Efficient sensitivity computations in 3D air quality models

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Abstract

The prediction of ground level ozone for air quality monitoring and assessment is simulated through an integrated system of gridded models (meteorological, photochemical), where the atmosphere is represented with a three-dimensional grid that may include thousands of grid cells. The continuity equation solved by the Photochemical Air Quality Model (PAQM) reproduces the atmospheric processes (dynamical, physical, chemical and radiative), such as moving and mixing air parcels from one grid cell to another, calculating chemical reactions, injecting new emissions. The whole modeling procedure includes several sources of uncertainty, especially in the large data sets that describe the status of the domain (boundary conditions, emissions, chemical reaction rates and several others). The robustness of the photochemical simulation is addressed in this work through the deterministic approach of sensitivity analysis. The automatic differentiation tool ADIFOR is applied on the 3D PAQM CAMx and augments its Fortran 77 code by introducing new lines of code that additionally calculate, in only one run, the gradient of the solution vector with respect to its input parameters. The applicability of the approach is evaluated through a sensitivity study of the modeled concentrations to perturbations at the boundary conditions and the emissions, for three essentially dissimilar European Metropolises of the Auto-Oil II programme (Athens, Milan, and London).

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Keywords: Sensitivity analysis; Air quality models; Ozone; Automatic differentiation; Deterministic approach

1. Introduction

Ozone (O₃) in the troposphere is produced in a series of reactions involving nitrous oxides (NOₓ), hydrocarbons (VOC) and sunlight. Its concentration varies from day to day depending on the emissions of its precursors (NOₓ, VOC) and on the weather conditions. The weather conditions do not only affect the production of ozone but also its transport. Stagnant meteorological situations can trap O₃, obstructing its dispersion and causing high pollution levels. The accurate prediction of O₃ concentration is one of the challenges in atmospheric science.
The best available tool for predicting the concentrations of air pollutants are the Photochemical Air Quality Models (PAQMs). Every atmospheric model needs quantities like meteorological data, topography and emission inventories defined as a function of time and space. Uncertainty in any of these will result in uncertainties in concentrations of ozone. Indeed recent studies (e.g., [26,27]) of photochemical formation in large urban environments conclude that a systematic evaluation of the sensitivity of an atmospheric chemical model due to perturbations in the input data is needed.

Some sensitivity studies utilizing 3D PAQMs have been published and these are summarized in Table 1. All these are based on a statistical approach, where PAQM calculations are repeated with appropriate variations in the input parameters of interest. The tremendous amounts of computer time required in the case of a complex 3D model usually limits the applicability of the statistical methodology to a small subset of the full parameter space. A deterministic approach is sometimes preferred (especially for large dimensionality problems) where one generates a set of differential sensitivity equations that approximate the changes in

<table>
<thead>
<tr>
<th>Reference</th>
<th>Model/Domain</th>
<th>Objective</th>
<th>Main findings</th>
</tr>
</thead>
</table>
| Winner et al. [40] | Model: CIT  
Domain: Los Angeles  
(250 km x 150 km)  
No Scenarios: 128 | Effect of alternative NOx and VOC emission reductions strategies, with 'observed' and 'clean' initial and boundary conditions | Only with clean boundary conditions, the emission reduction scenario can lead to a harmonization of the maximum concentration of O3 within the existing limits. |
| Jiang et al. [18]  | Model: OZIPR  
Domain: Lower Fraser valley in the northwest of Canada  
No Scenarios: 38 | Sensitivity of ozone concentrations to (total) variations in the emissions of VOC and NOx | (a) O3 concentration increases monotonically with the increase in the VOC emissions.  
(b) The sensitivity of O3 in the variations of the NOx emissions is not monotonic and reaches its maximum when the NOx emissions are reduced by 60%. |
| Hanna et al. [14]  | Model: UAM-IV  
Domain: New York  
(230 km x 290 km)  
Random sampling  
No Scenarios: 50 | Sensitivity of UAM-IV to variations at 109 input parameters, including the boundary conditions of O3, NOx and VOC and the emissions of VOC and NOx (both area and point) | The maximum concentration of O3 is affected mainly by the VOC emissions followed by the O3 boundary concentrations. |
| Ziomas et al. [41] | Model: UAM-IV  
Domain: Athens  
No Scenarios: 36 | Effect of alternative emission scenarios (total area) | The ozone control strategies should be focused more in the control of the VOC. The authors propose that in order to harmonize the concentrations of O3 in the whole basin with the European limit of 90 ppb, it is necessary to reduce the VOC emissions by 30–40%. |
| Bergin et al. [1]  | Model: CIT  
Domain: California  
No Scenarios: 200 | Estimate the uncertainty of emissions (46 uncertain parameters) | The most influential parameter in the uncertainty of the predicted O3 concentrations is the traffic emissions, with uncertainty range in O3 between 8% and 22.5%. |
| Vautard [35]       | Model: CHIMERE  
Domain: Paris | Impact of the boundary conditions in real time simulations by comparing the forecasted with the observed concentrations | About 50% of the prognostic error in the forecasted concentrations is due to bad prediction of the boundary conditions. |
model output as a function of changes in inputs. This approach is based on perturbation theory and assumes linearity.

The objectives of the current paper are:

– to develop a computationally efficient tool for sensitivity analysis of a 3D PAQM. Specifically, we generate the Tangent Linear Model (TLM) of the 3D Air Quality model CAMx (Comprehensive Air-Quality Model with eXtensions) [http://www.camx.com], which describes the linearized evolution of perturbations along a nonlinear base state [9,10,23,25,38,39]. The TLM of CAMx was created by utilizing the Automatic Differentiation (AD) tool ADIFOR (Automatic Differentiation in FORtran) [4];

– to validate the new model in different photochemical domains. Three cities of the Auto-Oil II Programme [http://europa.eu.int/comm/environment/autooil] [32] were selected;

– to compute and interpret the sensitivity coefficients in order to quantify the uncertainty arising from assumptions in the lateral boundary conditions and the emissions.

2. Sensitivity analysis using computational differentiation

Sensitivity analysis attempts to apportion quantitatively the variation in model predictions to different sources of variation (i.e. input variables). This is accomplished through either the global or local approach. In the global tactic the model is run several times, each time with slightly perturbed inputs, in order to calculate the statistical properties of the output variability. On the other hand, the idea behind the local approach is to differentiate the model output with respect to its inputs and hence provide in only one run the sensitivity indices. It is evident that the computation of derivatives is fundamental in the latter [3].

The computation of the derivatives for a numerical function is usually carried out through finite difference approximations [5]. An alternative technique that is faster and free of truncation and cancellation error is Automatic Differentiation. In this perspective, a code is mechanically enhanced with new lines that in addition to the calculation of a function simultaneously compute its derivatives. The core idea behind AD is very simple: it treats a computer program as a sequence of elementary operations and functions with known derivatives and applies the chain rule of differential calculus to each stage in this sequence of elementary operations [2,12,13,28].

A list of available tools for AD is accessible at http://www-unix.mcs.anl.gov/autodiff/AD_Tools/. In this sensitivity study, the model code was written in Fortran 77 and ADIFOR was employed to add the derivative statements. ADIFOR has already been applied in the past in sensitivity analysis of air quality models (box models) [6,17]. In the frame of three-dimensional modeling, it has been applied to the meteorological models MM5 (in a comparative study between AD- and DD-divided differences-computed sensitivities [5]) and ARPS (sensitivity of storm evolution to variations in initial conditions [25]).

One execution of the ADIFOR-augmented code is equivalent to \( k \) tangent linear model runs, where \( k \) is the number of (uncertain) input parameters. In addition, AD-computed sensitivities do not suffer from truncation and cancellation error [2,5], the sensitivity code is generated very easy (ADIFOR supports almost all of Fortran 77) [16] and has low computational demands (lower than \( k \) tangent linear model runs due to a hybrid technique that saves time [4]). However, as a derivative method, it assumes the solutions of the model are continuous with respect to changes in input parameters. This is normally a good assumption for small perturbations in the Taylor expansion. Validation of linear perturbation fields against the nonlinear ones [20] has shown that the solutions are accurate at least for perturbation magnitudes of 30%.

2.1. Methodology

The dimensions of the matrices in the enhanced version of the code are directly proportional to the number of independent variables. This limits the practical calculations of derivatives in 3D models due to the large number of independent variables (in the order of \( \sim 10^9 \) for a 3D model). We overcome this problem [24] by introducing a parameter \((e_j)\) that linearly interpolates between the unperturbed—\( C(x, y, z, t) \)— and perturbed—\( C(x, y, z, t, e_j) \)— initial states [19,20,24] of the chemical compound \( j \):

\[
C^j(x, y, z, t, e_j) = (1 + e_j)C^j(x, y, z, t).
\]  

(1)
The sensitivity of $C_i$ with respect to $e_j$ is defined as the first order term in the Taylor expansion of $C_i(e_j)$ about the reference solution $[C_i(e_j = 0)]$. We therefore modified CAMx in order to include perturbations $e_j$ to the lateral boundaries (BND) and to the area (ARE) and point (PNT) emissions and applied the ADIFOR tool to calculate the derivatives of $C_i$ with respect to $e_j$.

2.2. Interpretation of sensitivity information

2.2.1. Effect on a variable of perturbing another variable

The local sensitivity coefficient estimates the change in the output variable $i$ (e.g., concentration $C_i$) that originates from a unitary perturbation in the variable $j$ [29]. In dimensional mode, it has the form:

$$S_i^j = \frac{\partial C_i}{\partial e_j}.$$  

Relative sensitivity coefficients are more informative than the absolute ones and can be defined as:

$$S_i^j = \frac{\partial C_i}{C_i} \frac{e_j}{C_i}.$$  

$S_i^j$ indicates the linear estimation of the percentage change in the concentration $C_i$ as we perturb by 1% the parameter $e_j$. $S_i^j$ is non-dimensional, hence these coefficients can be compared.

2.2.2. Effect on the system of perturbing a variable

The global effect of perturbing a variable can be studied in terms of a control function of the form:

$$J = f \left( \sum_{i=1}^{n} w_i \frac{C_i - C_i^0}{C_i^0} \right) \cdot \left( \frac{C_i - C_i^0}{C_i^0} \right),$$

where the superscript $^0$ refers to the unperturbed concentration field and the operator $\bullet$ denotes the inner product of the matrices. The weights $w_i$ allow the study of the relative importance of the model’s parameters. Global sensitivities based on local sensitivity coefficients can be calculated as:

$$\frac{\partial J}{\partial e_j} = \sum_{i=1}^{n} S_i^j \cdot S_i^j.$$  

The global sensitivities are dimensional, hence we will normalize them in order to compare the relative importance of the different perturbations:

$$\frac{\partial J}{\partial e_j} = \frac{\sum_{i=1}^{n} S_i^j \cdot S_i^j}{\sum_{j=1}^{k} \sum_{i=1}^{n} S_i^j \cdot S_i^j}.$$  

The normalized global sensitivities sum up to one.

2.2.3. Effect on the system of perturbing several variables

The effect of simultaneous parameter changes on several variables, based on local sensitivities, can be estimated using Principal Component Analysis. Due to limited space, the reader is referred to the work of Vajda and Turanyi [34].

3. Model description and experimental design

3.1. The model

CAMx (for a review see [21]) is an Eulerian photochemical grid model that unifies all of the technical features required of “state-of-the-art” in research air quality models into a single system. The continuity equation is solved in a three-dimensional grid and describes the time dependency of the average species concentration within each grid cell volume as a sum of all of the physical and chemical processes operating on that volume, i.e. advection (horizontal + vertical), (turbulent) diffusion, chemical reactions (CB-IV, SAPRC97), emissions and removal (dry and wet deposition).

In addition to the features it shares with most photochemical models, the most notable characteristics of CAMx include Fast Plume-in-Grid Module, Treatment of Paniculate Matter and Source Apportionment, as well as an advanced photolysis model.

3.2. The domains

The selected domains for this application were three highly industrialized and populated cities, all test cases of the Auto-Oil II Programme (http://europa.eu.int/comm/environment/autooil) [32]. Athens, Milan and London are addressing several pollution episodes yearly, which however have in general different causes.
The city of Athens is located in a basin on the west coast of the Attica peninsula. It is surrounded by moderately high mountains, forming a channel, with only one major opening towards the sea to the south-west [8,41]. The whole area is characterized by high emissions in the centre of the domain and much lower in the rest.

Milan [31,36,37] is located in the Po valley. North of Milan (∼100 km) are the Alps, with a maximum elevation higher than 3000 m. The north-west area (vicinity of Milan) is characterized by higher emissions than the one of the south-east domain (vicinity of Bologna).

London [7] is essentially flat—the maximum elevation being approximately 220 metres—while the emissions in the domain are continuously very high all over the land surface.

The city dependent model parameters used in the calculations are presented in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Athens</th>
<th>Milan</th>
<th>London</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation day</td>
<td>28 July 1995</td>
<td>6 May 1995</td>
<td>7 May 1995</td>
</tr>
<tr>
<td>Coarse grid domain</td>
<td>300 × 282 × 2 km³</td>
<td>258 × 276 × 2 km³</td>
<td>294 × 276 × 2 km³</td>
</tr>
<tr>
<td>Computational domain</td>
<td>53 × 50 × 13</td>
<td>46 × 49 × 13</td>
<td>52 × 49 × 13</td>
</tr>
<tr>
<td>VOC/NOx (Area emissions)</td>
<td>2.01</td>
<td>3.38</td>
<td>1.32</td>
</tr>
<tr>
<td>VOC/NOx (Point emissions)</td>
<td>1.57</td>
<td>1.08</td>
<td>1.01</td>
</tr>
<tr>
<td>Vertical levels (m)</td>
<td>20, 50, 100, 150, 200, 250, 300, 400, 600, 900, 1200, 1500, 2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizontal grid spacing</td>
<td>6 km/2 km</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time step</td>
<td>5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical mechanism</td>
<td>CB IV with isoprene chemistry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Meteorological simulation</td>
<td>ARPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boundary conditions</td>
<td>Element</td>
<td>Concentration (ppb)</td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC (ppbC)</td>
<td>15.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1. Sensitivity to singular perturbations

In Fig. 1 we show the time evolution of the normalized global sensitivities in the fine grid (approximately 100 × 100 km² centred in the cities), which indicates the effect of each individual perturbation in the system. In the first hours, the system is dominated by the perturbations in the area emissions, since the ones in the boundaries have not reached the fine grid yet. Around midday, more than 80% of the variability of the system is driven mainly by only four perturbations. For example, at 14:00 LST:

- In Athens (Fig. 1(a)), 86% of the variability is due to the area emissions of NOx (29%), the boundary conditions of O₃ (28%), the boundary conditions of VOC (16%) and the area emissions of VOC (13%).
- In London (Fig. 1(b)), 83% of the variability is attributed to the boundary conditions of O₃ (31%), the point emissions of NOx (23%), the area emissions of NOx (16%) and the boundary conditions of VOC (13%).
- In Milan (Fig. 1(c)), 84% of the variability can be explained in terms of the boundary conditions of O₃ (31%), the area emissions of NOx (24%), the point emissions of NOx (17%) and the area emissions of VOC (12%).

4. Results and discussion

We now investigate the relationship of the sensitivity coefficients to the concentration field. Among the many available results (3 computational domains of 6 dimensions), we focus on the sensitivity arising from perturbations in O₃, NOx, VOC and CO.
Although photochemistry dynamics are different in each of the three domains, the boundary conditions of O$_3$ and the area emissions of NO$_x$ dominate the sensitivity in all of them. These results are consistent with those of other researchers utilizing different sensitivity analysis approaches as well as PAQMs.

The sensitivity fields for O$_3$, for the most important perturbations were then investigated in more detail.

**Fig. 2** illustrates the general features of O$_3$ sensitivity for the most important perturbations in Athens domain at 15:00 LST, and similar illustrations for the other domains are shown in **Fig. 3** (London, 18:00 LST) and **Fig. 4** (Milan, 14:00 LST). A lower bound of 40 ppb was used for the calculations of $S_{O3}$ in order to avoid excessive weighting of the sensitivity coefficient. Among all perturbations, the largest domain-wide sensitivity in O$_3$ is due to the $e_{B3}$ perturbation. The most observable characteristic of this field is its decrease downwind of the boundaries.

On the other hand, the sensitivity patterns arising from perturbations at NO$_x$ and VOC have as their main characteristic that they occupy complementary different areas. These results provide a direct qualitative indication on the “spatial accuracy” of the linear perturbation fields. An indirect indication for the “amplitude accuracy” is examined in the next paragraph.

Local enhancement in O$_3$ concentration depends mainly on the ratio among its precursors. We would expect perturbations of VOC (NO$_x$) emissions to enhance O$_3$ production in VOC- (NOX-)sensitive areas, e.g., in urban centres and downwind of urban centres. Comparison of first order sensitivity fields with certain indices can provide an indirect qualitative validation. It has been suggested that the local H$_2$O$_2$/HNO$_3$ ratio might be a useful indicator [33]. Areas with a high H$_2$O$_2$/HNO$_3$ ratio are characterized as relatively low-NO$_x$ areas, where we would expect high O$_3$ enhancement in response to disturbances. In contrast, in areas with a low H$_2$O$_2$/HNO$_3$ ratio the additional O$_3$ that is produced reacts with the NO$_x$, and thus the perturbation effect is smaller. **Fig. 5** illustrates the change in O$_3$ (O$_3$ [perturbed emissions] − O$_3$ [unperturbed emissions]) in the fine grid cells between the perturbed and unperturbed runs (25% reduction in emissions as calculated from the TLM) against the H$_2$O$_2$/HNO$_3$ ratio of the unperturbed solution. The curves represent a 5th-order regression line calculated from the values at each grid point in the fine grid cells. The linear perturbation fields represented very well in both location and magnitude the expected values. In all cities, the transition between NO$_x$ and VOC sensitive areas took place for a value of H$_2$O$_2$/HNO$_3$ between 0.2 and 0.3, specifically, 0.26 for Athens, 0.22 for London and 0.24 for Milan.

The smoothing procedure has an influence on these values. For instance, a 3rd-order regression gives a smaller value by 5–10%. Areas with high VOC sensitivity were the ones with a low H$_2$O$_2$/HNO$_3$ ratio (lower than 0.3) in the unperturbed trajectory, while regions with this ratio much higher than 0.3 were characterized as NO$_x$ sensitive areas. Therefore, **Figs. 2–5**

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**Fig. 1.** Time evolution of the normalized global sensitivities for grouped perturbations, for (a) Athens, (b) London, (c) Milan. The chart shows the relative importance among the various uncertain inputs for 1% perturbation. Results are for the nested fine grid.
indicate that the urban centres as well as the downwind regions in the investigated cities are VOC-sensitive areas, with the city of Milan the most sensitive (highest VOC/NOₓ ratio of area emissions) and the city of London the least sensitive (lowest VOC/NOₓ ratio of area emissions).

The sensitivity maps generated with each run of the model (Figs. 2–4), can be used in several different ways. For example, based on differential analysis, one can proceed with “superimposing” them, with the same or different perturbation size to assess the impact of a hypothetical policy on O₃. In the next section we show an approach based on eigenvalue–eigenvector decomposition of the sensitivity matrix.

The impacts in the urban centres can be estimated. Table 3 presents the relative sensitivity coefficients (mean ± standard deviation) at the time of the observed maximum O₃ concentration (576 km²).

<table>
<thead>
<tr>
<th></th>
<th>S JComboBox_2 (Athens)</th>
<th>S JComboBox_2 (Milan)</th>
<th>S JComboBox_2 (London)</th>
</tr>
</thead>
<tbody>
<tr>
<td>εₓₓ</td>
<td>0.06 ± 0.01</td>
<td>0.05 ± 0.02</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>εᵧᵧ</td>
<td>0.02 ± 0.004</td>
<td>0.06 ± 0.02</td>
<td>0.04 ± 0.006</td>
</tr>
<tr>
<td>εᵧₓ</td>
<td>0.34 ± 0.04</td>
<td>0.57 ± 0.20</td>
<td>0.71 ± 0.105</td>
</tr>
<tr>
<td>εᵧᵧ</td>
<td>−0.12 ± 0.09</td>
<td>−0.25 ± 0.12</td>
<td>−0.05 ± 0.028</td>
</tr>
<tr>
<td>εₓₓ</td>
<td>0.01 ± 0.004</td>
<td>0.11 ± 0.05</td>
<td>−</td>
</tr>
<tr>
<td>εᵧᵧ</td>
<td>−0.02 ± 0.003</td>
<td>0.01 ± 0.003</td>
<td>−</td>
</tr>
<tr>
<td>εᵧₓ</td>
<td>−0.01 ± 0.01</td>
<td>−0.06 ± 0.04</td>
<td>−0.02 ± 0.025</td>
</tr>
<tr>
<td>εₓₓ</td>
<td>−0.02 ± 0.01</td>
<td>−0.02 ± 0.01</td>
<td>−</td>
</tr>
</tbody>
</table>

The boundary conditions of O₃ and the area emissions of NOₓ, for all domains. However, the magnitude and the relative importance among the two most impor-
tant input factors were domain dependent. The higher the VOC/NOₓ ratio of the area emissions in the urban cells, the higher the absolute value of the \( S^{O_3 NO_X}_{2} \) and \( S^{O_3 VOC}_{2} \) coefficients (for emissions ratios in the range 1–4). Other important inputs found were the area emissions of VOC in Milan, and the boundary conditions of NOₓ in London. It is also worth mentioning the high coefficient of variation for perturbations at the area emissions of NOₓ, indicating the highly inhomogeneous field of \( S^{O_3 NO_X}_{2} \).

Table 3 indicates that an emission control strategy in the three metropolises should be very cautious about the effects of a policy only on NOₓ emissions.

4.2. Sensitivity of the system to multiple perturbations

The study of the effects of simultaneous perturbations to the system is now examined. Based on Principal Component Analysis, we will analyze the cross effects in the centred grid points by extracting the eigenvalues and eigenvectors of the sensitivity matrix. This is the only technique that, based on local sensitivities, provides the effects of simultaneous parameter changes to the system. The main idea is to transform the cost function (Eq. (4)) into a form:

\[
J = \sum_{i=1}^{n} \lambda_i (\Delta \Psi_i)^2,
\]

where \( \Delta \Psi = U^T \Delta e \), \( U \) is the matrix of normalized eigenvectors of \( S^1 S^2 \) and \( \lambda \) is the vector of eigenvalues.

Table 4 shows the eigenvectors corresponding to the highest eigenvalue (at midday). The study is performed for the central grid point of each domain. The first conclusion, common to all cities is that perturbations at the boundary conditions of \( O_3 \) and the area emissions of NOₓ (taken singularly plus interactions) have most influence. In the centre of Athens, the dis-

Fig. 3. Same as Fig. 2, but for London.
turbances at the boundary conditions of $O_3$ and the area emissions of $NO_x$ are responsible for 19% and 80% of the variation, respectively. The maximum influence in this area could be achieved by a simultaneous $x\%$ perturbation in the area emissions of $NO_x$ and $-0.5x\%$ in the boundary conditions of $O_3$. In London, there is a clear dominance of the boundary conditions of $O_3$ (89% contribution to the output variability), comparing to the area emissions of $NO_x$ (8.5% contribution). In Milan, the effects of the two dominant uncertain inputs are almost the same. This could be due to the Milan conurbation not being in the centre of the domain. The boundary conditions of $O_3$ account for 55% of the output variability and the area emissions of $NO_x$ for 40%. The maximum change in this area can be achieved by perturbing simultaneously by $x\%$ the boundary conditions of $O_3$ and by $-0.9x\%$ the area emissions of $NO_x$.

These results arise from equal perturbations in the uncertain inputs. It is obvious that one can utilize the method for different combinations of perturbation size (within the range of accuracy of the linear perturbation fields) on the uncertain inputs. This can improve the utility of the method. If we define a “system” by the concentration of $O_3$ (not shown), the importance of the boundary conditions of $O_3$ and area emissions of $NO_x$ remain dominant, however, the order changes and it is always the boundary conditions of $O_3$ dominating (66% in Athens and Milan, 80% in London).

5. Conclusions

A complex 3D photochemical model is enhanced with exact derivative computations through automatic differentiation. The augmented code is then used in a sensitivity study of the modeled concentrations to various perturbations at the input data. The selected cities and episodes were case studies in the AUTOOIL-II programme.
The results were interpreted in terms of main (single) as well as interaction effects. At the level of ‘photochemical system’, more than 80% of the variability in the concentrations arises from only four perturbations. The order and the importance of the most uncertain inputs varied among the domains, however, two of them were identified in all domains: the boundary conditions of O₃ and the area emissions of NOₓ. Using a different approach, we also found that the variation in these two inputs can produce the highest change in the output. Finally, all three city centres as well as the downwind areas were recognized as VOC-sensitive.

Our results provided estimates to the maximum change in O₃ or “photochemical system” (all species) concentrations predicted by a numerical model and arising from several different perturbations in the uncertain inputs. We found in some cases significant variations even with very small errors in measured or estimated inputs. Even though these results are based in linear perturbation theory, they provide in only one execution of the code accurate quantitative information in the changes of the solution vector.

A 3D photochemical model has many computational and data storage requirements. This limits practically the applicability of several sensitivity analysis methodologies into this field. The approach implemented here needs an order of magnitude less CPU and disk space when compared with a statistical approach, e.g., Monte Carlo while it does not require assumptions for the statistical distribution of the uncertain inputs. Overall, a systematic search in the input space of the uncertain variables could be achieved by a limited number of runs of the enhanced code. It is intended that this will be the next extension of the study.

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Table 4
Eigenvectors corresponding to the highest eigenvalue for the central grid point (urban centers)

<table>
<thead>
<tr>
<th>Grid point</th>
<th>Athens</th>
<th>London</th>
<th>Milan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (LST)</td>
<td>14:00</td>
<td>15:00</td>
<td>15:00</td>
</tr>
<tr>
<td>Maximum eigenvalue ($\lambda_{\text{MAX}}$)</td>
<td>0.38</td>
<td>0.22</td>
<td>0.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Eigenvector</th>
<th>(Athens)</th>
<th>(London)</th>
<th>(Milan)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{\text{BND NOX}}$</td>
<td>0.09</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>$\epsilon_{\text{BND VOC}}$</td>
<td>0.03</td>
<td>0.16</td>
<td>0.08</td>
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References