Comments to modifications

The presentation of results has considerably improved and at least the online source of the model and the urban data are now presented. Wording is also better but still problematic in parts, particularly towards the end of the manuscript, therefore, I am now more specific in my detailed comments (see below). I still think that the 'urban-rural part' of the title is misleading although this is not a major point since I can follow the argumentation of the authors. Similarly, I agree that the merging of results and discussion is not uncommon for ACP although the chapter gets very long. However, at least the headline should be changed from 'results' into 'results and discussion'.

We appreciate the anonymous reviewer's constructive comments. We revised the previously submitted manuscript to reflect the reviewer's comments. Here, we respond the comments line by line.

The diurnal cycle of the monoterpene concentrations and the obvious difference to isoprene concentration is still not explained or sufficiently discussed. I also pity the opinion of the authors that suggested literature is not relevant to discuss while the manuscript still presents discussion parts that seem not to be essential. Spaulding et al. 2003 is still missing in the reference list and uncertainties in the measurements are still not shown. The term KST has to be explained at first appearance (Fig. 1 not 2).

In the last revision, we considered what would be the optimal level of discussion on the observed diurnal variations of isoprene and monoterpenes. As the main discussion of this paper is about uncertainty in the radical distribution from incomplete understanding in isoprene oxidation chemistry, we feel a detailed discussion on the diurnal variations may distract the intended point of discussion considering an effort to adapt an 1-D model could easily result in in an additional paper worth of discussion (e.g. Bryan et al., 2012). In addition, as we noted in the revised manuscript, we are preparing a separate manuscript to describe the characteristics of observed trace gas temporal variations. Therefore, detailed discussion will be included in the upcoming publication. We appreciate the careful review of the references by the reviewer and we have double-checked the revised manuscript to match references in the manuscript in the reference list along with all the abbreviations that we used in the manuscript.

Some more specific comments

Line 116: An 'evolution of thought' cannot be derived from only one previous statement.

We corrected it as "(Spaulding et al. (2003) and references therein)" so that it can reflect the status quo of isoprene oxidation chemistry at that time.

Line 125: missing 'at' before low

We corrected it as suggested

Line 131: 'for' instead of 'in'

We corrected it as suggested.

L132: 'regarding' or similar instead of 'in'

We corrected it as suggested.

L142: replace 'alarming' by 'underlined' or similar

We corrected it and it now reads
"The could become especially a serious issue"

L166-168: not 'Methods'

We relocated the sentence to the introduction section.

L252: What specific parameters are listed where?

We corrected it and it now reads
The specific parameters, constrained by observations are described in section 2.1 and 2.2.

L278-285: I don't see the context of these lines (delete?)

We have retained this because we believe this is a valuable discussion. Two previous studies, Kim et al. (2012) and Na and Kim (2002), presented contrasting results in VOC distributions in Seoul, South Korea. Therefore, we believe that the discussion helps to reconcile the two contrasting previous reports.

L298: The MT is not highest during night but in the morning (sunset?) this could hardly be explained by the planetary boundary layer.

The MT level was observed in the highest at 7 am local time when the sunrise happened (Figure 1). We also do not intend to explain the diurnal variation solely by the boundary layer dynamics. Again, this observation of the MT diurnal variation is not an outlier from previous observations conducted in the forest canopy as described in the revised manuscript.

L299/300: repetition

We deleted the sentence in the revised manuscript

L301/302: I don't see how branch enclosure measures that were only done around midday could indicate how the emissions develop throughout the day.

We did not fully describe the extent of the branch enclosure sampling method and have now added this description to the manuscript. The data presented in Table 2 are all from sampling during the mid day. In addition, we conducted 3 consecutive days worth diurnal variation analysis to explore the diurnal variations of BVOC emissions. The statement is from the observational data. We made it clear about this point in the revised manuscript.

L311: replace 'suppresses' with 'masks' or similar

We replaced the word with ‘may prevent’ in the revised manuscript.

L313-315: So what? (delete?)

We think that we explained why this can be significant in the following sentences.

L321/322: Neither done nor shown (delete)

We deleted the sentence in the revised manuscript.

L327-331: Rather introduction than discussion. Is any of the investigated oaks relevant here? (if not delete?)

We think that it is relevant since isoprene has been observed in high levels and is the dominant OH chemical sink at the observational site. Since isoprene is not directly emitted from the forest immediately surrounding the observational site, it is necessary to discuss the potential origins of isoprene and its importance in the regional scale.

L334: delete 'observed'

We edited it as suggested in the revised manuscript

L338: does MEK count as AVOC?

It has both anthropogenic (industrial solvent) and biogenic (primarily from wounded and otherwise stressed plants) sources.

L356/357: More investigations are always required. If this statement is considered important, please specify specifically why and what for!

We assume this is about the discussion on HONO. We have described the importance of HONO thoroughly and have suggested specific research directions to apply new analytical techniques.

L372/373: Introduction

We are not sure what the reviewer is referring to.

L374-378: Repetition and not modeling results (delete)

We edited the paragraph to minimize repetition. However, we intentionally left the discussion about observed NO since it is a critical factor determining radical recycling, which is the main discussion for the section.

L381: insert 'simulations with' (or similar) before 'observed'

We could not find the word ‘observed’ in line 381.

L383-385: the mechanism is constrained by scenarios? (new wording)

We agreed that the wording is confusion and so we reworded the sentences so that we can convey our intention of highlighting roles of HONO in radical chemistry.

L388: 2.6 what? (new wording!)
We corrected it in the revised manuscript.

L395: 6 (not 5) Scenarios are shown in Fig. 3! (5 are shown in Fig. 3 top row)
We corrected it in the revised manuscript.

L412: delete 'is'
We corrected as suggested in the revised manuscript.

L414: delete 'Most', add 'in the' before 'model'
We corrected as suggested in the revised manuscript.

L419-421: This sentence is unclear and I don't see the logic in it. It also sounds as a conclusion, not a discussion point (delete)

We rephrased the sentence for clarity. We think it should be regarded as discussion so we did not delete the argument.

L423: bold letters
We corrected as suggested in the revised manuscript.

L437-439: unclear (new wording!)
We rephrased the sentence in the revised manuscript.

L448: replace 'conspicuous' by 'apparent' or similar
We corrected it in the revised manuscript as suggested

L458: R7, not R6
We corrected the typo.

L472-484: This paragraph makes a lengthy statement about relatively well known facts ending in the conclusion that isoprene is important for ozone formation – what has also been shown in previous studies. In my opinion this should be radically shortened or deleted at all.

We shortened the paragraph as suggested in the revised manuscript.

L498: delete 'evaluation'
We deleted the word as suggested.

L500: If ozone formation is always VOC limited, why is it then obvious to investigate the radical chemistry to determine ozone production – at least in this case? Please refine argumentation.

We revised the manuscript to clearly convey the argument, which is that the level of VOC reduction should be adjusted depending on the degree of VOC limited regimes.

L504-507: No, this paper doesn't address the difficulties of policy implementation at all (delete or reformulate considerably).

We agree that we are not addressing any of policy implications but we do think that we provide the quantitative analysis of potential uncertainty in ozone production regimes from uncertainty surrounding isoprene-OH interactions. We edited the paragraph to reflect this point.

L514/517: 'Most' studies are all presented in 'Sinha et al. 2010'? (check)

We included one more study (Nakashima et al., 2014) from the Manitou forest site, a conifer forest.

L519: replace 'as' by 'are the'

We corrected it as suggested.

L523: Paragraph end after compounds? Where is the link between the sentences?

We started a new paragraph after the sentence in the revised manuscript.

L543-545: SOA formation is not discussed previously and is not the topic here. Thus conclusions about this are misplaced (delete).

We were clear about our discussion point limited to uncertainty in OVOC formation. From there, we expanded the discussion to potential uncertainty in SOA formation, as OVOCs are precursors for SOA. We think we are clear about this in the manuscript.

L547: The summary should be in the abstract (stay with conclusions)

We believe that having a summary section in research papers especially submitted to ACP is a common practice. However, We also agree with the referee’s concerns that the summary and conclusions section should not be just a repetition of the abstract. We edited this section so that the summary is better integrated with conclusions.

L556: Again, I don't see any indication of aerosol formation from aged pollution in this paper.

We corrected the sentence accordingly in the revised manuscript.

L565: replace 'twice' by 'twofold'

We corrected as suggested.

L569: What is meant by 'indicate contrary results'?

We corrected the sentence to avoid any confusion

L572-574: More studies are always required. If this statement is considered important, please specify specifically why and what for!

We think we are clear about the specifics of required studies, characterizing existing available analytical techniques.

L582: R7, not R6

We corrected as suggested in the revised manuscript.

L590: What is meant by 'morning and afternoon show a very strong contrast with morning'?

We separate this sentence into two sentences for clarity in the revised manuscript.

L593-596: No, these results don't indicate that uncertainties in photochemistry propagate policy making processes. It is even quite uncertain if they should. Do you want to argue that NOx should be reduced because then trees would be less damaged by ozone? Since this is a strongly VOC limited regime measures would have to be unrealistically severe. (delete or strongly reword)

We edited this sentence to cautiously convey the importance of scientific understanding in radical chemistry in providing a scientific basis for policy decision making processes.

Fig. 1: KST not explained. Please give also weather information (at least temperature, possibly radiation and wind speed). Please show uncertainty ranges or explain why this is not possible.

KST stands for Korean Standard Time (GMT+9). We added the temperature diurnal variation since it was used for the model calculation input. We notated uncertainty in the manuscript and intentionally did not show in the plot because it makes the plot very hard to read.

Fig. 2: Put xylene at the top of the panel to match the order of compounds in the figure

We corrected as suggested in the revised manuscript.

Fig. 6: needs better indication of a) and b). Such a differentiation should be applied for figures 3 and 4 too.

We corrected as suggested in the revised manuscript. We updated Figure 3 as suggested in the revised manuscript. For Figure 4, we clearly annotated each figures with the each scenario number.

Urban-rural interactions in a South Korean forest in ozone and oxygenated volatile organic compound formation perspectives

[1]Saewung Kim, [2]So-Young Kim, [3]Meehye Lee, [3]Heeyoun Shim,
[4,5]Glenn M. Wolfe, [6]Alex B. Guenther, and [1]Amy He, [2]Youdeog Hong,
[2]Jinseok Han

1 Department of Earth System Science, School of Physical Sciences, University of California, Irvine, Irvine California, 92697 U.S.A.
2 National Institute Environmental Research, Incheon, South Korea
3 Department of Earth and Environmental Sciences, Korean University, Seoul, South Korea
4 Joint Center for Earth Systems Technology, University of Maryland Baltimore County, Baltimore, MD, USA
5 Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA
6 Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland WA USA

To be submitted to Atmospheric Chemistry and Physics “East Asian Megacity” Special Issue

Abstract

Rapid urbanization and economic development in East Asia in past decades has led to photochemical air pollution problems such as excess photochemical ozone and aerosol formation. Asian megacities such as Seoul, Tokyo, Shanghai, Gangzhou, and Beijing are surrounded by densely forested areas and recent research has consistently demonstrated the importance of biogenic volatile organic compounds (VOCs) from vegetation in determining oxidation capacity in the suburban Asian megacity regions. Uncertainties in constraining tropospheric oxidation capacity, dominated by hydroxyl radical, undermine our ability to assess regional photochemical air pollution problems. We present an observational dataset of CO, NO_X, SO_2, ozone, HONO, and VOCs (anthropogenic and biogenic) from Taehwa Research Forest (TRF) near the Seoul Metropolitan Area (SMA) in early June 2012. The data show that TRF is influenced both by aged pollution and fresh BVOC emissions. With the dataset, we diagnose HOx (OH, HO_2, and RO_2) distributions calculated using the University of Washington Chemical Box Model (UWCM v 2.1) with near-explicit VOC oxidation mechanisms from MCM 3.2 (The Master Chemical Mechanism). Uncertainty from unconstrained HONO sources and radical recycling processes highlighted in recent studies is examined using multiple model simulations with different model constraints. The results suggest that 1) different model simulation scenarios cause systematic differences in HO_X distributions especially OH levels (up to 2.5 times) and 2) radical destruction (HO_2+HO_2 or HO_2+RO_2) could be more efficient than radical recycling (HO_2+NO) especially in the afternoon. Implications of the uncertainties in radical chemistry are discussed with respect to ozone-VOC-NO_X sensitivity and VOC oxidation product formation rates. Overall, the VOC limited regime

Saewung Kim 10/21/2014 10:01 AM
Deleted: concentrations

in ozone photochemistry is assessed but the degree of sensitivity can significantly vary depending on the model scenarios. The model results also suggest that RO_2 levels are positively correlated with oxygenated VOCs (OVOCs) production that is not routinely constrained by observations. These unconstrained OVOCs can cause higher than expected OH loss rates (missing OH reactivity) and secondary organic aerosol formation. The series of modeling experiments constrained by observations strongly urge observational constraint of the radical pool to enable precise understanding of regional photochemical pollution problems in the East Asian megacity region.

1. **Introduction**

NOx (NO+NO_2) and volatile organic compounds (VOCs) are two important precursors that drive HOx radical cycles(Levy, 1971). In the presence of NO_X, VOC oxidation processes recycle OH and produce photochemical oxidation products such as ozone and oxygenated VOCs (OVOCs). This reaction cycle is highly non-linear. For example, excess NO_2 may expedite nitric acid formation (R1), limiting ozone production. In the same context, excess VOCs may expedite peroxy radical production (R2), which limits OH regeneration from peroxy radicals.

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (R1)$$

$$HO_2 + RO_2 \rightarrow ROOH \quad (R2)$$

The non-linearity in tropospheric photochemistry has been relatively well studied in the urban regions of developed countries and applied in ozone reduction policy. The Los Angeles Metropolitan Area has accomplished significant ozone reduction by implementing aggressive emission reductions of both NOx and VOC especially from mobile sources (Ryerson et al., 2013). The remarkable ozone abatement was possible due to the fact that there is no significant pollution transport from other metropolitan areas and no significant natural emission sources especially volatile organic compounds from vegetation (BVOCs; biogenic volatile organic compounds) compared with anthropogenic VOC mostly from mobile sources (Pollack et al., 2013;Huang et al., 2013). In the late 80s, Trainer et al. (1987) first demonstrated the importance of isoprene (C_5H_8) as a peroxy radical source that can contribute significant ozone production in rural areas. The importance of isoprene in ozone production in urban areas has also been highlighted, e.g. in the Atlanta Metropolitan Area (Chameides et al., 1988).

Isoprene is a hemiterpenoid species and is the globally dominant VOC emission from vegetation (Arneth et al., 2011;Guenther, 2013). Arguably, isoprene is the most frequently studied BVOC from the perspective of atmospheric oxidation processes and their implications for ozone and aerosol formation. However, significant uncertainty hinders assessing the roles of isoprene in regional and global photochemistry in three fronts. First, there is still significant uncertainty in estimating emission rates from each individual plant species on regional scales (Guenther, 2013). Second, limited isoprene inter-comparison results (Barket et al., 2001) suggest that there are large systematic biases among different analytical techniques. Lastly, recent laboratory, theoretical and field observations suggest significant uncertainty in tropospheric isoprene oxidation processes initiated by OH. Until early 2000, it was thought that three first generation isoprene oxidation products (methyl vinyl ketone, methacrolein, and formaldehyde) from OH oxidation were enough to constrain isoprene tropospheric oxidation processes for modeling purposes (e.g. Spaulding et al. (2003) and references therein). This is an interesting evolution of thoughts considering that Paulson and Seinfeld (1992), one of pioneering works describing isoprene oxidation, clearly claimed that 22 % of first generation isoprene oxidation products from the reaction with OH was not identified and likely included multifunctional C5 compounds. Recent advances in analytical techniques (Kim et al., 2013a) have shown that indeed significant C5-hydroxy carbonyl (e.g. isoprene hydroperxyenals, HPALD) and peroxide compounds are produced as first generation isoprene oxidation products (Crounse et al., 2011;Paulot et al., 2009;Wolfe et al., 2012;Zhao and Zhang, 2004). The product yields appeared to be a strong function of NO concentrations (Peeters and Muller, 2010). In general, at low to intermediate NO levels (~ 100 pptv or lower), the yields of C5-hydroxy carbonyl compounds become higher. These new findings in the isoprene oxidation process are also closely related with recent findings in unexpectedly high OH concentrations (Hofzumahaus et al., 2009;Lelieveld et al., 2008) and substantial missing OH sinks also known as unexpectedly high OH reactivity in high isoprene environments (Di Carlo et al., 2004;Edwards et al., 2013;Kim et al., 2011;Lou et al., 2010).

Saewung Kim 10/21/2014 10:30 AM
Deleted: and

ABG 10/28/2014 8:12 AM
Deleted: are

These new findings have significant implications for regional air quality especially regarding photochemical ozone and SOA production. Despite the strong anthropogenic pollutant emissions in East Asia (China, Japan and South Korea), recent research has shown that isoprene accounts for a major OH chemical sink in suburban areas near Beijing (Ran et al., 2011), the Pearl River Delta region (Lu et al., 2012), Taipei, Taiwan (Chang et al., 2014) and Seoul (Kim et al., 2013d;Kim et al., 2013b). Consequently, modeling studies also clearly show that isoprene contributes significantly to ozone formation in Asian megacity regions. Kim et al. (2013d) reported that simulated ozone levels with isoprene chemistry are up to 30 % higher than ozone simulation without isoprene chemistry using the WRF-Chem model, indicating an urgent need to implement improved isoprene chemistry schemes in these models in order to simulate the unexpected higher levels of OH in isoprene rich environments. This could become an especially serious issue as Hofzumahaus et al. (2009) reported significantly higher (~ 2.6 times at noon) than expected OH levels in the Pearl River Delta region in China. Therefore, the current assessments based on the conventional OH photochemistry could

Saewung Kim 10/16/2014 11:00 AM
Deleted: in

Saewung Kim 10/16/2014 11:00 AM
Deleted: in

Saewung Kim 10/16/2014 11:04 AM
Deleted: is

ABG 10/28/2014 8:12 AM
Deleted: a

Saewung Kim 10/16/2014 11:04 AM
Deleted: alarming

significantly misdiagnose regional air-quality status and mislead policy implementation to reduce photochemical air pollution in the East Asian region. Furthermore, as the importance of BVOC in regional air-quality issues in ozone and SOA formation has been also highlighted in Europe and North America, the uncertainty in isoprene photochemistry has significant implications in urban and suburban air quality in general (Zhang et al., 2008a;Sartelet et al., 2012).

We present atmospheric observations of NO_X, CO, VOCs, ozone, and HONO in the Taehwa Research Forest (TRF) in the Seoul Metropolitan Area (SMA), South Korea. We use observed data from June, 2013 to conduct observationally constrained box model (University of Washington Chemical Box Model; UWCM) calculations to estimate OH, HO_2 and RO_2 concentrations with different sets of observational parameters. We discuss current uncertainty in OH-isoprene photochemistry with perspectives of constraining photochemical ozone production and OVOCs precursors of secondary organic aerosols.

2. **Methods**

The Taehwa Research Forest (TRF) is located ~ 35 km from the center of Seoul, South Korea. The TRF is located at the southeastern edge of the Seoul metropolitan Area (SMA, population of ~ 23 million). TRF has a sampling tower located in the middle of a coniferous tree plantation (200 m by 200 m) with the canopy height of 18 m (*Pinus koraiensis*) surrounded by a deciduous forest mostly composed by oak. The TRF instrumentation has previously been described by Kim et al. (2013d) along with the previous trace gas observational results. Therefore, just brief descriptions of analytical techniques are given in this paper.

Saewung Kim 10/16/2014 11:12 AM
Moved (insertion) [1]

Saewung Kim 10/21/2014 10:45 AM
Deleted: Kim et al. (2013d) reported CO, NO_X, SO_2, ozone, and VOC observation results along with WRF-Chem assessments of ozone forming potential of isoprene photochemistry. The report found that isoprene was the most dominant OH chemical sink during daytime among the observed trace gases and explained up to 30 % of ozone production.We

Saewung Kim 10/16/2014 11:12 AM
Deleted: these

Saewung Kim 10/16/2014 11:12 AM
Moved up [1]: Kim et al. (2013d) reported CO, NO_X, SO_2, ozone, and VOC observation results along with WRF-Chem assessments of ozone forming potential of isoprene photochemistry. The report found that isoprene was the most dominant OH chemical sink during daytime among the observed trace gases and explained up to 30 % of ozone production.

2.1. CO, NO_X, SO_2, ozone, VOCs, and meteorological parameters

Thermo Fisher Scientific Enhanced Trace Level Gas Analyzers are used for CO, NO_X, SO_2, and ozone observations as summarized Table 1. VOC observations are conducted by a High-Sensitivity Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon GmbH). The atmospheric application of this technique is thoroughly reviewed by de Gouw and Warneke (2007). In addition, the instrument suite at TRF is thoroughly described in (Kim et al., 2013d). PTR-MS can quantify atmospheric VOCs that have higher proton affinity than the proton affinity of H_2O (691 kJ mol^{-1}). Most alkanes have lower proton affinity than water but alkene, aromatic and some OVOCs have higher proton affinity and are suitable for quantification using PTR-MS (Blake et al., 2009). These compounds are more reactive than alkane compounds so PTR-MS has capability to observe reactive atmospheric compounds. The TRF PTR-MS system was set to measure acetaldehyde, acetone, acetic acid, isoprene, methylvinylketone (MVK) + methacrolein (MACR), MEK, benzene, xylene (*p*, *m*, and *o*), and monoterpenes (MT). Each compound was set to be monitored for 1 second each resulting in a sample cycle of 15 seconds. Lower detection limits for the observed VOCs are estimated to be 20 ppt for a 5 second integration with sensitivity of 70 counts ppb^{-1} (2 σ). The uncertainty is estimated as 12 % (2 σ) for the same integration time. Meteorological parameters such as temperature and humidity are monitored by LSI LASTEM Meteorological Sensors. All the presented data is from the 15 m (the canopy height is 18 m) sampling line and meteorological sensors collocated at this height too.

Saewung Kim 10/21/2014 10:53 AM
Deleted: .

PTR-MS with a quadrupole mass filter has an intrinsic limitation that isobaric compounds are all collectively quantified with the same channel (m/z) with a resolution of unit mass. This limitation particularly becomes an issue for investigating the roles of different isomers of MT and sesquiterpenes (SQTs) in photochemistry. For this reason, we also occasionally collect sorbent cartridge samples to analyze MT and SQT speciation in both ambient air and branch enclosure emissions near the sampling tower. As described in (Kim et al., 2013d), Tenax GR and Carbotrap 5TD packed sorbent cartridges (Markes Int, Llanstrisant, UK) were used for sampling. The sampled cartridges were shipped to National Center for Atmospheric Research (NCAR), Boulder CO, USA for gas chromatography-mass spectrometer (GC-MS) analysis. An Agilent 7890 GC/5975 C Electron Impact Mass Spectrometer (GC-MS/FID) in conjunction with a MARKES Unity1/Ultra thermal desorption system optimized for terpenoid analysis quantifies speciated MT and SQT in the sorbent samples. Cartridge samples are both collected from ambient and branch enclosure air. Ambient samples were collected in the mid-day to early afternoon with a volume of 6 L. Ozone in the ambient air was removed using a Na_2SO_3 filter. Branch enclosure samples were also collected, mostly in the mid-day time frame, with a volume of 1 L without an ozone filter as zero air was introduced to the branch enclosure. To explore the diurnal differences in BVOC emissions, some branch enclosure sampling was conducted continuously for three consecutive days in mid June of 2013. We present these analytical results from GC-MS analysis limited to the qualification purpose to examine MT and SQT speciation.

ABG 10/28/2014 8:14 AM
Deleted: mostly

ABG 10/28/2014 8:14 AM
Deleted: we also

ABG 10/28/2014 8:15 AM
Deleted: cartridge samplings

ABG 10/28/2014 8:15 AM
Deleted: the

2.2 HONO quantification

HONO was measured with an ion chromatography (IC) coupled with diffusion scrubber. Air was introduced to diffusion scrubber (Lab solutions Inc., IL, USA) through a 2 m PFA tubing (1/4" i.d.) at 1.5 L m^{-1} using a filtered orifice restrictor (F-950, air logic, WI, USA). Air flowing through diffusion scrubber interfaced with deionized water, into which HONO was extracted. 50 µL of solution was injected into the IC system through a PEEK loop (Rheodyne, WA, USA) and 6-way valve (EV750-100, Rheodyne, WA, USA). Eluent was a mixture of Na_2CO_3 and $NaHCO_3$, which was pumped by a HPLC pump (DX-100, Dionex, CA, USA) into a guard column (Ionpax® AG 14, 4x50mm, Dionex, CA, USA) and then analytical column (Ionpax® AS 14, 4x250mm, Dionex, CA, USA). The column effluent passed through a suppressor (ASRS 300, Dionex, CA, USA) and HONO was detected as nitrite ion in conductivity detector (550, Alltech, IL, USA). The entire measurement processes of sampling, chemical analysis, and data acquisition were controlled by a digital timer and data acquisition software (DSchrom-n, DS science, Korea), by which we obtained two measurements every hour. The system was calibrated using a NO_2^- standard solution (Kanto chemical Co., Inc., Tokyo, Japan) whenever reagents were replaced. The detection limit was 0.15 ppb estimated from 3σ of the lowest working standard. Specific analytical characteristics are described in Simon and Dasgupta (1995) and Takeuchi et al. (2004).

Saewung Kim 10/21/2014 11:07 AM
Deleted: a

2.3 UWCM box model

UWCM 2.1 is an open source box model coded by MATLAB (MathWorks®). The model platform can be downloaded from a website (http://sites.google.com/site/wolfegm/code-archive). The box model is embedded its own

HO_X ($OH+RO_2$)-RO_X (peroxyradical and alkoxy radical)-NO_X coupling chemical mechanism. UWCM utilizes Master Chemical Mechanism version 3.2 (MCM 3.2) (Jenkins et al., 1997; Saunders et al., 2003) for near-explicit VOC photo-oxidation schemes. A more detailed model description can be found in Wolfe and Thornton (2011). To minimize uncertainty from the parameterizations of transport and emission, we constrained relatively long-lived trace gases presented in Figure 1. This box modeling technique has been commonly used for examination of OH levels that can be justified by the short chemical lifetime of OH (Kim et al., 2014;Kim et al., 2013c;Mao et al., 2012;Mao et al., 2010). Recently developed isoprene photo-oxidation mechanisms shown in Archibald et al. (2010) are also incorporated in the model. In addition, Kim et al. (2013c) and Wolfe et al. (2013) applied the model in the identical fashion as used for this study to probe radical distributions using comprehensive observational datasets. This study used the UWCM to simulate the diurnal variations of radical pool ($OH+HO_2+RO_2$) distributions as observational parameters such as CO, NO_X, ozone, and VOCs are constrained. To fully account for roles of OVOCs in the box model as radical sources, we simulated three consecutive days and presented diurnal variations from the third day. The specific parameters, constrained by observations are described in section 2.1 and 2.2.

Saewung Kim 10/16/2014 11:19 AM
Deleted: listed above

3. Results

3.1. Observational Results

Diurnal averages of observed trace gases (June 1st 2012 to June 6th 2012) are shown in Figure 1. The TRF observatory is in continuous operation and we choose this six day period because a regional high-pressure system caused a stagnant air pollution event in this period. In the center of Seoul (the real- time data available at http://www.airkorea.or.kr), carbon monoxide was observed in the similar levels during the focused period (June 1st to June 6th, 2012). On the other hand, the NO_2 level observed in central Seoul was much higher (20-50 ppb) compared with observed levels at TRF. The reason can be attributed to differences between the chemical lifetime of CO (~a month) and NO_2 (~a few hours to a day). The observations clearly indicate that the TRF is not directly influenced by fresh SMA pollution plumes although the TRF is very close to the center of Seoul (30 km away from the city center) as a regional modeling study shows most of CO and NO_X sources are located in the city center (Ryu et al., 2013). Similar observations were also reported for other East Asian megacities such as Beijing (Ma et al., 2012), where ~ 30 ppb and ~ 15 ppb of NO_2 were observed at noon in the urban and the adjacent rural sites, respectively. In contrast, there were no noticeable differences in CO levels between the urban and rural sites (~ 1-2 ppm). The observed CO, NO_X and SO_2 levels in TRF were much lower than those observed in the suburban regions of Chinese megacities such as Beijing (Ma et al., 2012), Shanghai (Tie et al., 2013), and the Pearl River Delta Region (Lu et al., 2012) and similar with the observed levels in Tokyo, Japan (Yoshino et al., 2012).

Saewung Kim 10/21/2014 11:26 AM
Deleted: also

Saewung Kim 10/21/2014 11:25 AM
Deleted: and

Previous VOC observations in the SMA consistently have shown that toluene is the dominant anthropogenic VOC followed by other aromatic compounds such as xylene and benzene (Kim et al., 2012;Na and Kim, 2001). Na and Kim (2001) reported high concentrations of propane from house hold fuel use. However, recent observation results from the photochemical pollution observational network managed by National Institute of Environmental Research (NIER) of South Korea in the SMA clearly indicate that propane levels have declined and are now much lower than the levels previously observed (NIER, 2010). This is probably caused by the implementation of a policy changing household fuel sources from propane to methane. Kim et al. (2012) presented detailed aromatic VOC distributions in the SMA from four different urban observational sites. In average, toluene concentrations were observed ~ 7 times higher than the observed levels of xylene and benzene. At the TRF, a similar anthropogenic VOC speciation distribution was observed as shown in Figure 1. The observed toluene and MEK (methyl ethyl ketone) mixing-ratios were much higher than benzene and xylene. MEK is detected in m/z of 73^+ by PTR-MS. Although methyl glyoxal, an atmospheric VOC oxidation product, is also detected on the same mass, we assumed that 73^+ of m/z signals are mostly from MEK, an anthropogenic VOC, since the temporal variation follows that of anthropogenic VOC such as toluene and xylene. In addition, atmospheric lifetime of methyl glyoxal is much shorter than MEK.

As the observation facility is located in the middle of a pine tree plantation (*Pinus koraiensis*), monoterpenes (MT) are consistently observed. The temporal variation of monoterpenes is affected by the planetary boundary layer evolution with a pattern of higher MT levels during night than those of mid-day as has been often reported in other forest environments (Bryan et al., 2012;Kim et al., 2010) This can be explained by interplays between boundary layer evolution and temperature dependent MT emission. It should also be noted that the continuous branch enclosure BVOC emission observations indicate that the daily maxima of MT and SQT emissions were observed in the midday (between noon to 2 pm in the local time). The observed MT and SQT speciation information in the midday is summarized in Table 2. Table 2a summarizes branch enclosure sample analysis results and ambient sample analysis results are summarized in Table 2b. In general, observed MT and SQT in the ambient air are consistent with previously observed distributions (Kim et al., 2013d). α-pinene and β-pinene were the dominant monoterpene and longifolene was the only detected SQT species. In contrast, the branch enclosure observation results, reflecting BVOC emission, indicate high emission of very reactive MT and SQT species such as β-myrcene, α-caryophyllene, and β-caryophyllene. The fast oxidation of these highly reactive terpenoid species is expected to limit the atmospheric presence of the compounds. Therefore, photochemical oxidation processes of these compounds may have been neglected. Investigating emissions and photochemistry of these reactive terpenoid compounds can constrain potential missing OH reactivity and SOA production from highly oxidized reaction products.

ABG 10/28/2014 8:17 AM
Deleted: may suppresses prevent

Isoprene is produced from carbon recently fixed through photosynthesis resulting in higher emissions and atmospheric concentrations during the daytime. The temporal variation shown in Figure 1 reveals an isoprene concentration maximum between 17:00 to 20:00. In addition, the ratios of MVK+MACR, major isoprene oxidation products and isoprene at this period, are significantly lower than those of late morning to early afternoon. The enhanced isoprene levels in the late afternoon or early evening have been also reported in previous studies (Apel et al., 2002;Bryan et al., 2012). The branch enclosure observations demonstrate that isoprene is not emitted from the pine plantation but rather transported from surrounding broadleaf forests as right outside of the pine plantation (200 m × 200 m) is a forested area dominated by oak trees. Oak comprises 85 % of broadleaf trees in South Korea (Lim et al., 2011). Lim et al. (2011) quantified isoprene emission rates for five representative oak species in South Korea and report a wide

Saewung Kim 10/17/2014 2:55 PM
Deleted: Further regional and 1-D modeling studies are being conducted to examine this observed temporal variations of isoprene and MVK+MACR

ABG 10/28/2014 8:18 AM
Deleted: .

Saewung Kim 10/21/2014 12:43 PM
Deleted: However, e

emission range from oaks that are negligible isoprene emitters (<0.004 μgC dw^{-1} h^{-1}; standard emission rates) to others with very high isoprene emission rates of 130 μgC dw^{-1} h^{-1}.

Contributions from each trace gas species towards ambient OH reactivity are shown in Figure 2. This is calculated as the product of the observed species concentration and its rate constant for reaction with OH. Observed OH reactivity from VOCs are much higher than from other trace gases such as CO, NOx, SO_2, and ozone. Among the observed VOC species, BVOCs such as isoprene, α-pinene and β-pinene accounted for significantly higher OH reactivity in comparison with the observed AVOCs such as toluene, benzene, xylene and MEK. Isoprene accounts the highest OH reactivity especially during the daytime. This analysis is consistent with reports from other suburban observations from East Asian megacities such as Beijing (Ran et al., 2011), the PRD region, China (Lou et al., 2010), and the Kinki region Japan (Bao et al., 2010).

Saewung Kim 10/17/2014 10:42 AM
Deleted: observed

Saewung Kim 10/21/2014 12:45 PM
Deleted:

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

Delta region near Guangzhou, where comparable NO_2 levels with TRF were observed. The high HONO levels (a few hundred ppt) especially during the daytime have been consistently reported near Eastern Asian megacities such as Beijing (Li et al., 2012), Shanghai (Hao et al., 2006), and Seoul (Song et al., 2009). Still these are limited datasets and further comprehensive analysis, especially more extensive observation is required. However, two recently proposed HONO production mechanisms may be able to explain the higher levels in the Eastern Asian megacity region. One is HONO production from NO_2 photo-excitation (Wong et al., 2012) as the region usually has high NO_2 concentrations and the other is HONO emission from soil bacteria (Oswald et al., 2013). Oswald et al. (2013) found differences as much as two orders of magnitude in HONO emissions from soil samples from different environments (e.g. pH and nutrient contents). In addition, as most of observations in the East Asia regions were conducted with ion chromatography based methods, more direct HONO quantification techniques such as a chemical ionization mass spectrometry technique (Roberts et al., 2010) need to be used to characterize any potential interferences such a high NO_X environment (e.g. N_2O_5).

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

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

Saewung Kim 10/22/2014 8:34 AM
Deleted: , secondary aerosol precursor

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

We conducted model simulation under six different scenarios. Each scenario is described in Table 3. The quantitative assessments of the impacts to radical concentrations (OH, HO_2, and RO_2) from unknown HONO sources are evaluated by examining the model outcomes of the scenarios with and without observed HONO. To evaluate the impacts of hydroperoxy-methyl-butenal (HPALD) photolysis and isoprene peroxy radical recycling in the radical pool, each chemical mechanism is selectively constrained by different scenarios. For HPALD chemistry, we adapted two different HPALD formation rate constants published by Peeters and Muller (2010) and Crounse et al. (2011). The formation rates from Peeters and Muller (2010) is about 40 times faster than those from Crounse et al. (2011) in 298 K. Finally, we applied the OH yield of 2.6 from isoprene peroxy radical and HO_2 reactions for the evaluation (Wolfe et al., 2011). Although, Liu et al. (2013) demonstrated significantly lower OH recycling contributions from HO_2 + isoprene peroxy radical reactions than those argued by Wolfe et al. (2011) by interpreting chamber experiment results, the high recycling rate from Wolfe et al. (2011) is applied in the model calculations to explore upper limit of uncertainty in radical estimations.

Modeled OH, HO_2, and RO_2 from the six different model scenarios are shown in Figure 3. A summary of averaged OH, HO_2, and RO_2 concentrations in the morning (08:00 – 11:00) and the afternoon (13:00 – 16:00) from each simulation is shown in Table 4. With respect to the base run results (Scenario I), Scenario III with the lower

Saewung Kim 10/17/2014 2:23 PM
Deleted: constrained

Saewung Kim 10/17/2014 2:24 PM
Deleted: constraining

Saewung Kim 10/17/2014 2:47 PM
Deleted: 2.6 of

Saewung Kim 10/22/2014 8:42 AM
Deleted: by

Saewung Kim 10/17/2014 2:56 PM
Deleted: five

HPALD formation rate does not cause noticeable differences in radical concentrations. Adapting higher HPALD formation rates (Scenario II) cause significant differences in radical distribution especially in RO_2. This difference is likely caused by the fact that significant isoprene peroxy radical is converted to HPALD. The higher levels of discrepancy is found in RO_2 between Scenario I and Scenario II in the afternoon when low NO concentrations are observed, which efficiently facilitates HPALD formation. Adding HO_2 + isoprene peroxy radical reactions as OH recycling processes (Scenario IV and V) results in significant enhancements in OH and HO_2 with respect to the base run (Scenario I). RO_2 concentrations are calculated in significantly different levels between Scenario IV and V. This can be again accounted by the applications of different HPALD formation rates in the two different model scenarios. The higher level of OH from the additional recycling process causes substantially higher RO_2 formation rates than those from the scenarios without the additional recycling process. The faster HPALD formation in Scenario IV appeared to cause faster loss of RO_2 resulting in low RO_2 concentrations.

Striking differences can be found in the model simulation results with or without constraining observed HONO as shown in Figure 3. Model calculation results from Scenario VI indicate significantly smaller OH, HO_2, and RO_2 concentrations than the concentrations calculated from the counter part (Scenario IV), which contains identical constraints and isoprene photochemistry except constraining observed HONO. Again, this clearly indicates that more thorough evaluations of the impacts of HONO on air quality are needed to precisely constrain photochemical processes in the region along with evaluations of the currently available analytical techniques as argued in section 3.1.

ABG 10/28/2014 8:36 AM
Deleted: is

Saewung Kim 10/17/2014 3:06 PM
Deleted: Most s

Saewung Kim 10/19/2014 3:29 PM
Deleted:

ABG 10/28/2014 8:20 AM
Deleted: on

Saewung Kim 10/19/2014 3:29 PM
Deleted: not only

ABG 10/28/2014 8:20 AM
Deleted: to

Saewung Kim 10/19/2014 3:29 PM
Deleted: but also analytical techniques

ABG 10/28/2014 8:20 AM
Deleted: should be followed

ABG 10/28/2014 8:20 AM
Deleted: n

3.3 Implications of uncertainty in HO_X model calculations in assessing photochemical ozone and OVOC production.

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

$$RO_2 + NO \rightarrow RO + NO_2 \ (R3)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \ (R4)$$

$$RO_2 + RO_2 \rightarrow ROOR + O_2 \ (R5)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \ (R6)$$

When the rate of R3 gets much faster than the sum of reaction rates of R4, R5, and R6 then radical recycling processes become more efficient than radical destruction processes. In this radical recycling regime, OH, a universal tropospheric oxidant, is well buffered to maintain the elevated OH levels. On the other hand, the radical destruction regime can be defined when the radical recycling rates (R3) are slower than the radical destruction reaction rates (R4+R5+R6). Although some recent findings (e.g. Lelieveld et al. (2008)) suggest that we may need to reconsider R4 as a radical recycling process rather than a radical destruction process, in this study, we follow the conventional classification of radical chemistry regimes. The temporal variations of radical-radical reaction rates from the model simulation scenarios are shown in Figure 4. In general, the radical reaction rates are elevated as much as twice once observed HONO is constrained in the model calculations (e.g. Scenario VI). This is because unaccounted HONO in the model calculations cause significant underestimations in the radical pool ($OH+HO_2+RO_2$)

Saewung Kim 10/19/2014 3:32 PM

Formatted: Font:Bold

Saewung Kim 10/19/2014 3:49 PM

Deleted: Although it is still controversial the yield of OH from (R4) for isoprene peroxy radicals which demands a serious discussion whether we should regard R4 as a radical destruction reaction, we stick with the classical categorization for radical recycling and destruction regimes in this study

ABG 10/28/2014 8:21 AM

Deleted: e

Saewung Kim 10/19/2014 3:56 PM

Deleted: .

size with respect to the constrained HONO scenarios as shown in Figure 4. In addition, as we include recently developed isoprene radical chemistry, the RO_2+HO_2 reaction rates, known for a radical destruction pathway becomes more faster. This becomes more obvious in the afternoon when NO concentration becomes lower. The RO_2 + HO_2 reaction rates get higher than those of RO_2 + NO in the afternoon for the Scenario IV and V. This is surprising, as the radical destruction regime is usually associated with low NO_X conditions. Suburban regions of megacities including the TRF in general show high NO_X conditions. However, radical recycling rates are determined by concentrations of NO. The fraction of NO in the NO_X pool is determined by competing reactions between NO_2 photolysis and oxidation reactions of NO by ozone, HO_2, and RO_2 radicals. Once we assume the pseudo-steady state of NO, then NO in NO_X pool can be expressed as

Saewung Kim 10/19/2014 4:06 PM
Deleted: is

Saewung Kim 10/19/2014 4:06 PM
Deleted: conspicuous

$$[NO] = J_{NO2}[NO_2]/(k_{NO+O3}[O_3] + k_{NO+HO2}[HO_2] + k_{NO+RO2}[RO_2]) \quad (R7)$$

Saewung Kim 10/19/2014 4:07 PM
Deleted: 6

This mathematical expression clearly shows that NO levels are dependent on NO_X mostly composed of NO_2. At the same time, the fraction of NO in NO_X is anti-correlated with ozone, HO_2, and RO_2 concentrations. Therefore, the size of the radical pool composed of HO_2 and RO_2 is relevant for determining the fractions of NO in given NO_X levels. High HO_2 and RO_2 are likely observed in high VOC regions such as forested areas. This could cause a smaller fraction of NO in the given NO_X pool so radical recycling gets relatively weaker compared with radical destruction reaction pathways. More quantitative approaches are required to categorize radical reaction pathways rather than qualitative categorization such as high or low NO_X regimes.

Conventionally, efficient ozone production can be achieved by the balance between nitric acid production rates (P_{HNO3}, OH + NO_2) and peroxide production rates (P_{ROOH}, HO_2+RO_2 or P_{H2O2} HO_2+HO_2) (Sillman and He, 2002). The imbalance will cause ozone production sensitivity towards either NOx or VOCs. A comprehensive photochemical model analysis (Tonnesen and Dennis, 2000a, b) demonstrated that in a wider range of ozone concentrations, the VOC and NOx limited regimes can be determined by the ratios of P_{H2O2} and P_{HNO3}. The ratio range (P_{H2O2}/P_{HNO3}) of 0.35 is regarded as the border range. In the VOC limited regime ($P_{H2O2}/P_{HNO3} < 0.35$), ozone production is expected to decrease with increasing NO_X and increase with increasing VOCs. In the NO_X limited regime ($P_{H2O2}/P_{HNO3} > 0.35$), ozone production gets efficient with increasing NO_X and is insensitive to changes in VOCs (Sillman and He, 2002). This categorization has guided policy-making processes whether NO_X or VOC controls will be more effective in ozone reduction. A series of modeling studies have been conducted to characterize ozone production regimes in the suburban regions of East Asian megacities and have consistently concluded that the role of isoprene is important in ozone production. However, most of these studies have concluded that East Asian megacity regions are mostly in the VOC limited regime (Tseng et al., 2009;Zhang et al., 2008b;Lim et al., 2011;Cheng et al., 2010;Shao et al., 2009a;Shao et al., 2009b;Xing et al., 2011). Recently, however, a modeling study by Li et al. (2013) in the Pearl River Delta region in China demonstrated the time dependence of ozone production regimes. Specifically, with high NOx emissions in the morning, the regional ozone production regime is categorized as VOC limited. In contrast, in the afternoon when the highest ozone concentrations are observed, a NOx limited regime is often found. The obvious

Saewung Kim 10/20/2014 8:25 AM

Deleted: High and low NO_X regimes also have been widely used to define ozone production regimes. As NO_X catalyzes ozone production and peroxy radicals expedite NO_X turnover, in general, higher NO_X and VOCs conditions result in higher ozone production. However, non-linearity in photochemistry of ozone production causes a complexity in ozone reduction strategy (Seinfeld, 1989).

issue to be addressed is that all of the above studies neglected how the uncertainty in hydroxyl radical chemistry would affect the ozone production regime. Moreover, HONO has been rarely constrained by observations in the previous modeling studies. Figure 5 shows the temporal variations of P_{H2O2}/P_{HNO3} from the all six different model scenarios. The VOC limited ozone formation regime was observed regardless of the HO_X simulation scenarios. Differences among the scenarios are not noticeable in the morning when NO is high but noticeable differences can be found in the afternoon which may cause uncertainty in assessing the optimal level of NO_X and VOC emission controls from a policy perspective. In general, the model calculation results with faster HPALD formation rates indicate higher $P(H_2O_2)/P(HNO_3)$ in the afternoon. This analysis indicates that it is difficult to determine an effective policy implementation for NO_X or VOC controls to achieve ozone abatement around Asian megaticities where isoprene is a significant OH sink without accurate understanding of radical isoprene interactions (e.g. Kim et al. (2013b)).

Another unresolved uncertainty in understanding tropospheric OH is its chemical loss rates. The limited observations of OH reactivity in BVOC dominant environments show consistent unaccounted OH chemical loss with observational datasets (Di Carlo et al., 2004;Edwards et al., 2013;Kim et al., 2011;Lou et al., 2010;Nolscher et al., 2012;Nakashima et al., 2014;Sinha et al., 2010). Two different processes are speculated to cause unaccounted OH loss known as missing OH reactivity: 1) primary emissions of unmeasured or unknown compounds and 2) oxidation products of well-known BVOCs especially isoprene. Most studies conducted in coniferous forests where monoterpenes are dominant primary BVOC emissions have concluded that unmeasured or unknown

Saewung Kim 10/20/2014 8:29 AM
Deleted: evaluation

Saewung Kim 10/22/2014 9:26 AM
Deleted: different

Saewung Kim 10/22/2014 9:27 AM
Deleted: noticed

Saewung Kim 10/22/2014 9:27 AM
Formatted: Subscript

ABG 10/28/2014 8:23 AM
Deleted: in

ABG 10/28/2014 8:23 AM
Deleted: the

Saewung Kim 10/20/2014 9:49 AM
Deleted: clearly shows

ABG 10/28/2014 8:24 AM
Deleted: the accurateppropriate

ABG 10/28/2014 8:24 AM
Deleted: in

ABG 10/28/2014 8:25 AM
Deleted: accounts

ABG 10/28/2014 8:25 AM
Deleted: s

primary BVOC emissions caused missing OH reactivity (Sinha et al., 2010;Nakashima et al., 2014). On the other hand, studies conducted in isoprene dominant environments in mostly broadleaf or mixed forests have concluded that the main cause of missing OH reactivity is the oxidation products of isoprene (Edwards et al., 2013;Kim et al., 2011). Edwards et al. (2013) presented a thorough analysis on potential impacts of isoprene oxidation products that are not routinely constrained by observations. The authors found significant contributions from secondary oxidation products such as multi-functional oxygenated compounds.

Figure 6a shows the temporal variations of total OH reactivity calculated from five different model scenarios (I through V). The highest and the lowest OH reactivity levels were predicted from model calculations of Scenario V and Scenario II, respectively. This observation is directly correlated with calculated RO_2 levels as the lowest and highest RO_2 levels were calculated from Scenario II and Scenario V, respectively. Since VOC precursors and trace gases were all constrained by observations in the model calculations, the differences in model calculated OH reactivity should be mainly caused by the oxidation products of VOCs. This can be confirmed by the comparisons of model calculated formaldehyde concentrations from Scenario II and V as formaldehyde is a dominant oxidation product of isoprene (Figure 6b). The differences in formaldehyde levels suggest differences in OH reactivity levels from OVOCs in each model simulation. In summary, uncertainty in radical distributions especially RO_2 levels is directly propagated into uncertainty in OVOC formation.

These calculated results provide an upper limit of potential contributions from the oxidation products of the constrained VOC precursors considering that the box-model

Saewung Kim 10/20/2014 11:17 AM
Deleted:

ABG 10/28/2014 8:25 AM
Deleted: are

Saewung Kim 10/20/2014 11:18 AM
Deleted: s

Saewung Kim 10/20/2014 11:24 AM
Deleted:

does not consider dry-deposition processes as Karl et al. (2010) and Edwards et al. (2013) suggested that there is significant uncertainty associated with the parameterizations of dry deposition especially OVOCs. Still, this analysis suggests that significant missing OH reactivity (~ up to factor of two to three) can be found without constraining OVOCs. OVOCs, especially multi-functional highly oxidized compounds are precursors for secondary organic aerosols (VOCs). Therefore, uncertainty surrounding missing OH reactivity significantly undermines our ability to constrain SOA formation and aerosol growth.

4. Summary and conclusions

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

Six different model scenarios are employed to investigate the radical (OH, HO_2, and RO_2) distributions using the UWCM box-model. The observed trace gas data were constrained and the photochemical mechanisms (MCM 3.2) of seven VOC species with

Saewung Kim 10/20/2014 4:02 PM
Deleted: aged pollution

ABG 10/28/2014 8:26 AM
Deleted: to

Saewung Kim 10/20/2014 4:02 PM
Deleted: on

Saewung Kim 10/20/2014 4:02 PM
Deleted: and aerosol formation

high levels at the TRF were integrated. The uncertainty in isoprene peroxy radical chemistry results in a wider range of OH, HO_2, and RO_2 distributions. Unconstrained HONO sources also cause a quite high level of underestimation in a radical pool ($OH+HO_2+RO_2$). OH simulation from the different model scenarios indicates much larger discrepancies (up to three times) than simulations for HO_2 and RO_2 (up to twofold). OH is simulated in much higher levels with the consideration of an additional OH recycling channel from isoprene peroxy radical + HO_2 reactions and fast HPALD formation chemistry Peeters and Muller (2010). On the other hand, the RO_2 simulations result in lower levels as HPALD formation depletes the RO_2 pool, which mostly composed by isoprene peroxy radicals. These results suggest that HO_2 and RO_2 observations can provide pivotal information about radical recycling and isoprene peroxy radical chemistry (Kim et al., 2013c;Wolfe et al., 2013). More studies on characterizing existing techniques to quantify HO_2 (Fuchs et al., 2011) and developing new techniques (Horstjann et al., 2013) are needed. In addition, the simulations with recently developed isoprene photo-oxidation chemistry show that radical termination processes (e.g. peroxide formation) get more efficient than radical recycling processes in the afternoon. This may come as a surprise as in general we expect the high NO_X conditions in the suburban regions of a megacity to have effective radical recycling. However, the critical factor determining competing reaction channels of recycling and peroxide formation is NO concentrations. Ratios of NO to NO_2 are not only correlated with NO_2 concentrations and photolysis constants but also anti-correlated with RO_2, HO_2 and ozone concentrations and relevant kinetic constants as shown in (R7). Therefore, a semi-quantitative term such

Saewung Kim 10/20/2014 4:19 PM
Deleted: ice

Saewung Kim 10/20/2014 4:32 PM
Deleted: indicate contrary results

Saewung Kim 10/20/2014 4:44 PM
Deleted: 6

as the high ‘NO_X’ regime is not a proper term to define radical recycle regimes especially in high radical environments (e.g. HO_2 and RO_2) such as forest environments.

These uncertainties in estimating the radical pool size and distribution directly affect our ability for constraining photochemical ozone and OVOC production. The non-linear response of ozone production to NO_X and VOC abundances are determined by OH, HO_2, RO_2 and NO_2 concentrations. Regardless of which model calculation scenario we adapt, the TRF photochemical state appears to be a VOC limited ozone production regime. However, morning and afternoon show a very strong contrast. The morning conditions indicate a stronger degree of VOC limitation. In addition, a noticeable range of VOC sensitivity was calculated from the six different model scenarios, especially in the afternoon. These analysis results, therefore, suggest that an accurate scientific understanding of isoprene-OH interactions should form the basis for an effective policy implementation to reduce photochemical pollution in the suburbs of Seoul and similar East Asian megacities. In addition, OVOC production is predicted to significantly vary depending on the model simulation scenarios. The fate of these OVOCs is uncertain and can include deposition, photolysis, or condensation. Our limited understanding of OVOCs contributes substantially to the overall uncertainty in radical photochemistry and should be addressed by studies that quantify the processes controlling OVOC production and loss.

Acknowledgements

Saewung Kim 10/20/2014 4:56 PM
Deleted: with m

Saewung Kim 10/20/2014 4:56 PM
Deleted: having

ABG 10/28/2014 8:27 AM
Deleted: s

Saewung Kim 10/20/2014 5:17 PM
Deleted: strongly indicate that uncertainty in radical photochemistry subsequently resulting in uncertainty in radical concentration estimations directly propagates in policy-making processes in effectiveness of NO_X or VOC controls in ozone reduction

ABG 10/28/2014 8:28 AM
Deleted: the

ABG 10/28/2014 8:28 AM
Deleted: in

ABG 10/28/2014 8:29 AM
Deleted: be . preceded

ABG 10/28/2014 8:29 AM
Deleted: the

ABG 10/28/2014 8:29 AM
Deleted: on

ABG 10/28/2014 8:29 AM
Deleted: reduction

ABG 10/28/2014 8:30 AM
Deleted: y

ABG 10/28/2014 8:31 AM
Deleted: As t

ABG 10/28/2014 8:31 AM
Deleted: ,

ABG 10/28/2014 8:32 AM
Deleted: the implications of the uncertainty in

ABG 10/28/2014 8:33 AM
Deleted: production

ABG 10/28/2014 8:32 AM
Deleted: caused by

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

ABG 10/28/2014 8:34 AM
Deleted: s

References

Apel, E. C., Riemer, D. D., Hills, A., Baugh, W., Orlando, J., Faloona, I., Tan, D., Brune, W., Lamb, B., Westberg, H., Carroll, M. A., Thornberry, T., and Geron, C. D.: Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive, J Geophys Res-Atmos, 107, Artn 4034 Doi 10.1029/2000jd000225, 2002.

Archibald, A. T., Jenkin, M. E., and Shallcross, D. E.: An isoprene mechanism intercomparison, Atmos Environ, 44, 5356-5364, Doi 10.1016/J.Atmosenv.2009.09.016, 2010.

Arneth, A., Schurgers, G., Lathiere, J., Duhl, T., Beerling, D. J., Hewitt, C. N., Martin, M., and Guenther, A.: Global terrestrial isoprene emission models: sensitivity to variability in climate and vegetation, Atmos Chem Phys, 11, 8037-8052, Doi 10.5194/Acp-11-8037-2011, 2011.

Bao, H., Shrestha, K. L., Kondo, A., Kaga, A., and Inoue, Y.: Modeling the influence of biogenic volatile organic compound emissions on ozone concentration during summer season in the Kinki region of Japan, Atmos Environ, 44, 421-431, Doi 10.1016/J.Atmosenv.2009.10.021, 2010.

Barket, D. J., Hurst, J. M., Couch, T. L., Colorado, A., Shepson, P. B., Riemer, D. D., Hills, A. J., Apel, E. C., Hafer, R., Lamb, B. K., Westberg, H. H., Farmer, C. T., Stabenau, E. R., and Zika, R. G.: Intercomparison of automated methodologies for determination of ambient isoprene during the PROPHET 1998 summer campaign, J Geophys Res-Atmos, 106, 24301-24313, Doi 10.1029/2000jd900562, 2001.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-Transfer Reaction Mass Spectrometry, Chem Rev, 109, 861-896, 2009.

Bryan, A. M., Bertman, S. B., Carroll, M. A., Dusanter, S., Edwards, G. D., Forkel, R., Griffith, S., Guenther, A. B., Hansen, R. F., Helmig, D., Jobson, B. T., Keutsch, F. N., Lefer, B. L., Pressley, S. N., Shepson, P. B., Stevens, P. S., and Steiner, A. L.: In-canopy gas-phase chemistry during CABINEX 2009: sensitivity of a 1-D canopy model to vertical mixing and isoprene chemistry, Atmos Chem Phys, 12, 8829-8849, Doi 10.5194/Acp-12-8829-2012, 2012.

Chameides, W. L., Lindsay, R. W., Richardson, J., and Kiang, C. S.: The Role of Biogenic Hydrocarbons in Urban Photochemical Smog - Atlanta as a Case-Study, Science, 241, 1473-1475, 1988.

Chang, C. C., Wang, J. L., Leung, S.-C. C., Chang, C. Y., Lee, P.-J., Chew, C., Liao, W.-N., and Ou-Yang, C.-F.: Seosonal characteristics of biogenic and anthropogenic isoprene in tropical-subtropical urban environments, Atmos Environ, 99, 298-308, 2014.

Cheng, H. R., Guo, H., Saunders, S. M., Lam, S. H. M., Jiang, F., Wang, X. M., Simpson, I. J., Blake, D. R., Louie, P. K. K., and Wang, T. J.: Assessing photochemical ozone formation in the Pearl River Delta with a photochemical trajectory model, Atmos Environ, 44, 4199-4208, Doi 10.1016/J.Atmosenv.2010.07.019, 2010.

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

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

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

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

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

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

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

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

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

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

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

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

Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra, Atmos Chem Phys, 10, 1759-1771, 2010.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Nakashima, Y., Kato, S., Greenberg, J., Harley, P., Karl, T., Turnipseed, A., Apel, E., Guenther, A., Smith, J., and Kajii, Y.: Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign, Atmos Environ, 85, 1-8, Doi 10.1016/J.Atmosenv.2013.11.042, 2014.

NIER: Annual Report for Atmospheric Environment, National Insititute of Environmetal Rsearch, 2010.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Spaulding, R. S., Schade, G. W., Goldstein, A. H., and Charles, M. J.: Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources, J Geophys Res-Atmos, 108, Artn 4247
Doi 10.1029/2002jd002478, 2003.

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

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

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

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

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

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

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

Wolfe, G. M., Thornton, J. A., Bouvier-Brown, N. C., Goldstein, A. H., Park, J. H., Mckay, M., Matross, D. M., Mao, J., Brune, W. H., LaFranchi, B. W., Browne, E. C., Min, K. E., Wooldridge, P. J., Cohen, R. C., Crounse, J. D., Faloona, I. C., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Huisman, A., and Keutsch, F. N.: The Chemistry of Atmosphere-Forest Exchange (CAFE) Model - Part 2: Application to BEARPEX-2007 observations, Atmos Chem Phys, 11, 1269-1294, Doi 10.5194/Acp-11-1269-2011, 2011.

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

Wolfe, G. M., Cantrell, C., Kim, S., Mauldin, R., Karl, T., Harley, P., Turnipseed, A., Zheng, W., Flocke, F., Apel, E., Hornbrook, R. S., Hall, S., Ullmann, K., Henry, S. B., Digangi, J., Boyle, E. S., Kaser, L., Schnitzhofer, R., Hansel, A., Graus, M., Nakashima, Y., Kajii, Y., Guenther, A., and Keutsch, F.: Missing peroxy radical sources within a rural forest canopy, Atmospheric Chemistry and Physics Discussion, 13, 31713-31759, 2013.

Wong, K. W., Tsai, C., Lefer, B., Haman, C., Grossberg, N., Brune, W. H., Ren, X., Luke, W., and Stutz, J.: Daytime HONO vertical gradients during SHARP 2009 in Houston, TX, Atmos Chem Phys, 12, 635-652, Doi 10.5194/Acp-12-635-2012, 2012.

Xing, J., Wang, S. X., Jang, C., Zhu, Y., and Hao, J. M.: Nonlinear response of ozone to precursor emission changes in China: a modeling study using response surface methodology, Atmos Chem Phys, 11, 5027-5044, Doi 10.5194/Acp-11-5027-2011, 2011.

Yoshino, A., Nakashima, Y., Miyazaki, K., Kato, S., Suthawaree, J., Shimo, N., Matsunaga, S., Chatani, S., Apel, E., Greenberg, J., Guenther, A., Ueno, H., Sasaki, H., Hoshi, J., Yokota, H., Ishii, K., and Kajii, Y.: Air quality diagnosis from comprehensive observations of total OH reactivity and reactive trace species in urban central Tokyo, Atmos Environ, 49, 51-59, Doi 10.1016/J.Atmosenv.2011.12.029, 2012.

Zhang, Y., Hu, X. M., Leung, L. R., and Gustafson, W. I.: Impacts of regional climate change on biogenic emissions and air quality, J Geophys Res-Atmos, 113, Artn D18310
Doi 10.1029/2008jd009965, 2008a.

Zhang, Y. H., Su, H., Zhong, L. J., Cheng, Y. F., Zeng, L. M., Wang, X. S., Xiang, Y. R., Wang, J. L., Gao, D. F., Shao, M., Fan, S. J., and Liu, S. C.: Regional ozone pollution and observation-based approach for analyzing ozone-precursor relationship during the PRIDE-PRD2004 campaign, Atmos Environ, 42, 6203-6218, Doi 10.1016/J.Atmosenv.2008.05.002, 2008b.

Zhao, J., and Zhang, R. Y.: Proton transfer reaction rate constants between hydronium ion (H3O(+)) and volatile organic compounds, Atmos Environ, 38, 2177-2185, 2004.

Zhou, X. L., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nat Geosci, 4, 440-443, Doi 10.1038/Ngeo1164, 2011.

Table 1. Analytical characteristics of trace gas analyzers at TRF

Chemical Species	Manufacturer and Model Number	Uncertainty	Lower Limit of Detection
CO	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

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

a)

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

b)

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

*Composition is calculated based on the mixing ratio scale

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	[+]Crounse et al. (2011)	0	[-]All
Scenario IV	[#]Peeters and Muller (2010)	2.6	[-]All
Scenario V	[+]Crounse et al. (2011)	2.6	[-]All
Scenario VI	[#]Peeters and Muller (2010)	2.6	[-]All but HONO

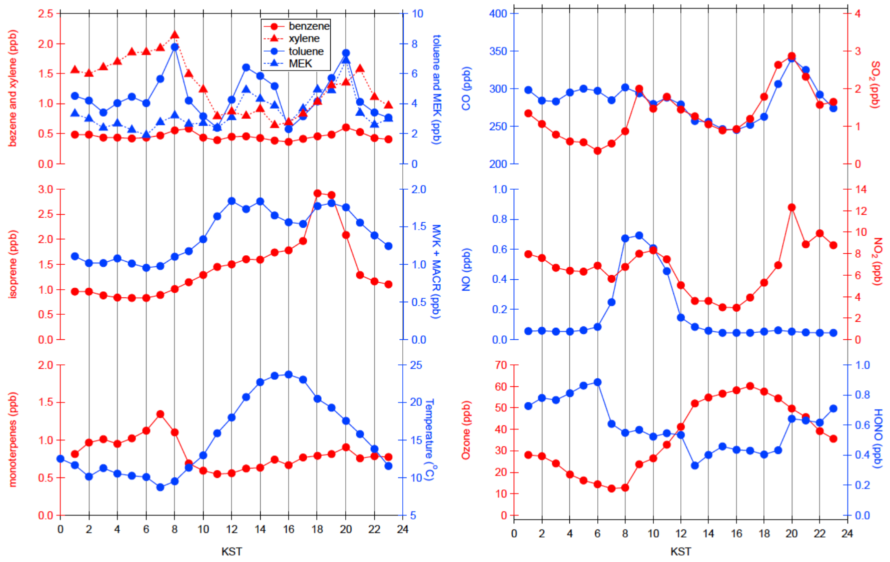
*α is an OH yield from reactions between an isoprene peroxy radical and HO_2, [#]k298 = ~ 0.08 for isoprene peroxy radical isomerization rate leading to produce HPALD, [+]k298 = 0.002 for isoprene peroxy radical isomerization rate, [-]All the observed diurnal variations, appeared in Figure 1 are constrained in the model along with ambient pressure and humidity.

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

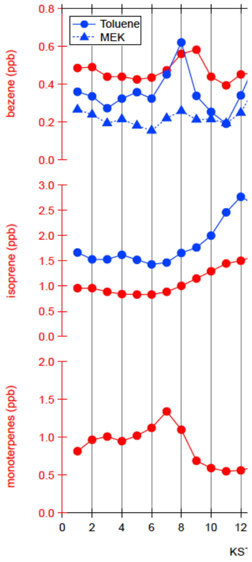
	OH		HO_2		RO_2		Constraints
Local Time	8:00-12:00	13:00-16:00	8:00-12:00	13:00-16:00	8:00-12:00	13:00-16:00	
Scenario I	3.85×10^6	3.08×10^6	4.10×10^8	7.02×10^8	3.65×10^8	1.14×10^9	All
Scenario II	3.99×10^6	3.69×10^6	3.99×10^8	7.86×10^8	3.51×10^8	9.62×10^8	All
Scenario III	3.86×10^6	3.13×10^6	4.09×10^8	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

unit: molecules cm^{-3}

Figure 1. Averaged temporal variations observed trace gases and ambient temperature at TRF (June 1st to June 6th, 2012, KST stands for Korean Standard Time GMT+9). The uncertainty for each observable is listed in the main text.



Saewung Kim 10/21/2014 9:40 AM

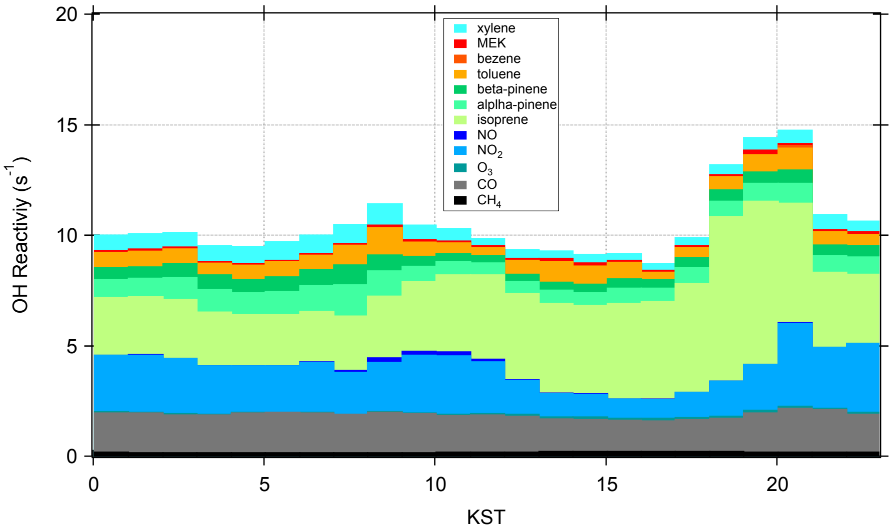


Deleted:

Unknown

Formatted: Font:(Default) Times New Roman

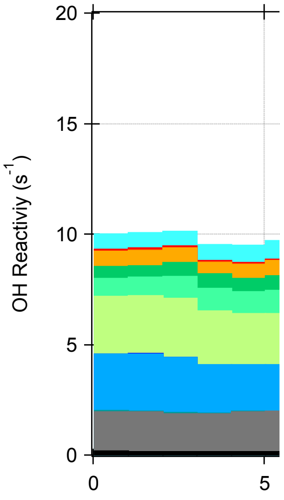
Figure 2. The temporal variations of OH reactivity calculated from the observed dataset at TRF (Figure 1).



Saewung Kim 10/22/2014 9:49 AM

Deleted: KST means Korean Standard Time (GMT+9).

Saewung Kim 10/21/2014 8:08 AM

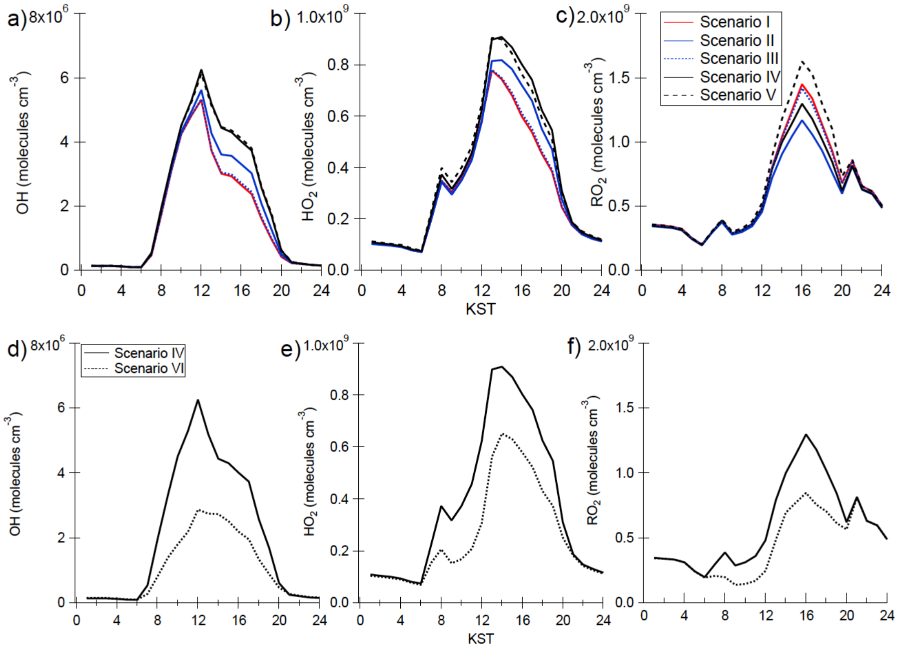


Deleted:

Unknown

Formatted: Font:(Default) Times New Roman

Figure 3. The temporal variations of OH (a) and d)), HO$_2$ (b) and e), and RO$_2$ (c) and f)) calculated by six different observationally constrained UWCM box model scenarios.



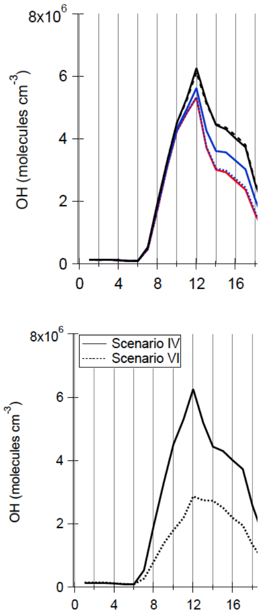
Saewung Kim 10/21/2014 8:29 AM

Formatted: Not Superscript/ Subscript

Saewung Kim 10/21/2014 8:30 AM

Deleted:

Saewung Kim 10/21/2014 8:24 AM



Deleted:

Unknown

Formatted: Font:(Default) Times New Roman

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

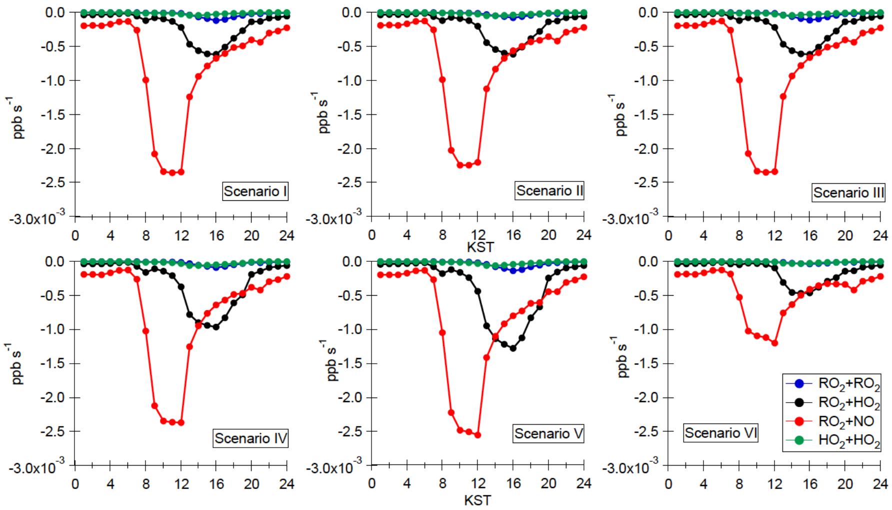


Figure 5. The temporal variations of P_{H2O2}/P_{HNO3} calculated from the UWCM box model from six different model scenarios

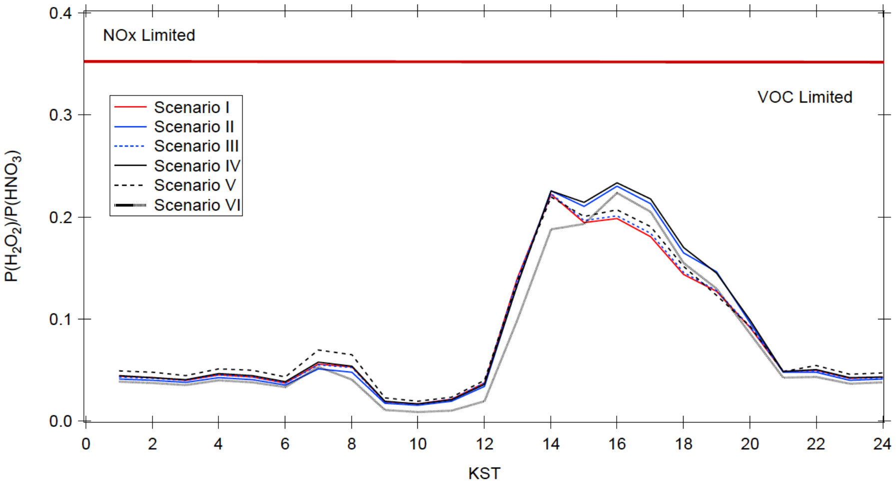


Figure 6. The temporal distributions of UWCM calculated OH reactivity (a) and formaldehyde (b)

Saewung Kim 10/21/2014 8:10 AM

Deleted: top panel

Saewung Kim 10/21/2014 8:10 AM

Deleted: bottom panel