Answer to reviewers

Referee #1 :

General comments The paper present 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.

Referee #2

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.
Koo, B., Wilson, G.M., Morris, R.E., Dunker, A.M. and Yarwood, G., 2009. Comparison of source apportionment and sensitivity analysis in a particulate matter air quality model. Environmental Science & Technology, 43(17), pp.6669-6675.

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., 299 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.
Dunker, A.M., 2015. Path-integral method for the source apportionment of photochemical pollutants. Geoscientific Model Development, 8(6), pp.1763-1773.
Simon, H., Baker, K.R., Akhtar, F., Napelenok, S.L., Possiel, N., Wells, B. and Timin, B., 2013. A direct sensitivity approach to predict hourly ozone resulting from compliance with the National Ambient Air Quality Standard. Environmental Science & Technology, 47(5), pp.2304-2313.

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: PPM → PM[PPM] NO2 + NH3 → PM[NH4NO3] SO2 + 2 NH3 → PM[(NH4)2SO4] 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

$$\frac{dx}{dt} = P - x^{\alpha}, \qquad\qquad (1)$$

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

(see Fig. 1). 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~~decoupled direct method (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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35 be acceptable in the context of the other uncertainties inherent to
36 complex models.
37
38 Moreover, when using sensitivity analysis for planning, it is
39 important to note that, under non-linear circumstances, the
40 calculated impacts will only provide information for the exact
41 conditions (e.g. emission reduction share) that are simulated.
42
43
44 **Keywords:** source apportionment, sensitivity analysis, abatement strategies,
45 air quality planning
46

1. Introduction

48
49 ~~The~~When pollutant concentrations exceed the thresholds set in the
50 legislation, competent authorities must take actions to abate
51 pollution. Those abatement strategies consist in reducing the
52 precursor's emission of the different activity sector to reduce
53 pollutant concentrations but they are challenging to design because
54 of the complex relationships that link emissions and pollutants.
55 Indeed, the concentration of a pollutant at a given location generally
56 results from direct emissions and from interactions in the
57 atmosphere among different emission precursors, emitted by a
58 variety of sources. For example, particulate matter (denoted here as
59 PM) results from the interaction and combination of ~~5~~five different
60 precursors (PPM, NO_x, SO_2, NH_3, and VOC) which can be emitted
61 by different activity macro-sectors (e.g. residential, transport,
62 industrial and agriculture~~).~~ [Seinfeld and Pandis, 2016]).
63
64 ~~Abatement strategies aim at reducing the precursor's emission of the~~
65 ~~different activity sector to reduce pollutant concentrations but these~~
66 ~~strategies are challenging to design because of the complex~~
67 ~~relationships that link precursors and pollutants.~~
68 Two different approaches are currently used to support air quality
69 decision makers: source apportionment and sensitivity analysis.
70

- 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:

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

where P_1, P_2 and P_3 are three constant coefficients.

107 On the other hand, the sensitivity of the concentration to a change of
108 a given emission source can be quantified via partial derivatives. For
109 expression (1) this gives:
110

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

111
112 In Clappier et al. (2017) the coefficients (P_1, P_2 and P_3) are referred
113 to "potencies". The ~~Authors~~authors used this concept of "potencies"
114 to analyze the model response to emission changes in different
115 European countries.
116
117 The consequences of a linear relationship between concentration and
118 emission sources are twofold:
119 1) all higher order derivatives (order 2 and beyond) are null,
120 including those involving two or more emission sources (crossed
121 derivatives) as the impact of a change in one emission source is
122 independent from all others.
123 2) the first-order partial derivatives are constant and can therefore be
124 calculated with finite differencing, between any couple of emission
125 levels, for example a base case (denoted BC) and a background
126 (denoted as 0).
127 The potency equations then read as:
128

$$P_1 = \frac{\Delta C_0^{BC_1}}{E_1^{BC}} \ ; \ P_2 = \frac{\Delta C_0^{BC_2}}{E_2^{BC}} \ ; P_3 = \frac{\Delta C_0^{BC_3}}{E_3^{BC}}$$

129
130 with $\quad \Delta C_0^{BC_1} = C(E_1^{BC}, 0, 0) - C(0,0,0),$
131 $\Delta C_0^{BC_2} = C(0, E_2^{BC}, 0) - C(0,0,0)$
132 $\Delta C_0^{BC_3} = C(0, 0, E_3^{BC}) - C(0,0,0)$
133
134 Together with "potencies", Clappier et al. (2017) also introduce the
135 concept of "potential", defined as the concentration change resulting
136 from a total reduction of the emissions (from BC to 0). The
137 "potential" can be calculated via relation (1) applied between the
138 base-case and background levels as:

139
$$\Delta C_0^{BC} = \Delta C_0^{BC_1} + \Delta C_0^{BC_2} + \Delta C_0^{BC_3} \qquad (2)$$

140

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

142

143 Equation (2) can directly be used for source apportionment purpose,
144 with $\Delta C_0^{BC_1}$ the concentration change resulting from a total reduction
145 of the emission source (or precursor) E_1, reflecting the contribution
146 of E_1 to the base case concentration. Similarly $\Delta C_0^{BC_2}$ and $\Delta C_0^{BC_3}$ are
147 the contributions of E_2 and E_3 . Equation (2) shows that, in the
148 linear case, the concentration change resulting from a simultaneous
149 reduction of all emission sources (ΔC_0^{BC}) is equal to the sum of the
150 emission sources contributions.

151

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

157

158 **3. Brute Force method**

159

160 The "brute force" method consists in estimating the concentration
161 change by performing and subtracting two simulations, one with and
162 the second without a specific emission source to be analysed
163 (Blanchard, 1999; Yarwood et al., 2004).
164 In non-linear situations, the concentration change resulting from a
165 set of emission sources is not anymore equivalent to the sum of the
166 concentration changes resulting from emission sources changed
167 individually. In the following, we will refer to the work of Stein and
168 Alpert (1993) who proposed an approach to decompose an overall
169 impact into single (one emission source only) and combined
170 (multiple emission sources) impacts.

171

172
173 3.1. Bottom-up formulation

174

175

176 We consider here three ~~precursor's~~ emission ~~precursors~~ E_1, E_2 and
177 E_3 that are changing from a low (denoted as "L") to a high level
178 (denoted as "H"). In a bottom-up approach, the low emission level is
179 chosen as the reference. With these definitions and notations, the
180 impact on concentration resulting from a change of one only of the
181 three precursor's emissions can be written as follows:

182

$$\Delta C_{\bar{L}}^{H_1} = C(E_1^H, E_2^L, E_3^L) - C(E_1^L, E_2^L, E_3^L)$$
$$\Delta C_{\bar{L}}^{H_2} = C(E_1^L, E_2^H, E_3^L) - C(E_1^L, E_2^L, E_3^L)$$
$$\Delta C_{\bar{L}}^{H_3} = C(E_1^L, E_2^L, E_3^H) - C(E_1^L, E_2^L, E_3^L)$$

183

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

186

$$\Delta C_{\bar{L}}^{H_1,H_2} = C(E_1^H, E_2^H, E_3^L) - C(E_1^L, E_2^L, E_3^L)$$
$$\Delta C_{\bar{L}}^{H_1,H_3} = C(E_1^H, E_2^L, E_3^H) - C(E_1^l, E_2^l, E_3^l)$$
$$\Delta C_{\bar{L}}^{H_2,H_3} = C(E_1^L, E_2^H, E_3^H) - C(E_1^L, E_2^L, E_3^L)$$
$$\Delta C_{\bar{L}}^{\bar{H}} = C(E_1^H, E_2^H, E_3^H) - C(E_1^L, E_2^L, E_3^L)$$

187 Using a similar notation, the decomposition of Stein and Alpert
188 (1993) applied to 2 variables (E_1 and E_2) would read as:

189

$$\Delta C_{\bar{L}}^{H_1,H_2} = \Delta C_{\bar{L}}^{H_1} + \Delta C_{\bar{L}}^{H_2} + \hat{C}^{int} \qquad (3)$$

190

191

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

195

196 It is clear from (3) that the impact of a simultaneous change of two
197 emission sources is not equivalent to the sum of the individual
198 impacts, as highlighted by the additional term $\hat{C}^{int}$. This term that

199 quantifies the interaction between the two emission sources can be
200 calculated using (3) as:
201

$$\hat{C}^{int} = \hat{C}_{\bar{L}}^{H_1,H_2} = \Delta C_{\bar{L}}^{H_1,H_2} - \Delta C_{\bar{L}}^{H_1} - \Delta C_{\bar{L}}^{H_2} \qquad (4)$$

202
203 The Stein and Alpert formulation can similarly be applied with 3
204 emission sources:
205

$$\Delta C_{\bar{L}}^{\bar{H}} = \Delta C_{\bar{L}}^{H_1} + \Delta C_{\bar{L}}^{H_2} + \Delta C_{\bar{L}}^{H_3} + \hat{C}^{int} \qquad (5)$$

206
207 Where $\Delta C_{\bar{L}}^{H_1}$, $\Delta C_{\bar{L}}^{H_2}$ and $\Delta C_{\bar{L}}^{H_3}$ are the impact on concentration
208 resulting from single emission changes in the sources and
209

$$\hat{C}^{int} = \hat{C}_{\bar{L}}^{H_1,H_2} + \hat{C}_{\bar{L}}^{H_1,H_3} + \hat{C}_{\bar{L}}^{H_2,H_3} + \hat{C}_{\bar{L}}^{H_1,H_2,H_3} \qquad (6)$$

210
211 where $\hat{C}_{\bar{L}}^{H_1,H_2}$, $\hat{C}_{\bar{L}}^{H_1,H_3}$ and $\hat{C}_{\bar{L}}^{H_2,H_3}$ are the double interaction terms that
212 can be further decomposed via equation (4). $\hat{C}_{\bar{L}}^{H_1,H_2,H_3}$ is the triple
213 interaction term (between E_1, E_2, E_3) which can be decomposed by
214 combining (5) and (6) as:
215

$$\hat{C}_{\bar{L}}^{H_1,H_2,H_3} = \Delta C_{\bar{L}}^{\bar{H}} - \Delta C_{\bar{L}}^{H_1} - \Delta C_{\bar{L}}^{H_2} - \Delta C_{\bar{L}}^{H_3}$$

$$\Delta C_{\bar{L}}^{H_1,H_2} - \Delta C_{\bar{L}}^{H_1,H_3} - \Delta C_{\bar{L}}^{H_2,H_3}$$

216
217   3.2. Top-down formulation
218
219 In a top-down formulation, the highest emission level is chosen as
220 reference. The Stein Alpert formulation for three precursors can then
221 be expressed similarly to the bottom-up formulation as:
222

$$\Delta C_{\bar{L}}^{\bar{H}} = \Delta C_{L_1}^{\bar{H}} + \Delta C_{L_2}^{\bar{H}} + \Delta C_{L_3}^{\bar{H}} + \hat{C}^{int} \qquad (7)$$

223
224 where $\Delta C_{L_1}^{\bar{H}}$, $\Delta C_{L_2}^{\bar{H}}$ and $\Delta C_{L_3}^{\bar{H}}$ are the impacts on concentration induced
225 by reducing E_1 , E_2 and E_3 independently whereas $\hat{C}^{int}$ is the

226 interaction term which itself can be decomposed into a series of
227 double interactions and a triple interaction terms:
228

$$\hat{C}^{int} = \hat{C}_{L_1,L_2}^{\bar{H}} + \hat{C}_{L_1,L_3}^{\bar{H}} + \hat{C}_{L_2,L_3}^{\bar{H}} + \hat{C}_{L_1,L_2,L_3}^{\bar{H}} \tag{8}$$

229
230 It is important to stress that the top-down single impacts are not
231 equivalent to their bottom-up counterparts. The relation between
232 these bottom-up and top-down impacts can be expressed as (here for
233 the case of E$_3$):
234

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

235
236

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

237

$$\Delta C_{L_3}^{\bar{H}} = \Delta C_{\bar{L}}^{\bar{H}} - \Delta C_{\bar{L}}^{H_1 H_2} \tag{9}$$

238
239 Using equations (3), (4), (5) and (6), equation (9) can be re-
240 expressed as:
241

$$\Delta C_{L_3}^{\bar{H}} = \Delta C_{\bar{L}}^{H_3} + \hat{C}_{\bar{L}}^{H_1,H_3} + \hat{C}_{\bar{L}}^{H_2,H_3} + \hat{C}_{\bar{L}}^{H_1,H_2,H_3} \tag{10}$$

242
243 In other words, the top-down impact on concentration of an emission
244 source (obtained by switching off the emission source while all
245 others remain unchanged) is not equivalent to its bottom-up
246 counterpart, (obtained by switching on the emission source while all
247 others are switched off). Relation (10) indeed clearly shows that
248 additional interaction terms need to be considered. The implications
249 resulting from these differences are highlighted in Section 5 in
250 which some theoretical examples are described.
251

252 **4. Source apportionment and sensitivity analysis**
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254

255  4.1. Tagged species techniques
256

257 Equation (2) shows that, when the relationship between
258 concentration and several emission sources is linear, the contribution
259 of a specific source (source apportionment) can be computed as the
260 impact on concentration obtained by a full reduction of this source
261 (sensitivity). Moreover, the sum of the impacts on concentration
262 obtained by reduction of the single sources ($\Delta C_0^{BC_1} + \Delta C_0^{BC_2} + \Delta C_0^{BC_3}$) is
263 equivalent to the impact on concentration resulting from a
264 simultaneous abatement of all sources (ΔC_0^{BC}). In such a case, the
265 concentration impacts are equal to source contributions and source
266 apportionment and sensitivity analysis lead to similar results. This is
267 not the case, however, when the relationship between concentrations
268 and emissions is nonlinear. In their approach, Stein and Alpert
269 express the difference between the impact caused by a simultaneous
270 abatement and the sum of the impacts caused by individual
271 abatement as interactions among the different sources. The Stein and
272 Alpert formulation applied between the base-case and background
273 levels is very close to equation (2) but with an additional term that
274 accounts for interactions:
275

$$\Delta C_0^{BC} = \Delta C_0^{BC_1} + \Delta C_0^{BC_2} + \Delta C_0^{BC_3} + \hat{C}^{int}$$

276

277 Because the interaction terms cannot not be attributed to a single
278 emission source as they represent the interaction between two and
279 more emission sources, the Stein and Alpert methodology does not
280 allow identifying the full contribution of each individual source. It
281 cannot therefore be used for source apportionment purpose, unless
282 the interaction terms are negligible as in the linear case.
283 Unlike the Stein and Alpert methodology, the tagged species
284 methodology is designed for source apportionment purposes. This
285 methodology tags each precursor and quantifies its contribution (in
286 terms of mass) to the pollutant concentration.
287 Tagged algorithms are implemented in several chemical transport
288 model systems (Yarwood et al., 2004; Wagstrom et al., 2008,
289 ENVIRON, 2014; Bhave et al., 2007; Wang et al., 2009;
290 Kranenburg et al., 2013).
291

292 In tagging approaches, the effect of the full reduction of all sources
293 is directly expressed as the sum of the source contributions:
294

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

295

296 where δC_1, δC_2, δC_3 are the contributions of sources E_1, E_2 and E_3
297 resulting from the tagged species approach resolution.

298

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

302

$$\delta C_1 = \Delta C_0^{BC_1} + \alpha \hat{C}^{int}$$

303

304

305 Because the tagged species approach mixes interaction terms and
306 single concentration impacts into sources contributions, it is not
307 suitable to estimate the effect of emission reduction when non-
308 linearities are present (Burr and Zhang 2011a, 2011b). Indeed these
309 two types of terms may react in very different ways to emission
310 reductions. This fact is detailed in the examples provided below.
311 On the other hand, the strength of this method is that it allows for a
312 direct comparison of the source contributions with measurements (or
313 measurement based methods like receptor models).

314

315 Note that similar tagging methods are also used in the frame of
316 climate-chemical studies at global scale (e.g. Horowitz and Jacob,
317 1999; Lelieveld and Dentener, 2000; Meijer et al., 2000; Grewe,
318 2004; Gromov et al., 2010; Butler et al.,2011; Emmons et al., 2012;
319 Grewe et al., 2012; Grewe et al., 2017).

320

321   4.2. DDM

322

323 The decoupled direct method (DDM) is designed to
324 estimatecalculate directly sensitivities to emission changes (Dunker
325 et al., 1984; Dunker et al., 2002). It aims to compute only the first
326 order derivatives (which correspond to the potencies mentioned in
327 paragraphsection 2).

328

$$\frac{\partial C}{\partial E_1} \; ; \; \frac{\partial C}{\partial E_2} \; ; \; \frac{\partial C}{\partial E_3}$$

329
330 The Taylor formula is applied at first order to calculate the
331 concentration change between two emission levels (denoted H and
332 L).
333

$$\Delta C_{\bar{L}}^{\bar{H}} = \Delta E_1 \left.\frac{\partial C}{\partial E_1}\right|_H + \Delta E_2 \left.\frac{\partial C}{\partial E_2}\right|_H + \Delta E_3 \left.\frac{\partial C}{\partial E_3}\right|_H$$

334
335   with $\Delta E_1 = E_1^H - E_1^L, \Delta E_2 = E_2^H - E_2^L, \Delta E_3 = E_3^H - E_3^L$
336
337 In the linear case, the first order derivatives are constant and the first
338 order approximation of the Taylor formula gives the exact
339 expression of the impact on concentration of an emission change
340 between H and L. When the emission-concentration relationship is
341 nonlinear, the first derivatives are not constants. The first order
342 Taylor formula cannot take into account the nonlinear effects. It is a
343 linear approximation based on derivatives computed at a given
344 emission reference level (level H in our example). The estimation of
345 the impact on concentration of an emission change between H and L
346 is accurate enough if level L is close enough to level H.
347
348 ~~The~~ HDDM is another method (Hakami et al., 2003) ~~aim~~which aims
349 to increase the accuracy of the DDM method by computing second
350 order derivatives.
351 DDM (and HDDM) gives similar information to the Stein Alpert
352 formulation applied with the Brute force top-down approach
353 (because the reference level is H). For the same reason than for the
354 Stein Alpert approach, these two methods are suitable for source
355 apportionment purpose only if the relation between concentration
356 and emission is close to linearity.
357
358 DDM (and HDDM) approximates the impact on concentration from
359 an emission change between the two level H and L, using
360 derivatives computed at level H. This impact is accurate enough if
361 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

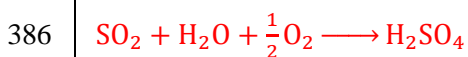
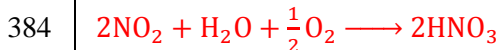
In this section, examples are designed to illustrate the differences in terms of contribution and impact estimates when the approaches discussed previously are used. In these examples, we focus on the formation of particulate matter (PM) in the atmosphere and only consider three formation processes: direct emissions (primary PM denoted as PPM); formation through reactions with nitrogen oxides (NO_2) and ammonia (NH_3) and formation through reactions with sulphur oxide (SO_2) and NH_3.

$$PPM \longrightarrow PM$$

$$2NO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2HNO_3$$

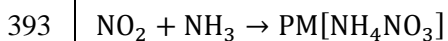
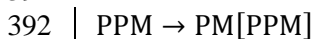
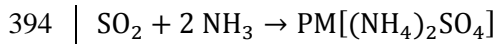
$$2NH_3 + 2HNO_3 \longrightarrow 2NH_4NO_3$$

$$SO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow H_2SO_4$$

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

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

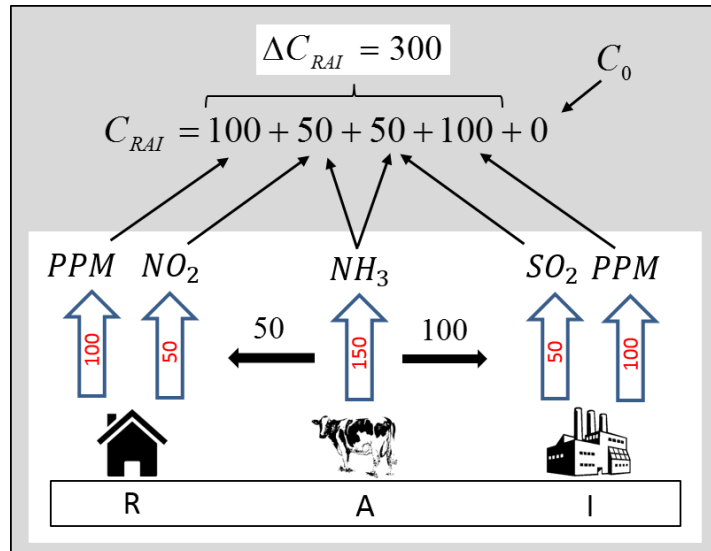
$$PPM \rightarrow PM[PPM]$$

$$NO_2 + NH_3 \rightarrow PM[NH_4NO_3]$$

$$SO_2 + 2\,NH_3 \rightarrow PM[(NH_4)_2SO_4]$$

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 NH_3 and 1 NO_2 moles or by the combination of 1 SO_2 and 2 NH_3 moles.

We also limit our examples to emissions from three activity sectors. The residential sector (R) only emits PPM and NO_2, the agricultural sector (A) only emits NH_3 and the industrial sector (I) only emits PPM and SO_2 (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 NH_3 quantity is sufficient to react with all moles of NO_2 and SO_2 and a "limited regime" where the NH_3 quantity of is not sufficient to react with all moles of NO_2 and SO_2.

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 NH_3 moles which can react with 50 NO_2 moles emitted by the residential sector and 50 SO_2 moles emitted by industrial sector. 100 PPM moles are emitted by the residential sector as well by the industrial sector. (Figure 1).

421
422 Figure 1~:~ Example of PPM, NO₂, SO₂ and NH₃ emissions released
423 by three activity sectors: residential (R), agricultural (A) and
424 industrial (I). For convenience, no units are associated to emissions
425 and concentrations
426
427 Let's first calculate the PM concentration produced with and without
428 each of the sources:
429
430 No source: C_0 is the PM concentration obtained when all emissions
431 are set to zero. Since we assumed a zero background pollution,
432 $C_0 = 0$.
433
434 One source only: C_R (resp. C_A and C_I) is the PM concentration
435 reached when only the residential (resp. agricultural and industrial)
436 sector releases emissions:
437   - $C_R = 100$ produced by PPM emissions (NO₂ emissions do not
438   produce PM as no NH₃ is available).
439   - $C_A = 0$ because NO₂ and SO₂ are not available to react with
440   NH₃.
441   - $C_I = 100$ produced by the PPM emissions (SO₂ emissions do not
442   produce PM as no NH₃ is available).
443

444 Two sources: C_{RA} C_{RI}, and C_{AI} are the concentrations obtained when
445 two (out of three) activity sectors release their emissions
446 simultaneously (the RA subscripts correspond to residential and
447 agriculture, RI to residential and industrial, AI to agriculture and
448 industrial):
449 - $C_{RA} = 150$: 100 produced by PPM emissions from the
450 residential sector and 50 produced by the 50 NO_2 released by the
451 residential sector reacting with the 50 NH_3 emitted by agriculture
452 (100 NH_3 moles remain unused).
453 - $C_{RI} = 200$: 100 produced by PPM emissions from the residential
454 sector and 100 produced by PPM emissions from the industrial
455 sector.
456 - $C_{AI} = 150$: 100 produced by PPM industrial emissions and 50
457 from the combination of 50 SO_2 (industry) and 100 NH_3
458 (agriculture).
459
460 Three sources: C_{RAI} is the concentrations obtained when all
461 emissions are released simultaneously.
462 - $C_{RAI} = 300$: 200 from PPM (residential and industry), 50 from
463 reaction between NO_2 and NH_3 and 50 from reaction between SO_2
464 and NH_3.
465
466 **Brute-force Bottom-up (BF-BU) method**
467
468 The contribution of each activity sector is calculated as the
469 concentration change resulting from a 100% emission increase from
470 the lowest emission level (previously denoted "L" or background) to
471 the highest level (denoted as "H", the base case C_{RAI} obtained with
472 all emissions)
473
474 In a bottom-up approach, the concentration associated with the
475 lowest emission level is considered as the reference. Concentration
476 impacts are then computed by the difference between any situation
477 (e.g. one, two or three sources present) and this reference.
478
479 - with one source: $\Delta C_R^{BU} = C_R - C_0 = 100$
480                        $\Delta C_A^{BU} = C_A - C_0 = 0$
481                        $\Delta C_I^{BU} = C_I - C_0 = 100$

482
483   - with two sources: $\Delta C_{RA}^{BU} = C_{RA} - C_0 = 150$
484                                   $\Delta C_{RI}^{BU} = C_{RI} - C_0 = 200$
485                                   $\Delta C_{AI}^{BU} = C_{AI} - C_0 = 150$
486
487   - with three sources: $\Delta C_{RAI} = C_{RAI} - C_0 = 300$
488
489 To calculate the interaction terms, we use the Stein-Alpert
490 formulation using Eq. (5) and Eq. (6):
491

$$\Delta C_{RAI} = \Delta C_R^{BU} + \Delta C_A^{BU} + \Delta C_I^{BU} + \hat{C}_{RA}^{BU} + \hat{C}_{RI}^{BU} + \hat{C}_{AI}^{BU} + \hat{C}_{RAI}^{BU}$$

492
493 from which the interaction terms are obtained by application of (4)
494 and (6):
495

$$\hat{C}_{RA}^{BU} = \Delta C_{RA}^{BU} - \Delta C_R^{BU} - \Delta C_A^{BU} = 50$$
$$\hat{C}_{RI}^{BU} = \Delta C_{RI}^{BU} - \Delta C_R^{BU} - \Delta C_I^{BU} = 0$$
$$\hat{C}_{AI}^{BU} = \Delta C_{AI}^{BU} - \Delta C_A^{BU} - \Delta C_I^{BU} = 50$$
$$\hat{C}_{RAI}^{BU} = \Delta C_{RAI} - \Delta C_R^{BU} - \Delta C_A^{BU} - \Delta C_I^{BU} - \hat{C}_{RA}^{BU} - \hat{C}_{RI}^{BU} - \hat{C}_{AI}^{BU} = 0$$

496
497 As can be seen from this example, the system behaves non-linearly
498 and the interaction terms (e.g. $\hat{C}_{RA}^{BU}$) are not-zero. Moreover the sum
499 of the individual impacts ($\Delta C_R^{BU} + \Delta C_A^{BU} + \Delta C_I^{BU} = 200$)
500 underestimates the overall impact ($\Delta C_{RAI} = 300$). These results are
501 graphically represented in Figure 2 (third column).
502
503
504 **Brute-force Top-down (BF-TD) method**
505
506 In a BF-TD approach, the higher emission level (base case, C_{RAI}) is
507 the reference and the impact of each activity sector is calculated as
508 the concentration change resulting from a 100% emission decrease
509 (of one, two or three sources) from this reference to the background
510 level.
511
512   - with one source: When all emissions from one sector are
513   reduced (e.g. residential), the other two sector remain active
514   (agricultural and industry). In this case, the Top-down impact is
515   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:

$$\Delta C_R^{TD} = C_{RAI} - C_{AI} = 150$$
$$\Delta C_A^{TD} = C_{RAI} - C_{RI} = 100$$
$$\Delta C_I^{TD} = C_{RAI} - C_{RA} = 150$$

- 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).

$$\Delta C_{RA}^{TD} = C_{RAI} - C_I = 200$$
$$\Delta C_{RI}^{TD} = C_{RAI} - C_A = 300$$
$$\Delta C_{AI}^{TD} = C_{RAI} - C_R = 200$$

- 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 ΔC_{RAI}:

$$\Delta C_{RAI} = \Delta C_R^{TD} + \Delta C_A^{TD} + \Delta C_I^{TD} + \hat{C}_{RA}^{TD} + \hat{C}_{RI}^{TD} + \hat{C}_{AI}^{TD} + \hat{C}_{RAI}^{TD}$$

The interaction terms are given by:

$$\hat{C}_{RA}^{TD} = \Delta C_{RA}^{TD} - \Delta C_R^{TD} - \Delta C_A^{TD} = -50$$
$$\hat{C}_{RI}^{TD} = \Delta C_{RI}^{TD} - \Delta C_R^{TD} - \Delta C_I^{TD} = 0$$
$$\hat{C}_{AI}^{TD} = \Delta C_{AI}^{TD} - \Delta C_A^{TD} - \Delta C_I^{TD} = -50$$
$$\hat{C}_{RAI}^{TD} = \Delta C_{RAI} - \Delta C_R^{TD} - \Delta C_A^{TD} - \Delta C_I^{TD} - \hat{C}_{RA}^{TD} - \hat{C}_{RI}^{TD} - \hat{C}_{AI}^{TD} = 0$$

With this approach, a non-linear behavior is also observed and interaction terms are not zero. It is also interesting to note that the

550 triple interaction term ($\hat{C}_{RAI}^{TD}$) is null. The sum of the individual
551 impacts ($\Delta C_R^{TD} + \Delta C_A^{TD} + \Delta C_I^{TD} = 400$) overestimates the overall
552 impact ($\Delta C_{RAI} = 300$). We further discuss these aspects at the end of
553 this section. These results are graphically represented in Figure 2
554 (fourth and fifth columns).
555
556
557 **Tagged species approach**
558
559 Compared to Brute-force, the tagged species approach calculates the
560 share of each source to the overall concentration change. These
561 shares are referred to as contributions and have the main property
562 that the sum of the individual contributions is equal to the overall
563 concentration impact, by definition, i.e.:
564

$$\Delta C_{RAI} = \delta C_R^{TAG} + \delta C_A^{TAG} + \delta C_I^{TAG}$$

565
566
567 The sector contributions are computed by tracking the mass of their
568 emitted species contributing to PM formation (in our example:
569 PM[PPM] , PM[NH_4NO_3] and PM[$(NH_4)_2SO_4$])
570
571 - PM[PPM] is formed from PPM. The 100 moles from the
572   residential sector lead to 100 moles of PM. The same applies to
573   the 100 moles from industry.
574
575 - PM[NH_4NO_3] is formed by combination of NH_3 and NO_2. The
576   share between these two contributions is obtained by application
577   of stoichiometric molar mass ratios:
578

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

579
580 In our example, 50 moles of PM[NH_4NO_3] are formed by
581 combination of NO_2 (50 moles) from the residential sector and
582 NH_3 (50 moles) from agriculture. The contribution attributed to
583 NO_2 is $50 \times a_1$ whereas the contribution attributed to NH_3 is
584 $50 \times (1 - a_1)$.

585
586
587   - PM$[(NH_4)_2SO_4]$ is formed by combination of NH_3 and SO_2. The
588   following stoichiometric mass ratio is used:
589

$$a_2 = \frac{[SO_4]_m}{[SO_4]_m + 2[NH_4]_m} = 0.73$$

590
591   The contribution attributed to SO_2 is $50 \times a_2$ whereas the
592   contribution attributed to NH_3 is $50 \times (1 - a_2)$.
593
594   The contribution of each sector is then obtained as the sum of their
595   precursor contribution shares as follows:
596
597    $\delta C_R^{TAG} = 100 + 50 \times a_1 = 138.7$
    $\delta C_A^{TAG} = 50 \times (1 - a_1) + 50 \times (1 - a_2) = 24.9$
    $\delta C_I^{TAG} = 100 + 50 \times a_2 = 136.4$
598
599   By definition the sum of the contributions ($\delta C_R^{TAG} + \delta C_A^{TAG} +$
600    $\delta C_I^{TAG} = 300$) is exactly equal to the overall concentration impact
601   ($\Delta C_{RAI} = 300$).
602
603   Note that a decomposition of the non-linear interaction terms
604   obtained in the top-down or bottom-up approach, using the above
605   stoichiometric ratios would lead to similar results than the tagged
606   approach. These results are graphically represented in Figure 2
607   (second column).
608
609
610   **DDM**
611
612   In this methodology, delta concentrations and interaction terms are
613   estimated with first order partial derivatives computed from the
614   highest emission level (base case in our example). Being a
615   sensitivity approach using level H as reference, DDM shows clear
616   analogies with the BF-TD.
617
618    $\left.\frac{\partial C}{\partial \alpha_R}\right|_{TD} = 150$ $\left.\frac{\partial C}{\partial \alpha_A}\right|_{TD} = 100$ $\left.\frac{\partial C}{\partial \alpha_I}\right|_{TD} = 150$

619
620
621 where α_R , α_A and α_I are percentage emission changes from the base
622 case for the residential, agricultural and industrial sectors.
623 The first-order derivatives are evaluated using finite differencing
624 between the base case and a level characterised by emissions that are
625 10% lower for each activity sector.
626 The concentration changes resulting from a 100% emission
627 reduction (i.e. between the base case and the zero emission case)
628 could be estimated by setting α_R, α_A and α_I to unity.
629

$$\Delta C_R^{HDDM} = \left.\frac{\partial C}{\partial \alpha_R}\right|_{TD} = 150$$

$$\Delta C_A^{HDDM} = \left.\frac{\partial C}{\partial \alpha_A}\right|_{TD} = 100$$

$$\Delta C_I^{HDDM} = \left.\frac{\partial C}{\partial \alpha_I}\right|_{TD} = 150$$

630
631
632 We see from this last example that both the total PM and the
633 contribution of the sources are then comparable with those obtained
634 with the BF-TD method. Their interpretation is similar (Figure 2,
635 sixth column). In their work, Koo et al. (2009) present a detailed
636 comparison between a DDM and a tagged species approach in a 3-D
637 PM model and show which sensitivities are similar to
638 apportionment, and which are not.
639

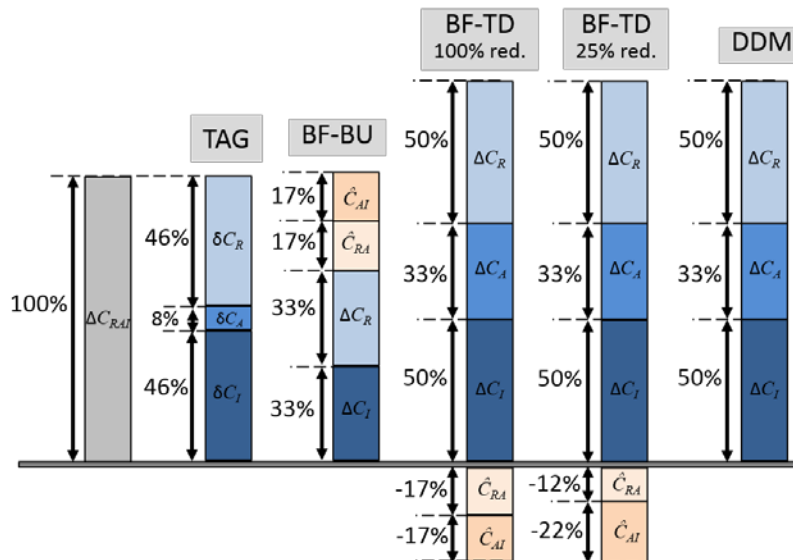
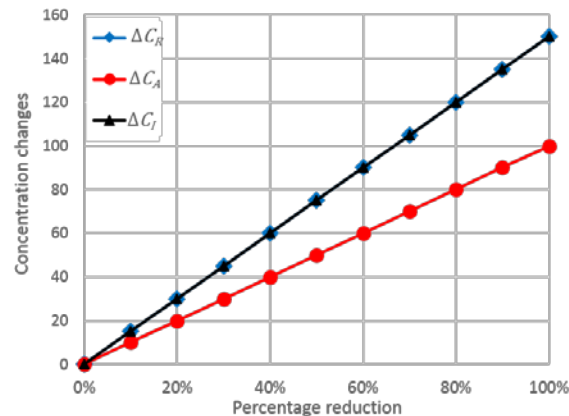
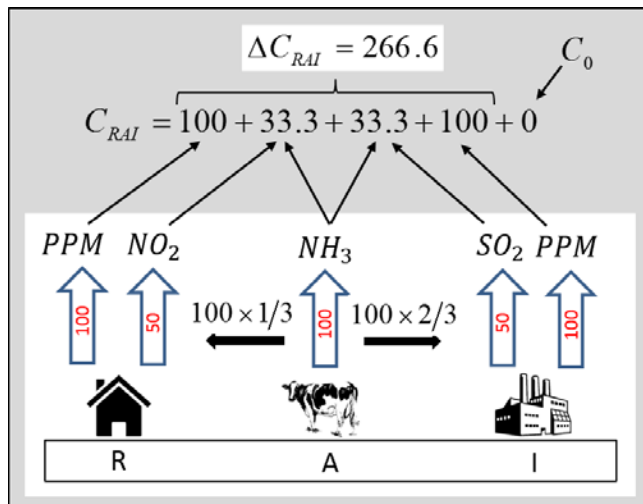



Figure 2.: Schematic representation of the allocation of PM to its
sources in the non-limited example. The expected total PM is
displayed in the grey bar on the left.

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 ($\Delta C_R^{TD} + \Delta C_A^{TD} = 250 \neq \Delta C_{RA}^{TD} = 200$). Note
that similarly to BF-TD, the concentration impacts computed as

662 increases from the background (BF-BU) show the same behaviour
663 ($\Delta C_R^{BU} + \Delta C_A^{BU} = 100 \neq \Delta C_{RA}^{BU} = 150$).
664
665 Figure 3 shows that the impact on concentration is proportional to
666 the emission reduction indicating that the relationship between
667 emission and concentration changes is linear. However, this example
668 also illustrates the fact that linearity encompasses two aspects: 1)
669 the interaction terms are zero ($\hat{C}^{int} = 0$); 2) the ratios between
670 concentration change and emission changes ($\Delta C/\Delta E$) remain
671 constant, regardless of the calculation bounds (denoted "H" and "L"
672 in Section 4). In the current example the ratios $\Delta C/\Delta E$ are constant
673 (linear trend of ΔC on Figure 3) but the relationship between
674 concentration and emission is not linear because of the non-zero
675 interaction terms (not shown) ($\hat{C}_{RA}^{TD} = -50$ and $\hat{C}_{AI}^{TD} = -50$).
676 However, even with zero interaction terms, we can still observe a
677 non-linear behaviour with the emission reduction percentage. The
678 evaluation of linearity therefore requires two tests: one to quantify
679 the interaction terms and the second to assess the deviation from a
680 linear trend with respect to the emission reduction percentage.
681

682
683 Figure 3: Evolution of the concentration changes resulting from
684 different percentage of source abatement (Top down approach) for
685 the three sectors (Residential, Agricultural and Industrial).
686
687

688
689   ## 5.2. Limited regime
690
691   This example is similar to the previous, except that the emissions of
692   NH_3 are reduced from 150 to 100 moles.
693   When all sources release emissions, the 100 moles of NH_3 are
694   shared into 100/3=33.3 moles which react with NO_2 to form 33.3
695   moles of $PM[NH_4NO_3]$ and 100×2/3=66.6 moles which react with
696   SO_2 to give 33.3 moles of $PM[(NH_4)_2SO_4]$. Because the mass of
697   NH_3 is not enough to react with all the NO_2 and SO_2 mass, 16.7
698   moles of NO_2 and 16.7 moles of SO_2 remain unused. (Figure 4).
699   Note that when the agricultural source is active with one only of the
700   two other sources (residential or industrial) the NH_3 100 moles are
701   then sufficient to consume all the NO_2 or SO_2 and lead to 50 moles
702   of PM in either case.
703

704
705   Figure 3.4: Example with three sources in an ammonia-limited
706   regime. The mass emitted by each source is expressed in moles.
707
708   The PM concentrations obtained when one or two sources are active
709   are similar to the previous example:
710
711    $$C_0 = 0 \; ; C_R = 100 \; ; C_A = 0 \; ; C_I = 100$$

712     $C_{RA} = 150$; $C_{RI} = 200$; $C_{AI} = 150$

713

714 But the result differ when all sources are active: $C_{RAI} = 266.6$ (200
715 from PPM (residential industry), 33.3 from reaction between NO_2
716 and NH_3 and 33.3 from reaction between SO_2 and NH_3).

717

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

719

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

723

724     $\Delta C_R^{BU} = 100$ $\hat{C}_{RA}^{BU} = 50$
725     $\Delta C_A^{BU} = 0$ $\hat{C}_{RI}^{BU} = 0$
726     $\Delta C_I^{BU} = 100$ $\hat{C}_{AI}^{BU} = 50$
727     $\Delta C_{RAI} = 266.6$ $\hat{C}_{RAI} = -33.3$

728

729 The limiting effect of NH_3 appears only in the negative triple
730 interaction term ($\hat{C}_{RAI}$). These results are graphically represented in
731 Figure 5 (third column).

732

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

734

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

738

739     $\Delta C_R^{TD} = 116.6$ $\hat{C}_{RA}^{TD} = -16.6$
740     $\Delta C_A^{TD} = 66.6$ $\hat{C}_{RI}^{TD} = 33.3$
741     $\Delta C_I^{TD} = 116.6$ $\hat{C}_{AI}^{TD} = -16.6$
742     $\Delta C_{RAI} = 266.6$ $\hat{C}_{RAI} = -33.3$

743

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

746

747 **Tagged approach**

748

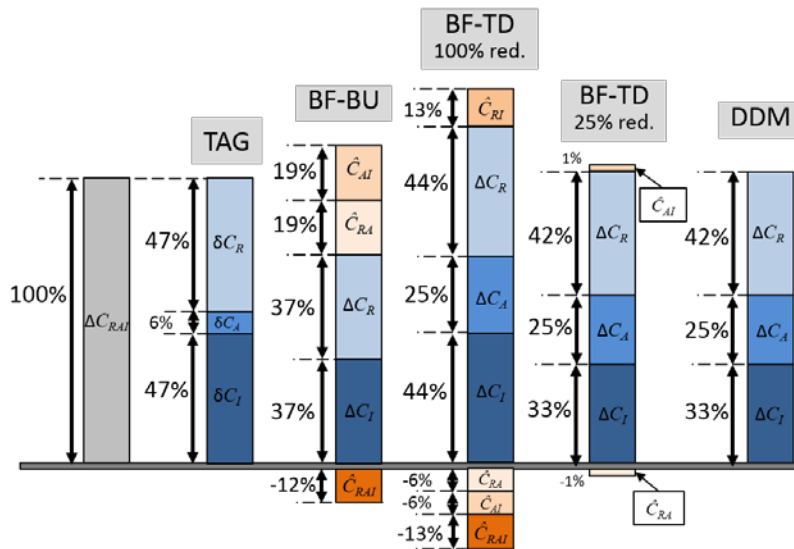
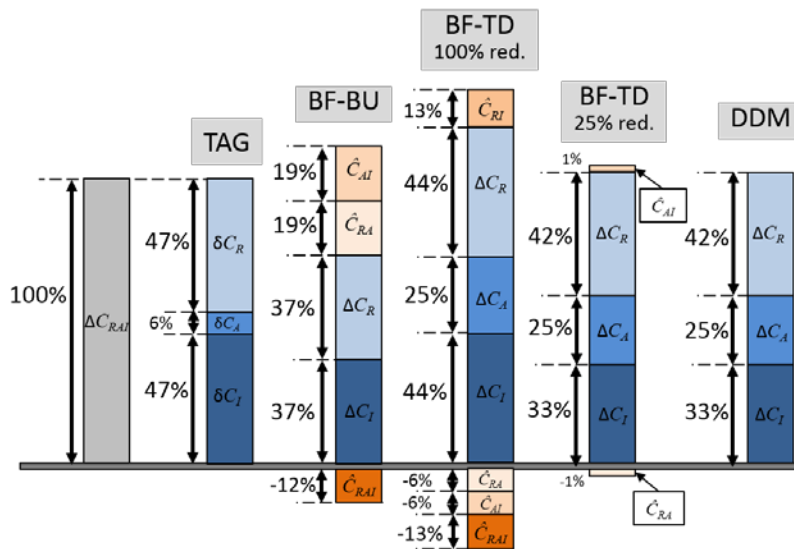
749 The contribution of each source is computed similarly to the non-
750 limited regime. The ~~productions~~production of 33.3 moles of
751 $PM[NH_4NO_3]$ and 33.3 moles of $PM[(NH_4)_2SO_4]$ are split among
752 the different sectors using the stoichiometric coefficients a_1 and a_2:
753
754
$$\delta C_R^{TAG} = 100 + 33.3 * a_1 = 125.8$$
$$\delta C_A^{TAG} = 33.3 * (1 - a_1) + 33.3 * (1 - a_2) = 16.6$$
$$\delta C_I^{TAG} = 100 + 33.3 * a_2 = 124.2$$

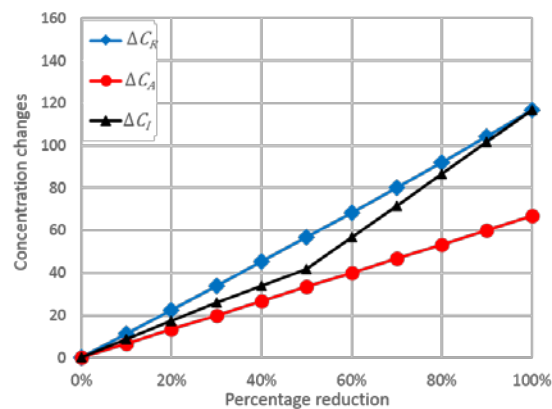
755
756 These results are graphically represented in Figure 5 (second
757 column).
758
759
760 **DDM**
761
762 As shown below, DDM only considers first derivatives, which are
763 not suitable to estimate higher order interaction terms. The
764 calculation of the first order derivatives in this example gives:
765

$$\Delta C_R^{HDDM} = \left.\frac{\partial C}{\partial \alpha_R}\right|_{TD} = 111.5$$

$$\Delta C_A^{HDDM} = \left.\frac{\partial C}{\partial \alpha_A}\right|_{TD} = 66.7$$

$$\Delta C_R^{HDDM} = \left.\frac{\partial C}{\partial \alpha_I}\right|_{TD} = 88.1$$

766

767
768 ~~Figure 4.~~These results are graphically represented in Figure 5 (sixth
769 column).

770
771 Figure 5: Schematic representation of the allocation of PM to its
772 sources in the ammonia-limited example. The expected total PM is
773 displayed in the grey bar on the left.

774
775
776 **Comparative overview**
777
778 The main difference with respect to the non-limited regime is the
779 appearance of a triple interaction term that will also lead to
780 differences between the BF-TD and the DDM approaches, given the
781 fact that the latter only accounts for first order terms.
782
783 In comparison to the non-limited regime, the calculation of the
784 concentration impacts resulting from different percentage of
785 emission reduction shows non-linear trends (Figure 56). A
786 discontinuity appears at 50% reduction for the abatement of
787 industrial emissions. This discontinuity corresponds to a change of
788 chemical regime. Below the 50% reduction level , the quantity of
789 NH_3 is not sufficient to feed the reactions with NO_2 and SO_2 (with
790 no SO_2 reduction, 50 moles of NO_2 and 50 moles of SO_2 would
791 require 150 moles of NH_3 but only 100 are available) while beyond
792 this 50% reduction level the quantity of NH_3 is then enough to feed
793 the reactions with NO_2 and SO_2 (with 50% SO_2 reduction, 50 moles
794 of NO_2 and 25 moles of SO_2 requires 100 moles of NH_3).
795

796
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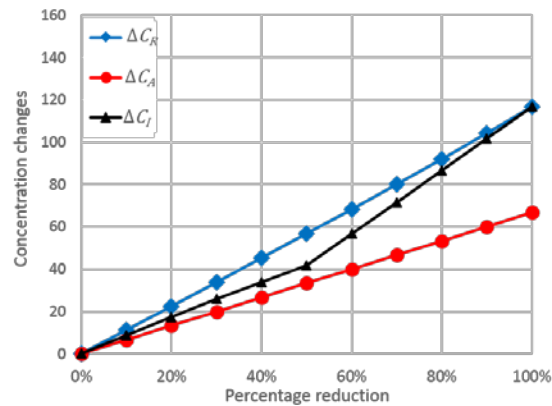
799

800 Figure 56: Evolution of the concentration changes resulting from
801 different percentage of source abatement (Top down approach) for
802 the three sectors (Residential, Agricultural and Industrial).

803

804

805 The methodologies presented in this section aim at decomposing the
806 impact of an ensemble of sources into different terms attributed to
807 each individual sources. The terms computed by methodologies
808 designed for source apportionment (like TAG) are named source
809 contributions. Their sum is always equal to the combined impact of
810 all sources. On the other hand, the terms computed by sensitivity
811 analysis represent the emission change of each individual source and
812 their sum is equal to the combined impact of all sources only if the
813 relationship between emissions and concentrations is linear (see
814 Section 2). Grewe at al. (2010) and Grewe (2013) who used simple
815 differential equations to reproduce the ozone tropospheric chemistry,
816 also highlighted this point in their work. In non-linear situations, the
817 source contributions computed for source apportionment and the
818 source impacts computed for sensitivity analysis are different (see
819 Figure 45 where column 2 shows different results than column 3 or
820 4). Non-linearity also imply that the calculation of the source
821 impacts depends from the bounds used to estimate the concentration
822 changes (denoted "H" and "L" in Section 4). The BF-BU and BF-
823 TD (columns 3 and 4 in Figure 45) give different results because
824 they are not using the same reference level ("L" for the BU and "H"

825   for the TD as defined in Section 4). Moreover, the results depend
826   from the percentage of emission changes applied to calculate the
827   source impacts as demonstrated by the different source impacts
828   computed with the BF-TD for 100% and 25% emission reductions
829   (columns 4 and 5 in Figure 45). We expect that lower percentage
830   emission reductions generate less non-linearity and lead to a better
831   agreement between the BF-TD and the DDM method (columns 5
832   and 6 in Figure 45).
833   In synthesis, the second example illustrates that all the
834   methodologies tested to find source contributions and source
835   impacts give different results when the relationship emissions-
836   concentrations is non-linear. ~~It is therefore important to determine~~
837   ~~the degree of non-linearity in order to understand the range of~~
838   ~~applicability of each methodology and apply it for the right~~
839   ~~purpose~~A quantification of the potential non-linearities should
840   therefore be the first step prior to source apportionment or planning
841   applications, to prevent any limitations in their use. When non-
842   linearity is mild, these limitations may however be acceptable in the
843   context of the other uncertainties inherent to complex models.
844

845   6. Conclusions

846
847   ~~When pollutant concentrations exceed the thresholds set in the~~
848   ~~legislation, competent authorities must take actions to abate~~
849   ~~pollution.~~ In the European legislation (Directive 2008/50/EC) both
850   source apportionment and planning are requested when designing air
851   quality plans. In practice, source apportionment is often used for
852   planning purposes. It is indeed intuitive to use source apportionment
853   to detect the activity sectors that need to be tackled in priority in an
854   air quality plan. On the other hand, sensitivity analysis is often used
855   as an approach to derive source contributions (e.g. SHERPA,
856   FASST, GAINS…).

857
858   In this work, we compared ~~the two above mentioned~~source
859   apportionment and sensitivity approaches and investigated their
860   domain of application. While sensitivity analysis refers to impacts to
861   characterize the concentration change resulting from a given

862   emission change, source apportionment aims to quantify
863   contributions, by attributing a fraction of the pollutant concentration
864   to each emission source. In the case of linear (or close to linear)
865   relationships between concentration and emissions, impacts and
866   contributions are equivalent (or close to) concepts. Source
867   apportionment may then be used for air quality planning purposes
868   and vice versa, sensitivity analysis may be used for quantifying
869   sources contributions.
870
871   In many cases, however, linearity is not a valid assumption. In such
872   cases, sensitivity approaches cannot be used to retrieve source
873   apportionment information, unless non-linear interaction terms are
874   explicitly accounted for. On the other hand, source apportionment
875   approaches (e.g. tagged species approach) intrinsically account for
876   these non-linear interactions into their source contributions. But
877   because it mix interaction terms and impacts, which may react in
878   opposite directions, source apportionment should not be used to
879   evaluate the impact of abatement strategies
880   Even when using sensitivity analysis for planning, it is important to
881   note that, under non-linear conditions, the calculated impacts will
882   only provide information for the exact conditions that are
883   considered. Impacts for an emission reduction of 50% are only valid
884   for exactly that percentage of reduction and extrapolation to air
885   quality planning with any other emission reduction levels would be
886   inappropriate, unless additional scenarios are tested. Along the same
887   line of reasoning, the importance of the non-linear interaction terms
888   (among precursors) should be quantified as well when assessing the
889   impact of more sources or precursors. Finally, these non-linear
890   interaction terms are in most cases not constant with the emission
891   reduction intensities, which would imposes the further need to
892   quantify them for different levels of emission reduction. Calculating
893   sensitivities and interactions at various level of emission reductions
894   seems the only alternative when non-linearities are important. In this
895   respect, new approaches like the path-integral methodology
896   proposed by Grewe et al. (2012) might represent a powerful
897   approach.
898

899 Fortunately, not all cases are so complex to require the full
900 quantification of all non-linear interaction terms. Thunis et al. (2015)
901 showed that for yearly average relationships between emission and
902 concentration changes, linearity is a realistic assumption, implying
903 the possible use of source apportionment and sensitivity analysis for
904 both purposes. Some integrated assessment tools (e.g. GAINS,
905 SHERPA) take advantage of this assumption to retrieve source
906 apportionment information from calculated CTM sensitivities.
907 Although non-linearities are important for short-term time averages
908 (e.g. daily means, episodes), they are likely not associated to every
909 process. For instance, non-linear interactions are expected to be
910 more relevant for secondary pollutants, especially under limited
911 regimes. The challenge consists, therefore, in screening the system
912 for significant non-linearities and account for them by calculating
913 explicitly the relevant non-linear interaction terms.
914
915 One main strength of source apportionment approaches is to provide
916 contribution estimates that can be cross validated with source
917 apportionment derived from measurements (i.e. receptor modelling,
918 for a detailed description see e.g. Belis et al., 2013). This step is
919 crucial for the evaluation of chemistry transport models.
920

7. Code availability

922 No specific code is attached to this work as all presented examples
923 can easily be replicated.
924
925

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