Review #3:

The authors would like to thank Referee #3 for his constructive comments and suggestions. They certainly helped us to improve the quality of the manuscript.

General comments

Comment 1:

This work would benefit from including more discussion of the merits of singular vector analysis vs other modes of sensitivity calculations (brute force, DDM or adjoint) for sensitivity studies of box-model photochemical calculations. How would they differ in their overall effort? What are the differences in the results they would provide? How well do the different methods scale when considering application to 3D CTMs?

Response 1:

Thank you for this comment. As already addressed in our responses to Referees #1 and #2, the proposed other methods of sensitivity calculations do not provide optimal perturbations, which we are looking for. Hence, an investigation of differences of methods must also include a study on the different type of information provided by these methods and their use.

In order to clarify the relation between singular vector analyses and other sensitivity methods, we added the following paragraph to the introduction:

"Singular vector analysis accomplishes the identification of measurement priorities by detecting the most sensitive species (here equated to the fastest growing uncertainties). Therefore the first objective of the present work is the singular vector based sensitivity analyses of specific photochemical scenarios, while the second objective is the generation of sensitivity based measurement strategies.

Common sensitivity analysis methods for chemical box models are the "brute force" approach, as well as adjoint sensitivity or direct decoupled method (DDM). While the brute force approach is simple to implement and computationally inexpensive, it will become infeasible for systems with a large number of input parameters. The implementation of adjoint sensitivity and DDM is technically challenging, but both methods provide greater efficiency and accuracy (Dunker et al., 2002). Brute force approach, adjoint sensitivity and DDM compute first-order local concentration sensitivity coefficients. In contrast, singular vector analysis provides optimised sensitivities, i.e. perturbations resulting in maximum error growth. Due to the latter feature, the singular vector analysis is indispensable and our method of choice. Since singular vector analysis is furthermore a well proven approach which allows keeping the dimension of the problem flexible, the anticipated later application to a three-dimensional chemistry transport model is feasible in a computational efficient way."

Comment 2:

There seems to be a disconnect between the reasoning for this study described in the introduction (targeted observations) and the actual application (sensitivity of a photochemical box model). Discussing how singular vector analysis will eventually be useful

for targeted observations is motivational, but perhaps not the most direct application of the results that are actually presented here. Could the authors instead find other applications of the kind of results they are generating in this initial application? For example, that NOx emissions have impacts according to the time of their emission is relevant to discussion of pollution control strategies. The temporal trends in the singular vector growth has implications for inverse modeling of emissions and the degree to which observations may reflect uncertainties in concentrations several days prior or several hundred km afar. I would encourage the authors to find more direct ways of making their existing results relevant.

Response 2:

We agree that there seems to be a disconnect. In order to clarify the link from sensitivities to observation targeting, we formulated the objectives in a clearer way and added a section in the theory part which establishes the link from sensitivities to observation targeting (for details see our Response 1 to Reviewer #1). Using optimal sensitivities for the identification of most useful observations is now discussed in a sounder way.

We are especially grateful for the advice of the Reviewer concerning the relevance of the results. Though the suggested approach of emission control strategies seems very interesting we decided to follow our original objectives of targeting observations, also in view of the other reviewers' comments. Therefore, we interpreted all sensitivity results in terms of targeted observations by adding a section called "Summary of sensitivity results and associated measurement strategy" at the end of each error growth investigation (for an example see our Response 3 to Reviewer #2). Finally, the summary of the different measurement strategies at the end of the revised paper (page 16780, line 23) reads:

"In a second step, the identified sensitivities are applied to address the problem of targeted observations. Sensitivity based measurement strategies are proposed, defining which species can be omitted for measurements and which species need to be measured to reduce the uncertainty of the ozone-forecast. Here, a measurement strategy is considered profitable if at least measurements of one species can be omitted for all considered measurement times and forecast intervals. Such profitable measurement strategies allow for a reduced instrumentation and are therefore desirable.

In terms of targeted observations the sensitivity results for the grouped error growth with respect to initial values suggest a profitable measurement strategy with focus on VOC measurements in polluted air (i.e. the measurement strategy is regime restricted). In case of the grouped error growth, a profitable measurement strategy is not feasible for the other environments considered in this study (i.e. an omission of VOC- or NO_x-measurements is not advisable). Considering the two other types of grouped error growth (grouped relative error growth with respect to initial values and with respect to emissions), their sensitivity rankings yield a multitude of measurement strategies. However, profitable measurement strategies can be achieved for all types of projected singular vectors. Since summation of the most important projected singular vector entries approximates the associated grouped singular vector entry, the profitable measurement strategies of the projected error growth can be utilised for both types of error growths. In detail, the projected relative error growth allows for regime dependent and regime independent measurement strategies which are both very profitable (i.e.

in both cases many compounds can be omitted for measurement). In contrast measurement strategies for the projected error with respect to initial values and for the projected error with respect to emission factors are much more profitable (i.e. much more compounds can be omitted for measurement) when regime restricted. The latter feature is due to the fact that reaction rates and emission sources themselves are regime dependent (in case of reaction rates the regime dependence is solely initiated by regime associated temperatures). The rather high profitability of a regime independent measurement strategy for the projected relative error growth with respect to initial values is caused by the fact that the magnitudes of concentration ratios of species within one family are approximately stable.

In summary it can be stated that singular vector analysis is a powerful tool, which can be used to identify sensitive chemical species. Here, this method was applied to analyse the time- and regime-dependence of the VOC versus NO_x limitation of the ozone formation for a set of six different scenarios. With the help of six different types of error growth, different chemical regimes could be characterised. While the sensitivity of ozone to the VOC or NO_x family varies with time and suggests therefore mostly time-dependent measurement strategies (i.e. for a time-independent measurement strategy all species have to be measured), the relevance ranking of species within one family remains scenario-wise relatively stable. Here time-invariant targeted observations can effectively be applied omitting measurements of several less sensitive compounds. Given the multitude of reactions and the time and scenario dependence of the chemical evolution, the potential of ranking species into less, middle or very important is a very positive result showing that singular vectors can be utilised effectively for optimal campaign and instrumentation planning."

Comment 3:

Clearly this approach generates more results than can be discussed in the paper. In some cases, the authors choose to focus on results from particular scenarios. Could they explain a bit more why they pick specific scenarios to plot the results over others, such as MARINE for Figs 4 and 5? At the moment it seems a bit arbitrary at times.

Response 3:

In most of the cases we selected those scenarios and/or chemical compounds for illustration which showed the most variability. In the special case of Fig. 4 and Fig. 5, scenario MARINE has been chosen for illustration because it features the largest reduction of standard deviation between category C_b and categories $C_{b1/2/3/4}$ on the one hand and the smallest reduction of standard deviation between category C_a and categories $C_{a1/2/3/4}$ on the other hand. In order to make our choices more comprehensible, each selection criterion is now described within the discussion of the associated figure.

Comment 4:

Regarding the box model, from what I can tell it contains only emissions and reactions. There are no loss rates or dilution factors. Wouldn't this lead to buildup of chemical concentrations beyond typical values? Is this perhaps why the influence of some perturbations is so pervasive

across multiple days, while in the real atmosphere it is typically assumed that the influence of NOx emissions are much more localized?

Response 4:

We agree. Nevertheless, to comply with the scenario definitions, we strived to adhere to the modelling conditions set out in Poppe et al. (2001), and intend to apply real world conditions in a follow up study. We hope this division can be accepted by the Referee.

Specific comments

Comment 5:

The abstract could contain less general background material, and more about the results of this paper.

Response 5:

We are grateful for this advice. Accordingly, we reformulated the abstract, which now reads

"Observations of the chemical state of the atmosphere typically provide only sparse snapshots of the state of the system due to their insufficient temporal and spatial density. One possibility to optimise the state estimate is provided by observation targeting of sensitive system states, to identify measurement configurations of best value for forecast improvements. In the present work, the technique of singular vector analyses is applied to atmospheric chemical modelling in order to identify the chemical compounds with most quickly growing errors over a given time period (i.e. most sensitive chemical compounds) and prioritise them for measurements. Besides initial values, emissions are investigated as target variables for adaptive observations. Special operators are introduced to adequately address particular problems of atmospheric chemistry resulting in different types of error growth.

The concept of adaptive observations is studied with a chemistry box model. For a set of six different scenarios and six types of error growth, the time and regime dependence of the VOC versus NO_x limitation of the ozone formation is investigated by singular vector based sensitivity analysis. Results reveal that singular vectors with initial values as target variables tend to be more sensitive to the start time in the diurnal cycle, while emission factors as target variables are more sensitive to the ageing of air. For both target variables the ozone sensitivity to the VOC and the NO_x family is strongly dependent on photochemical scenario and simulation interval. A time independent measurement strategy benefitting from omission of VOC- or NO_x-measurements is therefore difficult to achieve. However, the findings for the ozone sensitivity to VOC and NO_x compounds reveal that the particular chemical compounds of the VOC family can be classified into less, middle or very important for the ozone sensitivity to the VOC family. This coarse categorisation is independent of simulation interval and allows for time independent measurement strategies that effectively neglect less important species. Moreover, summation of the sensitivities of the very important VOC or NO_x compounds roughly approximates the sensitivity of the respective family. Accordingly, the

sensitivity analyses presented here can be used to devise profitable measurement strategies for each considered type of error growth."

Comment 6:

16754: Is the definition of the different families a bit arbitrary? Could one instead use the singular vectors themselves to define appropriate groupings?

Response 6:

Using the singular vectors themselves to define appropriate groupings (e.g. simply adding all singular vector entries belonging to one group and afterwards divide the sum by the number of species that belong to the particular group) would cause the problem that no preconditions are imposed on the composition of the initial perturbation. Therefore it is likely that the fastest growing initial perturbation found by the singular vector has comparatively large entries for some compounds of one group while other compounds have nearly negligible entries. Accordingly, the ozone sensitivity to one group would not be induced by the group in total but by particular species of the group. In this manner one and the same sensitivity result for two different simulation lengths could be induced by a completely different perturbation composition of the group. The application of the family operator within the grouped (relative) error ensures however that each member of one family has the same (relative) initial perturbation. Hence it is possible to directly interfere from the (relative) initial perturbation of the group to the (relative) initial perturbation of each compound of the group (see for example Fig. 1). Furthermore, a plain comparison between different sensitivity results of one group is possible. In order to clarify this feature the authors included the following sentences directly after the definition of the family operator: "The application of the family operator serves the purpose to allow for unique interferences from the error of one family to the error of each associated family member. In detail its application on the (relative) error causes all species belonging to one family to have the same (relative) disturbance. In this manner the perturbation composition of one family is clearly defined. Accordingly, each chemical species is only allowed to belong to one single family..."

Comment 7:

16761: In equation 46, why not use the previous definitions of FWD and TLM model (i.e., M and L)?

Response 7:

Eq. (46) and Eq. (47) are introduced for testing the tangent-linear approximation as well as for code-checking purposes. Since we tested new routines separately before examing the complete model, the new definitions are utilized to allow for code pieces of the forward or associated tangent linear/adjoint model. In order to clarify this matter, we extended the explanation on page 16761, line 3 to "The abbreviations FWD and TLM denote particular parts of the forward and associated tangent linear routines. These new abbreviations are introduced to allow for piecewise code-checking. [...] Within numerical limits, the new

tangent linear routines as well as the complete tangent linear model demonstrate the required characteristics for Eq. (46) for considered test cases."

Comment 8:

16761: In eq 47, doesn't this not rule out the possibility of cancelation of errors by checking the dot product on the left and right sides rather than the individual components? I realize it's much more computationally efficient to validate using this metric, but for box-model simulations I would think that element-by-element checking would not be overly burdensome.

Response 8:

For code-checking purposes the authors agree that element-by-element checking is not overly burdensome. Therefore we compared furthermore the elements of the tangent-linear model with the associated elements of the adjoint model. The comparison demonstrates good agreement between tangent linear and adjoint model. Therefore, we replaced lines 12-16 on page 16761 with the following text: "In order to verify the consistency of the tangent linear and adjoint model, each of these models is utilized to build a Jacobian. For construction of the Jacobians the equations $\delta y_i = TLM(\delta x_i)$ and $\delta z_i = ADJ(\delta x_i)$ are executed for i=1,...,n. Here, ADJ denotes particular parts of the adjoint routines associated to the considered tangent linear routines TLM. Furthermore each δx_i is a unit vector where the entry of the i-th element is one and all other entries are zero. Then δy_i builds the i-th row of the Jacobian constructed with the tangent linear model while δz_i builds the i-th column of the Jacobian constructed with the adjoint model. Consistency is verified if the elements of both Jacobians are equal within the limits of machine precision. Again, the new routines demonstrate correctness for both single routines as well as for the complete model."

Comment 9:

The ability to follow discussion related to individual chemical components would be greatly enhanced by providing a definition of the species abbreviations.

Response 9:

We added a Table with definitions of the RADM2 species abbreviations for the VOC-compounds and referred to this Table when first mentioning these species.

Comment 10:

Section 4.1: Does the second conclusion (on pages 16768/16769) apply to all scenarios, even FREE and URBAN?

Response 10:

The second conclusion does not apply to all scenarios; scenarios FREE and URBAN are excluded (indicated with "typically"). In order to emphasize this, we extended the second conclusion to "For simulations with initial time t_I at night, the ozone sensitivity to VOC is

typically decreasing with simulation length (this does not hold for scenarios FREE and URBAN). The decrement rate appears to be dependent on the degree of air pollution. “

Comment 11:

I found it a bit odd that there wasn’t much or any discussion of the NOx results in section 4.3.1 and 4.3.2.

Response 11:

In section 4.3.1, 4.3.2 and 4.3.3 only the ozone sensitivity to VOC is analysed, since the ozone sensitivity to NO_x can be directly derived from the latter due to the normalisation of the singular vectors. For clarification of these characteristics we extended page 16772, line 13 to: “Facing these difficulties, the qualitative features of the scenarios are analysed. Thereby the ozone sensitivity to VOC is evaluated scenario-wise initially. Due to the normalisation of the singular vectors, the ozone sensitivity to NO_x can be derived directly from the ozone sensitivity to VOC. In detail, low ozone sensitivity to VOC represents high ozone sensitivity to NO_x while increasing ozone sensitivity to VOC is equivalent to decreasing ozone sensitivity to NO_x. In order to clarify the implications for the NO_x sensitivity, the subsequent summary of the main qualitative features of all three scenarios is reflected in terms of the ozone sensitivity to NO_x.” Further, we revised page 16772, line 8 to “In summary, the key features of scenarios PLUME, URBAN and BIO are...”

Comment 12:

16746.18: no comma after reveal

Response 12:

We are happy to correct this.

Comment 13:

Overall, the grammar and punctuation is far from perfect and somewhat distracting. Below are listed a few places where it actually clouds the understanding; the entire paper would bennefit from a thorough editing.

- *16748.25: Point 1*

  Response 13a:

  We reformulated the sentence “The multitude of reactants enforces analyses which quantifies the species to be observed with preference, given limitations of the observational network and a well defined forecast time.” to “Observational networks are restricted by technical, financial or organisational limits. Given these limits of resources, it is of special interest to identify and assemble the most beneficial configuration, or likewise, a list of chemical compounds which have to be observed with preference.”

- *16768.23 (16768.14): that the results resemble*

Response 13b:

The sentence "For simulations with initial time t_I at night, Table 5 exhibits that the results resemble for scenarios LAND, MARINE, PLUME and BIO." has been revised to "For simulations with initial time t_I at night, Table 5 shows two common features for scenarios LAND, MARINE, PLUME and BIO. Firstly their mean ozone sensitivity to NO_x is smaller than 0.5 for the shortest time interval, which implies VOC dominance. Secondly these scenarios show decreasing ozone sensitivity to VOC with growing simulation length."

- *throughout, "to which extent" should be "to what extent"*

  Response 13c:

  The statements have now been reformulated accordingly.

- *16779.27* (16779.18): *"is at disposition"*

  Response 13d:

  We reformulated the statement "is at disposition" to "... a flexible algorithm is at our disposal".