Dr. Muller

I find interesting to test different oxidation mechanisms against the reported observations near Seoul, but I'm at a loss regarding the choice of the different scenarios. I understand that α is the OH yield in the reaction of isoprene peroxy radicals with HO_2. The reference given for its adopted value (2.6), Wolfe et al. (2012), is not appropriate. Such high yield was proposed by Lelieveld et al. (2008) as an artificial OH recycling re- action introduced in order to match the GABRIEL campaign measurements. But there is a wide consensus that the OH yield is of the order of 10% or less (e.g. Liu et al., 2013). I fail therefore to see the relevance of simulations combining HPALD chemistry with a high value of α.

Responses to Dr. Muller's comments

We appreciate Dr. Muller's very insightful comments. We acknowledge that the discussion about the recycling scenario in the original manuscript was not thorough enough to inform most up to dated isoprene oxidation photochemistry to the readers. In the revised manuscript, we introduced the laboratory experimental results by Liu et al. (2013) so that we can inform the readers that our recycling scenarios are upper limit of the OH recycling. However, we think that the upper limit scenario can be informative as our main purpose is to introduce the upper and lower limits of radical pool distributions for the assessments of photochemical product formation rates.

Referee #1

This paper presents interesting measurements of air chemistry compounds in a South- Asian forest and shows box-model simulations with various constraints applied. This is certainly a very well fitting into the current discussions about interactions between biogenic and anthropogenic emissions and how these influence the composition and quality of the air.

However, I found some irritating issues. First, nearby (?) urban measurements are discussed several times for comparison with the forest observations but are not presented in the paper. Given that the measurement period was only very short (6 days), which is a problem in itself, the explicit presentation of the mentioned data would greatly enhance the manuscript value.

As we agreed that we present a dataset from a relatively short time period, our focus is to study photochemical characteristics during the pollution episode with a significant BVOC influence. The given time frame provides a perfect opportunity to study the topic so we focus our discussion on the time frame. We stressed this point in the revised manuscript.

It would then also justify the title which is indicating that also urban air chemistry is investigated. Second, the article is not very clear and difficult to follow. This is partly due to an insufficient structure such as presenting results and discussions together without indicating so. Also the so called 'summary' (which should be indicated as 'conclusions') is really a mix of everything. Other reasons for the difficulties I have are that some essential descriptions are missing (e.g. use of abbreviation without explanation, presentation of constraints without explanations) or that language is improperly used (I should be careful without being a native speaker but I don't think that 'uncertainties surrounding the radical pool' is correct wording. I am also quite annoyed to read the word 'observed' in some variations in every second line (page 16700, total count in the text without references 92 times!).

Regarding the title, we do not have an intention to present 'urban air' rather as the title implies, we are exploring how regional pollution affects rural air quality. We read through the revised manuscript carefully to eliminate any redundancy that may cause confusions as the referee suggested. We do think that it is not an unusual way to present results and discussion in the same section. However, as the referee suggested we revised the manuscript for readers to easily follow the discussion. Especially, we separated the "3. Results and Discussion" section into three sections in the revised manuscript. As we believe the summary and conclusion section should be balanced between succinctly conveying main findings and urging the community moving into the new research directions, we edited accordingly in the revised manuscript.

Discussion by sections
As already indicated, I think the title is misleading due to the missing focus on urban- rural interactions. I also cannot see, why aerosols are mentioned which are not measured but modeling isn't.

What we meant by "urban-rural interaction" was urban influences over the rural region. We clearly mentioned this point in the revised manuscript. Also, we changed title as "OVOC productions" instead of "secondary organic aerosol" since our discussion mainly lies in OVOCs that are SOA precursors.

In the abstract it is stated as one result that different simulations cause different results (I am simplifying here). It would be better to tell which model settings have been found most appropriate and for which reason. The second result (radical destruction can be more efficient than radical recycling) is also quite general and should be better tailored to the case study: When and why is this so. What is the implication? The ozone photochemistry is probably not 'predicted' but the assumed mechanisms could represent the observed concentrations (using which assumptions/ constraints?). Also, there were no model 'scenarios' but model simulations under different settings, and the modeling experiments indicate that understanding can be improved by using constraint simulations but will never 'enable a precise understanding', right? I might be a bit picky but I feel using the terms right would greatly improve comprehension.

The point we would like to convey is that the lack of actual radical observations cause significant uncertainty in ozone and OVOC production rate estimation since there are a number of competing isoprene-OH interaction chemical mechanisms along with unconstrained HONO sources. This can still be true in the suburb of megacity where we usually assume that pollution would be a dominant driver for regional photochemistry. Therefore, we intend to quantitatively present the range of the uncertainty from insufficient understanding in isoprene-OH interactions in ozone and OVOC production depending upon the adaptation of competing model scenarios rather than evaluating specific chemical mechanisms for its validity in ambient conditions. We made this point clear in the revised manuscript. We choose the word "assessed" instead for "predicted" in the revised manuscript

The introduction seems fairly comprehensive with regard to air chemistry findings, al- though I doubt that biogenic emissions don't play a role in Los Angeles at least in the future (McPherson et al., 2011, Pincetl et al., 2013) or at the city boundaries

(Sartelet et al., 2012).

A recent analysis (Pollack et al., 2013, JGR Vol 118, 5893-5911) indicates that rapid decrease in anthropogenic VOCs past decades and no significant change in isoprene concentrations in the Greater Los Angeles Area. According to the described AVOC levels in Pollack et al. (2013) in 70s and 80s when photochemical smog issues were really serious in the LA area, AVOC composed much higher OH reactivity than that from BVOCs. Therefore, our argument on relatively insignificance of BVOCs in controlling Southern California photochemical smog issues still holds. We made this point clear in the revised manuscript.

I also like to hint that uncertainties in global BVOC emissions are better indicated in some recent publications (Arneth et al., 2011, Harrison et al., 2013, Williams et al., 2013) than in (Guenther, 2013a).

We updated the discussion as suggested

You might consider (Guenther, 2013b) though. Please note that the cited (Spaulding et al., 2003) is not in the reference list and also that papers from 2008 and 2009 cannot be referenced as 'new' anymore.

Spauling et al. (2003) was introduced to explain the previous status quo about isoprene photochemistry not to introduce the most up to dated isoprene photochemistry. We made this point clear in the manuscript.

I am not an expert here, but aren't there also contradicting findings regarding OH reactivity (Nölscher et al., 2013)? In the end, the link to forest measurements is quite poor. The objective why is it useful to study in a forest area close to Seoul and the benefits from model simulations should be much more clearly defined. Doing so, some similar exercises could be mentioned (Brilli et al., 2014, Bryan et al., 2012, Nakashima et al., 2014, Nölscher et al., 2012, Préndez et al., 2013).

We don't think Nolsher et al. (2013) is a particularly good example since they described individual leaf level observational results rather than results from the ecosystem ambient observations. Nakahima et al. (2014) and Nolscher et al. (2012) were observational results mainly from MT dominant ecosystems so they are not relevant in the discussion. Bryan et al. (2012) and Prendez et al. (2013) do not discuss specifically about OH reactivity observations.

Since my work is focused on modeling, I might be more critical here than about the measurements. Regarding the site, some more information, e.g. about leaf area index would be welcome but what strikes me most odd is that I cannot find a proper reference to this UWCM model. There is none given here and none given in the other papers of the author. There should be however, some indications on how the MCM is applied and how the boundary conditions are set.I also find that the single table is not enough to define the modeling scenarios. Some more details about what is supplied by measurements and what is calculated by the model in each setup would be very much welcome. I am particularly curious about how BVOC emission modelling is done under unconstrained conditions for those conditions that are apparently influenced by different forests (or is it always constrained?).

We introduced the UWCM reference, which is Wolfe and Thornton (2011). More thorough descriptions about how MCM was integrated in the UWCM model were included in the revised manuscript. Table 1 was presented to provide descriptions on the different model scenarios. We provide more information about each scenario in the table. By constraining relatively long-lived species such as CO, NOx, and VOCs with observations, we avoid uncertainty from boundary layer height and BVOC emission rate parameterizations. In other words, we utilized the UWCM model as a 0D-box model to calculate very short-lived chemical species (less than a second) for the evaluation of ozone and OVOC production rates. This approach has been widely used especially in radical observation community (e.g. Kim et al., 2013, Kim et al., 2014, and Mao et al., 2012). We add this explanation in the revised manuscript.

Results and discussion sections are merged (which should be indicated in the head- lines) and are separated into observations and modeling (unfortunately not called modeling but 'implications of uncertainties in isoprene-hydroxl radical interactions in assessments of regional ozone and organic aerosol precursor production').

We separated the 'Results and Discussion' section into three sub-sections.

Here (p 16700, L7ff) the authors discus measurements in the center of Seoul without presenting them or giving a reference. This is a bid odd. Are those for the same period? Is it reasonable to assume transport from one place to another? Has a model been applied to better characterize the interactions between the two sites (should be expected from the title)?

We compared CO concentrations during the same period. We clarified it in the revised manuscript. We think it is reasonable to assume for CO mostly from pollution to be transported from Seoul a nearby megacity. In addition, other regional 3d modeling studies (e.g. Ryu et al., 2012 ACP, 13, 2177-2194) clearly show that emitted trace gases in the Seoul city center are transported to the suburban region.

From the results, the different patterns in isoprene and monoterpenes are most striking. First, the isoprene maximum in the evening is discussed to originate from "different air masses" which are "consistently observed" at this site or from a "reduced vertical mixing". What does this mean? There should certainly be wind measurements from which the origin of air masses could be defined – these should be presented. The change of the mixing layer height is possible and it is unfortunate that no ceilometer measurements are available – but I wonder why the increase cannot be seen in the monoterpene concentration?

Since regional and vertical transport phenomena at the site will be presented in a separate paper, we removed the discussion on the regional transport. Rather, only discussion on diurnal patterns of isoprene and MT are presented. The late afternoon isoprene peak has been also reported in other forest environments (e.g. Apel et al., 2002 JGR Vol 107 D3 4034; and

Bryan et al., 2012 ACP 8829-8849). It should be also noted that the maxima of the BVOC emission and its ambient concentration are not necessarily coincided each other as the pervious studies clearly indicated. We also included this discussion in the revised manuscript.

Most of the discussion in the modeling section can only be judged when the model settings and parameters as well as the constraints are better known. So this is very difficult here. I just would suggest not touse the term 'scenarios' here which generally refer to different magnitudes of the same inputs but not to different pattern of inputs. The term HPALD, which seems to refer to something very important, is frequently used without any explanation. I gather this means isoprene-derived hydroperoxynals (Wolfe et al., 2012) but I would be happy if this could be indicated and some properties of the species group would be described. In general, the section develops throughout pages 16704 to 16709 from a discussion of study-observations into a general discussion and back. Perhaps this could be more clearly differentiated?

As described above, we expanded discussion describing model scenarios.

As mentioned above, I was surprised to find a 'summary' in addition to the 'abstract' and I gather this should better be a 'conclusion' section. The section is particularly suffering from language problems (e.g. 'HONO sources are also appeared to cause a quite high level of underestimation'). Some points are very interesting such as the high radical destruction rate in the afternoon which coincides with isoprene abundance or the VOC limited ozone formation despite being in a quite rural area. On the other hand, at least the latter has been discussed already in (Kim et al., 2013). I also miss a comparison between different case studies of similar kinds (Bryan et al., 2012, Fares et al., 2013, Lu et al., 2012, Nölscher et al., 2012, Ran et al., 2011, Wolfe et al., 2011) and a critical evaluation about the dependence of observations on seasonality (Llusia et al., 2012, Nölscher et al., 2013, Situ et al., 2013).

As suggested we changed the section title as '4. Summary and conclusion'. In addition, we edited this section to be well-read. In terms of comparisons with previous studies, we thoroughly discuss the points in the main text. In the '4. summary and conclusion' section, we would like to make a case why the in situ observation of radical species is a key to address regional photochemical air pollution issues along with a succinct summary. Therefore, we edited the section accordingly in the revised manuscript.

Regarding the figures, please note that the arrow to OVOCs in Figure 1 should have the same spin as the arrow coming from RO2 and that the abbreviation (i.e. OVOC) should be explained. In Figure 2 the term KST (probably hours per day) is not explained and variances (standard variations over the 6 days measured) are not given. Also, the axes labels are too small.

We corrected as referee commented.

Referee #2

General comments: The manuscript "Urban-rural interactions in a South Korean forest: uncertainties in isoprene-OH interactions limit understanding of ozone and secondary organic aerosols production" by Kim et al present a isoprene-OH study in forest area. This work was designed to investigate the urban-rural interactions by constraining key atmospheric chemical processes. I think that this research had contribution to better understand isoprene chemistry, and the methodology was encouraging. However, the way of presenting the scientific findings is not explicit and often confusing, and the current version needs more technical details.
Specific comments:
1 The title is too long, needs modification to highlight the aim of the work, I suggest the authors to remove ozone and SOA out ;

We changed the title as "Urban-rural interactions in a South Korean forest in ozone and OVOC formation perspectives"

2 The abstract and the whole text have a lot of well-known knowledge, the authors needs to do some housekeeping, and focus on the findings from this work, e.g., figure 1 and related text could be deleted;
We removed Figure 1 in the revised manuscript and edited the introduction section accordingly.

3 The section of method is weak. The authors published a paper on the measurements already, however as a follow-up work, one needs to know the area of the forest, statistics of the vegetation, meteorological parameters with the consideration of urban areas. 4 The measurements techniques needs to add data of QA/QC, especially for VOCs speciation and HONO when different technologies were used for the same pollutants;

We added further details on site information and instrument QA/QC procedures. We utilized the PTR-MS dataset for VOC quantification and the GC/MS dataset is only used for the qualification purpose. We made the points clear in the revised manuscript. We included the discussion about HONO quantification techniques in the results/discussion section since we thought it fits better to explain the significance of having accurate HONO observations in the East Asian region.

5 The whole measurements were done only for 6 days? Will this be representative for urban-rural interaction? 6 Figure 2 looks strange to me, the peak around 17:00-20:00 cames out as a surprise, and I did not find reasonable explanation for this pattern.

The observations are yearlong but we choose a 6-day period of a pollution episode caused by regional stagnation from a high-pressure system. We included this discussion in the revised manuscript.

Branch enclosure measurement results that were not presented but are being prepared for a separate manuscript clearly show mid-day maxima for BVOC emissions as expected. However, ambient BVOC concentrations are determined by not only emissions but also photochemistry and transports. Therefore, the temporal discrepancy between emission and ambient concentration maxima is expected and actually has been reported in the previous studies (e.g. Hansen et al., 2012; Apel et al., 2002). We added this discussion in the revised manuscript.

7 The title for section 3.2 is much too long, with a lot of ideas mixed up. I strongly suggest to break it down to several parts, to present the constrains on isoprene, intermediates, HONO, and radicals separately.

We separated section 3.2 in to two sections. The first section is describing HO_X levels from the different model calculation scenarios and the second section is describing implications of uncertainty in estimating HOX levels using model calculations in ozone and OVOC productions. We only present one HONO evaluation scenario as explained in the comment section 8 to simplify section 3.2 describing justifications for the model scenarios.

8 I do not understand the logic of the 7 scenarios in table 1 and the explanation in text.

We agree that there is a redundancy to present two scenarios without constraining observed HONO as the submitted manuscript. In the revised manuscript, we did not present Scenario VI.