) q only takes into account the regarded element not the whole molecule?

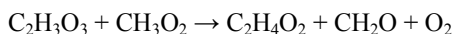
q is not the molecular mass. Apparently, the following sentences try to explain this, but not very clearly. The misunderstanding arises from the misplaced word "weight", which, if replaced by "weighting" (i.e., relative importance) clarifies what we mean. We will do so in the revised manuscript and reformulate:

The weightings q_e and q_n are taken from the molecular elemental composition of the educts, e.g. number of C or O atoms, depending on the isotope considered. Thus the branching ratios in (4) define a proportional isotope content share of both educts in the products composition.

We give the example in the text and in the following. The stoichiometry of the reaction implies the correct transfer of all atoms from the left to the right hand side, i.e.

$$q_e + q_n = \sum_{p \in P_r} s_{rp} \cdot q_p$$

for every element simultaneously. In reaction



the abovementioned condition for carbon is

$$2 + 1 = 2 + 1 .$$

For oxygen, it becomes

$$3 + 2 = 2 + 1 + 2 ,$$

respectively. The ratios η for the carbon isotopes are

$$\eta^{\text{C}_2\text{H}_3\text{O}_3 \rightarrow p} = 2/3, \quad \eta^{\text{CH}_3\text{O}_2 \rightarrow p} = 1/3 ,$$

but for oxygen isotopes these are

$$\eta^{C_2H_3O_3 \rightarrow p} = 3/5, \quad \eta^{CH_3O_2 \rightarrow p} = 2/5.$$

Above p denotes the products. Similarly to the current Sect. (2.3), we clarified the terminology in Sect. (3.2) with respect to the explanation of the weightings q (i.e. not masses, but number of atoms of the element in consideration in a molecule).

R#1: page 217 l 18-20. I am puzzled by this sentence. Probably k_r should read A_r in line 18? Otherwise eq (10) would lead to $k_r=A_r$?

We admit that this sentence may mislead the reader to understanding k_r as a constant. In fact, k_r varies within the regular chemistry internal integration, and A_r is simply an average of k_r over the integration time τ . We reformulate this part of the paragraph as follows:

Therefore, the final pair rates (Eq. (5)) have to be derived *a posteriori* from the integral value of k_r . In a first approximation, the estimated reaction rate A_r can be assumed to be constant throughout the integration time step:

$$A_r = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} k_r dt, \quad (10)$$

$$k^{e \rightarrow p} = \sum_{r \in R^{e \rightarrow p}} \eta_r^{e \rightarrow p} \cdot s_{rp} \cdot A_r$$

Here A_r is an average value of the regular reaction rate k_r over the time step of length τ . Such a primitive approximation ensues from the fact that the exact evolution of the reaction rates in the regular system during its internal integration procedure is not known.

R#1: page 224 Why is q_p/q_e "the probability of the rare isotope to be transferred to the current product" (which is again a rare isotope?) I have difficulties to understand the idea behind the formula. (Well, after I saw the examples, I think I got it. If the whole text is better linked to the examples, this comment will be obsolete.)

The term "probability" in this case is used to show that the creation of the minor isotopologue takes place unconditionally. Actually, this is a scaling term determining that exactly one minor isotopologue is created (see the explanation in Appendix C).

R#1: page 225 line 1: It would be helpful to see the calculation, either in the appendix or in the supplement.

We sketch the calculation in Appendix C. Generally, this is rather a detailed example on the transfer of the different isotopes in case of reaction of the minor isotopologue. The calculation is thus presented simply to show that the isotope balance is correct.

R#1: page 226 eq (15) 2nd line one 'maj' of Cb from the left side of the eq, should be moved to the right side of the eq.

Thank you, we will correct this in the revised manuscript.

R#1: page 229: The examples are very important for the understanding of the methodology! I suggest to change the order in chapter 3 and to start with these examples. Further there should be a direct link between the numbers in the example and the variables in the previous sections. So, if the order in section 3 is changed, there could be a reference to the examples in the description of the methodology, e.g. $q_e=...$ $q_n=...$ in the 1st example of section 3.1.

We have changed the order of the examples and extended the formulations in the respective sections.

R#1: page 231: eq 19: I was confused by the symbol e -, but it's probably a double "-" ?

This is indeed wrong, perhaps caused by the formula editor. The system (19) contains 3 lines, thus the second line was broken by the minus sign. The symbol e should be there, it is the index of the educt in the rate matrix. Thus $J_{p,e}$ denotes the pair rate between the educt C_e and the product C_p . We have reconstructed this equation in a more comprehensible form.

R#1: page 231: eq (20), again an example would be nice. So if $16O_2$ is regarded than $q_n=2$ and since you only consider 1 replaced O atom the rare chi is multiplied by $1/q_n = 1/2$.

An appropriate example is added.

R#1: page 232: For consistency reasons: the 1 in eq (21) should be bold.

Most probably this is a misprint from the conversion of the formulae. We will correct it.

R#1: page 233: Can you explain more detailed, why the equilibrium isotope effect introduce the deviations but not the 'normal isotope chemistry'? If I understand it right then MECCA produces a concentration c_n of specie C_n at time $t+\tau$. MECCA-TAG produces concentrations $\hat{c}_{n,maj}$ and $\hat{c}_{n,min,i}$ for time $t+\tau$. I would have expected that the schemes give $\hat{c}_{n,maj} + \sum_i \hat{c}_{n,min,i} = c_n$. This does not seem to be the case, which needs to be explained in more detail. It would be helpful, if (e.g. in the appendix / supplement) the authors could show mathematically that this holds or doesn't.

Thank you, the statement on page 233, line 15 apparently must not mention the equilibrium isotope effects. The trait of the isotope exchange is indeed in that it does not alter the species concentrations, but the isotope composition. One can note that directly from Eq. (24), where the derivatives for the major and minor isotopologues are adjusted with the equal non-zero term γ , if the isotope exchange takes place. The ratios of the minor to major isotopologues are affected by the isotope exchange, but not their sum. To proof that, we may simply sum all (major and minor isotopologues) derivatives so that γ cancels out.

The 'normal isotope chemistry' introduces deviations only if kinetic isotope effects in the regular reactions are considered. Otherwise, the sum of the concentrations calculated in the tagging system and MECCA are identical (within the numerical precision).

R#1: page 234: The re-scaling eq. (25) means that the left side is newly defined?

Correct. That is clarified in the revised version. In the Eq. (25) we change the equation sign to the "left arrow" sign, thus denoting the procedural form of the correction:

$$\begin{aligned} \hat{c}_{n,maj}^{(t_0+\tau)} &\leftarrow f_n^{maj} \cdot c_n^{(t_0+\tau)}, \\ \hat{c}_{n,min,i}^{(t_0+\tau)} &\leftarrow f_n^{min,i} \cdot c_n^{(t_0+\tau)} \end{aligned}$$

R#1: page 240 HL LL, it could be mentioned that this means high / low latitude ? (also in Fig. caption).

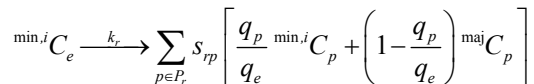
The respective sentence was changed to: "To assess the sensitivity of the mechanism to the OH level, the box was simulated in two distinctive regimes of OH seasonality emerging in the box positioned at the NH latitudes of 70°N (high-latitude setup, HL) and 30°N (low-latitude setup, LL)." The caption of Fig.5 is detailed as well.

R#1: page 253 l 18 "JJ."

Corrected.

Appendix C. Isotope transfer calculation

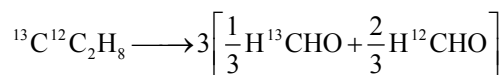
Below we elucidate the isotope transfer in the system (13). Consider the reaction of the rare isotopologue (line 2) in the Eq. (13):



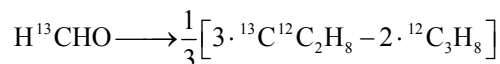
At the left hand side (LHS), an isotopologue possessing q_e isotopes of the element of interest is reacting. We consider the case when q_e is greater than unity; hence, the reacting isotopologue carries one rare and (q_e-1) abundant isotopes. For example, for the rare ^{13}C -isotopologue of propene (C_3H_6), $q_e=3$ and the isotopologue composition is $^{13}\text{C}^{12}\text{C}_2\text{H}_6$. Now, consider a case when the right hand side (RHS) has a single product C_p , with the number of the isotopes q_p . The stoichiometry condition (12) requires that $s_{rp} = q_e/q_p$. Three cases are possible then:

- 1) $q_e=q_p$, i.e. number of isotopes is equal in the educt and the product, and $s_{rp} = 1$;
- 2) $q_e>q_p$, i.e. the product species pool receives one rare and (q_p-1) abundant isotopologues;
- 3) $q_e<q_p$, i.e. the educt is incorporated into the product.

For the case 1), the transfer of the rare and abundant isotopes is unambiguous. In the cases 2) and 3), the stoichiometric coefficient is not equal to unity to create the same number of isotopes redistributed in the product molecules. Noteworthy, the LHS has only one rare isotope, thus only one rare isotope can be created at the RHS. The additional coefficient q_p/q_e next to the product minor isotopologue in the RHS ensures that; thus not more than one rare isotope is transferred as a part of one minor isotopologue. As an artificial example for the case 2), if a ^{13}C -propene isotopologue produces formaldehyde molecules (HCHO), then $s_{rp} = 3$ and only one of these HCHO carries ^{13}C isotope, the rest two acquire the abundant ^{12}C from propene:



The case 3) is somewhat intricate. Imagine, for the example only, that now HCHO produces propene. The stoichiometric coefficient in this case is $s_{rp} = 1/3$, i.e. one needs to assemble three carbons from the formaldehyde molecules to create C_3H_8 . But we allow the minor isotopologue of propane to carry not more than one ^{13}C atom, thus the rest atoms have to be ^{12}C . These can be taken only in from of the propene major isotopologues, so that the overall isotopic ratio of the propene pool is preserved. Conclusively, for this example of case 3) it follows:



Again, the coefficients require that only one rare isotopologue is created, and this isotopologue is completed with the abundant isotopes from the major isotopologues.

This argumentation can be straightforwardly extended to the cases when the RHS has more than one product. Finally, we calculate the number of rare and abundant isotopes at the LHS and RHS in the general formulation (13). First, we select the rare isotopes only:

$$n_{rare} = \sum_{p \in P_r} s_{rp} \frac{q_p}{q_e} = \frac{1}{q_e} \sum_{p \in P_r} s_{rp} q_p = 1$$

assuming one rare isotope in each minor isotopologue and recalling stoichiometry condition (12). Similarly, the number of the abundant atoms at the RHS is, respectively

$$n_{abu} = \sum_{p \in P_r} s_{rp} \left[\frac{q_p}{q_e} (q_p - 1) + \left(1 - \frac{q_p}{q_e} \right) q_p \right] = \frac{(q_e - 1)}{q_e} \sum_{p \in P_r} s_{rp} q_p = (q_e - 1)$$

taking into account that the major and minor isotopologue of the products have q_p and (q_p-1) abundant isotopes, respectively. Thus, the total number of transferred isotopes is q_e , of which one is rare.