

Reply to the Anonymous Referee #1:

We thank Referee #1 for his/her suggestions and comments, which helped improving the manuscript. Comments are addressed point by point below. Extract of the manuscript are indicated in italics.

Major comments:

Comment 1: The authors present a study of the impact of turbulent mixing and segregation of OH radicals and OH sinks on modelled reaction rates and OH reactivity. A number of simulations are presented for various cases, including regions dominated by biogenic and anthropogenic emissions. However, the paper is lacking an overall summary and conclusion on the impact of these effects on model simulations for [OH] and OH reactivity.

Reply 1: The conclusion has been rewritten in order to highlight both a summary of the results and the final conclusions of our study on the impacts of turbulent mixing and segregation on OH reaction rates and reactivity (please see Reply 3 for text modification). The abstract has been also rewritten to take into account these modifications:

“The hydroxyl radical (OH) is a highly reactive species and plays a key role in the oxidative capacity of the atmosphere. We explore the potential impact of a convective boundary layer on reconciling the calculation-measurement differences for OH reactivity (the inverse of OH lifetime) attributable to the segregation of OH and its reactants by thermals and the resulting modification of averaged reaction rates. The Large-Eddy simulation version of the Meso-NH model is used, coupled on-line with a detailed chemistry mechanism to simulate two contrasted biogenic and urban chemical regimes. In both environments, the top of the boundary layer is the region with the highest calculated segregation intensities but with the opposite sign. In the biogenic environment, the inhomogeneous mixing of isoprene and OH leads to a maximum decrease of 30% of the mean reaction rate in this zone. In the anthropogenic case, the effective rate constant for OH reacting with aldehydes is 16% higher than the averaged value. OH reactivity is always higher by 15 to 40% inside thermals in comparison to their surroundings as a function of the chemical environment and time of the day. Since thermals occupy a small fraction of the simulated domain, the impact of turbulent motions on domain-averaged total OH reactivity reaches a maximum decrease of 9% for the biogenic case and a maximum increase of 5% for the anthropogenic case. Accounting for the segregation of air masses by turbulent motions in regional and global models may increase OH reactivity in urban environments but lower OH reactivity in biogenic environments. In both cases, segregation alone is insufficient for resolving the underestimation between observed and modeled OH reactivity.”

Comment 2: The introduction provides an overview of some previous OH reactivity measurements and studies investigating the impacts of air mass segregation. However, the studies investigating air mass segregation are typically concerned more with simulations of OH radical concentrations rather than OH reactivity. Are measurements of OH reactivity typically made on a timescale sufficiently rapid for the impacts of turbulence and segregation to be investigated?

Reply 2: The time response of current OH reactivity measurement techniques is not sufficient to directly assess the impact of turbulence. This highlights the interest of such an LES study, which is able to simulate this effect. The paper is built in two stages. First, the paper focuses on the impact of turbulence on chemical reactions of representative OH reactants (isoprene, aldehydes). Second, the model is used to calculate the impact of the inhomogeneous mixing of the chemical species on OH reactivity.

The following text has been added to the introduction section (lines 25-32, p.2):

“One possible issue in total OH reactivity retrieval not mentioned by previous studies could lie in neglecting turbulent motions in the transport of chemical compounds in the boundary layer. Indeed, turbulence can spatially segregate or bring together chemical species, reducing or increasing the mean reaction rate and thus chemical reactivity. However, as far as we know this physical process has not been investigated in previous studies. The time response of current OH reactivity measurement techniques is not yet sufficient to directly resolve the smallest relevant turbulent spatial scales. The limitation in time resolutions range from 30 seconds for LIF-based methods (Kovacs and Brune, 2001; Sadanaga, 2004) to one minute for the CRM method (Sinha et al., 2008). Pugh et al. (2011) and Dlugi et al. (2010) used direct isoprene and OH measurements with temporal resolution of a few seconds, fast enough to estimate the segregation of the compounds.”

Comment 3: The discussion and conclusion would benefit from a discussion of the overall impacts of neglecting effects of turbulence and air mass segregation. Are the differences in [OH] and OH reactivity significant? How do they compare to measurement uncertainties? Uncertainties in the rate constant and mechanism for OH + isoprene? What is the ultimate impact of the results reported? Are there regimes for OH reactivity for which turbulence/air mass segregation is more or less significant (i.e. are there ranges of OH reactivity for which the effects can/cannot be neglected

Reply 3: To address this issue, several modifications have been made in the text as the following:

- In the discussion section (line 20-26, p. 15): *“The redistribution of chemical species by the boundary layer turbulence induces a different mean reaction rate between compounds when compared to a situation in which chemical species would be perfectly mixed (Krol et al. (2000), Ouwersloot et al. (2011), Kim et al. (2012), Kim et al. (2016), Li et al. (2016) and Li et al. (2017) among others). The perfectly mixed assumption used in regional and large scale atmospheric models leads to errors on the mean reaction rates between species as the turbulent mixing occurs at scales smaller than the grid length (Vinuesa and Vilà-Guerau de Arellano, 2005). This implies that the OH total reactivity has been calculated inaccurately, in turn leading to a modification in the lifetimes of the OH reactants such as ozone and carbon monoxide.”*
- In the discussion section (line 34, p.18 to line 6, p. 19): *“Moreover, the error made on the total OH reactivity neglecting the turbulent mixing could cumulate with the uncertainties reported in the literature regarding OH reactivity techniques such LIF with a flow tube (from 10 to 15%, Kovacs and Brune (2001)), LP-LIF (from 10 to 20%, Sadanaga (2004)) and the CRM measurement method (15 to 20%, Sinha et al. (2008)). In addition, uncertainties on reaction rate constants are also present in chemical schemes, including those used by numerical models. These uncertainties on reaction rate coefficients range from 5 to 15%, as suggested by Atkinson et al. (2006). It is likely that the unaccounted fraction of OH reactivity reported in the literature may be explained at least partially by a combination of the following phenomena similar in intensity: turbulence effects on chemical reactivity and uncertainties on the OH reactivity measurements and reaction rate coefficients.”*
- In the conclusion section (line 23, p. 19 to line 17, p20): *“The differentiated transport by thermals is dependent on the chemical lifetime of the compounds, represented by the Damköhler number. This transport induces inhomogeneous mixing of the species within the boundary layer, with an impact on the mean chemical rate between reactive species. In both natural and urban environments, the top of the boundary layer was the region with the highest calculated segregation intensities but of the opposite sign. Between isoprene and the OH radical, an effective maximum decrease of 30% of the reaction rate was calculated at the top of the boundary layer in a biogenic environment compared to a perfectly*

mixed case. In the urban case, the reduction of the mean chemical reaction rate between the OH radical and C>2 aldehydes reached 8% at the surface in the early morning while this reaction increased to 16% at the top of the boundary layer during most of the simulation. Thermals transporting species emitted at the surface can lead to different chemical regimes inside up-drafts and the environment. For both cases, the surface and the thermals are the preferential reaction zones, with highest chemical reactivity. This was especially the case for the OH radical whose precursors are either transported by thermals or created inside them. OH reactivity was always higher by 15 to 40% inside thermals compared to their surroundings depending on the time of day. For the natural case, the major OH precursors close to the surface were radicals originating from the oxidation of isoprene and its degradation products whereas O₁D+H₂O reaction became more predominant with increasing altitudes. In the urban case, OH was mainly produced through the reaction between HO₂ and NO, at the surface or higher in the boundary layer. This led to a higher oxidation capacity in the air transported by thermals for both cases.

The overall impact of turbulence on OH concentrations and reactivity at the domain scale differs depending on the chemical environment considered. In a biogenic environment with low OH mixing ratios varying from 0.18 to 0.24 ppt, turbulent structures had little impact on the redistribution of OH in the boundary layer. This was due to an efficient OH recycling initiated by peroxy radicals formed by BVOC oxidation. In the anthropogenic case, OH mixing ratios ranged from 0.26 to 0.50 ppt. The turbulence significantly impacted the spatial distribution of OH and its precursors in the boundary layer, with higher mixing ratios in thermals. The mean relative error on domain-averaged OH reactivity revealed that effective OH reactivity (taking into account segregation by turbulent motions) in the biogenic case was up to 9% below the OH reactivity calculated based on averaged boundary layer mixing ratios. Accounting for inhomogeneous mixing between OH and its reactants (primarily isoprene) in a regional or global model could lower the calculated OH reactivity and increase the discrepancies with observed OH reactivities. In the urban environment, the mean relative error was slightly positive which means that air mass segregation by turbulence increases OH reactivity. Considering the effect of turbulent motions could reduce the gap between modelled and observed OH reactivity. However, segregation alone is unlikely to resolve the underestimation between observed and modeled OH reactivity.”

Minor comments:

Comment 4: Page 1, lines 6, 7 & elsewhere: Please clarify the comparisons being made and the meaning and relevance of ‘resp’ throughout the manuscript.

Reply 4: We used the abbreviation resp for respectively in the first version of our manuscript. As it seems to be confused, we removed this abbreviation throughout the revised version.

Comment 5: Page 1, line 12: Insert ‘the’ in ‘during daytime’.

Reply 5: This has been done.

Comment 6: Page 1, line 13: Remove ‘the’ in ‘by the ozone photolysis’.

Reply 6: This has been removed.

Comment 7: Page 1, line 16: Change ‘measured reactivity’ and ‘calculated reactivity’ to ‘measured reactivities’ and ‘calculated reactivities’.

Reply 7: The changes have been made.

Comment 8: Page 1, line 17: Change ‘reaction constants’ to ‘reaction rate constants’.

Reply 8: The change has been made.

Comment 9: Page 1, line 18 onwards: Please make the distinction between calculated reactivity (from observed concentrations of OH sinks) and modelled OH reactivity (which includes concentrations of intermediates produced in the oxidation of the observed sinks), and clarify whether the studies referred to include any model intermediates.

Reply 9: To avoid this confusion, the text has been changed to (lines 4-11, p.2): *“Measured OH reactivity in urban areas has been shown to be similar (less than 10%) to calculated OH reactivity in New York (Ren, 2003), in Houston (Mao et al., 2010) and in a controlled urban environment (Hansen et al., 2015). However, discrepancies in urban areas have been observed between measured and calculated OH reactivity in Nashville (Kovacs et al., 2003) (35% less for calculated reactivity), in Mexico (Shirley et al., 2006) (25%) and in Tokyo (Sadanaga, 2004) (25%). The differences between measured and calculated total OH reactivity are even higher in forested areas. Di Carlo (2004) found an unexplained fraction of 50% in measured OH reactivity during the PROPHET campaign in Michigan. These results are comparable to the missing part (50 to 58%) calculated from measurements made in a boreal forest in Finland (Sinha et al., 2010; Nölscher et al., 2012). Similarly, Nölscher et al. (2016) calculated an accounted fraction of measured OH reactivity close to 49% in an Amazonian rainforest.”*

Comment 10: Page 2, lines 7-9: Provide some references and further details to the statements made.

Reply 10: The text has been changed to (lines 12-20, p. 3): *“Attempts to use numerical models to explain the missing fraction of OH reactivity have proved to be insufficient. Indeed, Edwards et al. (2013) found an underestimation of 30% of OH reactivity in a box model with a detailed chemical mechanism for the OP3 project. In the PRIDE-PRD campaign, Lou et al. (2010) found discrepancies of +/- 10% between the results of the OH reactivity model and the measurements, also using a box model. Similarly, Mogensen et al. (2011) used a column model to elucidate the missing part of OH reactivity, but only explained 30 to 50% of the OH reactivity measured over a forest in Finland. Chatani et al. (2009) used a three-dimensional model with coarse resolution to fill the gap in OH reactivity but 40% of the measured OH sinks remained unexplained. The difficulty of getting models to represent OH reactivity could be partly due to as yet non-discovered OH reaction pathways, and which are therefore not implemented in atmospheric models.”*

Comment 11: Page 2, line 10: ‘lox’ to ‘low’. Please include the definitions of NO_x and HO_x, and state the values for ‘low’ NO_x.

Reply 11: This sentence has been changed to: *“The OH recycling by the isoprene oxidation chain in forest environments characterized by low NO_x (sum of NO and NO₂) conditions (i.e. <1 ppb) was proposed to explain the uncertainties in the simulated HO_x (sum of OH and HO₂) budget”*

Comment 12: Page 2, line 13: Subscript in HO₂.

Reply 12: This has been done.

Comment 13: Page 3, line 2: ‘asses’ to ‘assess’.

Reply 13: The change has been made.

Comment 14: Page 3, line 25: Change 'whose' to 'in which' and 'in the spin-up' to 'of the spin-up'.

Reply 14: The change has been made.

Comment 15: Page 3, line 33: State the locations of the observation sites.

Reply 15: Locations of the observations sites are now stated (lines 1-3, p.5): *"The initial and forcing dynamical fields are taken from Couvreux et al. (2014) who used a single column model to study the representation of the diurnal cycles of meteorological parameters at four observation sites in West Africa (Agadez and Niamey in Niger, Parakou and Cotonou in Benin)."*

Comment 16: Page 4, line 13: 'ozone gaseous precursors' to 'gaseous ozone precursors'.

Reply 16: The change has been made.

Comment 17: Page 4, line 16: What is the justification for choosing this particular flight? Can the flight track be provided?

Reply 17: This particular flight is described in Stone et al. (2010): it is characteristic of the boundary layer of a tropical forest in West Africa in monsoon period.

More details are now given in the text (lines 18-21, p.5): *"For both simulations, the initial vertical profiles of the main primary chemical species are taken from airborne measurements made during the B235 flight of the AMMA campaign performed by the BAE-146 aircraft (Table 1). This particular flight gives access to measurements performed in the boundary layer over a tropical forest in the north of Benin (10.13oN, 2.69oE) during the early afternoon (Stone et al., 2010)."*

Comment 18: Page 4, line 18: Why not for NO?

Reply 18: Biogenic emissions for NO are not available in the MEGAN-MACC inventory. The only inventory given this emission is the global GEIAv1 inventory. However, available measurements of NO biogenic emissions from soil during the AMMA campaign show that biogenic fluxes for NO over West Africa from the GEIAv1 inventory are underestimated. This point is now better explained in the revised version (lines 22-27, p.5): *"Biogenic emissions (Table 2) are taken from the MEGAN-MACC (Model of Emissions of Gases and Aerosols from Nature -Monitoring Atmospheric Composition and Climate) inventory (Sindelarova et al., 2014) except for NO, which is not available in this inventory. Biogenic NOx emissions from the GEIAv1 (Global Emission Initiative) inventory (Yienger and Levy, 1995) proved to be too low for the region studied in comparison to estimations based on airborne measurements during the AMMA campaign (Stewart et al., 2008; Delon et al., 2010). Therefore, a maximum value of 10 ng.N.m⁻².s⁻¹ was set for nitrogen oxide emissions from soils in the simulation."*

Comment 19: Page 4, line 29: Please quantify 'very low'.

Reply 19: The text was modified as (line 33, p.5 to line 1, p.6): *"This is in agreement with Guenther et al. (1991) who showed that isoprene emissions are thought to be null when the Photosynthetically Active Radiation (PAR) is equal to zero and maximum when the PAR exceeds the value of 1000 μmol.m⁻².s⁻¹."*

Comment 20: Page 5, line 5: Is ALD2 C>2 or C#2?

Reply 20: ALD2 represent the lumped C>2 aldehydes in the chemical scheme used. This is now indicated in the revised manuscript (lines 9-10, p. 6): *"For the anthropogenic case, attention is given to*

the lumped C>2 aldehydes (ALD2 in the chemical scheme)”.

Comment 21: Page 5, line 15-18: What is the reason for the difference in the threshold values and why is the value of 1 taken as the threshold in this study?

Reply 21: Considering reaction between ozone and nitrogen oxide, Schuman (1989) noticed that turbulence influence on the reaction rate between these compounds is the highest for values of Damkholer number higher than 0.1. Later studies (e.g. Molemaker and Vilà-Guerau de Arellano, 1998; Vilà-Guerau de Arellano and Cuijpers, 2000; Vilà-Guerau de Arellano and Cuijpers, 2005) rather considered that turbulence effects on reactions rates are thought to be maximum when a threshold value of 1 is used to discriminate fast (>1) and slow (<1) chemistry.

To clarify this point, the text was modified as (lines 22-27, p.6):*”Schumann (1989) distinguished different chemical regimes for the reaction between nitrogen oxide and ozone and found that the impact of turbulence on this reaction rate is highest for $Da > 0.1$. Later studies (Molemaker and Vilà-Guerau de Arellano, 1998; Vilà-Guerau de Arellano and Cuijpers, 2000; Vilà-Guerau de Arellano et al., 2005) have shown that the impacts of turbulence on atmospheric chemistry are expected to be maximum when $Da \geq 1$. Therefore, this value will be used in the following to discriminate slow and fast chemical reactions in the boundary layer.”*

Comment 22: Page 5, line 21: ‘specie’ to ‘species’.

Reply 22: The change has been made.

Comment 23: Page 5, line 29: ‘ratios’ to ‘ratio’.

Reply 23: The change has been made.

Comment 24: Page 6, line 8: Italicise ‘i’ in ‘i-th’.

Reply 24: The change has been made.

Comment 25: Page 6, line 9: ‘in a similar way than’ to ‘in a similar way to’.

Reply 25: The change has been made.

Comment 26: Page 6, line 21: What is the impact of this error and its neglect in previous studies?

Reply 26: The impact of this error and the effect of neglecting it are now discussed in the revised manuscript (lines 8-15, p.8): *“The segregation intensity used to compute the mean error corresponds to the deviation from the averaged boundary layer values. This error on OH reactivity was not considered in previous numerical studies focused on identifying the missing part of OH reactivity. Indeed, using a box model or a single column model like Mogensen et al. (2011), Whalley et al. (2011) or Whalley et al. (2016) leads to neglecting the turbulent motions that could affect the redistribution of chemical species within the atmospheric boundary layer. This may imply an underestimation or an overestimation of OH reactivity as a function of the sign of E_{ROH} . If E_{ROH} is positive or negative, then the effective OH reactivity R_{OH}^E is either higher or lower, respectively, than the OH reactivity R_{OH} found by neglecting the turbulent motions. Due to the crucial aspect of the OH radical in the atmosphere, this could subsequently modify the lifetimes of gaseous OH reactants such as ozone and carbon monoxide.”*

Comment 27: Page 7, line 22: Please quantify 'slightly overestimates'.

Reply 27: The observations of potential temperature averaged in the lowest 500m from Gounou et al. (2012) are now added to Figure 1.b and the text has been changed as (lines 11-13, p.9): *"The range of simulated virtual potential temperature (Fig. 1b) overestimates the AMMA observations in Cotonou of Gounou et al. (2012) in the lowest 500m, as shown by Couvreur et al. (2014). At 0600 UTC, the model has a cold bias of -2K turning throughout the simulation to a simulated potential temperature overestimated by +2K at the end of the simulation."*

Comment 28: Page 9, line 1: Formaldehyde is not $C>2$.

Reply 28: The text has been changed to *"no aldehydes"*

Comment 29: Page 9, line 5: Subscript in HNO₄.

Reply 29: The change has been made.

Comment 30: Page 9, line 13: 'mn' to 'min'.

Reply 30: The change has been made.

Comment 31: Page 9, line 21 and page 10, line 20: Change 'chemical equilibrium' to 'steady state'.

Reply 31: The change has been made.

Comment 32: Page 10, lines 4&5: Change 'lower' to 'shorter' and 'low' to 'short'.

Reply 32: The change has been made.

Comment 33: Page 11, lines 8-11: Please clarify the meaning here. What, specifically, is implied about the reaction(s)?

Reply 33: This line refers to the modification of chemical reaction rates by turbulent motions. To clarify this point the text has been revised as (lines 2-5, p.13): *"The previous part emphasized the non-uniform mixing between isoprene and OH for the biogenic case and between OH and ALD2 for the urban case, and the modification of the reactions rates between these species. However, this feature must be taken into account for every OH reactant in order to obtain the full picture of total OH reactivity and gain insight into how the Meso-NH model computes the OH budget in different chemical regimes."*

Comment 34: Page 11, line 10: 'reactants' to 'reactant'.

Reply 34: The change has been made.

Comment 35: Page 11, line 12: Consider changing the section title, which 'environment' does this refer to? Would 'surroundings' be a better description?

Reply 35: Thank to reviewer for his/her suggestion, the title of the section has been changed to *"OH budget in thermals versus surroundings"*

Comment 36: Page 11, lines 24-25: Quantify the budgets.

Reply 36: The budget is now quantify in the revised manuscript (lines 14-19, p.13) : *"The OH budget for the anthropogenic case (Fig. 7b) shows that the chemical reactivity is higher inside thermals at the surface compared to the rest of the domain. The budget is largely dominated by the production of OH by NO+HO₂ (79.2% of its total source in updrafts and 71.2% of the total source in non-updrafts) and by*

O1D+H2O (14.4% of the total source in updrafts and 18.5% of its total source in the rest of the domain). Over the whole domain, ALD2+OH (21.6% of the total loss in updrafts and 26.0% of the total loss in the rest of the domain) is the most important sink at the surface and at 500 m, followed closely by the oxidation of carbon monoxide (17% of the destruction of OH in thermals and 18.8% in non-updrafts)."

Comment 37: Page 11, line 31: 'photochemistry' to 'photochemical'.

Reply 37: The change has been made.

Comment 38: Page 12, line 4: Change 'is maximum' to 'is at a maximum'.

Reply 38: The change has been made.

Comment 39: Page 12, lines 11 and 21: Can the errors be shown?

Reply 39: The error made on the OH reactivity is now shown for both simulations (Figure 10) and discussed in lines 25-29 p.14 and lines 3-14, p.15.

Comment 40: Page 12, line 19: 'reactants' to 'reactant'.

Reply 40: The change has been made.

Comment 41: Page 13, line 3: Please provide details of the 'simple chemistry'.

Reply 41: Details have been added as (line 32, p.15 to line 1, p.16): "*Using a simple chemistry scheme of 19 reactions representing the basic reactions of O3-NOx-VOC-HOx system, Ouwersloot et al. (2011) found an almost constant value of -7% for the segregation between OH and isoprene in the boundary layer over the Amazonian forest.*"

Comment 42: Page 13, line 35: Please re-word 'remains not negligible in the OH loss'. Do you mean it is significant for OH loss?

Reply 42: The original text has been changed to (lines 6-7, p.17): "*The formaldehyde mixing ratios were close to 2 ppbv, which explains that this is not a major sink like isoprene, but remains important for OH loss through the reaction OH+HCHO.*"

Comment 43: Page 14, line 5: 'imply' to 'implies'.

Reply 43: The change has been made.

Comment 44: Page 14, line 10: 'imply' to 'implies' and 'have' to 'has'.

Reply 44: The change has been made.

Comment 45: Page 14, line 21: 'percents' to 'percent'.

Reply 45: The change has been made.

Comment 46: Page 15, line 17: 'HO' to 'OH'.

Reply 46: The change has been made.

Comment 47: Page 26, Fig. 1a: Why does the blue line stop at 1800 hours?

Reply 47: It is because the tracer used for this diagnostic is emitted only from 0600 to 1800 UTC to optimize computing time. A sentence was added to clarify this point in the "Dynamics" subsection of

the "Simulation assessment" section (lines 9-10, p.9): *"The tracer used for this diagnostic is emitted only during the period of interest, from 0600 to 1800 UTC."*

Comment 48: Page 30, Table 3: Subscripts in O3 and NOx.

Reply 48: Subscripts have been added.

Comment 49: References: There are a number of formatting issues in the references, please check thoroughly prior to publication.

Reply 49: We apologize about that. The references have been carefully checked in the revised version.