Modelling pollutants sub-grid scale variability due to surface emission heterogeneity at urban areas

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Abstract.
We propose a sub-grid scale model, that takes into account surface emission heterogeneity and models pollutants variability at scales smaller than model resolution. Grid-average emission flux is split into a sub-grid mosaic of different types of emitting surfaces (traffic, residential, etc...). The model is implemented into a mesoscale chemistry transport model and results for a 3-months simulation over Paris (June 1st to August 31) are compared with surface measurements at traffic and background stations. The model is able to differentiate correctly pollutants concentrations over sub-grid scale micro-environments (close to streets or over residential areas) improving correlation with measurements up to 25% for $[PM_{10}]$ and up to 72% for $[NO_2]$. Decrease in model bias reaches 30% for $[NO]$ and 11% for $[O_3]$ compared to grid-average concentrations. Different sensitivity of ozone production to its precursors emission rates is observed between sub-grid simulations. Modelled $[O_3]$ sub-grid scale variability is found to vary by a factor of 3 depending on the photochemical regime, with the NO – $x$-sensitive photochemistry favouring variability creation compared to the VOC-sensitive regime.

1. Introduction

Recent studies confirm the evidence of atmospheric pollution adverse health effects (WHO [2004]; Bell et al. [2005]). Health risk evaluation in health impact assessment studies (HIA) may whether consider homogeneous exposure to air pollution, regardless pollutants spatial variability (Blanchard et al. [2008]; Medina [2006]), or keep record of individuals exposure during their daily activities (Penard-Morand et al. [2005]). Each one of these approaches uses different types of air quality data. The former, most commonly, uses measured concentrations at sites selected to represent background pollution (background sites), while the latter, uses high resolution simulations (few tenths of meters) of emissions dispersion within city-blocks (street canyons), where exposure actually takes place (Vardoulakis et al. [2003, 2005]).

The evaluation of an average citizens exposure has the evident inconvenience that in reality, variability in emission sources spatial distribution leads to sharp variations in pollutants concentrations inside cities (Menut [2003]). Dispersion models, on the other hand, are limited to simulations around localized emission sources; modelled concentrations at urban center scale are very sensitive to boundary conditions and models domain need to be large enough around all the included sources (Menut [2003]; Brucher et al. [2000]).

Mesoscale chemistry transport models (CTM), at least to the knowledge of the authors, have not been used in (HIA) evaluation. Even though they have been proved to provide reliable concentrations (van Loon et al. [2007]; Vautard et al. [2007]) over domains of tenths of kilometres around urban centers, their relatively low resolution (a few kilometres) prevents them from being directly associated with human exposure. In the present study, we propose a method that takes into account emission heterogeneity at scale smaller than CTM resolution (sub-grid scale) and attaches the associated variability on mesoscale CTM grid-average concentrations. This additional information, is of significant importance when human exposure comes into question.

Within a common CTM, emissions are diluted instantly in the entire grid-cell, an area of some squares of kilometres. At the moment of their release, all information on emissions spatial distribution at sub-grid scale is lost. Surface emission heterogeneity however, can affect modelled concentrations throughout the atmospheric boundary layer (Galmarini et al. [2007]; Auger and Legras [2007]). In reality, fast chemical reactions occur close to sources and emitted species are consumed locally rather than being directly dispersed in the entire grid-cell volume. By modelling pollutants concentrations at sub-grid
scales we obtain a description of the concentration field close to emission sources. The principal advantage of the proposed sub-grid model is the simplicity of its implementation and its low computational cost. Sub-grid variability in the context of this study represents the statistical probability distribution of pollutants concentration over a sub-grid mosaic of different types of emitting surfaces. In this sense, the proposed model combines the deterministic calculation of grid-average 'standard' CTM concentration with a statistical description of emission sources spatial distribution over the grid cell area. This hybrid approach between deterministic modelling and statistical downscaling, is the main difference with recent studies addressing the same issue of transferring emission sub-grid variability to mesoscale model output concentrations (Galmarini et al. [2007]), where concentration variance equation is added and explicitly solved by the Reynolds-Average Navier-Stokes model.

The case study and model setup are presented in section 1. The principal assumptions and methodological aspects of the implementation are discussed in section 2. Section 3 is an overall presentation of model validation based on the comparison of 3-months simulation results with surface measurements. In section 4 we zoom in measurement sites representing different types of air pollution (traffic and background) and we compare the temporal evolution of measured concentrations with sub-grid concentrations. In section 5 we focus on the sub-grid model response with respect to the non-linear aspects of NO$_2$-VOC-O$_3$ chemistry. The principal findings of the study are synthesized in section 4.

2. Case-study and model setup

The case-study is based on a 3-months (June 1st to August 31st 2006) simulation of gas and particulate matter chemistry and transport over Paris (France), with CHIMERE (www.lmd.polytechnique.fr/chimere) model. Model domain (160x130km$^2$) is centered around Paris city, with a 3km horizontal resolution and 10 vertical layers (995-500hPa).

Input meteorological data (off-line meteorology) are calculated with the MM5 model (Grell et al. [1994]) at a 5km horizontal resolution with 61 vertical layers (995-200hPa). Model configuration considers a simple ice scheme (Dudhia [1989a]), the planetary boundary layer (PBL) Medium Range Forecast Model (MRF) scheme Hong and Pan [1996] and the Land surface model 5-layer thermal scheme (Dudhia [1989a]). A meteorological diagnostic processing is applied within CHIMERE model providing the final turbulence-related parameters (Schmidt et al. [2001]; Vautard et al. [2001]) reducing CTM vertical resolution to the aforementioned 10 vertical layers.

Initial and boundary conditions are taken from a coarser CHIMERE domain simulation over France (15km horizontal resolution) following a one-way nesting method. Chemical boundary conditions for the coarse resolution simulation are driven by GO-CART model monthly climatologies (Ginoux et al. [2001]) for aerosol species and by the LMDz-INCA global chemical weather forecast system for gas-phase species (Van Leer [1979]; Tiedtke [1989]; Hourdin and Armengaud [1999]; Haughstaine et al. [2004]).

Emission input for Paris area are taken from the 1km resolution inventory issued by AIRPARIF (http://www.airparif.asso.fr under the ESMERALDA project (http://www.esmeralda-web.fr) providing hourly mean emission fluxes for gas and particulate matter species considered in model chemical mechanism.

At European level, sources of pollutants are defined by considering the type of emission activity, fuels and other criteria such as type of process, abatement techniques, operating conditions etc... (http://www.citepa.org/emissions/methodologie). AIRPARIF anthropogenic emission inventory provides mean annual emission flux rates for pollutants released from eleven different source types (table 1).

Source categories are characterized by different temporal profiles and chemical compositions. This a posteriori information is applied on raw emission data to provide refined emission input for CTM simulations. Total NMVOC mass, for example, is split into 375 volatile organic compounds according to the chemical composition of the corresponding source type. At a second level, different NMVOCs are aggregated to a limited number of model species taking into account their reactivity respectively to model chemistry.

A common CTM procedure, considers that emission is homogeneous over the grid-cell surface and wipes out all trace of the differentiation between source types at the moment of the aggregation of raw data to model grid-average emission flux rates.

$^1$NO$_2$, VOC, CO, CO$_2$, SO$_2$, NH$_3$, CH$_4$, black and organic carbon, particulate matter classified to three size bins

$^2$α-pinene (C$_{10}$H$_{16}$), ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$), propylene (C$_3$H$_6$), α-butane (C$_4$H$_{10}$), isoprene (C$_5$H$_{10}$), formaldehyde (C$_2$H$_2$O), acetaldehyde (C$_3$H$_4$O), methyl ethyl ketone (C$_4$H$_7$O), α-xylene (C$_8$H$_{10}$)
Table 1. Definition of the different emission sources, relating emission type and fuels, following the SNAP (Selected Nomenclature for Air Pollution) reference nomenclature (http://www.citepa.org/emissions/methodologie).

<table>
<thead>
<tr>
<th>#</th>
<th>Source type</th>
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<tbody>
<tr>
<td>1</td>
<td>Combustion in energy and transformation industries</td>
</tr>
<tr>
<td>2</td>
<td>Non-industrial combustion plants</td>
</tr>
<tr>
<td>3</td>
<td>Combustion in manufacturing industry</td>
</tr>
<tr>
<td>4</td>
<td>Production processes</td>
</tr>
<tr>
<td>5</td>
<td>Extraction and distribution of fossil fuels and geothermal energy</td>
</tr>
<tr>
<td>6</td>
<td>and other product use</td>
</tr>
<tr>
<td>7</td>
<td>Road transport</td>
</tr>
<tr>
<td>8</td>
<td>Other mobile sources and machineries</td>
</tr>
<tr>
<td>9</td>
<td>Waste treatment and disposal</td>
</tr>
<tr>
<td>10</td>
<td>Agriculture</td>
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<tr>
<td>11</td>
<td>Other sources and sinks</td>
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</tbody>
</table>

When different types of emitting sources coexist in the same model grid-cell, emission sub-grid variability acts as a source of variability around modelled grid-average concentration. Traffic transport emission, for example, is characterized by low \( \frac{VOC}{NO_x} \) ratios (mean daily \( \frac{VOC}{NO_x \text{ Traffic}} \approx 0.3 \)), whereas more \( VOC \) than \( NO_x \) is released over residential buildings (mean daily \( \frac{VOC}{NO_x \text{ Residential}} \approx 5 \)). Note that the difference in these ratios is much more due to variation in \( NO_x \) than \( VOC \) emission; similar \( VOC \) mass is emitted in both traffic or residential micro-environments \( \frac{NO_x \text{ Traffic}}{NO_x \text{ Residential}} \approx 10 \), \( \frac{VOC \text{ Residential}}{VOC \text{ Traffic}} \approx 1 \). Variability in its precursors emission ratios may in-duce \( O_3 \) formation under different local photochemical regimes.

3. Methodology

3.1. Preparation of the sub-grid scale emission input

For the present study we preserved the classification of emitted pollutants over different source types. Instead of a single, mean emission flux rate over the entire grid-cell we considered a sub-grid mosaic of four types of emitting surfaces: road traffic emission, residential/tertiary emission, emission due to outdoors leisure activity (e.g. gardening, river navigation etc...), all other source. Each sub-grid emission represents the contribution of a certain source type to the standard grid-average input flux. For instance, maps of figure 1 show \( NO \) emission flux due only to traffic (left) or only to polluting activities in residential households (right).

3.2. Implementation of the sub-grid scale calculation

In a common CTM calculation, the variation of pollutants grid-average concentration within a model time step interval integrates production and loss terms related to modelled physical and chemical processes under consideration (i.e. primary emission, chemical production or consumption, horizontal transport, vertical mixing, scavenging by rain, dry deposition on the underlying surface). All model variables are grid and time averaged. In the proposed sub-grid model, sub-grid emission flux \( E_i \) is released over the sub-grid area \( A_i \) considering that the corresponding source lies over the \( \frac{A_i}{A} \) area fraction \( (E = \sum_{i=1}^{n} E_i A = \sum_{i=1}^{n} A_i) \). In this sense, we assume for instance that traffic emission \( E_{\text{Traffic}} \) is released over the \( \frac{A_{\text{Traffic}}}{A} \) sub-grid fraction of the grid-cell area which is covered with roads (figure 2).

A schematical representation of sub-grid model implementation is shown in figure 3. Grid-cell area is divided in the following 4 sub-grid surfaces, each corresponding to a single emission source type: i)roads for traffic, ii)buildings for residential emission, iii)parks, gardens, rivers etc... for outdoor leisure activity related emission, iv)the rest of grid-cell area is attributed to the rest of emission sources (left part of figure 3). Note that the division in three emission types, illustrated in figure 3, is only an indicative ex-
Figure 1. NO emission fluxes over Paris due to week day morning traffic (left) and residential activities (right) at 1×1km² horizontal resolution on 02/06/2006 at 07:00. Red triangles show the location of measurement stations of the local air quality network (AIRPARIF) assigned to measure atmospheric pollutants concentrations close to traffic sources and black circles give the location of background stations.

Figure 2. The fraction of model grid-cells occupied by streets and avenues in Paris city at 1×1km² resolution.

ample and that in fact, an unconditional number of sub-grid emissions can be defined.

Independent simulations over each sub-grid space calculate pollutants concentration variation during a time-step interval. Sub-grid model provides different concentration values (sub-grid concentrations) representing the deviation range around the ‘standard’ grid-average concentration due to the proximity to local emission sources (middle part of figure 3). In the following we will use the terms traffic and residential sub-grid concentrations. At the end of each time-step, sub-grid concentrations define the concentration sub-grid scale variability and they are averaged to the ‘standard’ grid-average concentration for the continuation of the simulation (right part of figure 3).

It should be noted that we have made the assumption that air parcels are neither transported nor mixed in between sub-grid areas and only emission is considered at sub-grid scale. Mass transport inwards and outwards model grid-cells at each time-step always considers grid-average terms for both meteorological
variables (wind speed for transport, eddy coefficient for mixing etc...) and species concentrations.

In this context, sub-grid space should be seen as the probability that during a model time-step interval an air parcel is found over a certain type of emitting surface, rather than it has been physically advected there by the wind. The absence of sub-grid transport ensures that each sub-grid simulation remains completely unaffected by any other emission source.

Sub-grid emission flux rates can not enter directly in the calculation; less mass is emitted over sub-grid space since sub-grid emission \( E_i \) is always smaller than grid-average emission \( E > E_i \). This artificial mass discontinuity would lead to erroneous advection and mixing of air parcels at grid-average scale. For this reason sub-grid emission flux is normalized by the area fraction so that sub-grid emission no longer represents the part of the total emission due to a certain source but rather what the total emission would be if the whole grid-cell surface was occupied by the corresponding surface type.

4. Overall comparison of model results with surface measurements

Sub-grid model implementation is applied on the central part of the domain representing downtown Paris (12 model grid-cells over \( 12 \times 9 \text{km}^2 \)), including the largest and more complex part of anthropogenic emission sources (figure 4).

We use the two available types of measurements sites, namely, background and traffic stations, for model validation (see also figure 4 for locations). We compare both ‘standard’ model grid-average concentration and traffic and residential sub-grid concentrations with measurements. The comparison includes \( NO_2 \), \( PM10 \), \( NO \) and \( O_3 \). It should be noted that only background measurements exist for ozone.

Sub-grid concentrations other than traffic and residential could not be compared with measurements since no measurement site could be directly associated with the corresponding micro-environment. Given that traffic and residential related emission represent the largest part of emission burden over the studied area, we assume that pollutants variability can be well represented by the difference between traffic and residential sub-grid concentrations. The following analysis is hence, based on this consideration and ignores the rest of modelled sub-grid concentrations.

4.1. Sub-grid model validation

Model results for a 3-months simulation period (June 1st to August 31st 2006) are compared with measurements according to common validation criteria (Honore et al. [2008]). The interest of the comparison is to test whether sub-grid model, by running independent simulations over different emission sources, is able to provide sub-grid concentrations closer to the measurements at the corresponding site type, than grid-average concentration. In this way we can validate our considerations on emission heterogeneity projection via land use fractions on model sub-grid space.

The surface type attributed to residential emission covers by far the largest part of the studied area and so we consider that residential sub-grid concentration represents background pollution and it is compared with measured concentration at background sites. Measured concentrations at traffic stations are compared with the traffic sub-grid concentrations.

For the calculation of model bias and root mean square error (RMSE) of \([NO_2]\), \([NO]\) and \([O_3]\) we use the daily measured and observed maximal values. For \([PM10]\) the mean daily values are compared instead (table 2).

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Formula</th>
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<tbody>
<tr>
<td>BIAS</td>
<td>( \frac{1}{N} \sum_{i=1}^{N} (M_i - O_i) )</td>
</tr>
<tr>
<td>RMSE</td>
<td>( \sqrt{\frac{1}{N} \sum_{i=1}^{N} (M_i - O_i)^2} )</td>
</tr>
<tr>
<td>CORR</td>
<td>( \sqrt{\frac{\sum_{i=1}^{N} (O_i - O_{mean})(M_i - M_{mean})}{\sum_{i=1}^{N} (M_i - M_{mean})^2}} )</td>
</tr>
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</table>

Table 2. Mathematical formulas of the criteria applied to compare model results with measurements: model error (BIAS), root mean square error (RMSE) and correlation coefficient, where ‘M’ stands for model value and ‘O’ for observations.

Grid-average model (‘standard’ simulation) overestimates \([NO_2]\), \([PM10]\) and \([NO]\) at all background stations and underestimates them at all traffic stations (figure 5 left). This model response is logical considering that these pollutants are directly emitted at the traffic network and their concentration decreases with the distance from source location. Smaller bias is observed with the residential sub-grid concentration than with the grid-average at background stations for \([NO_2]\) and \([PM10]\). For \([NO]\) model bias may increase or decrease with the residential sub-grid model depending on the station.
Figure 3. The blue arrows-pathway (top) represents a ‘Standard’ model procedure, where emission is instantly diluted to the volume of a grid-cell in the beginning of model time-step (left). Production/loss terms affect pollutants concentration during the time-step interval (middle) leading to a mean concentration value (right). The red arrows-pathway represents the implemented sub-grid model methodology (bottom), where emission heterogeneity (left) is preserved inside the time-step interval (middle) leading to discrete sub-grid concentrations and allowing the definition of sub-grid variability before averaged to the grid-average value.

Bias decrease in the sub-grid model is especially pronounced at traffic stations, for all sites and all primary pollutants.

Model bias for $[O_3]$ at background stations is also smaller when residential sub-grid concentrations are compared with measurements instead of the grid-average values. Grid-average model underestimates ozone at all sites most probably because dilution of high NO emissions at the entire grid-cell volume results in enhanced $[NO]+[O_3]$ reaction rate. The fact that more $O_3$ is modelled in the residential sub-grid simulation shows that differentiation in sources within the sub-grid model counteracts dilution effect.

Smaller RMS error is observed with the sub-grid traffic and residential model for all stations and pollutants (figure 5 middle). Note that even for $[NO]$ at background stations RMS error is lower when residential sub-grid concentrations are compared with measurements instead of the grid-average concentrations. Given that RMSE has the tendency to favour large discrepancies, we conclude that grid-average concentrations remain most of the time closer to measurements than sub-grid concentrations (lower BIAS), but when they miss grid-average model discrepancies are much larger than sub-grid model errors (larger RMS error).

At background stations sub-grid residential $[NO_2]$ is less correlated with measurements than grid-average concentrations but a much better correlation is observed at traffic stations (figure 5 right). At both traffic and background stations sub-grid $[PM_{10}]$ is more correlated with measured concentrations than grid-average concentrations. Sub-grid model results for NO show that sub-grid model is less correlated.
with measurements at background sites, whereas at traffic sites correlation may improve or worsen depending on the station.

$O_3$ sub-grid concentrations are more correlated with measurements at all background stations but the improvement is clearly less pronounced than for the rest of the studied pollutants. This is probably due to the fact that $O_3$ is a secondary pollutant, while the other discussed species are directly emitted from traffic sources. Emission heterogeneity has logically greater influence on primary pollutants variability. Synthesizing those remarks we conclude that the separation between traffic and residential micro-environments within the sub-grid model provides a more realistic representation of pollutants concentration. This conclusion is more pronounced at areas at the proximity to traffic sources than for background pollution. Sub-grid modelled $[NO]$ concentrations enhance overestimation of measured concentrations at background stations and they are less correlated with measurements.

### 5. Zoom in individual stations

'Standard' model output concentration is a $9km^2$ grid-average value. Sub-grid concentrations give the deviation range around this mean value due to emission heterogeneity inside the cell. By selecting surface stations included in the same grid-cell, one can compare 'real' variability with modelled sub-grid variability. Figure 6 compares the difference between traffic and residential sub-grid concentrations with the difference in measured $[NO_2]$ at the traffic (TR3) and background stations (BG5) (see figure 4 for locations). Even though modelled variability has a tendency to underestimate the measured one, a good correlation exists between the two values ($R^2 \approx 0.7$). Figure 7 compares the temporal evolution of sub-grid modelled $[NO_2]$ concentrations with measurements at the traffic and background sites (TR3 and BG5), from June 30th to July 30th. Traffic station (TR3) and background station (BG5) are both within the same model grid-cell; differences between traffic and residential sub-grid concentrations for $[NO_2]$ can reach $100\mu g/m^3$. Traffic sub-grid concentration follows much closer the temporal evolution of nitrogen dioxide at the traffic station, whereas the residential sub-grid concentration is more competent to reproduce $[NO_2]$ evolution at the background station.

There are no $[PM10]$ measurements at traffic and background stations both located in the same model grid-cell. Traffic and residential sub-grid concentrations are consequently compared with measurements at traffic and background stations included in the corresponding grid-cell. Sub-grid model response is studied respectively to the grid-average concentration.

Traffic sub-grid concentration better represents measured $[PM10]$ temporal evolution at the traffic station (TR1) and residential sub-grid concentration is closer to measurements at the residential station.
Figure 5. Comparison between ‘Standard’ simulation (blue crosses) and sub-grid model (red crosses) at for $NO_2$, $PM_{10}$, $NO$ and $[O_3]$, based on bias error (left), root mean square error (middle) and correlation with measurements (right) at background and traffic stations.

Figure 6. Hourly comparison between modelled and measured $NO_2$ sub-grid variability from June 1st to August 31st, calculated for measurements at the background station ‘Paris 1st’ (GB5) and the traffic station at ‘Bonaparte street’ (TR3).

(BG3) (figure 8). The time series of grid-average concentration is also shown in figure 8 and modelled sub-grid variability is expressed as the difference between traffic and residential sub-grid concentrations. In a significant number of cases, measured maximal or minimal concentration values are within the shadowed area representing the range of modelled variability. This remark suggests that attaching modelled sub-grid variability on the ‘standard’ grid-average model output concentration overcomes model discrepancies and gives a more realistic picture of $[PM_{10}]$ concentration. Another remark is that residential sub-grid concentration remains very close to the ‘standard’ model output concentration. This justifies our decision to compare background measurements to residential sub-grid modelled concentrations and on the same time suggests that our initial considerations concerning emission split into different sources and their projection in sub-grid surfaces is realistic.

In what concerns $O_3$ concentration, only background measurements were available. Figure 9 (top panel) shows a week-simulation of $O_3$ concentration compared to measurements at the background sta-
Figure 7. Measured and modelled $[NO_2]$ at the traffic station on Bonaparte street (TR3) in Paris center (top panel) and at the background station ‘Paris 1st’ (BG5) (bottom panel). Time series of measured values (black crosses) and modelled traffic sub-grid concentration (red line) and residential sub-grid concentration (blue line), from June 30th to July 30th. Sub-grid variability is expressed as the difference between traffic and residential sub-grid concentrations (grey shadow).

ation BG5 in the center of Paris. ‘Standard’ model grid-average simulation has the tendency to underestimate $[O_3]$, especially during days of exceptionally high photochemical activity (July 12th to 15th). This underestimation is quite common at urban areas with high sources of nitrogen oxides. Even though $NO$ emission is localized over high sources (e.g. streets) a ‘standard’ simulation dilutes emission at the entire grid-cell volume and consequently overestimates $O_3 + NO$ reaction rate (see also previous section). The impact of this reaction becomes clear by the low ozone concentrations modelled with traffic sub-grid simulation. On the contrary, more $[O_3]$ is produced in the residential sub-grid simulation than in the ‘standard’ grid-average simulation.

At days where ozone concentration remains low (≈ 80 µg/m$^3$), sub-grid model is able to predict correctly the measured daily maximal values with the residential sub-grid simulation (e.g. July 7th, July 10th). This remark shows that separation of emission sources in independent sub-grid scale simulations counteracts dilution effect. During days of very high ozone concentration model underestimation is large. Adding modelled sub-grid variability to the grid-average $[O_3]$ concentration (error bars in figure 9) shows that the difference between traffic and residential sub-grid concentrations is of the same order of magnitude as model discrepancies. This suggests that dilution effect is at large extent responsible for ozone model bias.

Having shown that $[NO]$ sub-grid concentrations may worsen grid-average model results, without affecting neither $NO_2$ nor $O_3$, it is interesting to study $[NO]$ and $[O_3]$ concentrations coevolution. Traffic and residential sub-grid and grid-average $[NO]$ concentrations are compared with measurements at the same background station BG5 as $[O_3]$ (figure 9 middle panel). Modelled and measured concentrations temporal profiles show a clear anticorrelation between $[NO]$ and $[O_3]$. Traffic sub-grid simulation models the highest $[NO]$ and lowest $[O_3]$. Measured background $[NO]$ concentration is lower than in all simulations while measured background $[O_3]$ concentrations are the highest. If we compare modelled
and measured concentrations at the traffic station TR3 (figure 9 bottom panel), we may argue that modelled traffic and residential sub-grid concentrations define a realistic sub-grid variability. Nevertheless correlation with measurements for $[NO]$ is much worse than for all other studied pollutants.

An interesting remark is that contrary to $[O_3]$, $[NO_2]$ and $[PM10]$, grid-average $[NO]$ concentration detaches from the residential sub-grid concentration. Both traffic and residential sub-grid $[NO]$ concentrations are significantly higher than grid-average concentration. This indicates strong chemical reactivity within sub-grid simulations that has a non-linear effect on grid-average modelled concentration. However, this sign of non-linearity does not affect directly sub-grid modelled $[O_3]$ (residential and traffic sub-grid $[O_3]$ concentrations are always on oposite sides of grid-average value). This suggests that the non-linear features of $NO_x$-$VOC$-$O_3$ photochemistry does not affect ozone formation locally (close to emission sources), where ozone concentration is more driven by the fast $O_3+NO$ reaction, but further downwind at longer temporal scales.

The same effect is also present in the grid-average, 'standard' simulation; the large $[NO]$ morning peak modelled on July 10th (figure 9) does not have a direct impact on ozone production on the same afternoon (nevertheless, $[NO]$ afternoon peak on the same day depletes all ozone during night-time). The non-linear response observed for modelled $[NO]$ concentrations leads to the question whether $NO_x$-$VOC$-$O_3$ chemistry within traffic and residential sub-grid simulations is driven by different photochemical regimes.

6. Modelled ozone sub-grid scale variability as a function of the chemical regime

Up to this point we showed that sub-grid model is able to represent correctly small scale variability at the proximity to emission sources, especially for pollutants directly emitted at the traffic network ($PM10$...
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Figure 9. Measured and modelled $[O_3]$ and $[NO]$ concentration from July 7th to July 15th at the background station 'PARIS01' (BG5) (top and middle pannels) and $[NO]$ concentrations at the traffic station 'Bonaparte str.' (TR3) (bottom pannel). Time series of measured (black crosses), modelled traffic sub-grid concentration (red line), residential sub-grid concentration (blue line), and 'standard' grid-average model output concentration (green line). Sub-grid variability is expressed as the the range of deviation from the grid-average concentration and it is calculated by the difference between traffic and residential sub-grid concentrations (grey shadow). The error bar around the 'standard' simulation equals the same difference on the hour of the simulation daily maximal and minimal values.

and $NO_2$). Non-linear effects appear when species chemical reactivity becomes high. In this section we setup a sensitivity experiment that allows a closer study of $NO_x$-VOC-O$_3$ photochemistry within the sub-grid model. The first step is to put in evidence the non-linear dependence of ozone formation with respect to $NO_x$ emission. We identify two days, where ozone formation is driven by different photochemical regimes. We study ozone sub-grid scale variability creation as a function of ozone precursors emission ratios.

We set up 36 simulations by varying $NO_x$ and VOC emission rates by steps of 0.25 around their value at the reference simulation. Variation in emission was applied on the whole data set independent of source type (e.g. the same coefficient is applied on $NO_x$ emission released by traffic or residential source). By varying the ratio of ozone precursors emission, we define areas of different photochemical regimes (Sillman [1995, ]; Sillman and H.Dongyang [2002]; Kanaya et al. [2008]).

On July 10th, ozone concentration at the reference simulation reduces with decrease in VOC emission and increases with $NO_x$ emission increase. This response defines a VOC-sensitive regime (Sillman [1995]). Four days later, on July 14th, modelled ozone production is driven by a different regime, where decrease in $NO_x$ emission inhibits ozone production ($NO_x$-sensitive regime). The remark that ozone production over Paris is often on the transition zone between different regimes agrees with previous studies over the same area (Menut et al. [2000], Sillman et al. [2003]; Deguillaume et al. [2008]).

Comparing ozone production on each of the studied
days, we observe rapid change in ozone concentration under $VOC$-sensitive regime ($[O_3]$ increases from 67 to 127 ppb on 10 July 10th), whereas the same fluctuations in precursors emission rates leads to a much lower sensitivity under a $NO_x$ sensitive regime ($[O_3]$ increases from 64 to 72 ppb on 10 July 14th).

The response of $O_3$ sub-grid scale variability to the same perturbation precursors emission rates is shown in figure 10 (right). Different response is observed depending on the chemical regime. On July 10th, most of the emission ratios map is dominated by $VOC$-sensitive chemistry. For low $NO_x$ emission, ozone variability is relatively low but it increases rapidly and almost linearly with $NO_x$ ($NO_x$-limited regime). For higher $NO_x$ emission (above 50% of the reference emission rate) the regime becomes saturated in $NO_x$ and ozone variability change rate slows down.

On July 14th, $NO_x$-sensitive regime dominates most part of precursors emission ratio plan. The fast linear increase in ozone sub-grid variability remains present at relatively high $NO_x$ emission rates (up to the reference simulation), where $NO_x$ saturation is observed. Variability becomes much less sensitive to further increase in $NO_x$ emission.

On both days, sub-grid ozone variability increases by an equivalent factor of 3 under the same fluctuation in precursors emission ratios. Note that on July 10th ($VOC$-sensitive regime) ozone concentration varied 10 times more than on July 14th ($NO_x$-sensitive regime) over the same precursors ratio plan.

Synthesizing those remarks we can argue that $[O_3]$ sub-grid variability increases linearly with increase in $NO_x$ emission and is practically insensitive in $VOC$ variations under a $NO_x$-limited regime. Sensitivity in $VOC$ emission is significantly less pronounced for ozone sub-grid variability than for ozone concentration itself under a $VOC$-sensitive regime.

Ozone sub-grid variability dependence on the chemical regime is explained by the different $\frac{VOC}{NO_x}$ ratios characterizing emission sources (see also the section 3.1). The main difference between traffic and residential emission is in $NO_x$ burden. Consequently, $NO_x$ sensitive regime favours ozone sub-grid variability creation. Even if modelled ozone concentration is less sensitive in precursors emission ratios under a $NO_x$ regime, modelled sub-grid variability is highly unstable.

7. Conclusions

A sub-grid scale model was implemented in a mesoscale chemistry transport model accounting for the variability of surface emission at scales smaller than model resolution. This method allowed to attach pollutants variability to the mean output CTM concentration and better define pollution within an urban context. The proposed implementation is based on the division of grid-cells in sub-grid surfaces representing areas releasing different types of emission. Emission heterogeneity or turbulence-related sub-grid scale effects on CTM mean output concentrations have been previously identified and quantified using explicit methods (e.g. large eddy simulations) Krol et al. [2000]; Galmarini et al. [2007]; Ebel et al. [2007]; Vinuesa and Port-Agel [2008]. The advantage of the proposed model is that the effect of smaller scales on model grid-average output is calculated in a statistical manner without explicitly resolving the finer scale. We are based on the consideration that a statistical distribution of emission sources over model sub-grid space can generate concentration variability at sub-grid scale. This hybrid approach, combining deterministic modelling with statistical description of sub-grid scale heterogeneity, makes the implementation of the model relatively simple and at low computational cost.

Model results for nitrogen oxides, $PM10$ and ozone were compared with measurements at different types of stations, showing that sub-grid model is able to differentiate correctly pollutants concentrations at the proximity to emission sources. Given that urban emissions are principally released over the traffic network or over residential buildings we focused the study on the variability induced by the spatial distribution of these two emission types. It was shown that modelled variability was well correlated to the measured one, suggesting that our initial considerations concerning the projection of emission heterogeneity within model sub-grid scale were correct. Model showed, however, a tendency to underestimate measured variability, indicating that other sources of variability have been neglected.

Modelled sub-grid concentrations had a non-linear impact on grid-average concentration for highly reactive species as $NO$. We focused on $NO_x$-$VOC$-$O_3$ photochemistry within the sub-grid model and showed that ozone sub-grid scale variability may vary by a factor of 3 depending on the photochemical regime. Ozone concentration was shown to vary more
rapidly with emission perturbations under the $NO_x$-sensitive regime than under a $VOC$-sensitive one, but the $NO_x$-sensitive regime had a clear tendency to favour sub-grid variability creation. These findings suggest that photochemical regime indicators may be also useful for ozone small scale variability prediction.

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