

Response to Referee Comments

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Reviewer comments are shown in black. Our responses are shown in blue and indented. Quoted manuscript text is further indented; within quotations, added text is shown in **bold**, deleted text is shown in ~~striketrough~~, and unchanged text is shown in normal font. Each quotation gives the line numbers in the original (orig.) and revised (rev.) manuscripts.

Response to RC1

The manuscript titled “GEOS-Chem-hyd: enabling source-oriented sensitivity analysis with GEOS-Chem” presents the development of a new sensitivity calculation method using hyperdual numbers in the widely used GEOS-Chem chemistry transport model. The authors provide background on hyperdual numbers, use a 1-day simulation to evaluate the model’s sensitivities to finite difference sensitivity approaches, and apply it in 1-week simulation to demonstrate its capabilities.

As the authors advocate, source-oriented sensitivities of atmospheric composition to emissions (and other parameters) can be a very valuable tool for policy-making, and as a result this development is a very interesting one. The paper is structured well, and clearly written

- We would like to first thank the reviewer for this accurate summary and for the favorable assessment of this work.

Simulation length: What was the decision-driver for the two choices: 1-day evaluation, 1-week application?

- **1-day evaluation.** The 24-hour episode was chosen to verify the implementation rather than to support scientific conclusions. It spans a full diurnal cycle, so the evaluation includes the day–night transitions in photolysis and chemistry where implementation errors commonly appear, while keeping the several finite-difference simulations needed for comparison computationally tractable. The GEOS-Chem adjoint was verified in the same way, with finite-difference tests over one-day and one-week simulations (Henze et al., 2007).
- **1-week application.** The one-week application was chosen to limit computational cost at this stage of development, not because of a limitation of the method. To show this, we extended the restart capability to the non-real components and extended the application to four weeks (August 1–28, 2019). Figure 8 and Sect. 3.3 now present the four-week results, and the archived code includes the restart capability.

L. 476–477 (orig.) → L. 523–525 (rev.): GEOS-Chem-hyd is archived at <https://doi.org/10.5281/zenodo.16575028> **16575027** (Akinjole and Capps, ~~2025~~ **2026a**). Both the GEOS-Chem and the GEOS-Chem-hyd models are under MIT licenses. The input data configuration for the simulation experiments is available at <https://doi.org/10.5281/zenodo.16575028> **22699829** (Akinjole and Capps, ~~2025~~ **2026b**).

- We added the following sentence to Sect. 2.2:

L. 167–169 (orig.) → L. 185–187 (rev.): Additional diagnostics were added to obtain the non-real components for species concentrations and aerosol mass using the same structure as those of the real components. **Likewise, the restart capability was extended for the non-real components to enable sensitivity propagations for longer simulations.**

- We updated Fig. 8 with the four-week simulation and revised its caption (L. 410–413 (orig.) → L. 449 (rev.)):

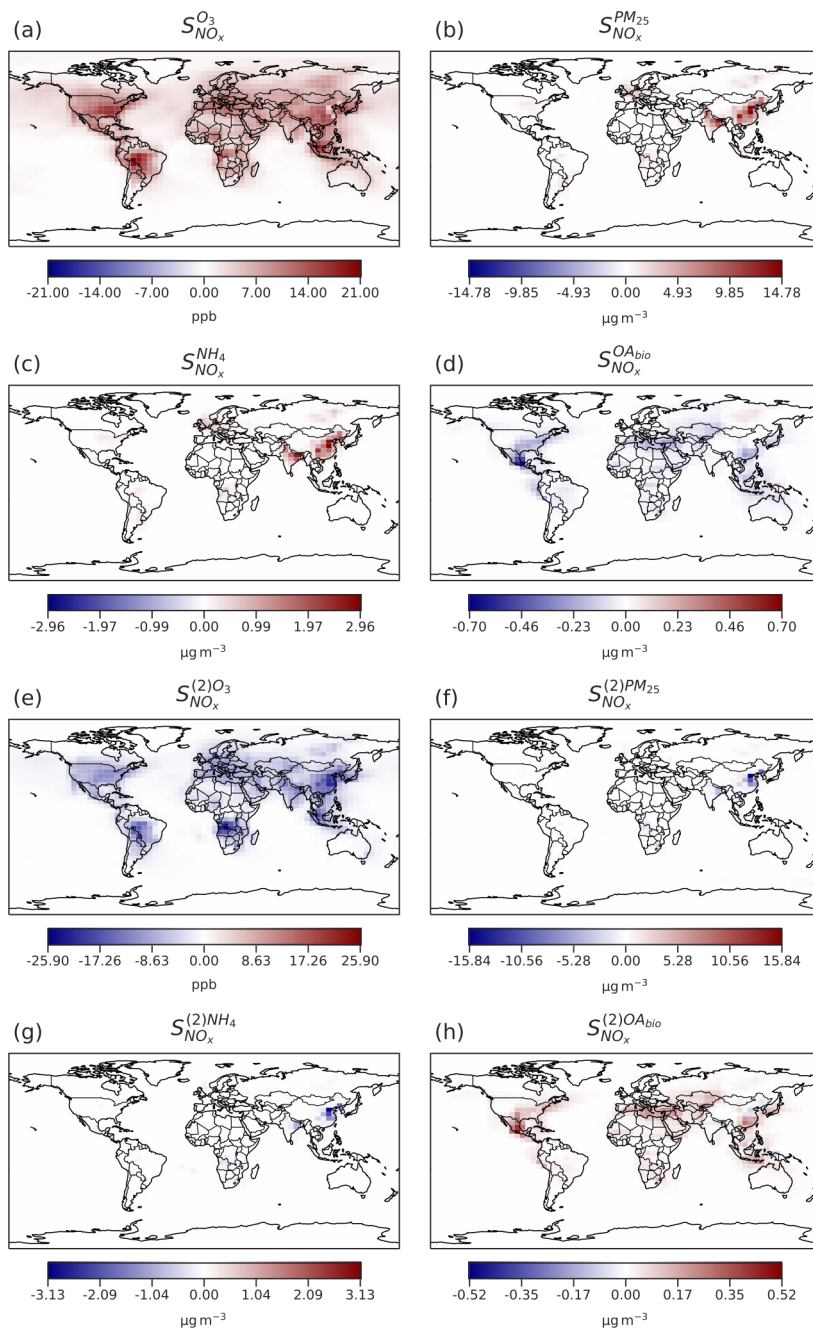


Figure 8. First- and second-order semi-normalized sensitivities of time-averaged O_3 , $\text{PM}_{2.5}$, NH_4^+ , and OA_{bio} concentrations with respect to NO_x emissions on the ground layer for a 4-week simulation. Panels (a–d) show the first-order sensitivities and (e–h) show the second-order sensitivities.

- The four-week average shows a more spatially coherent positive response of O_3 to NO_x than the first week alone. In particular, the negative first-order sensitivities over industrial eastern China in the first week are not sustained over the four weeks, so we removed the discussion of NO_x titration in that region from Sect. 3.3. The revised opening of Sect. 3.3 and the discussion of the second-order effect on O_3 read:

L. 377–380 (orig.) → L. 415–419 (rev.): **To demonstrate the practical value of simultaneously calculating first- and second-order source-oriented sensitivities, the effects of domain-wide NO_x emissions on concentrations were quantified with a single GEOS-Chem-hyd simulation of August 01–28, 2019. The time-averaged, first- and second-order semi-normalized sensitivities of ground-layer O_3 , $\text{PM}_{2.5}$, ammonium (NH_4^+ , and biogenic organic aerosol (OA_{bio}) concentrations to domain-wide NO_x emissions provide adequate information for assessing how a fractional change in domain-wide emissions would impact the concentrations in any ground layer grid cell (Figure Fig. 8). →**

L. 401–413 (orig.) → L. 428–447 (rev.): The second-order sensitivities, $S_{\text{NO}_x}^{(2)\text{O}_3}$, are predominantly negative (**Fig. 8e**), indicating a ~~convex~~ **concave** nonlinear relationship. Accordingly, first-order estimates alone would ~~indicate~~ **underestimate a larger** the influence of NO_x emission reductions on O₃ concentrations ~~than~~ **but would overestimate** ~~the influence of NO_x emission increases on O₃ concentrations~~. For example, in the central-west region of Brazil (18° S, 60° W) where the first-order sensitivity is approximately ~~15~~ **11** ppb, a 20 % reduction in **domain-wide** NO_x emissions ~~should~~ **would be predicted to** lead to a reduction of O₃ concentrations by ~~3~~ **2.2** ppb **considering only the first-order sensitivity**. However, including the second-order sensitivity of around -20 ppb adjusts this estimate for a 20 % reduction in **domain-wide** NO_x emissions to a more realistic O₃ concentration reduction of approximately 2.6 ppb.

Numerical stability: Sensitivity calculations are prone to instabilities. Is GEOS-Chem-hyd also susceptible to instabilities? Did this drive the simulation length choice?

- Thank you for this question. The simulation length was not driven by numerical stability; it was driven by computational cost, as described in our previous response, and has now been extended to a 4-week simulation, which revealed the need for revision of ISORROPIA to maintain stability in the sensitivities in longer simulations.
- The real part of each hyperdual variable does not depend on the non-real parts, so the hyperdual formulation cannot destabilize the simulated concentrations and adds no stiffness or time-step constraint. Apart from the numerical refinements to ISORROPIA listed in Table S1, which alter the simulated concentrations only at the level of round-off error and near-zero thresholds, the real part is computed exactly as in GEOS-Chem. The non-real parts can, however, expose operations whose derivatives are unbounded even where the concentrations are well behaved. We found such operations only in the aerosol thermodynamics module, ISORROPIA, and we describe how each was resolved in our response to the next comment, in Sect. 2.2, and in Table S1. After these refinements, the sensitivities remained bounded throughout the four-week simulation (Fig. 8).
- To confirm stable behaviour in other chemical regimes, we also conducted one-week simulations for the first weeks of February, May, and November 2019 (Fig. S7):

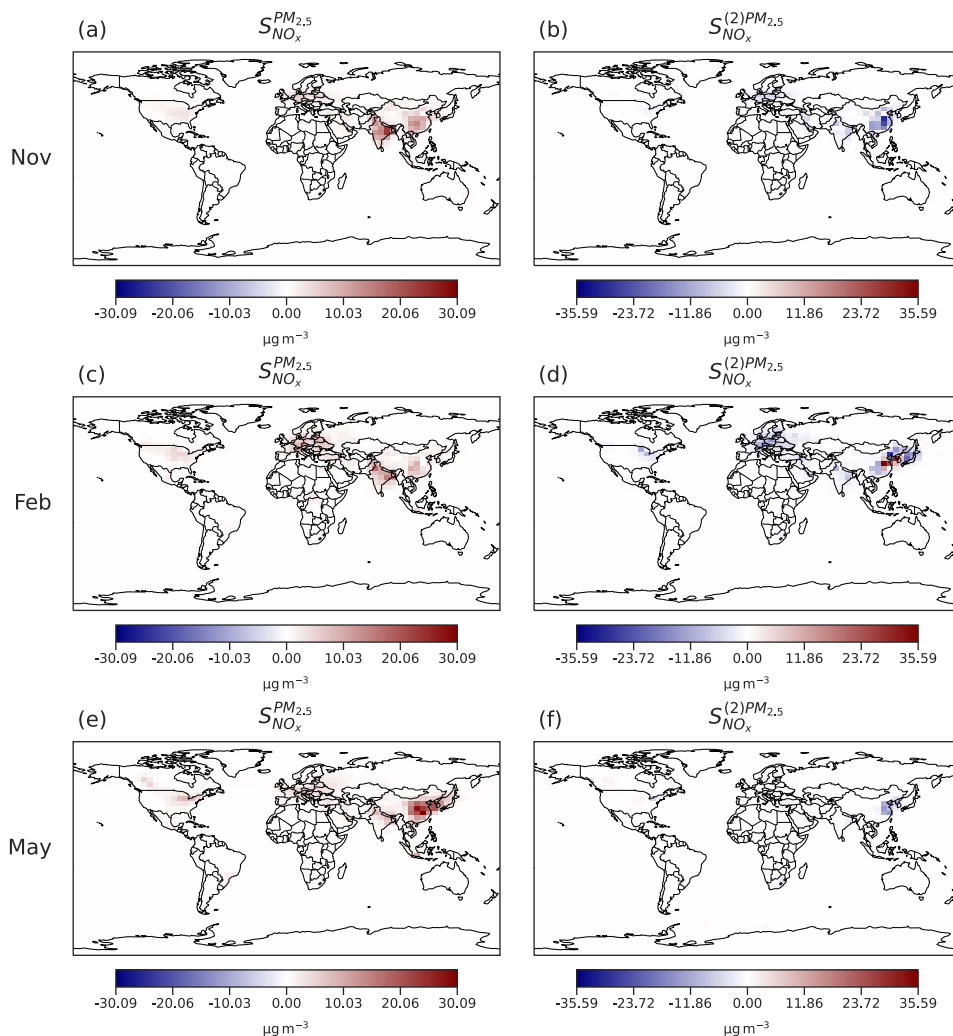


Figure S7. First- and second-order semi-normalised sensitivities of 1-week, time-averaged $PM_{2.5}$ concentrations with respect to domain-wide NO_x emissions on the ground layer for the first week simulation in November (a-b), February (c-d), and May (e-f) of 2019. The first column shows the first-order sensitivities, and the second column shows the second-order sensitivities.

- We added the following to Sect. 3.3:

L. 481–482 (rev.): **We also conducted one-week simulations for the first week of February, May, and November of 2019, to confirm the stability of the GEOS-Chem-hyd sensitivity calculations across different model states (Fig. S7).**

Semi-normalized sensitivities: the authors mention (line 192-194) that “We apply multiplicative perturbations in the dual space in GEOS-Chem-hyd to produce semi-normalized sensitivities without the need for post-processing with additional information about the denominator.” What additional information would you require for this post-processing (and at what temporal resolution, if any)? Please comment on the potential practical applications of semi-normalized sensitivities

- GEOS-Chem-hyd returns semi-normalized sensitivities directly because the dual-space perturbation is multiplicative with magnitude unity. The resulting derivative is therefore already scaled by the baseline emissions to which the perturbation is applied, and no post-processing is needed to express it in the units of the concentration.
- Converting to an absolute (unnormalized) sensitivity (e.g., concentration change per kg emitted) requires dividing by the baseline emissions that were perturbed, summed over the grid cells and timesteps to which the perturbation was applied. For the domain-wide, episode-long perturbations in this work, this quantity is the single value $E_{NO_x,dom}$ defined in Eq. (15). For a perturbation applied to a subset of grid cells or timesteps, the emissions summed over that subset are needed.
- We revised the passage to state the purpose of semi-normalization:

L. 190–194 (orig.) → L. 230–234 (rev.): **Semi-normalization allows the sensitivities to be expressed in the same units as the numerator in response to a fractional change in the denominator, which is particularly useful when estimating relative concentration responses to fractional emissions changes using a Taylor-series approximation.** We apply multiplicative perturbations of **magnitude unity** in the dual space in GEOS-Chem-hyd to produce semi-normalized sensitivities without the need for post-processing. ~~with additional information about the denominator.~~

- A practical application of semi-normalized sensitivities is the rapid estimation of concentration responses to percentage-based emission scenarios, such as a 10 % reduction in regional NO_x emissions. Because the sensitivities are expressed directly in concentration units, they can be easily combined with fractional emission changes to estimate expected concentration responses without requiring additional normalization steps (Bastien et al., 2019). This makes the sensitivities particularly useful for policy-relevant scenario analysis.

Could you explain what was contributing “unrealistic sensitivities” in ISORROPIA (lines 267-268)?

- We thank the reviewer for requesting clarification. In this context, “unrealistic sensitivities” refer to abnormally large or oscillatory first- and second-order sensitivities that are numerical artifacts of differentiating an iterative, piecewise-defined equilibrium solver rather than a defect of the equilibrium solution itself: the computed concentrations remain physical and bounded, and are unaffected by the sensitivity calculation, since the real part of a hyperdual variable is independent of its dual parts.
- Because the hyperdual formulation evaluates derivatives analytically, it exposes operations in ISORROPIA that are benign for the concentration but ill-conditioned for its derivative. The revised Sect. 2.2 describes three refinements:
 1. **Activity coefficients.** ISORROPIA recalculates activity coefficients iteratively at nearly every set of aqueous concentrations on the path to the equilibrium solution, and differentiating this loop occasionally produced extremely large sensitivities. We therefore compute the activity coefficients from the real parts only. This neglects their dependence on the perturbed concentrations, but standalone tests showed that it does not substantially change the first- or second-order sensitivities when the solution is stable.
 2. **Quadratic roots.** When $b^2 \gg |4ac|$, the textbook root subtracts nearly equal numbers. Instead, we adopted the numerically stable form recommended by Press et al. (2007), as in HETP (Miller et al., 2024), which replaced ISORROPIA as the default in GEOS-Chem 14.4.0. When $b^2 \rightarrow 4ac$, the root remains smooth, but its first and second derivatives diverge. Here, a safeguard detects the near-degenerate case and prevents the amplified derivative from propagating while leaving the concentration unchanged.
 3. **Bisection.** The G5 and H6 sub-cases are solved by bisection, which is not differentiable. We appended a two-step Newton–Raphson refinement after convergence, which recovers the sensitivity of the root, as described in our response to Reviewer 2 (comment on line 250).
- The second and third refinements change the equilibrium solution by no more than round-off error and the convergence tolerance of the solver. The first is an approximation for the derivatives only. Table S1 in the revised Supplement lists all modifications.
- The revised Sect. 2.2 reads:

L. 266–272 (orig.) → L. 198–217 (rev.): **Finally, the refinements to the inorganic aerosol thermodynamics module, ISORROPIA, were the most extensive. Accordingly, we extended a standalone version of ISORROPIA developed for testing conditions encountered in GEOS-Chem (Berman et al., 2023) to develop ISORROPIA-hyd with stable sensitivities over the extensive range of conditions encountered throughout the troposphere. We made three types of refinement in the hyperdual space. First, the nested nature of ISORROPIA leads to activity coefficients being calculated at nearly every set of aqueous concentrations on the path to determining the equilibrium solution. Accordingly, we kept only the real part of these calculations, which influence the concentrations along the solution path. By testing ISORROPIA in a standalone manner, this** This adjustment was shown not to alter the first- or second-order sensitivities substantially in the usual case of a stable result while eliminating the rare cases in which activity coefficient calculations led to extremely large sensitivities. This approach also improved computational efficiency marginally. **Secondly, we refined the quadratic solution in the two limiting cases of the elements of the discriminant, $\sqrt{(b^2-4ac)}$. In the first, $b^2 \gg |4ac|$, so that $-b + \sqrt{(b^2-4ac)}$ subtracts nearly equal floating-point numbers. In this case, the root loses precision, so we instead adopted the numerically stable quadratic formulation recommended by Press et al. (2007), which was implemented in HETP (Miller et al., 2024). In the second, $b^2 \rightarrow 4ac$, so that the discriminant approaches zero. In this case, the root itself remains smooth as the two roots merge, but its first and second derivatives scale as $D^{-1/2}$ and $D^{-3/2}$ and diverge. For this case, we introduced safeguards that**

detect the near-degenerate configuration and prevent the amplified derivatives from propagating while maintaining the real result. Finally, the equilibrium sub-cases for the sulphate-poor and sodium-poor (G5) and the sulphate-poor and sodium-rich (H6) are solved by bisection, which is non-differentiable. We, therefore, augment bisection with a two-step post-convergence Newton–Raphson refinement following previous works (Capps et al., 2012; Griewank and Walther, 2008). The analytic residual derivatives, which were generated with Tapenade (Hascoet and Pascual, 2013), make this step differentiable. Table S1 summarizes the modifications implemented in ISORROPIA to ensure a stable hyperdual formulation.

Limitations and future work: It would have been interesting to read at the concluding section a bit more about limitations of the hyperdual approach as well as suggestions for next steps.

- Thank you for this valuable suggestion. We have expanded the concluding section of the manuscript to discuss both the limitations of the hyperdual approach and potential future research directions.
- The revised manuscript now states the current limitations. Only the HEMCO components needed for domain-wide perturbations have been made hyperdual, so sector-specific perturbations are not yet available. The implementation is limited to GEOS-Chem Classic and does not yet support GCHP or specialized configurations such as TOMAS. GEOS-Chem-hyd requires approximately four times the wall time and three times the memory of GEOS-Chem (Sect. 3.2). Future work is also outlined:

L. 194–197 (rev.): **The full HEMCO-hyd is work currently in progress. The first-order sensitivities from the GEOS-Chem external arrays to the HEMCO arrays evaluate well against finite difference (Fig. S1), and the second-order sensitivities evaluate well against the hybrid method (Fig. S2). The current implementation is limited to GClassic; support for GEOS-Chem High Performance (GCHP) and for specialized configurations such as the TOMAS aerosol microphysics scheme constitutes future work.**

L. 465–466 (orig.) → L. 506–510 (rev.): Future work includes fully integrating the hyperdual method within the ~~Harmonized Emissions Component~~ (HEMCO) for sector-specific applications. **Longer simulations in GEOS-Chem-hyd are fully supported and can be explored in future scientific applications as computational resources permit. In future work, the framework could also be extended to the high-performance configuration of GCHP (Eastham et al., 2018; Martin et al., 2022). Specialized configurations, such as the TOMAS aerosol microphysics scheme, are likewise not yet supported.**

Line 129-130: “Perturbations are either additive or multiplicative, as with finite difference methods. We use only multiplicative perturbations.”: What was the reason for this choice?

- Thank you for this question. We adopt multiplicative perturbations because policy-relevant emission changes are typically expressed as fractional adjustments (e.g., a 20 % reduction), which correspond naturally to multiplicative perturbations.
- An additive perturbation, in contrast, applies the same absolute increment to every grid cell. This is difficult to interpret across grid cells whose emissions differ by orders of magnitude, and it would introduce emissions into grid cells that have none.
- We added this explanation to Sect. 2.1:

L. 129–130 (orig.) → L. 140–144 (rev.): Perturbations are either additive or multiplicative, as with finite difference methods. **In this work, we use multiplicative perturbations (5% unless stated otherwise) because they provide a physically meaningful representation of emission scaling. Policy-relevant emission adjustments are typically expressed as fractional changes (e.g., percentage reductions), which correspond naturally to multiplicative perturbations and provide consistent scaling across grid cells with widely varying emission magnitudes.**

Why did you choose to develop this for GEOS-Chem Classic vs GCHP?

- Thank you for this question. Development began in 2021 in GEOS-Chem Classic because of the familiarity to the group. The hyperdual formulation is not specific to GEOS-Chem Classic, and the refinements developed here would carry over to GCHP.
- We now state this in Sect. 2.2 and in the Conclusion:

L. 508–510 (rev.): **In future work, the framework could also be extended to the high-performance configuration of GCHP (Eastham et al., 2018; Martin et al., 2022). Specialized configurations, such as the TOMAS aerosol microphysics scheme, are likewise not yet supported.**

Line 161: typo

- Thank you; we corrected the typo and clarified the sentence:

L. 161 (orig.) → L. 175–176 (rev.): The ~~hyperdual~~ **hyperdual** version of GEOS-Chem, GEOS-Chem-hyd, enables the ~~application~~ **calculation of derivatives using** the hyperdual step method.

Figure 1: Why isn't dry deposition modified to hyperdual numbers?

- Thank you for this question. To clarify at the outset: sensitivities are propagated through dry deposition in GEOS-Chem-hyd. What was not converted to hyperdual arithmetic is the calculation of the deposition velocity itself, and we explain below why this is sufficient for the sensitivities reported in this work.
- In the GEOS-Chem architecture, the dry deposition flux F can be written as

$$F = V_d \cdot C$$

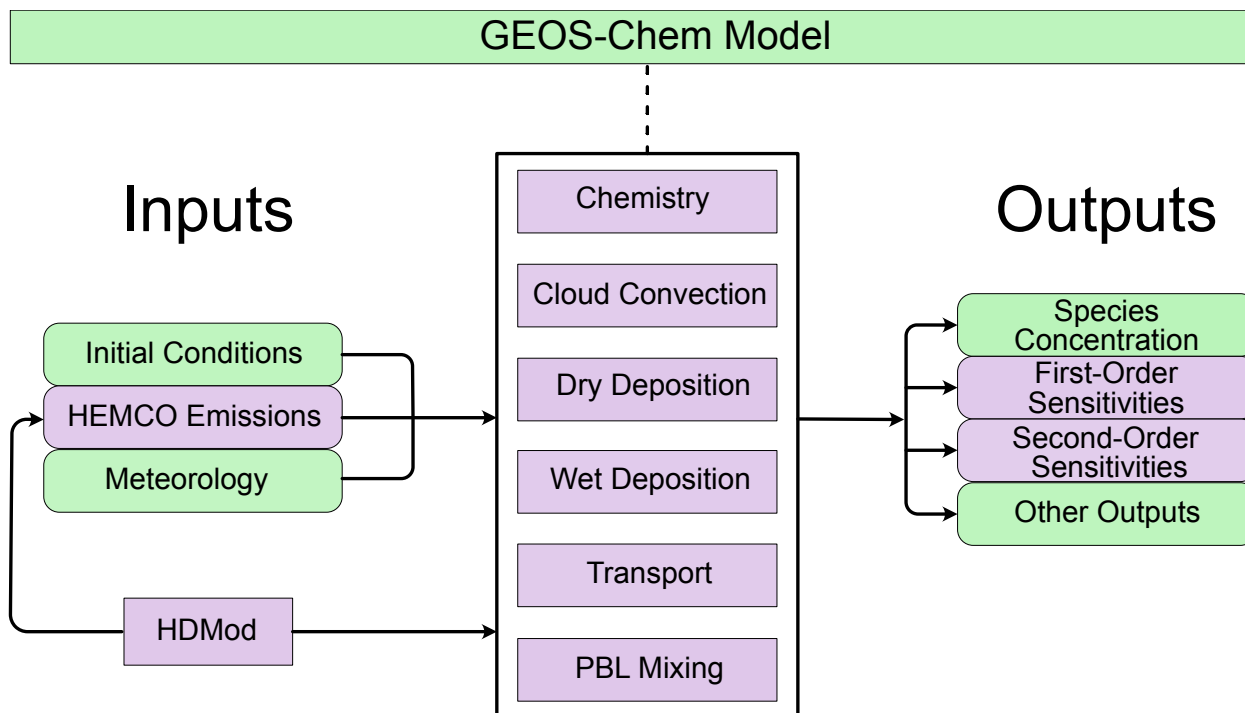
where V_d is the deposition velocity, and C is the concentration. Because C is hyperdual, the derivative still propagates automatically through this multiplication though V_d remains real.

- The deposition velocity was not converted because the quantities that control its calculation are independent of the hyperdual perturbation variables used in this study. In GEOS-Chem-hyd, the hyperdual perturbations are applied to the species concentration array (`State_Chm%Species(ID)%Conc(I,J,L)`) and to emissions (`HCO_State%Spc(ID)%Emis%Val(I,J,L)`), which are the variables of interest for computing concentration-to-concentration and concentration-to-emission sensitivities.
- In the dry deposition module (`drydep_mod`), the deposition velocity calculations depend on meteorological variables, land surface properties, and species-specific parameters such as molecular diffusivity, molecular weight, and Henry's law constants. These quantities are independent of the hyperdual perturbation variables used in this work, so the deposition velocity remains a real variable and does not need to be modified for the derivative calculations performed here.
- Some specialized dry deposition schemes, such as those in the TOMAS aerosol microphysics configuration, use species concentrations directly. GEOS-Chem-hyd does not yet support these configurations, which we now state in Sect. 2.2 and in the Conclusion:

L. 196–197 (rev.): **The current implementation is limited to GCClassic; support for GEOS-Chem High Performance (GCHP) and for specialized configurations such as the TOMAS aerosol microphysics scheme constitutes future work.**

L. 509–510 (rev.): **Specialized configurations, such as the TOMAS aerosol microphysics scheme, are likewise not yet supported.**

- We agree that the original figure was ambiguous on this point. Sensitivities are propagated through the dry deposition flux, but the original figure showed which modules were converted to hyperdual arithmetic rather than which processes propagate sensitivities. We revised Fig. 1 (caption at L. 183 (orig.) → L. 221 (rev.)) to show that sensitivities propagate through dry deposition:



Additional changes

We have also added Jiachen Liu as a co-author for leading the standalone testing of ISORROPIA-hyd, and we revised the author contributions:

L. 481–482 (orig.) → L. 530–532 (rev.): *Author contribution*. **SLC conceived of the idea and designed the model development.** SOA developed the model code, performed the simulations, and developed the figures with direction from SLC. **JL led the standalone ISORROPIA testing.** SOA and SLC drafted the manuscript, which JL improved.

Beyond the changes described above, we made the following revisions:

- We reorganized the Introduction around forward, reverse, and tagging approaches, and we updated the burden-of-disease statistics to GBD 2023, reporting the contributions of PM_{2.5} and O₃ separately (Global Burden of Disease Collaborative Network, 2025).
- We merged the evaluations of first- and second-order sensitivities into Sect. 3.1, so the computational cost and application sections are now Sects. 3.2 and 3.3.
- We regenerated Figs. 2, 5, 6, and 7 and Tables 1 and 2 after the ISORROPIA bisection correction, and we added the factors by which gas-phase chemistry (10.5) and photolysis (28.7) increase in cost (Sect. 3.2).
- We added a worked example for OA_{bio} in southern Hebei, China, to Sect. 3.3, and we revised the description of the second-order effects in Sect. 3.3 and the Conclusion.
- We stated the exact base version (GEOS-Chem Classic 14.0.0-rc.3 with HEMCO 3.5.0), cited the GEOS-Chem Classic code, and archived the simulation configuration separately from the code.
- We added a Supplement statement, renumbered the supplementary figures, and updated the author contributions and acknowledgements.

References

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