Atmos. Chem. Phys. Discuss., 10, C2083–C2089, 2010
www.atmos-chem-phys-discuss.net/10/C2083/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone reservoir layers in a coastal environment – a case study in Southern Taiwan" *by* C.-H. Lin et al.

C.-H. Lin et al.

chlin@mail.fy.edu.tw

Received and published: 25 April 2010

The authors would like to thank the reviewer for the valuable suggestions. We have addressed all the concerns raised.

1.General comment:

This study is done based on the tethersonde measurements. Findings are interesting and worthy to be published. Some suggestions are listed below to make the paper more readable.

Response: All suggestions proposed by the reviewer have been adopted and we believe that these suggestions have clearly improved the quality of our work.

2.Specific comments:

Comment 1: (a) If the measurement site is at coast, will there be an ozone reservoir layer? (b) Also, if the measurement site is located downwind of those major emission plumes, will there be an ozone reservoir layer? (c) Further, if the prevailing wind is strong, from surface up to the top of the boundary layer, will there be an ozone reservoir layer? Clearly, all these matter. A discussion on these possibilities is necessary when describing the experimental design and the selection of the study site.

Response 1: Clearly, the coastal ozone reservoir layers observed at the study site are formed by the invasion of cooler, marine air masses into the inland warm, ozone-rich mixing layer. Accordingly, the coastal ozone reservoir layers are expected to have particular characteristics. The ozone reservoir layer can form at any coastal place where a cooler, marine air mass invades a warm, inland ozone-rich mixing layer. Therefore, the coastal ozone reservoir layer is expected to form over a considerably large coastal region and parallel to the coastline. This region may begin at some distance from the coastline in the sea-land direction and end at the line of penetration of the sea breeze.

(a) In a near-coast area, no ozone reservoir layer is expected to form, because a marine air mass may arrive in the area so early that the area does not have enough time to develop a deep, convective mixing layer unless the sea breeze develops late.

(b) An ozone reservoir layer is expected to form even at a site downwind of a coastal emission area, because the invasion of a marine air mass will not be influenced by the existence of the emission area. However, in this case, the arriving marine air mass can mix with abundant ozone precursors that are emitted from the emission area. Additional ozone can be produced within the arriving marine air mass. Therefore, the ozone concentration in the arriving marine air mass can exceed the marine background level. If a marine air mass is mixed with a large amount of NO and the site is very close to the emission area, then the ozone concentration in the arriving marine air mass is expected to be lower than the marine background level owing to the titration of ozone by NO.

(c) Finally, when the prevailing wind is strong, no sea breeze will develop. Therefore, the invasion will not occur. Consequently, the formation of an ozone reservoir layer is not expected.

The above discussions are now included in our revised manuscript.

Comment 2: (a) The assumption of ozone coming downward from the ozone reservoir layer to contribute on the build-up of ozone concentration next-day is interesting. However, as the wind observation data indicates a significant land-sea breeze happening locally. The horizontal extent of the ozone reservoir layer has to be identified to support such assumption. The air is not stagnant or only moving upward or downward. The trajectory plot in Fig. 9 supports this point. (b) By the way, how these trajectories are plotted. There is no spatially-dense measurement data to allow such calculation.

Response 2: (a) Our observations of the ozone reservoir layers do support that the horizontal dimensions of the reservoir layers are large. The followings are our explanations. On the four experimental days, the atmosphere was not stagnant but associated with light, northerly ambient flow and sea-land breeze circulations (Fig. 6). Daily formed ozone reservoir layers were, therefore, expected to move and follow those flows. Daily, from the late afternoon to the mid-morning hours of the next day, a period of more than 16 hours, the observed ozone reservoir layers were expected to move for a considerable distance. However, during this period on each of the four experimental days, ozone reservoir layers were continuously observed at the study site (Fig. 6), suggesting that the horizontal dimensions of the ozone reservoir layers were large.

(b) The trajectory is plotted based on the wind field which uses the surface winds at the air stations shown in Fig. 1 and the vertical sounding data of this experiment. The method to calculate the wind field and the trajectory is else where (Lin et al., 2002; Lin et al., 2004).

The above discussions are now included in our revised manuscript.

Comment 3: How reliable is the calculation given in Fig. 11, after following Eq. 4-9? It should be expressed in a statistical manner. The equations do not consider the effects of horizontal and vertical transport and diffusion, but taking the mixing of upper and lower layers as the major dynamic process. The complexity of the local circulation has been simplified in Eq. 4-9. Discussion on the uncertainty and possible errors embedded is needed.

Response 3: The uncertainties associated with the calculation of the concentration of the old ozone, the ozone carried over from the preceding day, and the new ozone, the ozone generated on the current day, are given in the followings.

(a) The uncertainties associated with the calculation of the old ozone concentration are mostly caused by neglecting the horizontal transport and net chemical production terms in the original, governing Eq. (1). Apparently, the horizontal transport term in Eq. (1) has only a small effect when the wind is light and/or the horizontal gradient of the old ozone concentration is small, or when the transport term is smaller than the other terms. Light winds within the mixing layers were found from sunrise to noon on the four experimental days (Fig. 6). The net entrainment term was also expected to dominate the overall variation of the old ozone concentration in the late morning hours. Therefore, neglecting the horizontal transport term in Eq. (1) in this study was expected to have only a small effect in the morning hours.

The observed ozone reservoirs were expected to have a large horizontal dimension (see our responses to comment 2). The horizontal gradient of the old ozone concentration was small when the study site was under the moving ozone reservoir layers. The arrival of relatively clean marine air masses at the study site in the late afternoon daily probably indicates that the edges of the ozone reservoir layers at the seaward side had probably just passed over. Therefore, neglecting the horizontal transport term may generate relatively large uncertainties after the arrival of the marine air masses at the study site, typically late in the afternoons.

The net chemical production above the mixing layer should be trivial owing to the lack of reactive species there. When the old ozone came into contact with newly emitted species, such as NO and VOCs, within the mixing layers, the old ozone may have been depleted and NO2 and some peroxide radicals produced in. However, the produced NO2 and peroxide radicals are expected to have reproduced new ozone in a short period, as described by NRC (1991). The chemical production and loss rates were, therefore, roughly the same for the old ozone, indicating that neglecting the net chemical production for the old ozone is acceptable.

(b) The hourly concentration of the new ozone is estimated simply by subtracting the hourly estimated concentration of the old ozone from the total ozone concentration. Actually, all processes that are likely to affect the hourly variations of the new ozone concentration as indicated in Eq. (1) are implicitly accounted for when this subtracting method is used. Therefore, the uncertainties associated with the estimated concentration of the new ozone are only related the uncertainties associated the estimation of the concentration of the old ozone. Relatively large uncertainties associated with the calculation of the new ozone concentration may appear in the late afternoon because in this period the uncertainties associated with the calculation of the old ozone concentration become large as mentioned above. The above discussions are now included in our revised manuscript.

Comment 4: The plot in Fig. 10 is useful. Some caution is needed. Sea breeze happening in the evening is questionable. From Fig. 6a, it stops around sunset. Also, a relative sense of magnitude is needed. Otherwise, the comparison of Fig. c with respect to Figs. a,b will lead to a misconception that the ozone level in the early morning is the highest in one day. Same consideration is needed for U and PT.

Response 4: We have made suitable modification about the original Fig. 10. The evolution of the coastal ozone reservoir layer are now stated at the developing stage,

fully-developed stage, and descending stage. The new Fig. 10 and their explanation are given in the attached figure.

Comment 5: The description of events and related figures can be shortened to make the paper much more concise, while discussions suggested above can be elaborated.

Response 5: We have carefully checked our manuscript again and made some suitable modification in our revised manuscript. Discussion is extended to include the suggestions raised by the reviewer. Additionally, grammatical and writing-style errors in the original version have been corrected by our colleague, who is a native English speaker.

Reference

Lin, C.-H., and Chang, L.-F. W.: Relative source contribution analysis using an air trajectory statistical approach. J. Geophys. Res., 107, 4583-4592, 2002.

Lin, C.-H, Wu, Y.-L., Lai, C.-H., Lin, P.-H., Lai, H.-C., and Lin, P.-L.: Experimental investigation of ozone accumulation overnight during a wintertime ozone episode in south Taiwan, Atmos. Environ., 38, 4267-4278, 2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1719, 2010.

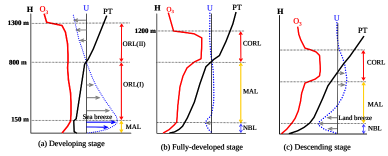

Figure 10. General evolution of vertical ozone distribution (O_3), wind (U) and potential temperature (PT) at various stages of the ozone reservoir layer. In the developing stage (a), a cooler, marine air mass arrives at the study site and an ozone reservoir layer forms at altitudes of 150-1300 m by the invasion of the marine air mass into a warmer, ozone-rich mixing layer. In this stage, the air layer below 150 m, MAL, is filled with marine air. The lower part of the ozone reservoir layer at 150-800 m, ORL(I), is a sea-breeze-like layer. However, it is filled with air masses that originate over land. The upper part of the ozone reservoir layer at 800-1300 m, ORL(II), is a return-flow layer that is filled with air masses that originated inland. The fully-developed stage is associated with the stopping of sea-breeze circulation by midnight when (b) a concentrated, elevated ozone reservoir layer, CORL, forms at 800-1200 m, and is filled with air masses that originated inland. The air layer in the previous ORL(I) is now filled with recently-arrived, less polluted marine air masses, MAL. Additionally, a stable nocturnal boundary layer (NBL) is formed by surface cooling. The descending stage is from midnight to the following morning (c). A land-breeze circulation is fully developed. The CORL gradually descends and the previous MAR becomes shallow owing to nocturnal subsidence.

Fig. 1. Fig. 10