

Interactive comment on “Urban-rural interactions in a South Korean forest: uncertainties in isoprene-OH interactions limit understanding of ozone and secondary organic aerosols production” by S. Kim et al.

Anonymous Referee #1

Received and published: 17 July 2014

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

C5041

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. 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!).

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.

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.

C5042

The introduction seems fairly comprehensive with regard to air chemistry findings, although 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). 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). 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. 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).

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?).

Results and discussion sections are merged (which should be indicated in the headlines) and are separated into observations and modeling (unfortunately not called modeling but 'implications of uncertainties in isoprene-hydroxyl radical interactions in

C5043

assessments of regional ozone and organic aerosol precursor production'). 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)? 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? 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 to use 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 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

C5044

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).

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.

Mentioned references

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

Brilli F., Gioli B., Zona D., Pallozzi E., Zenone T., Fratini G., Calfapietra C., Loreto F., Janssens I.A. & Ceulemans R. (2014) Simultaneous leaf- and ecosystem-level fluxes of volatile organic compounds from a poplar-based SRC plantation. *Agricultural and Forest Meteorology*, 187, 22-35.

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. & Steiner A.L. (2012) 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.

Fares S., Schnitzhofer R., Jiang X., Guenther A., Hansel A. & Loreto F. (2013) Observations of diurnal to weekly variations of monoterpene-dominated fluxes of volatile organic compounds from Mediterranean forests: implications for regional modeling.

C5045

Environmental Science & Technology, 47, 11073–11082

Guenther A. (2013a) Biological and Chemical Diversity of Biogenic Volatile Organic Emissions into the Atmosphere. *ISRN Atmospheric Sciences*, 2013, 1-27.

Guenther A. (2013b) Upscaling Biogenic Volatile Compound Emissions from Leaves to Landscapes. In: *Biology, Controls and Models of Tree Volatile Organic Compound Emissions* (eds Ü. Niinemets & R.K. Monson), pp. 391-414. Springer Netherlands.

Harrison S.P., Morfopoulos C., Srikanta Dani K.G., Prentice I.C., Arneth A., Atwell B.J., Barkley M.P., Leishman M.R., Loreto F., Medlyn B., Niinemets Ü., Possell M., Peñuelas J. & Wright I.J. (2013) Volatile isoprenoid emissions from plastid to planet. *New Phytologist*, 197, 49-57.

Kim S.-Y., Jiang X., Lee M., Turnipseed A., Guenther A., Kim J.-C., Lee S.-J. & Kim S. (2013) Impact of biogenic volatile organic compounds on ozone production at the Taehwa Research Forest near Seoul, South Korea. *Atmospheric Environment*, 70, 447-453.

Llusia J., Peñuelas J., Seco R. & Filella I. (2012) Seasonal changes in the daily emission rates of terpenes by *Quercus ilex* and the atmospheric concentrations of terpenes in the natural park of Montseny, NE Spain. *Journal of Atmospheric Chemistry*, 69, 215-230.

Lu K.D., Rohrer F., Holland F., Fuchs H., Bohn B., Brauers T., Chang C.C., Häsel R., Hu M., Kita K., Kondo Y., Li X., Lou S.R., Nehr S., Shao M., Zeng L.M., Wahner A., Zhang H. & Hofzumahaus A. (2012) 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.

McPherson E.G., Simpson J.R., Xiao Q. & Wu C. (2011) Million trees Los Angeles canopy cover and benefit assessment. *Landscape and Urban Planning*, 99, 40-50.

Nakashima Y., Kato S., Greenberg J., Harley P., Karl T., Turnipseed A., Apel E., Guen-

C5046

ther A., Smith J. & Kajii Y. (2014) Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign. *Atmospheric Environment*, 85, 1-8.

Nölscher A.C., Bourtsoukidis E., Bonn B., Kesselmeier J., Lelieveld J. & Williams J. (2013) Seasonal measurements of total OH reactivity emission rates from Norway spruce in 2011. *Biogeosciences*, 10, 4241-4257.

Nölscher 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., Vilà-Guerau de Arellano J. & Lelieveld J. (2012) Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010. *Atmos. Chem. Phys.*, 12, 8257-8270.

Pincetl S., Gillespie T., Pataki D.E., Saatchi S. & Saphores J.-D. (2013) Urban tree planting programs, function or fashion? Los Angeles and urban tree planting campaigns. *GeoJournal*, 78, 475-493.

Préndez M., Carvajal V., Corada K., Morales J., Alarcón F. & Peralta H. (2013) Biogenic volatile organic compounds from the urban forest of the Metropolitan Region, Chile. *Environmental Pollution*, 183, 143-150.

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. & Chen L.L. (2011) VOC reactivity and its effect on ozone production during the HaChi summer campaign. *Atmos. Chem. Phys.*, 11, 4657-4667.

Sartelet K.N., Couvidat F., Seigneur C. & Roustan Y. (2012) Impact of biogenic emissions on air quality over Europe and North America. *Atmospheric Environment*, 53, 131-141.

Situ S., Guenther A., Wang X., Jiang X., Turnipseed A., Wu Z., Bai J. & Wang X. (2013) Impacts of seasonal and regional variability in biogenic VOC emissions on surface

C5047

ozone in the Pearl River delta region, China. *Atmos. Chem. Phys.*, 13, 11803-11817.

Spaulding R.S., Schade G.W., Goldstein A.H. & Charles M.J. (2003) Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources. *Journal of Geophysical Research-Atmospheres*, 108, doi:10.1029/2002JD002478.

Williams J.E., van Velthoven P.F.J. & Brenninkmeijer C.A.M. (2013) Quantifying the uncertainty in simulating global tropospheric composition due to the variability in global emission estimates of Biogenic Volatile Organic Compounds. *Atmos.Chem.Phys.*, 13, 2857-2891.

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

Wolfe G.M., Thornton J.A., McKay M. & Goldstein A.H. (2011) Forest-atmosphere exchange of ozone: sensitivity to very reactive biogenic VOC emissions and implications for in-canopy photochemistry. *Atmos.Chem.Phys.*, 11, 7875-7891.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 16691, 2014.

C5048