Atmos. Chem. Phys. Discuss., 15, C5668–C5677, 2015
www.atmos-chem-phys-discuss.net/15/C5668/2015/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Spatiotemporal variations of air pollutants (O_3, NO_2, SO_2, CO, PM_{10}, and VOCs) with land-use types" *by* J.-M. Yoo et al.

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Received and published: 5 August 2015

We appreciate the reviewers' comments for improving our manuscript. Our response to the comments is given below. All responses refer to the revised version. Response to Referee #3 Q1) Generally, the current manuscript is not well organized and not concisely written, which makes it hard to read. For instance, in section 2 'Data and Method', the authors referred to Figures 7 and 8 (Page 16994) and discussed the land-use types (Page 16996). These explanation and discussion related to results should not be included in section2.

A1) The corresponding phrase was revised in the New Version (Line 207).

Q2) Lots of sentences in the current manuscript are not concise, for example, in Page

16999 Line 17-18), I don't think the authors need to list all the air pollutants investigated in Flemming et al. and Meng et al.

A2) The list of air pollutants in the two references was deleted (New Version; Lines 367-368, 333, 531, 884).

Q3) Examples of not concise writing include: in Page 17009 Line 14, listing the unit of NO2 is not necessary; explanation about the instruments in section 2 is good but it contains too many details.

A3) The unit was deleted. In section 2, one sentence and two phrases were removed (New Version; Lines 215-223, 641).

Q4) There are so many places are redundant or repeat presenting same information. Especially in the conclusion part (section 8), the authors just list all the results discussed in previous chapters.

A4) Redundant parts were removed in the text. The conclusion was revised by reducing 20-25 % of the previous part. Please see New Version (Conclusion of section 9, Lines 157, 164, 165, 199, 333, 367-368, 486, 531, 553, 559, 708, 884).

Q5) It lacks emphasizing the major significance of this paper and does not discuss the possible uncertainty/error introduced in this analysis. In summary, careful revision of the manuscript is suggested to make it more concise and focused on the scientific contribution of this study.

A5) Uncertainty of the measurement instrument for each pollutant is shown In Table A1 (NIER, 2010). The uncertainties for the CO and SO2 are relatively large compared to other pollutants (O3, NO2, PM10, and VOCs). For the uncertainty, the values of standard deviation have been shown in the pollutant average calculation in Tables 5-6, 9-11, and Fig. 9. The 95 % confidence intervals which have been calculated by the bootstrap method (Wilks, 1995) are also shown in the trend analysis of the pollutant time series. Based on the statistics of the above uncertainties, we think that overall the results of this study are significant and reliable. The pollutant data except VOCs had been utilized in the previous 'Washout' study of Yoo et al. (2014). The uncertainty of the measuring instrument for each pollutant has been included in the New Version (Lines 231-237, 1069-1071). Please see A4 about the careful revision.

Table A1. Minimum requirement for the accuracy of the pollutant measuring instruments (NIER, 2010).

Pollutant Accuracy O3 $\leq$ 0.005 ppm CO $\leq$ 0.5 ppm NO2 $\leq$ 0.005 ppm SO2 $\leq$ 0.005 ppm PM10 $\leq$ 2% of measuring range VOC Within $\pm$ 20% of true value Q6) The authors used two spatial resolutions of grids, 0.1 D and 0.25 D. However, after reading section 2, I still do not understand how these 283 site data are averaged into the 0.25 and 0.1 degree grids. Do the grids cover the whole South Korea and data are grouped into each grid? I also find one grid could be attributed to multiple land-use type, e.g. in Figure 5 areas near Seoul have been attributed to R, C, and I. How the data are processed? Also for readers who are not familiar with South Korea, it is hard to tell if the grids are urban, suburban, or rural, as well as the locations of major cities such as Seoul, Daegu, and Busan. Therefore, one map showing the raw AVHRR or MODIS land-use data and locations of the major cities is suggested. Another question is, after using 0.25 and 0.1 gridded data, what conclusion the author achieved? What are the pros/cons for each method? I found the current manuscript used both of them simultaneous and discuss the difference, but have any conclusions have been drawn? Overall, since the land-use types gridded are so important, I suggest the author add a separate section discussing this important part.

A6) We provided one additional map showing the satellite data and the major cities (Fig. 1f). Figure 1e has been revised to identify the VOC sites (New Version, Figs. 1e-f, Lines 190-191). In this study we rearranged the non-gridded pollutant data on the two spatial grids ($0.1^\circ \times 0.1^\circ$ and $0.25^\circ \times 0.25^\circ$) to examine urban characteristics of the gridded land-use type data due to the non-uniform distribution of the pollution monitoring stations. The pollutants, except for VOCs, were investigated as time-averaged in the

two spatial grids after categorizing the 283 station data in the four land-use types. The stations are mostly located in the urban areas with a very sparse distribution in the rural areas (Fig. 1). The higher spatial resolution of the $0.1^\circ \times 0.1^\circ$ grid generally tends to represent the characteristics of large urban cities better than in suburban regions, when they were compared to those of coarser resolution (i.e., $0.25^\circ \times 0.25^\circ$). For example, the more urbanized stations over the SMA contribute more to the number of the high resolution grid than that of the low resolution grid. In other words, since the number of stations are larger in the big cities (i.e., more urban features) than in the small cities (i.e., fewer urban features), the higher resolution grid displays more in the former cities than in the latter. Although this tendency is also shown in the lower resolution grids, the weighting effect of the big city characteristics is more substantial in the $0.1^\circ \times 0.1^\circ$ grid than in the $0.25^\circ \times 0.25^\circ$ grid. Because of the difference in the numbers of stations in each grid, the grid numbers that returned the valid grid-averages of observations at the $0.1^\circ \times 0.1^\circ$ and $0.25^\circ \times 0.25^\circ$ resolutions with respect to the non-gridded 283 stations were reduced to 196 (R; 89, C; 42, I; 32, G; 33) for the $0.1^\circ \times 0.1^\circ$ and 146 (R; 59, C; 30, I; 25, G; 32) for the $0.25^\circ \times 0.25^\circ$ resolutions, respectively. Different land-use type data (e.g., two residential and three greenbelt stations) can coexist in a given grid. In this case, the pollution data in the grid have been utilized for the arithmetic average calculation for the residential and greenbelt types, respectively. The choice of either $0.1^\circ \times 0.1^\circ$ or $0.25^\circ \times 0.25^\circ$ grid boxes as an optimal spatial grid scale represents a compromise based on keeping the intrinsic spatial variability of the pollutants (O3, CO, NO2, SO2 and PM10) of interest, namely their concentrations, at comparable levels and still having large enough total sample size, i.e. the number of grid boxes with the pollutant data, for a robust computation. The variability has been examined in terms of some dimensionless measure (i.e., the ratio of standard deviation (σ) to mean (X ÌĚ); Yoo et al., 2014) in the climatological annual average distribution of the pollutants. The σ/X ÌĚ values for the five air pollutants at the two different types of grids range from 15.0 % to 45.0 %. Since the σ/X ÌĚ values at a $0.1^\circ \times 0.1^\circ$ grid are 16.3-44.0 %, they are within the range (15.0-44.9 %) at a $0.25^\circ \times 0.25^\circ$ grid (Table A2). As suggested by Referee #3, a separate section (i.e., section 3) was added to the text in order to address the grid issue (New Version; section 3, Lines 169-170, 273-305).

Table A2. Values (%) of intrinsic spatial variability for pollutant concentrations at the two spatial grids of 0.1o x 0.1o and 0.25o x 0.25o, respectively, in terms of σ/X ÌĚ. Here the values of mean (X ÌĚ) and standard deviation (σ) for the pollutant variables can be obtained from the annual average distribution. σ/X ÌĚ (%) at a 0.1o x 0.1o grid σ/X ÌĚ (%) at a 0.25o x 0.25o grid O3 23.5 24.3 CO 22.4 22.2 NO2 44.0 44.9 SO2 36.6 34.9 PM10 16.3 15.0

Q7) Data presented in this study are very comprehensive, and show the regional nature and trends of air pollution in South Korea. However, the current manuscript doesn't discuss the possible influence from the changing world in the past decade. For instance, can the change of Asian summer monsoon influence the summertime ozone pollution? How are the effects of land-use change on air pollution? Has any member from monitoring sites, 0.1 or 0.25 girds been influenced by the recent expanded urbanization? For instance, how the Seoul or SMA expanded in the past decade, did the land-use types of sites in or near SMA change from G to R/C? The revised manuscript should take them into account and discuss their potential impacts.

A7) In the text, Fig. 3 shows the interannual variations in the MODIS-derived land-cover types (%) versus the MEK four land-use types from 2002 to 2012. The interannual variations in the MODIS land-covers with respect to the MEK types were not significant during that time period. It is reasonable that MODIS 'forest/wood' covers were the greatest (37.2%) in the MEK 'greenbelt' type (Fig. 3a). In the MEK 'residence' type, the MODIS 'forest/wood' cover was slightly increased, but the 'grass/shrub' cover had decreased (Fig. 3a-b). The MODIS 'urban/build-up' was at a minimum (16.4%) in the MEK 'greenbelt' and at a maximum (32.2%) in the 'commerce' (Fig. 3c and Table 4). Considering the time series of the MODIS-derived land-covers of 'forest/wood' and 'urban/build-up', the urbanization over South Korea is not significant, probably due to the government control in the recent decade. Please see New Version (Lines 258-265).

Yes, we agree with your point about Asian summer monsoon. We think that the change of convective rain and typhoons during the monsoon can affect the summertime ozone pollution. According to Yoo et al. (2014, AE, 82, 226-237), the rainfall washout on the pollutants has been estimated in the order: PM10 > SO2 > NO2 > CO > O3. The surface O3 concentration tends to be rather enhanced by vertical mixing associated with the convection leading to the downward O3 transport from lower stratosphere/upper troposphere (see also Martin, 1984; Jain et al., 2005). This convective activity seems to be more effective than the reduction of O3 due to the direct washout (New Version; Lines 898-900).

Detailed Remarks/Suggestions for Revision: Q8) Page 16988 Line 14: As discussed above, details such as 'for NOx' are not necessary. Using 'Kim et al. 2011' is suggested. Also 'Wang et al. 2013' does not discuss the transport of air pollutants from China, please consider using the following two papers as references:

A8) The two references of Zhang et al. (2009) and Wang et al. (2003) were removed, while the papers of Li et al. (2010) and He et al. (2012) were cited (New Version; Lines 55-56, 983-986, and 1041-1043).

Q9) Page 16994 Line 19: Why Figure 7 & 8 were introduced before Figure 2-6? This section should only describe the dataset and method used in this study, so I don't think Figures that are discussed later should be mentioned here.

A9) Corrected. Please see A1.

Q10) Page 16992 Line 10-12: As discussed in the general comments, please provide detailed information about how to create these grids.

A10) Please see A6.

Q11) Page 17000 Line 3: As discussed above, please provide a map of South Korea showing the major cities. Line 23-30: It is hard for me to comprehend the Table 6 and 7. For instance, in line 24, it states 'Table 6 shows the magnitude order : : :'. What is the definition of 'magnitude order'? Also I didn't see any information about the order. Does Table 6 accidently have the content of Table 7? Please re-write these sentences. Line 18: The production of O3 is through 'photochemical reactions'

A11) Yes, that's right. Please see A6 for the map question. Thank you for your comments for the captions of Tables 6-7. The captions were not clear. The caption of Table 6 was switched with the caption of Table 7. The word 'photolysis' was replaced by 'photochemical reactions'. The captions of Tables 6-7 were revised. (New Version; Figs. 1e-f, captions of Tables 6-7, and Line 395)

Q12) Page 17003: Line 9-10: The high concentrations of NO2 could also be caused by shallow PBL and slow photolysis rate. Line 20-22: Due to faster photochemical reactions in summer, the atmospheric lifetimes of SO2 and NO2 are substantially shorter. So if the transport from China dominates, it could be as important as summer Asian monsoon. Further discussion is suggested here. Line 26-27: As discussed in the general comments, this sentence described the different characteristics of 0.1 and 0.25 degree grids. It should be emphasized in the conclusion part.

A12) Further discussion for the photolysis and lifetime was included in the text by citing an additional reference (Levy II et al., 1999). The sentence which related with the grid characteristics was moved into the conclusion (New Version; Lines 479-481, 870-872, 1038-1040).

Q13) Page 17008 Line 23-26: It is hard to comprehend, especially 'Seoul was defined as part of the SMA' while you have 3 regions with/without the capital city. I found Figure 9b has this information, so it should be mentioned here.

A13) The sentence has been revised in the text to clarify (New Version; Lines 624-625). The SMA is composed of i) Seoul and ii) SMA except for Seoul.

Q14) Page 17010: Line 2-3: The 'residence' areas should also be close to main and secondary roads. Why all the regions next to roads are attributed to 'commerce' in this

study? Line 20: Same questions as above, 'residence' areas should have lots of traffic emissions, so how can all the areas close to roads are grouped to 'commerce'. I am confused, and further explanation/discussion is expected.

A14) We agree with the reviewer. Although we are using the area names similar in Kuttler and Strassburger (1999), please note that the area in our study may not be exactly same as them. We have compared the land use classification by MEK with the satellite-observed land cover. The sentence has been revised by adding the phrase of 'particularly in the urban area (e.g., the SMA)' to the text. Please see New Version (Line 658).

Q15) Page 17012 Line 25-25: What could be the cause? Any possible explanation? Is Seokmo downwind of major sources? A map showing these monitoring sites as well as major cities is suggested.

A15) The contrast in O3 between the two sites (Seokmo and Simgok) is explained by NOx titration. The high O3 in Seokmo (greenbelt) also has found from a previous study. We have stated in the manuscript that "According to the study of Seo et al. (2014), larger NOx emissions over the metropolitan cities (e.g., the Simgok commerce) in the short-term and seasonality showed lower O3 minima because of NOx titration and a nocturnal NOy chemical process. They also reported that the higher O3 levels near the Seokmo greenbelt (i.e., Ganghwa) were induced due to lower NOx emissions and the regional O3 influxes from both the Yellow Sea (and China) and the SMA.". We provided one additional map showing the satellite data and the major cities (Fig. 1f). Figure 1e has also been revised to identify the VOC sites. Please see New Version (Lines 738-743, Figs. 1e-f).

Q16) Page 17016 Line 4-7: The authors cited the studies in South California to discuss the 'VOCs-limiting' photochemistry intensively in this manuscript. Based on VOCs concentrations presented in Figure 10 (VOCs in G is much lower than VOCs in R/I/C), VOC measurements only focus on the traces of anthropogenic VOC emissions such as benzene, and toluene. However, at least in the G areas biogenic VOCs emissions such as isoprene could dominate. Are there any measurements or previous studies confirming that the anthropogenic VOCs suppress the influences from biogenic sources in South Korea as the study in Southern California of late 1990's? i.e., do South Korea and South California have the similar ozone photochemistry.

A16) In our study, a total of 56 VOC species were identified and quantified using a combination of the on-line thermal desorption system (Unity/Air Server, Markes) and the GC/Deans switch/Dual FID system (Varian3800 GC, USA). These VOC compounds could be grouped into alkyne (1), aromatic (16), olefin (10), and paraffin (29) groups (Nguyen et al., 2009). They are emitted from both anthropogenic and biogenic sources. Although identification of sources of these compounds is very complicated due to complex chemical and photochemical processes, some of them are produced mainly by biogenic sources (isoprene) and others are anthropogenic (benzene, toluene, ethylbenzene, and ortho-, meta-, and para-xylenes). Lower VOCs in greenbelt areas than other land cover types in Fig. 10 indicate a weak contribution of the anthropogenic VOCs in greenbelt areas. Therefore the competing role between biogenic- and anthropogenic sources highly depends on the locations and conditions. A previous study has concluded that anthropogenic VOCs have greatly increases in VOC pollution at a monitoring station in Seoul in 2004 (Nguyen et al., 2009). On the other hand, biogenic VOCs sometimes play an important role on ozone formation (Kim et al., 2013b). Please see New Version (Lines 840-843).

Q17) Page 17017 Line 15: The current conclusion part only re-listed all the results, and some of the materials are redundant. Rewriting (focusing on the scientific contribution of this study) is suggested. Also adding discussion of the possible uncertainty of this analysis is necessary.

A17) Please see A4 and A5.

Please also note the supplement to this comment:

http://www.atmos-chem-phys-discuss.net/15/C5668/2015/acpd-15-C5668-2015-supplement.zip

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 16985, 2015.