“Estimation of volatile organic compound emissions for Europe using data assimilation”
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Response to Reviewer #3

We thank the reviewer for his/her useful comments and suggestions.

General comments:
This manuscript describes an application of inverse modeling to quantify the extent to which emissions of a selected set of VOCs are accurately represented in existing emission inventories. The authors assimilate “true” observational data from a network of EMEP monitoring sites in an adjoint model based on a 3D air quality model to backcalculate what the emissions should be in order to be consistent with the observations. This addresses a topic which is highly important to air quality modelers and regulators, but an issue in which little progress has been made to date. We don’t really know how good the overall VOC inventories are. It is a difficult problem, as the authors clearly describe in their introduction, and the results of this study show that it is limited by sparse observations, especially for more reactive species – and the ones that may be of most concern for health impacts. The two conclusions I can make from this work are 1.) there may be substantial errors in emissions of some VOCs, which justifies additional work and 2.) if using this technique, a non-truncated Gaussian estimation technique gives the best overall results (?).

We assume you meant “if using this technique, a truncated Gaussian estimation technique gives the best overall results” as demonstrated by the cross-validation results.

The conclusions of this manuscript could be more substantial if it included some discussion of the implications of these results. Does it make sense that propane is underestimated by a factor of 2 or that butene is underestimated by 30%? Why? Is butene underestimated by 30% across-the-board or is it estimated well in some places but poorly in others (and where)? What are the largest potential consequences of these results – why should the reader care?

We agree that the interpretation of the results can appear a bit frustrating. The results we get from this inversion study are consistent with roughly estimated uncertainties of the VOC inventories. The method we propose here does not aim to explain the possible cause of discrepancies between EMEP emissions estimation and potentially more realistic emissions, it aims to assess the magnitude of these discrepancies. The section “4.1.4 Spatial distribution”, supported by the figure 7, provides a discussion concerning the spatial heterogeneity of the corrections; so does the new section on the posterior uncertainty. The introduction section presents the main causes of concern related to the assessment of VOC emissions (why we should care). A comprehensive study of the impact (on ozone concentration fields for instance) of the a posteriori emission fields it out of the scope of the present paper.

I cannot fully evaluate the methodology because the manuscript employs terminology (i.e. “hyperparameters”, “gain matrix”, “value screening”) and conventions that are unfamiliar to many readers. It requires more basic explanation of the methodology (maybe putting more of the details in the appendix). Although I try to read sections 2.4 and 2.5, I always end up skipping over these. I hope that other commenters weigh in on the validity of the technique.

Thank you for your suggestions. We have clarified those key concepts in the revised manuscript. Note that some of them such as the gain matrix is merely a name and does bear more than its formal definition given by Eq.(9) in this case. We wish that our manuscript be readable by the atmospheric chemistry data assimilation community but also to a significant extent by the inventory community.

Note that several definitions had been provided in the original manuscript. For instance, the definition of “hyperparameters” had been introduced in the original submission (beginning of section 2.5) using standard concepts of atmospheric chemistry data assimilation. To make it more accessible, this definition has been extended into:

“The parameters of the prior statistics, such as r_s and m_s, give a measure of the magnitude of the prior uncertainties. For a reliable emission inverse modelling, these often need to be estimated, in addition to the emission fluxes, because their first guess is usually inaccurate, while the dependence of the retrieval on these parameters can be dramatic (Davoine and Bocquet, 2007). When those r_s and m_s are considered as parameters to be themselves estimated on top of the flux parameters, they are usually coined *hyperparameters*.”

The overall presentation could be clarified, with the evaluation of the validity of the assumptions easier to determine with additional explanations. By submitting to ACP, this manuscript strives to appeal to a wider audience (as it should, due to the practical application to a very real modeling problem), therefore the authors should include more text to “state the obvious” – what is the main point being made by Table 9? By Figures 3 and 4? Readers don’t have to fully understand every detail but the figures and tables should communicate something to the reader and they don’t to me. I suspect that these figures and tables could be eliminated.

Ok. Specifically, Table 3 and 4 are typical examples of the likelihood of the parameters m and r given the observation. It is important to show them for the reader fluent in data assimilation/inverse modelling. This is not so important if one is more concerned by the results and their interpretation.

Table 9 might be too much in the balance between the methodology and the results. That is why we removed this section. Given your reaction towards this section, and given another suggestion of reviewer 2, we replaced it in the revised manuscript by the objective estimation of the uncertainty of the retrieved emissions, which you may find more interesting.

Specific comments:

There are some variables (and indices) that are not defined, such as T (line 134) or the components of the error covariance matrices I (line 147). Definitions for rs and ms are missing (line 147). The manuscript would benefit from making these definitions very clear up front.

We do so in the revised manuscript. Thank you for the suggestions.

Section 2.1: Errors in the oxidants can mask errors in the emission inventory; the manuscript should present any evidence to support that the CTM is predicting OH, O3 and NO3 that are reasonably accurate.

The study has been completed by an uncertainty analysis (cf. response to reviewer 1) that partly answer to this question. The methodology advocated here take into account implicitly all the possible errors. The model has been evaluated in another paper (Kim et al, 2009), cited in this work, with a configuration similar to the one used in the present study. To clarify this point our text has been modified:

section “2.1 Full chemical transport model and reduced VOC model”

... In order to simulate the concentrations of these species, the RACM 2 (Regional Atmospheric Chemistry Mechanism, version 2) chemical kinetic mechanism (Goliff et al., 2013) is used within the CTM. The model has been satisfactorily evaluated with a similar configuration in Kim et al. (2009).

p. 4, line 97: how are the additional, explicit VOCs "..written in a way that does not affect RACM2?" Are they removed from the lumped species? Do they consume oxidants (as written in Table 1)? A large change in the emissions of any individual VOC could affect the parameters of the lumped species in which that VOC is included, unless you have rederived the lumped species coefficients.

We have now clarified this point by adding the following text: "The emissions of the explicit species continue to be treated as part of the lumped species of RACM2 and the oxidant species involved in the additional oxidation reactions of the explicit species (see Table 1) are included as a product of the oxidation reaction so that their concentrations are not affected by those additional reactions. This approach has been used previously and has been shown not to affect the concentrations of the original mechanism, here RACM2 (e.g., Pun et al., 2003; Kim et al., 2011)."

References:

Kim, Y., K. Sartelet, C. Seigneur, 2011. Formation of secondary aerosols over Europe: comparison of two gas-phase chemical mechanisms, Atmos. Chem. Phys., 11, 583-598.

Pun, B., S.-Y. Wu, C. Seigneur, J.H. Seinfeld, R.J. Griffin, S.N. Pandis, 2003. Uncertainties in modeling secondary organic aerosols: three-dimensional modeling studies in Nashville/Western Tennessee, Environ. Sci. Technol., 37, 3647-3661.

Table 4: Need to define rs and ms in this table (especially since they are not defined well in the text). Include the units of ms and ms+. What is meant by "background"? Does it mean concentrations induced by initial and boundary conditions, or does it mean transported concentrations, or the initial guess in emissions? It is not clear.

Ok. Thank you for the suggestions. ms and ms+ are unit-less because they scale the error covariance matrix on the alpha variables which have no dimension. The background is the initial guess in the emissions. As rightfully pointed out by Reviewer 1, we have been using several expression for the background/first guess/prior which is not to ease the reading. This has been corrected in the revised manuscript as much as possible.

p. 8, line 173: I can't find anything in the text giving an indication of the uncertainty in the observations. Since these are used to constrain the emissions, it is important to know how reliable they are.

We have added a brief description of the observation uncertainties at the end of Section 3.1.

"The uncertainties associated with the measurements have been analyzed in detail by Sauvage (2008) for three stations of the monitoring network considered here (stations 9, 10 and 11 of Figure 1). For the VOC considered here, the measurement uncertainties were estimated to consist of a heteroscedastic component ranging from 11% (ethane) to 25% (m- & p-xylene) of the measured concentration and a constant component of 0.01 ppb associated with the detection limit."

However, our methodology determines the magnitude of these errors (in addition to representativeness and part of model errors) in an objective manner. That is the point of finding the optimal r_s. The value of r_s gives the typical standard deviation of the observation errors encompassing instrumental and representativeness errors.

Reference:

Sauvage, S., 2008. Origine et comportement des composés hydrocarbonés non-méthaniques (HCNM) en zone rurale, Ph.D. thesis, Université des Sciences et Technologies de Lille, France (in

French).

p. 9, line 206: It seems odd that the boundary conditions of most species are normalized to propane. Need to include some justification that this does not affect the results.

We agree it would be better to have specific boundary conditions for each of the treated species. The choice of the propane is pragmatic but also supported by the references cited in the section “3.2 Inversion and validation setup” Rudolph and Ehhalt (1981), Rudolph and Johnen (1990) and Penkett et al. (1993). As explained to Reviewer 1, we have performed for the revision a comparison of the results of the Mozart 2 model (used for the boundary conditions of our study), to the observations used for the inversion. From this comparison we roughly assess average relative errors ranging from 1% (for propane) to 116% (for propene). Among the species with boundary conditions derived from the propane concentration fields, the errors range from 4% (for n-butane) to 84% (for benzene). The worse situation occurs for acetylene that combines a significant potential error (-60%) with a long lifetime (110 days). Several comments have been added about the acetylene case in the revised manuscript to emphasize this point.

p. 10, line 269, and all simulations using a posteriori emissions; similar to comment on line 97: Did you rederive the emissions of the RACM2 lumped species where applicable or just increase the emissions of the explicit species (I assume the former). Did you need to adjust the parameters for species HC3 in order to account for changes in the components of HC3 (especially propane and isobutane)?

Both were done: the change in the emissions of a given VOC (e.g. propane) were reflected in the emissions of the corresponding lumped species (i.e., HC3 for propane) and in the emissions of the explicit species (i.e., propane). No change was made to the parameterisation of the lumped species, because the lumped species parameters are fixed in RACM2 and taken as a weighted average corresponding to U.S. emissions (Goliff et al., 2013), unlike the SAPRC mechanisms where those parameters can be recalculated based on the relative fractions of the individual VOC species contributing to a lumped species).

Reference:

Goliff, W.S., W.R. Stockwell, C.V. Lawson, 2013. The regional atmospheric chemistry mechanism, version 2, *Atmos. Environ.*, 68, 174-185.

Figure 7: The discussion of Figure 7 omits the spatial variation in the correction factor, even near to the monitors. While the inversion results (Table 6) imply that emissions for isopentane are close to the a priori emissions, Figure 7 shows a posteriori emissions that vary from 0.10 of the a priori to 5.0 times the a priori. This is important information!
To leave the reader with the impression that these emissions are consistent (based on the fact that the overall correction factor is close to 1) is wrong. Why are these four species selected for presentation? Since isobutane and ethene both show substantial error corrections relative to the a priori emissions, these would be more informative than isopentane and o-xylene, and would display the same range of lifetimes.

The figure 7 has been modified to account for your comments. We have added a column showing the base emissions and we now present results for acetylene, ethane, isobutane, ethylene and isoprene. The text in the section “4.1.4 Spatial distribution” is modified as follows:
“...the prior EMEP emissions for the species acetylene (ACE, with an average lifetime of 110$\,$days), ethane (C$_2$H$_6$, with an average lifetime of about 60$\,$days), isobutane (IBUT, with an average lifetime of about 7.5$\,$days), ethylene (C$_2$H$_4$, with an average lifetime of about 1.45$\,$days) and isoprene (ISO, with an average lifetime of about 1.7$\,$hour), respectively.

Obviously the corrections extend much farther from the monitoring stations for the long-lived species, such as ACE and ETH than for the short-lived species...”

The statement “*To leave the reader with the impression that these emissions are consistent (based on the fact that the overall correction factor is close to 1) is wrong*” should be nuanced. Firstly we hope that the reader is more impressed by the cross-validation and forecast studies which proved that the corrections go in the right direction, rather than by the fact that the correction factor is close to 1. Secondly, it is a well known fact in the atmospheric chemistry data assimilation literature or more generally in the inverse modelling literature, that the estimation of aggregated variables is less prone to error than high-resolution local flux variables, a basic statistical effect that also necessarily applies to our study. We hope that the new section on the posterior uncertainty will illustrate and emphasise this aspect.

p. 14, line 342: The comparison with the Cursi et al study raises a lot of questions. Odd that the isoprene inventory is 2.5 times larger than MEGAN, yet your difference in error is only about 20% from the Curci study. I also have not seen a good explanation of error in the assumed yield of HCHO from isoprene, especially in Europe, especially when it is highly spatially and temporally variable, especially based on one chemical mechanism, so I do not agree that the remote sensing option is necessarily more satisfying – it would be preferable to use isoprene directly, as you do.

When comparing to the Curci et al. study, we were interested in the directions of the corrections rather than in reconciling the revised isoprene emission inventories. One important point is that those studies pertain to different periods and biogenic emissions vary with season and from year to year because they depend on solar radiation and temperature. Therefore, we have reworded the text to clarify this point. We have also added some cautionary statement regarding the uncertainties associated with inverse modelling of isoprene emissions using formaldehyde (and glyoxal) satellite observations.

“…with the former leading to greater isoprene emissions on average over Europe, for example by a factor of about 2.5 for the July-August 2006 period (Sartelet et al., 2012).”

“On the contrary, satellite observations are well suited…snapshot of the concentrations, although uncertainties are associated with using oxidation products (formaldehyde, glyoxal) of isoprene to retrieve the isoprene emissions”.

Table 9: State either in this table of in the text, what the reader should be looking for in the use of ratios in this table. Is a low ratio an indicator of a superior data assimilation system? (see general comment #5)

This table has been discarded in the revised manuscript. The related section has been replaced by an estimation of the uncertainty of the retrieved emission. (The table was correct but arguably too much in terms of data assimilation techniques.)

Technical corrections:

Abstract, line 11: “. . . the retrieval leads to. . .” What is the retrieval? Do you mean the a posteriori emissions?

Yes. We replaced it by “... the retrieved emissions lead to...”.

p. 7, line 166:” . . .where rs+ and ms+ refer respectively to the standard deviation of the error and of the emission noise. . .” Which error? Do you really mean the standard deviation of the emission noise?

rs+ is the standard deviation of the prior observation error in the C case. ms+ is the standard deviation of the prior source error in the C case. Their optimal values are given by maximising their likelihood with the VOC observations. Hence, their optimal values are *per se* estimations of the magnitude of the prior errors.

The phrase was incorrect (missing word) and has been corrected. Thank you to pointing it out.

p. 15, line 410: “For all species the ratio is greater for B1.” Do you mean “For all species the ratio is greater for B1 than B2”?

Yes. But this section has now been removed (on your implicit suggestion) and replaced by an estimation of the uncertainties in the retrieved emissions.

p. 15, line 414: “The DFS, 4% in the B2 case and 7% is consistent. . .” Which case is 4% and which is 7% or is it 4% and 7% for B2?

Same as before.

References: Line 490: need a better reference for RACM2 – not a conference presentation.

The reference has been updated. Thank you.

Goliff, W.S., W.R. Stockwell, C.V. Lawson, 2013. The regional atmospheric chemistry mechanism, version 2, *Atmos. Environ.*, 68, 174-185.