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Atmospheric Chemistry and Physics Discussions

Interactive comment on "ANISORROPIA: the adjoint of the aerosol thermodynamic model ISORROPIA" *by* S. L. Capps et al.

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Anonymous Referee #2

I come to this review with expertise in aerosol and solution thermodynamics, but not in atmospheric modelling, nor in the mathematical techniques involved in inverse modelling. . . . should be rectified.

We appreciate the considerable effort put forth in writing this review, as it uniquely combines important comments with colourful overtones. Our responses to the issues raised are presented below.

(1) The division of chemical composition by ISORROPIA . . . figure makes better sense - although my comments about the pattern of values are unchanged - if the bottom left

apex is HNO3, the top one is H2SO4, and the bottom right one is NH3. It is important that the authors both correct the figure, and produce a comparison plot in which the same quantity is calculated using some general thermodynamic model of the system in which no division into composition regimes is made. This will be valuable (here and perhaps elsewhere) to evaluate the effects of this division.

As stated in our response to Dr. Kelly, branching and discontinuity is not unique to ISORROPIA but exists in every science code that contains "GO TO", "IF", "MAX/MIN", "ABS", etc. Calculation of sensitivity using finite difference approximation often fails to reflect the behavior of the model because of this (and other issues discussed in the manuscript). ANISORROPIA does not suffer from these problems however, because it is a discrete adjoint with a continuous set of solutions and derivatives in each sub-domain of the code. Thus, the division of the solution space into separate regimes motivates the local sensitivity analysis approach to calculate the relationships defined by ISORROPIA. The authors leave the assessment of the accuracy of the underlying model to earlier studies (Ansari & Pandis 1999; Yu et al. 2005).

Comparing ANISORROPIA against another more comprehensive thermodynamic code (e.g., E-AIM) is beyond the scope of this manuscript (because the main point is to demonstrate consistency with the original model) but is nevertheless an interesting quest. Such a comparison however is *not feasible* at this time, because to carry it out correctly would require at least the application of CVM. This needs a COMPLEX version of the more comprehensive code (e.g., E-AIM) which, to our knowledge does not exist.

We apologize for the oversight in the switched axes labels. This is now corrected and the discussion revised.

(2) The development of ISORROPIA in terms of a series of different 'composition spaces' also seems to have led to the development of shorthand language that, . . . good enough for publication unless these descriptions are corrected throughout.

ACPD

11, C12869–C12875, 2011

The parenthetical description in Section 2.2 (p.23478, lines 17-18) has been removed. As the reviewer demonstrated in the first comment, “neutralization” is a common description of the interactions of non-H^+_positive ions with the atmospherically-formed acids. Perhaps the persistence of the metastable assumption in CTMs and, consequently, ANISORROPIA was not made sufficiently clear and led to the confusion regarding formation of salts; the revised manuscript clarifies this point.

(3) I agree with Kelly’s comment about Pitzer vs. K&M: Pitzer is more . . . the use of K&M.

Thank you for clarifying. The text now states “K-M compares well with experimental results as does Pitzer but also continues to produce physically reasonable results at higher ionic strengths (i.e., greater than $30m$) (Harvie et al. 1984; Cohen et al. 1987; Kim et al. 1993).”.

(4) The introduction places the present . . . problems.

p23471 (lines 9-10): "as well as providing a means of refining emissions estimates with observations." Do you mean inferring emissions directly, or working out what emissions values need to be known most/more accurately? If the former, then the process seems rather circular.

The text now reads “. . . with observations in an inverse modeling framework.” Inverse modeling is a well-established practice for refining model input.

p23471 (lines 12-13) "..challenges the robust assessment.." Language for a bad press release.

Thank you! The text now reads “makes the robust assessment of emissions influences challenging.”.

p23472 (p. 23471, line 28 – p.23472, line 1)"..reveals the impact .. without perturbing the model state.”

ACPD

11, C12869–C12875, 2011

The text now reads "...can be used to understand the impact ...without changing emissions parameters...".

p23472 (line 2) "..source oriented sensitivities.."

This is a term used in the community. No change needed.

p23472 (lines 22-23) "..gas phase sensitivity relationships.." Be specific: sensitivity of what to what?

The text now reads "...to explore relationships of concentrations of gaseous species and emissions (Menut...".

p23472 (line 27) "Gas phase 4D-Var data assimilation..." Introduced without explanation.

The use of the acronym on line 27 was preceded by an introduction on lines 17-19 of the same page.

p23473 (lines 5-6) "recently increased impetus for their utility."

The text now reads "...as well as recent attention to refining aerosol concentration estimates in CTMs.".

p23474 (line 9) "..the entire deliquescence curve.." Do you just mean RH range? See also Kelly's comment.

"Deliquescence curve" now reads "water uptake curve". ISORROPIA could treat the formation of salts and the process of deliquescence; however, the standard in CTMs is to approximate the aerosol as metastable across the entire range of RH.

p23475 (lines 24-25) "weights the difference of modeled concentrations translated into observation space" Difference from what? The first part of the sentence isn't any clearer.

As noted elsewhere, Section 2.1 of the revised manuscript is limited in scope to species

ACPD

11, C12869–C12875, 2011

as opposed to the time and space dimensions of the original manuscript, which removes this sentence entirely.

p23476 (line 1) "a priori pa" . ?

The cost function described in the revised manuscript does not include model parameters, which may be the source of confusion here. This statement is removed.

p23476 (line 1): "model parameters". Parameters are usually fitted coefficients within a model. Here they seem to mean, much more loosely, the quantities of interest that are either output by the model or are input to it. Some specific examples, and more exact use of language, would be helpful.

The revised manuscript clarifies that in the context of inverse modeling with CTMs, model parameters indicate model input, including emissions rates.

p23479 (line 3-6): "If the governing equations are differentiated and then transformed into a numerical algorithm, the adjoint is termed a continuous adjoint; hence, the discretization of the adjoint model may not be in accordance with the underlying model." I do not understand what is meant by the last part.

The text now reads “hence, the algorithmic treatment of the adjoint model may differ significantly from the underlying model.”.

p23479 (line 18): "checkpoint the solution regime".

This is standard terminology in the field. To clarify, the text now reads to read “checkpoint, or store to a file, the selected solution regime”.

p23479 (lines 25-27): "was used to augment the forward model with sensitivity calculations capable of treating adjoint forcing vectors provided in a box modeling context". Clarify.

The text now reads “. . . was used to apply the chain rule of derivative calculus line by line such that derivatives of dependent variables with respect to intermediate variables

ACPD

11, C12869–C12875, 2011

can accumulate through this adjoint model in accordance with an adjoint forcing vector to produce the sensitivity of a dependent-variable with respect to independent variables *(Autodiff.org)".*

Autodiff.org: http://www.autodiff.org/?module=Introduction&submenu=FAQ#7, last access: 16 Nov 2011.

p23481 (lines 23) "differentiable calculation".

Lines 12 and 13 outline the need for this "differentiable calculation" described on line 23.

p23482 (lines 5-6) "Partitioned concentrations". I think this just means "results".

No. Concentrations together with the sensitivities are the "results" of ANISORROPIA.

p23482 (lines 5-6) "metastable assumption". I know what this means (even though it comes out of the blue); others may not.

In the revised manuscript, this is clearly described in the introduction (p. 23474, line 10).

p23485 (line 12): "Model input ranges"

The text now reads "Modeling experiments were . . . ".

p23485 (line 14) "...so that calculations, not variable writing processes, were evident in the comparisons." This is about execution time. Say so.

The text now reads ". . . were evident in the timing comparisons.".

p23487. The differentials are all unitless, but are either on a molar or mass basis. Writing "mol mol-1" is not the best way to express this.

Good point. The text now reads "on a molar basis" ("on a mass basis").

p23487 (lines 18, 24): molar mass not molecular weight. Nitrate is not a molecule.

ACPD

11, C12869–C12875, 2011

Indeed, it should have read “ionic weight”. The text now reads “molar mass” in both cases.

p23492: (lines 22-23)"..is used the reveal the sensitivity regimes..". "Reveal" suggests a stage performance, such as pulling a rabbit out of a hat, or (an old IBM term, I'm told) "opening the kimono". I'll leave that one to your imagination. "Determine" is a more appropriate word in a scientific manuscript.

We feel “reveal” is appropriate, because the sensitivity was “there” in the equations, but required the development of ANISORROPIA to correctly bring it out. No change made.

References

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