

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 HO₂. 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 reaction 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 relative 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.

Spaulding 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 Nölscher et al. (2013) is a particularly good example since they described individual leaf level observational results rather than results from the ecosystem ambient observations. Nakashima et al. (2014) and Nölscher et al. (2012) were observational results mainly from MT dominant ecosystems so they are not relevant in the discussion. Bryan et al. (2012) and Préndez 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, NO_x, 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-hydroxyl 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 discuss measurements in the center of Seoul without presenting them or giving a reference. This is a bit 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 comes 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.

1
2
3
4 **Urban-rural interactions in a South Korean forest in ozone**
5 **and oxygenated volatile organic compound formation**
6 **perspectives**
7

8 ¹Saewung Kim, ²So-Young Kim, ³Meehye Lee, ³Heeyoun Shim,
9 ^{4,5}Glenn M. Wolfe, ⁶Alex B. Guenther, and ¹Amy He, ²Youdeog Hong,
10 ²Jinseok Han
11

12
13
14
15
16 1 Department of Earth System Science, School of Physical Sciences, University
17 of California, Irvine, Irvine California, 92697 U.S.A.

18 2 National Institute Environmental Research, Incheon, South Korea

19 3 Department of Earth and Environmental Sciences, Korean University, Seoul,
20 South Korea

21 4 Joint Center for Earth Systems Technology, University of Maryland Baltimore
22 County, Baltimore, MD, USA

23 5 Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space
24 Flight Center, Greenbelt, MD, USA

25 6 Atmospheric Sciences and Global Change Division, Pacific Northwest National
26 Laboratory, Richland WA USA
27

28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44 To be submitted to Atmospheric Chemistry and Physics “East Asian Megacity”
45 Special Issue

Saewung Kim 8/29/2014 2:38 PM

Deleted: : Uncertainties in isoprene-OH interactions limit understanding of ozone and secondary organic aerosols production

50 Abstract

51 Rapid urbanization and economic development in East Asia in past decades has
52 led to photochemical air pollution problems such as excess photochemical ozone and
53 aerosol formation. Asian megacities such as Seoul, Tokyo, Shanghai, Gangzhou, and
54 Beijing are surrounded by densely forested areas and recent research has consistently
55 demonstrated the importance of biogenic volatile organic compounds (VOCs) from
56 vegetation in determining oxidation capacity in the suburban Asian megacity regions.
57 Uncertainties in constraining tropospheric oxidation capacity, dominated by hydroxyl
58 radical concentrations, undermine our ability to assess regional photochemical air
59 pollution problems. We present an observational dataset of CO, NO_x, SO₂, ozone,
60 HONO, and VOCs (anthropogenic and biogenic) from Taehwa Research Forest (TRF)
61 near the Seoul Metropolitan Area (SMA) in early June 2012. The data show that TRF is
62 influenced both by aged pollution and fresh BVOC emissions. With the dataset, we
63 diagnose HO_x (OH, HO₂, and RO₂) distributions calculated using the University of
64 Washington Chemical Box Model (UWCM v 2.1) with near-explicit VOC oxidation
65 mechanisms from MCM 3.2 (The Master Chemical Mechanism). Uncertainty from
66 unconstrained HONO sources and radical recycling processes highlighted in recent
67 studies is examined using multiple model simulations with different model constraints.
68 The results suggest that 1) different model simulation scenarios cause systematic
69 differences in HO_x distributions especially OH levels (up to 2.5 times) and 2) radical
70 destruction (HO₂+HO₂ or HO₂+RO₂) could be more efficient than radical recycling
71 (HO₂+NO) especially in the afternoon. Implications of the uncertainties in radical
72 chemistry are discussed with respect to ozone-VOC-NO_x sensitivity and VOC oxidation

Saewung Kim 9/19/2014 11:28 AM

Deleted: with

74 product formation rates. Overall, the VOC limited regime in ozone photochemistry is
75 assessed but the degree of sensitivity can significantly vary depending on the model
76 scenarios. The model results also suggest that RO₂ levels are positively correlated with
77 oxygenated VOCs (OVOCs) production that is not routinely constrained by observations.
78 These unconstrained OVOCs can cause higher than expected OH loss rates (missing OH
79 reactivity) and secondary organic aerosol formation. The series of modeling experiments
80 constrained by observations strongly urge observational constraint of the radical pool to
81 enable precise understanding of regional photochemical pollution problems in the East
82 Asian megacity region. ▾

Saewung Kim 8/29/2014 3:45 PM

Deleted: predicted

Saewung Kim 9/3/2014 11:11 AM

Deleted: 0

Saewung Kim 9/19/2014 11:30 AM

Deleted: -

86 1. Introduction

87 NO_x (NO+NO₂) and volatile organic compounds (VOCs) are two important
88 precursors that drive HO_x radical cycles (Levy, 1971). In the presence of NO_x, VOC
89 oxidation processes recycle OH and produce photochemical oxidation products such as
90 ozone and oxygenated VOCs (OVOCs). This reaction cycle is highly non-linear. For
91 example, excess NO₂ may expedite nitric acid formation (R1), limiting ozone production.
92 In the same context, excess VOCs may expedite peroxy radical production (R2), which
93 limits OH regeneration from peroxy radicals.



97
98 The non-linearity in tropospheric photochemistry has been relatively well studied
99 in the urban regions of developed countries and applied in ozone reduction policy. The
100 Los Angeles Metropolitan Area has accomplished significant ozone reduction by
101 implementing aggressive emission reductions of both NO_x and VOC especially from
102 mobile sources (Ryerson et al., 2013). The remarkable ozone abatement was possible due
103 to the fact that there is no significant pollution transport from other metropolitan areas
104 and no significant natural emission sources especially volatile organic compounds from
105 vegetation (BVOCs; biogenic volatile organic compounds) compared with anthropogenic
106 VOC mostly from mobile sources (Pollack et al., 2013; Huang et al., 2013). In the late 80s,
107 Trainer et al. (1987) first demonstrated the importance of isoprene (C₅H₈) as a peroxy
108 radical source that can contribute significant ozone production in rural areas. The

Saewung Kim 9/2/2014 1:48 PM

Deleted: as shown in Figure 1

Saewung Kim 9/2/2014 1:52 PM

Deleted: Peroxy radical (HO₂ and RO₂) chemistry becomes the backbone of OH recycling. In addition, subsequent interactions with peroxy radicals and NO_x (NO+NO₂) produce ozone and oxygenated VOCs (OVOCs) that are precursors for secondary organic aerosols. In summary, i

117 importance of isoprene in ozone production in urban areas has also been highlighted, e.g.
118 in the Atlanta Metropolitan Area (Chameides et al., 1988).

119 Isoprene is a hemiterpenoid species and is the globally dominant VOC emission
120 from vegetation (Arneth et al., 2011; Guenther, 2013). Arguably, isoprene is the most
121 frequently studied BVOC from the perspective of atmospheric oxidation processes and
122 their implications for ozone and aerosol formation. However, significant uncertainty
123 hinders assessing the roles of isoprene in regional and global photochemistry in three
124 fronts. First, there is still significant uncertainty in estimating emission rates from each
125 individual plant species on regional scales (Guenther, 2013). Second, limited isoprene
126 inter-comparison results (Barket et al., 2001) suggest that there are large systematic
127 biases among different analytical techniques. Lastly, recent laboratory, theoretical and
128 field observations suggest significant uncertainty in tropospheric isoprene oxidation
129 processes initiated by OH. Until early 2000, it was thought that three first generation
130 isoprene oxidation products (methyl vinyl ketone, methacrolein, and formaldehyde) from
131 OH oxidation were enough to constrain isoprene tropospheric oxidation processes for
132 modeling purposes (e.g. Spaulding et al., 2003). This is an interesting evolution of
133 thoughts considering that Paulson and Seinfeld (1992), one of pioneering works
134 describing isoprene oxidation, clearly claimed that 22 % of first generation isoprene
135 oxidation products from the reaction with OH was not identified and likely included
136 multifunctional C5 compounds. Recent advances in analytical techniques (Kim et al.,
137 2013a) have shown that indeed significant C5-hydroxy carbonyl (e.g. isoprene
138 hydroperxyenals, HPALD) and peroxide compounds are produced as first generation
139 isoprene oxidation products (Crouse et al., 2011; Paulot et al., 2009; Wolfe et al.,

Saewung Kim 8/29/2014 3:59 PM

Deleted: (Guenther, 2013)

Saewung Kim 9/19/2014 11:45 AM

Deleted: ment of

142 2012;Zhao and Zhang, 2004) and are a strong function of NO concentrations (Peeters and
143 Muller, 2010). In general, low to intermediate NO levels (~ 100 pptv or lower), the yields
144 of C5-hydroxy carbonyl compounds become higher. These new findings in the isoprene
145 oxidation process are also closely related with recent findings in unexpectedly high OH
146 concentrations (Hofzumahaus et al., 2009;Lelieveld et al., 2008) and substantial missing
147 OH sinks also known as unexpectedly high OH reactivity in high isoprene environments
148 (Di Carlo et al., 2004;Edwards et al., 2013;Kim et al., 2011;Lou et al., 2010).↓

149 These new findings have significant implications in regional air quality especially
150 in photochemical ozone and SOA production. Despite the strong anthropogenic pollutant
151 emissions in East Asia (China, Japan and South Korea), recent research has shown that
152 isoprene accounts for a major OH chemical sink in suburban areas near Beijing (Ran et
153 al., 2011), the Pearl River Delta region (Lu et al., 2012), and Seoul (Kim et al.,
154 2013d;Kim et al., 2013b). Consequently, modeling studies also clearly show that isoprene
155 contributes significantly to ozone formation in Asian megacity regions. Kim et al. (2013d)
156 reported that simulated ozone levels with isoprene chemistry are up to 30 % higher than
157 ozone simulation without isoprene chemistry using the WRF-Chem model, indicating an
158 urgent need to implement improved isoprene chemistry schemes in these models in order
159 to simulate the unexpected higher levels of OH in isoprene rich environments. This is
160 especially alarming as Hofzumahaus et al. (2009) reported significantly higher (~ 2.6
161 times at noon) than expected OH levels in the Pearl River Delta region in China.
162 Therefore, the current assessments based on the conventional OH photochemistry could
163 significantly misdiagnose regional air-quality status and mislead policy implementation
164 to reduce photochemical air pollution in the East Asian region. Furthermore, as the

Saewung Kim 8/29/2014 4:18 PM

Comment [1]: Nolscher et al., 2012 should be removed

Saewung Kim 9/4/2014 10:00 AM

Deleted: (Di Carlo et al., 2004;Edwards et al., 2013;Kim et al., 2011;Lou et al., 2010;Nolscher et al., 2012).

168 importance of BVOC in regional air-quality issues in ozone and SOA formation has been
169 also highlighted in Europe and North America, the uncertainty in isoprene
170 photochemistry has significant implications in urban and suburban air quality in
171 general(Zhang et al., 2008a;Sartelet et al., 2012).

Saewung Kim 9/19/2014 11:55 AM

Deleted: reporte

Saewung Kim 9/19/2014 11:55 AM

Deleted: potential

172 We present atmospheric observations of NO_x, CO, VOCs, ozone, and HONO in
173 the Taehwa Research Forest (TRF) in the Seoul Metropolitan Area (SMA), South Korea.
174 We use these data to conduct observationally constrained box model (University of
175 Washington Chemical Box Model; UWCM) calculations to estimate OH, HO₂ and RO₂
176 concentrations with different sets of observational parameters. We discuss current
177 uncertainty in OH-isoprene photochemistry with perspectives of constraining
178 photochemical ozone production and OVOCs precursors of secondary organic aerosols.
179

Saewung Kim 9/19/2014 11:56 AM

Formatted: Subscript

Saewung Kim 9/19/2014 11:56 AM

Formatted: Subscript

Saewung Kim 9/4/2014 9:57 AM

Deleted: oxygenated

180 2. Methods

181 The Taehwa Research Forest (TRF) is located ~ 35 km from the center of Seoul,
182 South Korea. The TRF is located at the southeastern edge of the Seoul metropolitan Area
183 (SMA, population of ~ 23 million). TRF has a sampling tower located in the middle of a
184 coniferous tree plantation (200 m by 200 m) with the canopy height of 18 m (*Pinus*
185 *koraensis*) surrounded by a deciduous forest mostly composed by oak. Kim et al. (2013d)
186 reported CO, NO_x, SO₂, ozone, and VOC observation results along with WRF-Chem
187 assessments of ozone forming potential of isoprene photochemistry. The report found that
188 isoprene was the most dominant OH chemical sink during daytime among the observed
189 trace gases and explained up to 30 % of ozone production. The TRF instrumentation has

193 previously been described by Kim et al. (2013d). Therefore, just brief descriptions of
194 analytical techniques are given in this paper.

195

196 2.1. CO, NO_x, SO₂, ozone, VOCs, and meteorological parameters

197 Thermo Fisher Scientific Enhanced Trace Level Gas Analyzers are used for CO,
198 NO_x, SO₂, and ozone observations as summarized Table 1. VOC observations are
199 conducted by a High-Sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS,
200 Ionicon GmbH). The atmospheric application of this technique is thoroughly reviewed by
201 de Gouw and Warneke (2007). In addition, the instrument suite at TRF is thoroughly
202 described in (Kim et al., 2013d). PTR-MS can quantify atmospheric VOCs that have
203 higher proton affinity than the proton affinity of H₂O (691 kJ mol⁻¹). Most alkanes have
204 lower proton affinity than water but alkene, aromatic and some QVOCs have higher
205 proton affinity and are suitable for quantification using PTR-MS (Blake et al., 2009).

206 These compounds are more reactive than alkane compounds so PTR-MS has capability to
207 observe reactive atmospheric compounds. The TRF PTR-MS system was set to measure
208 acetaldehyde, acetone, acetic acid, isoprene, methylvinylketone (MVK) + methacrolein
209 (MACR), MEK, benzene, xylene (*p*, *m*, and *o*), and monoterpenes (MT). Each compound
210 was set to be monitored for 1 second each resulting in a sample cycle of 15 seconds.

211 Lower detection limits for the observed VOCs are estimated to be 20 ppt for a 5 second
212 integration with sensitivity of 70 counts ppb⁻¹ (2 σ). Meteorological parameters such as

213 temperature and humidity are monitored by LSI LASTEM Meteorological Sensors. All

214 the presented data is from the 15 m (the canopy height is 18 m) sampling line and

215 meteorological sensors collocated at this height too.

Saewung Kim 9/4/2014 9:57 AM

Deleted: oxygenated

Saewung Kim 9/20/2014 4:12 PM

Deleted: s in the atmosphere

Saewung Kim 9/2/2014 11:02 PM

Deleted:

Saewung Kim 9/2/2014 11:02 PM

Formatted: Superscript

Saewung Kim 9/20/2014 4:13 PM

Deleted: (the canopy height is 18 m)

220 PTR-MS with a quadrupole mass filter has an intrinsic limitation that isobaric
221 compounds are all collectively quantified with the same channel (m/z) with a resolution
222 of unit mass. This limitation particularly becomes an issue for investigating the roles of
223 different isomers of MT and sesquiterpenes (SQTs) in photochemistry. For this reason,
224 we also occasionally collect sorbent cartridge samples to analyze MT and SQT speciation
225 in both ambient air and branch enclosure emissions near the sampling tower. As
226 described in (Kim et al., 2013d), Tenax GR and Carbotrap 5TD packed sorbent cartridges
227 (Markes Int, Llanstrisant, UK) were used for sampling. The sampled cartridges were
228 shipped to National Center for Atmospheric Research (NCAR), Boulder CO, USA for
229 gas chromatography-mass spectrometer (GC-MS) analysis. An Agilent 7890 GC/5975 C
230 Electron Impact Mass Spectrometer (GC-MS/FID) in conjunction with a MARKES
231 Unity1/Ultra thermal desorption system optimized for terpenoid analysis quantifies
232 speciated MT and SQT in the sorbent samples. Cartridge samples are both collected from
233 ambient and branch enclosure air. Ambient samples were collected in the mid-day to
234 early afternoon with a volume of 6 L. Ozone in the ambient air was removed using a
235 Na₂SO₃ filter. Branch enclosure samples were also collected in the mid-day time frame
236 with a volume of 1 L without an ozone filter as zero air was introduced to the branch
237 enclosure. We present these analytical results from GC-MS analysis limited to the
238 qualification purpose to examine MT and SQT speciation.

239

240 **2.2 HONO quantification**

241 HONO was measured with an ion chromatography (IC) coupled with diffusion
242 scrubber. Air was introduced to diffusion scrubber (Lab solutions Inc., IL, USA) through

243 a 2 m PFA tubing (1/4" i.d.) at 1.5 L m⁻¹ using a filtered orifice restrictor (F-950, air
244 logic, WI, USA). Air flowing through diffusion scrubber interfaced with deionized water,
245 into which HONO was extracted. 50 µL of solution was injected into the IC system
246 through a PEEK loop (Rheodyne, WA, USA) and 6-way valve (EV750-100, Rheodyne,
247 WA, USA). Eluent was a mixture of Na₂CO₃ and NaHCO₃, which was pumped by a
248 HPLC pump (DX-100, Dionex, CA, USA) into a guard column (Ionpax® AG 14,
249 4x50mm, Dionex, CA, USA) and then analytical column (Ionpax® AS 14, 4x250mm,
250 Dionex, CA, USA). The column affluent passed through a suppressor (ASRS 300,
251 Dionex, CA, USA) and HONO was detected as nitrite ion in conductivity detector (550,
252 Alltech, IL, USA). The entire measurement processes of sampling, chemical analysis, and
253 data acquisition were controlled by a digital timer and data acquisition software
254 (DSchrom-n, DS science, Korea), by which we obtained two measurements every hour.
255 The system was calibrated using a NO₂⁻ standard solution (Kanto chemical Co., Inc.,
256 Tokyo, Japan) whenever reagents were replaced. The detection limit was 0.15 ppb
257 estimated from 3σ of the lowest working standard. Specific analytical characteristics are
258 described in Simon and Dasgupta (1995) and Takeuchi et al. (2004).

259

260 2.3 UWCM box model

261 UWCM 2.1 is an open source box model coded by MATLAB (MathWorks®).
262 The model platform can be downloaded from a website
263 (<http://sites.google.com/site/wolfegm/code-archive>). The box model is embedded its own
264 HO_x (OH+RO₂)-RO_x (peroxyradical and alkoxy radical)-NO_x coupling chemical
265 mechanism. UWCM utilizes Master Chemical Mechanism version 3.2 (MCM 3.2)

Saewung Kim 8/30/2014 8:21 PM

Formatted: Subscript

Saewung Kim 8/30/2014 8:21 PM

Formatted: Subscript

Saewung Kim 8/30/2014 8:21 PM

Formatted: Subscript

Saewung Kim 8/30/2014 8:22 PM

Formatted: Subscript

Saewung Kim 8/30/2014 7:14 PM

Deleted: UWCM

Saewung Kim 8/30/2014 7:04 PM

Deleted: (v.2.1)

Saewung Kim 8/30/2014 7:33 PM

Deleted: has the capability to adapt the Master Chemical

270 (Jenkins et al., 1997; Saunders et al., 2003) for near-explicit VOC photo-oxidation
271 schemes. A more detailed model description can be found in Wolfe and Thornton (2011).
272 To minimize uncertainty from the parameterizations of transport and emission, we
273 constrained relatively long-lived trace gases presented in Figure 1. This box modeling
274 technique has been commonly used for examination of OH levels that can be justified by
275 the short chemical lifetime of OH (Kim et al., 2014; Kim et al., 2013c; Mao et al.,
276 2012; Mao et al., 2010). Recently developed isoprene photo-oxidation mechanisms
277 shown in Archibald et al. (2010) are also incorporated in the model. In addition, Kim et al.
278 (2013c) and Wolfe et al. (2013) applied the model in the identical fashion as used for this
279 study to probe radical distributions using comprehensive observational datasets. This
280 study used the UWCM to simulate the diurnal variations of radical pool (OH+HO₂+RO₂)
281 distributions as observational parameters such as CO, NO_x, ozone, and VOCs are
282 constrained. To fully account for roles of QVOCs in the box model as radical sources, we
283 simulated three consecutive days and presented diurnal variations from the third day. The
284 specific parameters, constrained by observations are listed above.

285

286 3. Results

287 3.1. Observational Results

288 Diurnal averages of observed trace gases (June 1st 2012 to June 6th 2012) are
289 shown in Figure 1. The TRF observatory is in continuous operation and we choose this
290 six day period because a regional high-pressure system caused a stagnant air pollution
291 event in this period. In the center of Seoul (the real-time data available at
292 <http://www.airkorea.or.kr>), carbon monoxide was observed in the similar levels during

Saewung Kim 8/30/2014 7:44 PM

Deleted: including all the chemical species and reactions

Saewung Kim 9/3/2014 11:12 AM

Deleted: 0

Saewung Kim 9/4/2014 9:57 AM

Deleted:

Saewung Kim 9/3/2014 10:47 AM

Deleted: 2

Saewung Kim 8/29/2014 1:44 PM

Deleted: During this period, the weather was mostly clear and the trace gases were observed in the typical ranges observed during the previous summer (Kim et al., 2013b). Regionally,

Saewung Kim 8/29/2014 1:58 PM

Deleted: high pressure

304 | the focused period (June 1st to June 6th, 2012). On the other hand, the NO₂ level observed
305 | in central Seoul was much higher (20-50 ppb) compared with observed levels at TRF.
306 | The reason can be attributed to differences between the chemical lifetime of CO (~a
307 | month) and NO₂ (~a few hours to a day). The observations also clearly indicate that the
308 | TRF is not directly influenced by fresh SMA pollution plumes although the TRF is very
309 | close to the center of Seoul (30 km away from the city center) and a regional modeling
310 | study shows most of CO and NO_x sources are located in the city center (Ryu et al., 2013).
311 | Similar observations were also reported for other East Asian megacities such as Beijing
312 | (Ma et al., 2012), where ~ 30 ppb and ~ 15 ppb of NO₂ were observed at noon in the
313 | urban and the adjacent rural sites, respectively. In contrast, there were no noticeable
314 | differences in CO levels between the urban and rural sites (~ 1-2 ppm). The observed
315 | CO, NO_x and SO₂ levels in TRF were much lower than those observed in the suburban
316 | regions of Chinese megacities such as Beijing (Ma et al., 2012), Shanghai (Tie et al.,
317 | 2013), and the Pearl River Delta Region (Lu et al., 2012) and similar with the observed
318 | levels in Tokyo, Japan (Yoshino et al., 2012).

319 | Previous VOC observations in the SMA consistently have shown that toluene is
320 | the dominant anthropogenic VOC followed by other aromatic compounds such as xylene
321 | and benzene (Kim et al., 2012; Na and Kim, 2001). Na and Kim (2001) reported high
322 | concentrations of propane from house hold fuel use. However, recent observation results
323 | from the photochemical pollution observational network managed by National Institute of
324 | Environmental Research (NIER) of South Korea in the SMA clearly indicate that propane
325 | levels have declined and are now much lower than the levels previously observed (NIER,
326 | 2010). This is probably caused by the implementation of a policy changing household

Saewung Kim 8/29/2014 1:58 PM

Deleted: observed

Saewung Kim 8/29/2014 1:58 PM

Formatted: Superscript

Saewung Kim 8/29/2014 1:58 PM

Formatted: Superscript

Saewung Kim 9/20/2014 4:42 PM

Deleted: is

Saewung Kim 9/20/2014 4:42 PM

Deleted: interpreted as due

Saewung Kim 8/29/2014 2:08 PM

Deleted: Seoul metropolitan area

Saewung Kim 9/3/2014 10:35 AM

Formatted: Subscript

331 fuel sources from propane to methane. (Kim et al., 2012) presented detailed aromatic
332 VOC distributions in the SMA from four different urban observational sites. In average,
333 toluene concentrations were observed ~ 7 times higher than the observed levels of xylene
334 and benzene. At the TRF, a similar anthropogenic VOC speciation distribution was
335 observed as shown in Figure 1. The observed toluene and MEK (methyl ethyl ketone)
336 mixing-ratios were much higher than benzene and xylene. MEK is detected in m/z of 73⁺
337 by PTR-MS. Although methyl glyoxal, an atmospheric VOC oxidation product, is also
338 detected on the same mass, we assumed that 73⁺ of m/z signals are mostly from MEK, an
339 anthropogenic VOC, since the temporal variation follows that of anthropogenic VOC
340 such as toluene and xylene. In addition, atmospheric lifetime of methyl glyoxal is much
341 shorter than MEK.

342 As the observation facility is located in the middle of a pine tree plantation (*Pinus*
343 *koraiensis*), monoterpenes (MT) are consistently observed. The temporal variation of
344 monoterpenes is affected by the planetary boundary layer evolution with a pattern of
345 higher MT levels during night than those of mid-day as has been often reported in other
346 forest environments (Bryan et al., 2012; Kim et al., 2010). This can be explained by
347 interplays between boundary layer evolution and temperature dependent MT emission. It
348 should be noted that the branch enclosure BVOC emission observations indicate that the
349 daily maxima of MT and SQT emissions were observed in the midday (between noon to
350 2 pm in the local time). The observed MT and SQT speciation information is summarized
351 in Table 2. Table 2a summarizes branch enclosure sample analysis results and ambient
352 sample analysis results are summarized in Table 2b. In general, observed MT and SQT in
353 the ambient air are consistent with previously observed distributions (Kim et al., 2013d).

Saewung Kim 9/3/2014 10:47 AM

Deleted: 2

Saewung Kim 9/20/2014 4:52 PM

Deleted: ,

Saewung Kim 9/20/2014 4:52 PM

Deleted: which

Saewung Kim 9/4/2014 11:44 AM

Deleted: 2

Saewung Kim 9/4/2014 11:44 AM

Deleted: 2

Saewung Kim 9/4/2014 11:44 AM

Deleted: 2

360 α -pinene and β -pinene were the dominant monoterpene and longifolene was the only
361 detected SQT species. In contrast, the branch enclosure observation results, reflecting
362 BVOC emission, indicate high emission of very reactive MT and SQT species such as β -
363 myrcene, α -caryophyllene, and β -caryophyllene. The fast oxidation of these highly
364 reactive terpenoid species suppresses the atmospheric presence of the compounds.
365 Therefore, photochemical oxidation processes of these compounds may have been
366 neglected. Investigating emissions and photochemistry of these reactive terpenoid
367 compounds can constrain potential missing OH reactivity and SOA production from
368 highly oxidized reaction products.

369 Isoprene is produced from carbon recently fixed through photosynthesis resulting
370 in higher emissions and atmospheric concentrations during the daytime. The temporal
371 variation shown in Figure 1 reveals an isoprene concentration maximum between 17:00
372 to 20:00. In addition, the ratios of MVK+MACR, major isoprene oxidation products and
373 isoprene at this period, are significantly lower than those of late morning to early

374 afternoon. Further regional and 1-D modeling studies are being conducted to examine
375 this observed temporal variations of isoprene and MVK+MACR. However, enhanced
376 isoprene levels in the late afternoon or early evening have been also reported in previous
377 studies (Apel et al., 2002; Bryan et al., 2012). The branch enclosure observations

378 demonstrate that isoprene is not emitted from the pine plantation but rather transported
379 from surrounding broadleaf forests as right outside of the pine plantation (200 m \times 200 m)
380 is a forested area dominated by oak trees. Oak comprises 85 % of broadleaf trees in South
381 Korea (Lim et al., 2011). Lim et al. (2011) quantified isoprene emission rates for five
382 representative oak species in South Korea and report a wide emission range from oaks

Saewung Kim 9/3/2014 11:01 AM

Deleted: 2

Saewung Kim 8/30/2014 10:19 PM

Deleted: This may indicate that two distinctive air masses were observed during early afternoon and late afternoon time periods. In general, this pattern is consistently observed at TRF and probably governed by local and regional atmospheric advection systems as described in Ryu et al. (2013). Another possibility is that the reduced vertical mixing and lower photochemical losses at this time of day results in higher isoprene concentrations

Saewung Kim 8/30/2014 10:21 PM

Deleted: .

395 that are negligible isoprene emitters ($<0.004 \mu\text{gC dw}^{-1} \text{h}^{-1}$; standard emission rates) to
396 others with very high isoprene emission rates of $130 \mu\text{gC dw}^{-1} \text{h}^{-1}$.

397 Contributions from each observed trace gas species towards ambient OH
398 reactivity are shown in Figure 2. This is calculated as the product of the observed species
399 concentration and its rate constant for reaction with OH. Observed OH reactivity from
400 VOCs are much higher than from other trace gases such as CO, NO_x, SO₂, and ozone.
401 Among the observed VOC species, BVOCs such as isoprene, α -pinene and β -pinene
402 accounted for significantly higher OH reactivity in comparison with the observed
403 AVOCs such as toluene, benzene, xylene and MEK. Isoprene accounts the highest OH
404 reactivity especially during the daytime. This analysis is consistent with reports from
405 other suburban observations from East Asian megacities such as Beijing (Ran et al.,
406 2011), the PRD region, China (Lou et al., 2010), and the Kinki region Japan (Bao et al.,
407 2010).

408 HONO levels up to 1 ppb were observed in the early morning and were
409 consistently higher than 0.5 ppb during the daytime. These observed levels are
410 substantially higher than reported observations from forest environments in North
411 America (Ren et al., 2011; Zhou et al., 2011), where NO_x (~ 1 ppb) is substantially lower
412 than the level observed at TRF. Ren et al. (2011) reported 30 – 60 ppt of HONO at the
413 Blodgett Forest Research Station in the western foothills of the Sierra Nevada Mountains
414 in the late summer of 2007. Zhou et al. (2011) also reported the similar levels of HONO
415 (below 100 ppt) from the PROPHET forest, a mixed hardwood forest in northern
416 Michigan (Pellston, MI). However, significantly higher HONO levels (~ 200 ppt to ~ 2
417 ppb) were reported by Li et al. (2012) from a rural observational site in the Pearl River

Saewung Kim 9/4/2014 11:43 AM

Deleted: 3

419 Delta region near Guangzhou, where comparable NO₂ levels with TRF were observed.
420 The high HONO levels (a few hundred ppt) especially during the daytime have been
421 consistently reported near Eastern Asian megacities such as Beijing (Li et al., 2012),
422 Shanghai (Hao et al., 2006), and Seoul (Song et al., 2009). Still these are limited datasets
423 and further comprehensive analysis, especially more extensive observation is required.
424 However, two recently proposed HONO production mechanisms may be able to explain
425 the higher levels in the Eastern Asian megacity region. One is HONO production from
426 NO₂ photo-excitation (Wong et al., 2012) as the region usually has high NO₂
427 concentrations and the other is HONO emission from soil bacteria (Oswald et al., 2013).
428 Oswald et al. (2013) found differences as much as two orders of magnitude in HONO
429 emissions from soil samples from different environments (e.g. pH and nutrient contents).
430 In addition, as most of observations in the East Asia regions were conducted with ion
431 chromatography based methods, more direct HONO quantification techniques such as a
432 chemical ionization mass spectrometry technique (Roberts et al., 2010) need to be used to
433 characterize any potential interferences such a high NO_x environment (e.g. N₂O₅). ▾

434 ▾

435 **3.2 HO_x Model calculations with different isoprene photo-oxidation scenarios and**
436 **the roles of unconstrained HONO sources in HO_x model evaluations.**

437 The presented observational results are used to constrain the UWCM box model. ▾
438 We evaluate uncertainties in the tropospheric oxidation capacity and how it affects our
439 ability to constrain ozone and OVOCs, secondary aerosol precursor production. The
440 observational results clearly indicate that isoprene is the most dominant OH sink among
441 the observed VOCs. In addition, NO concentrations were higher in the 600 to 800 ppt

Saewung Kim 9/2/2014 2:36 PM

Deleted: -

Saewung Kim 9/2/2014 2:36 PM

Deleted: 3.2 Implications of uncertainties in isoprene-hydroxyl radical interactions in assessments of regional ozone and organic aerosol precursor production

Saewung Kim 9/3/2014 11:05 AM

Formatted: Subscript

Saewung Kim 9/2/2014 2:28 PM

Formatted: Subscript

Saewung Kim 9/21/2014 9:51 PM

Deleted: and

448 range in the morning. On the other hand, afternoon levels were substantially lower in the
449 50 to 100 ppt range. The environment provides a unique opportunity to examine
450 implications of isoprene photochemistry in various NO conditions.

451 We conducted model simulation under six different scenarios. Each scenario is
452 described in Table 3. The quantitative assessments of the impacts to radical
453 concentrations (OH, HO₂, and RO₂) from unconstrained HONO sources are evaluated by
454 examining the model outcomes of the scenarios with and without constraining observed
455 HONO. To evaluate the impacts of hydroperoxy-methyl-butenal (HPALD) photolysis
456 and isoprene peroxy radical recycling in the radical pool, each chemical mechanism is
457 selectively constrained by different scenarios. For HPALD chemistry, we adapted two
458 different HPALD formation rate constants published by Peeters and Muller (2010) and
459 Crouse et al. (2011). The formation rates from Peeters and Muller (2010) is about 40
460 times faster than those from Crouse et al. (2011) in 298 K. Finally, we applied 2.6 of the
461 OH yield from isoprene peroxy radical and HO₂ reactions for the evaluation (Wolfe et al.,
462 2011). Although, Liu et al. (2013) demonstrated significantly lower OH recycling
463 contributions from HO₂ + isoprene peroxy radical reactions than those argued by Wolfe et
464 al. (2011) by interpreting chamber experiment results, the high recycling rate by Wolfe et
465 al. (2011) is applied in the model calculations to explore upper limit of uncertainty in
466 radical estimations.

467 Modeled OH, HO₂, and RO₂ from the five different model scenarios are shown in
468 Figure 3. A summary of averaged OH, HO₂, and RO₂ concentrations in the morning
469 (08:00 – 11:00) and the afternoon (13:00 – 16:00) from each simulation is shown in
470 Table 4. With respect to the base run results (Scenario I), Scenario III with the lower

Saewung Kim 9/3/2014 1:48 PM

Deleted: calculations

Saewung Kim 9/3/2014 1:48 PM

Deleted: seven

Saewung Kim 9/4/2014 11:23 AM

Deleted: 1

Saewung Kim 9/4/2014 3:22 PM

Deleted: Peeters et al

Saewung Kim 9/4/2014 3:22 PM

Deleted: .

Saewung Kim 9/4/2014 3:22 PM

Deleted: 09

Saewung Kim 9/4/2014 3:22 PM

Deleted: et al.

Saewung Kim 9/4/2014 3:22 PM

Deleted: 09

Saewung Kim 9/3/2014 1:50 PM

Deleted: W

Saewung Kim 9/2/2014 2:23 PM

Formatted: Subscript

Saewung Kim 9/4/2014 11:43 AM

Deleted: 4

Saewung Kim 9/4/2014 11:48 AM

Deleted: a

Saewung Kim 9/4/2014 11:44 AM

Deleted: 3

483 | HPALD formation rate does not cause noticeable differences in radical concentrations.
484 | Adapting higher HPALD formation rates (Scenario II) cause significant differences in
485 | radical distribution especially in RO₂. This difference is likely caused by the fact that
486 | significant isoprene peroxy radical is converted to HPALD. The higher levels of
487 | discrepancy is found in RO₂ between Scenario I and Scenario II in the afternoon when
488 | low NO concentrations are observed, which efficiently facilitates HPALD formation.
489 | Adding HO₂+isoprene peroxy radical reactions as OH recycling processes (Scenario IV
490 | and V) results in significant enhancements in OH and HO₂ with respect to the base run
491 | (Scenario I). RO₂ concentrations are calculated in significantly different levels between
492 | Scenario IV and V. This can be again accounted by the applications of different HPALD
493 | formation rates in the two different model scenarios. The higher level of OH from the
494 | additional recycling process causes substantially higher RO₂ formation rates than those
495 | from the scenarios without the additional recycling process. The faster HPALD formation
496 | in Scenario IV is appeared to cause faster loss of RO₂ resulting in low RO₂
497 | concentrations.

Saewung Kim 9/3/2014 1:51 PM
Deleted: observation

Saewung Kim 9/3/2014 1:52 PM
Deleted: observe

Saewung Kim 9/3/2014 1:52 PM
Deleted: in low

498 | Most striking differences can be found model simulation results with or without
499 | constraining observed HONO as shown in Figure 3. Model calculation results from
500 | Scenario VI indicate significantly smaller OH, HO₂, and RO₂ concentrations than the
501 | concentrations calculated from the counter part (Scenario IV), which contains identical
502 | constraints and isoprene photochemistry except constraining observed HONO. Again,
503 | this clearly indicates that more thorough evaluations not only impacts of HONO to air
504 | quality but also analytical techniques should be followed to precisely constrain
505 | photochemical processes in the region as argued in section 3.1.

Saewung Kim 9/3/2014 1:53 PM
Deleted: were observed

Saewung Kim 9/4/2014 11:56 AM
Deleted: 4b and Figure 4c

Saewung Kim 9/4/2014 12:03 PM
Deleted: C

Saewung Kim 9/3/2014 11:23 AM
Deleted: both

Saewung Kim 9/2/2014 4:10 PM
Deleted: and VII

Saewung Kim 9/2/2014 4:10 PM
Deleted: s Scenario I and

Saewung Kim 9/2/2014 4:11 PM
Deleted: I

Saewung Kim 9/3/2014 11:24 AM
Deleted: are constrained by observed HONO

Saewung Kim 9/2/2014 4:11 PM
Deleted: , respectively

518

519 3.3 Implications of uncertainty in HO_x model calculations in assessing photochemical
520 ozone and OVOC production.

521 Two competing chemical reactions (R3 vs. R4,5,6) determine radical distribution
522 regimes.



527

528 When the rate of R3 gets much faster than the sum of reaction rates of R4, R5,
529 and R6 then radical recycling processes become more efficient than radical destruction
530 processes. In this radical recycling regime, OH, a universal tropospheric oxidant, is well
531 buffered to maintain the elevated OH levels. On the other hand, the radical destruction
532 regime can be defined when the radical recycling rates (R3) are slower than the radical
533 destruction reaction rates (R4+R5+R6). Although it is still controversial the yield of OH
534 from (R4) for isoprene peroxy radicals which demands a serious discussion whether we
535 should regard R4 as a radical destruction reaction, we stick with the classical
536 categorization for radical recycling and destruction regimes in this study. The temporal
537 variations of radical-radical reaction rates from the model simulation scenarios are shown
538 in Figure 4. In general, the radical reaction rates are elevated as much as twice once
539 observed HONO is constrained in the model calculations (e.g. Scenario VI). This is
540 because unaccounted HONO in the model calculations cause significant underestimations

Saewung Kim 9/2/2014 2:27 PM

Deleted:

Saewung Kim 9/2/2014 4:07 PM

Formatted: Subscript

Saewung Kim 9/2/2014 2:31 PM

Deleted:

Saewung Kim 9/4/2014 12:12 PM

Deleted: 5

Saewung Kim 9/3/2014 11:30 AM

Deleted: (Scenario VI and VII)

545 in the radical pool (OH+HO₂+RO₂) size with respect to the constrained HONO scenarios
546 as shown in Figure 4. In addition, as we include recently developed isoprene radical
547 chemistry, the RO₂+HO₂ reaction rates, known for a radical destruction pathway becomes
548 more faster. This is more conspicuous in the afternoon when NO concentration becomes
549 lower. The RO₂ + HO₂ reaction rates get higher than those of RO₂ + NO in the afternoon
550 for the Scenario IV and V. This is surprising, as the radical destruction regime is usually
551 associated with low NO_x conditions. Suburban regions of megacities including the TRF
552 in general show high NO_x conditions. However, radical recycling rates are determined by
553 concentrations of NO. The fraction of NO in the NO_x pool is determined by competing
554 reactions between NO₂ photolysis and oxidation reactions of NO by ozone, HO₂, and
555 RO₂ radicals. Once we assume the pseudo-steady state of NO, then NO in NO_x pool can
556 be expressed as

557

$$558 \quad [\text{NO}] = J_{\text{NO}_2}[\text{NO}_2]/(k_{\text{NO}+\text{O}_3}[\text{O}_3] + k_{\text{NO}+\text{HO}_2}[\text{HO}_2] + k_{\text{NO}+\text{RO}_2}[\text{RO}_2]) \quad (\text{R6})$$

559

560 This mathematical expression clearly shows that NO levels are dependent on NO_x
561 mostly composed of NO₂. At the same time, the fraction of NO in NO_x is anti-correlated
562 with ozone, HO₂, and RO₂ concentrations. Therefore, the size of the radical pool
563 composed of HO₂ and RO₂ is relevant for determining the fractions of NO in given NO_x
564 levels. High HO₂ and RO₂ are likely observed in high VOC regions such as forested areas.
565 This could cause a smaller fraction of NO in the given NO_x pool so radical recycling gets
566 relatively weaker compared with radical destruction reaction pathways. More quantitative

Saewung Kim 9/3/2014 11:32 AM

Deleted: V and

568 approaches are required to categorize radical reaction pathways rather than qualitative
569 categorization such as high or low NO_x regimes.

570 High and low NO_x regimes also have been widely used to define ozone
571 production regimes. As NO_x catalyzes ozone production and peroxy radicals expedite
572 NO_x turnover, in general, higher NO_x and VOCs conditions result in higher ozone
573 production. However, non-linearity in photochemistry of ozone production causes a
574 complexity in ozone reduction strategy (Seinfeld, 1989). Conventionally, efficient ozone
575 production can be achieved by the balance between nitric acid production rates (P_{HNO_3} ,
576 $\text{OH} + \text{NO}_2$) and peroxide production rates (P_{ROOH} , $\text{HO}_2 + \text{RO}_2$ or $P_{\text{H}_2\text{O}_2}$ $\text{HO}_2 + \text{HO}_2$)
577 (Sillman and He, 2002). The imbalance will cause ozone production sensitivity towards
578 either NO_x or VOCs. A comprehensive photochemical model analysis (Tonnesen and
579 Dennis, 2000b, a) demonstrated that in a wider range of ozone concentrations, the VOC
580 and NO_x limited regimes can be determined by the ratios of $P_{\text{H}_2\text{O}_2}$ and P_{HNO_3} . The ratio
581 range ($P_{\text{H}_2\text{O}_2}/P_{\text{HNO}_3}$) of 0.35 is regarded as the border range. In the VOC limited regime
582 ($P_{\text{H}_2\text{O}_2}/P_{\text{HNO}_3} < 0.35$), ozone production is expected to decrease with increasing NO_x and
583 increase with increasing VOCs. In the NO_x limited regime ($P_{\text{H}_2\text{O}_2}/P_{\text{HNO}_3} > 0.35$), ozone
584 production gets efficient with increasing NO_x and is insensitive to changes in VOCs
585 (Sillman and He, 2002). This categorization has guided policy-making processes whether
586 NO_x or VOC controls will be more effective in ozone reduction. A series of modeling
587 studies have been conducted to characterize ozone production regimes in the suburban
588 regions of East Asian megacities and have consistently concluded that the role of
589 isoprene is important in ozone production. However, most of these studies have
590 concluded that East Asian megacity regions are mostly in the VOC limited regime (Tseng

591 et al., 2009;Zhang et al., 2008b;Lim et al., 2011;Cheng et al., 2010;Shao et al.,
592 2009a;Shao et al., 2009b;Xing et al., 2011). Recently, however, a modeling study by Li et
593 al. (2013) in the Pearl River Delta region in China demonstrated the time dependence of
594 ozone production regimes. Specifically, with high NO_x emissions in the morning, the
595 regional ozone production regime is categorized as VOC limited. In contrast, in the
596 afternoon when the highest ozone concentrations are observed, a NO_x limited regime is
597 often found. The obvious issue to be addressed is that all of the above studies neglected
598 how the uncertainty in hydroxyl radical chemistry would affect the ozone production
599 regime evaluation. ~~Moreover~~, HONO has been rarely constrained by observations in the
600 previous modeling studies. Figure 5 shows the temporal variations of P_{H₂O₂}/P_{HNO₃} from
601 the all six different model scenarios. The VOC limited ozone formation regime was
602 observed regardless of the HO_x simulation scenarios. Differences among different
603 scenario are not noticeable in the morning when NO is high but noticeable differences
604 can be noticed in the afternoon. In general, the model calculation results with faster
605 HPALD formation rates indicate higher P(H₂O₂)/P(HNO₃) in the afternoon. ~~This analysis~~
606 clearly shows that it is difficult to determine the appropriate policy implementation for
607 NO_x or VOC controls to achieve ozone abatement in Asian megacities without accurate
608 understanding of radical isoprene interactions (e.g. Kim et al. (2013b)).

609 Another unresolved uncertainty in understanding tropospheric OH is its chemical
610 loss rates. The limited observations of OH reactivity in BVOC dominant environments
611 show consistent unaccounted OH chemical loss with observational datasets (Di Carlo et
612 al., 2004;Edwards et al., 2013;Kim et al., 2011;Lou et al., 2010;Nolscher et al., 2012).
613 Two different processes are speculated to cause unaccounted OH loss known as missing

Saewung Kim 9/3/2014 3:04 PM

Deleted: In addition

Saewung Kim 9/4/2014 12:23 PM

Deleted: 6

Saewung Kim 9/3/2014 3:23 PM

Deleted: four

Saewung Kim 9/3/2014 3:28 PM

Deleted: are

Saewung Kim 9/3/2014 3:28 PM

Deleted: observed

Saewung Kim 9/3/2014 3:23 PM

Deleted: The identical tendency was found in the model calculation results without constraining observed HONO (not shown in Figure 6).

623 OH reactivity: 1) primary emissions of unmeasured or unknown compounds and 2)
624 oxidation products of well-known BVOCs especially isoprene. Most studies conducted in
625 coniferous forests where monoterpenes are dominant primary BVOC emissions have
626 concluded that unmeasured or unknown primary BVOC emissions caused missing OH
627 reactivity (Sinha et al., 2010). On the other hand, studies conducted in isoprene dominant
628 environments in mostly broadleaf or mixed forests concluded the main cause of missing
629 OH reactivity as oxidation products of isoprene (Edwards et al., 2013; Kim et al., 2011).
630 Edwards et al. (2013) presented a thorough analysis on potential impacts of isoprene
631 oxidation products that are not routinely constrained by observations. The authors found
632 significant contributions from secondary oxidation products such as multi-functional
633 oxygenated compounds. Figure 6a shows the temporal variations of total OH reactivity
634 calculated from five different model scenarios (I through V). The highest and the lowest
635 OH reactivity levels were predicted from model calculations of Scenario V and Scenario
636 II, respectively. This observation is directly correlated with calculated RO₂ levels as the
637 lowest and highest RO₂ levels were calculated from Scenario II and Scenario V,
638 respectively. Since VOC precursors and trace gases were all constrained by observations
639 in the model calculations, the differences in model calculated OH reactivity should be
640 mainly caused by the oxidation products of VOCs. This can be confirmed by the
641 comparisons of model calculated formaldehyde concentrations from Scenario II and V as
642 formaldehyde is a dominant oxidation product of isoprene (Figure 6b). The differences in
643 formaldehyde levels suggest differences in OH reactivity levels from OVOCs in each
644 model simulation. In summary, uncertainty in radical distributions especially RO₂ levels
645 is directly propagated into uncertainty in OVOC formation.

Saewung Kim 9/4/2014 12:29 PM

Deleted: 7

647 These calculated results provide an upper limit of potential contributions from the
648 oxidation products of the constrained VOC precursors considering that the box-model
649 does not consider dry-deposition processes as Karl et al. (2010) and Edwards et al. (2013)
650 suggested that there is significant uncertainty associated with the parameterizations of dry
651 deposition especially OVOCs. Still, this analysis suggests that significant missing OH
652 reactivity (~ up to factor of two to three) can be found without constraining OVOCs.
653 OVOCs, especially multi-functional highly oxidized compounds are precursors for
654 secondary organic aerosols (VOAs). Therefore, uncertainty surrounding missing OH
655 reactivity significantly undermines our ability to constrain SOA formation and aerosol
656 growth.

657

658 **4. Summary and conclusion**

659 We presented trace gas observation results from the TRF near the center of Seoul,
660 South Korea. The dataset provides important constraints to evaluate the HO_x pool at the
661 site where both anthropogenic and biogenic influences become important factors in
662 determining oxidation capacity. Although the site is in the vicinity of a megacity with 25
663 million people, isoprene accounted for most of the OH loss from observed atmospheric
664 hydrocarbon species during the 6-day focus period in early June 2012 during a regional
665 pollution episode. In addition, observed NO_x levels were substantially lower than
666 observed values in the center of the SMA. These observations indicate that impacts of
667 aged pollution on BVOC photochemistry and aerosol formation can be observed at the
668 TRF.

Saewung Kim 9/3/2014 3:44 PM

Deleted: the SMA

Saewung Kim 9/3/2014 3:44 PM

Formatted: Font:(Default) 바탕

Saewung Kim 9/3/2014 3:46 PM

Deleted: the observational

671 Six different model scenarios are employed to investigate the radical (OH, HO₂,
672 and RO₂) distributions using the UWCM box-model. The observed trace gas data were
673 constrained and the photochemical mechanisms (MCM 3.2) of seven VOC species with
674 high levels at the TRF were integrated. The uncertainty in isoprene peroxy radical
675 chemistry results in a wider range of OH, HO₂, and RO₂ distributions. Unconstrained
676 HONO sources also cause a quite high level of underestimation in a radical pool
677 (OH+HO₂+RO₂). OH simulation from the different model scenarios indicates much
678 larger discrepancies (up to three times) than simulations for HO₂ and RO₂ (up to twice).
679 OH is simulated in much higher levels with the consideration of an additional OH
680 recycling channel from isoprene peroxy radical + HO₂ reactions and fast HPALD
681 formation chemistry Peeters and Muller (2010). On the other hand, the RO₂ simulations
682 indicate contrary results as HPALD formation depletes the RO₂ pool, which mostly
683 composed by isoprene peroxy radicals. These results suggest that HO₂ and RO₂
684 observations can provide pivotal information about radical recycling and isoprene peroxy
685 radical chemistry (Kim et al., 2013c; Wolfe et al., 2013). More studies on characterizing
686 existing techniques to quantify HO₂ (Fuchs et al., 2011) and developing new techniques
687 (Horstjann et al., 2013) are needed. In addition, the simulations with recently developed
688 isoprene photo-oxidation chemistry show that radical termination processes (e.g.
689 peroxide formation) get more efficient than radical recycling processes in the afternoon.
690 This may come as a surprise as in general we expect the high NO_x conditions in the
691 suburban regions of a megacity to have effective radical recycling. However, the critical
692 factor determining competing reaction channels of recycling and peroxide formation is
693 NO concentrations. Ratios of NO to NO₂ are not only correlated with NO₂ concentrations

Saewung Kim 9/3/2014 4:19 PM

Deleted: even

Saewung Kim 9/3/2014 4:20 PM

Deleted: calculation

Saewung Kim 9/3/2014 4:20 PM

Deleted: as summarized in Table 1

Saewung Kim 9/3/2014 3:49 PM

Deleted: observed in

Saewung Kim 9/3/2014 4:21 PM

Deleted: different scenarios

Saewung Kim 9/3/2014 3:56 PM

Deleted: are also appeared to

Saewung Kim 9/4/2014 2:15 PM

Deleted: A larger difference is observed in

Saewung Kim 9/4/2014 2:15 PM

Deleted: s

Saewung Kim 9/4/2014 2:17 PM

Deleted: s

703 and photolysis constants but also anti-correlated with RO₂, HO₂ and ozone concentrations
704 and relevant kinetic constants as shown in (R6). Therefore, a semi-quantitative term such
705 as the high 'NO_x' regime is not a proper term to define radical recycle regimes especially
706 in high radical environments (e.g. HO₂ and RO₂) such as forest environments.

707 These uncertainties in estimating the radical pool size and distribution directly
708 affect our ability for constraining photochemical ozone and OVOC production. The non-
709 linear response of ozone production to NO_x and VOC abundances are determined by OH,
710 HO₂, RO₂ and NO₂ concentrations. Regardless of which model calculation scenario we
711 adapt, the TRF photochemical state appears to be a VOC limited ozone production
712 regime. However, morning and afternoon show a very strong contrast with morning
713 having a stronger degree of VOC limitation. In addition, a noticeable range of VOC
714 sensitivity was calculated from the six different model scenarios especially in the
715 afternoon. These analysis results, therefore, strongly indicate that uncertainty in radical
716 photochemistry subsequently resulting in uncertainty in radical concentration estimations
717 directly propagates in policy-making processes in effectiveness of NO_x or VOC controls
718 in ozone reduction. In addition, OVOC production is predicted to significantly vary
719 depending on the model simulation scenarios. As the fate of these OVOCs is uncertain
720 and can include deposition, photolysis, or condensation, the implications of the
721 uncertainty in OVOC production caused by the uncertainty in radical photochemistry
722 should be addressed.

723

724 **Acknowledgements**

Saewung Kim 9/3/2014 5:06 PM

Deleted: surrounding

Saewung Kim 9/4/2014 2:25 PM

Deleted: SOA

Saewung Kim 9/3/2014 4:27 PM

Deleted: , which is defined by a stronger nitric acid formation in comparison with peroxide formation

Saewung Kim 9/4/2014 2:26 PM

Deleted: four

731 This research is financially supported by National Institute of Environmental
732 Research of South Korea. The authors appreciate logistical supports from the research
733 and supporting staff at Taehwa Research Forest operated by Seoul National University.

734

735 **References**

736

- 737 Apel, E. C., Riemer, D. D., Hills, A., Baugh, W., Orlando, J., Faloon, I., Tan, D., Brune,
738 W., Lamb, B., Westberg, H., Carroll, M. A., Thornberry, T., and Geron, C. D.:
739 Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and
740 methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive, *J*
741 *Geophys Res-Atmos*, 107, Artn 4034
742 Doi 10.1029/2000jd000225, 2002.
- 743 Archibald, A. T., Jenkin, M. E., and Shallcross, D. E.: An isoprene mechanism
744 intercomparison, *Atmos Environ*, 44, 5356-5364, Doi
745 10.1016/J.Atmosenv.2009.09.016, 2010.
- 746 Arnth, A., Schurgers, G., Lathiere, J., Duhl, T., Beerling, D. J., Hewitt, C. N., Martin, M.,
747 and Guenther, A.: Global terrestrial isoprene emission models: sensitivity to
748 variability in climate and vegetation, *Atmos Chem Phys*, 11, 8037-8052, Doi
749 10.5194/Acp-11-8037-2011, 2011.
- 750 Bao, H., Shrestha, K. L., Kondo, A., Kaga, A., and Inoue, Y.: Modeling the influence of
751 biogenic volatile organic compound emissions on ozone concentration during
752 summer season in the Kinki region of Japan, *Atmos Environ*, 44, 421-431, Doi
753 10.1016/J.Atmosenv.2009.10.021, 2010.
- 754 Barkot, D. J., Hurst, J. M., Couch, T. L., Colorado, A., Shepson, P. B., Riemer, D. D., Hills,
755 A. J., Apel, E. C., Hafer, R., Lamb, B. K., Westberg, H. H., Farmer, C. T., Stabenau, E. R.,
756 and Zika, R. G.: Intercomparison of automated methodologies for determination of
757 ambient isoprene during the PROPHET 1998 summer campaign, *J Geophys Res-*
758 *Atmos*, 106, 24301-24313, Doi 10.1029/2000jd900562, 2001.
- 759 Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-Transfer Reaction Mass
760 Spectrometry, *Chem Rev*, 109, 861-896, 2009.
- 761 Bryan, A. M., Bertman, S. B., Carroll, M. A., Dusanter, S., Edwards, G. D., Forkel, R.,
762 Griffith, S., Guenther, A. B., Hansen, R. F., Helmig, D., Jobson, B. T., Keutsch, F. N.,
763 Lefer, B. L., Pressley, S. N., Shepson, P. B., Stevens, P. S., and Steiner, A. L.: In-canopy
764 gas-phase chemistry during CABINEX 2009: sensitivity of a 1-D canopy model to
765 vertical mixing and isoprene chemistry, *Atmos Chem Phys*, 12, 8829-8849, Doi
766 10.5194/Acp-12-8829-2012, 2012.
- 767 Chameides, W. L., Lindsay, R. W., Richardson, J., and Kiang, C. S.: The Role of Biogenic
768 Hydrocarbons in Urban Photochemical Smog - Atlanta as a Case-Study, *Science*, 241,
769 1473-1475, 1988.
- 770 Cheng, H. R., Guo, H., Saunders, S. M., Lam, S. H. M., Jiang, F., Wang, X. M., Simpson, I.
771 J., Blake, D. R., Louie, P. K. K., and Wang, T. J.: Assessing photochemical ozone
772 formation in the Pearl River Delta with a photochemical trajectory model, *Atmos*
773 *Environ*, 44, 4199-4208, Doi 10.1016/J.Atmosenv.2010.07.019, 2010.

774 Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical
775 isomerization in the oxidation of isoprene, *Phys Chem Chem Phys*, 13, 13607-13613,
776 Doi 10.1039/C1cp21330j, 2011.

777 de Gouw, J., and Warneke, C.: Measurements of volatile organic compounds in the
778 earths atmosphere using proton-transfer-reaction mass spectrometry, *Mass*
779 *Spectrom Rev*, 26, 223-257, 2007.

780 Di Carlo, P., Brune, W. H., Martinez, M., Harder, H., Leshner, R., Ren, X. R., Thornberry,
781 T., Carroll, M. A., Young, V., Shepson, P. B., Riemer, D., Apel, E., and Campbell, C.:
782 Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs,
783 *Science*, 304, 722-725, Doi 10.1126/Science.1094392, 2004.

784 Edwards, P. M., Evans, M. J., Furneaux, K. L., Hopkins, J., Ingham, T., Jones, C., Lee, J.
785 D., Lewis, A. C., Moller, S. J., Stone, D., Whalley, L. K., and Heard, D. E.: OH reactivity in
786 a South East Asian tropical rainforest during the Oxidant and Particle Photochemical
787 Processes (OP3) project, *Atmos Chem Phys*, 13, 9497-9514, Doi 10.5194/Acp-13-
788 9497-2013, 2013.

789 Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., and
790 Wahner, A.: Detection of HO₂ by laser-induced fluorescence: calibration and
791 interferences from RO₂ radicals, *Atmos Meas Tech*, 4, 1209-1225, Doi 10.5194/Amt-
792 4-1209-2011, 2011.

793 Guenther, A.: Biological and chemical diversity of biogenic volatile organic emissions
794 into the atmosphere, *Atmospheric Sciences*, 2013, ArticleID 786290, 2013.

795 Hao, N., Zhou, B., Chen, D., and Chen, L. M.: Observations of nitrous acid and its
796 relative humidity dependence in Shanghai, *J Environ Sci-China*, 18, 910-915, Doi
797 10.1016/S1001-0742(06)60013-2, 2006.

798 Hofzumahaus, A., Rohrer, F., Lu, K. D., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H.,
799 Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S. R., Shao, M., Zeng, L. M., Wahner, A., and
800 Zhang, Y. H.: Amplified Trace Gas Removal in the Troposphere, *Science*, 324, 1702-
801 1704, 10.1126/science.1164566, 2009.

802 Horstjann, M., Andres Hernandez, M. D., Nenakhov, V., Chrobry, A., and Burrows, J.
803 P.: Peroxy radical detection for airborne atmospheric measurements using cavity
804 enhanced absorption spectroscopy of NO₂, *Atmospheric Measurement Techniques*
805 *Discussion*, 6, 9655-9688, 2013.

806 Huang, M., Bowman, K. W., Carmichael, G. R., Pierce, R. B., Worden, H. M., Luo, M.,
807 Cooper, O. R., Pollack, I. B., Ryerson, T. B., and Brown, S. S.: Impact of Southern
808 California anthropogenic emissions on ozone pollution in the mountain states:
809 Model analysis and observational evidence from space, *J Geophys Res-Atmos*, 118,
810 12784-12803, Doi 10.1002/2013jd020205, 2013.

811 Karl, T., Harley, P., Emmons, L., Thornton, B., Guenther, A., Basu, C., Turnipseed, A.,
812 and Jardine, K.: Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by
813 Vegetation, *Science*, 330, 816-819, Doi 10.1126/Science.1192534, 2010.

814 Kim, K. H., Ho, D. X., Park, C. G., Ma, C. J., Pandey, S. K., Lee, S. C., Jeong, H. J., and Lee, S.
815 H.: Volatile Organic Compounds in Ambient Air at Four Residential Locations in
816 Seoul, Korea, *Environ Eng Sci*, 29, 875-889, Doi 10.1089/Ees.2011.0280, 2012.

817 Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and
818 Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic

819 Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass
820 spectra, *Atmos Chem Phys*, 10, 1759-1771, 2010.

821 Kim, S., Guenther, A., Karl, T., and Greenberg, J.: Contributions of primary and
822 secondary biogenic VOC to total OH reactivity during the CABINEX (Community
823 Atmosphere-Biosphere Interactions Experiments)-09 field campaign, *Atmos Chem*
824 *Phys*, 11, 8613-8623, 2011.

825 Kim, S., Guenther, A., and Apel, E.: Quantitative and qualitative sensing techniques
826 for biogenic volatile organic compounds and their oxidation products, *Environ Sci-*
827 *Proc Imp*, 15, 1301-1314, Doi 10.1039/C3em00040k, 2013a.

828 Kim, S., Lee, M., Kim, S., Choi, S., Seok, S., and Kim, S.: Photochemical characteristics
829 of high and low ozone episodes observed in the Taehwa Forest observatory (TFO) in
830 June 2011 near Seoul South Korea, *Asia-Pacific Journal of Atmospheric Sciences*, 49,
831 325-331, Doi 10.1007/S13143-013-0031-0, 2013b.

832 Kim, S., Wolfe, G. M., Mauldin, L., Cantrell, C., Guenther, A., Karl, T., Turnipseed, A.,
833 Greenberg, J., Hall, S. R., Ullmann, K., Apel, E., Hornbrook, R., Kajii, Y., Nakashima, Y.,
834 Keutsch, F. N., DiGangi, J. P., Henry, S. B., Kaser, L., Schnitzhofer, R., Graus, M., Hansel,
835 A., Zheng, W., and Flocke, F. F.: Evaluation of HO_x sources and cycling using
836 measurement-constrained model calculations in a 2-methyl-3-butene-2-ol (MBO)
837 and monoterpene (MT) dominated ecosystem, *Atmos Chem Phys*, 13, 2031-2044,
838 Doi 10.5194/Acp-13-2031-2013, 2013c.

839 Kim, S., VandenBoer, T. C., Young, C. J., Riedel, T. P., Thornton, J. A., Swarthout, B.,
840 Sive, B., Lerner, B., Gilman, J. B., Warneke, C., Roberts, J. M., Guenther, A., Wagner, N.
841 L., Dube, W. P., Williams, E., and Brown, S. S.: The primary and recycling sources of
842 OH during the NACHTT-2011 campaign: HONO as an important OH primary source
843 in the wintertime, *J Geophys Res-Atmos*, 119, 6886-6896, Doi
844 10.1002/2013jd019784, 2014.

845 Kim, S. Y., Jiang, X. Y., Lee, M., Turnipseed, A., Guenther, A., Kim, J. C., Lee, S. J., and
846 Kim, S.: Impact of biogenic volatile organic compounds on ozone production at the
847 Taehwa Research Forest near Seoul, South Korea, *Atmos Environ*, 70, 447-453, Doi
848 10.1016/J.Atmosenv.2012.11.005, 2013d.

849 Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder,
850 H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric
851 oxidation capacity sustained by a tropical forest, *Nature*, 452, 737-740, 2008.

852 Levy, H.: Normal Atmosphere - Large Radical and Formaldehyde Concentrations
853 Predicted, *Science*, 173, 141-143, 1971.

854 Li, X., Brauers, T., Haseler, R., Bohn, B., Fuchs, H., Hofzumahaus, A., Holland, F., Lou,
855 S., Lu, K. D., Rohrer, F., Hu, M., Zeng, L. M., Zhang, Y. H., Garland, R. M., Su, H., Nowak,
856 A., Wiedensohler, A., Takegawa, N., Shao, M., and Wahner, A.: Exploring the
857 atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China,
858 *Atmos Chem Phys*, 12, 1497-1513, Doi 10.5194/Acp-12-1497-2012, 2012.

859 Li, Y., Lau, A. K. H., Fung, J. C. H., Zheng, J. Y., and Liu, S. C.: Importance of NO_x control
860 for peak ozone reduction in the Pearl River Delta region, *J Geophys Res-Atmos*, 118,
861 9428-9443, Doi 10.1002/Jgrd.50659, 2013.

862 Lim, Y. J., Armendariz, A., Son, Y. S., and Kim, J. C.: Seasonal variations of isoprene
863 emissions from five oak tree species in East Asia, *Atmos Environ*, 45, 2202-2210, Doi
864 10.1016/J.Atmosenv.2011.01.066, 2011.

865 Liu, Y. J., Herdinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl
866 vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation,
867 *Atmos Chem Phys*, 13, 5715-5730, Doi 10.5194/Acp-13-5715-2013, 2013.

868 Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H.,
869 Haseler, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang,
870 W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta -
871 China in summer 2006: measurement and model results, *Atmos Chem Phys*, 10,
872 11243-11260, 2010.

873 Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Haseler,
874 R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner,
875 A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of OH and HO₂
876 concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich
877 atmosphere, *Atmos Chem Phys*, 12, 1541-1569, Doi 10.5194/Acp-12-1541-2012,
878 2012.

879 Ma, J. Z., Wang, W., Chen, Y., Liu, H. J., Yan, P., Ding, G. A., Wang, M. L., Sun, J., and
880 Lelieveld, J.: The IPAC-NC field campaign: a pollution and oxidization pool in the
881 lower atmosphere over Huabei, China, *Atmos Chem Phys*, 12, 3883-3908, Doi
882 10.5194/Acp-12-3883-2012, 2012.

883 Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J. H., Goldstein, A. H.,
884 Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B.,
885 Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.:
886 Insights into hydroxyl measurements and atmospheric oxidation in a California
887 forest, *Atmos Chem Phys*, 12, 8009-8020, Doi 10.5194/Acp-12-8009-2012, 2012.

888 Mao, J. Q., Ren, X. R., Chen, S. A., Brune, W. H., Chen, Z., Martinez, M., Harder, H., Lefer,
889 B., Rappengluck, B., Flynn, J., and Leuchner, M.: Atmospheric oxidation capacity in
890 the summer of Houston 2006: Comparison with summer measurements in other
891 metropolitan studies, *Atmos Environ*, 44, 4107-4115, Doi
892 10.1016/J.Atmosenv.2009.01.013, 2010.

893 Na, K., and Kim, Y. P.: Seasonal characteristics of ambient volatile organic
894 compounds in Seoul, Korea, *Atmos Environ*, 35, 2603-2614, Doi 10.1016/S1352-
895 2310(00)00464-7, 2001.

896 NIER: Annual Report for Atmospheric Environment, National Institute of
897 Environmental Research, 2010.

898 Nolscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R.,
899 Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J.,
900 Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot,
901 H. G., de Arellano, J. V. G., and Lelieveld, J.: Summertime total OH reactivity
902 measurements from boreal forest during HUMPPA-COPEC 2010, *Atmos Chem Phys*,
903 12, 8257-8270, Doi 10.5194/Acp-12-8257-2012, 2012.

904 Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek,
905 A., Mougou, E., Delon, C., Loubet, B., Pommerening-Roser, A., Sorgel, M., Poschl, U.,
906 Hoffmann, T., Andreae, M. O., Meixner, F. X., and Trebs, I.: HONO Emissions from Soil
907 Bacteria as a Major Source of Atmospheric Reactive Nitrogen, *Science*, 341, 1233-
908 1235, Doi 10.1126/Science.1242266, 2013.

909 Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P.
910 O.: Isoprene photooxidation: new insights into the production of acids and organic
911 nitrates, *Atmos Chem Phys*, 9, 1479-1501, 2009.

912 Paulson, S. E., and Seinfeld, J. H.: Development and evaluation of a photooxidation
913 mechanism for isoprene, *Journal of Geophysical Research*, 97, 20703-20715, 1992.

914 Peeters, J., and Muller, J. F.: HOx radical regeneration in isoprene oxidation via
915 peroxy radical isomerisations. II: experimental evidence and global impact, *Phys
916 Chem Chem Phys*, 12, 14227-14235, Doi 10.1039/C0cp00811g, 2010.

917 Pollack, I. B., Ryerson, T. B., Trainer, M., Neuman, J. A., Roberts, J. M., and Parrish, D.
918 D.: Trends in ozone, its precursors, and related secondary oxidation products in Los
919 Angeles, California: A synthesis of measurements from 1960 to 2010, *J Geophys Res-
920 Atmos*, 118, 5893-5911, Doi 10.1002/Jgrd.50472, 2013.

921 Ran, L., Zhao, C. S., Xu, W. Y., Lu, X. Q., Han, M., Lin, W. L., Yan, P., Xu, X. B., Deng, Z. Z.,
922 Ma, N., Liu, P. F., Yu, J., Liang, W. D., and Chen, L. L.: VOC reactivity and its effect on
923 ozone production during the HaChi summer campaign, *Atmos Chem Phys*, 11, 4657-
924 4667, Doi 10.5194/Acp-11-4657-2011, 2011.

925 Ren, X., Sanders, J. E., Rajendran, A., Weber, R. J., Goldstein, A. H., Pusede, S. E.,
926 Browne, E. C., Min, K. E., and Cohen, R. C.: A relaxed eddy accumulation system for
927 measuring vertical fluxes of nitrous acid, *Atmos Meas Tech*, 4, 2093-2103, Doi
928 10.5194/Amt-4-2093-2011, 2011.

929 Ryerson, T. B., Andrews, A. E., Angevine, W. M., Bates, T. S., Brock, C. A., Cairns, B.,
930 Cohen, R. C., Cooper, O. R., de Gouw, J. A., Fehsenfeld, F. C., Ferrare, R. A., Fischer, M.
931 L., Flagan, R. C., Goldstein, A. H., Hair, J. W., Hardesty, R. M., Hostetler, C. A., Jimenez, J.
932 L., Langford, A. O., McCauley, E., McKeen, S. A., Molina, L. T., Nenes, A., Oltmans, S. J.,
933 Parrish, D. D., Pederson, J. R., Pierce, R. B., Prather, K., Quinn, P. K., Seinfeld, J. H.,
934 Senff, C. J., Sorooshian, A., Stutz, J., Surratt, J. D., Trainer, M., Volkamer, R., Williams, E.
935 J., and Wofsy, S. C.: The 2010 California Research at the Nexus of Air Quality and
936 Climate Change (CalNex) field study, *J Geophys Res-Atmos*, 118, 5830-5866, Doi
937 10.1002/Jgrd.50331, 2013.

938 Ryu, Y. H., Baik, J. J., Kwak, K. H., Kim, S., and Moon, N.: Impacts of urban land-surface
939 forcing on ozone air quality in the Seoul metropolitan area, *Atmos Chem Phys*, 13,
940 2177-2194, Doi 10.5194/Acp-13-2177-2013, 2013.

941 Sartelet, K. N., Couvidat, F., Seigneur, C., and Roustan, Y.: Impact of biogenic
942 emissions on air quality over Europe and North America, *Atmos Environ*, 53, 131-
943 141, Doi 10.1016/J.Atmosenv.2011.10.046, 2012.

944 Seinfeld, J. H.: Urban Air-Pollution - State of the Science, *Science*, 243, 745-752, Doi
945 10.1126/Science.243.4892.745, 1989.

946 Shao, M., Lu, S. H., Liu, Y., Xie, X., Chang, C. C., Huang, S., and Chen, Z. M.: Volatile
947 organic compounds measured in summer in Beijing and their role in ground-level
948 ozone formation, *J Geophys Res-Atmos*, 114, Artn D00g06
949 Doi 10.1029/2008jd010863, 2009a.

950 Shao, M., Zhang, Y. H., Zeng, L. M., Tang, X. Y., Zhang, J., Zhong, L. J., and Wang, B. G.:
951 Ground-level ozone in the Pearl River Delta and the roles of VOC and NO(x) in its
952 production, *J Environ Manage*, 90, 512-518, Doi 10.1016/J.Jenvman.2007.12.008,
953 2009b.

954 Sillman, S., and He, D.: Some theoretical results concerning O₃-NO_x-VOC chemistry
955 and NO_x-VOC indicators, *Journal of Geophysical Research*, 107,
956 4659, doi:4610.1029:2001JD001123, 2002.

957 Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen,
958 H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH Reactivity
959 Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions,
960 *Environ Sci Technol*, 44, 6614-6620, Doi 10.1021/Es101780b, 2010.

961 Song, C. H., Park, M. E., Lee, E. J., Lee, J. H., Lee, B. K., Lee, D. S., Kim, J., Han, J. S., Moon,
962 K. J., and Kondo, Y.: Possible particulate nitrite formation and its atmospheric
963 implications inferred from the observations in Seoul, Korea, *Atmos Environ*, 43,
964 2168-2173, Doi 10.1016/J.Atmosenv.2009.01.018, 2009.

965 Tie, X., Geng, F., Guenther, A., Cao, J., Greenberg, J., Zhang, R., Apel, E., Li, G.,
966 Weinheimer, A., Chen, J., and Cai, C.: Megacity impacts on regional ozone formation:
967 observations and WRF-Chem modeling for the MIRAGE-Shanghai field campaign,
968 *Atmos Chem Phys*, 13, 5655-5669, Doi 10.5194/Acp-13-5655-2013, 2013.

969 Tonnesen, G. S., and Dennis, R. L.: Analysis of radical propagation efficiency to assess
970 ozone sensitivity to hydrocarbons and NO_x 2. Long-lived species as indicators of
971 ozone concentration sensitivity, *J Geophys Res-Atmos*, 105, 9227-9241, Doi
972 10.1029/1999jd900372, 2000a.

973 Tonnesen, G. S., and Dennis, R. L.: Analysis of radical propagation efficiency to assess
974 ozone sensitivity to hydrocarbons and NO_x 1. Local indicators of instantaneous odd
975 oxygen production sensitivity, *J Geophys Res-Atmos*, 105, 9213-9225, Doi
976 10.1029/1999jd900371, 2000b.

977 Trainer, M., Williams, E., Parrish, D. D., Buhr, M. P., Allwine, E. J., Westberg, H.,
978 Fehsenfeld, F. C., and Liu, S. C.: Models and observations of the impact of natural
979 hydrocarbons on rural ozone, *Nature*, 329, 705 - 707, 1987.

980 Tseng, K. H., Wang, J. L., Cheng, M. T., and Tsuang, B. J.: Assessing the Relationship
981 between Air Mass Age and Summer Ozone Episodes Based on Photochemical
982 Indices, *Aerosol Air Qual Res*, 9, 149-171, 2009.

983 VandenBoer, T., Murphy, J. G., Roberts, J. M., Middlebrook, A. M., Brock, C., Lerner, B.
984 M., Wolfe, D. E., Williams, E., Brown, S. S., Warneke, C., De Gouw, J., Wagner, N. L.,
985 Young, C. C., Dube, W. P., Bahreini, R., Riedel, T., Thornton, J. A., Ozturk, F., Keene, W.,
986 Maben, J. R., Pszenny, A., Kim, S., Grossberg, N., and Lefer, B.: Understanding the role
987 of the ground surface in HONO vertical structure: High resolution vertical profiles
988 during NACHTT-11, submitted, 2013.

989 Wolfe, G. M., and Thornton, J. A.: The chemistry of atmosphere-forest exchange
990 (CAFE) model - PART1: Model description and characterization, *Atmos Chem Phys*,
991 11, 77-101, 2011.

992 Wolfe, G. M., Crouse, J. D., Parrish, J. D., St Clair, J. M., Beaver, M. R., Paulot, F., Yoon,
993 T. P., Wennberg, P. O., and Keutsch, F. N.: Photolysis, OH reactivity and ozone
994 reactivity of a proxy for isoprene-derived hydroperoxyenals (HPALDs), *Phys Chem*
995 *Chem Phys*, 14, 7276-7286, 2012.

996 Wolfe, G. M., Cantrell, C., Kim, S., Mauldin, R., Karl, T., Harley, P., Turnipseed, A.,
997 Zheng, W., Flocke, F., Apel, E., Hornbrook, R. S., Hall, S., Ullmann, K., Henry, S. B.,
998 Digangi, J., Boyle, E. S., Kaser, L., Schnitzhofer, R., Hansel, A., Graus, M., Nakashima, Y.,
999 Kajii, Y., Guenther, A., and Keutsch, F.: Missing peroxy radical sources within a rural

1000 forest canopy, Atmospheric Chemistry and Physics Discussion, 13, 31713-31759,
1001 2013.
1002 Wong, K. W., Tsai, C., Lefer, B., Haman, C., Grossberg, N., Brune, W. H., Ren, X., Luke,
1003 W., and Stutz, J.: Daytime HONO vertical gradients during SHARP 2009 in Houston,
1004 TX, Atmos Chem Phys, 12, 635-652, Doi 10.5194/Acp-12-635-2012, 2012.
1005 Xing, J., Wang, S. X., Jang, C., Zhu, Y., and Hao, J. M.: Nonlinear response of ozone to
1006 precursor emission changes in China: a modeling study using response surface
1007 methodology, Atmos Chem Phys, 11, 5027-5044, Doi 10.5194/Acp-11-5027-2011,
1008 2011.
1009 Yoshino, A., Nakashima, Y., Miyazaki, K., Kato, S., Suthawaree, J., Shimo, N.,
1010 Matsunaga, S., Chatani, S., Apel, E., Greenberg, J., Guenther, A., Ueno, H., Sasaki, H.,
1011 Hoshi, J., Yokota, H., Ishii, K., and Kajii, Y.: Air quality diagnosis from comprehensive
1012 observations of total OH reactivity and reactive trace species in urban central Tokyo,
1013 Atmos Environ, 49, 51-59, Doi 10.1016/J.Atmosenv.2011.12.029, 2012.
1014 Zhang, Y., Hu, X. M., Leung, L. R., and Gustafson, W. I.: Impacts of regional climate
1015 change on biogenic emissions and air quality, J Geophys Res-Atmos, 113, Artn
1016 D18310
1017 Doi 10.1029/2008jd009965, 2008a.
1018 Zhang, Y. H., Su, H., Zhong, L. J., Cheng, Y. F., Zeng, L. M., Wang, X. S., Xiang, Y. R.,
1019 Wang, J. L., Gao, D. F., Shao, M., Fan, S. J., and Liu, S. C.: Regional ozone pollution and
1020 observation-based approach for analyzing ozone-precursor relationship during the
1021 PRIDE-PRD2004 campaign, Atmos Environ, 42, 6203-6218, Doi
1022 10.1016/J.Atmosenv.2008.05.002, 2008b.
1023 Zhao, J., and Zhang, R. Y.: Proton transfer reaction rate constants between
1024 hydronium ion (H₃O⁽⁺⁾) and volatile organic compounds, Atmos Environ, 38, 2177-
1025 2185, 2004.
1026 Zhou, X. L., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M.,
1027 Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid
1028 photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nat
1029 Geosci, 4, 440-443, Doi 10.1038/Ngeo1164, 2011.

1030
1031

Saewung Kim 9/4/2014 4:06 PM

Formatted: Indent: Left: 0", Hanging:
0.31"

1032
1033

1034
1035

Table 1. Analytical characteristics of trace gas analyzers at TRF

Chemical Species	Manufacturer and Model Number	Uncertainty	Lower Limit of Detection
CO _x	Thermo Scientific 48i TLE	10%	40 ppb
NO _x	Thermo Scientific 42i-TL	15%	50 ppt
SO ₂	Thermo Scientific 43i-TLE	10%	50 ppt
ozone	Thermo Scientific 49i	5%	< 1 ppb

- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [1]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [2]
- Saewung Kim 9/4/2014 10:07 AM
Formatted Table ... [3]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [5]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [6]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [7]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [4]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [8]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [9]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [10]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [11]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [12]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [13]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [14]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [15]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [16]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [17]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [18]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [19]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [20]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [21]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [22]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [23]
- Saewung Kim 9/4/2014 10:06 AM
Formatted ... [24]
- Saewung Kim 9/4/2014 10:04 AM
Formatted ... [25]

1036

1037 Table 2. Terpenoid speciation analysis results from GC-MS a) branch enclosure and b)
 1038 ambient air samples.

1039

1040

a)

<u>Terpenoids</u>	<u>*Composition(%)</u>	<u>Speciation</u>	<u>*Composition(%)</u>
<u>Isoprene</u>	<u>0.5</u>		
		<u>α-pinene</u>	<u>36.7</u>
		<u>camphene</u>	<u>13.1</u>
<u>Monoterpenes</u>	<u>92.9</u>	<u>β-pinene</u>	<u>12.0</u>
		<u>β-myrcene</u>	<u>27.7</u>
		<u>α-terpinolene</u>	<u>1.9</u>
		<u>d-limonene</u>	<u>8.6</u>
<u>Sesquiterpenes</u>	<u>6.6</u>	<u>β- caryop hyllene</u>	<u>53.2</u>
		<u>α- caryop hyllene</u>	<u>46.8</u>

1041

1042

b)

<u>Terpenoids</u>	<u>*Composition(%)</u>	<u>Speciation</u>	<u>*Composition(%)</u>
		<u>α-pinene</u>	<u>38.8</u>
<u>Monoterpenes</u>	<u>98.6</u>	<u>β-piene</u>	<u>36.5</u>
		<u>camphene</u>	<u>13.5</u>
		<u>d-limonene</u>	<u>11</u>
<u>Sesquiterpenes</u>	<u>1.4</u>	<u>longifolene</u>	<u>100</u>

1043 *Composition is calculated based on the mixing ratio scale

1044

1045

1046
1047
1048
1049
1050

Table 3. A summary of critical differences in input parameters for four different model simulation scenarios presented in this study

	HPALD chemistry	* α	Observational Constraints
Scenario I	No	0	All
Scenario II	Peeters and Muller (2010)	0	All
Scenario III	Crouse et al. (2011)	0	All
Scenario IV	Peeters and Muller (2010)	2.6	All
Scenario V	Crouse et al. (2011)	2.6	All
Scenario VI	Peeters and Muller (2010)	2.6	All but HONO

1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1075

* α is an OH yield from reactions between an isoprene peroxy radical and HO₂, $k_{298} \sim 0.08$ for isoprene peroxy radical isomerization rate leading to produce HPALD, $k_{298} = 0.002$ for isoprene peroxy radical isomerization rate, All the observed diurnal variations, appeared in Figure 1 are constrained in the model along with ambient pressure and humidity.

- Saewung Kim 9/4/2014 10:03 AM
Deleted: 1
- Saewung Kim 9/4/2014 2:36 PM
Deleted: HPALD Chemistr
- Saewung Kim 9/4/2014 2:28 PM
Deleted: y
- Saewung Kim 9/4/2014 2:43 PM
Formatted: Superscript
- Saewung Kim 9/4/2014 2:56 PM
Deleted: et al.
- Saewung Kim 9/4/2014 2:43 PM
Formatted: Superscript
- Saewung Kim 9/4/2014 2:56 PM
Deleted: 09
- Saewung Kim 9/4/2014 2:37 PM
Formatted: Superscript
- Saewung Kim 9/4/2014 2:43 PM
Formatted: Superscript
- Saewung Kim 9/4/2014 2:43 PM
Formatted: Superscript
- Saewung Kim 9/4/2014 2:56 PM
Deleted: Peeters et al. (2009)
- Saewung Kim 9/4/2014 2:43 PM
Formatted: Superscript
- Saewung Kim 9/2/2014 3:04 PM
Deleted: Scenario VI
- Saewung Kim 9/2/2014 3:04 PM
Deleted: 0
- Saewung Kim 9/4/2014 2:43 PM
Formatted: Superscript
- Saewung Kim 9/2/2014 3:04 PM
Deleted: All but HONO
- Saewung Kim 9/2/2014 3:04 PM
Deleted: No
- Saewung Kim 9/4/2014 3:19 PM
Formatted: Superscript
- Saewung Kim 9/4/2014 8:44 PM
Deleted: .
- Composition(%) ... [26]
- Saewung Kim 9/4/2014 8:43 PM
Deleted: .
- Composition(%) ... [27]

1091 | Table 4 A summary for radical distributions from the observationally constrained box-
1092 model simulation results
1093

Saewung Kim 9/4/2014 10:03 AM
Deleted: 3

Local Time	OH		HO ₂		RO ₂		Constraints
	8:00-12:00	13:00-16:00	8:00-12:00	13:00-16:00	8:00-12:00	13:00-16:00	
Scenario I	3.85×10 ⁶	3.08×10 ⁶	4.10×10 ⁸	7.02×10 ⁸	3.65×10 ⁸	1.14×10 ⁹	All
Scenario II	3.99×10 ⁶	3.69×10 ⁶	3.99×10 ⁸	7.86×10 ⁸	3.51×10 ⁸	9.62×10 ⁸	All
Scenario III	3.86×10 ⁶	3.13×10 ⁶	4.09×10 ⁸	7.09×10 ⁸	3.64×10 ⁸	1.12×10 ⁹	All
Scenario IV	4.27×10 ⁶	4.49×10 ⁶	4.29×10 ⁸	8.70×10 ⁸	3.66×10 ⁸	1.06×10 ⁹	All
Scenario V	4.21×10 ⁶	4.52×10 ⁶	4.55×10 ⁸	8.55×10 ⁸	3.86×10 ⁸	1.28×10 ⁹	All
Scenario VI	1.61×10 ⁶	1.61×10 ⁶	1.95×10 ⁸	4.82×10 ⁸	1.75×10 ⁸	7.25×10 ⁸	All but HONO
Scenario VII	1.82×10 ⁶	2.55×10 ⁶	2.09×10 ⁸	6.07×10 ⁸	1.80×10 ⁸	7.00×10 ⁸	All but HONO

1094 unit: molecules cm⁻³

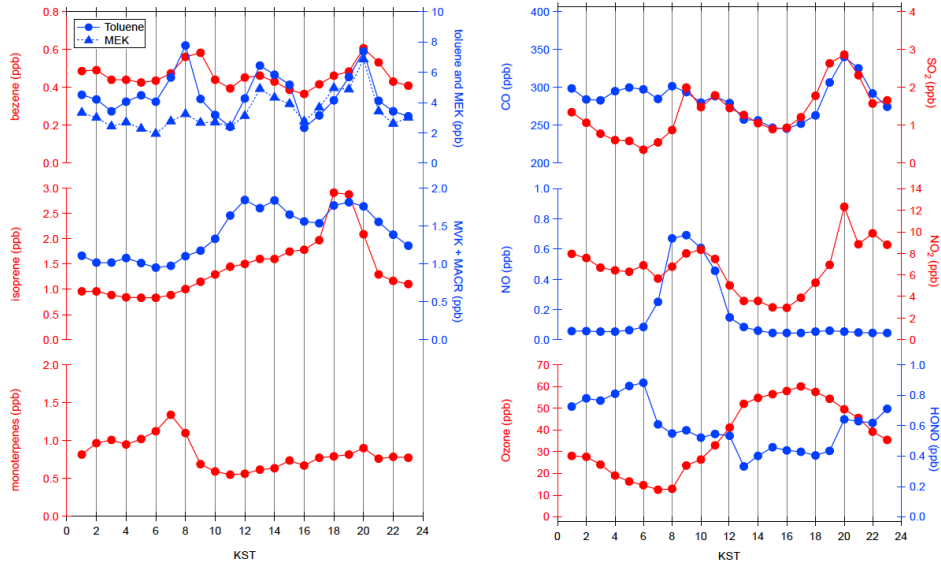
1095 |
1096

Saewung Kim 9/2/2014 2:25 PM
Deleted: Page Break
... [28]

Unknown
Formatted: Font:(Default) Times New Roman

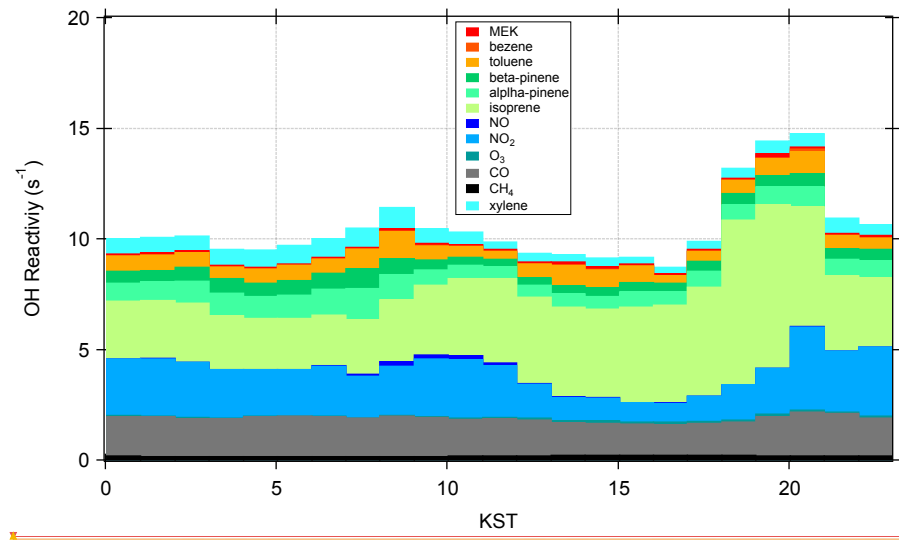
1101 | Figure 1. Averaged temporal variations observed trace gases at TRF (June 1st to June 6th,
1102 | 2012).
1103
1104

Saewung Kim 9/4/2014 11:57 AM
Deleted: 2



1105
1106
1107

1109 | Figure 2. The temporal variations of OH reactivity calculated from the observed dataset
1110 | at TRF (Figure 1). KST means Korean Standard Time (GMT+9).
1111 |
1112 |



1113 |
1114 |
1115 |
1116 |

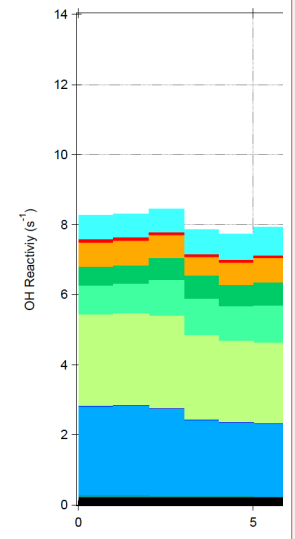
Saewung Kim 9/4/2014 11:57 AM

Deleted: 3

Saewung Kim 9/4/2014 3:24 PM

Deleted: 2

Saewung Kim 9/4/2014 3:29 PM

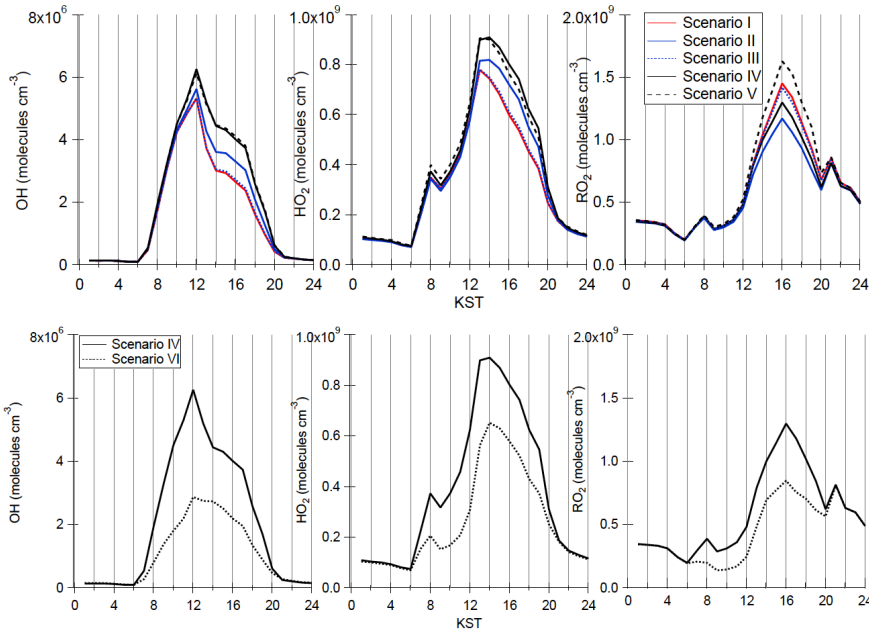


Deleted:

Unknown

Formatted: Font:(Default) Times New Roman

1120 | Figure 3. The temporal variations of OH, HO₂, and RO₂ calculated by six different
1121 | observationally constrained UWCM box model scenarios.
1122 |



1123 |
1124 |
1125 |

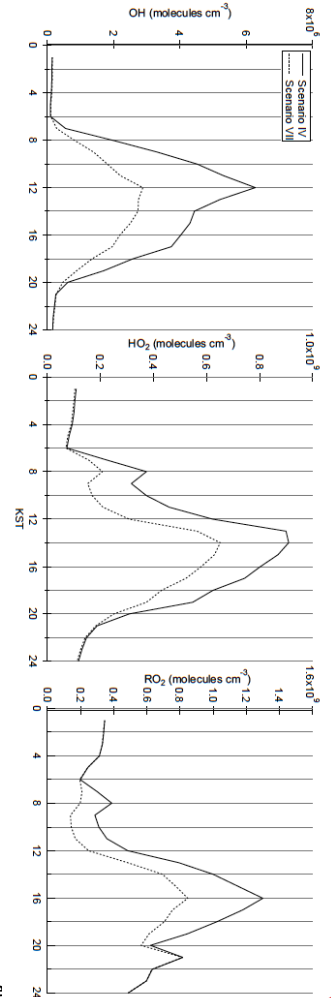
Saewung Kim 9/4/2014 11:57 AM

Deleted: 4

Saewung Kim 9/4/2014 3:26 PM

Deleted: seven

Saewung Kim 9/4/2014 3:29 PM



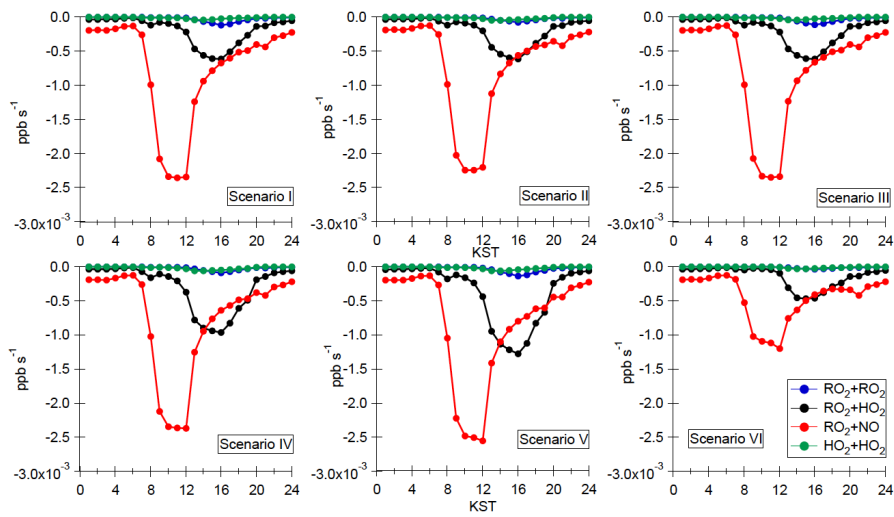
Dele

Unknown

Formatted: Font:(Default) Times New Roman

1129
1130
1131
1132

Figure 4 The temporal variations of radical recycling (red) and destruction (blue, black and green) rates calculated using the UWCM box model for different model scenarios



1133
1134
1135
1136
1137

Saewung Kim 9/4/2014 11:57 AM

Deleted: 5

Unknown

Formatted: Font:(Default) Times New Roman

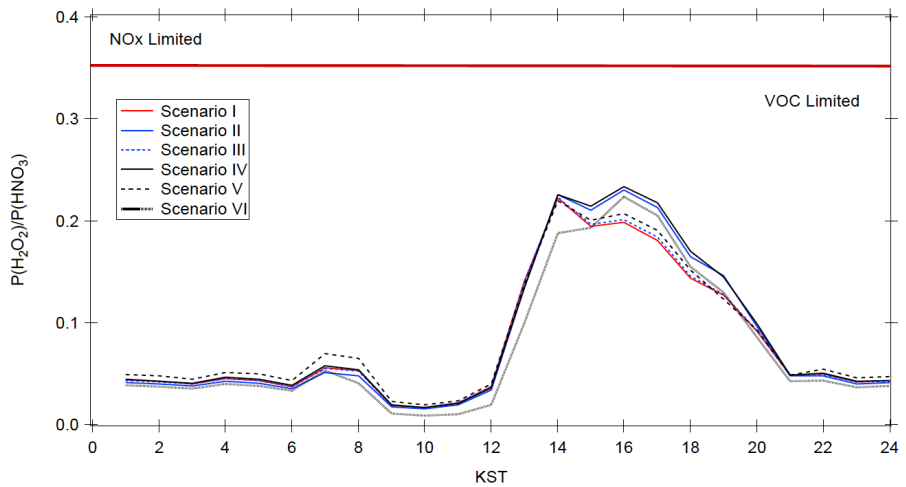
Saewung Kim 9/4/2014 3:51 PM

Deleted: <sp>

Unknown

Formatted: Font:(Default) Times New Roman

1140 Figure 5. The temporal variations of $P_{H_2O_2}/P_{HNO_3}$ calculated from the UWCM box model
1141 from six different model scenarios
1142



1143
1144
1145
1146

Saewung Kim 9/4/2014 11:57 AM

Deleted: 6

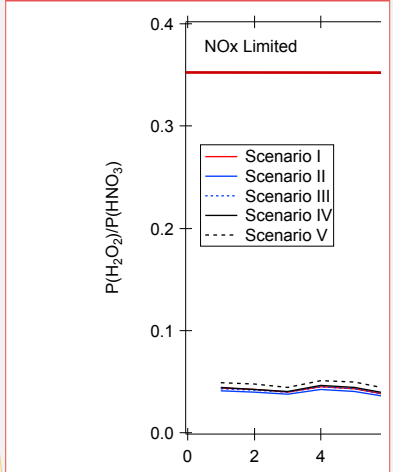
Saewung Kim 9/4/2014 3:52 PM

Deleted: five

Unknown

Formatted: Font:(Default) Times New Roman

Saewung Kim 9/4/2014 3:52 PM

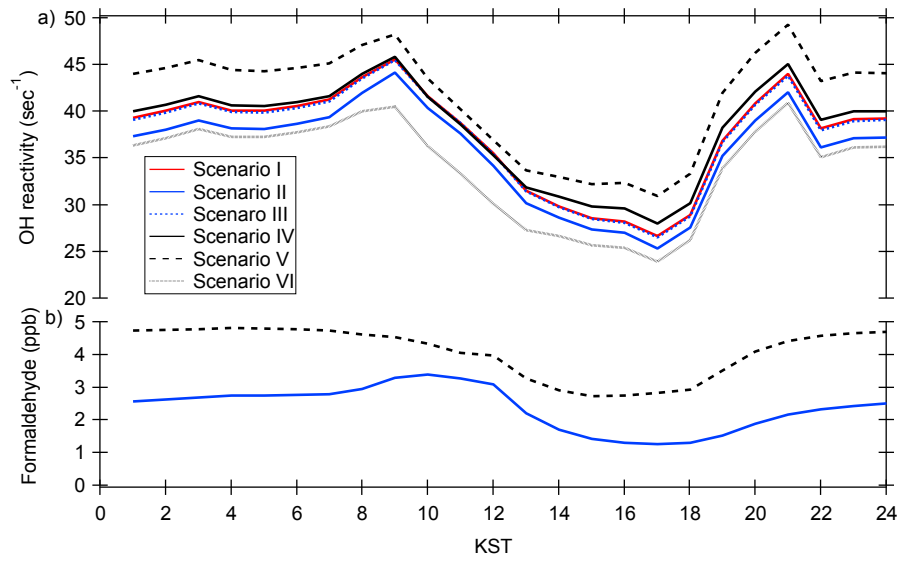


Deleted:

Unknown

Formatted: Font:(Default) Times New Roman

1150 | Figure 6. The temporal distributions of UWCM calculated OH reactivity (top panel) and
1151 formaldehyde (bottom panel)
1152
1153
1154
1155

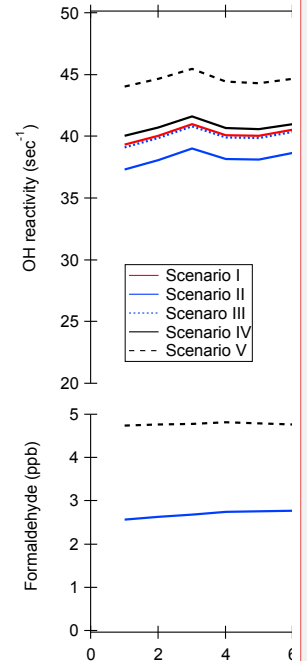


1156

Saewung Kim 9/4/2014 11:57 AM

Deleted: 7

Saewung Kim 9/4/2014 8:52 PM



Deleted:

Unknown

Formatted: Font:(Default) Times New Roman