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 5 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 Damkhöler 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 updrafts 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 inthe 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."

<u>Minor comments:</u>

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 NOx and HOx, and state the values for 'low' NOx.
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 NO_2) conditions (i.e. <1 ppb) was proposed to explain the uncertainties in the simulated HO_x (sum of OH and HO_2) 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 inWest 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 $\mu mol.m^{-2}.s^{-1}$.”*

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 >=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^{E}_{OH} 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 Couvreux 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 ‘surroudings’ 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*

$O1D+H_2O$ (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.

Reply to the Anonymous Referee #2:

We thank Referee #2 for his/her suggestions and valuable 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: This article describes the effect of turbulence on the reactivity of OH and two key volatile organic compounds, isoprene and lumped aldehydes (where there are more than 2 carbons). The authors find that turbulence can reduce isoprene and OH reaction rates by up to 30% for a biogenic environment with low NOx, and affect reaction rates of lumped aldehydes and OH by 16% or less for an anthropogenic environment. Thus, a box model or regional and global-scale models that assume each grid box is well mixed will potentially be in error of the OH reactivity by 10% or less because of covariance of reactants caused by turbulence.

Over the past 5 or so years, there have been some very similar studies with similar conclusions as what was presented here (Ouwersloot et al., 2011; Kim et al., 2012; 2016; Li et al., 2016; 2017). As a consequence, the only new advance for atmospheric chemistry science is the potential error to the OH reactivity calculation in models that assume a well-mixed box. Yet this error calculation was done for a limited time and space region. In its current state, this paper is not ready to be published. Most importantly, the paper needs to emphasize its uniqueness. Otherwise it will be viewed as a confirmation of the previous studies.

Reply 1: The originality of this work is now highlighted in the introduction section where it is specified that this work investigate the potential role of turbulent motions in explaining the observed-calculated OH reactivity discrepancies (discussed further in Reply 2). Moreover, the peculiar dynamic situation of the case study, which consists in a transition from stratus deck breaking up to form cumulus clouds, is now added in the introduction (discussed further in Reply 3).

Moreover, the differences between this study and previous works studying segregation (for example Ouwersloot et al., 2011; Kim et al., 2012; 2016; Li et al., 2016; 2017) result from differences in the chemical scheme (recycling of OH during oxidation of BVOC or not, discussed further in Reply 8) and from differences in chemical species repartition in the boundary layer. This leads to lower or higher concentrations anomalies, which induce different segregation values. As an example, higher segregation is calculated in our study than in Kim et al. (2016) in the cloudy layer due to the OH vertical profiles whose gradients are sharper, which induces higher OH anomalies. Regarding the positive values of segregation simulated in the afternoon, the differences with Kim et al. (2016) might lie in discrepancies in chemical mechanism used. The OH recycling in ReLACS 3.0 is likely more important than the one present in Mozart v2.2 used by Kim et al. (2016).

To address this point, the text was changed to (line 3-17, p.16): "*In the biogenic case in this study, the negative segregation of a few percent in the middle of the boundary layer is reproduced. As in this case, higher segregation values were simulated with altitude in Kim et al. (2016), especially in the cloudy layer. However, segregation computed in the cloudy layer in Kim et al. (2016) was equal to -0.1, a value lower to that computed in the biogenic case of the present study. The discrepancies in this study and Kim et al. (2016) are likely due to the* *vertical OH profiles. In the study by Kim et al. (2016), OH concentrations increased linearly with altitude. This implies lower OH covariances for ascending air parcels and thus lower segregation values (Eq. 2). On the contrary, in the present study, OH is relatively homogeneous in the boundary layer and a strong gradient is present only at the top of the boundary layer. This induces high covariances for OH concentrations inside air transported by thermals at the top of the boundary layer, implying higher segregation values. As segregation computed by Li et al. (2016) is not available above 1000m height, a direct comparison with results regarding the cloudy layer is not possible with the results from the biogenic case. The positive values of segregation simulated in the afternoon (Fig. 6a) in the biogenic case are not reproduced in other studies and might be the result of efficient OH recycling in ReLACS 3.0, initiated in particular inside the thermals due to peroxy radicals formed by isoprene oxidation. Indeed, this recycling is either absent or indirect in previous works like in the mechanism used by Kim et al. (2016) that produces only HO2 from peroxy radicals, which may explain the discrepancies in OH covariances."*

Comment 2: The paper needs to emphasize its uniqueness. The reactivity of OH should be discussed more thoroughly as it is the goal of the paper. The title of the paper, the introduction, and even the section heading (3.2 OH budget and reactivity in a convective boundary layer) say that we will learn about the convective boundary layer (CBL), yet only results at 20 m, the lowest model level, are discussed. I strongly recommend presenting OH reactivity results for the entire CBL adding a figure showing the error associated with OH reactivity when turbulence effects are considered, and stating the implications of this error on atmospheric chemistry in general. For this last part, it would be good to learn, besides the point that turbulence could explain the missing OH reactivity sink found in the Amazon, what the expectation of turbulence effects on OH reactivity is for the atmospheric oxidative capacity. Making these changes would very much align the paper's content with its title.

Reply 2: The introduction section has been modified to highlight the originality of this work, especially the role of turbulence on the discrepancies in OH reactivity mentioned in the literature:

- (lines 25-32, p2): *"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."*

- (lines 5-8, p4): *"The goal of this work is to evaluate the role of thermals on OH reactivity in the framework of a convective boundary layer with contrasted chemical environments in southern West Africa. It focuses in particular on investigating turbulence as a possible explanation of the discrepancies between calculated-*

> *measured OH reactivities mentioned in the literature. Two contrasted chemical regimes represented by a detailed chemical scheme are studied by using Large-Eddy Simulations."*

A figure was also added in the revised manuscript to show the diurnal evolution of the error associated with OH reactivity when turbulence effects are considered (Figure 10). The expectations for atmospheric chemistry and the oxidative capacity are discussed in the conclusion section (line 29, p.19 to line 9, p.20):

"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. This study addressed the impact of moist thermals on the oxidative capacity of the atmosphere on two contrasted chemical"

Comment 3: One other unique aspect of this investigation is the selected case study, which is a region in tropical West Africa that experiences stratus clouds in the morning subsequently breaking up to form cumulus clouds in the afternoon. Examining segregation of reactants with low-level stratus cloud has not been reported (to my knowledge). This aspect could be emphasized more by including the cloud fraction diurnal profile along with the other variables plotted, and address the question of what impact the cloud has on the intensity of segregation and OH reactivity. The effect is most likely limited to the effect on heat and moisture fluxes for the simulations shown, unless effects of cloud scattering on photolysis rates are included in Meso-NH. The authors could also speculate what effect the clouds have on isoprene emissions based on transmittance (cloud optical depth) and temperature effects.

Reply 3: The originality of this study looking at the segregation in an environment characterized by stratus cloud deck is now emphasized in the introduction. The paragraph presenting the cloud characteristics previously in the section 2.4.1 has been moved to the introduction section to complete this information (lines 21-29, p.3): "*Cloud cover over West Africa is an important feature of the African monsoon but is poorly represented by global models (Knippertz et al., 2011; Hannak et al., 2017). This could lead to overly low simulated clouds and overly high incoming radiation at the surface, implying excessively high diurnal* *temperature and relative humidity cycles over this region. The nocturnal low-level stratus was studied during the monsoon period at Parakou (Benin) by Schrage et al. (2007) with radiosondes. The authors found that turbulent processes are responsible for cloudy nights whereas clear nights are associated with a nocturnal inversion leading to the decoupling of the surface and lower atmosphere. Schrage and Fink (2012) investigated nighttime cloud formation. They observed that the presence of a nighttime low-level jet induces the shear-driven vertical mixing of moisture accumulated near the surface. This leads to stratus formation whose cover is likely to persist until the early afternoon when it breaks up to form cumulus clouds (Schrage et al., 2007; Schrage and Fink, 2012). However, studying the impact of this specific cloudy environment on the turbulent transport of chemical species in tropical West Africa has not been reported."*

The diurnal variation of cloud fraction is now added to the segregation plots. The possible cloud effects (thermodynamic fields and photolysis rates) on segregation are now discussed in the discussion section, as well as the possible impact on isoprene emissions. Finally, speculations are made on the impact of aqueous-phase chemistry on segregation of chemical compounds in the boundary layer. These specific points and the modification of manuscript are presented in Reply 15.

Specific Comments:

Comment 4: In general, the LES results show that the intensity of segregation is <10%. The 30% segregation that is stated in the abstract and conclusions is overstated, as this high value occurs for a small-time period (30 minutes) and region (top of boundary layer) of the model domain where isoprene is likely quite small.

Reply 4: The abstract and conclusions have been corrected. The revised abstract now stated: *"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 5: Although this paper does a good job of citing previous studies, I was surprised that Krol et al. (2000) was not cited. Krol et al. (2000) is one of the first to examine segregation effects on VOC + OH reaction rates.
Reply 5: We apologize for this missing; the pioneering work of Krol et al. (2000) is now added to the introduction section.

Comment 6: Page 2, line 33. Clouds scatter radiation resulting in regions of less solar radiation and more solar radiation.
Reply 6: "Decrease" was changed to "modify" in the sentence (lines 18-19, p.3) : "They also modify incoming solar radiation, which in turn disturbs photolysis reactions and alters the emissions of biogenic compounds, such as isoprene."

Comment 7: Page 3, lines 29-30. Could the definition of the thermals be presented in a little more detail? My understanding is that the definition is also based on vertical velocity greater than zero, the standard deviation of the decaying tracer, and for when cloud exists, liquid water content. In addition, I was wondering if radioactive-decay tracer is the correct terminology, as it could just be called a first-order decay tracer.
Reply 7: We use the terminology of radioactive-decay tracer because it is how it was introduced by Couvreux et al. (2010). However, we agree that first-order decay may be a more simple terminology. Moreover, the definition of thermals is now presented in more details (lines 28-33, p.4): *"The thermals are identified by the conditional sampling method implemented in the model by Couvreux et al. (2010), which relies on a first-order decay passive tracer mixing ratio emitted with a constant flux at the surface. In brief, in order to be considered as thermals, air parcels at a given altitude z must satisfy simultaneous conditions such as a positive vertical velocity anomaly w'>0 and tracer anomalies sv'(z) greater than the standard deviation of the tracer concentration* $\sigma_{sv}(z)$ *and a minimum threshold* $\sigma_{min}(z)=(0.05/z).\int_0^z \sigma_{sv}(z)k.dk$. *In the cloud layer, a supplementary condition is that the grid box has to be cloudy."*

Comment 8: Page 4, section 2.2. How does the ReLACS 3.0 chemistry mechanism compare to that used by Kim et al. (2012)? Just based on number of chemical species, they may be quite comparable, making the statement on p. 3, line 4 inappropriate. A key part is that they both include reactions that allow peroxy radicals to produce hydroxyl radical limiting the segregation effects.
Reply 8: We agree with this statement and modified the text as (line 31, p.3 to line 4, p.4): "*High resolution simulations which explicitly resolve the turbulent and convective advection terms were conducted (Vilà-Guerau de Arellano and Cuijpers, 2000; Vilà-Guerau de Arellano et al., 2005; Ouwersloot et al., 2011; Kim et al., 2012, 2016) to assess the impacts of clouds and the convective boundary layer on the mixing of chemical compounds. However, previous numerical studies on the impact of the turbulent mixing of chemical compounds mainly used relatively simple or only slightly more detailed chemical schemes (e.g., Vilà-Guerau de Arellano and Cuijpers (2000),Vilà-Guerau de Arellano et al. (2005) and Ouwersloot et al. (2011)), resulting in possible limitations in the representation of the atmospheric chemistry. However, more recent studies by Kim et al. (2012) and Kim et al. (2016) used a more detailed chemical scheme derived from Mozart v2.2, allowing the formation of OH radicals initiated by peroxy radicals. This limits the spatial heterogeneities caused by the reactions consuming the OH radical."*

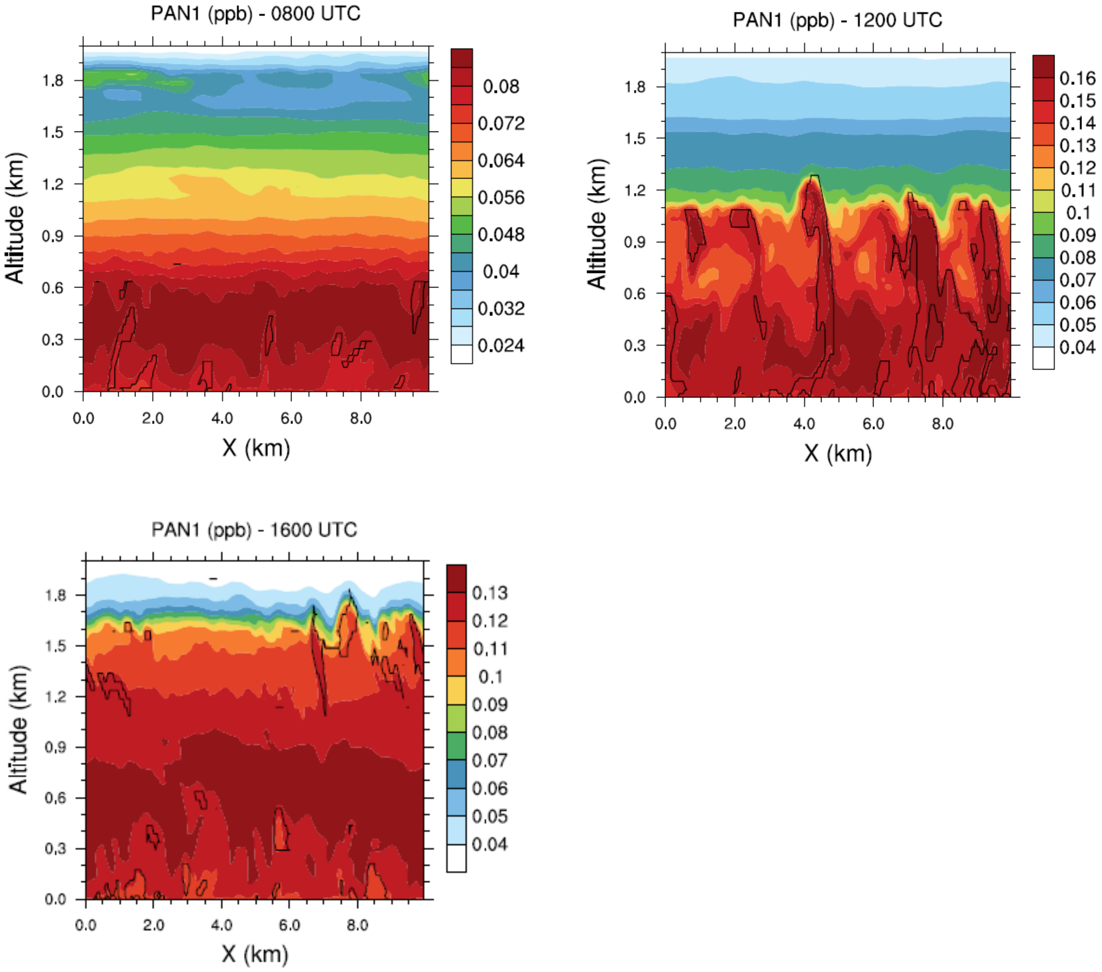
Comment 9: Page 5, section 2.3. How is the convective velocity calculated? There are different methods such that characterizing the turbulence is important.
Reply 9: The way how the convective velocity is calculated is now described in the "Metrics subsection" (lines 21-23, p.6) *: "The convective velocity is computed with g, the standard acceleration due to gravity, and Θ, the potential temperature, according to the relation* $w^{*} = (\frac{g}{\theta}.\overline{w'\theta'_{v,s}}.h)^{1/3}$ *where* $\overline{w'\theta'_{v,s}}$ *stands for the buoyancy flux at the surface."*

Comment 10: Page 6. In comparing equation 4 to equation 9, should ROH be in the denominator of equation 9?
Reply 10: R_{OH} is in the denominator of equation 9 to normalize the estimated error made on the OH reactivity. The construction of equation 9 is intended to be similar to the one used for the segregation coefficient.

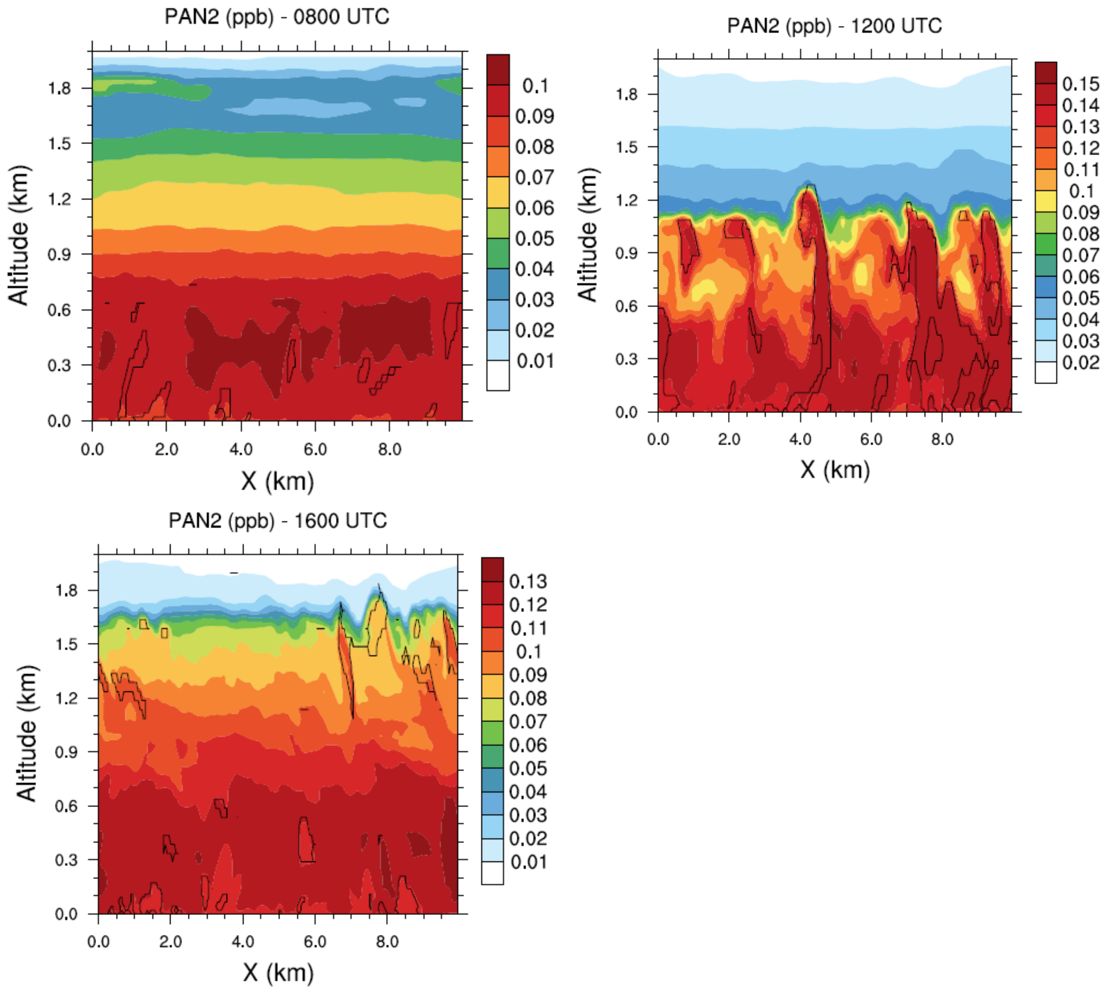
Comment 11: Page 7, lines 10-15, lines 22-24. It would be nice to see the observations overlaid on the figures displaying the model results.
Reply 11: Observations are now overlaid to the figures of boundary layer height and vertical profiles of potential temperature (Figures 1.a and 1.b). The boundary-layer height is in agreement with the observations but the models predicts a larger potential temperature diurnal cycle than observed which is similar to the results obtained with a single column models (Couvreux et al., 2014) or Numerical Weather Prediction models suggesting that at least part of those differences are due to the definition of the large-scale forcings.

Comment 12: Page 8, Is UTC same as local time (LT)? This information would be helpful when examining the diurnal profiles.
Reply 12: The local time (LT) is equal to UTC +1. This information is now given in the manuscript (lines 25-16, p.4): "The r*esults are shown only for the third day from 0600 to 1700 UTC (LT=UTC+1), when the convective boundary-layer is well developed*"

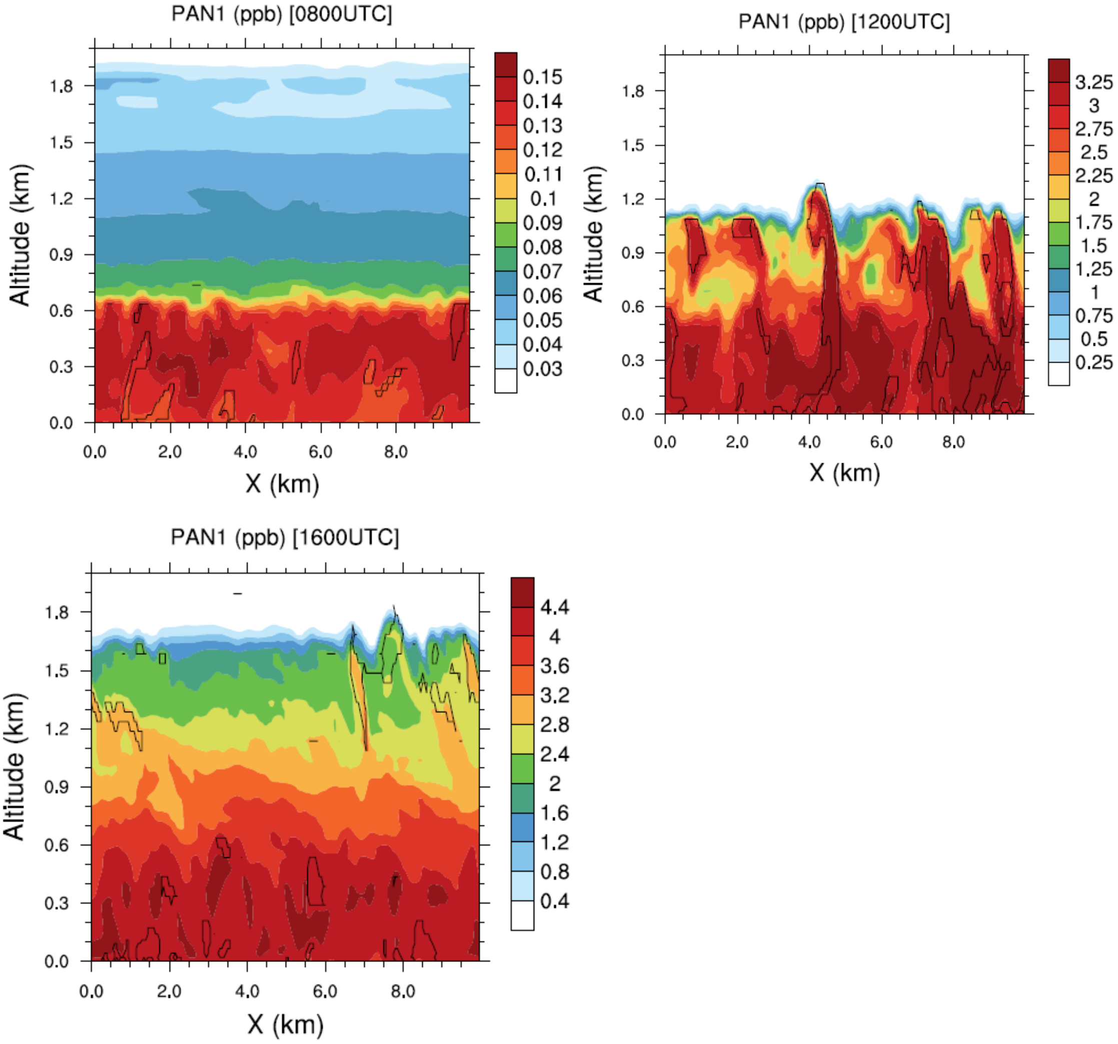
Comment 13: Page 9, lines 4-6. I am surprised production of HNO3 was not discussed. It seems a more likely outcome at temperatures near 300 K (as PAN thermally decomposes).
Reply 13: HNO$_3$ has now been explicitly mentioned in the list of reservoir species of NO$_2$. Besides, its production (by NO$_2$+OH) is taken into account in the percentages of the net conversion of NO$_2$. In the biogenic case, the low NO$_2$ mixing ratios induce a too low production of HNO$_3$ in the boundary layer. In the anthropogenic case, the production of HNO$_3$ through NO$_2$+OH reaction accounts for almost 15% of the instantaneous destruction of NO$_2$ at 1200 UTC near the surface. In the meantime, HNO$_3$+OH → NO3 +H$_2$O and the subsequent photolysis of NO$_3$ yields only a negligible amount of NO$_2$. Moreover, in the anthropogenic case, PAN is the most important reservoir of NO2 because of the efficient oxidation of carbonyls species, which produced peroxyles radicals, precursors of PAN. Even if PANs thermally decompose, they accumulate in the boundary layer, resulting in a net sink for NO$_2$ for both cases as shown in the following plots.



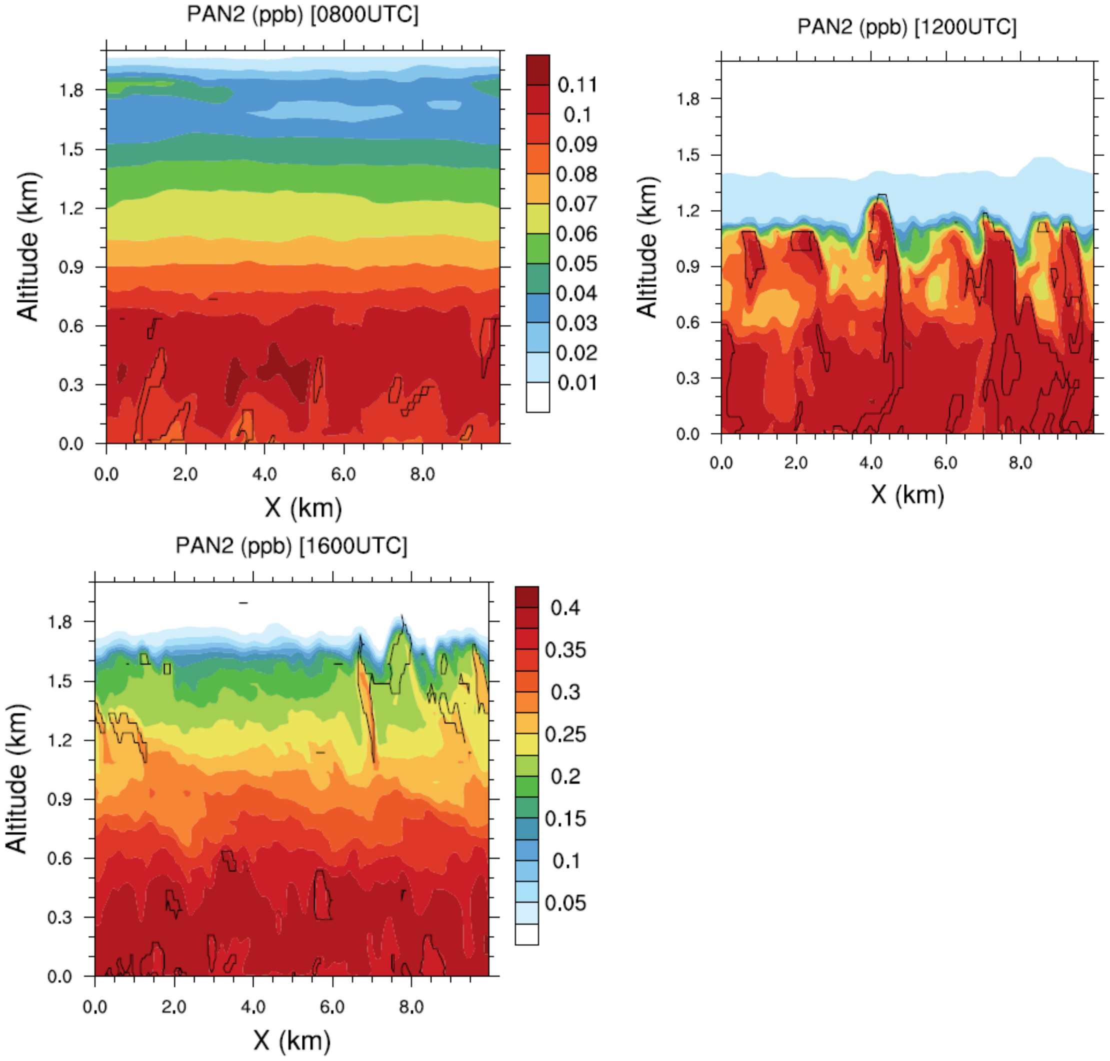
PAN1 (peroxy pentionyl nitrate) in the biogenic simulation.



PAN2 (peroxy acetyl nitrate) in the biogenic simulation.



PAN1 (peroxy pentionyl nitrate) in the anthropogenic simulation



PAN2 (peroxy acetyl nitrate) in the anthropogenic simulation.

The text was changed to (lines 19-24, p.10): *"A minimum of NOx was found around 1200 UTC for both cases and can be explained by two factors. The first is dynamical and is linked to the boundary layer. In the middle of the simulation, the boundary layer growth was maximal and induced dilution in a larger mixing volume. The second factor was chemical because at that instant, NO was efficiently converted into NO2. However, NO2 chemical transformations in a reservoir such as HNO3, HNO4 or PANs are net sinks for NO2. The chemical balance between reservoir species and NO2 represented 2.12% of the net destruction of NO2 averaged over the domain at 20 m and 1200 UTC for the biogenic case, and 34.2% for the anthropogenic case. For both cases, the main reservoirs of NO2 were PAN1 and PAN2. Therefore, less NO2 was available for conversion into NO, which explains the low NO mixing ratios at midday (Fig. 4b and d)."*

Comment 14: Page 10, section 3.1.2. It would be useful to show via figures why the intensity of segregation is negative or positive and why it changes with time as part of the discussion of Figure 6 on page 10. Examples of the isoprene and OH anomalies in the context of the OH production would help quantify and explain the results.

Reply 14: To clarify this point, as suggested by the reviewer, values of anomalies are now indicated.

For the biogenic case, the text was changed to (line 29, p.11 to line 24, p.12):

"Negative values of segregation coefficients up to -30% are calculated at the top of the cloudy boundary layer from 1000 to 1700 UTC which means that OH and isoprene are partly segregated in this frontier zone. In other words, the hypothesis of a well-mixed atmosphere would lead to a 30% overestimation of the reaction rate at the frontier between the boundary layer and the free troposphere. The negative segregation (Eq. 2) means the anomalies of isoprene and OH have opposite signs, as shown in figure 5a. This is due to lower OH mixing ratios in thermals than in the environment (Fig. 5b). These results are consistent with the previous studies of Li et al. (2016); Kim et al. (2016); Ouwersloot et al. (2011) (see Discussion).

In the biogenic case, isoprene anomalies in thermals are considerable from the surface (+0.48 ppbv on average at midday) to the top of the boundary layer (+0.1 ppbv on average at midday) and are thought to be always positive as OH is uniformly emitted at the ground (Fig. 5a). On the contrary, OH mixing ratios are almost constant in the boundary layer at 1200 UTC (Fig. 5b), so the magnitude of OH anomalies are expected to be low (-0.03 pptv on average at midday at the top of the boundary layer). Besides, due to its very short chemical lifetime, OH quickly reaches equilibrium with its surroundings, implying that its fluctuations are mostly due to thermals transporting air originating from different chemical environments. Thus, isoprene anomalies are thought to be the major driver of the magnitude of segregation over the boundary layer whereas changes in OH anomalies are related to changes in the segregation sign.

Positive values around +5% are calculated at 700 meters starting from 1400 to 1800 UTC (Fig. 6a). The intensity of segregation becomes positive due to positive anomalies of both compounds. Due to decrease in isoprene emissions in the afternoon, OH destruction slows down, especially inside thermals. They are still active in transporting enough NO to react with HO2 to produce OH, inducing higher OH mixing ratios inside updrafts than in the surroundings (+0.02 pptv on average at 1600 UTC).

Before 0900 UTC near the surface, the segregation coefficient in the anthropogenic simulation between OH and ALD2 is negative up to -8% in the lower 200m (Fig. 6b), due to the anthropogenic emission patch. As chemical equilibrium is not yet reached, more of the OH radical is destroyed through its reaction with recently emitted compounds than that which is produced (not shown). This means that OH is less concentrated inside updrafts at that moment so its anomalies are negative near the surface. Simultaneously, positive segregations develop at the top of the boundary layer from 0700 UTC to 1230 UTC with a maximum of 16% at 1000 UTC and from 1530 to 1730 UTC. The positive segregation is related to the concomitant transport of ALD2 and precursors of OH by thermals. Moreover, the high segregation values correspond to the presence of clouds between 0.6 and 0.9 km (Fig. 2c), simultaneously with a high cloud fraction over the domain (>0.6) (Fig. 6b). This specific point is discussed in the discussion section. As ALD2 is emitted at the surface, its anomalies are high and positive inside updrafts. For example, at midday, anomalies are +0.5 ppbv on average at the surface and nearly +4 ppbv at the top of the boundary layer. However, in this case, OH anomalies are more difficult to predict due to the spatial heterogeneities of chemical emissions. Local changes in OH production and destruction explain the changes in the segregation sign throughout the simulation."

Comment 15: Page 10, lines 27-33. It is interesting that there is a positive covariance of ALD2 and OH at the top of the boundary layer from 0700 to 1230 UTC, which is during the time period of the stratus cloud (Figure 1 shows cloud fraction > 0.5). How much of this positive covariance region coincide with the clouds? How might the cloud environment affect ALD2-OH covariance (e.g. high relative humidity, scattering of photolysis rates, etc.). How much would the results differ if aqueous chemistry (or just partitioning between gas and aqueous phases) were represented in the model? Finally, why is there a positive covariance for ALD2 and OH during morning at CBL top, yet a negative covariance for isoprene and OH?
Reply 15: The presence of clouds concomitant to high segregation between ALD2 and OH is now added in the section 3.1.2. (see manuscript changes in the previous comment for this specific point).
The modification of ALD2-OH covariance by the presence of clouds is now discussed in the discussion section (lines 23, p.17 to line 12, p.18): *"In the anthropogenic simulation, the high values of segregation computed at the top of the boundary layer are coincident with the presence of clouds. In the absence of aqueous-phase chemistry, clouds impacts on chemical species are dynamical and photochemical. They modify heat and moisture fluxes at their surroundings (Vilà-Guerau de Arellano et al., 2005) and thus the transport of compounds, as noted by Kim et al. (2012) who demonstrated that clouds presence could increase transport of chemicals to 1000m. In this set of simulations, the chemical impact of clouds on species involves photolysis rates as they are corrected at every time step due to the presence of clouds according to the work of Chang et al. (1987). At each point of the domain, photolysis rates are increased above clouds and decreased below them.*

Another effect of clouds on the atmospheric chemistry lies in isoprene emissions, as demonstrated by Kim et al. (2012). As isoprene emissions are dependent on incoming radiation and temperature near the surface, cloud shading could decrease the amount of isoprene emitted. Kim et al. (2012) showed that isoprene concentrations are decreased by 10% and OH concentrations increased by 5% in the boundary layer when isoprene emissions are reduced by up to 10%. The ultimate impact onsegregation cannot be anticipated since it corresponds to two compensating effects.

Finally, clouds impact atmospheric chemistry through aqueous phase reactivity. Aqueous-phase chemistry was not considered here, nor were the exchanges between gas and aqueous phases. However, it could have an impact on soluble species mixing ratios, such as formaldehyde and H2O2 through the capture and degassing cycles of these compounds. Lelieveld and Crutzen (1990) showed a decrease in oxidative capacity of the atmosphere through aqueous-phase reactions via a significant decrease in ozone mixing ratios, but 5 also OH, formaldehyde and nitrogen oxides. However, the effects of aqueous-phase chemistry on gas-phase compound concentrations are various (Barth et al., 2003) and OH concentrations could decrease in clouds (Mauldin et al., 1997). This result was confirmed by the study of Commane et al. (2010) who found that HOx concentrations decreased in clouds. Recently, Li et al. (2017) studied segregation effects in a biogenic environment when aqueous-phase chemistry is included. They found that isoprene concentrations are increased by up to 100% while OH concentrations decreased by 18%, resulting in a maximum segregation of 55% in the cloudy layer. In the anthropogenic environment, segregation effects are expected to be *enhanced due to the decrease of OH concentrations in gaseous phase in the cloud layer, reducing the cleansing capacity of the atmosphere."*

In the anthropogenic case, the positive covariance for ALD2 and OH at the top of the CBL during the morning is a consequence of transport of ALD2, emitted at the surface, and OH precursors, also emitted at the surface. In the biogenic case, isoprene, emitted at the surface, is more concentrated in thermals, which means positive anomalies of concentrations over the domain. The OH radical is slightly less concentrated in updrafts (-0.03 pptv at the top of the boundary layer). It is the result of a chemical balance characterized by its destruction (chemical reactions, especially isoprene) and its production (chemical production by NO+HO2 reaction but also its recycling by peroxy radicals). This balance changes over time depending of the local chemical regime, which changes the sign of OH covariance in the boundary layer and thus affects the segregation sign. In the morning and at the top of the boundary layer, this chemical balance induces lower OH concentrations in updrafts and so negative covariance for isoprene and OH.

Comment 16: Page 11, section 3.2.1. It may make more sense to calculate the OH budget for several model layers to reduce effects of the emissions being injected into the lowest model layer. The lowest model layer is subject to subgrid effects (e.g., Vinuesa and Vila-Guerau, 2003; not only subgrid-scale TKE but also subgrid-scale chemistry) and therefore more uncertainties can arise in these budget calculations.
Reply 16: The OH budget at 20m allows a comparison between model results and measurements. Nevertheless, the text had been modified to include the uncertainties rising from the subgrid effects (lines 3-6, p.13): *"This height is the first level in the model and computing the chemical budget at this height leads to uncertainties due to subgrid-scale mixing and chemistry (Vinuesa and Vilà-Guerau de Arellano, 2005). However, it makes it possible to compare the model results with the measurements in the literature."*

Moreover, figures showing the OH budget at the top of the boundary layer are now added to the manuscript with the following associated discussion in section 3.1.2 (lines 25, p.13 to line 17, p.14): *"The chemical budget at 1200 m (Fig. 8), namely at the top of the boundary layer, allows the investigation of chemical reactions inside the ascending air parcel lifted by thermals and its comparison with its surroundings. For the biogenic case, the major OH reactants in the thermals have a chemical lifetime greater than the turbulence timescale. At this altitude, only species whose Damkhöler numbers are lower than 1 are present in sufficient amounts to react with the OH radical. For example, carbon monoxide (26.2% of total OH destruction in thermals and 36.6% in the surroundings) is the major sink, but also methane (11.8% of total OH loss in updrafts and 18.4% in the environment). Chemical compounds with a secondary source like formaldehyde and C>2 aldehydes (ALD2) are other important sinks at 1200m. Isoprene, the major OH reactant close to the surface, is present only in thermals at this altitude due to its reaction with OH in the ascending air parcel and consumes 11.8% of OH in thermals. OH production by NO+HO2 reaction is null inside updrafts and low in the non-updraft area (3.2% of the total OH production) due to NO destruction in updrafts. The reaction between hydroxyl radicals RO2, secondary products, with HO2 is a major OH source in thermals (49.7% of total production) but also in the surroundings (36.1% of OH production in updraft-free region). Production of OH by O1D + H2O or H2O2 photolysis are similar in magnitude in thermals and in the non-thermal areas. The production and* *destruction terms are higher in the thermals compared to these terms in non-updrafts due to higher concentrations of OH reactants inside the thermals, but lower than at 20m.*

Regarding the anthropogenic case, species whose lifetimes are higher than the turbulence timescale are major OH reactants at 1200m. Carbon monoxide contributes 22% of the OH destruction in thermals and 34.3% in the rest of the domain. As with the biogenic case, chemical compounds with a secondary source are important OH sinks like formaldehyde (11.1% in thermals and 11.0% in updraft-free regions) and ALD2 (26.4% of total OH destruction in updrafts and 11.8% in the surroundings), corresponding to the major OH destruction term at the top of the boundary layer. The OH production terms in the anthropogenic case are similar in thermals compared to the surface with a high contribution of NO + HO2 reaction (66.9% of total OH production), followed by O1D + H2O reaction (15.3%) and RO2 + HO2 (10.6%). In the rest of the domain, NO + HO2 contribution drops to 16.9% while O1D + H2O (32.8%) and RO2 + HO2 (31.1%) are major production terms.

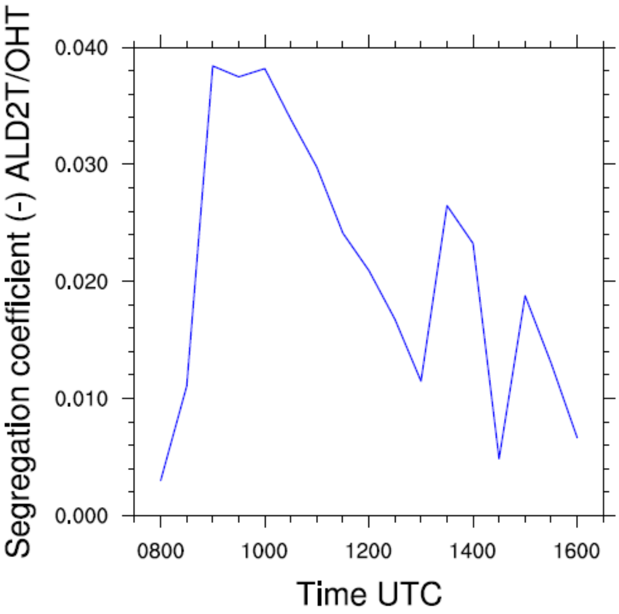
The differences between the OH reactivity at the surface and the top of the boundary layer are mainly driven by the changes in chemical mixing ratios of precursors caused by chemical reactions and consequently by their Damkhöler number, and by the secondary products formed inside the thermals."

Comment 17: Page 12, lines 11-25. It would be good to see a figure showing the error in the OH reactivity due to turbulence effects.

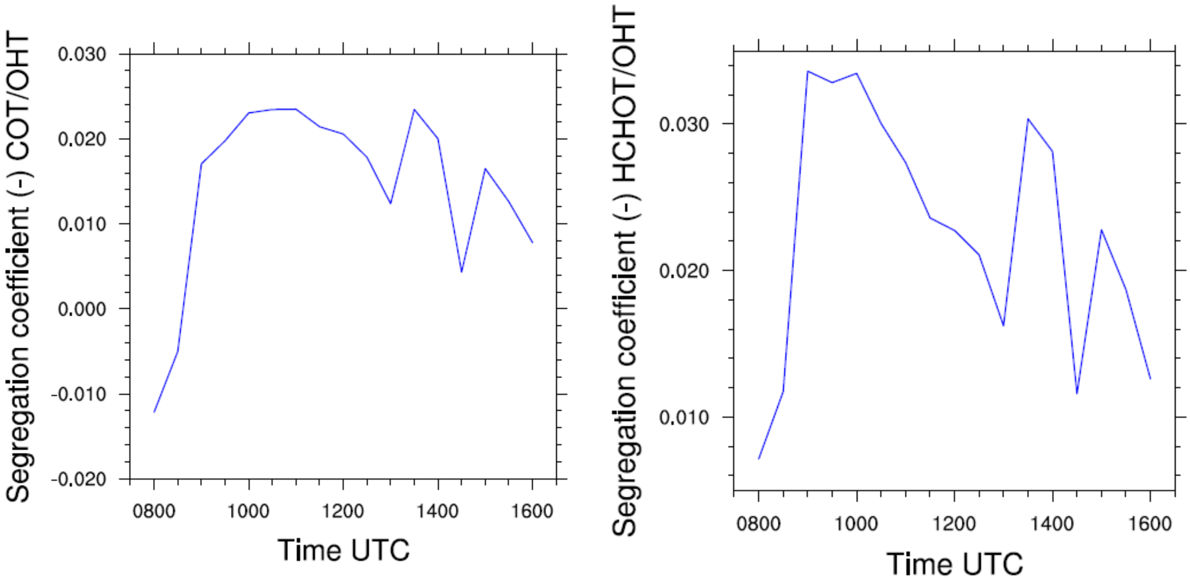
Reply 17: A figure showing the error in the OH reactivity had been added to the manuscript for both biogenic and anthropogenic cases with the following associated discussion in section 3.2.2 (lines 13-18, p.15): *"In both cases, the occurrence and development of clouds (Fig. 6, upper panel) is concomitant with linear increases of the error made on the OH reactivity while neglecting the impact of turbulence (Fig. 10). The diurnal cycle of E_{Roh} in each case is correlated to the development of the convective boundary layer. Firstly, a rapid change occurs during the first hours of the simulations, characterized by the occurrence of thermals and an increase in chemical emissions for the biogenic environment. Then, E_{Roh} is relatively stable from the end of the morning to the middle of the afternoon, with a maximum value computed around 1400 UTC, corresponding to the maximum turbulent activity in the convective boundary layer."*

Comment 18: Page 12, line 24. Since segregation happens only for compounds that have chemical lifetimes similar to the turbulence time scale, it seems unlikely that there is a compensating factor described in this line (unless isoprene + OH segregation compensates). Could the authors provide support for this statement?

Reply 18: Segregation between two compounds happens when at least one of the two compounds have chemical lifetimes lower than or equal to the turbulence time scale. In that sense, segregation might be important between OH and each of its reactants. Moreover, the segregation used to compute the error made on the OH reactivity is now calculated from boundary layer averaged values. In other words, covariances of each compound are computed relatively to concentration averaged over the whole boundary layer. Depending on the chemical species considered and their vertical distribution, averaging these covariances to compute the segregation coefficient can either induce negative values of segregation or lower positive values, even if positive values of segregation are computed when considering vertical segregation. As an example, the segregation computed relatively to boundary layer averages for ALD2 and OH is positive during daytime but does not exhibit the large values simulated in Fig. 6, because of the average over the boundary layer:



The error made on the OH reactivity is thus the result of every OH reactants segregation like CO or formaldehyde (major OH sinks in the boundary layer):



To clarify this point, the text was changed to (lines 10-12, p.15): *"Moreover, chemicals have either negative or positive segregation towards OH that may compensate or increase the positive values simulated for ALD2 and OH (Fig. 6b)."*

Comment 19: Page 13. I applaud the authors for discussing several previous studies in the context of their results. However, I found that there was often no explanation of why there are differences between this study and the previous work. For example, p. 13, line 1, why are the current segregation values higher than Kim et al. (2016)? Line 8, how are the boundary layer dynamics different between this study and Li et al. (2016)? Lines 20-28, do the previous studies report the same dominant OH production and loss reactions as the current study? If they are different why does that happen (e.g. different emissions causes more VOCs in one study or the other)?

Reply 19: The differences with Li et al. (2016) cannot be discussed for the cloudy layer as the segregation is only computed from the surface to 1000m in Li et al. (2016).

The higher segregation values computed in our study in the cloudy layer are the result of OH vertical profiles whose gradients are sharper, which induces higher OH covariances. Regarding the positive values of segregation simulated in the afternoon, the differences with Kim et al. (2016) might lie in discrepancies in chemical mechanism used. The OH recycling in ReLACS 3.0 is likely more important than the one present in Mozart v2.2 used by Kim et al. (2016).

To address this point, the text was changed to (line 3-17, p.16): *"In the biogenic case in this study, the negative segregation of a few percent in the middle of the boundary layer is reproduced. As in this case, higher segregation values were simulated with altitude in Kim et al. (2016), especially in the cloudy layer. However, segregation computed in the cloudy layer in Kim et al. (2016) was equal to -0.1, a value lower to that computed in the biogenic case of the present study. The discrepancies in this study and Kim et al. (2016) are likely due to the vertical OH profiles. In the study by Kim et al. (2016), OH concentrations increased linearly with altitude. This implies lower OH covariances for ascending air parcels and thus lower segregation values (Eq. 2). On the contrary, in the present study, OH is relatively homogeneous in the boundary layer and a strong gradient is present only at the top of the boundary layer. This induces high covariances for OH concentrations inside air transported by thermals at the top of the boundary layer, implying higher segregation values. As segregation computed by Li et al. (2016) is not available above 1000m height, a direct comparison with results regarding the cloudy layer is not possible with the results from the biogenic case. The positive values of segregation simulated in the afternoon (Fig. 6a) in the biogenic case are not reproduced in other studies and might be the result of efficient OH recycling in ReLACS 3.0, initiated in particular inside the thermals due to peroxy radicals formed by isoprene oxidation. Indeed, this recycling is either absent or indirect in previous works like in the mechanism used by Kim et al. (2016) that produces only HO2 from peroxy radicals, which may explain the discrepancies in OH covariances."*

Concerning OH chemical budget, the text has been modified to clarify whether the production/destruction terms are the same in previous studies or not (lines 22-35, p.16): *"Kim et al. (2012) studied by means of a LES the OH budget in a biogenic environment averaged over the domain and over time from 1330 to 1430 LT with a chemical scheme adapted from MOZART v2.2. They found, for a low NO_x case with ozone mixing ratios close to 64 ppbv, that the OH production was mostly influenced by four predominant reactions (including $O^1D + H_2O$, $HO_2 + O_3$, H_2O_2 photolysis and $HO_2 + NO$). These production terms are present in the biogenic case of the present study. However, the recycling by peroxy radical is not present in Kim et al. (2012) as peroxy radicals only formed HO_2 in the chemical scheme they used.*

Moreover, they found that the OH loss by reaction with isoprene was dominant near the surface, followed by the reactions with CO and formaldehyde, similarly to the current study.

The OH reactivity contribution of the BVOC species was simulated by Li et al. (2016) for three distinct biogenic cases of the DISCOVER-AQ (Deriving Information on Surface Conditions from

Column and Vertically Resolved Observations Relevant to Air Quality) campaign. The production terms of OH are not available but it was found that isoprene was a dominant sink for OH, about 25-30% of the OH reactivity was linked to BVOC reactions at 0.3 km during midday. This contribution is comparable to the percentage calculated for isoprene in the OH destruction in thermals (41.7%) or in updraft-free area (29.3%). The contribution of formaldehyde was comparable to isoprene at that height, with HCHO mixing ratios ranging from 2 to 4.5 ppbv at the surface. The higher formaldehyde contribution of Li et al. (2016) is the result of higher concentrations than in the current work."

Comment 20: Page 15, lines 11-13. This discussion states a 5-15% missing fraction of OH reactivity reported by Nölscher et al. (2016) are similar in magnitude as that caused by turbulence effects on OH reactivity. Although I agree that the assumption of the well- mixed "box" is an issue to be considered for studies like Nölscher et al. (2016), I wonder if uncertainties in the measurements and reaction rate constants are also sufficient to explain discrepancies between model and observation analyses of OH reactivity.
Reply 20: We agree that all this factors or a combination of them could explain the discrepancies. This was added in the discussion section (lines 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 5 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."*

Comment 21: Page 15, lines 14-20. The Li et al., 2017 study addresses segregation of reactants with aqueous phase chemistry included.
Reply 21: This publication is now present in the discussion section where clouds presence and segregation are discussed (see Reply 15).

Technical Comments

Comment 22: The paper needs to be proofread carefully and completely to improve the English. There are many places that could be improved, which should have been done as part of the Quick Review Process.
Reply 22: The revised manuscript was proofread by a native English speaker.

Comment 23: Could "resp." be spelled out ?
Reply 23: This abbreviation was not used anymore in the revised manuscript.

Comment 24: P. 12, lines 27-30, The first paragraph should cite other papers such as Krol et al.,2000; Ouwersloot et al., 2011; Kim et al., 2012; 2016; Li et al., 2016; 2017.

Reply 24: The paragraph is now modified to (lines 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."*

Comment 25: P. 18, There are two Hansen et al. (2015) references that appear to be the same.
Reply 25: This has been corrected.

Comment 26: Table 1. Instead of having the reader find the ReLACS3 paper, it would be helpful to explain the names of the lumped species.
Reply 26: Species names are now included in the Table 1 caption.

Comment 27: Figure 2, I find the title of each plot to be useful. Yet in this case I do not understand "MRC". It should be defined or rewritten into something meaningful.
Reply 27: "MRC" stands for cloud water mixing ratio. This is now stated in the title.

Comment 28: Figure 4 caption should be improved. That is, NO, NO2 should be added to a-b) description and OH, O3 should be added to c-d) description. The ALD2 line needs a scale.
Reply 28: The caption has been corrected and ALD2 line has now a scale.

Comment 29: Figure 5. What are the black lines contouring? I think thermals, but it does not say in the caption. The vertical profile lines need to be thicker.
Reply 29: Yes, black lines are thermals. The caption has been corrected.

Comment 30: Figure 6. I assume the results plotted must be an average in space, and needs to be stated in the caption.
Reply 30: The variable plotted in Fig.6 is the segregation coefficient that is, by definition, an average in space.

Comment 31: Figure 8 shows results for OH reactivity at an altitude of 20 m (the lowest model level) for "updrafts", "updrafts-free", and all horizontal grid points. I think it would be better to characterize these lines as thermals and non-thermals as vertical velocity is often very close to zero at/near the surface.
Reply 31: We agree with the reviewer and modified the caption in that sense.

LES study of the impact of moist thermals on the oxidative capacity of the atmosphere in southern West Africa

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Abstract. The hydroxyl radical (OH) is a highly reactive ~~specie~~ species and plays a key role in the oxidative capacity of the atmosphere. ~~The total OH reactivity , corresponding to~~ We explore the potential impact of a convective boundary layer on reconciling the calculation-measurement differences for OH reactivity (the inverse of OH lifetime~~, may have a significant fraction non-attributable to commonly measured compounds. The turbulence-driven~~) attributable to the segregation of OH and its reactants ~~can cause substantial~~ by thermals and the resulting modification of averaged reaction rates~~, and thus of the total OH reactivity, when compared to a perfectly mixed assumption. We study the impact of turbulent mixing on the OH reactivity with~~ . The Large-Eddy ~~Simulations from the~~ simulation version of the Meso-NH model is used, coupled on-line with a detailed chemistry mechanism ~~in two contrasted regimes. Our findings show that the non-mixing of isoprene (resp. aldehydes)~~ 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% ~~decrease (resp. 16% increase)~~ of the mean reaction rate ~~at the top of the boundary layer and consequently to 9% decrease (resp. 5% increase) of the OH total reactivity in a biogenic (resp. anthropogenic) environment. Moreover, the total OH reactivity is highest inside thermals in both cases.~~ 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.

1 Introduction

The hydroxyl radical (OH) is an efficient cleansing molecule present in the troposphere. It is mainly produced during the daytime through the reaction of water vapor with O(^{1}D), formed by ~~the~~ ozone photolysis, while nitrogen oxides and volatile organic compounds (VOC) are its major sinks. OH ~~has a very high reactivity~~ is highly reactive and reacts with numerous chemical species, controlling their chemical lifetimes (Ehhalt, 1999). Both OH concentrations and its reactivity are key elements of the oxidative capacity of the atmosphere. Several field campaigns have been conducted to study ~~the~~ total OH reactivity for urban ~~or~~ and forested environments. ~~The measured reactivity~~ Measured reactivities have been compared to ~~the calculated reactivity, obtained by the sum of OH reactants concentrations multiplied~~ calculated reactivities obtained by summing OH reactant concentrations and multiplying them by their reaction rate constants. A missing part, corresponding to the difference ~~in~~ between measured and calculated OH reactivity, is found not only under urban or biogenic conditions but also in clean remote regions. ~~OH reactivity measurements made~~ Measured OH reactivity in urban areas ~~proved to be in agreement~~ has been shown to be similar (less than 10%) ~~with the~~ to calculated OH reactivity in New York (Ren, 2003), in Houston (Mao et al., 2010) ~~or in a urban controlled environment (Hansen et al., 2015b)~~and in a controlled urban environment (Hansen et al., 2015a) . However, discrepancies in urban areas have been ~~noticed between the measured and the~~ observed between measured and calculated OH reactivity in Nashville (Kovacs et al., 2003) (35% less for ~~the~~ calculated reactivity), in Mexico (Shirley et al., 2006) (25%) ~~or~~ and in Tokyo (Sadanaga, 2004) (25%). The differences between ~~the measured and the~~ measured and calculated total OH reactivity are even higher in forested areas. Di Carlo (2004) found ~~a missing~~ 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~~ Amazonian rainforest.

As ~~addressed~~ shown by Williams and Brune (2015), atmospheric models do not correctly simulate ~~the~~ observed total OH reactivity. Attempts to use ~~box models with~~ 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 ~~or 3D-models~~ 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 ~~proved to be insufficient but the reasons still remain unclear. This~~ but 40% of the measured OH sinks remained unexplained. The difficulty of getting models to represent OH reactivity could be partly due to ~~not yet discovered OH reactions~~ as yet non-discovered OH reaction pathways, and ~~thus~~ which are therefore not implemented in atmospheric models. OH recycling ~~during~~ by the isoprene oxidation chain in forest environments characterized by ~~lox~~ low NO_x ~~conditions~~ (sum of NO and NO_2) conditions (i.e. <1 ppb) was proposed to explain the uncertainties in the simulated HO_x (sum of OH and HO_2) budget (Lelieveld et al., 2008; Butler et al., 2008; Peeters et al., 2009; Pugh et al., 2010; Stone et al., 2011). However, Stone et al. (2011) studied several proposed OH recycling ~~mechanism~~ mechanisms present in the literature and found that biases from OH and HO~~2~~ $_2$ concentrations still exist whatever the mechanism. One possible issue in ~~the~~ total OH reactivity retrieval not mentioned by previous studies could lie in neglecting ~~the~~ turbulent motions in the transport of chemical compounds in the boundary layer~~, which can segregate chemical species and reduce~~. 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). In comparison, Pugh et al. (2011) and Dlugi et al. (2010) used direct isoprene and OH concentrations measurements with temporal resolution of a few seconds, fast enough to estimate the segregation of the compounds.

The atmospheric boundary layer has a turbulent structure characterized by strong and narrow updrafts surrounded by weak and large descending areas (Molemaker and Vilà-Guerau de Arellano, 1998; Schumann, 1989). ~~Considering passive scalars , Wyngaard and Brost (1984) found that the~~ Wyngaard and Brost (1984) considered passive scalars and found that surface bottom-up transport ~~is more important to~~ plays a more important role in the vertical diffusion than the entrainment zone top-down transport in a convective boundary layer. Updrafts in the boundary layer ~~create a~~ lead to the spatial discrimination of ~~pollutants~~ pollutant concentrations between thermals and their environment. This heterogeneity in chemical species redistribution ~~influence~~ influences the mean reaction rate obtained ~~considering averaged reactants~~ when considering averaged reactant concentrations (Vilà-Guerau de Arellano and Cuijpers, 2000). ~~By~~ Using an idealized simulation, Molemaker and Vilà-Guerau de Arellano (1998) ~~have shown~~ showed that, for a second-order reaction implying a top-down and a bottom-up species, reaction rates are maximum in updrafts near the surface and in downdrafts at the top of the boundary-layer. Segregation between VOC and the OH radical was first addressed by the numerical study of Krol et al. (2000) who investigated the turbulence effects on the mean reaction rates of these species. Ouwersloot et al. (2011) studied the inefficiency of turbulent mixing over heterogeneous surfaces and found that the highest reaction rates for isoprene and OH are located in thermals at the top of the boundary layer. The chemical reactivity of the boundary layer is ~~then~~ therefore determined by the ~~ability~~ capacity of turbulence to mix reactive species (Molemaker and Vilà-Guerau de Arellano, 1998). However, modelling and experimental studies investigating heterogeneities in the boundary layer have focused on OH radical concentrations rather than on OH reactivity due to the instrumental limitations discussed above.

Vertical motions associated with clouds and sea-breeze impact the atmospheric chemistry and pollution levels near the surface since they dilute ~~the~~ chemical species and increase the upward transport of surface emissions (Chen et al., 2012). ~~When updrafts lead~~ In the case of updrafts leading to cloud formation, Vilà-Guerau de Arellano et al. (2005) found a decrease of 10 to 50% of tracer mixing ratios averaged over the boundary-layer with respect to a situation without clouds due to the deepening of the boundary-layer. Clouds have multiple impacts on the atmospheric boundary layer as they induce ~~a~~ turbulent mixing of chemical compounds ~~, which modifies the~~ which modifies reaction rates. ~~Then, they decrease the~~ They also modify incoming solar radiation, which in turn ~~disturb the~~ disturbs photolysis reactions and ~~alter~~ alters the emissions of biogenic compounds, such as isoprene. Finally, they alter atmospheric chemistry due to soluble gas washout and chemical reactions occurring in cloud droplets.

Cloud cover over West Africa is an important feature of the African monsoon but is poorly represented by global models (Knippertz et al., 2011; Hannak et al., 2017). This could lead to overly low simulated clouds and overly high incoming radiation at the surface, implying excessively high diurnal temperature and relative humidity cycles over this region. The nocturnal low-level stratus was studied during the monsoon period at Parakou (Benin) by Schrage et al. (2007) with radiosondes. The authors found that turbulent processes are responsible for cloudy nights whereas clear nights are associated with a nocturnal inversion leading to the decoupling of the surface and lower atmosphere. Schrage and Fink (2012) investigated nighttime cloud formation. They observed that the presence of a nighttime low-level jet induces the shear-driven vertical mixing of moisture accumulated near the surface. This leads to stratus formation whose cover is likely to persist until the early afternoon when it breaks up to form cumulus clouds (Schrage et al., 2007; Schrage and Fink, 2012). However, studying the impact of this specific cloudy environment on the turbulent transport of chemical species in tropical West Africa has not been reported.

High resolution simulations which explicitly resolve the turbulent and convective advection terms were conducted ~~(Vilà-Guerau de Arella~~ ~~in order to asses~~ (Vilà-Guerau de Arellano and Cuijpers, 2000; Vilà-Guerau de Arellano et al., 2005; Ouwersloot et al., 2011; Kim et al., 2 to assess the impacts of clouds and the convective boundary layer on the mixing of chemical compounds. However, previous numerical studies on the impact of the turbulent mixing of chemical compounds ~~used mainly rather simple or little~~ mainly used relatively simple or only slightly more detailed chemical schemes ~~,~~ (e.g., Vilà-Guerau de Arellano and Cuijpers (2000) ,Vilà-Guerau de Arellano et al. (2005) and Ouwersloot et al. (2011)), resulting in possible limitations in the representation of the atmospheric chemistry. Besides, more recent studies by Kim et al. (2012) and Kim et al. (2016) used a more detailed chemical scheme derived from Mozart v2.2, allowing the formation of OH radicals initiated by peroxy radicals. This limits the spatial heterogeneities caused by the reactions consuming the OH radical.

The goal of this work is to evaluate the role of thermals on OH reactivity in the framework of a convective boundary layer with contrasted chemical environments in southern West Africa. ~~This region is characterized by high occurrence of low-level stratus and stratus deck poorly represented in climate models, leading to errors in radiative forcing (Schrage et al., 2007; Knippertz et al., 20~~ ~~. Two~~ It focuses in particular on investigating turbulence as a possible explanation of the discrepancies between calculated-measured OH reactivities mentioned in the literature. Two contrasted chemical regimes represented by a detailed chemical scheme are ~~contrasted in LES studies~~studied by using Large-Eddy Simulations. The first simulation is influenced by biogenic emissions whereas the second ~~one~~ is characterized by anthropogenic emissions representative of Cotonou (Benin) in the center of the domain. Based on a conditional sampling implemented in the model, the thermals are discriminated in these simulations, allowing the specific chemical regime inside thermals to be investigated. The model experiments are presented in section 2. ~~The section~~ Section 3 ~~present~~ presents the dynamical and chemical results for the two cases ~~and~~ while section 4 ~~the discussion on~~ presents the discussion relating to these results.

2 Simulation description

2.1 Model configuration

LES simulations are performed with the mesoscale non-hydrostatic atmospheric model Meso-NH ~~version 5.2.1~~ (http://mesonh.aero.obs-mip.fr/mesonh/) ~~, jointly developed~~ version 5.2.1, developed jointly by the Laboratoire d'Aérologie and the Centre National de le Recherche Météorologique ~~(?)~~(Lac et al., 2018). Cloud microphysical processes are represented by the ICE3 scheme (Pinty and Jabouille, 1998) that includes six different types of hydrometeors. The turbulence is solved by a 3-dimensional scheme using a prognostic equation for the turbulent kinetic energy (Cuxart et al., 2000) with the turbulent mixing length given by the mesh size. Surface processes and interactions with the atmosphere are simulated by the SURFEx model (Masson et al., 2013) coupled with Meso-NH.

The resolution used is ~~$50m * 50m$~~ 50m × 50m for a domain size of 10 km × 10 km (200 × 200 grid points)~~; the boundary conditions are cyclic~~. 10 km is the targeted mesh size of an increasing number of current large-scale chemistry models. Along the vertical, 121 levels are stretched from Δz = 20 m at the surface to 250 m on top of the domain at 20 km and the boundary conditions are cyclic.

The simulation is run for three days ~~whose~~ in which two days consist ~~in~~ of the spin-up for chemistry. ~~Each day uses the~~ The same dynamical conditions and ~~has~~ the same initial and forcing thermodynamical fields ~~. Results~~ are used for each day. The results are shown only for the third day and from 0600 to 1700 UTC (LT=UTC+1), when the convective boundary-layer is well developed. A passive scalar is emitted only during this part of the simulation with a constant emission rate and is used to determine the boundary layer height (see section 2.4.1). ~~Thermals~~ The thermals are identified by the conditional sampling method implemented in the model by Couvreux et al. (2010), which relies on a ~~radioactive-decay~~ first-order decay passive tracer mixing ratio ~~and vertical velocity anomalies.~~ emitted with a constant flux at the surface. In brief, in order to be considered as thermals, air parcels at a given altitude z must satisfy simultaneous conditions such as a positive vertical velocity anomaly $w' > 0$and tracer anomalies $sv'(z)$ greater than the standard deviation of the tracer concentration $\sigma_{sv}(z)$ and a minimum threshold $\sigma_{min}(z) = (0.05/z)\int_0^z \sigma_{sv}(k)dk$. In the cloud layer, a supplementary condition is that the grid box has to be cloudy. This passive tracer is emitted ~~starting~~ from the beginning of the third day of simulation.

~~Initial~~ The initial and forcing dynamical fields ~~come~~ are taken from Couvreux et al. (2014) who ~~studied by means of~~ used a single column model to study the representation of the diurnal cycles of meteorological parameters ~~in~~ at four observation sites in West Africa (Agadez and Niamey in Niger, Parakou and Cotonou in Benin). Here we focus on the "cloudy" regime of Couvreux et al. (2014), representative of the climate encountered close to the ~~Guinean Gulf~~ Gulf of Guinea. The vegetation present in our simulation is dominated by tropical crops and open shrublands (35% of the domain for each type), sea (15%), inland water (5%), wetlands (5%) and tropical grasslands (5%) and a high moisture content is prescribed with ~~a soil water index~~ soil water indexes of 0.7 and 0.74 for the surface and the ground, respectively. ~~Initial~~ The initial conditions and composite large-scale advections ~~are extracted from~~ were extracted from the ECMWF re-analysis (Agustí-Panareda et al., 2010) prepared for the AMMA campaign (Redelsperger et al., 2006). The present simulation ~~is~~ was initialized at 0600 UTC with stable initial conditions ~~, extracted from~~ extracted from the ECMWF AMMA reanalysis (black curve in Fig. 1b). The large-scale conditions from the ECMWF re-analysis ~~also~~ are weak in magnitude but includes sea-breeze circulations from the surface to 500 m, linked to moist and cool advection throughout the simulation, topped by the advection of dry and warm air from 1000 to 3000 m.

2.2 Chemical model setup

The ~~applied~~ chemical scheme ReLACS 3.0 (Reduced Lumped Atmospheric Chemical Scheme version 3.0) (Tulet et al., 2006) ~~,~~ applied is a reduced version of the Caltech Atmospheric Chemistry Mechanism (CACM) (Griffin, 2002). This mechanism describes the ~~reactions system of ozone gaseous~~ reaction system of gaseous ozone precursors as well as of Secondary Organic ~~Aerosol~~ Aerosols (SOA) with 365 reactions involving 87 species.

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 ~~(Table 1)~~ in the north of Benin (10.13^{o}N, 2.69^{o}E) during the early afternoon (Stone et al., 2010).

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~~. A maximum value of 10 ng.N.m^{-2}.s^{-1} is prescribed for nitrogen oxide emissions by soils in the simulation~~, which is not available in this inventory. Biogenic NO$_x$ emissions from the GEIAv1 (Global Emission InitiAtive) inventory (Yienger and Levy, 1995) ~~were~~ proved to be too low for the ~~studied region~~ 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.

The emissions are constant in space and time except for NO, isoprene and monoterpenes, for which a ~~gaussian~~ Gaussian diurnal cycle is used. For biogenic NO, the maximum emission ~~is~~ occurs at 1300 UTC and the standard deviation of the ~~gaussian~~ Gaussian curve is equal to 3 hours~~, these~~. These parameters are set in order to approximate the ground temperature ~~as~~ since Mamtimin et al. (2016) and Yienger and Levy (1995) noted that NO emissions from soils are closely linked to soil temperature. For isoprene and the sum of monoterpenes (represented as ISOP, BIOL and BIOH in the chemical scheme), the maximum ~~is~~ occurs at 1200 UTC and the standard deviation is equal to 2.5 hours, chosen to fit the diurnal evolution of the solar radiation reaching the surface. This is in agreement with Guenther et al. (1991), who showed that isoprene emissions are thought to be ~~very low when the~~ null when Photosynthetically Active Radiation ~~decreases.~~(PAR) is equal to zero and maximum when the PAR exceeds the value of 1000 μmol.m^{-2}.s-1. For isoprene and monoterpenes, the maximum emission values were defined to ensure that an equal amount of chemical species is emitted ~~during~~ over one day compared to the constant value provided by MEGAN-MACC.

The anthropogenic emissions are provided by a squared patch in the center of the domain. Its area is chosen ~~to be~~ as equal to half the domain area. However, the cyclic boundary conditions applied for these simulations tend to homogenize the chemical mixing ratios. This ~~affects especially~~ especially affects long-lived species in the boundary layer and leads to the deletion of the biogenic ~~emissions signature. Values~~ emission signature. The values of anthropogenic emissions are representative of Cotonou (Table 2) (Junker and Liousse, 2008).

In the following, the study focuses on isoprene for the biogenic case because it is the major biogenic VOC emitted ~~to~~ into the atmosphere and influences ~~the~~ ozone and secondary organic aerosol formation (Guenther et al., 2006). For the anthropogenic case, ~~a focus is made on~~ attention is given to the lumped C>2 aldehydes (ALD2 in the chemical scheme) because they have both primary and secondary sources and their role is very important in the troposphere as they contribute to the production of radicals and are precursors of ozone (Williams et al., 1996).

2.3 Metrics

In order to study the competition between chemical reactivity and turbulent mixing, ~~as well as the~~ and inhomogeneity in chemical species mixing ratios, Schumann (1989) introduced two dimensionless numbers~~,~~ : the Damkhöler number and the segregation coefficient. The first ~~one~~ corresponds to the ratio between the ~~turbulence characteristic~~ characteristic turbulence timescale τ_{turb} and the chemical reactivity timescale τ_{chem}. For a given compound A, the Damkhöler number D_a is :

$$D_a(A) = \frac{\tau_{turb}}{\tau_{chem}(A)} \text{ with } \tau_{turb} = \frac{w^*}{h} \text{ and } \tau_{chem}(A) = \frac{r_A}{\sum sinks(A)} \tag{1}$$

Where w^* and h refer to the convective velocity and the boundary-layer height, r_A is the mixing ratio of A and $\sum sinks(A)$ corresponds to the total chemical loss rate of A. ~~Schumann (1989) used a threshold value of 0.1 for the Damkhöler number to distinguish slow (lower than~~ The convective velocity is computed with g, the standard acceleration due to gravity, and θ, the potential temperature, according to the relation $w^* = (\frac{g}{\theta} \cdot (\overline{w'\theta'_{v,s}}) \cdot h)^{1/3}$ where $\overline{w'\theta'_{v,s}}$ stands for the buoyancy flux at the surface. 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 $D_a > 0.1$~~) and fast (higher than 0.1) reactions~~. Later studies ~~(Vilà-Guerau de Arellano and Cuijpers, 2000; Vilà-Guerau de Arellano et al., 2005; Molemaker and Vilà-Guerau de Arellano, 1998) used a threshold value of 1 to~~ (Molemaker and Vilà-Guerau de Arellano, 1998; Vilà-Guerau de Arellano and Cuijpers, 2000; Vilà-Guerau d have shown that the impacts of turbulence on atmospheric chemistry are expected to be maximum when $D_a \geq 1$. Therefore, this value will be used in the following to discriminate slow and fast chemical reactions ~~and this method will be used in the following~~in the boundary layer. If $D_a < 1$, then the turbulent mixing is more efficient than the chemistry. If $D_a \simeq 1$, ~~one can expect strong competition~~ strong competition can be expected between dynamics and chemical reactivity. Finally, if $D_a > 1$, the chemical reactions occur faster than turbulent mixing. ~~This~~

The turbulent mixing causes fluctuations of chemical ~~specie~~ species mixing ratios in the LES domain, which can be quantified by the intensity of segregation. For a second order reaction ~~implying~~ involving two species A and B with a reaction constant k: $A + B \rightarrow C$, the intensity of segregation $I_S(A,B)$ is defined as:

$$I_S(A,B) = \frac{\overline{a'b'}}{\bar{a}.\bar{b}} \tag{2}$$

The lower case letters represent species mixing ratios at a grid point. The overbar denotes a spatial average, and the prime a deviation from this average. If $I_S(A,B) = -1$, then the two species are completely segregated and no reaction will take place between them. If $I_S(A,B) = 0$, the compounds are perfectly mixed. A positive segregation coefficient means that the covariance between species is similar and thus the mean chemical reaction rate would be higher in comparison to ~~a~~ perfect mixing. The segregation is calculated with mixing ~~ratios~~ ratio anomalies related to spatial averages in numerical models. Ouwersloot et al. (2011) stated that these averages should correspond to the complete mixing volume in order to allow comparisons between models and measurements. In the following, the large-scale spatial average is calculated over the 10 km x 10 km model domain. ~~One can define an~~ An effective average reaction rate ~~$\overline{R}$~~ R_e can be defined that includes the ~~turbulent mixing impact on the~~ impact of turbulent mixing on chemical reactivity as:

$$R_e = k_e \cdot \overline{a} \cdot \overline{b} \text{ with } k_e = k \cdot (1 + I_S(A,B)) \tag{3}$$

Here, k$_e$ is the effective mean reaction constant~~and bars over species denote averages over the domain.~~. In the current LES experiments, chemical reaction rates are calculated with a focus on OH. ~~The~~ OH radical reactivity R_{OH} corresponds to the inverse of OH lifetime τ_{OH} and is defined as:

$$R_{OH} = \frac{1}{\tau_{OH}} = \sum_i^n k_{(\chi_i+OH)} \cdot \chi_i \tag{4}$$

In Equation 4, $k_{(\chi_i+OH)}$ represents the reaction constant between OH and the ~~i-th~~ i-th reactant, and χ_i corresponds to its concentration. ~~In a similar way than~~ As with the effective reaction constant R$_e$, ~~an~~ effective reactivity for the OH radical R$^e_{OH}$ is defined by including the effect of turbulent mixing in Equation 4 as:

$$R^e_{OH} = \sum_i^n k^e_{(\chi_i+OH)} \cdot \chi_i \tag{5}$$

$$= \sum_i^n k_{(\chi_i+OH)} \cdot (1 + I_S(OH,\chi_i)) \cdot \chi_i \tag{6}$$

$$R^e_{OH} = R_{OH} + \sum_i^n k_{(\chi_i+OH)} \cdot I_S(OH,\chi_i) \cdot \chi_i \tag{7}$$

R_{OH} denotes the OH total reactivity calculated with averaged values. In order to obtain the relative deviation of the total OH reactivity from the reactivity computed with averaged mixing ratios, ~~a~~ factorization is performed on Equation 7, which results in:

$$R^e_{OH} = R_{OH}.(1 + \frac{\sum_i^n k_{(\chi_i+OH)} \cdot I_S(OH,\chi_i) \cdot \chi_i}{R_{OH}}) \tag{8}$$

$$R^e_{OH} = R_{OH}.(1+E_{R_{OH}}) \tag{9}$$

From Equation 9 the mean relative error, ~~$E_{k_{OH}}$, made on the~~ $E_{R_{OH}}$, found on total OH reactivity ~~only considering~~ considering only averaged values is :

$$E_{R_{OH}} = \frac{\sum_{i}^{n} k_{(\chi_i+OH)} \cdot I_S(OH,\chi_i) \cdot \chi_i}{R_{OH}} \tag{10}$$

The segregation intensity used to compute the mean error corresponds to ~~deviation from boundary layer averaged~~ the deviation from the averaged boundary layer values. This error ~~is~~ on OH reactivity was not considered in previous numerical studies ~~looking at the identification of the~~ 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, 2016) could lead~~ 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 $E_{R_{OH}}$. If $E_{R_{OH}}$ is positive or negative, then the effective OH reactivity R^e_{OH} 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.

2.4 Simulation assessment

2.4.1 Dynamics

The diurnal evolution of the boundary-layer height (BLH) is analyzed in Fig. 1a. It is diagnosed ~~from~~ using two different methods. The first ~~one~~ corresponds to a determination according to the bulk Richardson number method as presented in Zhang et al. (2014). The boundary layer height is defined as a threshold value for the bulk Richardson number Ri_b, ~~which is~~ computed at a given height with the virtual potential temperature θ_v and horizontal wind speeds u_z and v_z at this altitude and at the surface:

$$Ri_b = \frac{(g/\theta_{v0})(\theta_{vz}-\theta_{v0})z}{u_z^2+v_z^2} \tag{11}$$

A clear diurnal cycle is observed, with the maximum height ~~being~~ at 1400 UTC and the minimum during nighttime (Fig. 1a, red line). This first diagnostic did not include the cloud layer on the boundary layer. Daytime BLH is consistent with observations from Cotonou in West Africa studied by Gounou et al. (2012), who noticed daily variabilities ranging from 400 to 600 m ~~. In this work~~ (Fig. 1a, black dots). In Gounou et al. (2012), the boundary-layer height is derived from ~~radiosoundings~~ radio soundings by comparing the virtual potential temperature at one level and the averaged value below. ~~The LES Meso-NH model fails to reproduce the observed shallow nocturnal BL of about 100 m deep during the AMMA campaign. Couvreux et al. (2014)~~

~~explained the very low nighttime BL by the strong stratification in the model. This first diagnostic does not include the cloud layer on the boundary layer~~The slight differences between the simulated BLH and observations reveal the same biases noticed in the 1D-simulation performed by Couvreux et al. (2014). This may be explained by uncertainties on the derivations of large-scale advection fields.

The second method determines the boundary layer height according to Vilà-Guerau de Arellano et al. (2005) by identifying the height at which a passive bottom-up scalar emitted ~~the third day~~ at the surface is equal to 0.5% of its surface value. Kim et al. (2012) mentioned that this definition could be valuable when studying ~~the~~ boundary layer deepening due to clouds. This diagnostic ~~captures~~ captured the growth of the boundary layer height due to the development of cumulus clouds (Fig. 1a, blue line) and is used to mark the BL height in the following. The tracer used for this diagnostic was emitted only during the period of interest, from 0600 to 1800 UTC.

The range of simulated virtual potential temperature (Fig. 1b) ~~slightly~~ overestimates the AMMA observations in Cotonou of Gounou et al. (2012) in the lowest 500m, as shown by Couvreux 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. Both the dry and cloudy layers are identified by two inflections on the vertical profiles of the virtual potential temperature (Fig. 1b). The first inflection increases from 400 m at 0600 UTC to 600 m at 1700 UTC~~corresponds~~, corresponding to a thin inversion zone between the well-mixed dry layer and the cloudy layer above it. The second inflection defines the top of the boundary layer ranging from 500 m at 0600 UTC to 1600 m at 1700 UTC.

~~Cloud cover over~~ The southern part of West Africa is ~~an important feature of the African monsoon but is poorly represented by global models (Hannak et al., 2017). This could lead to too low simulated clouds and too high incoming radiation at the surface that imply too high diurnal cycles of temperature and relative humidity over this region. The nocturnal low-level stratus have been studied during the monsoon period at Parakou (Benin) by Schrage et al. (2007) with radiosondes. The authors found that turbulent processes are responsible for cloudy nights whereas clear nights are associated with a nocturnal inversion promoting the decoupling of surface and lower atmosphere. Schrage and Fink (2012) investigated the nighttime cloud formation. They stated that the presence of a nighttime low-level jet induces a shear-driven vertical mixing of moisture accumulated near the surface. This leads to cloud formation whose cover is likely to persist until the early afternoon (Schrage et al., 2007; Sc~~ a region characterized by high diurnal variability in cloud occurrence. Low-level stratus clouds form during the night and persist in the morning, these stratus then break up during the afternoon into cumulus clouds (Schrage et al., 2007). This feature is simulated in this work as low level stratus clouds that occupy a large fraction of the simulated domain in the morning (Fig. ~~1a and 2a ;2~~2a and c). In the afternoon, the cloud deck breaks up and less uniform but higher cumulus clouds are simulated (Fig. ~~1a, 2c~~ 2b and d).

Throughout the growth of the boundary layer, dry thermals develop capped by the temperature inversion zone. Some thermals penetrate this inversion (Fig. 2) and cloud formation ~~occur~~ occurs at the upper part of the updrafts. The vertical profiles of the fraction area (Fig. 3) occupied by thermals exhibit a local maximum at the height corresponding to the separation between the two layers. This altitude is variable through the simulation but tends to stabilize between 500 and 600m in the early afternoon and is associated ~~to a favored~~ with a preferential detrainment zone. The peaks observed at the surface and at the top of the cloudy layer correspond to two ~~others~~ other local maxima. Due to the deepening of the boundary-layer, the top of the cloudy layer ~~is increasing~~ increases throughout the simulation (Fig. 2,3). Simulated convective velocity w^* ~~(resp.~~ ranges from $1cm.s^{-1}$ in the morning to $1m.s^{-1}$ at midday, and the turbulence characteristic timescale τ_{turb} ~~) ranges from $1cm.s^{-1}$ (resp.~~ from $6h$ ~~)~~ in the morning to ~~$1m.s^{-1}$ (resp.~~ 20 min ~~)~~ at midday.

2.4.2 Atmospheric chemistry

Typical diurnal cycles are obtained for isoprene in the biogenic case and for OH in the biogenic and anthropogenic cases ~~,~~ ~~where~~ in which both compounds exhibit maximum mixing ratios around midday (Fig. 4). For the biogenic case, the simulated isoprene mixing ratios averaged from the surface to 600 m reach a maximum close to 1 ppbv (Fig. 4a) at noon, when isoprene emissions are ~~the highest. It is on~~ highest. This is in the same range as the AMMA measurement studied by Saxton et al. (2007), who found a maximum of 1.5 ppbv on the composite diurnal cycle of isoprene at midday. In our study, the ozone mixing ratios ~~do~~ did not exhibit strong variability throughout the day. The simulated values around 18 ppbv ~~are lower than observations collected~~ were lower than the observations recorded over forested areas (Table 3), ranging from 22 to 30 ppbv. The NO_x mixing ratios ~~are~~ were close to 0.2 ppbv on average around midday (Fig. 4b) and are in agreement with AMMA measurements where a mean value of 0.1 ppbv of NO_x ~~has been~~ was observed. Simulated OH mixing ratios ~~vary~~ varied between 0 and 0.18 pptv (Fig. 4a), within the observational range of 0.05 to 0.15 pptv during the AMMA campaign (Table 3). The biogenic environment is characteristic of a limited NO_x ~~limited~~ regime.

The chemical regime induced by the anthropogenic emissions is contrasted with the previous biogenic case (Fig. 4c ~~,~~ and d), including NO_x emissions nearly forty times higher at 1300 UTC. ~~Averaged~~ The averaged NO_x mixing ratio ~~is~~ was 1.5 ppbv at midday (Fig. 4d), which is similar to the averaged value of 1 ppbv measured during a flight over Cotonou during the AMMA campaign (Table 3). The increase in NO and NO_2 ~~leads to important~~ led to considerable oxidant formations. OH mixing ratios ~~vary~~ varied between 0 and 0.40 pptv in the simulation, in agreement with the AMMA measurements ranging from 0 to 0.50 pptv over Lagos (Table 3). Ozone ~~is~~ was produced throughout the simulation but ~~does~~ did not exhibit strong spatial variabilities. Its mixing ratios ~~vary~~ varied from 17 ppbv in the morning to 82 ppbv in late afternoon. This ~~is higher than observations collected~~ was higher than the observations recorded over several cities in West Africa, varying between 26 and 40 ppbv (Table 3). ALD2 ~~is continuously increasing~~ increased continuously during this case through chemical production and emissions (Table 2). Its mixing ratios ~~range~~ ranged from less than 1 ppbv in the morning to 11 ppbv at the end of the simulation. Unfortunately, no ~~C>2 aldehydes~~ aldehyde observations, except formaldehyde, were available from the AMMA experiment despite the use of a PTR-MS due to interferences during the measurements for m/z=45 identified as acetaldehyde (Murphy et al., 2010).

A minimum of NO~~is~~$_x$ was found around 1200 UTC for both cases ~~. At that time, NO is~~ and can be explained by two factors. The first is dynamical and is linked to the boundary layer. In the middle of the simulation, the boundary layer growth was maximal and induced dilution in a larger mixing volume. The second factor was chemical because at that instant, NO was efficiently converted into NO_2. However, NO_2 chemical transformations in ~~reservoir species such as peroxy pentionyl nitrate (PAN1 in the chemical scheme), peroxy acetyl nitrate (PAN2) or HNO4~~ a reservoir such as HNO_3, HNO_4 or PANs are net sinks for NO_2. The chemical balance between reservoir species and NO_2 ~~represent~~ represented 2.12% of the net destruction of NO_2 averaged over the domain at 20 m and 1200 UTC for the biogenic case, and 34.2% for the anthropogenic case. ~~As a consequence,~~ For both cases, the main reservoirs of NO2 were PAN1 and PAN2. Therefore, less NO_2 ~~is available to convert~~ was available for conversion into NO, which ~~explain the midday~~ explains the low NO mixing ratios at midday (Fig. 4b and d).

3 Vertical transport and chemical reactions in the convective boundary layer

3.1 Impact of turbulent mixing on the OH reactions

3.1.1 Vertical transport and Damkhöler numbers

Isoprene is highly reactive, especially towards OH, and is rapidly consumed in the boundary layer linked to its chemical lifetime τ_{ch} approximately equal to 30 ~~mn~~ min in the biogenic case. The Damkhöler number of isoprene is close to 1 (Table 4), indicating that the isoprene chemical lifetime is comparable with the timescale of turbulent mixing. This implies that chemical reactions and turbulent mixing are competing processes for this compound. Isoprene is both transported and consumed inside the thermals and ~~exhibit~~ exhibits vertical and horizontal gradients (Fig. 5a). ~~Average~~ The average profiles of isoprene ~~are decreasing~~ decrease with altitude (Fig. 5a). The lower mixing ratios ~~on the dashed line, denoting updrafts-free region,~~ in the updraft-free region (dashed line) are close to the domain averaged values due to ~~the~~ domain coverage by thermals (Fig. 3). ~~Updrafts regions contain isoprene higher mixing ratios and anomalies are consequent~~ Updraft regions contain higher isoprene mixing ratios with significant anomalies over the whole boundary layer~~.~~, although decreasing with altitude.

For the biogenic case, OH has a very short chemical lifetime of the order of 0.2 s. The OH radical ~~reaches rapidly a chemical equilibrium and is nearly~~ rapidly reaches steady state and is relatively undisturbed by the turbulent mixing~~as shown~~, as evidenced by its large Damkhöler number (Table 4). ~~As a consequence~~Therefore, OH mixing ratios (Fig. 5b) ~~has nearly~~ have almost homogeneous values below 600 m with no distinction between thermals and their environment. Average ~~profiles of OH~~ OH profiles (Fig. 5b) ~~shows~~ show no strong variability below 600 m in the boundary layer. Above this height, ~~thermals are less concentrated in OH on average but differencesare relatively low~~the thermals have lower OH concentrations on average with relatively small differences. The differences between thermals and their surroundings are more pronounced in the cloudy layer because clouds arise from air parcels transported by thermals and characterized by lower OH mixing ratios than the rest of the domain. Since OH is almost constant over the boundary layer, the highest reaction rate for the oxidation of isoprene by OH ($k_{OH+ISOP}\,[ISOP]\,[OH]$) is located where the isoprene mixing ratios are the highest. This implies that both the surface and air lifted by thermals are preferential reaction zones in the boundary layer.

For the anthropogenic simulation, ~~ALD2 reaction rate~~ the reaction rate of ALD2 with OH is lower than the reaction rate of OH with isoprene. Its calculated Damkhöler number ($\approx$ 0.17) indicates that turbulent mixing dominates over chemical reactions (Table 4). Consequently, ALD2 is efficiently transported by updrafts (Fig. 5c). The contrast between concentrated air parcels lifted ~~up~~ upwards by thermals and relatively diluted air outside is illustrated by the large differences in the ALD2 average profile in thermals and in the environment (Fig. 5c). ~~Similarly to~~ As with isoprene in the biogenic case, ~~two local~~

~~maxima are present 600 and 1100m, representing~~ the two-layer structure presented above ~~.~~ is present on the vertical profiles. It results from the mixing in the sub-cloud layer and from the mixing within clouds.

OH mixing ratios are nearly twice ~~higher~~ as high in the anthropogenic environment ~~than~~ as in the biogenic case~~. That induces~~ , inducing a more reactive atmosphere and a ~~lower~~ shorter chemical lifetime for species whose OH is the main sink in the boundary layer. OH has a very ~~low~~ short chemical lifetime of 0.07s in this simulation, which represents a large Damkhöler number close to 12 000. OH mixing ratios are ~~maximum~~ maximal in thermals (Fig. 5d) due to the transport of OH precursors, such as NO$_x$, and fast ~~chemical equilibrium~~steady state. Conversely, lower mixing ratios ~~on OH average~~ in average OH profiles (Fig. 5d) ~~corresponds~~ correspond to regions without updrafts, leading to strong OH anomalies ~~inside updrafts~~ within updrafts from the surface to the top of clouds.

3.1.2 Vertical profile of segregation intensity

Negative values of segregation ~~coefficient~~ coefficients up to -30% are calculated at the top of the cloudy boundary layer from 1000 to 1700 UTC which means that OH and isoprene are partly segregated in this frontier zone. In other words, ~~a well mixed atmosphere hypothesis would conduct~~ the hypothesis of a well-mixed atmosphere would lead to a 30% overestimation of the reaction rate at the frontier between the boundary layer and the free troposphere. The negative segregation ~~means covariances~~ (Eq. 2) means the anomalies of isoprene and OH ~~are of opposite signs(Eq. 2).~~ have opposite signs, as shown in figure 5a. This is due to lower OH mixing ratios in thermals than ~~the environment.~~ in the environment (Fig. 5b). These results are consistent with the previous studies of Li et al. (2016); Kim et al. (2016); Ouwersloot et al. (2011) (see Discussion).

In the biogenic case, isoprene anomalies in thermals are ~~important~~ considerable from the surface (+0.48 ppbv on average at midday) to the top of the boundary layer (+0.1 ppbv on average at midday) and are thought to be always positive as ~~it~~ OH is uniformly emitted at the ground (Fig. 5a). On the ~~opposite~~contrary, OH mixing ratios are almost constant in the boundary layer at 1200 UTC (Fig. 5b), so the magnitude of ~~its~~ OH anomalies are expected to be low (-0.03 pptv on average at midday at the top of the boundary layer). Besides, due to its very short chemical lifetime~~induces that OH is quickly in~~ , OH quickly reaches equilibrium with its surroundings, ~~which implies~~ implying that its fluctuations are mostly due to thermals transporting air originating from ~~a different chemical environment~~different chemical environments. Thus, isoprene anomalies are thought to be the major driver ~~in segregation magnitude~~ of the magnitude of segregation over the boundary layer whereas changes in OH anomalies are related to changes in the segregation sign.

Positive values around +5% are calculated at 700 meters starting from 1400 to 1800 UTC (Fig. 6a). The ~~segregation intensity become~~ intensity of segregation becomes positive due to positive anomalies of both compounds. Due to ~~the decreasing~~ decrease in isoprene emissions in the afternoon, OH destruction slows down, especially inside thermals. They are still active ~~to transport~~ in transporting enough NO to react with HO$_2$ to produce OH, ~~which induces~~ inducing higher OH mixing ratios inside updrafts than in the surroundings (+0.02 pptv on average at 1600 UTC).

Before 0900 UTC near the surface, the segregation coefficient in the anthropogenic simulation between OH and ALD2 is negative up to -8% in the lower 200m (Fig. 6b), due to the anthropogenic emission patch. As chemical equilibrium is not yet reached, more of the OH radical is destroyed through its reaction with recently emitted compounds than that which is produced (not shown). This means that OH is less concentrated inside updrafts at that moment so its anomalies are negative near the surface. Simultaneously, positive segregations develop at the top of the boundary layer from 0700 UTC to 1230 UTC with a maximum of 16% at 1000 UTC and from 1530 to 1730 UTC. The positive segregation is related to the concomitant transport of ALD2 and precursors of OH by thermals. Moreover, the high segregation values correspond to the presence of clouds between 0.6 and 0.9 km (Fig. 2c), simultaneously with a high cloud fraction over the domain (>0.6) (Fig. 6b). This specific point is discussed in the discussion section. As ALD2 is emitted at the surface, ~~thus~~ its anomalies are high and positive inside updrafts. ~~As an~~ For example, at midday, anomalies are +0.5 ppbv on average at the surface and nearly +4 ppbv at the top of the boundary layer. However, in this case, OH anomalies are more difficult to predict ~~.~~ due to the spatial heterogeneities of chemical emissions. Local changes in OH production and destruction explain the changes in the segregation sign throughout the simulation. Except for positive segregation simulated between 500 and 1400 m from 1130 to 1600 UTC with values ranging from 2 to 4%, ALD2 and OH can be considered ~~well mixed~~ well-mixed in the central part of the boundary layer. The ALD2 oxidation reaction by OH is accelerated up to 16% at the top of the cloudy layer from the morning to the early afternoon compared to a perfect mixing assumption.

Regarding the two simulations, the segregation has both spatial and temporal variations. The maximum values of the segregation coefficient are calculated near the top of the boundary layer. Below and during daytime, the considered species are ~~well mixed~~ well-mixed for both cases. ~~It means that~~ This means that in the biogenic environment, the highest decrease induced by the thermals of isoprene + OH reaction is located near the top of the boundary layer. It also implies that in the anthropogenic environment, the highest increase induced by the ~~highest decrease (resp. increase) induced by~~ thermals of isoprene ~~(resp.~~ and ALD2 ~~)~~ + OH reaction is also located near the ~~boundary layer top~~top of the boundary layer.

3.2 OH budget and reactivity in a convective boundary layer

The ~~precedent part emphasizes the non uniform~~ 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 ~~implication for the reaction~~ modification of the reactions rates between these species. However, this feature ~~has to be accounted~~ must be taken into account for every OH ~~reactants~~ reactant in order to ~~have~~ obtain the full picture of ~~the~~ total OH reactivity and ~~understand~~ gain insight into how the Meso-NH model ~~compute~~ computes the OH budget in different chemical regimes.

3.2.1 OH budget in thermals versus ~~environment~~surroundings

In order to identify and quantify the major OH sources and sinks in the boundary layer, the instantaneous chemical budget of OH at 20 meters above ground level is investigated at 1200 UTC for both environments (Fig. 7). This height is the first ~~model level and allows a comparison between the results from the simulations and from~~ level in the model and computing the chemical budget at this height leads to uncertainties due to subgrid-scale mixing and chemistry (Vinuesa and Vilà-Guerau de Arellano, 2005) . However, it makes it possible to compare the model results with the measurements in the literature.

The budget distinguishes between ~~updrafts and updrafts-free~~ updraft and updraft-free columns. Percentages are related to the fraction of the overall production and destruction ~~in~~ within or outside thermals. In the biogenic case (Fig. 7a), the OH budget is dominated by its destruction by isoprene oxidation (41.7% of the total loss in updrafts and 29.3% of the total loss in the rest of the domain) and its production by ~~peroxy radicals reaction~~ the reaction of peroxy radicals with HO_2 (37.2% of its total source in updrafts and 42.4% of the total source in ~~non updrafts~~non-updrafts) and NO reaction with HO_2 (32.4% of the total source in updrafts and 17.8% of its total source in the rest of the domain). In ~~that~~ this case, the peroxy radicals are mainly formed by the oxidation of isoprene and its degradation products. The absolute value of OH reactivity is higher in thermals than in the rest of the domain.

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+HO_2 ~~and~~ (79.2% of its total source in updrafts and 71.2% of the total source in non-updrafts) and by O^1D+H_2O (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 ~~or~~ 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).

The chemical budget at 1200 m (Fig. 8), namely at the top of the boundary layer, allows the investigation of chemical reactions inside the ascending air parcel lifted by thermals and its comparison with its surroundings. For the biogenic case, the major OH reactants in the thermals have a chemical lifetime greater than the turbulence timescale. At this altitude, only species whose Damkhöler numbers are lower than 1 are present in sufficient amounts to react with the OH radical. For example, carbon monoxide (26.2% of total OH destruction in thermals and 36.6% in the surroundings) is the major sink, but also methane (11.8% of total OH loss in updrafts and 18.4% in the environment). Chemical compounds with a secondary source like formaldehyde and C>2 aldehydes (ALD2) are other important sinks at 1200m. Isoprene, the major OH reactant close to the surface, is present only in thermals at this altitude due to its reaction with OH in the ascending air parcel and consumes 11.8% of OH in thermals. OH production by NO+HO_2 reaction is null inside updrafts and low in the non-updraft area (3.2% of the total OH production) due to NO destruction in updrafts. The reaction between hydroxyl radicals RO_2, secondary products, with HO_2 is a major OH source in thermals (49.7% of total production) but also in the surroundings (36.1% of OH production in updraft-free region). Production of OH by $O^1D + H_2O$ or H_2O_2 photolysis are similar in magnitude in thermals and in the non-thermal areas. The production and destruction terms are higher in the thermals compared to these terms in non-updrafts due to higher concentrations of OH reactants inside the thermals, but lower than at 20m.

~~Similar results are obtained at 500 m (not shown)that confirm the higher chemical reactivity inside thermals compared to their environment~~Regarding the anthropogenic case, species whose lifetimes are higher than the turbulence timescale are major OH reactants at 1200m. Carbon monoxide contributes 22% of the OH destruction in thermals and 34.3% in the rest of the domain. As with the biogenic case, chemical compounds with a secondary source are important OH sinks like formaldehyde (11.1% in thermals and 11.0% in updraft-free regions) and ALD2 (26.4% of total OH destruction in updrafts and 11.8% in the surroundings), corresponding to the major OH destruction term at the top of the boundary layer. The OH production terms in the anthropogenic case are similar in thermals compared to the surface with a high contribution of NO + HO_2 reaction (66.9% of total OH production), followed by $O^1D + H_2O$ reaction (15.3%) and $RO_2 + HO_2$ (10.6%). In the rest of the domain, NO + HO_2 contribution drops to 16.9% while $O^1D + H_2O$ (32.8%) and $RO_2 + HO_2$ (31.1%) are major production terms.

The differences between the OH reactivity at the surface and the top of the boundary layer are mainly driven by the changes in chemical mixing ratios of precursors caused by chemical reactions and consequently by their Damkhöler number, and by the secondary products formed inside the thermals.

3.2.2 OH reactivity in the convective boundary layer

The OH reactivity for the biogenic case (Eq. 4) at 20 m is maximum around midday and is equal to 6.0 s^{-1}, 4.25 s^{-1} and 4.55 s^{-1} respectively in updrafts, non-updrafts and averaged over the domain (Fig. 9a). This feature is linked to the ~~photochemistry~~ photochemical maximum activity at noon, and the diurnal cycle of emissions amplifies this phenomenon. At that time and near the surface, many chemical compounds are available to react with OH, which leads to a high value of reactivity. The values in updrafts are higher than outside due to higher ~~reactants~~ reactant mixing ratios inside thermals (Fig. 5a). The ~~arithmetic~~ arithmetical difference between updrafts and non-updrafts ~~is~~ reaches a maximum at 1200 UTC and is about 1.75 s^{-1}. ~~As~~ However, as the thermals occupy less than 15% of the domain (Fig. ~~3~~ 3), the evolution of the domain-averaged OH reactivity is very similar to ~~these related to updrafts-free region~~that linked to updraft-free regions.

The diurnal cycle of OH total reactivity with a maximum around midday in a biogenic environment is well documented in ~~literature from~~ the literature on observations of OH reactivity for a Mediterranean forest (Zannoni et al., 2016), for temperate forests (Sinha et al., 2008; Ramasamy et al., 2016) ~~but also~~ and for tropical forests (Nölscher et al., 2016; Williams et al., 2016). The values of OH reactivity in or outside thermals in the present study are the lower ~~bound of measurements~~ bounds of measurements taken over forests and gathered in Yang et al. (2016), between 1 and 76 s^{-1}.

The mean relative error made on OH reactivity is calculated ~~following~~ by Equation 10 (~~not shown). It is generally~~ Fig. 10). This diagnostic includes the segregation, computed relative to the boundary layer averaged values, between OH and every one of its reactants in the chemical scheme. It is negative throughout the simulation, increases during the morning and is ~~maximum~~ maximal in the early afternoon with a peak at -9% at 1430 UTC. In other words, neglecting the segregation of reactive species by turbulent mixing in the boundary layer would ~~overestimate the~~ lead to overestimating OH reactivity by 9% at ~~the maximum~~ most in an environment dominated by biogenic emissions.

For the anthropogenic case, ~~the~~ total OH reactivity (Eq. 4) in thermals ~~or~~ and in the rest of the domain does not ~~display~~ present a clear diurnal cycle (Fig. 9b). From the 0800 UTC value of 11.6 s^{-1}, the domain-averaged OH reactivity fluctuates but tends to increase to 14.2 s^{-1} at 1600 UTC. The evolution of the OH reactivity in thermals is similar and ranges from 14.8 s^{-1} at 0800 UTC to 17.7 s^{-1} at 1600 UTC. For the same period, the values in ~~updrafts-free domain~~ updraft-free domains vary between 11 and 13.5 s^{-1}.

~~As a consequence of the increased OH reactants~~ The consequence of higher OH reactant mixing ratios in the boundary layer (Fig. 4c and d), ~~OH reactivity is higher~~ is higher OH reactivity in this case compared to the biogenic simulation.

The mean relative error of the OH reactivity (Eq. 10) is generally positive throughout the simulation (~~not shown~~Fig. 10). It ranges between 0 to 4% from 0900 to ~~1730~~ 1600 UTC with a maximum value of ~~6% at 1800~~ 4.5% at 1330 UTC. In ~~that~~ this case, the turbulent mixing induces a moderate increase up to ~~6~~4.5% of the total OH reactivity for two reasons. The segregation effect is limited to the last 200 m of the boundary layer. Thus averaging on the whole boundary layer ~~suppress~~ cancels the extreme values. Moreover, ~~some chemicals could have negative~~ chemicals have either negative or positive segregation towards OH that may compensate or increase the positive values simulated for ALD2 and OH (Fig. 6b).

In both cases, the occurrence and development of clouds (Fig. 6, upper panel) is concomitant with linear increases of the error made on the OH reactivity while neglecting the impact of turbulence (Fig. 10). The diurnal cycle of $E_{R_{OH}}$ in each case is correlated to the development of the convective boundary layer. Firstly, a rapid change occurs during the first hours of the simulations, characterized by the occurrence of thermals and an increase in chemical emissions for the biogenic environment. Then, $E_{R_{OH}}$ is relatively stable from the end of the morning to the middle of the afternoon, with a maximum value computed around 1400 UTC, corresponding to the maximum turbulent activity in the convective boundary layer.

4 Discussion

The redistribution of chemical species ~~in~~ by the boundary layer turbulence induces a different mean reaction rate between compounds when compared to a situation ~~where~~ in which chemical species would be perfectly mixed ~~. This~~ (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 ~~or~~ and large scale atmospheric models leads to errors on ~~chemical reactivity~~ 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 a biogenic environment characterized by low NO_x conditions, Kim et al. (2016) found negative segregation between isoprene and OH varying between -3% near the surface to -10% in the cloud layer due to increasing OH mixing ratios in thermals with altitude. That implied positive isoprene anomalies and negative ones for OH in the frontier region between the boundary layer and the free troposphere~~, these~~. These features are reproduced in our biogenic simulation ~~even though our values of segregation~~ although our segregation values are higher in the cloud layer (Fig. 6) due to sharper gradients of OH mixing ratios at the top of the cloudy layer.

Using a simple chemistry scheme of 19 reactions representing the basic reactions of O_3-NO_x-VOC-HO_x system, Ouwersloot et al. (2011) found an almost constant value of -7% for the segregation between OH and isoprene ~~over the amazonian forest~~ in the boundary layer ~~. It was the results~~ over the Amazonian forest. This was the result of positive isoprene anomalies due to transport by thermals and negative OH anomalies due to consumption therein. Negative segregation ranging from -2% to -5% inside the convective boundary layer ~~have been~~ was simulated by Li et al. (2016) and Kim et al. (2016). In the biogenic case ~~of our work,~~ in this study, the negative segregation of a few percent in the middle of the boundary layer is reproduced. ~~The discrepancies between this last simulation and the previous cited studies are partly due to differences between the convective boundary layer dynamics, resulting in different characteristics of turbulent structure. Moreover, using simple chemistry rather than a comprehensive chemical mechanism could lead to an insufficient representation of the OH chemistry. This results in neglecting some OH destruction reactions and eventually some OH recycling pathways. Besides,~~ As in this case, higher segregation values were simulated with altitude in Kim et al. (2016), especially in the cloudy layer. However, segregation computed in the cloudy layer in Kim et al. (2016) was equal to -0.1, a value lower to that computed in the biogenic case of the present study. The discrepancies in this study and Kim et al. (2016) are likely due to the vertical OH profiles. In the study by Kim et al. (2016), OH concentrations increased linearly with altitude. This implies lower OH covariances for ascending air parcels and thus lower segregation values (Eq. 2). On the contrary, in the present study, OH is relatively homogeneous in the boundary layer and a strong gradient is present only at the top of the boundary layer. This induces high covariances for OH concentrations inside air transported by thermals at the top of the boundary layer, implying higher segregation values. As segregation computed by Li et al. (2016) is not available above 1000m height, a direct comparison with results regarding the cloudy layer is not possible with the results from the biogenic case. The positive values of segregation simulated in the afternoon (Fig. 6a) in the biogenic case are not reproduced in other studies and might be the result of efficient OH recycling in ReLACS 3.0, initiated in particular inside the thermals due to peroxy radicals formed by isoprene oxidation. Indeed, this recycling is either absent or indirect in previous works like in the mechanism used by Kim et al. (2016) that produces only HO_2 from peroxy radicals, which may explain the discrepancies in OH covariances. Furthermore, Ouwersloot et al. (2011) and Kim et al. (2016) investigated the sensitivity of segregation to NO_x. It was found that different NO_x levels imply ~~discrepancies~~ differences in the segregation of OH and other compounds as they contribute to ~~the~~ OH production.

~~The segregations between isoprene and OH inferred from observations are higher than numerical studies calculated. Butler et al. (2008) found a segregation close to -13% over a forest in Suriname and Dlugi et al. (2010) calculated over a deciduous forest a reduction of 15% in the effective reaction rate between OH and isoprene at the surface due to incomplete mixing. This is higher than the segregation computed at the surface in the biogenic case of the present study but when considering the complete mixing volume, the segregation computed with boundary layer averaged mixing ratios is negative and its maximum value is -16% at 1300 UTC.~~

~~Kim et al. (2012) studied by means of a LES the~~ Kim et al. (2012) used LES to study the OH budget in a biogenic environment averaged over the domain and over time from 1330 to 1430 LT with a chemical scheme adapted from MOZART v2.2. ~~They found, for~~ For a low NO_x case with ozone mixing ratios close to 64 ppbv, ~~that the~~ they found that OH production was mostly influenced by four predominant reactions (including O^1D + H_2O, HO_2 + O_3, H_2O_2 photolysis and HO_2 + NO). ~~They found that the~~ These production terms are present in the biogenic case of the present study. However, Kim et al. (2012) did not take into account recycling by peroxy radicals as the latter formed only HO_2 in the chemical scheme they used. Moreover, they found that OH loss by reaction with isoprene was dominant near the surface, followed by ~~the~~ reactions with CO and formaldehyde~~. The OH reactivity contribution of the BVOC species~~ , as in the present study. The contribution of BVOC species to OH reactivity was simulated by Li et al. (2016) for three distinct biogenic cases of the DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) campaign. ~~Isoprene was~~ The production terms of OH were not available but it was found that isoprene was a dominant sink for OH~~,~~ ; about 25-30% of the OH reactivity was linked to BVOC reactions at 0.3 km during midday. This contribution is comparable to the percentage calculated for isoprene in the OH destruction in thermals (41.7%) or in an updraft-free area (29.3%). The contribution of formaldehyde was comparable to isoprene at that height, with HCHO mixing ratios ranging from 2 to 4.5 ppbv at the surface. The higher formaldehyde contribution of Li et al. (2016) is the result of higher concentrations than in the current work.

Yang et al. (2016) found that in forest areas the OH budget was largely dominated by isoprene and its oxidation products. ~~As an example, over a Mediterranean forest, Zannoni et al. (2016) measured the OH reactivity , as well as~~ For example, Zannoni et al. (2016) measured OH reactivity and the concentration of biogenic compounds over a Mediterranean forest. They found that isoprene was the dominant sink for OH and ~~contributes~~ contributed up to 74% of ~~OH total~~ total OH reactivity during daytime due to its high reactivity towards OH and its high concentration over the forested area. ~~The isoprene~~ Isoprene predominance in OH loss ~~is~~ was reproduced in the OH budget of the biogenic environment of the present study, ~~as well as~~ and for carbon monoxide. ~~Formaldehyde mixing ratios are~~ The formaldehyde mixing ratios were close to 2 ppbv, which explains that this is not a ~~important sink as~~ major sink like isoprene, but remains ~~not negligible in the OH loss . The~~ important for OH loss through the reaction OH+HCHO. OH production in the biogenic case ~~is~~ was similar to Kim et al. (2012), as almost the same production terms are present. However, ~~the overall production is dominated by peroxy radicals reaction~~ overall production was dominated by the reaction of peroxy radicals with HO_2 and the ozone mixing ratios of 18 ppbv decrease the importance of O^1D + H_2O source for OH.

However, the mechanism used to represent atmospheric chemistry in our simulation has ~~a~~ fast OH cycling ~~through~~ due to the reaction of peroxy radicals RO_2 with HO_2. ~~An uncertainty comes from this reaction yield that is higher than~~ This reaction yield in OH is greater than in the laboratory studies (Hasson et al., 2004; Jenkin et al., 2007; Groß et al., 2014; Winiberg et al., 2016)~~. This imply~~ , implying an overestimation of OH mixing ratios, especially in the biogenic case where RO_2 are ~~important~~high. As the hydroxyl radical is recycled through the isoprene oxidation products, it tends to reduce the impact of isoprene chemistry on OH mixing ratios and thus ~~influence~~ influences the low segregation simulated in the core of the boundary layer. This is similar to a case considered by Stone et al. (2011) where ~~a recycling mechanism~~ an ISOPO2 + HO_2 → ISOPOOH + 3 OH ~~have been~~ recycling mechanism was proposed to increase the simulated OH concentrations and provided the best agreement with OH observations. This reaction ~~imply that isoprene have~~ implied that isoprene has no net impact on OH concentrations. This conclusion ~~is drawn also~~ was also reached by Kubistin et al. (2010) who found better agreement between simulated and measured HO_x concentrations by ignoring ~~the~~ isoprene chemistry. As the chemistry of isoprene is not well understood, the results obtained in our work are subject to these uncertainties.

Aldehydes have not been considered in previous works ~~studying~~ on segregation. Auger and Legras (2007) calculated ~~the~~ segregation at 250 m and 1100 UTC between each species of the chemical model CHIMERE used in their simulation. They found ~~a~~ segregation ranging from 0 to -1% between OH and acetaldehyde. This is comparable to range of results of the anthropogenic case of the present study (Fig. 6b) considering the incomplete mixing between OH and C>2 aldehydes at the same height. ~~The segregation computed relatively to boundary layer averaged values is very similar to the mean relative error (Eq. 10) made on the OH reactivity~~

In the anthropogenic simulation, the high values of segregation computed at the top of the boundary layer are coincident with the presence of clouds. In the absence of aqueous-phase chemistry, clouds impacts on chemical species are dynamical and photochemical. They modify heat and moisture fluxes at their surroundings (Vilà-Guerau de Arellano et al., 2005) and thus the transport of compounds, as noted by Kim et al. (2012) who demonstrated that clouds presence could increase transport of chemicals to 1000m. In this set of simulations, the chemical impact of clouds on species involves photolysis rates as they are corrected at every time step due to the ~~strong predominance of ALD2 in the OH budget. It is generally negative throughout the simulation and varies from -0.02 at 0700 UTC to -0.015 at 1730 UTC. As pointed out by~~ presence of clouds according to the work of Chang et al. (1987). At each point of the domain, photolysis rates are increased above clouds and decreased below them.

Another effect of clouds on the atmospheric chemistry lies in isoprene emissions, as demonstrated by Kim et al. (2012). As isoprene emissions are dependent on incoming radiation and temperature near the surface, cloud shading could decrease the amount of isoprene emitted. Kim et al. (2012) showed that isoprene concentrations are decreased by 10% and OH concentrations increased by 5% in the boundary layer when isoprene emissions are reduced by up to 10%. The ultimate impact on segregation cannot be anticipated since it corresponds to two compensating effects.

Finally, clouds impact atmospheric chemistry through aqueous phase reactivity. Aqueous-phase chemistry was not considered here, nor were the exchanges between gas and aqueous phases. However, it could have an impact on soluble species mixing ratios, such as formaldehyde and H_2O_2 through the capture and degassing cycles of these compounds. Lelieveld and Crutzen (1990) showed a decrease in oxidative capacity of the ~~vertical profiles of segregation (Fig. 6b), the impact of turbulent mixing on the chemical reactivitydepends on the considered time of the day. In this case, a reduction of few percents of the reaction rate of ALD2+OH is found in the early morning and the late afternoon, and an increase up to 4% is simulated between 0800 and 1600 UTC over the whole boundary layer. This reveals a small impact of turbulent mixing on the chemical reactivity~~atmosphere through aqueous-phase reactions via a significant decrease in ozone mixing ratios, but also OH, formaldehyde and nitrogen oxides. However, the effects of aqueous-phase chemistry on gas-phase compound concentrations are various (Barth et al., 2003) and OH concentrations could decrease in clouds (Mauldin et al., 1997). This result was confirmed by the study of Commane et al. (2010) who found that HO_x concentrations decreased in clouds. Recently, Li et al. (2017) studied segregation effects in a biogenic environment when aqueous-phase chemistry is included. They found that isoprene concentrations are increased by up to 100% while OH concentrations decreased by 18%, resulting in a maximum segregation of 55% in the cloudy layer. In the anthropogenic environment, segregation effects are expected to be enhanced due to the decrease of OH concentrations in gaseous phase in the cloud layer, reducing the cleansing capacity of the atmosphere.

Several instrumental studies ~~looked at the~~ examined OH total reactivity in urban environments, and ~~especially at~~ more especially the OH budget. Hansen et al. (2015a) found ~~in an urban environment~~ that NO_x contribution (50 to 55%) ~~was the most important to the OH lossranging~~ in an urban environment had the greatest effect on OH loss, considering NO_x mixing ratios between 10 and 300 ppbv. The next most important contribution came from ~~the~~ OVOCs (especially aldehydes and ketones) ~~that varied from~~ leading to 15 to 25% of ~~the~~ OH destruction with mixing ratios close to 20 ppbv. Some discrepancies exist between this experimental study and the OH budget for the anthropogenic case in our study (Fig. 7b). Given the NO_x mixing ratios simulated in the present study (< 3 ppbv at midday), they are not an important sink for OH as measured by Hansen et al. (2015a). However, the range of ~~OVOCs~~ OVOC contribution reported by Hansen et al. (2015a) is comparable to what ~~is~~ was found for ALD2 in the anthropogenic case.

In the city of Tokyo, Sadanaga et al. (2004) found that the OH budget was dominated by NMHCs and by OVOCs. In their study, the OVOC ~~category grouping~~ group including acetaldehyde, formaldehyde, methanol, ethanol and acetone, ~~can~~

~~contribute~~ contributed up to 18% of ~~the~~ OH reactivity. If aggregated, the species constituting the ~~NMHCs category~~ NMHC group are the predominant sink for OH in our anthropogenic simulation, as observed by Sadanaga et al. (2004). However, C>2 aldehydes ~~have higher contribution in the~~ contribute more to OH destruction in our study than in ~~Sadanaga et al. (2004). It could be a consequence of~~ that of Sadanaga et al. (2004). This could result from the cyclic boundary conditions prescribed at the borders of our domain, which can cause the ageing of air masses and increase the mixing ratios of secondary products such as aldehydes.

Lelieveld et al. (2016) studied the global distribution and budget of OH radical using the ~~model EMAC~~ EMAC model (ECHAM/Messy Atmospheric Chemistry) coupled with the ~~the~~ Mainz Organics Chemistry (MOM). They found that the annual mean OH reactivity near the surface ranged from 10 to 20 s^{-1} in southern West Africa, which is in agreement with the results of the anthropogenic case but slightly higher than the values obtained in our biogenic case. However, Nölscher et al. (2016) studied, by means of observations, the effects of seasonality in rainforest air reactivity and noticed that ~~the~~ total OH reactivity was much lower during the wet season than during the dry season due to ~~a lowering in temperature~~ lower temperatures and incoming radiation. More ~~precisely~~specifically, measurements of reactivity ~~made~~ performed during the wet season varied between 6 and 12 s^{-1} with an average value of 9.9±5.2 s^{-1} at 24 meters, which is much closer to the Meso-NH model results. Moreover, the ~~estimations of Nölscher et al. (2016) OH reactivity missing fraction, between 5 and 15 %, are of the order of the overestimation of the~~ error made on the total OH reactivity neglecting the turbulent mixing ~~over a rainforest in a convective boundary layer (Fig. 9a)~~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.

~~Aqueous-phase chemistry was not considered here, nor the exchanges between gas and aqueous phases. However, it could have an impact on soluble species mixing ratios, such as formaldehyde and H_2O_2 through the capture and degassing cycles of these compounds. Lelieveld and Crutzen (1990) showed a decrease in oxidative capacity of the atmosphere through aqueous-phase reactions via a significant decrease in ozone mixing ratios, but also HO, formaldehyde and nitrogen oxides. However, variables effects of aqueous-phase chemistry on gas-phase compounds concentrations exist (Barth et al., 2003) and OH concentrations could decrease in clouds (Mauldin et al., 1997), reducing the cleansing capacity of the atmosphere and potentially increasing the segregation between OH and its reactants.~~

5 Conclusions

A numerical simulation coupled with a realistic chemical mechanism ~~is~~ was performed with the atmospheric model Meso-NH to study the impact of thermals on the oxidizing capacity of the atmosphere. The fine grid resolution of the LES version of the model ~~allows the thermals to be explicitly resolved~~ made it possible to explicitly resolve the thermals spatially and temporally. Identification of thermals was based on a conditional sampling method relying on a ~~radioactive-decay~~ first-order decay passive scalar. The ~~study of~~ impact of turbulent mixing on ~~the~~ chemical species redistribution, ~~but also~~ and of the consequences on ~~the OH reactivity , is performed~~ OH reactivity was determined in a natural environment and a more contrasted urban case.

The differentiated transport by thermals is dependent ~~of~~ on the chemical lifetime of ~~compounds, which is~~ the compounds, represented by the Damkhöler number. This transport induces ~~heterogeneities in the species repartition~~ inhomogeneous mixing of the species within the boundary layer, ~~but also has~~ 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, ~~a~~ an effective maximum decrease of 30% ~~affective decrease~~ of the reaction rate ~~is~~ 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 ~~can reach~~ reached 8% at the surface in the early morning while this reaction ~~is increased up~~ increased to 16% at the top of the boundary layer during most ~~part~~ of the simulation.

Thermals transporting species emitted at the surface can lead to different chemical regimes inside updrafts and the environment. For both cases, the surface and the ~~transported parcel correspond to~~ thermals are the preferential reaction zones, ~~where the reactivity is the highest . This is~~ 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 ~~are~~ were radicals originating from the oxidation of isoprene and its degradation products whereas O~~^{1}~~$_1$D+H_2O reaction ~~become~~ became more predominant with increasing altitudes. In the urban case, OH ~~is~~ was mainly produced through the reaction between HO_2 and NO, at the surface or higher in the boundary layer. This ~~leads~~ led to a higher oxidation capacity in the air transported by thermals for both cases. ~~The heterogeneity in OH reactivity within the boundary layer have repercussions on the mean OH reactivity. In order to evaluate this impact, the mean relative error is introduced and includes the effect of turbulence on the mean effective reaction rate between OH and its reactants. A maximum overestimation close to 9% of the total OH reactivity~~

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 ~~is found compared to a reactivity that would be calculated with boundary layer averaged values. This is in the range of OH reactivity missing fraction, from 5 to 15%, found by Nölscher et al. (2016) during the wet season at midday over the amazonian forest but lower than Lelieveld et al. (2016). The segregation cannot~~

~~fully reconcile the OH concentration measurements and simulations, but it remains an interesting candidate to consider while studying the total OH reactivity over a tropical forest during the wet season~~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 ~~is not constant over time but fluctuates between an overestimation of 5% and an underestimation of 6%~~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.

~~This study addresses~~

This study addressed the impact of moist thermals on the oxidative capacity of the atmosphere on two contrasted chemical situations in a wet environment represented by the monsoon flow. However, Nölscher et al. (2016) ~~noticed a consequent~~ observed a substantial seasonal cycle in ~~the~~ OH reactivity over an ~~amazonian~~ Amazonian forest ranging from 10 s s^{-1} in the wet season to 62 s^{-1} in the dry season. It ~~could~~ would be interesting to assess the impact of turbulent mixing on chemistry in the dry season over the southern part of West Africa. Moreover, the influence of urban area in this study was only linked to chemical emissions. This work should be repeated by taking into account the dynamical forcing due to the presence of the urban area ~~in the same way that Ouwersloot et al. (2011)~~ as in Ouwersloot et al. (2011) in which the authors introduced heterogeneous surface conditions over forest and savannah patches. ~~These authors~~ They showed that the difference in buoyancy fluxes at the surface could have an impact on the redistribution of species, and thus on ~~the~~ segregation. Finally, the presence ~~or clouds was only considered~~ of clouds was considered only from a dynamical view. Adding ~~the~~ aqueous phase chemistry in ~~those~~ these simulations could provide ~~a~~ further insight into the impact of moist thermals on ~~the~~ chemical reactivity.

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Table 1. Initial vertical profiles of mixing ratios and associated profiles. ~~Number~~ Numbers in brackets ~~refers~~ refer to (1) uniform profile, (2) stratospheric profile (initial profile multiplied by 1 from 0 to 2000m, then by 0.5 from 3000m to 13000m, by 0.75 at 14000m and 1 above), (3) boundary-layer profile (multiplied by 1 from 0 to 1000m, by 0.10 from 2000 to 13000m and 0.05 above). Chemical names are those used in the ReLACS3 chemical mechanism. ALD2 corresponds to aldehydes C>2, ALKL to lumped alkanes C_2C_6, ALKH to lumped alkanes C_7C_{12}, OLEL to lumped alkenes C_3-C_6, OLEH to lumped alkenes C>6, ETHE to ethene, ISOP to isoprene, AROL to lumped low SOA yield aromatic species, AROH to lumped high SOA yield aromatic species , AROO to lumped phenolic species, ARAC+ to lumped aromatic monoacids, MEOH to methanol, ARAL to lumped aromatic monoaldehydes, MVK to methyl-vinyl-ketone, MCR to methacrolein, HCHO to formaldehyde, KETL to lumped ketones C_3-C_6 and PAN2 to peroxy acetyl nitrate

Species	Initial mixing ratio	Species	Initial mixing ratio
O_3	21.19 ppb (2)	HO_2	2.48 ppt (1)
OH	0.07 ppt (1)	NO	55.25 ppt (2)
CO	149.23 ppb (3)	HCHO	747.47 ppt (3)
ALD2	896.82 ppt (3)	PAN2	35.70 ppt (3)
ALKL	282.90 ppt (3)	ALKM	3.67 ppt (3)
ALKH	0.60 ppt (3)	ETHE	277.12 ppt (3)
OLEL	104.71 ppt (3)	OLEH	0.94 ppt (3)
ISOP	1.23 ppb (3)	AROH	53.29 ppt (3)
AROL	14.11 ppt (3)	AROO	4.66 ppt (3)
ARAC+	0.69 ppt (3)	ARAL	1.98 ppt (3)
MEOH	564.54 ppt (3)	KETL	72.69 ppt (3)
MVK	537.74 ppt (3)	MCR	268.87 ppt (3)

Table 2. ~~Emissions~~ Emission values for the biogenic and the anthropogenic cases, in kg.m^2.s^{-1}. For compounds in bold ~~character~~characters, Gaussian shape emissions ~~have been prescribed~~ were set and only the maximum value is indicated here. Please see text for details.

Chemical species	Molar mass $(g.mol^{-1})$	Biogenic patch emissions $(kg.m^{-2}.s^{-1})$	Anthropogenic patch emissions $(kg.m^{-2}.s^{-1})$
NO	30	$2.23 * 10^{-11}$	$5.68 * 10^{-10}$
NO_2	46	-	$2.44 * 10^{-10}$
CO	28	$2.13 * 10^{-11}$	$2.43 * 10^{-08}$
ETHE	28	$7.72 * 10^{-12}$	$8.06 * 10^{-10}$
OLEL	70	$3.26 * 10^{-12}$	$8.68 * 10^{-10}$
OLEH	126	$4.20 * 10^{-14}$	$1.91 * 10^{-11}$
ALKL	72	$2.72 * 10^{-14}$	$3.92 * 10^{-10}$
ALKM	128	$6.13 * 10^{-15}$	$1.31 * 10^{-10}$
ALKH	226	$8.76 * 10^{-16}$	$2.16 * 10^{-11}$
AROH	134	$2.75 * 10^{-13}$	$2.95 * 10^{-10}$
AROL	120	-	$1.98 * 10^{-10}$
AROO	122	-	$8.94 * 10^{-11}$
ARAC+	136	-	$1.32 * 10^{-11}$
ARAL	120	-	$3.81 * 10^{-11}$
ALD2	86	$2.99 * 10^{-12}$	$2.41 * 10^{-10}$
HCHO	30	$8.32 * 10^{-13}$	$8.39 * 10^{-11}$
ACID	74	-	$1.12 * 10^{-10}$
ORA1	46	$6.24 * 10^{-13}$	$5.75 * 10^{-10}$
ORA2	60	$6.24 * 10^{-13}$	$6.01 * 10^{-10}$
KETL	86	$6.80 * 10^{-13}$	$8.04 * 10^{-12}$
KETH	114	$2.51 * 10^{-14}$	$4.14 * 10^{-13}$
MEOH	32	$3.61 * 10^{-11}$	$2.64 * 10^{-11}$
ETOH	46	$2.15 * 10^{-12}$	$2.95 * 10^{-10}$
ALCH	102	-	$1.45 * 10^{-10}$
ISOP	68	$2.76 * 10^{-10}$	-
BIOL	154	$3.29 * 10^{-11}$	-
BIOH	88	$4.94 * 10^{-11}$	-
SO_2	64	-	$1.60 * 10^{-10}$
NH_3	17	-	$6.02 * 10^{-11}$
MTBE	88	-	$2.30 * 10^{-10}$

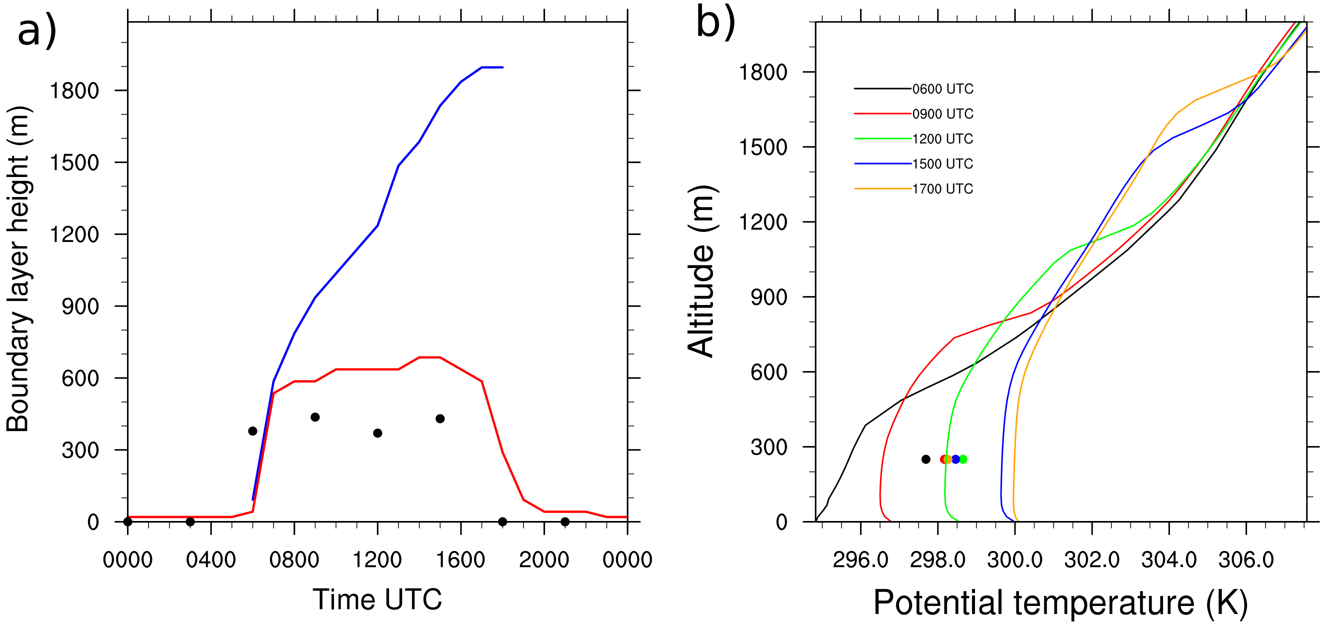

Figure 1. (a) ~~Cloud fraction (dotted black) and boundary~~ Boundary layer height diurnal evolution computed from the bulk-Richardson method (red)~~and~~ , the tracer method (blue) ~~,~~ and composite values of boundary layer height for the sOP-2 period (08/01/06-08/15/06) based on Gounou et al. (2012) (black dots). (b) ~~potential temperature~~ Potential vertical temperature profiles at 0600 (black), 1000 (red), 1400 (green) and 1700 UTC (blue)

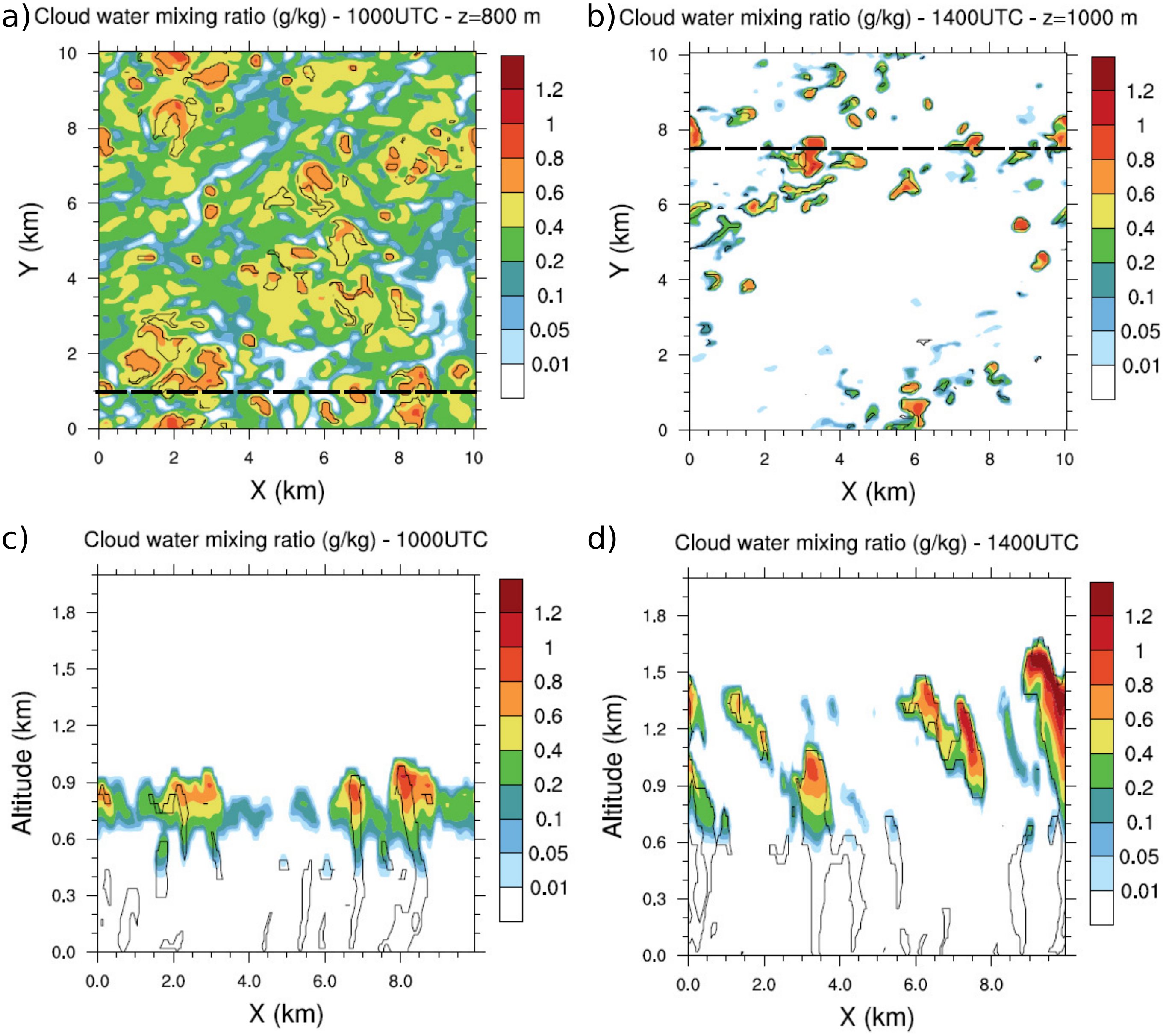

Figure 2. (a) Cloud water mixing ratio horizontal cross-sections at 1000 UTC and 800m height and (b) at 1400 UTC and 1000m height . Black dashed lines represent the vertical cross-sections at (c) 1000 UTC and y=1km and at (d) 1400 UTC and y=7.5km. Black isolines denote thermals identified by the conditional sampling method.

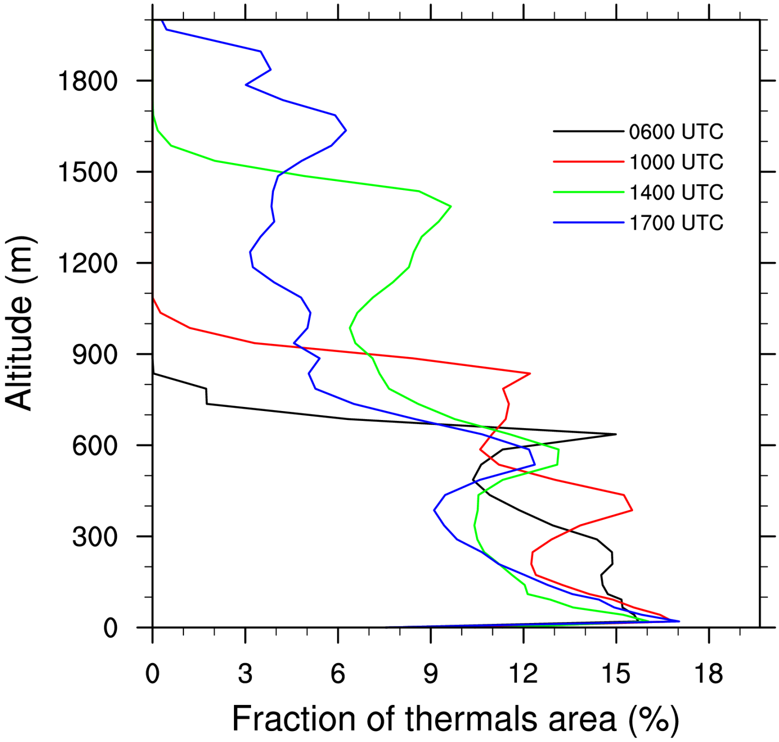

Figure 3. Vertical profiles of the fraction occupied by thermals at 0600 (black), 1000 (red), 1400 (green) and 1700 UTC (blue).

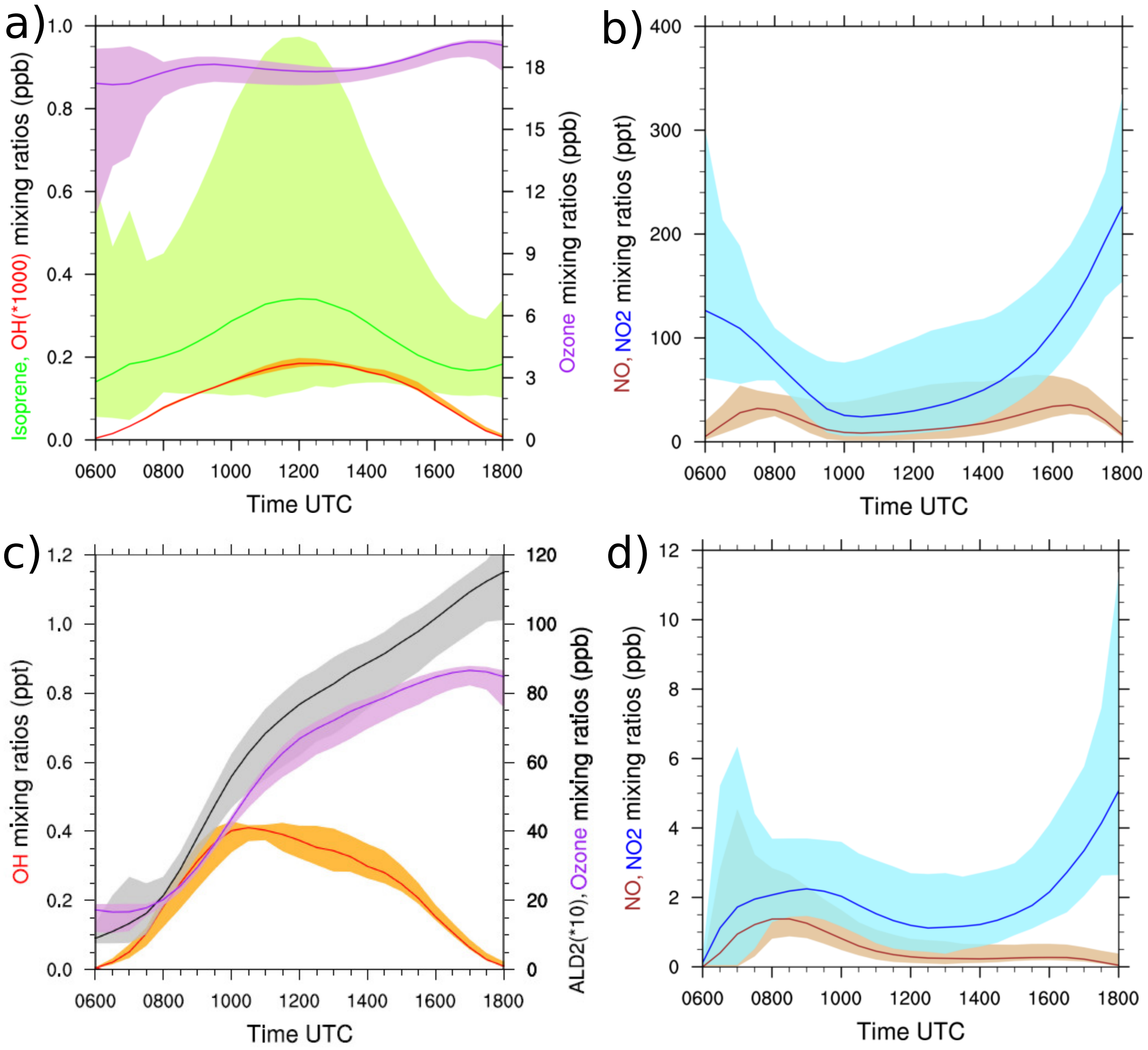

Figure 4. (a)-(b) LES simulated diurnal cycles for isoprene (green), OH (red), ozone (purple), NO (brown), NO_2 (blue), (c)-(d) ALD2 (grey), OH (red), ozone (purple), NO (brown) and NO_2 (blue). (a)-(b) corresponds to the biogenic environment, (c)-(d) to the anthropogenic environment. The shaded areas ~~denotes~~ denote the minimum and ~~the~~ maximum of mean vertical profiles between the surface and 600m height, and the colored lines correspond to the ~~average~~ averages of these profiles

Table 3. Measurements collected during the AMMA campaign over forested ~~area~~ areas (upper part) and over cities (lower part). The last column corresponds to the concerned period.

Species	Mixing ratio	Altitude	Location	References	Comments
O_3	24 ppbv	500 m	10°N	Commane et al. (2010)	1340 UTC - 17/08
	25 ppbv	<900 hPa	10°N	Reeves et al. (2010)	Median value (20/07 - 21/08)
	25-30 ppbv	300 - 1700 m	12-13°N	Borbon et al. (2012)	0800 -1800 UTC
	22 ppbv	<700 m	7.2-13.1°N	Murphy et al. (2010)	Mean value (17/07 - 17/08)
Isoprene	1.2 ppbv	<700 m	10°N	Ferreira et al. (2010)	1345 UTC - 17/08
	0.604 ppbv	<700 m	7.2-13.1°N	Murphy et al. (2010)	Mean value (17/07 - 17/08)
	1 - 1.5 ppbv	400 -1450 m	10°N		1200 UTC - 17/08
	0.2-1.5 ppbv	Surface	9.42°N;1,44°E	Saxton et al. (2007)	Composite diurnal cycle (07/06 - 13/06)
OH	0.05 - 0.15 pptv	500 m	10°N	Commane et al. (2010)	1345 UTC - 17/08
NO_x	0.2 ppbv	<900 hPa	10°N	Reeves et al. (2010)	Median value (20/07 - 21/08)
	0.1 ppbv	<700 m	9°N	Delon et al. (2010)	Mean value (05/08 - 17/08)
O_3	40 ppbv	<2km	Cotonou	Ancellet et al. (2009)	08/19 p.m. flight
	24-30 ppbv	0-2 km	Cotonou	Thouret et al. (2009)	Mean value (August 2006)
	26 ppbv	<700m	Lagos	Murphy et al. (2010)	B229 flight - Mean value (17/07 - 17/08)
	31 ppbv		Niamey		
NO_x	1 ppbv	<2km	Cotonou	Ancellet et al. (2009)	08/19 p.m. flight
OH	0-0.5 pptv	500m	Lagos	Commane et al. (2010)	B229 flight

Table 4. Simulated Damkhöler number of chemical species averaged from the surface to 0.6 km at 1200 UTC for the two cases calculated with $\tau_{turb} \approx 20$ ~~mn~~min.

	Damkhöler number (unitless)	
	Biogenic case	Anthropogenic case
OH	4402.7	12002.5
HO_2	50.4	137.5
ISOP	0.54	1.08
O_3	0.66	0.79
NO	80.2	81.0
NO_2	24.3	17.9
ALD2	0.086	0.17

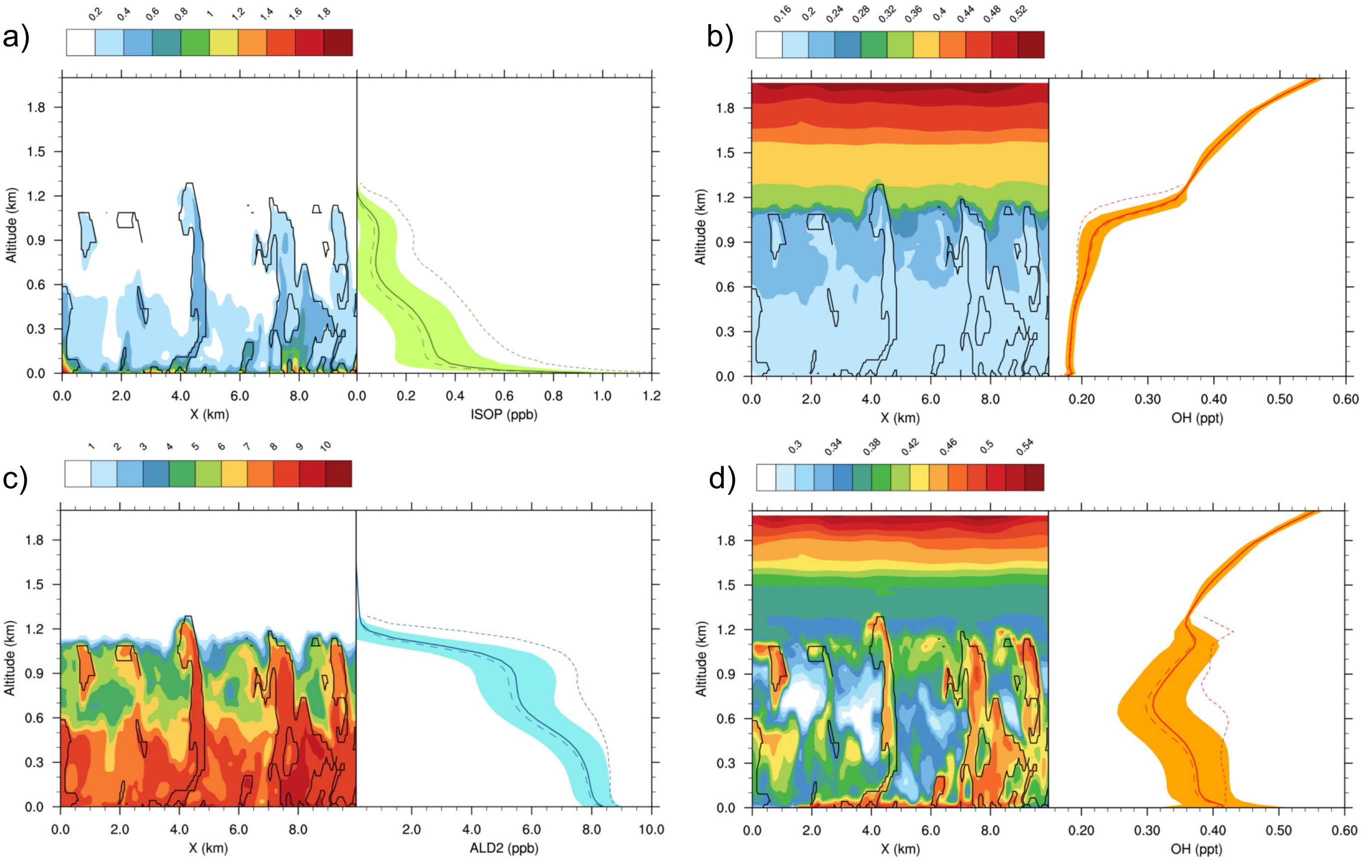

Figure 5. (a) Isoprene (ppb) and (b) OH radical (ppt) mixing ratios for the biogenic case at 1200 UTC. (c) ALD2 (ppb) and (d) OH radical (ppt) mixing ratios for the anthropogenic case at the same time. For each figure, the left part consists ~~in~~ of a vertical ~~cross section~~ cross-section at the middle of the domain (y = 5km). Black isolines denote thermals identified by the conditional sampling method. In the right part of each panel, the shaded areas denote ~~two times~~ twice the standard deviation at a given altitude and the line represents the horizontal average over the domain. The dashed line ~~correspond~~ corresponds to the average in the environment and the dotted lines inside thermals.

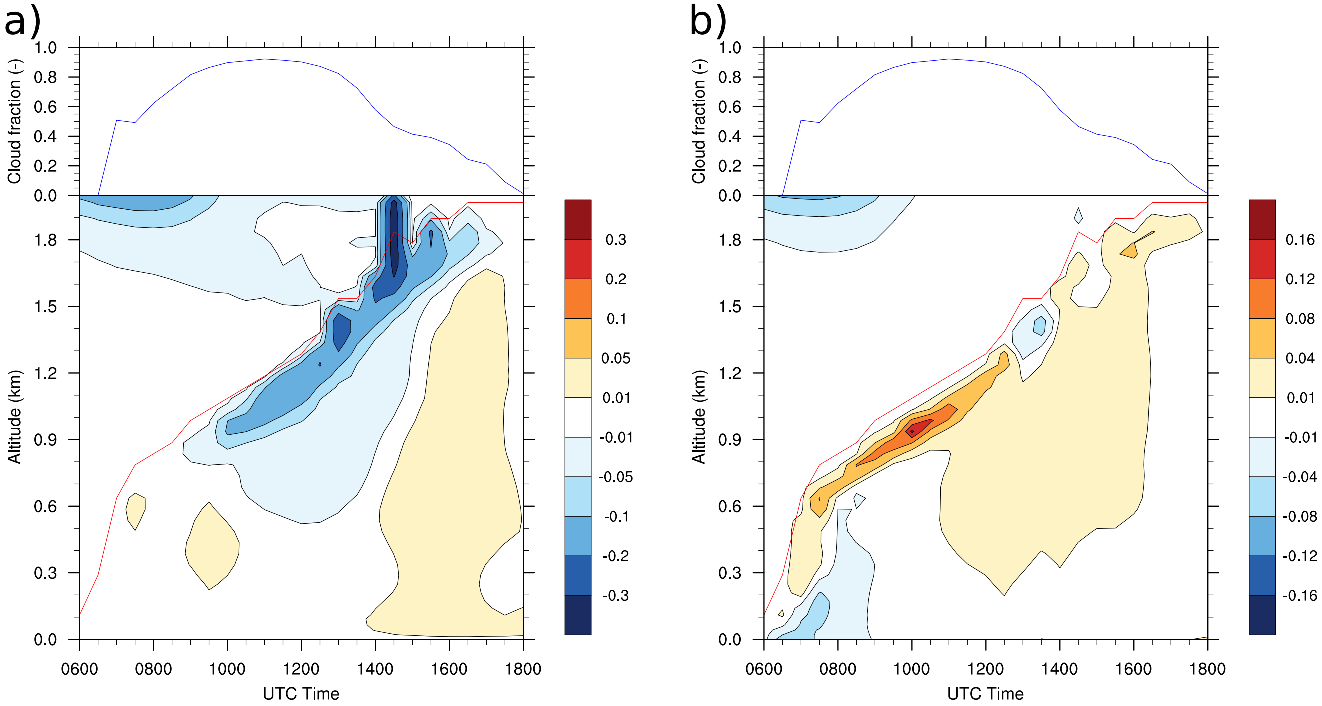

Figure 6. (a) Diurnal evolution of the segregation coefficient for isoprene and OH in the biogenic case and (b) for ALD2 and OH in the anthropogenic case. The red line represents the boundary layer height as determined by the tracer approach.

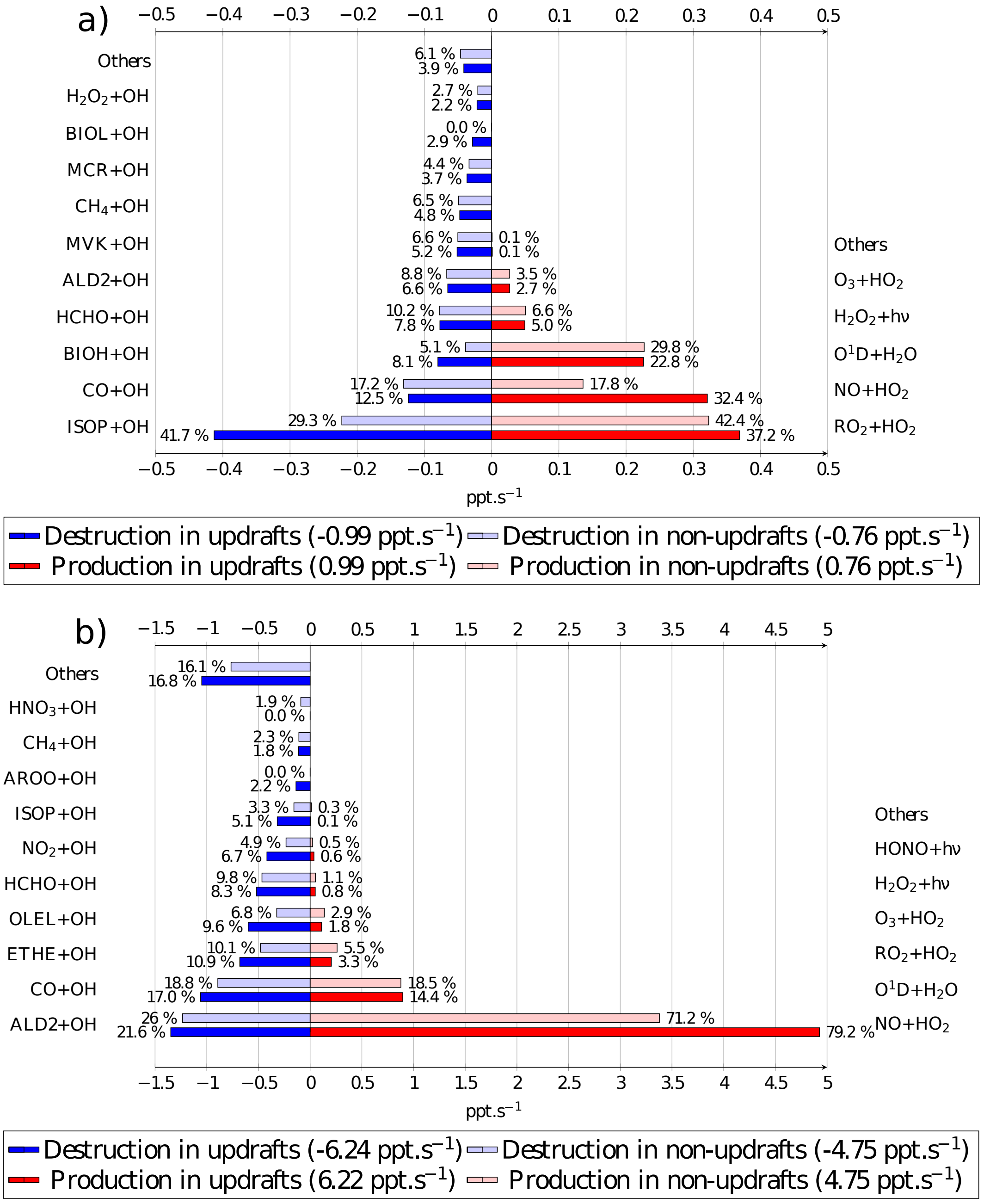

Figure 7. OH radical chemical budget at 1200 UTC averaged at 20 m for the biogenic (a) and the anthropogenic case (b). Source terms are in red for updrafts and pale red for non-updrafts. Destruction terms are in blue for updrafts and pale blue for non-updrafts. The bar lengths determine the absolute values and the relative contributions for destruction and production are given by the percentage near each bar. ~~Number~~ Numbers between ~~parenthesis~~ parentheses in the legend box are the OH production and destruction rates in updrafts and in non-updrafts. Chemical names correspond to ~~name~~ the names given in the ReLACS 3 mechanism.

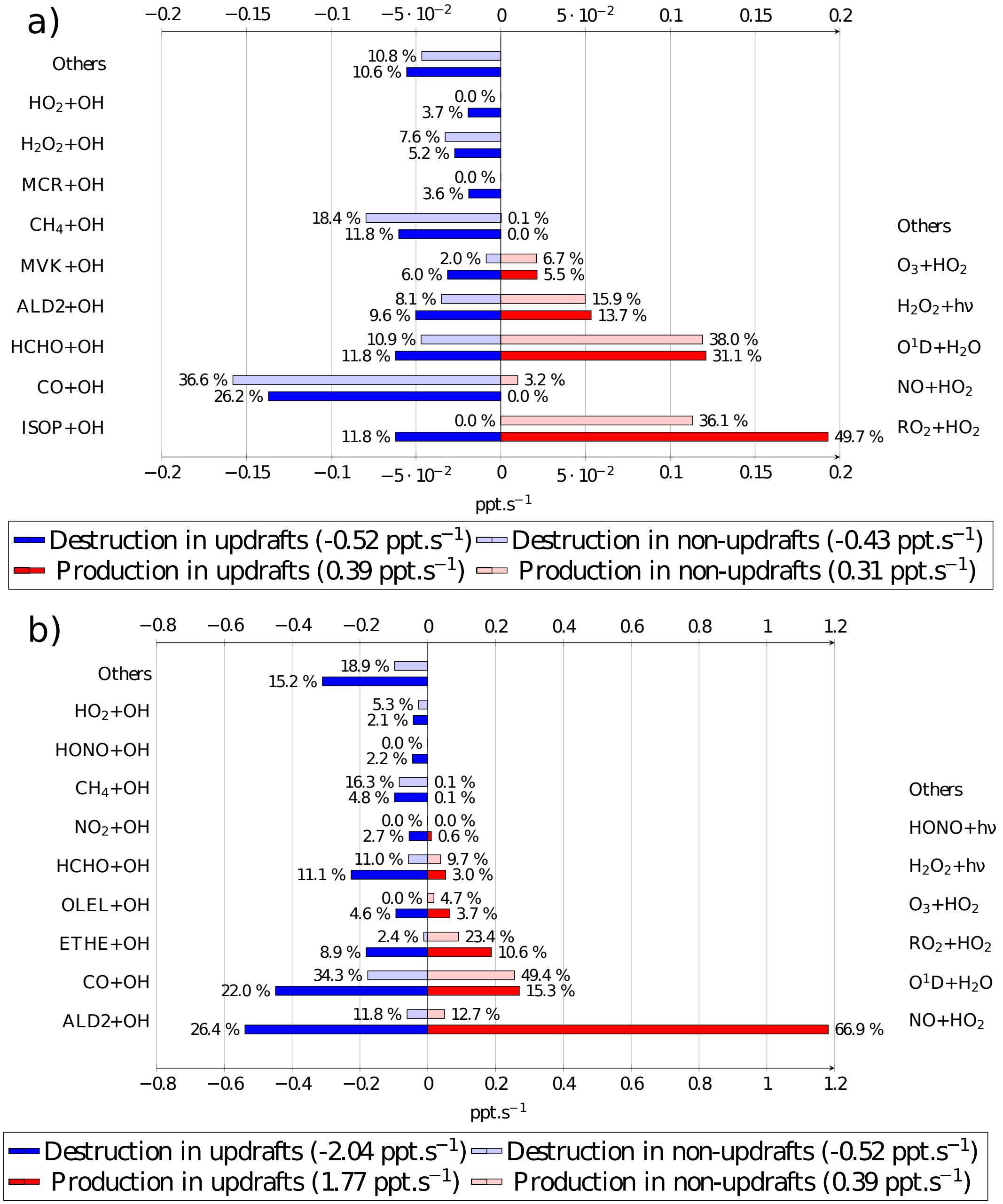

Figure 8. Same as figure 7 for the height of 1200m.

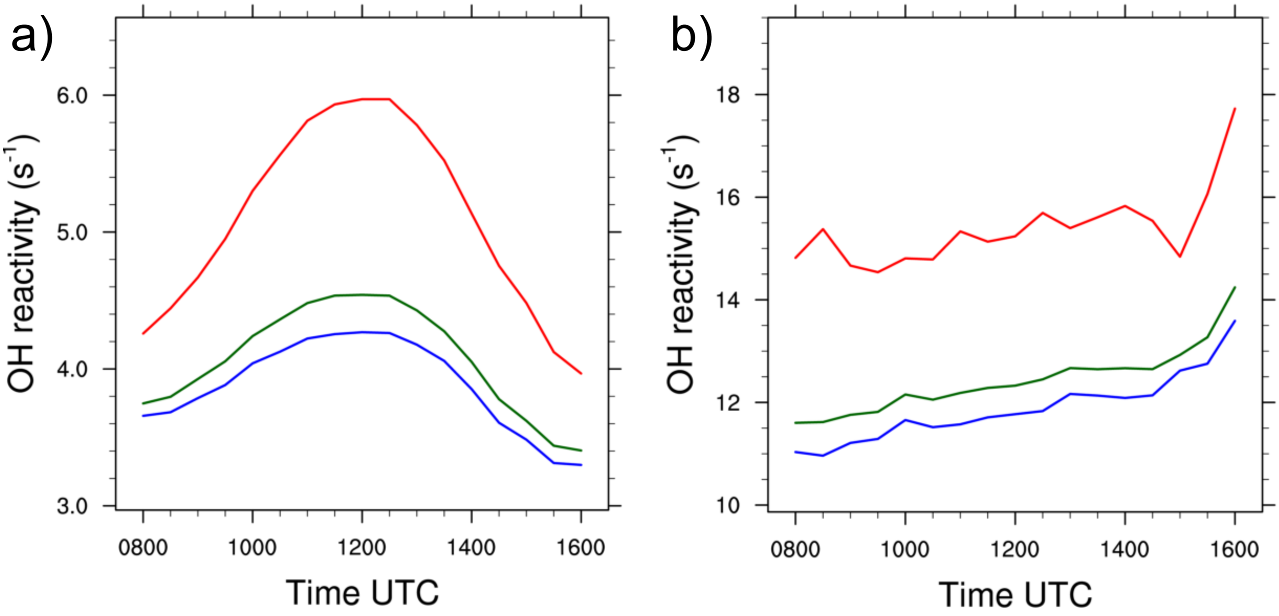

Figure 9. (a) OH reactivity (s^{-1}) in ~~updrafts~~ thermals (red), domain averaged (green) and in ~~updrafts-free~~ non-thermals region (blue) averaged at z = 20 m for the biogenic and (b) the anthropogenic case.

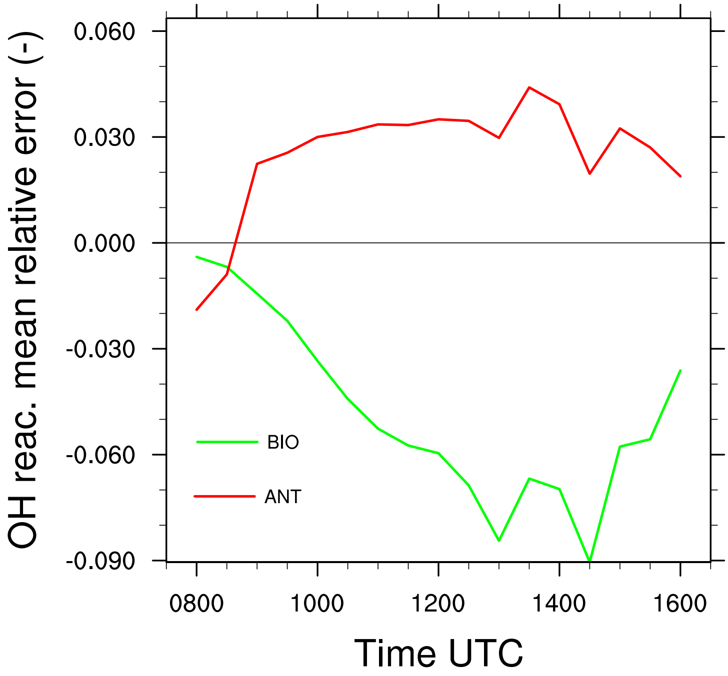

Figure 10. Mean relative error $E_{R_{OH}}$ made on the OH reactivity by neglecting turbulent motions for the biogenic case (green) and the anthropogenic case (red).