Answer to reviewers

Referee #1:

General comments The paper presents an interesting research about the difference between source apportionment and sensitivity analysis, supported by theoretical examples, and helps clarifying the purpose of each approach and when it should be applied. The paper is in general well-written and structured with references supporting it. Only minor changes and some specific and technical comments are suggested before publication.

Specific comments Introduction: This section is poor on references and state-of-art about the subject (source apportionment and sensitivity analysis methods). The authors should improve this section refereeing what have been done already by other authors about these two methods and the assessment of “contribution” and “impact”.

We agree with the Reviewer. The introduction has been re-structured (also according to Reviewer 2 suggestions) and additional references have been introduced in the text.

Lines 41-48: a reference to support this statement is missing and is necessary

A reference has been introduced

Line 373: please introduce the regimes that are will be analysed in the following sections

The two regimes are now mentioned and detailed prior to the example section

Line 667-676: Figure 4 should be refereed/introduced in the text

Figure 4 is now referenced in the different sub-sections of the example section

Line 735: Figure 5 should be refereed/introduced in the text

Done as suggested

Lines 768-798: This text (or at least part of that) should be placed at Conclusions section

We agree with the Reviewer and introduced new sub-sections (comparative overview) in the two examples sections to highlight the fact that the parts of text are meant as summary of all approaches discussed earlier.

Lines 801-810: This text should be placed at the “Introduction” section Conclusions: Authors should revised this section: part of that is state-of-art, other is too much detail about what was done and finnaly the last part should be part of the discussion of results. This last section (Conclusions) should be a summary of what was presented before and not enter in detail in what was done and obtained. Technical corrections”: typing errors, etc.).

We agree with the Reviewer and re-structured the introduction and conclusion sections according to suggestions.

Line 18: Define DDM

DDM is now defined in the text.

Line 23: Rephrase this sentence: the use of vice-versa in the middle of the sentence it is not clear

Rephrased as suggested
Line 92: authors instead of “Authors”

Done as suggested

Line 114: missing the year on “Clappier et al”

Year has been added

Line 156: write “precursor’s emission” instead of “emission precursors”

Done as suggested

Line 167: missing the year on the reference “Stein and Alpert”

Year has been added

Line 307: replace “paragraph” by “section” or “chapter”

Done as suggested

Line 437: “computed by the difference”

Done as suggested

Line 679: Figure 4 instead of figure 3 Figures: it is not used the same format for the captions

Harmonized as suggested

Line 721: “production” instead of “productions”

Done as suggested

Line 741: Figure 5 instead Figure 4

Done as suggested

Line 752: Figure 6 instead Figure 5

Done as suggested

Line 753: The text (analysis and interpretation of the results) should be after Figure 6

Moved as suggested

Line 764: Figure 6 instead Figure 5

Done as suggested

References: they are not all in the same format (very different formats are used among the list of references) and not by alphabetic Order

We have harmonized the references format and re-order them by alphabetical and chronological order

Line 884-886: this paper is still in preparation: : :should not make part of the list of references

This paper has been removed from the reference list.
The manuscript discusses relationships between source sensitivity and source contribution for air quality model simulations involving non-linear chemistry. Hypothetical examples are provided that may help readers better understand the concepts involved. Although this work does not present new concepts and results, it does provide in-depth discussion of issues that have sometimes created confusion when air quality model results are used to develop public health policy. I support publication. I request the following clarifications.

Lines 25-29: However, this study demonstrates that when the relationship between emissions and concentrations is non-linear, sensitivity approaches are not suitable to retrieve source contributions and source apportionment methods are not appropriate to evaluate the impact of abatement strategies. The phrases “not suitable” and “not appropriate” suggest that there should be a brightline, yes or no, test for when sensitivity and source apportionment methods can be used. Instead, I suggest using more subtle wording to explain that these methods will encounter limitations when applied to non-linear cases. When non-linearity is mild these limitations may be acceptable in the context of the other uncertainties inherent to complex models. In other words, source apportionment may provide useful information about model sensitivity, and vice-versa, for mildly non-linear cases. In the main manuscript, it would be useful to cite Koo et al. (2009) who present a detailed comparison of source apportionment and sensitivity in a 3-D PM model that shows which sensitivities are similar to apportionment, and which are not.


We agree with the Reviewer and adapted the text in several instances to smooth the wording. The Koo et al. reference has been inserted in the text.

Lines 297 - 298: The decoupled direct method (DDM) is designed to estimate sensitivities to emission changes (Dunker et al., 1984; Dunker et al., 2002). The DDM explicitly calculates sensitivity, as opposed to making an estimate. If a sensitivity calculated by a specific model turns out to be imprecise, that is a limitation of how the DDM is implemented.

This has been changed in the text according to reviewer comment

Lines 303 - 319: This discussion might be understood to suggest that Taylor series expansions are the only way to use sensitivity coefficients computed using the DDM. Dunker (2015) showed how to use first-order sensitivity to determine source contributions to the difference between two model cases, e.g., to apportion the difference between the current atmosphere and natural conditions to specific human activities. Simon et al. used first order sensitivity to construct emission response surfaces. It would be useful to mention other ways in which sensitivity information can be applied. It would be useful to note that computing first-order sensitivity at several emission levels is a powerful alternative to high-order sensitivity.

We agree. Sensitivity can be obtained with DDM as first order derivatives but also from a brute force approach. We tried to clarify this in the text. We also inserted the useful references suggested by the Reviewer.

Lines 348 to 356:

\[
\text{PPM} \rightarrow \text{PM[PPM]} \quad \text{NO}_2 + \text{NH}_3 \rightarrow \text{PM[NH}_4\text{NO}_3] \\
\text{SO}_2 + 2 \text{NH}_3 \rightarrow \text{PM[(NH}_4\text{)SO}_4]}
\]

The fact that reactions in lines 349 and 350 are non-stoichiometric may cause confusion. Changing NO2 to NOx and SO2 to SOx may make it more apparent that these reactions are intended to be conceptual. The subsequent statements about the stoichiometry of these reactions in lines 354 to 356 are chemically inaccurate and should be re-worded. The reaction in line 348 seems not needed because no atmospheric reactions are involved for primary PM, it is simply emitted.

A set of chemical stoichiometric equations has been added to explain from the origin of our simplified equation system. We hope this now clarifies the issue.
Inclusion of global studies may strengthen the paper

Volker Grewe and Mariano Mertens

Congratulations to the authors for this well-written comparison of methods related to the evaluation of emission impacts! We think that an inclusion of similar discussions from the chemistry-climate community would even strengthen the paper. Four aspects may be especially of interest:

1. We believe that the tagging method presented in Section 4.1 is identical to tagging approaches used in global model. (e.g. Horowitz and Jacob, 1999; Lelieveld and Dentener, 2000; Meijer et al., 2000; Grewe, 2004; Gromov et al., 2010; Butler et al., 2011; Emmons et al., 2012; Grewe et al., 2012, 2017) Is that correct? Can you comment on this?

We agree. The tagging methods used in global model are similar to those used to estimate contributions in the frame of climate-chemical studies at global scale. We added a paragraph at the end of section 4.1 and included the suggested references.

2. Are the results of your comparison deviating from earlier intercomparisons between the two methods (source apportionment and sensitivity analysis)? Here we refer to Grewe (2013) where the simple differential equation

\[ \frac{dx}{dt} = P - x^n, \]  

(1)

with $x$ the concentration of a chemical species, is used to analyse the differences between the two approaches. Further, we refer to Grewe et al. (2010) where a more complex chemical system (3 species: pseudo NOy, pseudo VOC and pseudo O3 and 3 differential equations) is investigated. This system shows the characteristics similar to that of tropospheric ozone chemistry and is hence well suited as a test bed. This system was evaluated with respect to the differences between both methods. Grewe et al. (2010) and Grewe (2013) also nicely show that both methods are equal in a linear regime, which supports the author’s statement.

We agree and added a couple of lines (and references) referring to those works in the text.

3. We agree that depending on the purpose of the analysis one or the other method is appropriate, as discussed by the authors. However, we miss a clear statement that the combination of both methods give a much better basis for the interpretation of mitigation options.

This is an important point, made by one of the Reviewers as well. We now inserted a few lines to address it in the text. Rather than a combination of the two approaches, we stressed the need to calculate sensitivities at different levels of emission reduction whenever non-linearity is important. New approaches like the path-integral method are in this respect very useful. We stressed this point again in the conclusions.

4. On top of the previous point, a more in depth discussion on the effectiveness and suitability of the discussed methods for the use in political and economic frameworks, which try to provide incentives for mitigation options might be helpful to understand the implications of using those methods. For example, only the sensitivity method (or also called perturbation method) is suitable to evaluate the impact of a mitigation measure. However, while having said this, deducing from this statement that only the sensitivity measure should be used in any political and economic framework for incentivising measures, might be plainly false. We think that this is an important point which should be raised in the paper. Let’s take exemplarily the response of the ozone chemistry on a decrease of NOx emissions
In a saturated chemical regime a decrease of NOx from e.g. road traffic (Fig. 1a) might not lead to any change in the ozone concentration (Fig. 1b). As NOx emission decrease, but not the ozone concentration, the net-ozone production (NO3P) per NOx-molecule (Fig. 1c) increases. Hence this mitigation measure leads to important change in the chemistry without affecting the ozone concentration. The chemistry might have left the saturation regime because of this first measure. If a second NOx emission reduction is implemented, this second measure reduces the ozone concentration, since the chemical regime is not anymore saturated and hence takes advantage of the first measure. An ozone reduction is only achieved because the first measure took place. Assessing the two measures by the sensitivity analysis makes the effectiveness prone to the order of implementation. This has been touched in the conclusion (line 802), but might be clarified. On the other hand tagging methods would be more suitable in assessing the effectiveness of mitigation measures, since they are largely (of course not totally) independent of the order of implementation. This is sketched in Fig 1d). The perturbation approach would not see a change of the road traffic impact, as the ozone concentration would not change. The contribution, however, as calculated with a tagging method would be lowered as less NOx molecules from road traffic are involved in the production of ozone.

A first discussion of these effects were given in Grewe et al. (2012) and will further discussed in a paper which we will submit this summer to ACPD (Mertens et al. 2017). The Fig. 2 is taken from that paper and nicely illustrates the impact of the degree of saturation of a chemical regime on the assessment of mitigation options.

Additionally to our response to point 3 above, we believe that calculating sensitivities and interactions at various level of emission reductions seems the only alternative when non-linearities are important. Source apportionment would provide the impact of reducing all emissions by 100% (and could be considered as an overall sensitivity) but this overall sensitivity might represent far away conditions from the limited reductions (e.g. 30 or 50%) considered by policymakers. Even if used in combination, the gap between the source apportionment and sensitivity approaches might still be too large to provide useful information to policymakers. As mentioned above, new approaches like the path-integral methodology represent a powerful approach (although on the expense of additional computer calculations). This point is now addressed in the text.
Interactive comment on “Source apportionment and sensitivity analysis: two methodologies with two different purposes” by Alain Clappier et al.

A. Dunker

My co-workers and I have recently developed a method that provides a direct, mathematical connection between sensitivity analysis and source apportionment. (See references below.) The path-integral method involves integrating sensitivity coefficients over a range of emissions between two simulations. The integrals correspond to the contributions of the different emission sources to the change in concentrations between the two simulations. If the two simulations are a base simulation with anthropogenic emissions included and a background simulation without anthropogenic emissions, then the change in concentrations is the anthropogenic increment to ozone and other pollutants. This path-integral method has a number of advantages, and it would be good if A. Clappier et al. included the method in their review.

Thanks for making us aware of this new interesting methodology which has been included in the text as follows (in the DDM section)

Dunker (2015) showed how to use first-order sensitivity to determine source contributions between two model cases, e.g., to apportion the difference between the current atmosphere (and natural conditions) to specific human activities. Along the same lines, Simon et al. (2013) used first order sensitivity to construct emission response surfaces. To cope with potential non-linearities and the need to compute higher-order derivatives, a powerful alternative is to compute first-order sensitivities at several emission levels.
Source apportionment and sensitivity analysis: two methodologies with two different purposes.

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Abstract

In this work are reviewed the existing methodologies for source apportionment and sensitivity analysis to identify key differences and stress their implicit limitations. The emphasis is laid on the differences between source “impacts” (sensitivity analysis) and “contributions” (source apportionment) obtained by using four different methodologies: brute force top-down, brute force bottom-up, tagged species and DDM. A simple theoretical example to compare these approaches is used highlighting differences and potential implications for policy. When the relationships between concentration and emissions are linear, impacts and contributions are equivalent concepts. In this case, source apportionment and sensitivity analysis may be used indifferently for both air quality planning purposes and vice versa, sensitivity analysis may be used for quantifying sources contributions. However, this study demonstrates that when the relationship between emissions and concentrations is non-linear, sensitivity approaches are not suitable to retrieve source contributions and source apportionment methods are not appropriate to evaluate the impact of abatement strategies. A quantification of the potential non-linearities should therefore be the first step prior to source apportionment or planning applications, to prevent any limitations in their use. When non-linearity is mild, these limitations may however

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be acceptable in the context of the other uncertainties inherent to complex models.

Moreover, when using sensitivity analysis for planning, it is important to note that, under non-linear circumstances, the calculated impacts will only provide information for the exact conditions (e.g. emission reduction share) that are simulated.

**Keywords:** source apportionment, sensitivity analysis, abatement strategies, air quality planning

### 1. Introduction

When pollutant concentrations exceed the thresholds set in the legislation, competent authorities must take actions to abate pollution. Those abatement strategies consist in reducing the precursor’s emission of the different activity sector to reduce pollutant concentrations but they are challenging to design because of the complex relationships that link emissions and pollutants. Indeed, the concentration of a pollutant at a given location generally results from direct emissions and from interactions in the atmosphere among different emission precursors, emitted by a variety of sources. For example, particulate matter (denoted here as PM) results from the interaction and combination of five different precursors (PPM, NOx, SO2, NH3, and VOC) which can be emitted by different activity macro-sectors (e.g. residential, transport, industrial and agriculture). [Seinfeld and Pandis, 2016].

Abatement strategies aim at reducing the precursor’s emission of the different activity sector to reduce pollutant concentrations but these strategies are challenging to design because of the complex relationships that link precursors and pollutants. Two different approaches are currently used to support air quality decision makers: source apportionment and sensitivity analysis.
Source apportionment quantifies the contribution of an emission source (or precursor) to the concentration of one pollutant at one given location.

- Sensitivity analysis estimates the impact on pollutant concentration that results from a change of one or more emission sources.

In practice, source apportionment is often used for planning purposes. It is indeed intuitive to use source apportionment to detect the activity sectors that need to be tackled in priority in an air quality plan. On the other hand, sensitivity analysis is often used as an approach to derive source contributions, e.g., SHERPA (Thunis et al. 2017), FASST (Crippa et al. 2017), GAINS (Kiesewetter et al. 2015)...

The main objective of this work is to review the existing methodologies, identify key differences and stress their implicit limitations. We will particularly focus on the differences between concentration “impacts” (sensitivity) and “contributions” (source apportionment) obtained with different methodologies. We make use of a simple theoretical example to compare the approaches, highlight differences and potential implications in terms of policy. In the following sections, we analyze first how these methodologies work in a simple linear case before generalizing it to more complex non-linear situations.

2. Linear simplification and implications

Let’s consider $C$ a pollutant concentration at one location that is a function of three variables ($E_1$, $E_2$ and $E_3$), i.e., the emissions of three precursors or sources within a given domain: $C = C(E_1, E_2, E_3)$. For a linear relationship between the function $C$ and the three variables $E_1$, $E_2$ and $E_3$, we can write:

$$C(E_1, E_2, E_3) = C(0, 0, 0) + P_1 E_1 + P_2 E_2 + P_3 E_3 \quad (1)$$

where $P_1$, $P_2$ and $P_3$ are three constant coefficients.
On the other hand, the sensitivity of the concentration to a change of a given emission source can be quantified via partial derivatives. For expression (1) this gives:

\[ \frac{\partial C}{\partial E_1} = P_1 \; ; \; \frac{\partial C}{\partial E_2} = P_2 \; ; \; \frac{\partial C}{\partial E_3} = P_3 \]

In Clappier et al. (2017) the coefficients \((P_1, P_2 \text{ and } P_3)\) are referred to “potencies”. The authors used this concept of “potencies” to analyze the model response to emission changes in different European countries.

The consequences of a linear relationship between concentration and emission sources are twofold:

1) all higher order derivatives (order 2 and beyond) are null, including those involving two or more emission sources (crossed derivatives) as the impact of a change in one emission source is independent from all others.

2) the first-order partial derivatives are constant and can therefore be calculated with finite differencing, between any couple of emission levels, for example a base case (denoted BC) and a background (denoted as 0).

The potency equations then read as:

\[ P_1 = \frac{\Delta C_{0}^{BC_1}}{E_1^{BC}} \; \; ; \; P_2 = \frac{\Delta C_{0}^{BC_2}}{E_2^{BC}} \; \; ; \; P_3 = \frac{\Delta C_{0}^{BC_3}}{E_3^{BC}} \]

with

\[ \Delta C_{0}^{BC_1} = C(E_1^{BC}, 0, 0) - C(0,0,0) \]
\[ \Delta C_{0}^{BC_2} = C(0, E_2^{BC}, 0) - C(0,0,0) \]
\[ \Delta C_{0}^{BC_3} = C(0,0, E_3^{BC}) - C(0,0,0) \]

Together with "potencies", Clappier et al. (2017) also introduce the concept of “potential”, defined as the concentration change resulting from a total reduction of the emissions (from BC to 0). The “potential” can be calculated via relation (1) applied between the base-case and background levels as:
\[ \Delta C_0^{BC} = \Delta C_0^{BC_1} + \Delta C_0^{BC_2} + \Delta C_0^{BC_3} \quad (2) \]

where \( \Delta C_0^{BC} = C(E_1^{BC}, E_2^{BC}, E_3^{BC}) - C(0,0,0) \)

Equation (2) can directly be used for source apportionment purpose, with \( \Delta C_0^{BC_1} \) the concentration change resulting from a total reduction of the emission source (or precursor) \( E_1 \), reflecting the contribution of \( E_1 \) to the base case concentration. Similarly \( \Delta C_0^{BC_2} \) and \( \Delta C_0^{BC_3} \) are the contributions of \( E_2 \) and \( E_3 \). Equation (2) shows that, in the linear case, the concentration change resulting from a simultaneous reduction of all emission sources (\( \Delta C_0^{BC} \)) is equal to the sum of the emission sources contributions.

In the next sections, we will explore how this simple conclusion changes when non-linear relationships are considered. In particular, we will assess which implications (and limitations) these non-linearities have in terms of source apportionment and sensitivity analysis.

3. Brute Force method

The “brute force” method consists in estimating the concentration change by performing and subtracting two simulations, one with and the second without a specific emission source to be analysed (Blanchard, 1999; Yarwood et al., 2004).

In non-linear situations, the concentration change resulting from a set of emission sources is not anymore equivalent to the sum of the concentration changes resulting from emission sources changed individually. In the following, we will refer to the work of Stein and Alpert (1993) who proposed an approach to decompose an overall impact into single (one emission source only) and combined (multiple emission sources) impacts.

3.1. Bottom-up formulation
We consider here three precursor’s emission precursors $E_1$, $E_2$, and $E_3$ that are changing from a low (denoted as “L”) to a high level (denoted as “H”). In a bottom-up approach, the low emission level is chosen as the reference. With these definitions and notations, the impact on concentration resulting from a change of one only of the three precursor’s emissions can be written as follows:

$$
\Delta C_L \rightarrow H_1 = C(E_1^H, E_2^L, E_3^L) - C(E_1^L, E_2^L, E_3^L)
$$

$$
\Delta C_L \rightarrow H_2 = C(E_1^L, E_2^H, E_3^L) - C(E_1^L, E_2^L, E_3^L)
$$

$$
\Delta C_L \rightarrow H_3 = C(E_1^L, E_2^L, E_3^H) - C(E_1^L, E_2^L, E_3^L)
$$

While the impact on concentration resulting from the simultaneous changes of two or three precursor’s emissions would be written as:

$$
\Delta C_L \rightarrow H_1, H_2 = \Delta C_L \rightarrow H_1 + \Delta C_L \rightarrow H_2 + C^{int}
$$

Using a similar notation, the decomposition of Stein and Alpert (1993) applied to 2 variables ($E_1$ and $E_2$) would read as:

$$
\Delta C_L^{H_1, H_2} = \Delta C_L^{H_1} + \Delta C_L^{H_2} + \tilde{C}^{int}
$$

where $\Delta C_L^{H_1}$ and $\Delta C_L^{H_2}$ are the impacts induced by the change in emission sources $E_1$ and $E_2$ taken independently and $\Delta C_L^{H_1, H_2}$ the impact induced from $E_1$ and $E_2$ taken simultaneously.

It is clear from (3) that the impact of a simultaneous change of two emission sources is not equivalent to the sum of the individual impacts, as highlighted by the additional term $\tilde{C}^{int}$. This term that
quantifies the interaction between the two emission sources can be calculated using (3) as:

\[
\hat{C}_{int} = \hat{C}^{H_1,H_2}_{L} = \Delta C^{H_1}_{L} - \Delta C^{H_2}_{L}
\]  

(4)

The Stein and Alpert formulation can similarly be applied with 3 emission sources:

\[
\Delta C^H_L = \Delta C^H_{L1} + \Delta C^H_{L2} + \Delta C^H_{L3} + \hat{C}_{int}
\]  

(5)

Where \(\Delta C^H_{L1}, \Delta C^H_{L2}\) and \(\Delta C^H_{L3}\) are the impact on concentration resulting from single emission changes in the sources and

\[
\hat{C}_{int} = \hat{C}^{H_1,H_2}_{L} + \hat{C}^{H_1,H_3}_{L} + \hat{C}^{H_2,H_3}_{L} + \hat{C}^{H_1,H_2,H_3}_{L}
\]  

(6)

where \(\hat{C}^{H_1,H_2}_{L}, \hat{C}^{H_1,H_3}_{L}\) and \(\hat{C}^{H_2,H_3}_{L}\) are the double interaction terms that can be further decomposed via equation (4). \(\hat{C}^{H_1,H_2,H_3}_{L}\) is the triple interaction term (between \(E_1, E_2, E_3\) which can be decomposed by combining (5) and (6) as:

\[
\hat{C}^{H_1,H_2,H_3}_{L} = \Delta C^{H_1}_{L} - \Delta C^{H_1}_{L2} - \Delta C^{H_2}_{L} - \Delta C^{H_3}_{L} - \Delta C^{H_1,H_2,H_3}_{L}
\]

3.2. Top-down formulation

In a top-down formulation, the highest emission level is chosen as reference. The Stein Alpert formulation for three precursors can then be expressed similarly to the bottom-up formulation as:

\[
\Delta C^H_L = \Delta C^H_{L1} + \Delta C^H_{L2} + \Delta C^H_{L3} + \hat{C}_{int}
\]  

(7)

where \(\Delta C^H_{L1}, \Delta C^H_{L2}\) and \(\Delta C^H_{L3}\) are the impacts on concentration induced by reducing \(E_1, E_2\) and \(E_3\) independently whereas \(\hat{C}_{int}\) is the
interaction term which itself can be decomposed into a series of
double interactions and a triple interaction terms:

\[ \tilde{C}^{\text{int}} = \tilde{C}_{L_1L_2}^H + \tilde{C}_{L_1L_3}^H + \tilde{C}_{L_2L_3}^H + \tilde{C}_{L_1L_2L_3}^H \]  

(8)

It is important to stress that the top-down single impacts are not
equivalent to their bottom-up counterparts. The relation between
these bottom-up and top-down impacts can be expressed as (here for
the case of \( E_3 \)):

\[ \Delta C_{L_3}^H = C(E_1^H, E_2^H, E_3^H) - C(E_1^L, E_2^L, E_3^L) \]  

(9)

\[ \Delta C_{L_3}^H = C(E_1^H, E_2^H, E_3^H) - C(E_1^L, E_2^L, E_3^L) \]  

\[ - [C(E_1^H, E_2^H, E_3^L) - C(E_1^L, E_2^L, E_3^L)] \]  

(9)

\[ \Delta C_{L_3}^H = \Delta C_{L_3}^L - \Delta C_{L_3}^{H_2H_3} \]  

(9)

Using equations (3), (4), (5) and (6), equation (9) can be re-
expressed as:

\[ \Delta C_{L_3}^H = \Delta C_{L_3}^L + \tilde{C}_{L_1}^{H_1H_3} + \tilde{C}_{L_2}^{H_2H_3} + \tilde{C}_{L_3}^{H_1H_2H_3} \]  

(10)

In other words, the top-down impact on concentration of an emission
source (obtained by switching off the emission source while all
others remain unchanged) is not equivalent to its bottom-up
counterpart, (obtained by switching on the emission source while all
others are switched off). Relation (10) indeed clearly shows that
additional interaction terms need to be considered. The implications
resulting from these differences are highlighted in Section 5 in
which some theoretical examples are described.

4. Source apportionment and sensitivity analysis
4.1. Tagged species techniques

Equation (2) shows that, when the relationship between concentration and several emission sources is linear, the contribution of a specific source (source apportionment) can be computed as the impact on concentration obtained by a full reduction of this source (sensitivity). Moreover, the sum of the impacts on concentration obtained by reduction of the single sources ($\Delta C_0^{BC1} + \Delta C_0^{BC2} + \Delta C_0^{BC3}$) is equivalent to the impact on concentration resulting from a simultaneous abatement of all sources ($\Delta C_0^{BC}$). In such a case, the concentration impacts are equal to source contributions and source apportionment and sensitivity analysis lead to similar results. This is not the case, however, when the relationship between concentrations and emissions is nonlinear. In their approach, Stein and Alpert express the difference between the impact caused by a simultaneous abatement and the sum of the impacts caused by individual abatement as interactions among the different sources. The Stein and Alpert formulation applied between the base-case and background levels is very close to equation (2) but with an additional term that accounts for interactions:

$$\Delta C_0^{BC} = \Delta C_0^{BC1} + \Delta C_0^{BC2} + \Delta C_0^{BC3} + \hat{C}^{int}$$

Because the interaction terms cannot not be attributed to a single emission source as they represent the interaction between two and more emission sources, the Stein and Alpert methodology does not allow identifying the full contribution of each individual source. It cannot therefore be used for source apportionment purpose, unless the interaction terms are negligible as in the linear case.

Unlike the Stein and Alpert methodology, the tagged species methodology is designed for source apportionment purposes. This methodology tags each precursor and quantifies its contribution (in terms of mass) to the pollutant concentration.

Tagged algorithms are implemented in several chemical transport model systems (Yarwood et al., 2004; Wagstrom et al., 2008, ENVIRON, 2014; Bhave et al., 2007; Wang et al., 2009; Kranenburg et al., 2013).
In tagging approaches, the effect of the full reduction of all sources is directly expressed as the sum of the source contributions:

\[ \Delta C_0^{BC} = \delta C_1 + \delta C_2 + \delta C_3 \]

where \( \delta C_1, \delta C_2, \delta C_3 \) are the contributions of sources \( E_1, E_2 \) and \( E_3 \) resulting from the tagged species approach resolution.

Tagging methodologies split the interaction terms into fractions and attribute these fractions to the source contributions, on the basis of mass weighting factors.

\[ \delta C_1 = \Delta C_0^{BC} + \alpha \hat{C}_{int} \]

Because the tagged species approach mixes interaction terms and single concentration impacts into sources contributions, it is not suitable to estimate the effect of emission reduction when non-linearities are present (Burr and Zhang 2011a, 2011b). Indeed these two types of terms may react in very different ways to emission reductions. This fact is detailed in the examples provided below.

On the other hand, the strength of this method is that it allows for a direct comparison of the source contributions with measurements (or measurement based methods like receptor models).

Note that similar tagging methods are also used in the frame of climate-chemical studies at global scale (e.g. Horowitz and Jacob, 1999; Lelieveld and Dentener, 2000; Meijer et al., 2000; Grewe, 2004; Gromov et al., 2010; Butler et al., 2011; Emmons et al., 2012; Grewe, 2012; Grewe et al., 2017).

4.2. DDM

The decoupled direct method (DDM) is designed to estimate calculate directly sensitivities to emission changes (Dunker et al., 1984; Dunker et al., 2002). It aims to compute only the first order derivatives (which correspond to the potencies mentioned in paragraph 2).
The Taylor formula is applied at first order to calculate the concentration change between two emission levels (denoted H and L).

\[ \Delta C_L^H = \Delta E_1 \frac{\partial C}{\partial E_1} \bigg|_H + \Delta E_2 \frac{\partial C}{\partial E_2} \bigg|_H + \Delta E_3 \frac{\partial C}{\partial E_3} \bigg|_H \]

with \( \Delta E_1 = E_1^H - E_1^L, \Delta E_2 = E_2^H - E_2^L, \Delta E_3 = E_3^H - E_3^L \)

In the linear case, the first order derivatives are constant and the first order approximation of the Taylor formula gives the exact expression of the impact on concentration of an emission change between H and L. When the emission-concentration relationship is nonlinear, the first derivatives are not constants. The first order Taylor formula cannot take into account the nonlinear effects. It is a linear approximation based on derivatives computed at a given emission reference level (level H in our example). The estimation of the impact on concentration of an emission change between H and L is accurate enough if level L is close enough to level H.

The HDDM is another method (Hakami et al., 2003) which aims to increase the accuracy of the DDM method by computing second order derivatives.

DDM (and HDDM) gives similar information to the Stein Alpert formulation applied with the Brute force top-down approach (because the reference level is H). For the same reason than for the Stein Alpert approach, these two methods are suitable for source apportionment purpose only if the relation between concentration and emission is close to linearity.

DDM (and HDDM) approximates the impact on concentration from an emission change between the two level H and L, using derivatives computed at level H. This impact is accurate enough if the level L is close enough to the reference level H.
Dunker (2015) showed how to use first-order sensitivity to determine source contributions between two model cases, e.g., to apportion the difference between the current atmosphere (and natural conditions) to specific human activities. Along the same lines, Simon et al. (2013) used first order sensitivity to construct emission response surfaces. To cope with potential non-linearities and the need to compute higher-order derivatives, a powerful alternative is to compute first-order sensitivities at several emission levels.

5. Example

In this section, examples are designed to illustrate the differences in terms of contribution and impact estimates when the approaches discussed previously are used. In these examples, we focus on the formation of particulate matter (PM) in the atmosphere and only consider three formation processes: direct emissions (primary PM denoted as PPM); formation through reactions with nitrogen oxides (NO₂) and ammonia (NH₃) and formation through reactions with sulphur oxide (SO₂) and NH₃.

\[ \text{PPM} \rightarrow \text{PM} \]

\[ 2\text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{HNO}_3 \]

\[ 2\text{NH}_3 + 2\text{HNO}_3 \rightarrow 2\text{NH}_4\text{NO}_3 \]

\[ \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \]

\[ 2\text{ NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 \]

These reactions pathways are summarised by the following system of reactions:

\[ \text{PPM} \rightarrow \text{PM}\left[\text{PPM}\right] \]

\[ \text{NO}_2 + \text{NH}_3 \rightarrow \text{PM}\left[\text{NH}_4\text{NO}_3\right] \]
SO₂ + 2 NH₃ → PM[(NH₄)₂SO₄]

This system is further simplified by assuming that all reactions have comparable kinetics (reaction speed) and have reached their equilibrium. From these three reactions, 1 PM mole can be produced by 1 PPM mole, by the combination of 1 NH₃ and 1 NO₂ moles or by the combination of 1 SO₂ and 2 NH₃ moles.

We also limit our examples to emissions from three activity sectors. The residential sector (R) only emits PPM and NO₂, the agricultural sector (A) only emits NH₃ and the industrial sector (I) only emits PPM and SO₂ (Figure 1). We assume for convenience that no background pollution is present (i.e. there is no PM when all emissions are zero). Two situations are considered: a “non-limited regime” where the NH₃ quantity is sufficient to react with all moles of NO₂ and SO₂ and a “limited regime” where the NH₃ quantity of is not sufficient to react with all moles of NO₂ and SO₂.

5.1. Non-limited regime

In this first example, the quantity of precursors (in terms of mass) is large enough to feed all reactions. The agricultural sector emits 150 NH₃ moles which can react with 50 NO₂ moles emitted by the residential sector and 50 SO₂ moles emitted by industrial sector. 100 PPM moles are emitted by the residential sector as well by the industrial sector (Figure 1).
Figure 1: Example of PPM, NO$_2$, SO$_2$ and NH$_3$ emissions released by three activity sectors: residential (R), agricultural (A) and industrial (I). For convenience, no units are associated to emissions and concentrations.

Let’s first calculate the PM concentration produced with and without each of the sources:

- **No source:** $C_0$ is the PM concentration obtained when all emissions are set to zero. Since we assumed a zero background pollution, $C_0 = 0$.

- **One source only:** $C_R$ (resp. $C_A$ and $C_I$) is the PM concentration reached when only the residential (resp. agricultural and industrial) sector releases emissions:
  - $C_R = 100$ produced by PPM emissions (NO$_2$ emissions do not produce PM as no NH$_3$ is available).
  - $C_A = 0$ because NO$_2$ and SO$_2$ are not available to react with NH$_3$.
  - $C_I = 100$ produced by the PPM emissions (SO$_2$ emissions do not produce PM as no NH$_3$ is available).
Two sources: $C_{RA}$, $C_{RI}$, and $C_{AI}$ are the concentrations obtained when two (out of three) activity sectors release their emissions simultaneously (the $RA$ subscripts correspond to residential and agriculture, $RI$ to residential and industrial, $AI$ to agriculture and industrial):

- $C_{RA} = 150 : 100$ produced by PPM emissions from the residential sector and 50 produced by the 50 NO$_2$ released by the residential sector reacting with the 50 NH$_3$ emitted by agriculture (100 NH$_3$ moles remain unused).

- $C_{RI} = 200 : 100$ produced by PPM emissions from the residential sector and 100 produced by PPM emissions from the industrial sector.

- $C_{AI} = 150 : 100$ produced by PPM industrial emissions and 50 from the combination of 50 SO$_2$ (industry) and 100 NH$_3$ (agriculture).

Three sources: $C_{RAI}$ is the concentrations obtained when all emissions are released simultaneously.

- $C_{RAI} = 300 : 200$ from PPM (residential and industry), 50 from reaction between NO$_2$ and NH$_3$ and 50 from reaction between SO$_2$ and NH$_3$.

**Brute-force Bottom-up (BF-BU) method**

The contribution of each activity sector is calculated as the concentration change resulting from a 100% emission increase from the lowest emission level (previously denoted “L” or background) to the highest level (denoted as “H”, the base case $C_{RAI}$ obtained with all emissions).

In a bottom-up approach, the concentration associated with the lowest emission level is considered as the reference. Concentration impacts are then computed by the difference between any situation (e.g. one, two or three sources present) and this reference.

- with one source:
  \[ \Delta C^B_{RU} = C_R - C_0 = 100 \]
  \[ \Delta C^B_{AU} = C_A - C_0 = 0 \]
  \[ \Delta C^B_{IU} = C_I - C_0 = 100 \]
To calculate the interaction terms, we use the Stein-Alpert formulation using Eq. (5) and Eq. (6):

\[
\Delta C_{RAI} = \Delta C_{RB} + \Delta C_{RA} + \Delta C_{RI} + \hat{C}_{RA} + \hat{C}_{RI} + \hat{C}_{AI} + \hat{C}_{RAI}
\]

from which the interaction terms are obtained by application of (4) and (6):

\[
\begin{align*}
\hat{C}_{RA} &= \Delta C_{RA} - \Delta C_{RB} - \Delta C_{RA} = 50 \\
\hat{C}_{RI} &= \Delta C_{RI} - \Delta C_{RB} - \Delta C_{RI} = 0 \\
\hat{C}_{AI} &= \Delta C_{AI} - \Delta C_{RB} - \Delta C_{AI} = 50 \\
\hat{C}_{RAI} &= \Delta C_{RAI} - \Delta C_{RB} - \Delta C_{RA} - \Delta C_{RI} - \hat{C}_{RA} - \hat{C}_{RI} - \hat{C}_{AI} = 0
\end{align*}
\]

As can be seen from this example, the system behaves non-linearly and the interaction terms (e.g. \(\hat{C}_{RA}\)) are not-zero. Moreover, the sum of the individual impacts (\(\Delta C_{RB} + \Delta C_{RA} + \Delta C_{RI} = 200\)) underestimates the overall impact (\(\Delta C_{RAI} = 300\)). These results are graphically represented in Figure 2 (third column).

**Brute-force Top-down (BF-TD) method**

In a BF-TD approach, the higher emission level (base case, \(C_{RAI}\)) is the reference and the impact of each activity sector is calculated as the concentration change resulting from a 100% emission decrease (of one, two or three sources) from this reference to the background level.

- **with one source:** When all emissions from one sector are reduced (e.g. residential), the other two sector remain active (agricultural and industry). In this case, the Top-down impact is the difference between the base case concentration and the
concentration resulting from the agricultural and industrial emissions only. A similar reasoning can be made for all sectors:

\[
\Delta C_{R_A}^{TD} = C_{RAI} - C_{AI} = 150
\]
\[
\Delta C_{A}^{TD} = C_{RAI} - C_{RI} = 100
\]
\[
\Delta C_{I}^{TD} = C_{RAI} - C_{RA} = 150
\]

- with two sources: The Top-down impact due to a full reduction of two sectors (e.g. residential and agriculture) is similarly computed as the difference between the base case concentration and the concentration resulting from the remaining sector (industry).

\[
\Delta C_{RAI}^{TD} = C_{RAI} - C_{I} = 200
\]
\[
\Delta C_{RI}^{TD} = C_{RAI} - C_{A} = 300
\]
\[
\Delta C_{AI}^{TD} = C_{RAI} - C_{R} = 200
\]

- with three sources: The impact resulting from the simultaneous reduction of all three sources is similar in the Top-down and Bottom-up approaches:

\[
\Delta C_{RAI} = C_{RAI} - C_0 = 300
\]

The interaction terms can be obtained in a similar way to the bottom-up approach by using the Stein and Alpert formulation for \( \Delta C_{RAI}^{TD} \):

\[
\Delta C_{RAI} = \Delta C_{R}^{TD} + \Delta C_{A}^{TD} + \Delta C_{I}^{TD} + \ddot{C}_{RAI}^{TD} + \ddot{C}_{R}^{TD} + \ddot{C}_{A}^{TD} + \ddot{C}_{I}^{TD}
\]

The interaction terms are given by:

\[
\ddot{C}_{RAI}^{TD} = \Delta C_{RAI}^{TD} - \Delta C_{R}^{TD} - \Delta C_{A}^{TD} - \Delta C_{I}^{TD} = -50
\]
\[
\ddot{C}_{R}^{TD} = \Delta C_{RAI}^{TD} - \Delta C_{R}^{TD} - \Delta C_{I}^{TD} = 0
\]
\[
\ddot{C}_{A}^{TD} = \Delta C_{RAI}^{TD} - \Delta C_{R}^{TD} - \Delta C_{I}^{TD} = -50
\]
\[
\ddot{C}_{I}^{TD} = \Delta C_{RAI}^{TD} - \Delta C_{R}^{TD} - \Delta C_{A}^{TD} - \Delta C_{I}^{TD} - \ddot{C}_{RAI}^{TD} = 0
\]

With this approach, a non-linear behavior is also observed and interaction terms are not zero. It is also interesting to note that the
triple interaction term ($\delta_{RAI}$) is null. The sum of the individual
impacts ($\Delta C_{RD} + \Delta C_{AD} + \Delta C_{ID} = 400$) overestimates the overall
impact ($\Delta C_{RAI} = 300$). We further discuss these aspects at the end of
this section. These results are graphically represented in Figure 2
(fourth and fifth columns).

**Tagged species approach**

Compared to Brute-force, the tagged species approach calculates the
share of each source to the overall concentration change. These
shares are referred to as contributions and have the main property
that the sum of the individual contributions is equal to the overall
concentration impact, by definition, i.e.:

$$\Delta C_{RAI} = \delta_{RA} + \delta_{AI}$$

The sector contributions are computed by tracking the mass of their
emitted species contributing to PM formation (in our example:
PM[PPM], PM[NH4NO3] and PM[(NH4)2SO4])

- PM[PPM] is formed from PPM. The 100 moles from the
residential sector lead to 100 moles of PM. The same applies to
the 100 moles from industry.

- PM[NH4NO3] is formed by combination of NH3 and NO2. The
share between these two contributions is obtained by application
of stoichiometric molar mass ratios:

$$a_1 = \frac{[NO_3]_m}{[NO_3]_m + [NH_4]_m} = 0.78$$

In our example, 50 moles of PM[NH4NO3] are formed by
combination of NO2 (50 moles) from the residential sector and
NH3 (50 moles) from agriculture. The contribution attributed to
NO2 is $50 \times a_1$ whereas the contribution attributed to NH3 is
$50 \times (1 - a_1)$. 
PM\[(\text{NH}_4)_2\text{SO}_4\] is formed by combination of \text{NH}_3 and \text{SO}_2. The following stoichiometric mass ratio is used:

\[ a_2 = \frac{[\text{SO}_4]_m}{[\text{SO}_4]_m + 2[\text{NH}_4]_m} = 0.73 \]

The contribution attributed to \text{SO}_2 is \(50 \times a_2\) whereas the contribution attributed to \text{NH}_3 is \(50 \times (1 - a_2)\).

The contribution of each sector is then obtained as the sum of their precursor contribution shares as follows:

\[ \delta C_{\text{R}}^{\text{TAG}} = 100 + 50 \times a_1 = 138.7 \]
\[ \delta C_{\text{A}}^{\text{TAG}} = 50 \times (1 - a_1) + 50 \times (1 - a_2) = 24.9 \]
\[ \delta C_{\text{I}}^{\text{TAG}} = 100 + 50 \times a_2 = 136.4 \]

By definition the sum of the contributions (\(\delta C_{\text{R}}^{\text{TAG}} + \delta C_{\text{A}}^{\text{TAG}} + \delta C_{\text{I}}^{\text{TAG}} = 300\)) is exactly equal to the overall concentration impact (\(\Delta C_{\text{RAI}} = 300\)).

Note that a decomposition of the non-linear interaction terms obtained in the top-down or bottom-up approach, using the above stoichiometric ratios would lead to similar results than the tagged approach. These results are graphically represented in Figure 2 (second column).

**DDM**

In this methodology, delta concentrations and interaction terms are estimated with first order partial derivatives computed from the highest emission level (base case in our example). Being a sensitivity approach using level H as reference, DDM shows clear analogies with the BF-TD.

\[ \frac{\partial c}{\partial a_R} |_{TD} = 150 \quad \frac{\partial c}{\partial a_A} |_{TD} = 100 \quad \frac{\partial c}{\partial a_I} |_{TD} = 150 \]
where $\alpha_R$, $\alpha_A$, and $\alpha_I$ are percentage emission changes from the base case for the residential, agricultural and industrial sectors. The first-order derivatives are evaluated using finite differencing between the base case and a level characterised by emissions that are 10% lower for each activity sector. The concentration changes resulting from a 100% emission reduction (i.e. between the base case and the zero emission case) could be estimated by setting $\alpha_R$, $\alpha_A$, and $\alpha_I$ to unity.

\[
\Delta C_{R}^{HDDM} = \frac{\partial C}{\partial \alpha_R} = 150
\]
\[
\Delta C_{A}^{HDDM} = \frac{\partial C}{\partial \alpha_A} = 100
\]
\[
\Delta C_{I}^{HDDM} = \frac{\partial C}{\partial \alpha_I} = 150
\]

We see from this last example that both the total PM and the contribution of the sources are then comparable with those obtained with the BF-TD method. Their interpretation is similar (Figure 2, sixth column). In their work, Koo et al. (2009) present a detailed comparison between a DDM and a tagged species approach in a 3-D PM model and show which sensitivities are similar to apportionment, and which are not.
Comparative overview

In the linear case (second paragraph) we have seen that a single source contribution can be computed as the impact resulting from a full reduction of this source. However, source contributions and concentration impacts should not be confused as they are different in most situations. The example presented in this paragraph illustrates this clearly for a non-linear system. Indeed the contributions of the single sources computed by the tagged species approach ($\delta C_{R}^{TAG} = 138$; $\delta C_{A}^{TAG} = 24$; $\delta C_{I}^{TAG} = 136$) differ from the concentration impacts resulting from a total abatement of these single sources computed by the BF-TD ($\Delta C_{R}^{TD} = 150$; $\Delta C_{A}^{TD} = 100$; $\Delta C_{I}^{TD} = 150$) method. Moreover, the sum of the concentration impacts obtained with either the BF-TD approach for single sources does not equal the total concentration impact ($\Delta C_{RAI} = 300$). This is also valid for any selection of two sectors ($\Delta C_{R}^{TD} + \Delta C_{A}^{TD} = 250 \neq \Delta C_{RAI} = 200$). Note that similarly to BF-TD, the concentration impacts computed as...
increases from the background (BF-BU) show the same behaviour
\(\Delta C_B^T + \Delta C_A^T = 100 \neq \Delta C_B^T = 150\). Figure 3 shows that the impact on concentration is proportional to the emission reduction indicating that the relationship between emission and concentration changes is linear. However, this example also illustrates the fact that linearity encompasses two aspects: 1) the interaction terms are zero \(\hat{C}^{\text{int}} = 0\); 2) the ratios between concentration change and emission changes \(\Delta C/\Delta E\) remain constant, regardless of the calculation bounds (denoted “H” and “L” in Section 4). In the current example the ratios \(\Delta C/\Delta E\) are constant (linear trend of \(\Delta C\) on Figure 3) but the relationship between concentration and emission is not linear because of the non-zero interaction terms (not shown) \(\hat{C}^{\text{int}}_{RA} = -50\) and \(\hat{C}^{\text{int}}_{AI} = -50\).

However, even with zero interaction terms, we can still observe a non-linear behaviour with the emission reduction percentage. The evaluation of linearity therefore requires two tests: one to quantify the interaction terms and the second to assess the deviation from a linear trend with respect to the emission reduction percentage.

Figure 3: Evolution of the concentration changes resulting from different percentage of source abatement (Top down approach) for the three sectors (Residential, Agricultural and Industrial).
5.2. Limited regime

This example is similar to the previous, except that the emissions of NH$_3$ are reduced from 150 to 100 moles. When all sources release emissions, the 100 moles of NH$_3$ are shared into $100/3=33.3$ moles which react with NO$_2$ to form 33.3 moles of PM[$(NH_4)NO_3$] and $100\times2/3=66.6$ moles which react with SO$_2$ to give 33.3 moles of PM[$(NH_4)_2SO_4$]. Because the mass of NH$_3$ is not enough to react with all the NO$_2$ and SO$_2$ mass, 16.7 moles of NO$_2$ and 16.7 moles of SO$_2$ remain unused. (Figure 4).

Note that when the agricultural source is active with one only of the two other sources (residential or industrial) the NH$_3$ 100 moles are then sufficient to consume all the NO$_2$ or SO$_2$ and lead to 50 moles of PM in either case.

---

Figure 3.4: Example with three sources in an ammonia-limited regime. The mass emitted by each source is expressed in moles.

The PM concentrations obtained when one or two sources are active are similar to the previous example:

$C_0 = 0$; $C_R = 100$; $C_A = 0$; $C_I = 100$
But the result differ when all sources are active: $C_{RAI} = 266.6$ (200 from PPM (residential industry), 33.3 from reaction between NO$_2$ and NH$_3$ and 33.3 from reaction between SO$_2$ and NH$_3$).

**Bottom-up brute-force method (BF-BU)**

The BF-BU approach computes all concentration impacts from the background concentration ($C_0$). The Stein-Alpert terms are similar to the non-limited case, except for $\Delta C_{RAI}$ and $\hat{C}_{RAI}$:

$$
\begin{align*}
\Delta C^B_B &= 100 \\
\hat{C}^B_B &= 50 \\
\Delta C^B_A &= 0 \\
\hat{C}^B_A &= 0 \\
\Delta C^B_I &= 100 \\
\hat{C}^B_I &= 50 \\
\Delta C_{RAI} &= 266.6 \\
\hat{C}_{RAI} &= -33.3
\end{align*}
$$

The limiting effect of NH$_3$ appears only in the negative triple interaction term ($\hat{C}_{RAI}$).

**Top-down brute-force method (BF-TD)**

The Top-down approach uses the base case ($C_{RAI}$) concentration as reference to compute the concentration impact. In this case, all Stein-Alpert terms are different from the non-limited regime:

$$
\begin{align*}
\Delta C^T_R &= 116.6 \\
\hat{C}^T_R &= -16.6 \\
\Delta C^T_A &= 66.6 \\
\hat{C}^T_A &= 33.3 \\
\Delta C^T_I &= 116.6 \\
\hat{C}^T_I &= -16.6 \\
\Delta C_{RAI} &= 266.6 \\
\hat{C}_{RAI} &= -33.3
\end{align*}
$$

These results are graphically represented in Figure 5 (fourth and fifth columns).

**Tagged approach**
The contribution of each source is computed similarly to the non-limited regime. The production of 33.3 moles of PM[NH$_4$NO$_3$] and 33.3 moles of PM[(NH$_4$)$_2$SO$_4$] are split among the different sectors using the stoichiometric coefficients $a_1$ and $a_2$:

\[
\begin{align*}
\delta C_{T_A}^{TAG} &= 100 + 33.3 \times a_1 = 125.8 \\
\delta C_{A}^{TAG} &= 33.3 \times (1 - a_1) + 33.3 \times (1 - a_2) = 16.6 \\
\delta C_{I}^{TAG} &= 100 + 33.3 \times a_2 = 124.2
\end{align*}
\]

These results are graphically represented in Figure 5 (second column).

**DDM**

As shown below, DDM only considers first derivatives, which are not suitable to estimate higher order interaction terms. The calculation of the first order derivatives in this example gives:

\[
\begin{align*}
\Delta C_R^{HDDM} &= \frac{\partial C}{\partial a_R} \bigg|_{TD} = 111.5 \\
\Delta C_A^{HDDM} &= \frac{\partial C}{\partial a_A} \bigg|_{TD} = 66.7 \\
\Delta C_I^{HDDM} &= \frac{\partial C}{\partial a_I} \bigg|_{TD} = 88.1
\end{align*}
\]
Figure 4: These results are graphically represented in Figure 5 (sixth column).

Figure 5: Schematic representation of the allocation of PM to its sources in the ammonia-limited example. The expected total PM is displayed in the grey bar on the left.
Comparative overview

The main difference with respect to the non-limited regime is the appearance of a triple interaction term that will also lead to differences between the BF-TD and the DDM approaches, given the fact that the latter only accounts for first order terms.

In comparison to the non-limited regime, the calculation of the concentration impacts resulting from different percentage of emission reduction shows non-linear trends (Figure 56). A discontinuity appears at 50% reduction for the abatement of industrial emissions. This discontinuity corresponds to a change of chemical regime. Below the 50% reduction level, the quantity of NH$_3$ is not sufficient to feed the reactions with NO$_2$ and SO$_2$ (with no SO$_2$ reduction, 50 moles of NO$_2$ and 50 moles of SO$_2$ would require 150 moles of NH$_3$ but only 100 are available) while beyond this 50% reduction level the quantity of NH$_3$ is then enough to feed the reactions with NO$_2$ and SO$_2$ (with 50% SO$_2$ reduction, 50 moles of NO$_2$ and 25 moles of SO$_2$ requires 100 moles of NH$_3$).
The methodologies presented in this section aim at decomposing the impact of an ensemble of sources into different terms attributed to each individual source. The terms computed by methodologies designed for source apportionment (like TAG) are named source contributions. Their sum is always equal to the combined impact of all sources. On the other hand, the terms computed by sensitivity analysis represent the emission change of each individual source and their sum is equal to the combined impact of all sources only if the relationship between emissions and concentrations is linear (see Section 2). Grewe et al. (2010) and Grewe (2013) who used simple differential equations to reproduce the ozone tropospheric chemistry, also highlighted this point in their work. In non-linear situations, the source contributions computed for source apportionment and the source impacts computed for sensitivity analysis are different (see Figure 45 where column 2 shows different results than column 3 or 4). Non-linearity also imply that the calculation of the source impacts depends from the bounds used to estimate the concentration changes (denoted “H” and “L” in Section 4). The BF-BU and BF-TD (columns 3 and 4 in Figure 45) give different results because they are not using the same reference level (“L” for the BU and “H” for the TD).
for the TD as defined in Section 4). Moreover, the results depend from the percentage of emission changes applied to calculate the source impacts as demonstrated by the different source impacts computed with the BF-TD for 100% and 25% emission reductions (columns 4 and 5 in Figure 45). We expect that lower percentage emission reductions generate less non-linearity and lead to a better agreement between the BF-TD and the DDM method (columns 5 and 6 in Figure 45).

In synthesis, the second example illustrates that all the methodologies tested to find source contributions and source impacts give different results when the relationship emissions-concentrations is non-linear. It is therefore important to determine the degree of non-linearity in order to understand the range of applicability of each methodology and apply it for the right purpose. A quantification of the potential non-linearities should therefore be the first step prior to source apportionment or planning applications, to prevent any limitations in their use. When non-linearity is mild, these limitations may however be acceptable in the context of the other uncertainties inherent to complex models.

6. Conclusions

When pollutant concentrations exceed the thresholds set in the legislation, competent authorities must take actions to abate pollution. In the European legislation (Directive 2008/50/EC) both source apportionment and planning are requested when designing air quality plans. In practice, source apportionment is often used for planning purposes. It is indeed intuitive to use source apportionment to detect the activity sectors that need to be tackled in priority in an air quality plan. On the other hand, sensitivity analysis is often used as an approach to derive source contributions (e.g. SHERPA, FASST, GAINS...).

In this work, we compared the two above mentioned source apportionment and sensitivity approaches and investigated their domain of application. While sensitivity analysis refers to impacts to characterize the concentration change resulting from a given
emission change, source apportionment aims to quantify contributions, by attributing a fraction of the pollutant concentration to each emission source. In the case of linear (or close to linear) relationships between concentration and emissions, impacts and contributions are equivalent (or close to) concepts. Source apportionment may then be used for air quality planning purposes and vice versa, sensitivity analysis may be used for quantifying sources contributions. In many cases, however, linearity is not a valid assumption. In such cases, sensitivity approaches cannot be used to retrieve source apportionment information, unless non-linear interaction terms are explicitly accounted for. On the other hand, source apportionment approaches (e.g. tagged species approach) intrinsically account for these non-linear interactions into their source contributions. But because it mix interaction terms and impacts, which may react in opposite directions, source apportionment should not be used to evaluate the impact of abatement strategies. Even when using sensitivity analysis for planning, it is important to note that, under non-linear conditions, the calculated impacts will only provide information for the exact conditions that are considered. Impacts for an emission reduction of 50% are only valid for exactly that percentage of reduction and extrapolation to air quality planning with any other emission reduction levels would be inappropriate, unless additional scenarios are tested. Along the same line of reasoning, the importance of the non-linear interaction terms (among precursors) should be quantified as well when assessing the impact of more sources or precursors. Finally, these non-linear interaction terms are in most cases not constant with the emission reduction intensities, which would imposes the further need to quantify them for different levels of emission reduction. Calculating sensitivities and interactions at various level of emission reductions seems the only alternative when non-linearities are important. In this respect, new approaches like the path-integral methodology proposed by Grewe et al. (2012) might represent a powerful approach.
Fortunately, not all cases are so complex to require the full quantification of all non-linear interaction terms. Thunis et al. (2015) showed that for yearly average relationships between emission and concentration changes, linearity is a realistic assumption, implying the possible use of source apportionment and sensitivity analysis for both purposes. Some integrated assessment tools (e.g. GAINS, SHERPA) take advantage of this assumption to retrieve source apportionment information from calculated CTM sensitivities. Although non-linearities are important for short-term time averages (e.g. daily means, episodes), they are likely not associated to every process. For instance, non-linear interactions are expected to be more relevant for secondary pollutants, especially under limited regimes. The challenge consists, therefore, in screening the system for significant non-linearities and account for them by calculating explicitly the relevant non-linear interaction terms.

One main strength of source apportionment approaches is to provide contribution estimates that can be cross validated with source apportionment derived from measurements (i.e. receptor modelling, for a detailed description see e.g. Belis et al., 2013). This step is crucial for the evaluation of chemistry transport models.

7. Code availability
No specific code is attached to this work as all presented examples can easily be replicated.

References


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