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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of ozone and its precursors in Beijing during summertime: impact of urban plumes on ozone pollution in downwind rural areas" *by* J. Xu et al.

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Responses to the referee's comments Referee 1# General Comment: The manuscript Measurements of ozone and its precursors in Beijing during summer time: Impact of urban plumes on ozone pollution in downwind rural areas by Xu et al present a ïňĄeld measurement on ozone and its precursors in 4 sequential sites in Beijing city, to investigate the effects of transportation and local chemistry in ozone concentrations. The experimental design is very interesting, and could be valuable for the proposed research goal. However, the current manuscript could not provide convincing evidence for the relative importance of regional transportation and local production in observed

ozone levels. I would recommend a major revision before the MS could be accepted for publication. Authors: Thanks a lot for the referee's comments. We have made major revisions as suggested by the referee. In particular, we give an estimate of the LOH and OFP of CO and related discussions in the revised manuscript. Our multiple analyses including air mass types and correlations of O3 with CO and photochemical age have indicated the effect of transport on observed ozone levels at the rural site SDZ. The relative importance of regional transportation and local production, as proposed by the referee, is really an interesting topic, and will be quantified in our future modeling work.

SpeciïňĄc comments: (1) The referee: I wonder why the author use the current title suggesting the importance of transport, in fact, from the data evaluation, e.g. the correlation between ozone and chemical aging, it seems to me that the local chemistry might be more relevant. Authors: Note that our measurements were carried out not only at the urban sites, but also at a rural site (SDZ), both of which belong to the Beijing Municipality. Our data analysis shows that that the local chemistry might be more relevant in the urban area and the transportation of urban pollution might have a large impact on the photochemisty in the rural area. Considering that the latter is the main issue addressed in this paper, we would like to still use the current title in the revised manuscript.

(2) The referee: The author provide very high levels of biogenic VOCs, namely isoprene, a-pinene and b-pinene, due to their high reactivity, the actually contribution could be much higher to ozone formation (because these species were largely consumed after being emitted into air); and secondly, their chemistry in ozone formation will be very local. I suggest the authors to do more detailed evaluation for these species. Authors: We have taken biogenic VOCs as one of four VOC groups in the attribution of LOH and OFP (see Fig. 5 and Fig. 6 in the revised manuscript) with related discussions including sources of biogenic VOCs in the urban areas (see Section 3.2 of the revised manuscript).

(3)The referee: I doubt the use of the ratio between benzene and toluene for source

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identiïňĄcation. The ratio could be very different from current source measurements, and also the ratio will change due to aging processes, I think it would not be appropriate when long-range transport was considered. Authors: We have removed this part in the revised manuscript. (4)The referee: The LOH and OFP analysis did not provide support for the relative importance of transport and local chemistry, and this section uses mainly well known method, I would suggest largely shorten this discussion, and pay more attention to evaluate the role of transport and local production. Authors: We have revised this section substantially (see "3.2 NMHC reactivity and ozone formation potential"). In particular, we give an estimate of the LOH and OFP of CO with related discussions in the revised manuscript. Although the method is well known, the mixing ratios of CO and NHMHs, which are needed to calculate the LOH and OFP, are unique and obtained by our measurements. Comparisons of LOH and OFP between the BL (urban) and SDZ (rural) sites have provided valuable information on the photochemical characteristics in both urban and rural areas of Beijing. Relative higher percentage contributions of CO to LOH and OFP and higher correlation between O3 and CO at SDZ than at BL may indicate an importance role of transport in ozone production in the rural area.

Referee 2# General Comment: This paper presents the measurements of ozone and its precursors at four stations in Beijing area, which are in line along the regional transport route of air pollutants. The air quality impacts of ozone transported from urban to the downwind rural areas have been investigated in several megacities, e.g., Mexico City. Nevertheless, ïňĄeld measurement data from a network in Beijing is still rather limited. Given the unique features of ozone precursors in Beijing, this paper is still helpful to improving our understandings of the transport and chemistry of ozone in a megacity. Authors: Thanks a lot for the referee's comments. We have made revisions according to the referee's specific comments, which are very helpful for us to improve the manuscript.

SpeciïňĄc Comment: (1) The referee: It was indicated, and actually hypothesized,

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that the concentration and composition of ozone precursors were different in urban and downwind rural areas. However, the results (as shown in Figure 4) show that the compositions of NMHCs were rather similar at the BL and SDZ sites in spite of the substantially lower HC levels observed at SDZ. While some differences were actually indicated in the text and Table 3, it seems very confusing on the characteristics of O3 precursors at the two sites. Authors: It is true that the percentage contributions of aromatics, alkanes and alkenes to the total NMHCs are rather similar at the BL and SDZ sites. As suggested by the referee, we estimated the LOH and OFP of CO. As shown in Fig. 6 of the revised manuscript, the percentage contributions from CO and biogenic NMHCs to the total OFP are about twice greater at SDZ than at BL. In addition, the contributions of individual NMHC species to the total LOH and OFP are quite different at the two sites (Fig. 7). Moreover, the NOx level is rather lower at SDZ than at BL (see Table 2, Fig.8 and Fig. 9). These indicate different chemical characteristics of O3 precursors at the two sites.

(2) The referee: The mixing ratio of isoprene at BL was signiïňĄcantly higher than at SDZ, 13.36 vs. 2.79 ppbv. The authors suggested that the anthropogenic sources of isoprene were negligible in Beijing. In this context, the lower isoprene level observed at the rural site, SDZ, needs to be explained. Authors: In this study, isoprene shows negative and poor correlation with CO, however, it shows good correlation with temperature. It means isoprene is mostly biogenic rather than anthropogenic in summer in Beijing. Deciduous trees, which are often used to decorate the urban roads, and holly coniferous trees, which are common in most of the urban parks, can release substantial amounts of isoprene and monoterpenes into urban atmosphere in Beijing, respectively (Wang et al., 2003). The SDZ site is surrounded mainly by crops and fruit trees with much less emissions of isoprene and monoterpenes. Therefore, higher biogenic VOCs were observed at BL than at SDZ. We have added the discussions above into Section 3.2 in the revised manuscript.

(3) The referee: CO was used as an indicator of polluted air mass in this study. In

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addition to that, CO (and CH4) is also an important precursor of O3, in particular in a highly polluted area like Beijing. I suggest adding CO and CH4 into the calculation of OFP (Table 3) and make some discussion upon this point. Authors: Thank the referee for constructive comments. As mentioned above, we have added CO into the calculation of LOH and OFP and given related discussions in the revised manuscript. We have also added the CO emission strength for each county and distinct in Beijing into Fig. 1. The importance of CO in the ozone production at the rural site is also highlighted in the "summary and conclusions". We have no measurement of CH4 at our sites. The source profile of CH4 is rather different from NOx and CO, the latter originating mainly from fossil fuel usage and biomass burning. Therefore, we do not consider CH4 when calculating the LOH and OFP.

(4) The referee: The ratios of HCs with different lifetimes were used to infer the photochemical ages of air masses. Such an analysis should be made along the transport of an air parcel or for a stagnant air mass. The current analysis shows different HC ratios at BL and SDZ, respectively, but seems ignoring the differences in the emission proïňĄles at the two locations. Will this result in any bias in the analysis of O3 formation/transport? Given that the samples were collected along the transport route, it could be useful to analyze the data in the context of upwind/downwind relationship. Authors: The difference in HC ratios at BL and SDZ can be attributed to both the age of air masses and the differences in the emission profiles at the two locations. It should be noted that we focus on the changes in O3 as a function of the HC ratio at the same site, either BL or SDZ, as shown in Fig. 12. In this case, the effect of emission profiles can be neglected. It is a good idea to analyze the data in the context of upwind/downwind relationship. However, at present we do not have sufficient data to perform such analysis. Maybe we can continue such investigation in the next field experiment.

Technical Suggestion: (1) The referee: The unit of radiation in Figure 2 could be in error. Authors: We have corrected this.

(2) The referee: The resolution in Figure 3 is not enough. It's rather hard to see the

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differences among the data from respective stations. Authors: The resolution in Figure 3 and some other figures has been increased.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C9453/2011/acpd-11-C9453-2011-supplement.pdf

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