H14-92

STUDY OF OZONE SENSITIVITY TO PRECURSORS AT HIGH SPATIAL RESOLUTION USING THE CMAQ-ADJOINT MODEL

H. Dang[1], A. Hakami[2], J.J. Sloan[1]

[1]University Of Waterloo, Department of Earth and Environmental Science, Waterloo, Canada
[2] Carleton University, Department of Civil and Environmental Engineering, Ottawa, Canada.

Abstract: We apply the adjoint of the Community Multiscale Air Quality model (CMAQ-ADJ) in a high spatial resolution study of the sensitivity of ozone to several of its precursors in two selected regions of the Province of Ontario, Canada. For this study, we modified a version of CMAQ-ADJ (Hakami *et al*. 2007) that was developed for low spatial resolution. The modifications included eliminating restrictions on the synchronization time-steps of CMAQ and CMAQ-ADJ, eliminating an advection problem and improving the meteorology interface. We used the modified CMAQ-ADJ to analyse the sensitivity of ozone to precursor species for cases of high ozone levels that led to non-attainment of Provincial standards in the two selected regions. The studies examined the upwind influences of ozone, NO_X, anthropogenic VOCs and isoprene for the three days immediately preceding the non-attainment event.

Key words: *Chemical transport model, CMAQ-Adjoint, Ozone precursor, Sensitivity analysis* **.**

INTRODUCTION

Adjoint methods have been used for data assimilation in meteorological modelling and numerical weather forecasting for more than two decades, but their use in chemical transport models (CTMs) is much more recent. For the case of CMAQ, the basis for the adjoint approach (Sandhu *et al*. 2005) and the development of the first gas phase adjoint code, CMAQ-ADJ, (Hakami *et al*.2007) occurred within the last few years and now the first applications of CMAQ-ADJ are beginning to appear (Resler, *et al*. 2008; Gou, *et al*. 2009). Here we report an application of CMAQ-ADJ in which we determine the sensitivity of ozone to its precursors during a non-attainment event that occurred in Ontario in 2007.

The sensitivities of selected species (usually pollutants) to their precursors and to meteorological conditions were among the first applications of regional chemical transport modelling. This was motivated by the need to identify and regulate the emissions of precursors that caused unacceptable levels of atmospheric pollutants at sensitive receptor locations. Early approaches to this problem involved perturbing selected emissions and observing the effects using forward CTM calculations. This "brute force" approach is useful to assess domain-wide effects of selected emissions, but it is inefficient for finding the most important influences on a selected receptor, because it is often unclear whether the most important emissions have been selected and also it uses significant computational resources to produce information for locations that are not of interest. The Direct Decoupled Method (DDM) (Dunker, A.M. 1984; Dunker, A.M. *et al*. 2002) is a more efficient and elegant way to find sensitivities using forward calculations, but it also relies on selection of the most important sources, which is sometimes difficult.

In contrast to the determination of sensitivities by means of direct forward calculations, the adjoint approach uses a backward (in time) calculation. It determines the sensitivity of a cost function defined at a selected time and target receptor location to the model parameters at previous times. In the simplest implementation, the cost function is the pollutant concentration at the target receptor. The concentration is perturbed at the selected time and the perturbation is propagated backward in time and space using the gradients of the cost function with respect to changes in the model state at earlier times. In this way, the adjoint procedure determines the sensitivity of the selected pollutant to precursors released at earlier times at any location in the model domain. The adjoint approach also very efficient; a single integration of the adjoint model backward in time yields the sensitivity of the selected pollutant to the spatial and temporal distributions of all species defined in the chemical mechanism included in the adjoint model. The same advantages can also be exploited in 4-D Var data assimilation (Zhang *et al*. 2008).

For the present application, we modified the CMAQ-ADJ code reported in (Hakami *et al*. 2007) as described earlier and used it to analyse the sensitivity of ozone to precursor species and pre-existing ozone in two selected regions of south-central Ontario during two three-day periods immediately preceding the occurrence of high ozone levels that exceeded Provincial standards. The results show the dependence of the ozone sensitivities on time and distance for each of the precursors and ofr the meteorology.

FORWARD MODEL CALCULATIONS

This study was intended primarily to be a demonstration of CMAQ-ADJ, so simple and well-tested model components and emission inventories were used. A forward calculation was carried out to create concentration fields for all species. This used CMAQ v4.5, which was driven by offline meteorology generated by the MM5 v3.6 Mesoscale Meteorology Model. The 1995 and 2001 Canadian and US emission inventories were used with SMOKE v2.3.2 to create emissions. Two nested domains were used. The outer domain, had western and eastern boundaries at 135^{o}W (in the Pacific Ocean) and 60^{o}W (in the Atlantic Ocean) and northern and southern boundaries at 47^{o}N (in James Bay) and 20^{o}N (in Mexico). The inner domain is shown in Figure 1. This Figure also shows the surface ozone mixing ratio predicted by the forward calculation for 18 July at 16:00H local time and the two target areas (enclosed by black dashed lines) selected for the sensitivity calculations. The southerly target area (denoted W-T) includes Windsor/Detroit and Toronto/Hamilton; the northerly one (called T-O) includes Toronto/Hamilton and Ottawa urban areas.

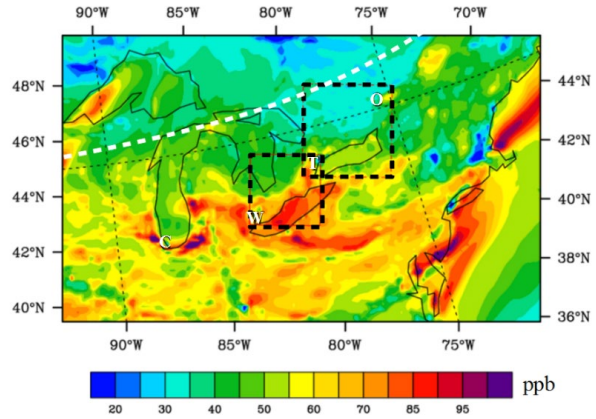

Figure 1: Model domain showing O_3 mixing ratio during the test period and target areas for sensitivity calculations. C: Chicago; W: Windsor/Detroit; T: Toronto/Hamilton; O: Ottawa

A total of 9 days were calculated for this study: a 3-day spin-up period from 13-15 July and two 3-day test periods from 16-18 and 19-21 July. The test periods coincided with a period of high ozone mixing ratios that exceeded the Province of Ontario's 1-hour Ambient Air Quality Criterion of 80 ppb at several locations. The high ozone episode developed over a period of several days, reaching a maximum in the W-T target area towards the end of the first test period. Thereafter, during the second test period, strong north-westerly winds swept the pollutants out of both target areas. When considering the sensitivity results, it is important to note that the part of the domain above and to the left of the dashed white line has low population density, significant forest cover and VOC/NO_X ratios mostly greater than 15, whereas the part below it has higher population density and non-urban areas that are mostly agricultural. The VOC/NO_X ratio in the lower part falls to values between 8 and 4 over large regions during a significant part of the diurnal cycle. Thus, roughly speaking, ozone creation in the upper left part is NO_X limited, while in the lower right, it is VOC limited.

The forward calculation reproduced the observed ozone fields reasonably well, despite the relatively old emissions inventories. Regression of the modelled *vs.* observed ozone levels showed R^2 values exceeding 0.6 in most parts of the domain. Meteorology during the 13-15 July period was influenced first by a high pressure region in the lower part of the domain and thereafter by a strong low pressure trough that passed through the upper part of the domain, drawing air northward. After the passage of this trough there was a period of weak high pressure and relatively lower winds throughout the domain and high levels of ozone developed in the target regions. During this time, the effects of lake breezes originating in the lower Great Lakes were evident in the diurnal circulation.

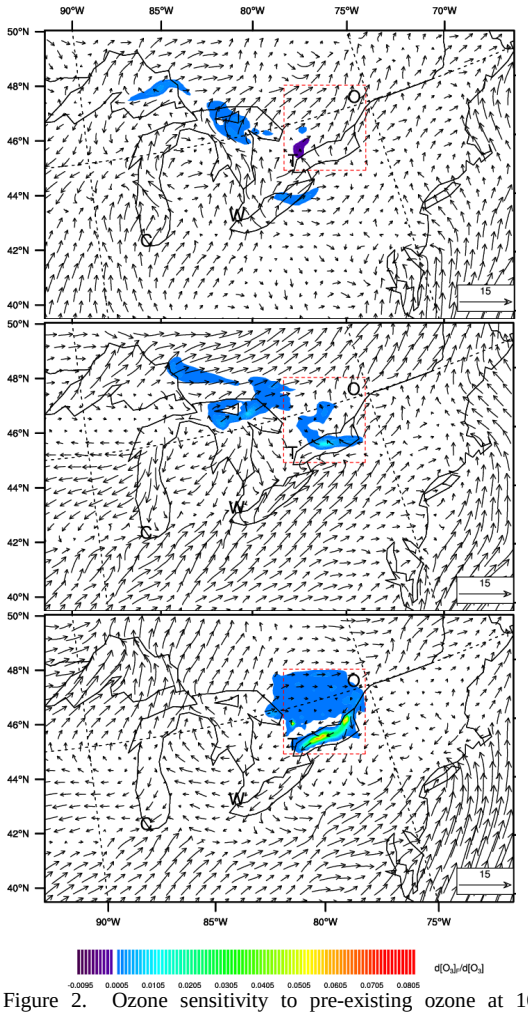

Figure 2. Ozone sensitivity to pre-existing ozone at 16 July;20:00h, 17 July;13:00h and 18 July;16:00h

ADJOINT CALCULATIONS

We used the results of the forward calculations in the adjoint study to determine the ozone sensitivities in the two target areas. The adjoint model was run for each of the two three-day periods and each of the target areas. In the following, we will discuss the results for the 16-18 July period only, since this gave more information about the sensitivities of the ozone to chemical precursors than the second period.

The adjoint approach to determining sensitivities requires that the mixing ratio of the selected chemical species in the target area be perturbed and the perturbation be traced backward in time through the use of the adjoint. The perturbation for each target area was done as follows: starting with the results of the forward calculation, the mixing ratio of the ozone in the target area was increased to 100 ppb, then the original ozone mixing ratios obtained in the forward calculation were subtracted at every grid cell in the domain. The resulting ozone mixing ratios, which were zero everywhere in the domain except in the target area, were used as input to the modified CMAQ-ADJ code. The reverse calculation was then carried out for three days and the sensitivities of ozone to each of the precursors were recorded at each hour preceding the time of the perturbation. To confirm that the result is not dependent on the size of the perturbation, the same procedure was carried out with a different perturbation level (40 ppb) and the result was found to be independent of this parameter.

Ozone Sensitivity

Figure 2 shows the sensitivity of ozone in the T-O target area to ozone in the rest of the domain at three selected times before the perturbation. (All times are local.) This sensitivity includes everything that affects the final ozone mixing ratio during its advection to the target area. The three panels from top to bottom show the ozone sensitivities on 16 July;20:00h, 17 July;13:00h and 18 July;16:00h . These are respectively -44 hours, -27 hours and -5 hours from the time of the perturbation, which was at 16:00h on 18 July. Evident in the top panel is an area of negative sensitivity,

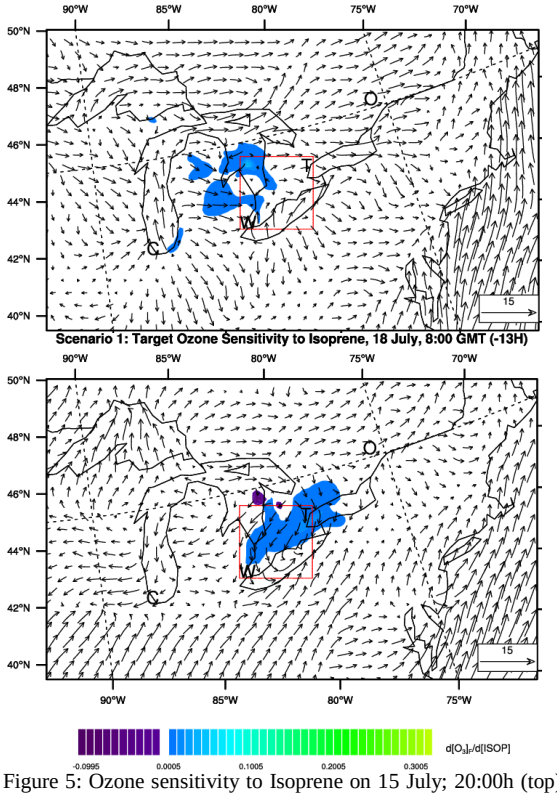

Figure 5: Ozone sensitivity to Isoprene on 15 July; 20:00h (top) and on 17 July at 03:00h (bottom) in the W-T target area

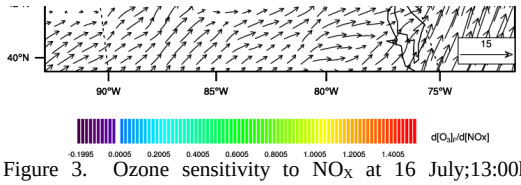

Figure 3. Ozone sensitivity to NO_X at 16 July;13:00h, 17 July;12:00h and 18 July;11:00h in the W-T target area

those to which the sensitivity is quite complicated. Of course, all sensitivities in a given example are dominated by the meteorology and emissions extant during that case. As a result, the sensitivities share a number of characteristics, such as transport pathways and chemical environment (*e.g.* the NO_X-limited conditions in the upper left part of the domain). Some of these points are exemplified by Figure 4, which shows the sensitivity of the ozone in the W-T area to CO. While CO is not normally associated with ozone sensitivity studies, it does have an effect on ozone, primarily through its reaction with OH to produce HO_2, followed by the reaction of the latter with NO, creating NO_2. Additionally, it is long-lived, so the sensitivity of the final ozone mixing ratio in the target area does not have the strong diurnal variation that is characteristic of the initial OH reaction. Emphasizing these points, the top panel of Figure 4 shows that the final ozone mixing ratio is sensitive to CO that is emitted at the earliest time examined by the adjoint calculation, which is on 15 July; 20:00h (-69 hours). This sensitivity persists throughout the study period, but is higher during the day, when the OH concentration is higher, as shown in the lower panel of Figure 4, which gives the target ozone sensitivity to CO on 17 July at 11:00h local time.

The sensitivity to isoprene is more complex. Isoprene is a significant natural source of ozone due to its daytime reaction with OH, which can add to the two double bonds, which indicates that the final ozone mixing ratio in the target area is decreased by a net removal of the ozone in the Toronto-Hamilton area. This area of negative sensitivity persists from the end of the reverse calculation at 19:00h on 16 July (-67 hours) to 01:00h on 17 July (-39 hours). It can be ascribed to the overnight titration of ozone in the Toronto-Hamilton area. Similar overnight reductions in ozone occur near all large urban areas. This case is evident because its effects are felt by the ozone in the T-O target area at the time of the perturbation. The lowest panel of Figure 2 shows the effect of Lake Ontario, which consists of a significant positive sensitivity coefficient due to reduced ozone deposition on the lake. This effect, which can also be detected in the middle panel, begins to become pronounced at Lake Ontario about 23:00 on 17 July when the north-westerly circulation brings the ozone-containing air parcels to the edge of the lake. Thereafter, there is an increasingly positive sensitivity in the area of the lake as the ozone mixing ratio increases more rapidly there than over the land surface.

NO_X Sensitivity

The sensitivity of ozone in the W-T target area to NO_X is shown in Figure 3. The three panels (from top to bottom) show the results at 16 July;13:00h (-51 hours), 17 July;12:00h (-28 hours) and 18 July;11:00h (-5 hours). These illustrate the fact that the greatest sensitivity of ozone in the target area to NO_X is in the upper part of the domain. This has two causes: the prevailing winds bring the air parcels through this region early in the test period and the ozone formation in this region is strongly NO_X limited. These results also show that the ozone sensitivities to NO_X are higher above large bodies of water (Lake Huron and Georgian Bay). This is consistent with the low solubility of ozone; the ozone produced in these locations is not removed by deposition and thus contributes disproportionately to the final ozone mixing ratio in the target region.

Other Sensitivities

Using the adjoint technique, the sensitivity of ozone in the target area to all relevant precursors can be examined, including

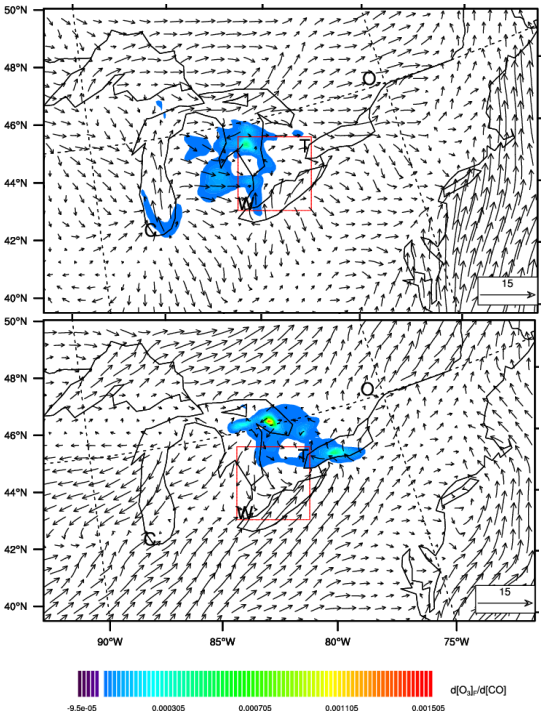

Figure 4. Ozone sensitivity to CO on 15 July; 20:00h (top) and 17 July; 11:00h (bottom) in the W-T target area

producing four different radical adducts. In the presence of NO, each of these creates an NO_2 molecule, which creates photochemical ozone. In the absence of sunlight, however, isoprene reacts with O_3 and although the rate constant is seven orders of magnitude slower than that of the OH reaction, the O_3-isoprene reaction removes ozone at night. Unlike the CO case, in which the ozone sensitivity varies from positive to zero during the diurnal cycle, the isoprene reaction directly reduces the ozone mixing ratio in the absence of sunlight. Thus we expect that in low NO_X regions (where formation of organic nitrates do not complicate the result), the sensitivity of ozone to isoprene will be positive during sunlit periods but can be negative for forested regions where high isoprene levels deplete ozone during the night. The adjoint study shows one example of this, which is illustrated in Figure 5. The top panel shows the expected (positive) ozone sensitivity on 15 July; 20:00h local time. The bottom panel, which refers to the sensitivity on 17 July at 03:00h shows a very small area of negative O_3 sensitivity to isoprene in the Lake Huron-Georgian Bay region. This negative sensitivity is only observed when the air parcels arriving at the target area have passed through a forested area during the night. In this case, the effect is observed in the W-T target area about 36 hours later.

CONCLUSION

The CMAQ adjoint provides a powerful way to explore the sensitivities of pollutants to the concentrations of their precursors and to other model parameters such as meteorology. We have applied a recently-developed version of the CMAQ adjoint to a study of the sensitivities of ozone mixing ratios in two selected areas of Southern Ontario to selected chemical species. This application has shown that the adjoint can provide information about the spatial distributions and strengths of the ozone sensitivities for the selected examples. Further studies with different target regions, pollutants and meteorological conditions will allow the generalisation of these results, elucidating both the causes of and possible remedies for poor air quality in this region.

REFERENCES

Dunker, A. M., 1984: The decoupled direct method for calculating sensitivity coefficients in chemical kinetics. *J. Chem. Phys.* **81**, 2385-2393.

Dunker, A. M., G. Yarwood, J. P. Ortmann, and G. M. Wilson (2002), The Decoupled Direct Method for Sensitivity Analysis in a Three-Dimensional Air Quality Model - Implementation, Accuracy, and Efficiency, *Environmental Science & Technology*, *36*, 2965-2976.

Gou, T., K. Singh, and A. Sandu (2009), Chemical Data Assimilation with CMAQ: Continuous vs. Discrete Advection Adjoints, in *Computational Science - ICCS 2009*, edited by G. Allen, *et al*., pp. 312-321..

Hakami, A., Henze, D. K., Seinfeld, J. H., Singh, K., Sandu, A., Kim, S. T., Byun, D. W., and Li, Q. B., 2007: The adjoint of CMAQ, *Environmental Science & Technology*, **41**, 7807-7817.

Resler, J., K. Eben, P. Jurus, and P. Krc (2008), Inverse Modelling of Emissions Using the CMAQ Adjoint Model, in *7th Annual CMAS Conference*, edited, Chapel Hill, NC.

Sandhu, A, D.N. Daescu, G.R. Carmichael and T. Chai, 2005, Adjoint sensitivity analysis of regional air quality models, *Journal of Computational Physics* **204** 222–252

Zhang, L., E. M. Constantinescu, A. Sandu, Y. Tang, T. Chai, G. R. Carmichael, D. Byun, and E. Olaguer (2008), An adjoint sensitivity analysis and 4D-Var data assimilation study of Texas air quality, *Atmospheric Environment*, *42*(23), 5787-5804.