

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 RC2

The manuscript by Akinjole and Capps presents the implementation of hyperdual sensitivities in GEOS-Chem. This is a significant and novel achievement that allows them to accurately compute second order sensitivities, and the approach also has benefits for computing first order sensitivities. The sensitive are evaluated, numerically, and the tool is briefly applied. Overall, the manuscript is very thoughtful and well written. My main suggestion at this point is to dig a bit deeper into the postulated reasons for the discrepancies between FD and hyperdual first-order sensitivities. Below I provide some additional comments, and I believe addressing these would make the work well suitable for publication in GMD.

- We would first like to thank Professor Henze for this valuable feedback. The careful attention to detail and deep understanding of this work has served to strengthen not only the manuscript but also what we are offering the modeling community. We are deeply grateful and hope this revision will be received favorably.
- Following this suggestion, we examined the discrepancies between the FD and hyperdual first-order sensitivities in detail. This led us to identify and correct a non-differentiable operation in ISORROPIA, as described in our response to the comment on line 250.

Comments:

48: I know that DDM is effectively the same as tangent linear, but you might also call it out as an approach here, in particular as DDM methods have been expanded to 2nd order sensitivities (i.e., Amir Hakami's work).

- Thank you for this helpful suggestion.
- We agree that the decoupled direct method (DDM) is mathematically equivalent to tangent linear approaches and is one of the most widely used forward sensitivity methods in chemical transport models. We now include additional examples of forward sensitivity analysis approaches that have been extended to second-order and cross-sensitivities, including DDM.
- We revised this passage in the Introduction:

L. 44–48 (orig.) → L. 46–56 (rev.): **Forward sensitivity methods reflect the influence of select model parameters or sources on all modelled results or concentrations. Examples of approaches that provide forward sensitivities are the finite difference method derived from Taylor's theorem, the complex and multicomplex step method (Lantoiné et al., 2012; Martins et al., 2003; Squire and Trapp, 1998), dual and hyperdual step methods (Fike and Alonso, 2011), the decoupled direct method (DDM) (Dunker et al., 2002a; Koo et al., 2007), and other tangent linear models (Vukicevic and Errico, 1993). Among these methods, DDM is one of the most prominent and has been more widely applied to CTMs. DDM was introduced to propagate sensitivities through stiff chemical kinetic systems by solving auxiliary sensitivity equations separately from the model equations while retaining the same time steps and numerical approximations (Dunker, 1984). It was subsequently extended to three-dimensional photochemical models (Dunker et al., 2002a; Yang et al., 1997), to particulate matter and aerosol thermodynamics (Koo et al., 2007; Napelenok et al., 2006), and to higher orders, which yield second-order and cross-sensitivities at a per-sensitivity computational cost comparable to that of first-order sensitivity calculations (Cohan et al., 2005; Hakami et al., 2003; Hakami et al., 2004; Zhang et al., 2012).**

51: I think there's actually quite a bit of work with tagging for reactive species. The MOZART model had a tagging scheme for O₃ — see papers from Louisa Emmons. Tim Butler does tagging — with WRF-Chem I believe. And Mike Kleeman's CTM includes tagging for aerosol species, all the way through the aerosol microphysics. That being said, I agree with the statement that tagging, as a method, can be somewhat set aside here given it is fundamentally different in objective and implementation than the sensitivity methods being discussed.

- We thank the reviewer for this insightful comment and for pointing us to the substantial body of work on tagging for reactive species. We have expanded the relevant passage to acknowledge tagged O₃ schemes in MOZART-4 and CAM-chem (Emmons et al., 2012), in WRF-Chem (Romero-Alvarez et al., 2022), and CESM (Butler et al., 2018), and the source-oriented aerosol treatments that carry tags through aerosol thermodynamics and microphysics (Kleeman and Cass, 2001; Ying and Kleeman, 2006).
- We also agree that tagging can be set aside here, and the revised passage now says why. Tagging quantifies the absolute contribution of a source to a modelled concentration, whereas sensitivity methods quantify the response of the concentration to a change in the source, and the two diverge where the chemistry is nonlinear (Belis et al., 2021; Cohan et al., 2005; Dunker et al., 2002b; Grewe et al., 2010).

L. 51–55 (orig.) → L. 67–77 (rev.): **Finally, an alternative approach is tagging parameters. This technique is most straightforward to implement for species whose chemistry is linear or negligible (e.g., Fisher et al., 2017; Ikeda et al., 2017; Kim et al., 2015). For reactive species, tracers may be carried alongside the host chemical mechanism as for O₃ and its precursors in both global and regional models (e.g., Butler et al., 2018; Emmons et al., 2012; Han et al., 2019; Romero-Alvarez et al., 2022; Wang et al., 2011; Whaley et al., 2015) and for aerosol species, including source-oriented treatments that carry the tag through aerosol thermodynamics and microphysics (Kleeman and Cass, 2001; Ying and Kleeman, 2006). Tagging quantifies the absolute contribution of a source to a modelled concentration, whereas the sensitivity methods described above quantify the relative response of that concentration to a change in the source. The two are not interchangeable. For instance, where nonlinear chemistry leads to a precursor inhibiting formation, the sensitivity would be negative while the apportioned contribution remains small and positive (Belis et al., 2021; Cohan et al., 2005; Dunker et al., 2002b; Grewe et al., 2010). Since this approach yields information valuable for source apportionment yet distinct from the derivatives of other sensitivity analysis approaches, implementations of tagging will not be further addressed.**

59: One of the biggest uses of FD sensitivities in the GC community is the analytic inversions of CH₄, including the calculations within the IMI. These papers all compute the entire Jacobian through ensembles of 100s to 1000s of FD sensitivities. However, these are for linear tracers, so there would not be a benefit in moving to higher-order sensitivity methods.

- We thank the reviewer for highlighting this application. Analytic inversions of CH₄ emissions, including those conducted with the Integrated Methane Inversion (IMI), are among the most extensive uses of finite difference sensitivities in the GEOS-Chem community. In these inversions, the Jacobian matrix is constructed column by column from simulations that each perturb one element of the state vector (Maasakkers et al., 2019; Varon et al., 2022).
- We agree that these applications would not benefit from the hyperdual method. Because CH₄ is simulated as a linear tracer in these inversions, the finite difference Jacobian is exact apart from round-off error, regardless of the perturbation size. Furthermore, a single hyperdual simulation propagates perturbations to at most two parameters, so it would not reduce the number of simulations needed to construct a Jacobian with hundreds to thousands of columns. The hyperdual method is instead intended for nonlinear responses, such as those of O₃ and secondary aerosol, for which finite difference sensitivities depend on the perturbation size and second-order sensitivities are informative. We now note this application and the distinction in the Introduction:

L. 59–64 (orig.) → L. 81–89 (rev.): **Primarily, the finite difference approach is used to evaluate the impact of a new science module (e.g., Croft et al., 2014; Johnson et al., 2016; Vinken et al., 2011; Sun et al., 2022; Yan et al., 2019). The finite difference-based sensitivities have also been applied in (Sun et al., 2022; Vinken et al., 2011; Yan et al., 2019), conducting mass balance inversions to improve emissions of select species based on satellite observations (Choi et al., 2022; Cooper et al., 2017; Li et al., 2019). Additionally, the finite difference method is used to evaluate, and assessing the accuracy of models instrumented to conduct sensitivity analysis (Constantin and Barrett, 2014; Dunker et al., 20022002a; Henze et al., 2007; Koo et al., 2007). For the case of analytic inversions of methane (CH₄) emissions, the full Jacobian is constructed from ensembles of hundreds to thousands of perturbation simulations (Maasakkers et al., 2019; Varon et al., 2022). Because CH₄ is simulated as a linear tracer in these inversions, the finite difference sensitivities are exact apart from round-off error, and higher-order sensitivity methods would offer no benefit. The hyperdual method instead targets nonlinear responses, such as those of O₃ and secondary aerosol, for which finite difference sensitivities depend on the perturbation size.**

126/Eq 3: Could you comment on this identity? It's not clear to me why these terms can't equal each other, or why they are non-zero. It also seems to me, naively, to conflict with later equations. When the perturbation H_a is introduced on line 131, the ϵ_{12} term is zero (even though Eq 3 states that ϵ_{12} is not zero). Also, as a_1 and a_2 are arbitrary and thus could be equal), wouldn't that make ϵ_1 and ϵ_2 equal to other, from inspection of Eq 7? I don't doubt that your final equations are correct, but there's just something about this presentation that I'm not grasping, and it would be useful if the text could explain this aspect in a little more detail.

- We appreciate the reviewer's careful inspection of Eq. 3. We realize the initial text did not sufficiently explain the algebraic properties of hyperdual numbers that allow these terms to remain distinct and non-zero.
- Our intent in Eq. 3 was to define the hyperdual basis algebra, not to imply that every perturbed variable must have a nonzero mixed term. In hyperdual arithmetic, ϵ_1 and ϵ_2 are independent infinitesimal directions, and ϵ_{12} is a distinct basis element that is nonzero in the algebra.
- However, the coefficient multiplying ϵ_{12} in a particular initialized variable can be zero. Thus, when H_a is introduced on line 131, the ϵ_{12} coefficient is zero by construction because that perturbation is seeded in only the ϵ_1 and ϵ_2 direction initially; the mixed term appears only after nonlinear operations combine two perturbed directions. Likewise, although a_1 and a_2 are arbitrary scalars and may take the same numerical value, that does not make ϵ_1 and ϵ_2 the same basis element. If we were to fully write the expression of H_a it would be:

$$H_a = 1 + a_1\epsilon_1 + a_2\epsilon_2 + 0\epsilon_{12}$$

Where the term ' $0\epsilon_{12}$ ' is zero and can be neglected from the expression, but the ' ϵ_{12} ' term here is not zero.

- We revised Sect. 2.1 to make this distinction explicit:

L. 138–139 (rev.): **Here, ϵ_{12} denotes a nonzero hyperdual basis element; however, its coefficient in a given variable may be zero at initialization and become nonzero only after nonlinear propagation.**

176: Does this mean that GEOS-Chem-hyd doesn't support GCHP? I think that's fine, just thought it would be good to state this clearly.

- Thank you for this question. The current implementation of GEOS-Chem-hyd is limited to GCClassic and does not yet support GCHP. We have clarified this in the manuscript in lines **192–197** and **508–510**, and note that extending support to GCHP is planned as future work.

L. 175–176 (orig.) → L. 192–197 (rev.): For the purposes of introducing GEOS-Chem-hyd, the emission routines that interface with GEOS-Chem Classic (**GCClassic**) are made **compatible with hyperdual operations. 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 GCClassic; support for GEOS-Chem High Performance (GCHP) and for specialized configurations such as the TOMAS aerosol microphysics scheme constitutes future work.**

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.**

180: Is this correct? I'm familiar with the parlance of "active variables" in adjoint code development, and I would have assumed it would be the same set of variables needed to convert to hyper dual. This would not include variables like temperature, RH, etc., which are not impacted by the emissions or initial conditions. Is that not the case here? If not, what is an example of a variable that does not impact concentrations, for which hyper dual type wasn't necessary?

- Thank you for this question. We agree that the concept of "active variables" is closely related to its use in adjoint and tangent linear model development, where it typically refers to variables that influence the quantity of interest (e.g., concentrations) through the model's computational graph, and are associated with the chosen control space (e.g., emissions or initial conditions).
- In the context of hyperdual implementation, we adopt a similar definition and focus on sensitivities of concentration to concentrations or to emissions. Active variables are, therefore, those impacted emissions or concentrations as in adjoint

development. Consistent with adjoint development, variables such as temperature and RH are not treated as active variables and are not converted to a hyperdual type.

- We revised the definition in Sect. 2.2:

L. 180–181 (orig.) → L. 181–183 (rev.): Specifically, the species concentration array and all other **active** variables that ~~depend on~~ **propagate sensitivities to** the species concentration array across GEOS-Chem were changed to the hyperdual type (Figure Fig. 1). **Here, active variables are defined as those that are impacted by emissions or initial concentrations.**

Fig 1: Why was dry dep not modified? Because it is linear? This pertains to my comment regarding line 180, where I suspect the text is incorrect; otherwise, dry dep would need to be modified as terms like dry dep velocities influence the species concentrations.

- Thank you for this question. To clarify, sensitivities are propagated through dry deposition in GEOS-Chem-hyd. As suspected, the linear nature of the deposition flux calculation enabled us to avoid the hyperdualization of the deposition velocity calculation itself. 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

$$F = V_d \cdot C$$

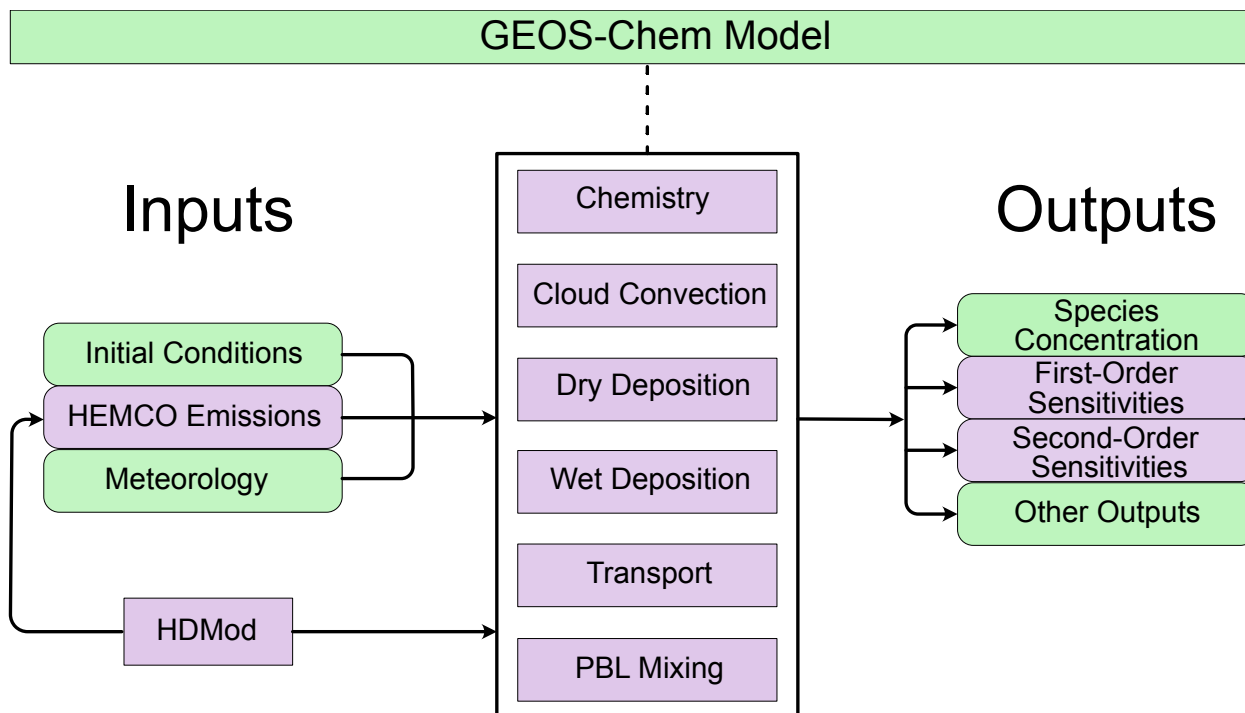
where V_d is the deposition velocity, and C is the concentration. Because C is hyperdual, the derivative still propagates automatically through this multiplication though V_d remains real.

- 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:



208/Eq 17: When viewing the manuscript pdf on a mac, there are two “?” that appear in the numerator of the right hand side.

- Thank you for pointing this out. The appearance of “?” symbols in Eq. 17 is due to incorrect formatting of the subscript expression (e.g., $\epsilon_{2\text{part}}$), which led to rendering issues in the PDF. We have corrected this by properly separating the subscript and typesetting ‘part’ as a text within math mode (e.g., using ϵ_{part}), since it is not a mathematical variable.
- The same correction has been applied to Eqs. 18-24 to ensure consistent and robust rendering across platforms.

250: That is true. Or, there may be a mistake in the hyper-dual implementation, or some differences owing to the approximations made in omitting hyper dual calculations (lines 268-272) within the activity coefficients or kinetic rate constants. I’d expect the authors to do a bit more here to identify the sources of these differences. This could readily be done by several methods, and it would be worth exploring one or more of these. One could try changing the FD perturbation size and seeing how the FD sensitivities respond. If nonlinearity is the reason for the discrepancy, the agreement should improve for smaller perturbations. If discontinuities are the issue, then the agreement should improve for larger perturbations. One could examine one-sided FD sensitivities — hyper dual can be considered valid if they lie between these, even if they don’t match the central FD estimate. One could take a deep dive on a few of the extreme outlier points and examine the forward model response to verify if it really is responding nonlinearly, or if values are all so small that roundoff error is degrading the FD.

- Thank you for this detailed and constructive comment. We agree that differences between hyperdual and finite-difference (FD) sensitivities may arise from several sources, including nonlinearity, discontinuities, numerical precision, or potential implementation errors, as well as approximations introduced where hyperdual propagation is not applied (e.g., activity coefficients and kinetic rate constants).
- Using the standalone ISORROPIA II implementation to examine several of the extreme outlier points individually, we identified one source of the discrepancy: the bisection root-finding used in the G5 (CALCG5) and H6 (CALCH6) sub-cases. Bisection is non-differentiable because it is an implicit root-finding approach. As a result, the dependence of the PSI6 root on the perturbed inputs is not propagated. By the implicit function theorem, the correct sensitivity of a root x^* of $f(x; p) = 0$ is $dx^*/dp = -(\partial f / \partial p) / (\partial f / \partial x)$, evaluated at x^* ; bisection does not form this quantity, so the first- and second-order sensitivities carried out of CALCG5/CALCH6 were effectively spurious.
- To resolve this, we retained bisection to robustly locate the real-valued root, then appended a post-convergence two-step Newton–Raphson algorithm. Because the Newton update $x_{n+1} = x_n - f(x_n)/f'(x_n)$ is differentiable, propagating it in hyperdual arithmetic from the converged root recovers exactly the implicit-function-theorem sensitivity. A single step corrects the first-order dual part, and a second step is required for the second-order part, whose dual component

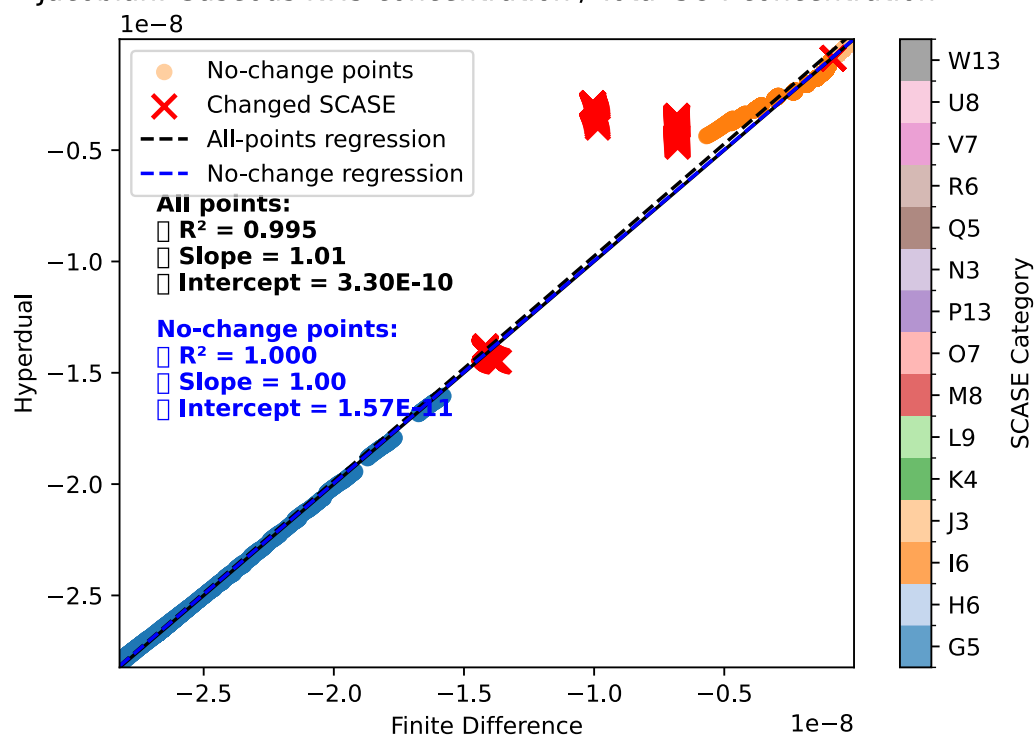
depends on products of the (now corrected) first-order parts. The required residual derivatives for FUNCG5A and FUNCH6A were generated with Tapenade (tangent mode), yielding FUNCG5A_D and FUNCH6A_D. After this correction, the hyperdual first- and second-order sensitivities for the G5 and H6 cases agree with the central finite-difference estimates to within the FD truncation error, which confirmed that the bisection non-differentiability was the principal cause of the divergence of the earlier version. The updated routines are included in the revised code.

- The Newton step is rejected when it would leave the bracket found by bisection (Table S1, category 11). Over the 24-hour simulation, this occurred in 0.03 % of Newton steps, in 0.8 % of the grid boxes where ISORROPIA is active, and mainly in cold mid-tropospheric air (mean 257 K and median 429 hPa, versus 276 K over all active boxes). When the Newton step is rejected, this call of ISORROPIA does not add any sensitivity information.
- We added this refinement to Sect. 2.2:

L. 212–216 (rev.): **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.**
- Another identified source of the discrepancy is the regime switching between thermodynamic cases as illustrated in Figure S3. Points marked with “X” indicate cases where perturbed simulations fall into different thermodynamic regimes. In these situations, finite-difference sensitivities become poorly defined, whereas the hyperdual formulation remains consistent and gives the derivative at that model state.

(a)

Jacobian: Gaseous NH3 concentration / Total SO4 concentration



(b)

Hessian: Gaseous NH3 concentration / Total SO4 concentration

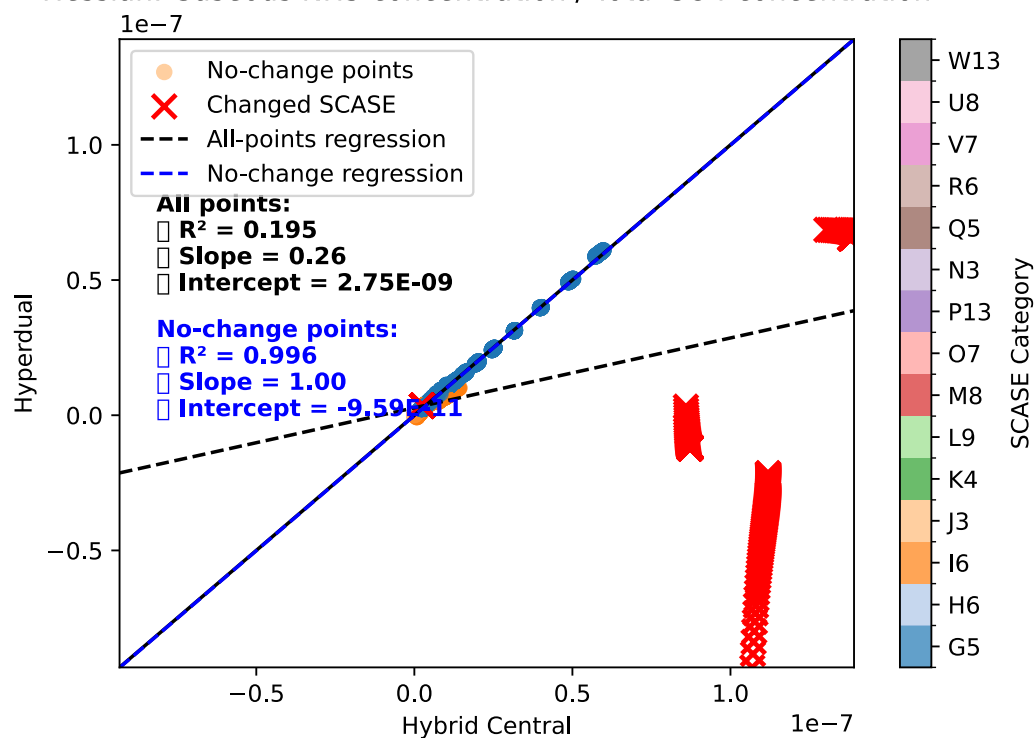


Figure S3. Comparison of the first-order (a) and second-order (b) hyperdual results to the central finite difference (a) and hybrid-hyd finite difference (b) results using standalone ISORROPIA II at 5 % perturbation. Tests were conducted at 297 K and 77 % RH, with NH4 and NO3 ranging from 1.0d-9 to 1.0d-7 mol/m3. The input conditions for TNA, TSO4, TNH3, TNO3, TCL were fixed at 4.712d-9, 1.338d-8, 5.03d-8, 1.101d-8, and 1.35d-8 mol/m3 respectively. X points represent scenarios in which case changes occur between the two perturbed runs when calculating the finite-difference sensitivities.

- We added this to Sect. 3.1:

L. 249–251 (orig.) → L. 293–296 (rev.): The deviation from unity for some relationships expected to exhibit nonlinear behaviour (e.g., ~~secondary-SO₂^{NH₄}, aerosol-SO₂^{NH₃}, formation-SNO_x^{PM_{2.5}}, and SNO_x^{OAbio}) may be attributed to **the nonlinearity of the relationship or** the model state changing with the FD method in a manner not required in the hyperdual approach, **such as regime switching between thermodynamic cases (Fig. S3).**~~

- Following the reviewer's suggestions, we also varied the FD perturbation size and compared the hyperdual sensitivities with forward, central, and backward FD estimates (Fig. 4). For the sensitivity of O₃ to NO_x emissions, all three FD estimates agree closely with the hyperdual sensitivities at a 5 % perturbation, agreement worsens for all three at 100 %, and the central FD estimate lies between the forward and backward estimates. Together, these results show that nonlinearity of the model response explains the differences at large perturbations for this relationship.

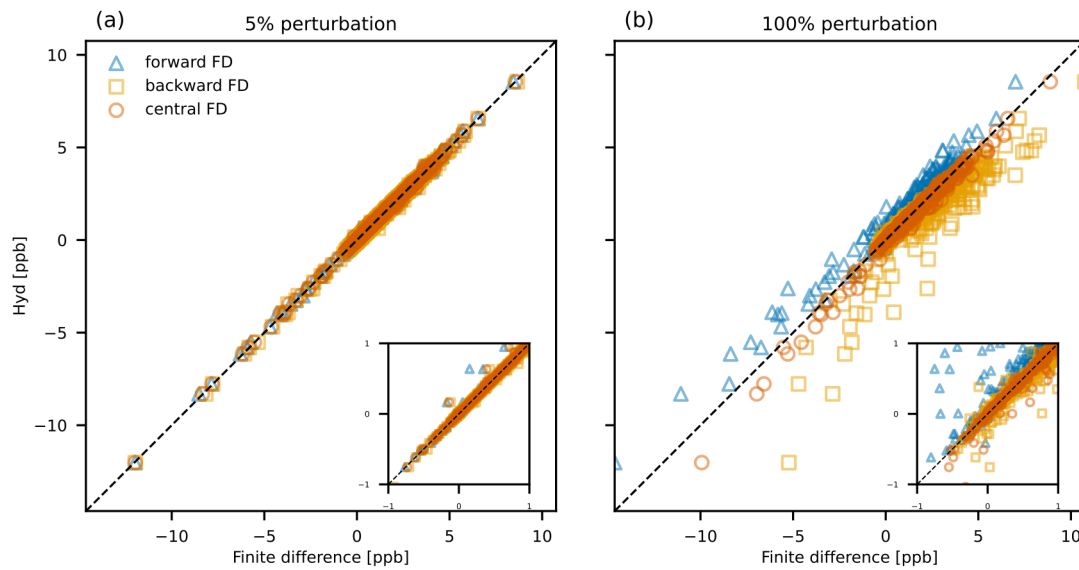


Figure 4. Comparison of first-order semi-normalized sensitivities of the time-averaged, ground layer ozone concentrations with respect to domain-wide, persistent perturbation of NO_x emissions throughout the 24-hour episode using the hyperdual step method (Hyd) and various FD methods with a 5 % (a) and 100 % perturbation (b) in each direction.

- We performed the same test for the sensitivity of PM_{2.5} to NO_x emissions (Fig. S4). With a 5 % perturbation, the three FD estimates agree with each other but deviate consistently from the hyperdual sensitivities for a subset of grid cells. With a 100 % perturbation, the forward and backward FD estimates usually bracket the hyperdual values. Because the three FD estimates agree with one another at 5 %, nonlinearity alone does not explain this deviation. It is consistent with the thermodynamic regime changes illustrated in Fig. S3, and the activity-coefficient approximation discussed above could also contribute, although standalone tests showed that approximation to have little effect when the solution is stable.

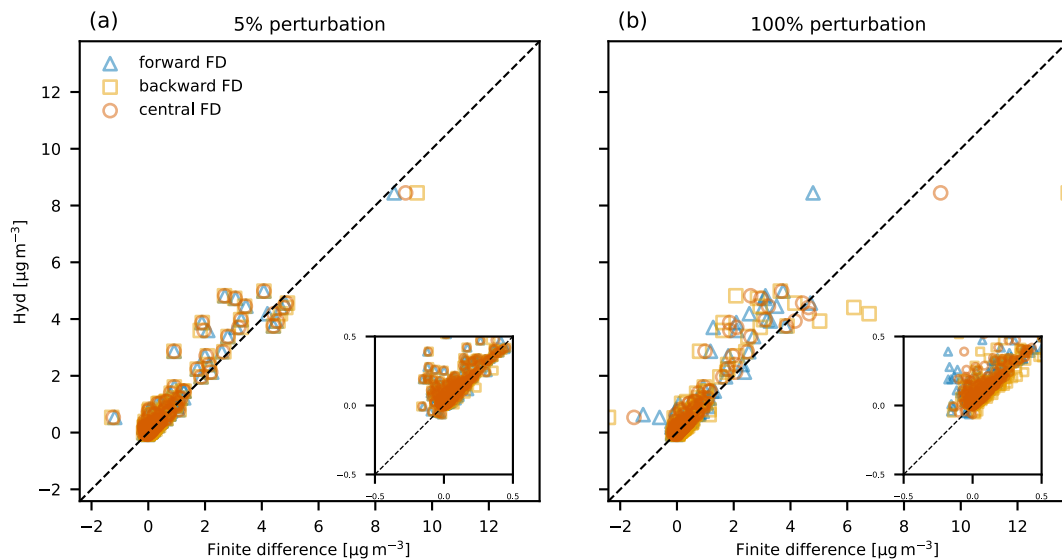


Figure S4. Comparison of first-order semi-normalized sensitivities of the time-averaged, ground layer PM_{2.5} concentrations with respect to domain-wide, persistent perturbation of NO_x throughout the 24-hour episode using the hyperdual step method (Hyd) and forward, central, and backward FD methods with a 5 % (a) and 100 % (b) perturbation in each direction.

- We revised the corresponding paragraph in Sect. 3.1:

L. 289–304 (orig.) → L. 322–342 (rev.): Comparing $S_{\text{NO}_x^{\text{O}_3}}$ hyperdual sensitivities to the forward, central, and backward finite difference sensitivities following Henze et al. (2007) provides further insight into the accuracy of the augmented model (Fig. 4). The tight agreement of the hyperdual sensitivities with the three finite difference methods at a 5% perturbation confirms the assessment of strong performance of the augmented model for this relationship (Fig. 4a). Worsening agreement with all FD methods with an increased perturbation size (100%) (Fig. 4b) indicates a nonlinear model response. Additionally, these results align with the expectation that the central FD sensitivity should lie between the forward and backward FD sensitivities. For the $S_{\text{NO}_x^{\text{PM}_{2.5}}}$ (Fig. S4), the smaller perturbation results in consistent deviation from the one-to-one line for all three FD methods. With the larger perturbation, the backward and forward FD points usually bound the one-to-one line (Fig. S4b), which suggests that the hyperdual sensitivities are correct though the model state may differ with the real perturbation. Collectively, these results further demonstrate the validity of the first-order hyperdual sensitivities.

Ok, I see that this is somewhat investigated in Fig 4. However, this figure is used more as a demonstration of the weakness of FD rather than as a method to verify that the central FD estimates differ from hyper dual owing to nonlinearity. Also, Fig 4 and the manuscript text don't state what sensitivity is being plotted. Is this again the sensitivity of O₃ with respect to NO_x emissions?

- We agree. Figure 4 now serves as the diagnostic described in the reviewer's previous comment. For the sensitivity of O₃ to NO_x emissions, agreement worsens for all three FD methods as the perturbation increases, which confirms that the differences from the central FD estimate at large perturbations arise from nonlinearity.
- Thank you for noting omission of the sensitivity being plotted. The text (L. 322 (rev.)) and the caption of Fig. 4 (L. 300 (orig.) → L. 334 (rev.)) now state that the figure shows the first-order sensitivity of O₃ concentrations with respect to NO_x emissions:

Figure 4. Comparison of first-order semi-normalized sensitivities of the time-averaged, ground layer ozone concentrations at the ground-layer with respect to domain-wide, persistent perturbation of NO_x the emissions throughout the 24-hour episode using the hyperdual step method (Hyd) and various FD methods with a 5 % (a) and 100 % perturbation (b) in each direction.

General: can the axis of the sensitivity plots be adjusted such that the 0,0 lines are visible? For example, I'm trying to understand Fig 5 (a) - (d), and it would be a lot easier I could clearly tell which clusters of sensitivities are around 0.

- Thank you for this helpful suggestion. We added zero-reference lines on both axes to Figs. 2 and 5 and adjusted the axis limits so that the origin is visible in each panel.

Sensitivity Equations: All of the sensitivity equations showing emissions in the denominator have subscripts i,j,l,t on the emissions. However, it seems that the applications only use emissions that are defined domain-wide, is that correct? Would it be useful / simpler to show the notation for that?

- Thank you for this observation. In all of the applications presented here, the emissions are perturbed by a single, uniform fractional amount applied to every grid cell and every emission timestep, so the quantity in the denominator is a domain-wide, persistent emission rather than a set of grid-resolved ones.
- We agree that the notation is simpler if this is shown explicitly, and have revised the equations accordingly. We define

$$E_{NO_x,dom} = \sum_{i,j,l} \sum_{t=0}^{t_f} E_{NO_x,i,j,l,t}$$

- as the domain-wide, episode-total emission of NO_x , and write the semi-normalized sensitivities as

$$S_{NO_x}^{O_3} = \left. \frac{\partial C_{O_3,i,j,l=0,t}}{\partial E_{NO_x,dom}} \right|_t E_{NO_x,dom}^{\text{def}}$$

$$S_{NO_x}^{(2)O_3} = \left. \frac{\partial^2 C_{O_3,i,j,l=0,t}}{\partial E_{NO_x,dom}^2} \right|_t (E_{NO_x,dom}^{\text{def}})^2$$

- The revised text notes that any subset of species, space, and time could be perturbed. Assigning perturbations by region, sector, or grid cell recovers the fully source-oriented case that motivates this development.
- $E_{NO_x,dom}$ is now defined in Eq. (15), and Eqs. (16)–(27) are written in terms of it. The revised text introducing the definition reads:

L. 236–238 (rev.): **Although any subset of species, space, and time could be selected for investigation, these perturbations are applied uniformly to every grid cell and every emission timestep, so the emissions in the denominator are represented by the domain-wide, episode-total emissions:**

L. 235–236 (orig.) → L. 240–241 (rev.): **Here, we perturb emissions at every 20-minute chemistry timestep throughout a 24-hour episode.**

Figures: Following on my above comment, for any panel of e.g. Fig 2, 5, etc., are the different points the different i,j locations of the numerator, as the emissions perturbation is domain wide?

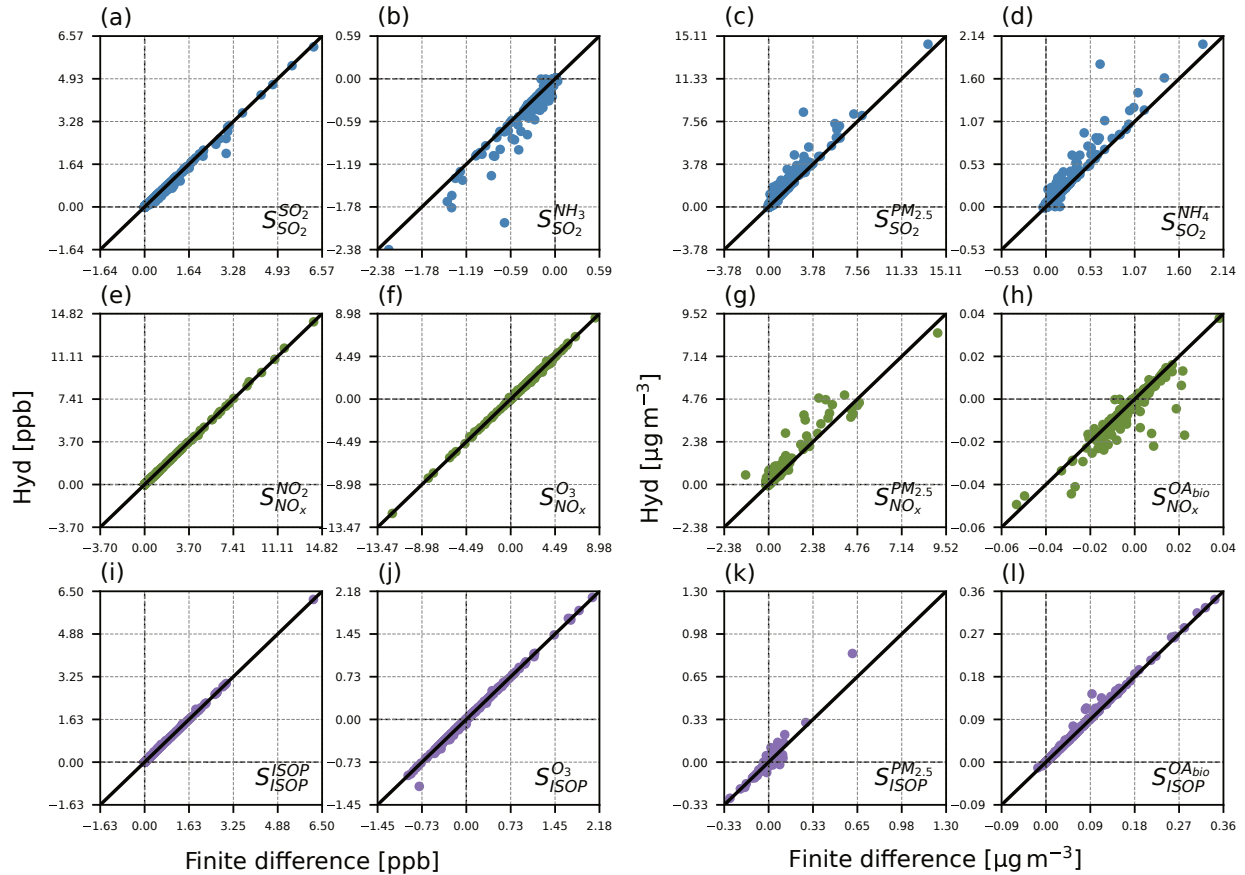
- Yes. Each point is one ground-level grid cell (i, j) of the concentration field, because the emission perturbation is applied domain-wide. We revised the captions of Figs. 2 and 5 to state this explicitly:

L. 256–261 (orig.) → L. 300–305 (rev.): Figure 2. Comparisons of first-order semi-normalized sensitivities of the time-averaged concentration **at the ground layer in each ground layer cell** to the **domain-wide** emissions throughout the 24-hour episode using the hyperdual step method (Hyd) and the central finite difference method with a 5 % perturbation in each direction. The sensitivity plots are polychromed by the domain-wide perturbed emissions of SO_2 , NO_x , or isoprene (ISOP) as indicated in the subscript. The superscript indicates the concentration. ~~OA_{bio} denotes organic aerosol attributable to biogenic sources.~~ The calculated sensitivities are labelled at the bottom right corner of each panel. The left two panels show examples of gas-phase species concentrations with respect to corresponding emissions, ~~while the right.~~ **The right** two panels show examples of aerosol-phase products with respect to their gaseous precursors.

L. 311–315 (orig.) → L. 348–353 (rev.): Figure 5. Comparisons of second-order semi-normalized sensitivities of the species indicated in the superscript **at the ground layer in each ground layer cell** averaged over the 24-hour episode to **domain-wide** emissions of the species indicated in the subscript using the hyperdual step (Hyd) and the hybrid methods. The sensitivity plots are polychromed by the domain-wide perturbed emissions of SO_2 , NO_x , or ISOP as indicated in the subscript. The calculated sensitivities are labelled in the bottom right corner of each panel. The left two panels show examples of gas-phase species concentrations with respect to corresponding emissions, while the right two panels show examples of aerosol-phase products with respect to their gaseous precursors.

320-324: Plausible, however the amount of disagreement for the SO₂ sensitivities in 2(c) seem comparable to those for NO_x in 2(g), however the second order sensitivities for NO_x seem fine. Is it true that in 5(c) the hybrid sensitivities are almost all negative? If so, can one think about the mechanism and chemistry, and make some arguments about whether or not the range of values spanned by the hyd sensitivities makes more physical sense (these seem to be clustered around 0) than the hybrid?

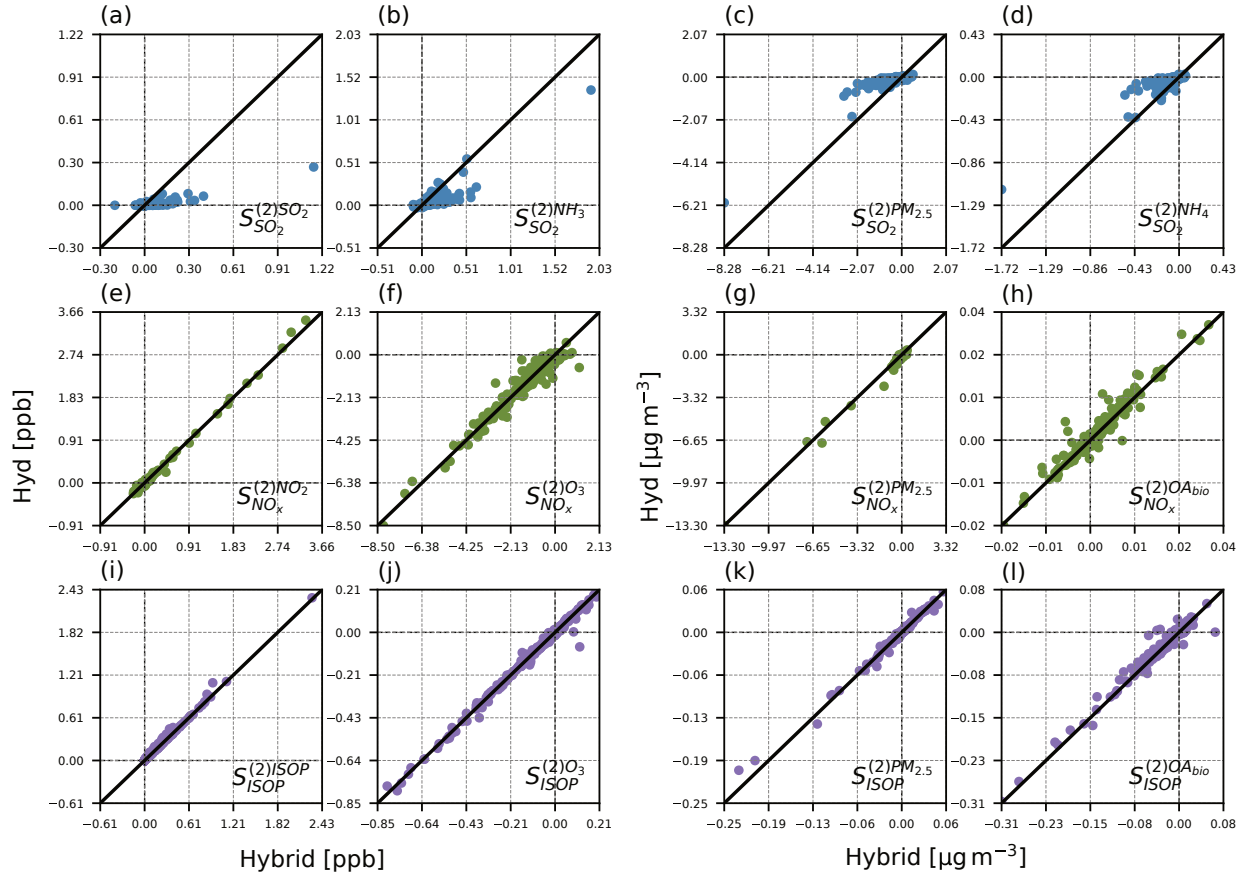
- Thank you for this comment. All figures and tables in this section were regenerated following the ISORROPIA bisection correction described in our response to the comment on line 250 above; the updated Fig. 2, Fig. 5, Fig. 6, Tables 1 and 2, and the revised slope in lines 329-330 are shown below.
- Updated Fig. 2 (caption at L. 256 (orig.) → L. 300 (rev.)):



- Updated Table 1 (caption at L. 262 (orig.) → L. 306 (rev.)):

First-order sensitivity: slope, R ²			
$S_{SO_2}^{SO_2}$: 0.96, 0.99	$S_{SO_2}^{NH_3}$: 1.17, 0.94	$S_{SO_2}^{PM_{2.5}}$: 1.14, 0.95	$S_{SO_2}^{NH_4}$: 1.17, 0.94
$S_{NO_x}^{NO_2}$: 1.00, 1.00	$S_{NO_x}^{O_3}$: 1.00, 1.00	$S_{NO_x}^{PM_{2.5}}$: 1.06 , 0.92	$S_{NO_x}^{OA_{bio}}$: 0.96, 0.82
S_{ISOP}^{ISOP} : 1.00, 1.00	$S_{ISOP}^{O_3}$: 1.01, 1.00	$S_{ISOP}^{PM_{2.5}}$: 1.12 , 0.93	$S_{ISOP}^{OA_{bio}}$: 1.02, 1.00

- Updated Fig. 5 (caption at L. 311 (orig.) → L. 348 (rev.)):



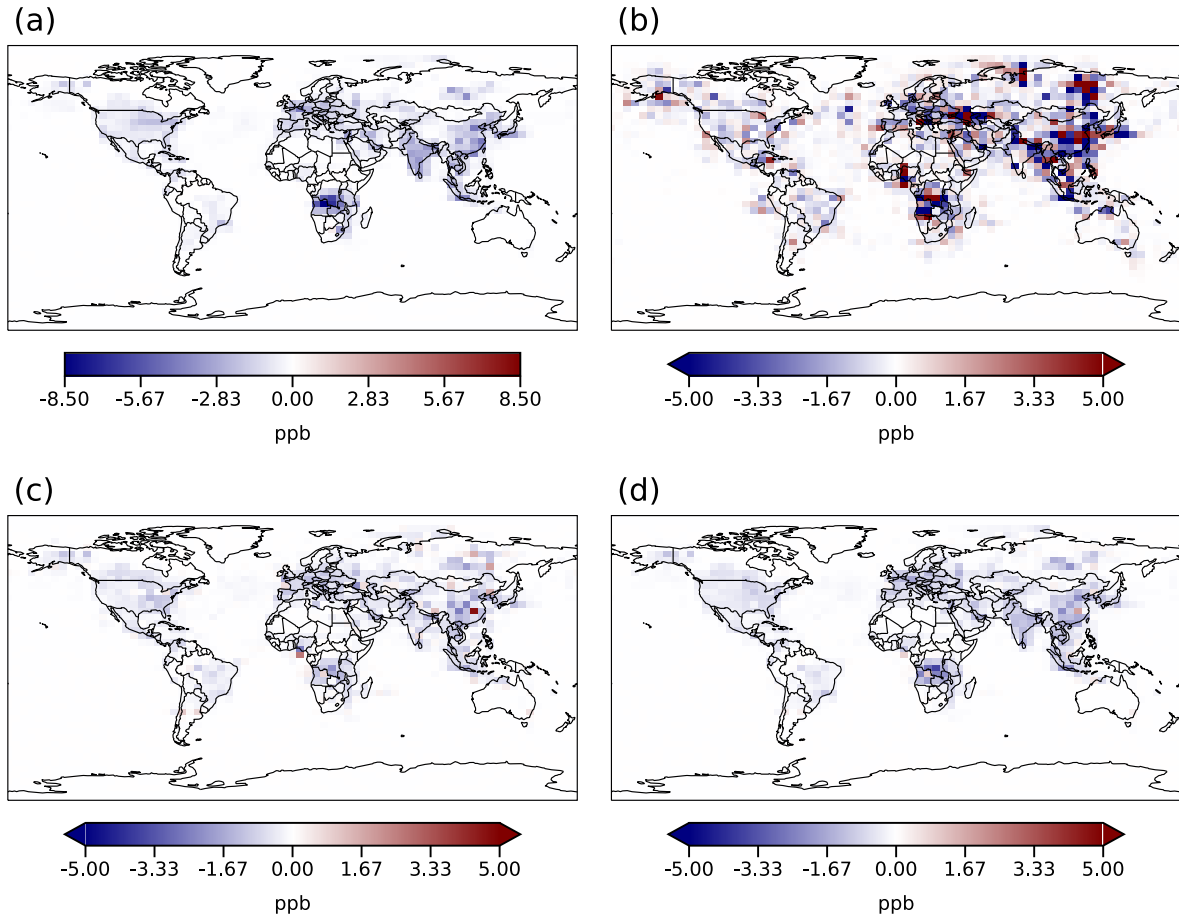
- Updated Table 2, with a naming typo corrected (caption at L. 316 (orig.) → L. 355 (rev.)):

Second-order sensitivity: slope, R^2			
$S_{SO_2}^{(2)SO_2}$: 0.18, 0.78	$S_{SO_2}^{(2)NH_3}$: 0.53, 0.78	$S_{SO_2}^{(2)PM_{2.5}}$: 0.50, 0.79	$S_{SO_2}^{(2)NH_4}$: 0.52, 0.80
$S_{NO_x}^{(2)NO_2}$: 1.02, 1.00	$S_{NO_x}^{(2)O_3}$: 0.98, 0.97	$S_{NO_x}^{(2)PM_{2.5}}$: 1.01, 0.99	$S_{NO_x}^{(2)OA_{bio}}$: 1.00, 0.93
$S_{ISOP}^{(2)ISOP}$: 1.03, 1.00	$S_{ISOP}^{(2)O_3}$: 1.00, 0.99	$S_{ISOP}^{(2)PM_{2.5}}$: 0.95, 0.99	$S_{ISOP}^{(2)OA_{bio}}$: 0.94, 0.97

- Updated slope value (L. 329–330 (orig.) → L. 374–375 (rev.)):

L. 329–330 (orig.) → L. 374–375 (rev.): The $S_{NO_x}^{(2)OA_{bio}}$ relationship has a slope of 1.00 and an R^2 value of 0.943, indicating no proportional bias between the hyperdual and hybrid sensitivities but some scatter.

- Updated Fig. 6 (caption at L. 343 (orig.) → L. 387 (rev.)):



- Although the first-order spread in Fig. 2c (SO_2) and Fig. 2g (NO_x) is comparable, it does not propagate to second order in the same way. ISORROPIA selects its equilibrium sub-case from the sulfate ratio (total sodium plus total ammonium, divided by total sulfate) and the sodium ratio (total sodium divided by total sulfate); nitrate enters neither. Perturbing SO_2 emissions therefore changes the denominator of both ratios directly and can place the base and perturbed states in different sub-cases, whereas perturbing NO_x emissions influences the sub-case only indirectly, through its effect on sulfate and ammonium. Where a 5 % SO_2 perturbation crosses a regime boundary (Fig. S3), the FD component of the hybrid estimator forms a difference quotient across a discontinuity in the solver response rather than a local curvature. The second-order NO_x sensitivities therefore remain well behaved even though the first-order FD scatter is of comparable size, while the second-order SO_2 sensitivities inherit the regime-crossing error.

- The hybrid sensitivities in Fig. 5c are shown in a joint heatmap and marginal distribution of the cells, which we added to the Supplement as Fig. S5. The highest concentration is a zero, and some spread exists in both the positive and negative direction, which is evident when shown in log-space.

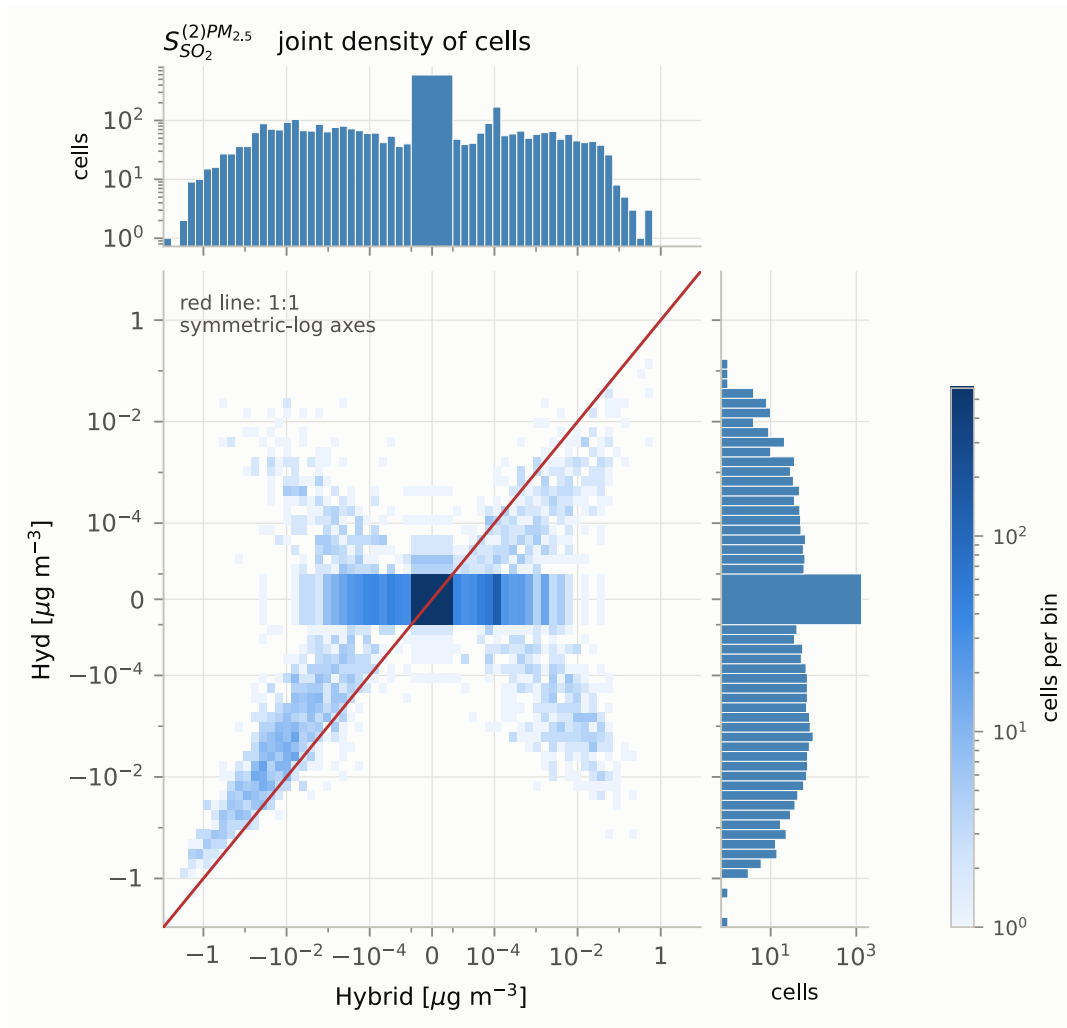


Figure S5. Joint heatmap and marginal distributions of second-order semi-normalized sensitivities of the time-averaged, ground layer $PM_{2.5}$ concentrations with respect to domain-wide, persistent perturbation of SO_2 emissions throughout the 24-hour episode, using the hyperdual step method (Hyd) and the hybrid hyperdual-finite difference method (Hybrid) with a 5 % perturbation in each direction. By cell count, 52.5 % of the hybrid values and 63.8 % of the hyperdual values are negative: the hyperdual values are negative more often but are clustered near zero, whereas in the hybrid it is the large-magnitude values that are predominantly negative.

- Nevertheless, the hyperdual values are indeed clustered around zero more tightly than the hybrid, and we regard that range as the physically meaningful one. The hyperdual value is the exact derivative of the model at the base state, whereas the hybrid value contains a finite difference across a ± 5 % perturbation; where that perturbation crosses a regime boundary, the resulting quotient is set partly by the size of the discontinuity and is not an estimate of the second derivative at that state. Consistent with this, the 2 % of cells with the largest $|\text{hybrid} - \text{hyd}|$ (Fig. S6), which we added to the Supplement, are concentrated where ship SO_2 emissions and coal emissions in industrial areas are largest, which is where a 5 % change in SO_2 emissions is most likely to move a cell across a regime boundary between perturbed runs.

Top 2% of $|\text{Hybrid} - \text{Hyd}|$, $S_{\text{SO}_2}^{(2)PM_{2.5}}$ (66 cells)

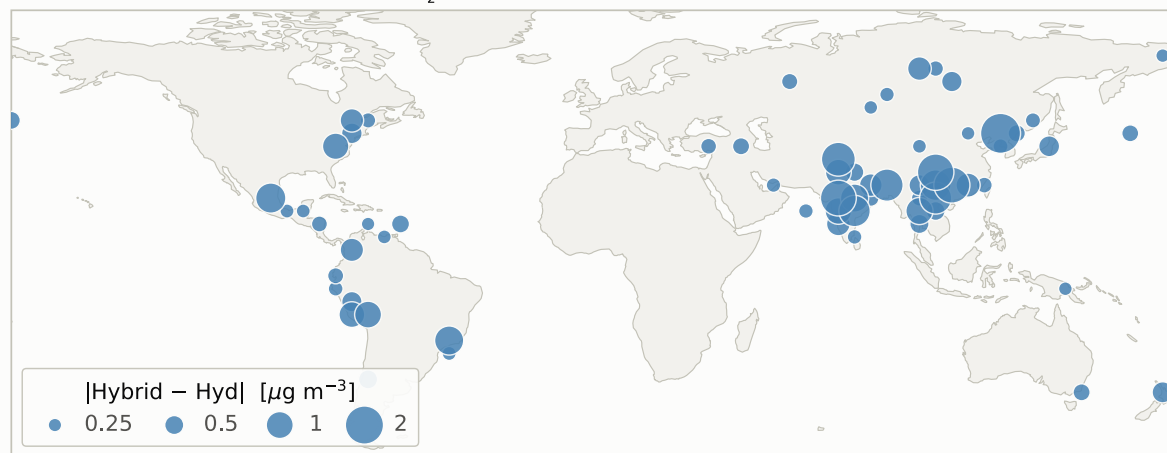


Figure S6. The 2 % of cells with the largest $|\text{hybrid} - \text{hyd}|$, sized by that difference of second-order semi-normalized sensitivities of the time-averaged, ground layer $\text{PM}_{2.5}$ concentrations with respect to domain-wide, persistent perturbation of SO_2 emissions throughout the 24-hour episode using the hyperdual step method (Hyd) and the hybrid hyperdual-finite difference method (Hybrid) with a 5 % perturbation in each direction.

- We revised the paragraph as follows:

L. 319–324 (orig.) → L. 357–369 (rev.): The statistics of the linear regression of the data in each subplot of Figure 4 5 (Table 2) indicate that the agreement between hyperdual and hybrid sensitivities with respect to SO_2 are ~~poor~~ **weak** while those with respect to NO_x and ISOP are strong. As noted in Liu et al. (2024), the disagreement between the hybrid and hyperdual sensitivities for SO_2 is attributable to the dependence on FD within the hybrid method, which ~~introduce~~ **introduces** disagreement in the first-order sensitivities with respect to SO_2 emissions (Fig. 2a-d). **This disagreement is primarily due to the regime switching in the sulfate response (Fig. S3): ISORROPIA selects its equilibrium sub-case from the sulfate and sodium ratios, in which nitrate does not appear, so perturbing SO_2 emissions can place the base and perturbed states in different thermodynamic regimes while perturbing NO_x emissions affects the sub-case only indirectly. Where a regime boundary is crossed, the FD component of the hybrid estimator forms a difference quotient across a discontinuity in the solver response rather than a local curvature. Further analysis shows that the hybrid values are in fact less often negative than the hyperdual (52.5 % versus 63.8 % of cells; Fig. S5), with the one-sidedness apparent in Fig. 5c confined to the large-magnitude tail. These cells with the large differences from hyperdual occur in areas where point source SO_2 emissions (e.g., shipping, coal-fired power plants) are expected and are more likely to lead to regime changes influencing the $\text{PM}_{2.5}$ response when emissions are perturbed in a multiplicative manner (Fig. S6).**

370-376: I appreciate the comparison of hyperdual sensitivities to adjoint sensitivities. However, it feels a bit out of place here, as section 3.4 should focus on results of the application, which does not include any adjoint modeling. Should this be move to / integrated into the introduction?

- We agree. We moved the comparison with the adjoint to the Introduction, where it now follows the review of the GEOS-Chem adjoint and opens the paragraph that introduces this work. We deleted the paragraph at L. 368–376 (orig.), so that Sect. 3.3 (formerly Sect. 3.4) opens directly with the application, and we updated the outline at the end of the Introduction.

L. 104–106 (orig.) → L. 112–119 (rev.): **This paper describes the implementation, evaluation, and demonstration of the hyperdual step method in GEOS-Chem. The hyperdual method is complementary to the receptor-oriented sensitivities calculated with the GEOS-Chem adjoint (Henze et al., 2007): the hyperdual method resolves the influence of a specific set of sources on the entire set of concentrations (Jacobian rows), while the adjoint resolves the influence of all sources on a select set of concentrations (Jacobian columns). The hyperdual approach additionally yields higher-order sensitivities with respect to the same source in a single model run. Although adjoint-on-adjoint code could be implemented to calculate second-order sensitivities, applications of the GEOS-Chem adjoint often assess the first-order sensitivities to be adequate for the extent of change assessed in the system or involve iteration in which the sensitivities are recalculated at different emissions levels.**

L. 369–376 (orig.): ~~The hyperdual method efficiently provides source-oriented first-, second-, or cross-sensitivities, which are complementary to the receptor-oriented sensitivities calculated with a model adjoint (Henze et al., 2007).~~

~~Specifically, the hyperdual method is practical for simultaneously quantifying the impact of select input parameters on all model outputs. As such, the hyperdual method complements the adjoint by easily exploring the influence of a specific source on the entire set of concentrations (Jacobian rows), while the adjoint computes the influence on a select set of concentrations of all sources (Jacobian columns). The hyperdual approach also provides higher-order sensitivities, which would require differentiating the adjoint model or conducting numerous adjoint simulations. In contrast, the hyperdual method yields first- and second-order derivatives in a single model run, which enables the quantification of the influence of emissions of selected species on concentrations through nonlinear chemical reactions.~~

L. 377–378 (orig.) → L. 415–417 (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.**

L. 115–117 (orig.) → L. 124–127 (rev.): In Sections 3.1–2, we evaluate the accuracy and computational cost of GEOS-Chem-hyd. **In Section 3.3, we demonstrate the usefulness of GEOS-Chem-hyd by evaluating the response of O₃, PM_{2.5}, ammonium (NH₄⁺), and biogenic organic aerosol (OA_{bio}) concentrations to perturbations in domain-wide NO_x emissions over a four-week simulation.**

Minor:

6: suggest “quantification of how changes in emission impact air quality”

- We thank the reviewer for this suggestion. We have revised lines 6–7 of the manuscript:

L. 7–8 (orig.) → L. 7 (rev.): Effective environmental policymaking requires accurate quantification of ~~the impacts on air quality of~~ **how changes in emissions impact air quality.**

420: NO_x

- Thank you. That sentence was removed when we revised Sect. 3.3, and we checked the remaining instances of NO_x.

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

- Belis, C. A., Pirovano, G., Villani, M. G., Calori, G., Pepe, N., and Putaud, J. P.: Comparison of source apportionment approaches and analysis of non-linearity in a real case model application, *Geoscientific Model Development*, 14, 4731-4750, 10.5194/gmd-14-4731-2021, 2021.
- Butler, T., Lupascu, A., Coates, J., and Zhu, S.: TOAST 1.0: Tropospheric Ozone Attribution of Sources with Tagging for CESM 1.2.2, *Geosci. Model Dev.*, 11, 2825-2840, 10.5194/gmd-11-2825-2018, 2018.
- Cohan, D. S., Hakami, A., Hu, Y., and Russell, A. G.: Nonlinear response of ozone to emissions: source apportionment and sensitivity analysis, *Environmental Science & Technology*, 39, 6739-6748, 10.1021/es048664m, 2005.
- Dunker, A. M.: The decoupled direct method for calculating sensitivity coefficients in chemical kinetics, *The Journal of Chemical Physics*, 81, 2385-2393, 10.1063/1.447938, 1984.
- Dunker, A. M., Yarwood, G., Ortmann, J. P., and Wilson, G. M.: The Decoupled Direct Method for Sensitivity Analysis in a Three-Dimensional Air Quality Model Implementation, Accuracy, and Efficiency, *Environmental Science & Technology*, 36, 2965-2976, 10.1021/es0112691, 2002a.
- Dunker, A. M., Yarwood, G., Ortmann, J. P., and Wilson, G. M.: Comparison of source apportionment and source sensitivity of ozone in a three-dimensional air quality model, *Environmental Science & Technology*, 36, 2953-2964, 10.1021/es011418f, 2002b.
- Eastham, S. D., Long, M. S., Keller, C. A., Lundgren, E., Yantosca, R. M., Zhuang, J., Li, C., Lee, C. J., Yannetti, M., Auer, B. M., Clune, T. L., Kouatchou, J., Putman, W. M., Thompson, M. A., Trayanov, A. L., Molod, A. M., Martin, R. V., and Jacob, D. J.: GEOS-Chem High Performance (GCHP v11-02c): a next-generation implementation of the GEOS-Chem chemical transport model for massively parallel applications, *Geoscientific Model Development*, 11, 2941-2953, 10.5194/gmd-11-2941-2018, 2018.
- Emmons, L. K., Hess, P. G., Lamarque, J. F., and Pfister, G. G.: Tagged ozone mechanism for MOZART-4, CAM-chem and other chemical transport models, *Geosci. Model Dev.*, 5, 1531-1542, 10.5194/gmd-5-1531-2012, 2012.
- Grewe, V., Tsati, E., and Hoor, P.: On the attribution of contributions of atmospheric trace gases to emissions in atmospheric model applications, *Geoscientific Model Development*, 3, 487-499, 10.5194/gmd-3-487-2010, 2010.
- Hakami, A., Odman, M. T., and Russell, A. G.: High-order, direct sensitivity analysis of multidimensional air quality models, *Environmental Science & Technology*, 37, 2442-2452, 10.1021/es020677h, 2003.
- Hakami, A., Odman, M. T., and Russell, A. G.: Nonlinearity in atmospheric response: A direct sensitivity analysis approach, *Journal of Geophysical Research: Atmospheres*, 109, <https://doi.org/10.1029/2003JD004502>, 2004.
- Hascoet, L. and Pascual, V.: The Tapenade automatic differentiation tool: Principles, model, and specification, *ACM Trans. Math. Softw.*, 39, Article 20, 10.1145/2450153.2450158, 2013.
- Kleeman, M. J. and Cass, G. R.: A 3D Eulerian Source-Oriented Model for an Externally Mixed Aerosol, *Environmental Science & Technology*, 35, 4834-4848, 10.1021/es010886m, 2001.
- Koo, B., Dunker, A. M., and Yarwood, G.: Implementing the decoupled direct method for sensitivity analysis in a particulate matter air quality model, *Environ Sci Technol*, 41, 2847-2854, 10.1021/es0619962, 2007.
- Maasakkers, J. D., Jacob, D. J., Sulprizio, M. P., Scarpelli, T. R., Nesser, H., Sheng, J.-X., Zhang, Y., Hersher, M., Bloom, A. A., Bowman, K. W., Worden, J. R., Janssens-Maenhout, G., and Parker, R. J.: Global distribution of methane emissions, emission trends, and OH concentrations and trends inferred from an inversion of GOSAT satellite data for 2010–2015, *Atmos. Chem. Phys.*, 19, 7859-7881, 10.5194/acp-19-7859-2019, 2019.
- Napelenok, S. L., Cohan, D. S., Hu, Y., and Russell, A. G.: Decoupled direct 3D sensitivity analysis for particulate matter (DDM-3D/PM), *Atmospheric Environment*, 40, 6112-6121, <https://doi.org/10.1016/j.atmosenv.2006.05.039>, 2006.
- Romero-Alvarez, J., Lupascu, A., Lowe, D., Badia, A., Archer-Nicholls, S., Dorling, S., Reeves, C. E., and Butler, T.: Sources of surface O₃ in the UK: tagging O₃ within WRF-Chem, *Atmos. Chem. Phys.*, 22, 13797-13815, 10.5194/acp-22-13797-2022, 2022.
- Varon, D. J., Jacob, D. J., Sulprizio, M., Estrada, L. A., Downs, W. B., Shen, L., Hancock, S. E., Nesser, H., Qu, Z., Penn, E., Chen, Z., Lu, X., Lorente, A., Tewari, A., and Randles, C. A.: Integrated Methane Inversion (IMI 1.0): a user-friendly, cloud-based facility for inferring high-resolution methane emissions from TROPOMI satellite observations, *Geosci. Model Dev.*, 15, 5787-5805, 10.5194/gmd-15-5787-2022, 2022.
- Yang, Y.-J., Wilkinson, J. G., and Russell, A. G.: Fast, direct sensitivity analysis of multidimensional photochemical models, *Environmental Science & Technology*, 31, 2859-2868, 10.1021/es970117w, 1997.
- Ying, Q. and Kleeman, M. J.: Source contributions to the regional distribution of secondary particulate matter in California, *Atmospheric Environment*, 40, 736-752, <https://doi.org/10.1016/j.atmosenv.2005.10.007>, 2006.
- Zhang, W., Capps, S. L., Hu, Y., Nenes, A., Napelenok, S. L., and Russell, A. G.: Development of the high-order decoupled direct method in three dimensions for particulate matter: enabling advanced sensitivity analysis in air quality models, *Geoscientific Model Development*, 5, 355-368, 10.5194/gmd-5-355-2012, 2012.