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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Theoretical implication of reversals of the ozone weekend effect systematically observed in Japan" *by* A. Kannari and T. Ohara

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(Reviewer Comment, RC) The paper proposes an interpretation of the reversals in the "ozone weekend effect"(called here OWE) depending on distance from city centre, meteorology and VOC reactivity. It proposes an analysis of a large measurement dataset as well as a model restitution of this phenomenon. In terms of understanding of ozone formation, but also as a preliminary step for the establishement of emission control policies, this constitutes a relevant issue for atmospheric chemistry, and for this journal. The observation of the OWE (change in the mean ozone value between sunday and weekdays) and its reversal (the sunday/weekday ratio above or below 1) are

deeply investigated here. In particular, the osbervation of the weekend effect versus the ozone percentile rank is very interesting and brings a quantitative view of the importance of this effect and its variability around the value of 1 close to large urban areas. This is why publication is recommended. Then, this phenomenon is discussed with an advection reaction model, first by the mean of isopleth diagrams, then by the lagrangianãĂĂsimulation of the evolution of air masses leaving the city at different times. In this part, it is much less clear what is the new information brought by this study to the atmospheric chemistry and pollution research field. Many things should be mentioned, cleared or detailed. Also, the text is not always easy to read. This is why major revisions are recommended. The following remarks are presented here so as to guide the authors to enhance their paper in view of publication.

(RC) At the end of part2, it is mentioned that many works have been conducted on the spatial reversal of the OWE, and mainly its dependance on meteorology. The authors should make clear here what is their contribution then : an application to a specific area? a first new quantification of this phenomenon (distance to city centre, intensity of the reversal...)? A more detailed investigation of this phenomenon? New links to ozone percentiles? In this version of the manuscript, it is not sure whether this study brings or not fundamental elements to the understanding of this phenomenon. And the structure of the paper becomes confuse, as we don't know what is important in the results.

(Author Comment, AC) We would like to note that the definition of OWE is "increases in ozone concentration on the weekend despite decreases in the concentrations of both precursors". Also, we did not say that "many works have been conducted on the spatial reversal of the OWE". Although there are many works on the OWE, there are not very many on the reversal of the OWE. Moreover, the studies cited in our manuscript reported only fragmentary results on the spatial reversal of the OWE or its reversal in response to changes in the meteorological conditions. Our study is the first to report systematic reversals of the OWE in relation to both distance from the source and changes in meteorological conditions. Our findings were obtained with the use

of our original methodology, which is based on comparisons between weekdays and weekends at every ozone percentile rank interval in relation to changes in the ozone chemistry. We will describe these facts in the revised manuscript.

(RC)The presentation of the isopleth diagram and the visualization they provide of the reversal in the OWE is too long. Isopleth diagrams are well known and the authors should inferr more rapidly what kind of new quantitative information these diagrams bring to the understanding of pollution events in this (or in such an) area. Only qualitative information is given here, on the fact that a different reduction in VOC and NOx can bring "point B" in a NOx-limited regime. This is somehow expected and new information would be to quantify this phenomenon in terms of intensity, location of the reversal, or to interpret it in terms of geographical ozone control by emissions around the urban area.

(AC) The aim of the advection-reaction model is to explain the reversals of the OWE by changes in the ozone formation regime. It is well known that the ozone formation regime in an air mass changes from a VOC-limited to an NOx-limited regime during transport on a Lagrangian basis, and the regime boundary on an ozone isopleth diagram at a specific time depends only on the initial VOC/NOx ratio (“similarity theory”) (e.g., Sillman, 1999). However, in order to explain the mechanism of the observed systematic spatial reversal of the OWE with regard to the ozone daily maximum concentration (O3max), it was necessary for us to confirm that the chemical regime affecting O3max changes with distance from the source in a Eulerian framework, and, further, that the regime boundary for O3max also depends only on the initial VOC/NOx ratio, similarly to chemical regime changes viewed with a Lagrangian perspective. We believe that these findings are not self-evident and that they must be proved by a new approach and scientific considerations. We will revise Sect. 3.2 to explain the relation between the Lagrangian basis chemical regimes and the Eulerian basis O3max chemical regimes, as well as common similarity of the regime boundary determined by the initial VOC/NOx ratio.

(RC) Part 3.4 brings quantitative information on the link between percentile of ozone and distance of the reversal. However, this part is a little confuse (which sentences refer to model, to measurements...?) and the tables and figures are not fully described, the values and results from the tables and figures are not discussed, and only final conclusions - thus, difficult to follow - are drawn. In particular, the complex Figure 10 should be described before it is interpretated.

(AC) Both Table 2 and Fig. 10 are based on the advection-reaction model simulations. We will revise Table 2 as shown below. For example, for the case of an initial VOC/NOx ratio of 11.3 (representative Sunday value), an NOx-limited regime is attained within D $\sim$ 5 h under the 95–100 percentile rank meteorology. However, a normalized distance D $\sim$ 8 h is required for the regime to become NOx-limited under the 75–80 percentile rank meteorology. Further, under the 65–70 percentile rank meteorology, an NOx-limited regime cannot be attained within a single day because the solar intensity is too low. In Fig. 10, the relation between the percentile rank and the reversal distance of the OWE was obtained by simulations using the initial weekday and Sunday concentrations shown by points A and B in Fig. 8. Increases in the reversal distance D under less suitable meteorological conditions clearly explain the mechanism of the observed systematic changes in relation to the percentile rank, shown in Figs. 2 and 3. The regime boundary shown in Fig. 10 indicates the VOC/NOx ratio at the regime boundary for each reversal distance between points A and B (see Fig. 8b). At each percentile rank, the boundary is located at a point that divides a line connecting A and B into two segments with a ratio of roughly 8:2. We will revise Sect. 3.4 in accordance with these comments.

(RC) The same remarks can be made for part 4. A long time is spent in the explanation of the ozone formation regimes which is well-known, and could be shortened, especially because only general ideas about regimes and only few examples are presented (case ot ETH, FORM...) and no general tendency is presented and discussed, except at the end of 4.1. In this last part, many values are given, but the only conclusion is

that many parameters (VOC reactivity, solar intensity...) play on the chemical regime, which is too general.

(AC) 1. We will shorten Sect. 4.1 as much as possible. However, for logical explanation in this section, a brief explanation of the regime change in ozone daily maximum concentrations on a Eulerian basis (as mentioned above) is necessary here. 2. The important result in the simulation using the CBIV chemical mechanism is that photochemically highly reactive species such as ISOP and OLE have a lower regime boundary. 3. We don't agree with the reviewer's comment that the last paragraph in Sect. 4.1 is 'too general'. The paragraph describes the minimum regime boundary attainable within a single day and its dependency on the source size. For example, we can estimate that the attainable minimum regime boundary changes from 7.7 to 8.4 for sources of size L = 0 and 4 h, respectively, under the 95–100 percentile meteorology. This means that an air mass released from a large source (L = 4 h) with an initial VOC/NOx of less than 8.4 cannot reach an NOx-limited regime within a single day, whereas an air mass released from a small source requires less time to reach an NOx-limited regime. We think that these results are new findings.

(RC) In the same way, the conclusion of Part 4.2 could be discussed within the scope of effective emission control, and not only general comments should be made ("release time (...) is earlier in the day for more remote points compared with points closer to the source"). Especially because this part is untitled "Applicability to the real world".

(AC) The purpose of Sect. 4.2 is to qualitatively consider factors that could not be introduced to the model, from the viewpoint of ascertaining whether a simple advection-reaction model is applicable to the real world. Therefore, we think that the description in this section is inevitably general to some extent, but we will add the following sentence, "For example, emission controls implemented before 9 LT in the urban area would effectively reduce high O3 concentrations in rural areas where O3max occurs after 15 LT ." to the last paragraph.

(PC) Part 4.3 finally brings some interesting quantitative elements, as the mean distance from the source of the regime transition depending on locations. But the mention that "the above inference is made for specified meteorological conditions and a specified initial VOC/NOx ratio" prevents from using this information. Can authors provide any idea of the representativity of this result? If it is meaningless, then the paragraph is meaningless.

(AC) The sentence, "the above inference is made for specified meteorological conditions and a specified initial VOC/NOx ratio" means that the transition point from a VOC-limited chemistry to an NOx-limited chemistry is essentially and systematically influenced by meteorological conditions and the initial VOC/NOx ratio, as shown in Table 4. We believe that "the location of the regime boundary of O3max formation in an urban plume released from a source with VOC/NOx $\sim$ 10.5 is about 30 km from the source under the 98th percentile rank meteorology" is important and meaningful information necessary for understanding the regime transition in the TMA. We will revise the related sentences to make them easier to understand.

(RC) If the authors can make clearer their contribution and highlight their results in the frame of ozone formation and emission control, but also better support the representativity of the model studies and results, then the work should be published. Before, major revisions are proposed.

(AC) On the basis of our comments above and the probable comments of other anonymous referees, we will endeavor to revise our manuscript. We acknowledge the comments of anonymous referee #1.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12927, 2009.

Draft revised Table 2 Comparison of the boundary VOC/NOx ratio (ppbC/ppb) on ozone isopleths obtained by the advection-reaction model under different ozone formation conditions.

Normalized distance D (h)	Boundary VOC/NOx calculated for various ozone percentile rank meteorological conditions in the TMA				Release time [a] (LT)	Arrival time [a] $(LT)_a$
	65–70	75–80	85–90	95–100	(95–100 percentile rank) [b]	
2	54.0	43.0	35.5	30.6	11.0	13.0 ± 0.0
3	33.4	26.4	21.8	18.8	10.4	13.4 ± 0.1
4	23.2	18.6	15.5	13.6	9.9	13.9 ± 0.1
5	18.4	15.0	12.5	11.1	9.3	14.3 ± 0.1
6	15.8	12.9	11.0	9.7	8.8	14.8 ± 0.1
7	14.4	11.8	10.0	8.9	8.3	15.3 ± 0.2
8	13.5	11.1	9.4	8.4	7.8	15.8 ± 0.2
9	13.0	10.7	9.0	8.0	7.3	16.3 ± 0.2
10	12.6	10.4	8.8	7.9	7.0	17.0 ± 0.1

*a Mean release and arrival times (± SD) of the air mass bringing O_{3max} to the regime boundary.
*b Release and arrival times under the meteorological conditions for the other percentile rank intervals of O_{3max} are similar to those for the 95–100 percentile rank interval, except when D > 9 h.

Fig. 1.