Anonymous Referee #2

We would like to thank the Referee #2 for his very constructive comments and recommendations. We would like also to mention that according to Referee's#1 suggestions we have applied the Factor Separation (FS) method of Stein and Alpert (1993) in order to quantify the contributions of biomass burning and biogenic emissions on O_3 production. Thus, the results of section (3) have been reorganized. In the revised manuscript, section 3.1 discusses the episode analysis as simulated by the reference run, section 3.2 refers to the evaluation of O_3 predictions, section 3.3 discusses the results of the FS analysis and finally section 3.4 presents the results of the sensitivity tests. The presentation of the FS method and the necessary simulations are presented in section 2. Regarding the case study we consider, we would like to emphasize that during the spring widespread wildland fires over western Russia, the burning material mainly consisted of previous-year grass remnants, which were dried up by the beginning of the fires. In particular, the daily distribution of the total Fire Radiative Power (FRP) from each land-use class (forest, grass, mixed) revealed that the case of spring fires 2006 represents mainly a dry grass fire; however emissions from forest and mixed areas also existed.

<u>**General comments**</u>

1. **Results are mainly presented for the period between the 2nd and the 7th of May. Why this period? From figure 4 it looks the major emitting period happened at the first days of the event.**

We would like to clarify that the model simulations cover the period of the whole episode from 24 April to 10 May 2006. Our decision to focus on the episode 2-8 May was driven by the high concentrations over Europe and not by the fires' intensity. Before that (late April), severe degradation of air quality was registered in Finland where the smoke had been transported (Saarikoski et al., 2007). During that period, the O_3 concentrations over Europe were relatively low. At the beginning of May (2-8 May), the resulting pollution cloud was blown towards the west leading to strong deterioration of air quality in most of Central and Northern Europe up to Iceland (Stohl et al., 2007).

2. **The comparison between isoprene predicted values and measured ones indicates a weak performance of the model (see figure 2); can we trust biogenic emissions simulations with this not so good behaviour? Please, develop a little bit more this topic.**

This section has been revised accordingly:

"*Unfortunately, the number of stations with available isoprene measurements is quite small (9) and the sampling period too coarse. Canister grab samples were taken at the EMEP stations twice a week and were analyzed with Gas Chromatography/Flame Ionization Detector (GC/FID). Only in Rigi-Switzerland (CH0005), a continuous GC monitor was operating. The comparative hourly observation-prediction pairs at this station represent only the 12% of the total simulation hours. In Figure 2, time series of* *predicted and observed isoprene concentrations are presented at six stations; two in France (FR0015 and FR0008), one in Finland (FI0009), one in Slovakia (SK0006), one in Switzerland (CH0005), and one in Czech Republic (CZ0003). Out of these, only CH0005 provides sufficient amount of observations to represent the diurnal variations of the concentrations. The comparison showed that at this station, the diurnal cycle is reproduced with temporal correlation coefficient 0.366. The mean observed and mean simulated isoprene values in all but one stations agree within a factor up to 3. The mean observed levels are underestimated at the French stations FR0008R and FR0013 and at the Czech station CZ0003. At the rest stations, the mean observed levels are overestimated. Significant discrepancies were found only for the DE008 station (agreement within a factor of 8). The discrepancy at that station has been also discussed in Poupkou et al. (2010) and has been attributed to the different correspondence between the satellite-derived and the ground-based land-use characterization for the area where the station is located. Our results are in conjunction with the uncertainties reported in the literature for biogenic emissions estimates of a factor 3-5 (Simpson et al., 1999). Although this data set cannot constitute the basis for a full scale evaluation, the comparison can give an indication of whether the model predictions reproduce the order of the observations magnitude. Using the same limited data set, Poupkou et al. (2010) evaluated hourly isoprene predictions by CAMx model in a study of BVOC estimations over Europe while Zare et al. (2012, in ACPD) compared isoprene estimates using the MEGAN model and the Global Emissions Inventory Activity (GEIA) inventory (Guenther et al., 1995) and concluded that MEGAN estimates had a better agreement in the mean observed values than GEIA.*"

3. **Fire characteristics, such as daily burnt area and type of consumed vegetation are needed; without this information it is difficult to assess results, particularly the fire impact on ozone production.**

The Fire Assimilation System (FAS) is based on the MODIS FRP product, which represents actual on-going fires and their intensity. In turn, fire intensity is directly converted into emission using empirical scaling coefficients. Therefore, there is a principal difference between the burnt-area based approached and FAS, which does not consider this information, instead it uses the active fires to directly obtain emissions. The methodology used for the calculation of fire emissions is explicitly analyzed in detail in Sofiev et al. (2009) thus, it is beyond the scope of this paper. The daily distribution of the total FRP release from each land-use class revealed that the fire event investigated in this study represents mainly a dry grass fire (Sofiev et al., 2009). The burning material mainly consisted of previous-year grass remnants, which were dried up by the beginning of the fires. Thus, in the reference run, the grassland was considered as burning material while the case of agricultural residues was also examined in order to quantify the sensitivity of the O_3 production on the fire emission properties. According to the reviewer's suggestion a short discussion has been added in the revised manuscript:

"*The daily pattern of PM emission fluxes, generated by the FMI FAS system (Sofiev et al., 2009), is based on MODIS FRP product and the recalibrated methodology of Ichoku and Kaufman (2005). In particular, Sofiev et al. (2009) continued the work of Ichoku and Kaufman (2005) and provided estimations of total PM emission coefficients for each land* *type. They concluded to total PM emission coefficients of 0.1 kg MJ^{-1} for forest, 0.05 kg MJ^{-1} for grass lands, and an average of 0.075 kg MJ^{-1} for mixed areas. The detailed discussion about FAS system is discussed in Sofiev et al. (2009).*

The daily distribution of the total FRP release from each land-use class (mixed, forest, grass) revealed that the fire event, investigated in this study, represents mainly a dry grass fire (Sofiev et al., 2009). The patterns of all gaseous emission fluxes follow the PM ones and are based on scaling factors relative to total PM considering grass as the burning material. However, in order to quantify the sensitivity of the O_3 production on the fire emission properties a sensitivity run considering agricultural residues as burning material (AGRIC) is also examined."

4. **Emissions estimates are not clearly described; Sofiev et al. (2009) is referenced, but a better description of emissions (including the hourly variation of fire intensity and its relationship to emissions) and their analysis is needed. Smoke composition depends on the burnt fuel.**

A short description has been added in the text, see answer on comment 3. Regarding the hourly variation of emissions, a normalization function is used which is considered fixed for all days (day-time emission intensity is 25% higher than the daily-mean level while the night-time emission is 25% lower, Saarikoski et al., 2007). This information has been included in the text.

5. **There are European fire emission inventories developed by other authors. Please, compare your estimates with the available values.**

Such comparison at the area and for this specific episode already has been presented by Sofiev et al. (2009), where it is demonstrated that the top-down approaches (burnt-area -> fuel load -> burning efficiency -> speciation) and more direct bottom-up approaches (active fire intensity -> emission per fire) lead to differences of a factor of several times, which so far has not been explained despite on-going concerted efforts of several research groups. The FAS system is based on the bottom-up approach, thus showing noticeably higher estimates than top-down datasets. The application of the FAS system in combination with the dispersion model SILAM showed that FRP product is suitable for the evaluation of the emission fluxes from wild-land fires (Sofiev et al., 2009). In the framework of this study, the impact of this uncertainty is examined with a 20% cut-off of fire emissions. It was found that this run provokes differences in maximum O_3 predictions less than ± 10 ppb. On the contrary, the chemical properties of the emissions have been proved critical provoking differences of the order of 100 ppb (Table 3, in the revised manuscript).

6. **Modeling results do not catch the smoke plume along the fire episode (see figure 5); this problem has to be addressed and much better explained.**

We consider that the model successfully reproduces the two fire plumes discerned during the episode 2-8 May; one over Western Russia moving westwards and the second one extending over Eastern Europe up to North and Baltic Sea. We realize that there are some deviations, for example the underestimation of O_3 concentrations over Scandinavia on 2-3 May or the delay in the arrival of the plume over Central Europe, not earlier than 5 May, but we consider that the model follows the evolution of the episode quite successfully. Regarding the underestimation over Northern Europe it was revealed that the predictions are strongly dependent on the fire emissions properties. The sensitivity test considering agricultural residues as the burning material predicts higher concentrations in the area of the order of 100 ppb.

7. **There are some publications about this particular case study or about other wildland fire effects on the air quality and it would be interesting to compare and discuss the performance indicators obtained here with the others.**

Although there are other modeling studies on this specific episode or in this area, a straightforward comparison is not possible. Specifically, the modeling studies on this specific episode mainly assess the impact of biomass burning on aerosols (Saarikoski et al., 2007;Treffeisen et al., 2007; Stohl et al., 2007) and on air pollution levels in the European Arctic (Stohl et al., 2007). Regarding other studies in the area, they concentrate on fires in boreal forests. Thus, our study complements these studies since it assess the impact of grass fires on O_3 over Europe. However, according to the reviewer's suggestions, we have included in the revised manuscript comparison with other studies regarding the O_3-CO slopes: (Alvarado et al. 2010; Singh et al., 2010; Paris et al. 2009; Stohl et al., 2007).

"The slope between O_3 and CO predictions during 2-8 May and over the areas that are affected by the fresh fire plumes (Western Russia) range between -0.0046 – 0.017 ppb/ppb. The more efficient O_3 production, greater than 0.0002 ppb/ppb, is estimated during the last days of the episode (5, 6, 7 May) when NO_X have decreased to low mixing ratios (< 5 ppb). These values are comparable to values reported in the literature for fresh biomass burning plumes but mainly in boreal regions. For example, Alvarado et al. (2010) found O_3-CO slopes of 0.005±0.019 ppb/ppb over Canada, Singh et al. (2010) reported slopes of 0.03±0.04 ppb/ppb over Siberia and North America, Paris et al. (2009) found slopes of 0.14 ± 0.50 ppb/ppb over Siberia. According to the model predictions, the O_3 production is more efficient in the aged plumes reaching the northern edge of the modeling domain. In this area, the O_3-CO slopes range between 0.019 and 0.045 ppb/ppb. These slopes, although lower are comparable with the O_3-CO slopes measured at the research Zeppelin (11.9^{o}E, 78.9^{o}N) station during the period 1-8 May ranging between 0.34 and 0.58 (Stohl et al., 2007)."

Specific comments

1. Introduction

The state-of-the-art is very good clearly showing the scientific advance of the current paper. Anyway it can be improved with some recently published papers.

New references have been included in the Introduction: the recent review paper of Jaffe and Wigder (2012), some papers examining the impact of fires on photochemistry (Junquera et al., 2005; Alvarado and Prinn, 2009; Alvarado et al., 2010; Singh et al., 2010) and some new papers discussing O_3 from fires over Europe (Konovalov et al., 2011; Ø. Hodnebrog et al., 2012).

2. Methodology, modelling tool, and input data

2.1 Atmospheric chemistry-transport models

- page 3471, lines 10-11: initial and boundary conditions are not described enough; please improve.

The text has been revised accordingly: "*The initial and boundary conditions are temporally and spatially constant concentrations based on climatological data (Tarasova et al., 2007)*."

- **Page 3471, lines 16-21: I'm assuming that smoke clouds are not considered in the photolysis rates adjustments. Please, state this clearly, because this could have an effect on obtained results.**

The reviewer is correct. The text has been revised accordingly:

"….for each day of the simulation period. The aerosol impact on photolysis rates has not been taken into account although the "obscouring" effect of aerosols (Tzanis et al., 2009; Konovalov et al., 2011) may decrease the ozone production at the surface by up to 20% (Jaffe and Wigder, 2012).

2.2 Biogenic emissions

- page 3472, line 22: add a reference to MEGAN

Done

- page 3473, lines 4-5: revise English, please

The text has been revised from:

"The impact of fires on isoprene and monoterpenes emissions as these have been calculated by Alessio et al. (2004) has not been considered, in this study"

to:

"*This study does not consider the impact (direct and indirect) of fires on isoprene and monoterpenes emissions (e.g. direct leaf wounding, photosynthetic inhibition) as was measured by Alessio et al. (2004)*."

- page 3473, figure 1: why presenting the period from 2 to 7 May and not another one?

See answer on comment 1

- page 3473, line 9: delete "the" between "with" and "recent"

Done

- page 3474, line 7-8: improve the sentence starting with "During" and ending with "data". It is not clear enough

This sentence has been removed from the text. Now the text has been revised accordingly:

"*Unfortunately, the number of stations with available isoprene measurements is quite small (9) and the sampling period too coarse. Canister grab samples were taken at the EMEP stations twice a week and were analyzed with Gas Chromatography/Flame Ionization Detector (GC/FID). Only in Rigi-Switzerland (CH005), a continuous GC monitor was operating. The comparative hourly observation-prediction pairs at this station represent only the 12% of the total simulation hours."*

- page 3474, line 8: insert information stating that data in Figure 2 are measured and calculated.

The text has been revised accordingly: "*In Figure 2, time series of predicted and observed isoprene concentrations are presented at six stations; two….*"

2.3 Fire emissions

Please, also see my previous general comments.

- page 3474, line 24: why considering grass? Don't you have information about the fuel burnt?

The daily distribution of the total FRP release from each land-use class (forest, grass, mixed) revealed that the case of spring 2006 represents mainly a dry grass fire (Sofiev et al., 2009). A complete answer is given on general comment 3.

- **Figure 3 is not described in the main text**

In the first submitted paper, figure 3 is described in pp. 3475 (lines 1-2). In the revised manuscript the information regarding the burning material was added: *"In Figure 3, the daily patterns of NO_X emissions, originated from fires during the period 2 to 7 May, are presented for the reference run (grass)."*

- **page 3475, line 11: PM behaviour is mentioned, but not shown at all.**

Our study focuses on O_3 simulations. Although PM have been also included in the simulations, in this paper we have focused and analyzed only the ozone simulations. PM have been used in the emissions process to provide information on fire gaseous emissions estimates.

3. Results

Insert a sentence introducing this Results section. It would help the reader to follow the analysis.

According to Referee's#1 suggestions we have applied the Factor Separation method of Stein and Alpert (1993) in order to quantify the contributions of biomass burning and biogenic emissions on O_3 production. The results section (3) has been reorganized. According to the referee's suggestions a sentence has been inserted to introduce the Results section:

"*The presentation of the results is organized as follows: in section 3.1 the episode analysis as simulated by the reference run is discussed and in section 3.2 the evaluation of the O_3 predictions is assessed. In section 3.3, the results of the FS method are analyzed. In particular, the pure, total and synergistic effect of biomass burning and biogenic emission sources are presented. Finally in section 3.4, the results of the sensitivity tests are analyzed and compared with the results of the reference run.* "

3.1 Episode analysis – comparison with O3 observations

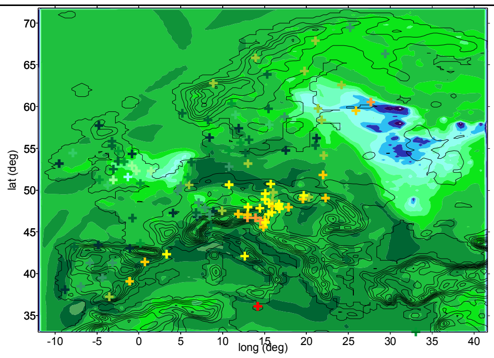
The first paragraph makes more sense in section 2.3.

This paragraph gives a short description of the episode and the prevailing meteorological conditions. In the revised manuscript, this paragraph has been moved in the Introduction section (1).

Figure 5 analysis reveals some modelling problems and I would like to see results from the first days of the fire event when emissions were higher. When comparing model results with EMEP measurements it looks modelling was not able to correctly catch the smoke plume. This problem has to be much better addressed in the paper.

Our decision to focus on the episode 2-8 May was driven by the high concentrations over Europe and not by the fires' intensity. We consider that the model successfully reproduces the two fire plumes discerned during the episode 2-8 May; one over Western Russia moving westwards and the second one extending over Eastern Europe up to North and Baltic Sea. The maximum hourly predicted and observed O_3 concentrations during the period 25 April to 1 May for the reference run considering grass as the burning material are presented in Figure 1. Regarding the underestimation over Western Russia and Northern Europe it was revealed that the predictions are strongly dependent on the fire emissions properties. The sensitivity test considering agricultural residues as the burning material (AGRIC run) predicts higher concentrations in these areas up to 150 ppb (Figure 2).

25/04/2006



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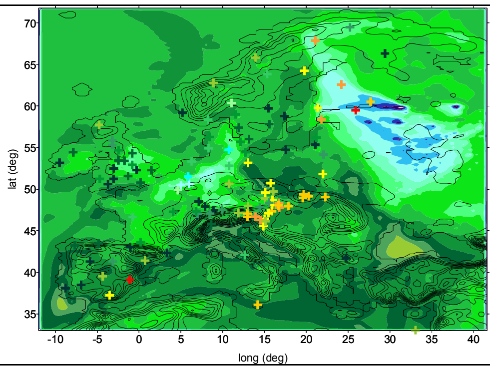

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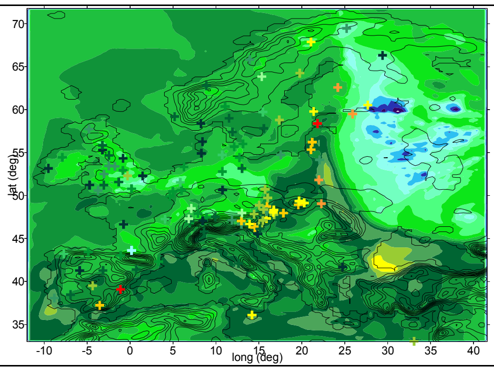

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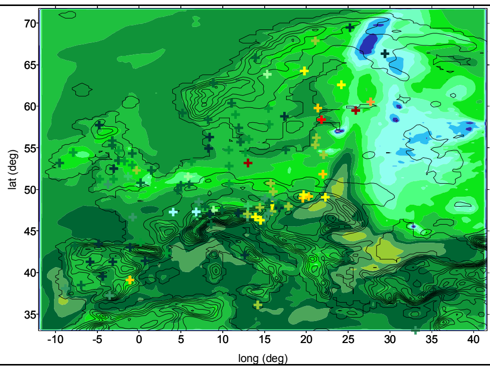

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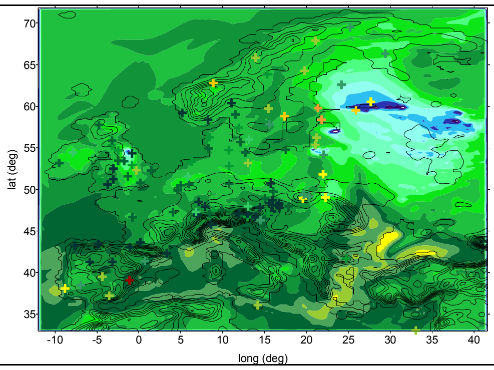

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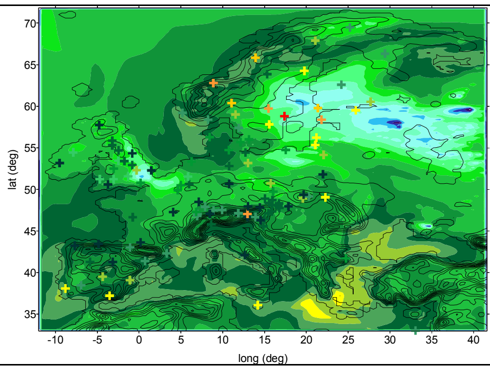

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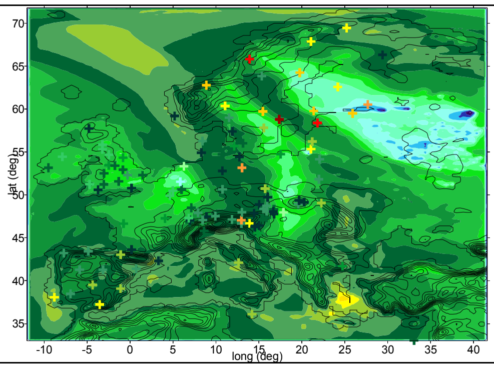


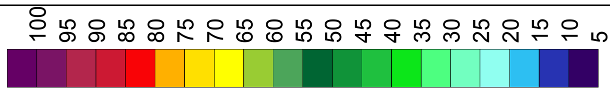
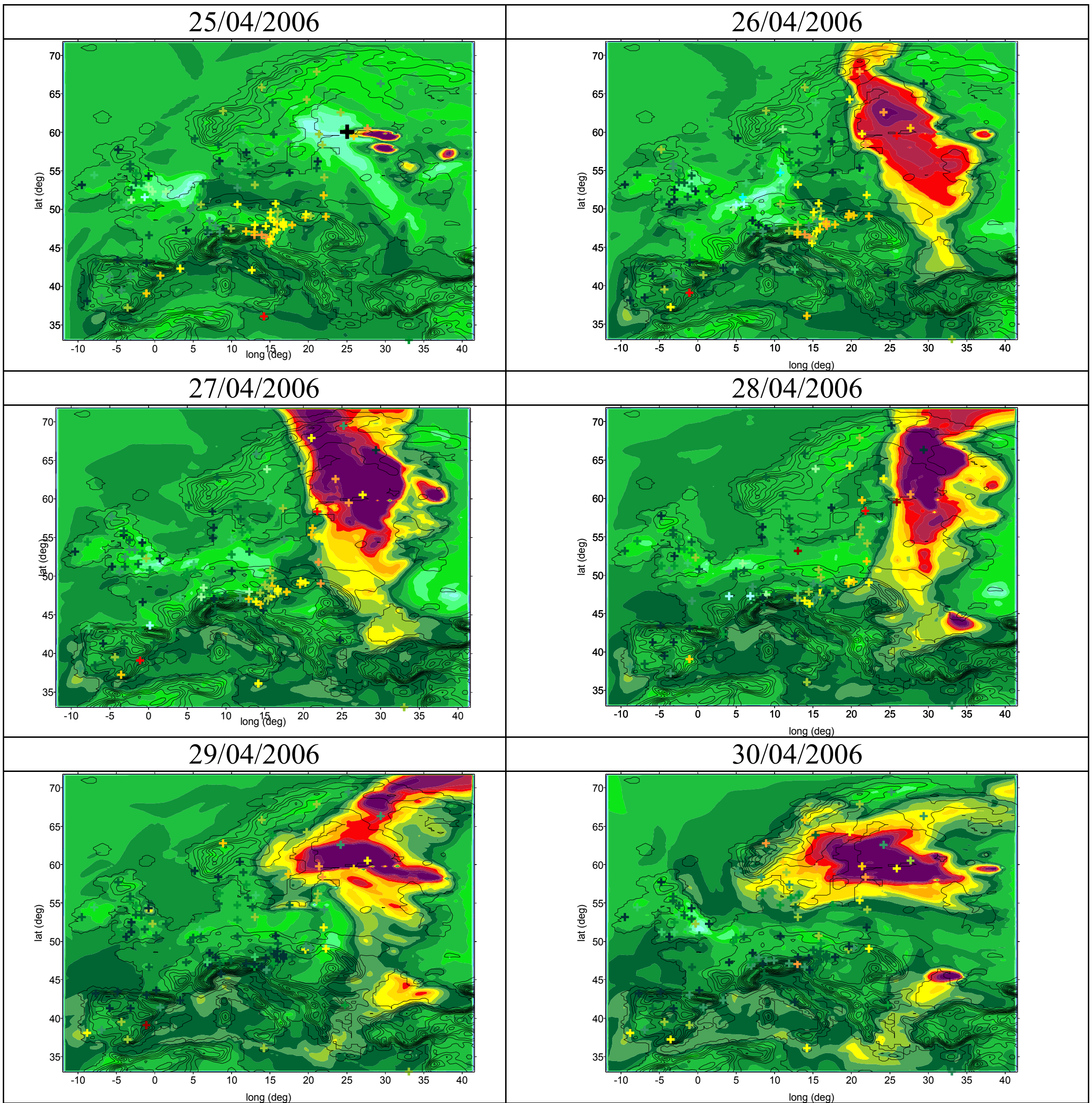


Figure 1: Predicted (color shade) and observed (symbols) daily maximum hourly O_3 concentrations (ppb) during 25/04-01/05/2006 for the reference run (considering grass as the burning material).



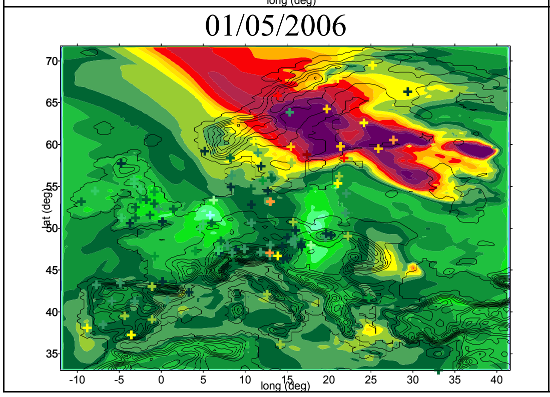


Figure 2: Predicted (color shade) and observed (symbols) daily maximum hourly O_3 concentrations (ppb) during 25/04-01/05/2006 for the AGRIC run (considering agricultural residues as the burning material).

- page 3476, line 17: why are you using US EPA metrics definition?

US EPA metrics are standard metrics and are often used by many researchers for studies over Europe (e.g. Jimenez et al., 2005 *in Atmos. Environ.*; Pay et al., 2010 *in Atmos. Environ*; Aksoyoglu et al., 2008 *in Ecological modelling*)

- In table 1 you're showing metrics for two NOx/CO ratios, which were not previously introduced

The reviewer is correct. In the revised manuscript, the simulation considering agricultural residues as burning material is introduced in section 2 'Methodology, modeling tool, and input data' and its assumptions are presented in section 2.3 'Fire emissions'.

- page 3477, lines 9-10 and figure 7: correlation values are mentioned, but they are not previously included in the description of the statistical parameters (page 3476), nor in table 1.

The reviewer is correct. The text has been revised accordingly: "*The statistical analysis includes the calculation of the predicted and observed average, the mean normalized bias (MNB), the mean normalized error (MNE), the mean fractional bias (MFB), the mean fractional error (MFE), the root mean square error (RMSE), correlation values and the time-paired and time-unpaired peak normalized bias and normalized error*."

The correlation values are also included in Table 2 (in the revised manuscript, the statistical metrics are presented in Table 2).

3.2 Impact of fire emissions

- page 3478, lines 25-26: fires release very large amounts of NOx, but also of VOCs.

The reviewer is correct. The text has been revised accordingly.

- page 3480, line 5: avoid mentioning figure 12 before including figure 11

In the revised manuscript the sequence of figures presentation has been changed. In particular, figure 11 is omitted in order to avoid an excess number of figures after the inclusion of the Factor Separation method.

3.4 Sensitivity to parameters of the fire emissions

- page 3482, lines 27-29: this information should be provided before when describing the fire event

The reviewer is correct. In the first submitted paper, the description of our case (grass fires) was not clearly stated in the Introduction section. In the revised manuscript this information has been included both in the Introduction section:

"The case study is the widespread wild-land fires over Western Russia during spring of 2006. This biomass smoke episode was exceptionally long, lasting about 12 days (24 April and 10 May 2006) (Saarikoski et al., 2007; Stohl et al., 2007; Treffeisen et al., 2007) and was mainly created by numerous small-scale dry-grass fires, largely man-made, that occurred under quite typical late-spring conditions (Sofiev et al., 2009). "

and section 2.3 'Fire emissions':

"*The daily distribution of the total FRP release from each land-use class (mixed, forest, grass) revealed that the fire event investigated in this study represents mainly a dry grass fire (Sofiev et al. 2009). The patterns of all gaseous emission fluxes follow the PM ones and are based on scaling factors relative to total PM considering grass as the burning material. However, in order to quantify the sensitivity of the O_3 production on the fire emission properties a sensitivity run considering agricultural residues as burning material (AGRIC) is also examined.*"

I understand the sensitivity studies, but it is not clear the use of injection heights typical of crown fires, if the studied event mainly was a dry grass fire.

For the case we considered, the daily distribution of the total FRP release from each land-use class (mixed, forest, grass) revealed that the fire event investigated in this study represents mainly a dry grass fire (Sofiev et al., 2009). However, emissions from forest and mixed areas are also substantial (Fig 2, *in Sofiev et al., 2009*) injecting releases also above the PBL (e.g. Labonne et al., 2007).

4. Conclusions

Part of the work was focused on performance of the application, but conclusions are too poor on this point. Only the last paragraph "touches" this issue. Please, include something about your performance evaluation work.

In the revised manuscript information on the performance of the simulations as well as on the results of the Factor Separation method and the sensitivity runs have been included.