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Synoptic-scale transport of ozone into Southern Ontario

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Abstract

This study focuses on synoptic-scale transport of ozone as it affects Southern Ontario. This process has been analyzed for the summer in 2001, as an example period of a frequent event that usually occurs during summer in this region. The work was carried out using the mesoscale modeling system generation 5 (MM5)/sparse matrix operator kernel emission modeling system (SMOKE)/community multiscale air quality (CMAQ) regional air quality modeling system, together with observational data from monitoring stations located throughout the modeling domain. Other different analyses have been carried out to supply more information apart from that obtained by the modeling system. A back-trajectory cluster methodology was used to evaluate the magnitude of the effects studied and an analysis of wind direction and cloud cover revealed a significant correlation with ozone concentration ($R^2 = 0.5$–0.6). Synoptic sea-surface level pressure (SLP) patterns were also analyzed to examine other meteorological aspects. The contribution of natural background ozone to the total amount within the region was compared with that from synoptic-scale transport. The influence of emission of pollutants from selected areas on ozone concentrations in Southern Ontario was also analyzed. As relevant results of these analyses, the model predicts that background ozone is the largest contribution to the ground-level ozone concentration during days in which low values were recorded. However, when smog episodes occurred, the model predicts that around 60% of the ozone formed by anthropogenic emissions of pollutants is due to releases from nearby US states.

Keywords: Ozone transport; Transboundary; Modeling; Back trajectory; Synoptic scale

1. Introduction

Tropospheric ozone is one of the major concerns for the air quality of Southern Ontario, mainly because of its effects on respiratory health (Ontario Medical Association, 2001), and agricultural crops (Linzon et al., 1984). Tropospheric ozone is also a major component of smog, and is formed through a series of complex photochemical reactions of various precursors emitted by multiple sources, so tracing its evolution by means of a chemical transport model is a difficult undertaking. These sources can be classified broadly as (Spicer et al., 1979):

(i) Natural or 'background' tropospheric ozone.
(ii) Local anthropogenic emissions.
(iii) Long-range transport (synoptic and intercontinental scale) and accumulation.
(iv) Vehicle-related urban plumes.
(v) Stratosphere injections.

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The importance of synoptic-scale transport of ozone has been noted by numerous authors (e.g., Yap et al., 1988; CEC, 1997; Farrell and Keating, 2002; Fiore et al., 2003; Brankov et al., 2003). Its magnitude depends heavily on the relative locations of the source and receptor regions and the meteorology connecting them. Some early studies (Yap et al., 1988) suggested that the contribution from transboundary transport could be the most important factor in the summertime high ozone concentration episodes that occur regularly in Southern Ontario. The Ontario Ministry of the Environment in its annual report in 2002 claims that more than 50 per cent of provincial ozone levels during widespread smog episodes are due to regional-scale transport of ozone and its precursors from neighboring US states. This report states that this contribution could be even higher in Ontario cities and towns on the northern shores of Lake Erie, the eastern shores of Lake Huron and in the extreme southwest near the US border (Ontario Ministry of Environment, 2002). Since this region contained a population of approximately 12 million in 2005 (Ontario Ministry of Finance, 2007), it is important to assess the sources of tropospheric ozone, including synoptic-scale transport, in order to design effective emission control strategies.

In the following, a study of the synoptic-scale transport of ozone in Southern Ontario is reported. The objective is to evaluate the magnitude of this process by means of different analyses, as an example to the capability of the methodology employed in the study of events like this. The combination of the mesoscale modeling system generation 5 (MM5) and the Model-3 community multiscale air quality (CMAQ), meteorology and chemical transport modeling systems, respectively, were used to simulate ozone concentration in the selected area. In the last decade the MM5-CMAQ system has been extensively employed to predict concentrations of different pollutants, particularly ground-level ozone and particulate matter (PM) (see e.g. recent studies of Zhang et al., 2004, 2006a, b, c, on the air quality in Southeastern US during summer). In addition, CMAQ has recently been selected for regulatory application by the US Environmental Protection Agengy (EPA) (e.g. Clean Air Interstate Rule, www.epa.gov). Back-trajectory modeling and analyses of key meteorological parameters calculated by MM5 model has been carried out to support the results obtained by CMAQ. A description of the air quality in the target area is given in Section 2. The methods used in this study are reported in Section 3, followed by the results in Section 4. Finally, Section 5 provides a summary of the main conclusions.

2. Target area

In this study, the attention is focused on Southern Ontario area (see Fig. 1), consisting of the Greater Toronto area (GTA), Central Ontario, Eastern Ontario, and Southwestern Ontario. Over 94 per cent of the Ontario population is included in this area. The air quality in this region can be represented by the air quality index (AQI), which is based on concentration of pollutants that have adverse effects on human health and the environment (Ontario Ministry of Environment, AQI, 2004). In 2001, ozone was responsible for 99 per cent of the hours during which the AQI was listed as 'poor' (in the case of ozone, a concentration larger than 81 ppb), but it must be noted that at that time this index did not include the particle matter. Fig. 2 shows the trend for the annual mean ozone concentration in Southern Ontario from 1993 to 2004. During this entire period of time, the annual average values exceeded 15 ppb, which is the maximum acceptable level specified by the National Ambient Air Quality Objectives and Guidelines for Canada (Health Canada, 2007). It is well known that ozone levels are strongly influenced by weather patterns (e.g. Zhang et al., 2007; Hogrefe et al., 2004; Krupa et al., 2003). The correlation between the number of 'hot days' (days in which the maximum air temperature is greater than 30 °C) and the annual mean ozone is overall apparent in Fig. 2. In this paper, the high ozone concentration episodes that took place during the period from 1 June to 31 July in 2001 are analyzed. By inspection of Fig. 2, it could be note that although 2001 was a 'hot year' with high-level ozone concentrations, these records were similar to those of other years in this region.

3. Methods

The synoptic meteorological pattern is the driver for the regional-scale transport of tropospheric ozone (Heidorn and Yap, 1986). An accurate representation of the evolution of the meteorological fields, therefore, is crucial for a good description of the ozone chemistry. In this study, the meteorological fields were obtained using the MM5 mesoscale

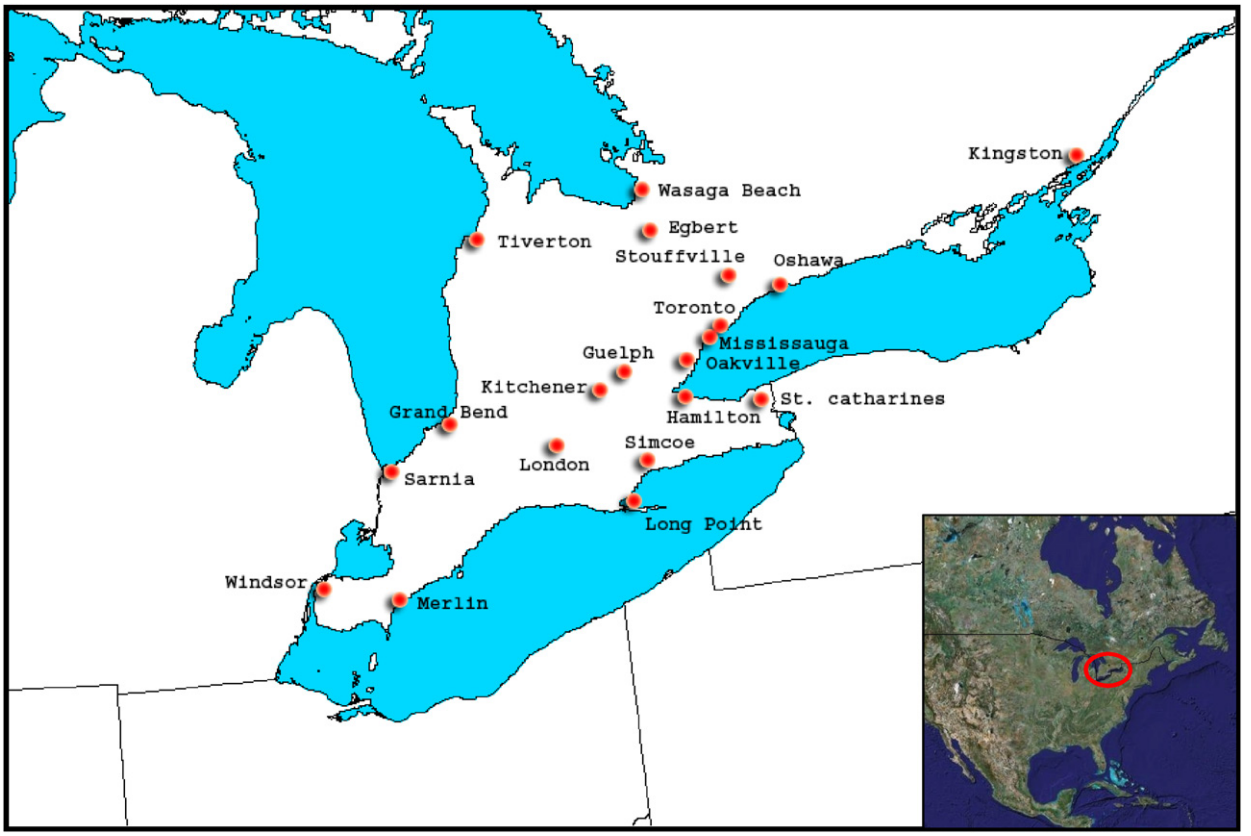

Fig. 1. Target area (Southern Ontario) of this study, including the location of relevant ozone monitoring sites of the National Air Pollution Surveillance (NAPS) network.

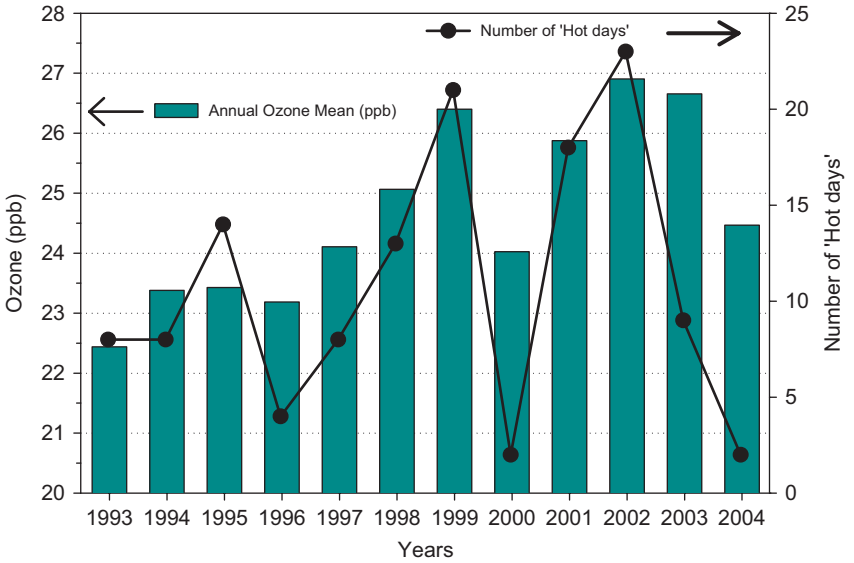

Fig. 2. 12-Year trend for annual mean ozone concentration in Southern Ontario and for 'Hot days' in Ontario (1993–2004). Annual mean ozone concentrations are based on 21 sites operated over 12 years. 'Hot days' (definition in Section 2) are based on eight meteorological sites in Ontario operated over 12 years. Data from Ontario Ministry of Environment (2002, 2004).

meteorology model, version 3 (Grell et al., 1994), which was applied in a nested-grid mode. The inner grid, which is illustrated in Fig. 3 and it is also the modeling domain of CMAQ, had a horizontal resolution of 36 km located in the Northeastern part of the US and Southeastern part of Canada (42 × 50 horizontal grid cells), and the outer grid had a horizontal resolution of 108 km covering most of North America. The results from the 36 km grid were used as input to perform the air quality simulations by CMAQ. Both MM5 and CMAQ were configured with 15 sigma layers (~6 below the planetary

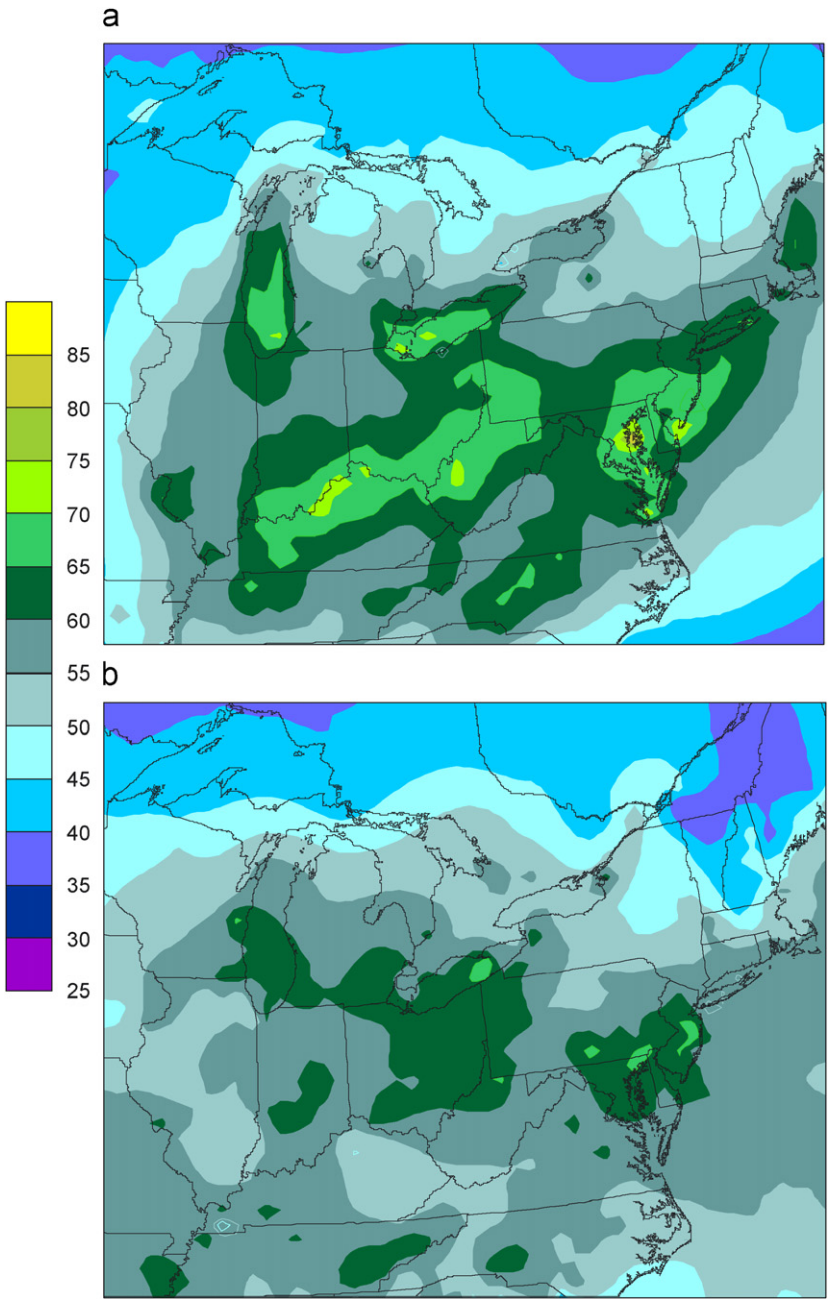

Fig. 3. CMAQ-predicted (a) and observed (b) 8-h daily maximum ozone concentrations, averaged over all summer days from 4 June to 31 July 2001. The contour levels in the map (b) were calculated using a Modified Simple Kriging interpolation method over 567 monitoring stations spread along the domain.

boundary layer), starting from the surface up to the top layer at 100 mbar (roughly 16 km height above sea level). The conventional medium range forecast (MRF) model boundary layer scheme (Hong and Pan, 1996) and Grell cumulus scheme (Grell et al., 1994) were selected in the MM5 parameterization.

To evaluate the effects of the synoptic-scale atmospheric transport patterns on ozone concentration levels observed at different locations in Southern Ontario, a trajectory-clustering methodology similar to that described by Brankov et al. (2003) has been used. The hybrid single particle lagrangian integrated trajectory (HYSPLIT4) model (Draxler and Hess, 1997) was employed to calculate 72-h back trajectories in the period of time under study, using the meteorological model's vertical velocity fields to model vertical motion. Three meteorological datasets were used for this study: FNL archive data (190 km of resolution), EDAS data (80 km), and MM5 data (36 km). FNL and EDAS archive data were provided by National Oceanic and Atmospheric Administration (2004), and the last one was calculated according to the methodology described above. The starting height was set at 925 mbar, which was found to provide good results for similar studies over Eastern North America (Haagenson et al., 1987). Due to the importance of overnight transport, and as it was chosen by Brankov et al. (2003) in their studies of transboundary transport of ozone, the starting time of each trajectory was set at 6:00 a.m. local time. To test the influence of this parameter, trajectories were also initialized at 12:00 noon, obtaining similar results. Starting points of trajectories were located in six cities spread throughout Southern Ontario: Kingston, Egbert, Tiverton, St. Catharines, Windsor, and Toronto (see Fig. 4), all of which have ozone monitoring stations. In order to cluster the trajectories, four 'transport sectors' were chosen for each location (East, West, North, and South), which were arbitrarily defined to denote regions with potentially different characteristics of sources of pollutants. North sector includes the large Canadian territories, East sector contains the US Northeastern Corridor, South sector covers the Ohio River Valley, and West sector encompasses the central part of US. Results from this analysis are shown in Section 4.3.

Version 4.3 of the CMAQ model (Byun and Ching, 1999) with the carbon bond IV mechanism

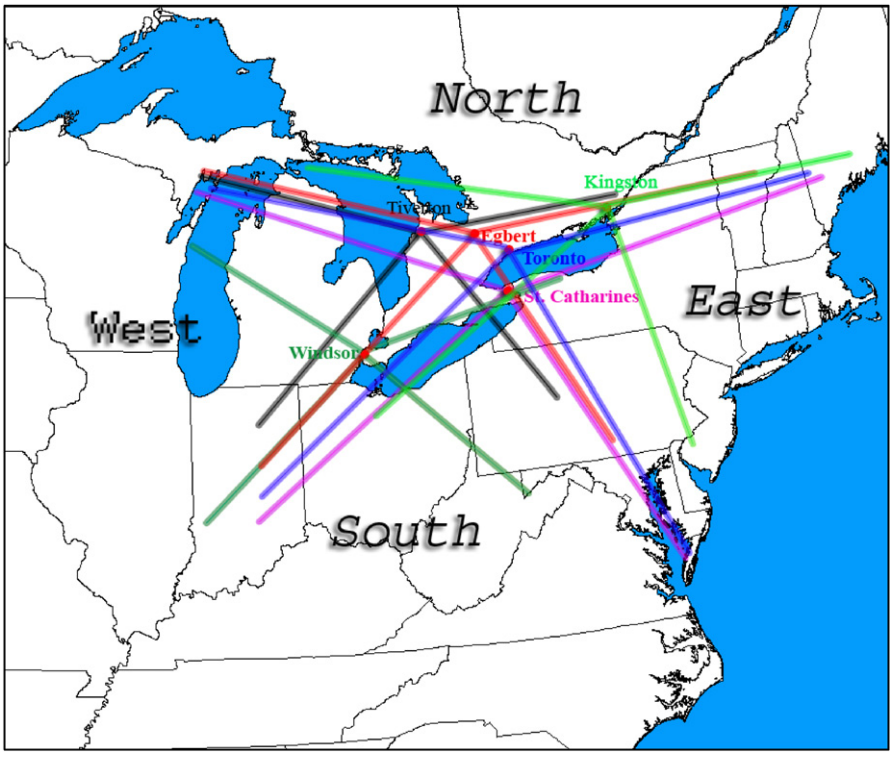

Fig. 4. Transport sector for six locations in Southern Ontario. Colors are used to distinguish the city at which lines are originated.

(CB-IV) (Gery et al., 1989) was used to perform the regional chemical transport modeling calculations. The default time-invariant boundary conditions of CMAQ were selected for ozone and precursors. Given that Southern Ontario is a small region located at the center of a considerably larger modeling domain, it must be expected that this choice should not affect the simulations, except for the 'zero' and 'bio' scenarios, as it will be discussed in Section 4.5. Meteorological fields were obtained from MM5, with the parameterization described previously. The 1996 EPA's National Emissions Inventory (NET96) for US and the 1995 Canadian emissions inventory were chosen to generate a gridded emission of pollutants for model simulation. These datasets contain county-level emissions from different categories of sources for both US and Canada. These emission inventories were processed with the version 2.0 of the sparse matrix operator kernel emission modeling system (SMOKE) (Carolina Environmental Programs, 2003), which generates the gridded-hourly-speciated emission input needed for CMAQ. The BEIS3 package integrated in SMOKE was used to simulate the biogenic emissions.

Observational data for 514 sites in the US were obtained from the aerometric information retrieval system (AIRS); data for 53 sites (33 located in Southern Ontario, see Fig. 1) in Canada were acquired from the National Air Pollution Surveillance (NAPS) network. Since both sources supply surface measurements, the model predictions corresponding to only the surface layer can be compared with observational data, which makes the comparison somewhat sensitive to model details of vertical transport and deposition algorithms.

4. Results and discussion

4.1. Air quality model evaluation

The ability of CMAQ to capture the spatial and temporal variability of ozone in the selected region has been tested. The spatial distribution of the observed and predicted daily 8-h maximum ozone concentrations averaged over all days from 4 June to 31 July 2001 (the first 3 days, i.e., 1–3 June, were neglected due to model spin up) is depicted in Fig. 3, showing a general qualitative agreement but some quantitative differences. Both plots confirm broad bands of high ozone concentration across the center of the domain, over lakes Michigan and Erie, and along the Eastern seaboard of the United States, and a gradual decrease towards the North part of the domain. The model predictions, however, overestimate in general the absolute concentrations by up to 20 ppb in some places, mainly in the Ohio River Valley and the Northeastern Corridor. These overestimations might be related to the use of the 1996 US emission inventory. Reductions in motor vehicle emissions and, to a lesser degree, point source emissions occurred from 1996 to 2001, so a probable decrease of the ozone concentration over these areas might be obtained with an updated emission inventories. Nonetheless, a better agreement is found in the evaluation of the temporal evolution of the ozone concentration in the target area, as shown in Fig. 5. The top panel (5a) gives the temporal pattern of observed and predicted 8-h daily maximum ozone concentration averaged over Southern Ontario during the study period. A general good agreement is found, although the model slightly underestimates (<10 ppb) the ozone concentration between days 26 and 30 (26–30 of June) and to a greater extent ($\sim$20 ppb) on day 19 (19 June), and overestimates (10–15 ppb) the ozone concentration between days 50 and 54 (20–24 of July). All these periods coincided with high ozone concentrations that were reported as official smog advisories in the annual air quality report of Ontario (Ontario Ministry of Environment, 2001). Despite these discrepancies, the temporal variation is predicted quite well, showing a correlation coefficient R^2 between observed and predicted 8-h daily maximum ozone concentration (averaged over 33 stations located in Southern Ontario) of 0.76, with a standard error of ca. 8 ppb. The hourly temporal variation between observed and predicted ozone concentration for Toronto region for the period of time from 23 June to 4 July, that included a representative smog episode, is shown in panel (5b). In this case, CMAQ predicts rather well the diurnal pattern of the variation of ozone concentration, even though chemical transport models usually overestimate nighttime minima (see for example Hogrefe et al., 2004). Nevertheless, the good agreement obtained is a bit fortuitous and in general the nighttime ozone concentrations are overestimated at other monitoring sites during smog episodes, particularly rural sites (results not shown). The correlation coefficient R^2 between the observed and predicted hourly ozone concentration averaged at 33 stations in Southern Ontario is 0.63, with a standard error of ca. 11 ppb.

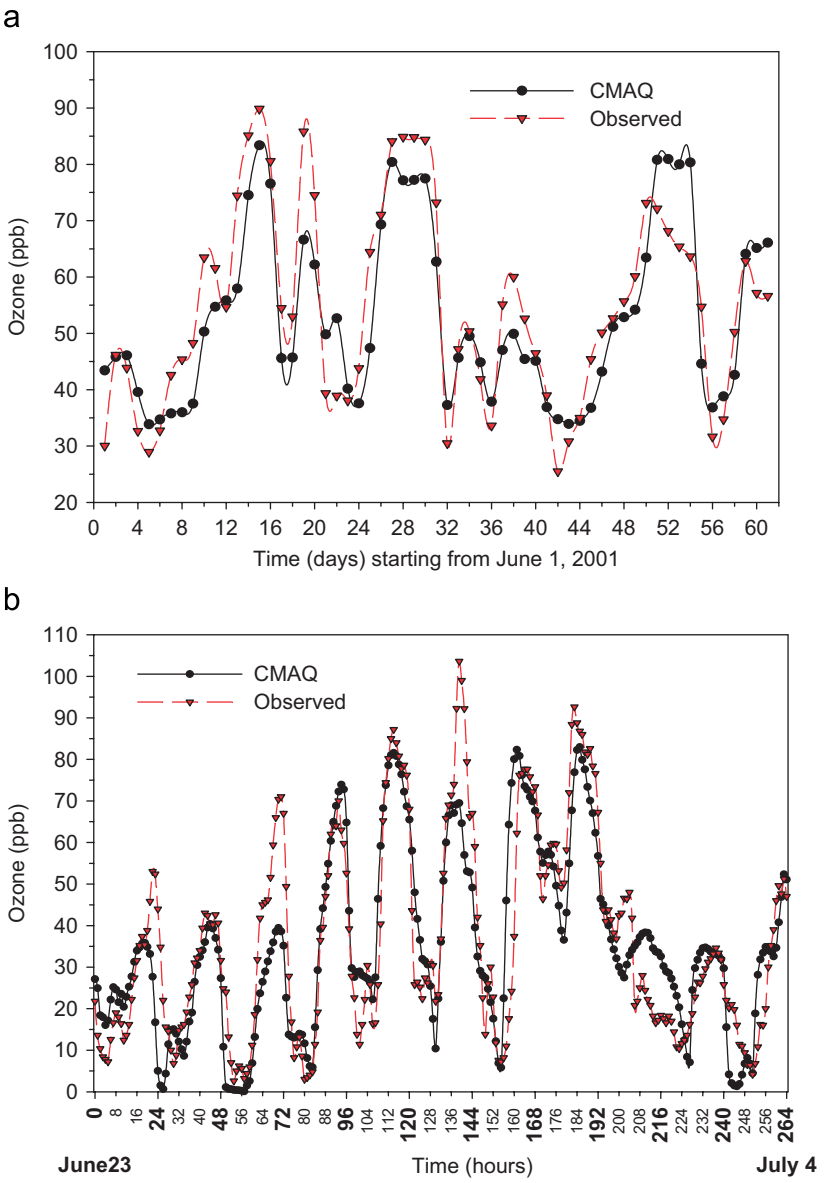

Fig. 5. (a) Observed and CMAQ-predicted 8-h daily maximum ozone concentrations averaged over Southern Ontario from 1 June to 31 July 2001. Observed data were averaged over 33 monitoring stations. Panel (b) shows the observed and CMAQ-predicted hourly ozone concentration from 23 June to 4 July 2001 for Toronto region. Observed data were averaged over 5 stations located in Toronto city or the neighborhood.

4.2. *Wind field analysis*

Statistical data as well as back-trajectory studies show that the ozone concentration in Southern Ontario is strongly influenced by synoptic-scale transport involving Southerly and Southeasterly air flows (CEC, 1997; Ontario Ministry of Environment, 2002). The photochemical history of these air masses as well as the meteorology patterns occurred during the high ozone episodes should be considered to treat the tropospheric ozone problem. Several efforts have been made to find reliable correlations between selected meteorological parameters and the ground-level ozone observed (e.g., Krupa et al., 2003), but these led in general to complicated expressions. With the aim of both scratching on the surface of this problem and showing the influence of meteorology in the ozone

concentration predicted in Southern Ontario, the correlation between two key meteorological parameters (wind direction and fraction of cloud cover) and ground-level ozone has been analyzed. For the area and period of time studied, an empirical correlation is obtained by considering mainly the North-South component (v) of the horizontal wind vector ($v=-1$ and 1 indicate Northerly and Southerly winds, respectively) in the US domain in Fig. 3 and, as a minor contribution, the fraction of cloud cover (CV) in Southern Ontario. Fig. 6 shows a comparison between predicted ozone concentration and 'effective meteorological forcing', F_{eff}, along the period of time studied. F_{eff} is defined as

$$F_{\text{eff}} = \frac{N_{v>0}}{N_{\text{Tot}}} - f \times CV, \quad (1)$$

where $N_{v>0}/N_{\text{Tot}}$ is the percentage of cells in the US domain in Fig. 3 which have a component of the horizontal wind direction at ground-level pointing towards the North ($v>0$). CV denotes the total cloud cover fraction (0–1) over Southern Ontario and f is an arbitrary factor to account for the influence of this parameter on F_{eff}. With the aim to achieve the highest correlation coefficient between F_{eff} and ozone concentration, different values of f were tried, finding 0.3 as the best result. This small value of f shows that the term $N_{v>0}/N_{\text{Tot}}$ in Eq. (1) is the dominant effect in F_{eff}. In fact, choosing $f=0$ yields similar values of F_{eff} to those shown in Fig. 6 but a slightly lower correlation coefficient between ozone concentration and F_{eff}. Fig. 6 shows that F_{eff} values close to 1 are obtained when the ozone concentration is high, i.e. Southerly winds are involved when high level ozone concentrations are predicted. If only the area belonging to the US states closest to Southern Ontario (the group of states consisting of Michigan, Ohio, Pennsylvania, and New York, hereafter referred to as 'Border') is taken into account for the calculation of $N_{v>0}/N_{\text{Tot}}$, similar results to those including all US territory in the domain are obtained. Due to the simplification of this analysis a high correlation coefficient between F_{eff} and ozone concentration is not expected; nevertheless, values of R^2 of 0.51 and 0.56 for US territories and 'Border' states, respectively, are obtained, showing at least the mutual dependence of both magnitudes. This result is in good agreement with a previous study by Mukammal et al. (1982), who observed higher ozone concentration in Simcoe city (located at north of lake Erie, see Fig. 1) in the presence of Southerly winds. The fact that the analysis over only the 'Border' states gives similar results to those obtained over all the US territory, suggests that the ozone concentration predicted in Southern Ontario could be strongly influenced by emissions of precursors or even ozone moving from these neighboring.

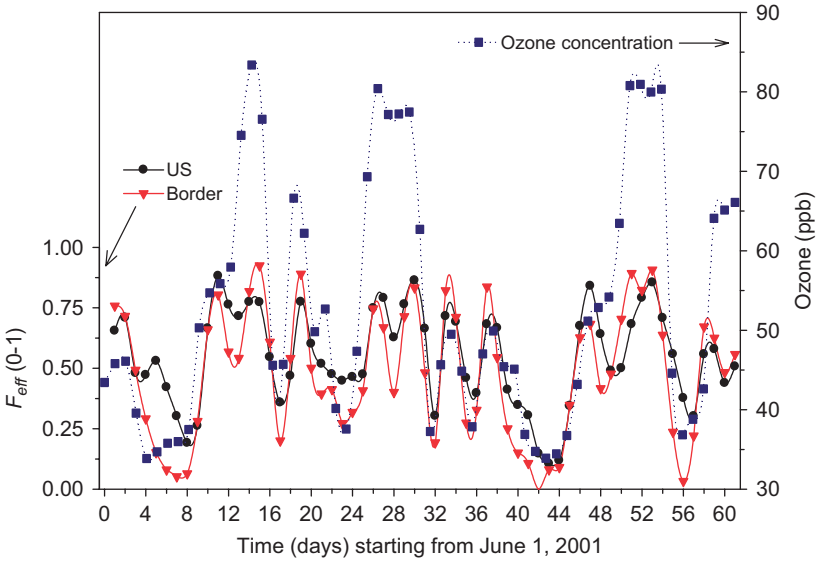

Fig. 6. Daily averaged values of F_{eff}, defined in Eq. (1), from 1 June to 31 July 2001. Circles represent data for US territories and down triangles data for 'Border' states (Michigan, Ohio, Pennsylvania and New York). 8-h daily maximum ozone concentrations predicted by CMAQ and averaged over Southern Ontario are also shown (squares).

4.3. Back-trajectory analysis

Back trajectories of the air masses were analyzed for six different locations in Southern Ontario. For each trajectory, their positions (longitude and latitude), given each hour over 3 days, are assigned to a specific transport sector (North, South, East and West; see Fig. 4), forming the transport history of the trajectory. For every site, each trajectory is assigned to a specific transport sector when a percentage value larger than a previously selected percentage of the transport history belonged to this sector. Trajectories not meeting this criterion were considered unclassifiable and denoted as "U". The selected percentage had to be a good representation of the transport history but not so stringent to generate a large number of unclassifiable trajectories. Due to the small number of trajectories per site calculated, a percentage of 70% has been selected, being this value slightly smaller than that proposed by Brook et al. (2002), 80%. The results obtained in this analysis, using the EDAS data set, are shown in Fig. 7. A good agreement (R^2~0.7) between the ozone calculated by CMAQ and that measured at monitoring stations is observed in the figure, emphasizing again the potential of CMAQ to account for the spatial ozone distribution in the selected domain. The major differences rise between predicted and observed 8-h maximum concentrations at St. Catharines and Toronto, for back-trajectories originating from the East, obtaining R^2~0.8 when these two points are neglected. Windsor site shows high levels of ozone (>80 ppb), especially for trajectories assigned to South and East sectors, in good agreement with the prediction by CMAQ. The monitoring stations of Egbert and Tiverton (cataloged as agricultural and undeveloped respectively) also measured similar high ozone values in the days when the trajectories came from the South sector too. It is well known that higher ozone concentrations are recorded in this kind of rural ambient than in urban sites (e.g. see Toronto site in Fig. 7), which agrees with the results predicted by CMAQ. Similar correlations between predicted and observed data were obtained comparing the different meteorological data sets (see Table 1).

As it is shown in Fig. 7, the ozone concentration measured when back-trajectories belong to East, West or South sectors is significantly higher than that for the North sector. Table 1 shows the average ozone concentration for each sector for the three meteorological data sets. Ozone concentration recorded for back-trajectories belonging to the North sector is ca. 38–40 ppb, depending on the meteorological data set, which is considerably lower (ca. 40%) than the value found for other transport sectors, indicating that less polluted air masses come from Northern territories. On the other hand, trajectories coming from Southern regions produce the highest ozone concentrations values, 64–74 ppb (67–79 ppb predicted by CMAQ). East and West sectors show slightly lower ozone concentrations: 58–64 ppb for the East (68 ppb predicted by CMAQ) and 61–62 ppb for the West (62–63 predicted by CMAQ). These slight overestimations of the ozone predictions when trajectories come from South, East and West sectors could be due to the use of the outdated 1996 US emission inventory, as it was mentioned in Section 4.1. Due to the smaller percentage (4–5%) of trajectories coming from the South and East sectors (see Table 1), more discrepancies between measured and CMAQ predictions or even among different meteorological data sets are obtained. The percentage of unclassifiable trajectories was ca. 27–29% (see Table 1), which is lower than that estimated by Brook et al. (2002), due to the fact that a smaller percentage of the transport history to cluster the trajectories has been selected. Finally, the average ozone concentration for trajectories classified as 'U' is ca. 62–64 ppb (in good agreement with the prediction of CMAQ, 63–64 ppb). The high ozone concentrations observed for this group suggest that most of these trajectories could cross the East, West or South sectors. The results are in good agreement with those reported by both Brook et al. (2002) for $PM_{2.5}$ or Brankov et al. (2003) for ozone, who considered a quite larger number (about 10–30 times) of back trajectories in their analysis.

4.4. Synoptic weather pattern description

The ozone concentration and the air parcel trajectory strongly depend on the in situ synoptic weather pattern under which they evolve. With the aim of illustrating the synoptic weather pattern predicted during the study-period, the sea-surface level pressure (SLP) fields calculated by MM5 for those days, following the parameterization described in Section 3, has been analyzed. Comparing the different patterns with the measured ozone concentration, it can be observed that high ozone concentrations in Southern Ontario were often

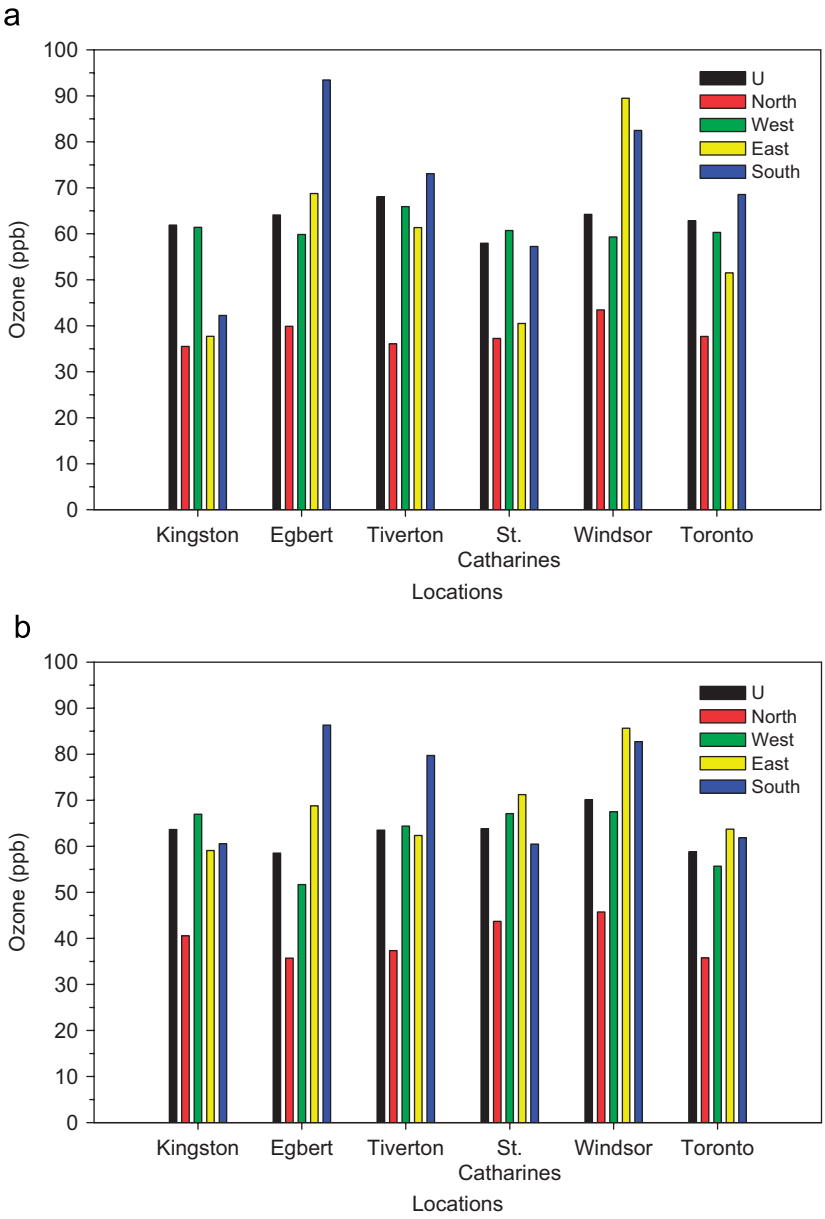

Fig. 7. CMAQ-predicted (a) and observed (b) 8-h daily maximum ozone concentration in different locations, averaged during the period of time from 4 June to 31 July in 2001 and classified according to the transport sector assigned to the 3 days back-trajectory history (defined in Section 4.3). EDAS (80 km) meteorological data set was used in this analysis.

associated with SLP which presents an amplitude ridge extending from a high pressure system (Bermuda high pressure pattern) situated over the Southeastern part of the modeling domain (see Fig. 8a). This kind of SLP pattern was found in the 2 five-days smog episodes that started on 26 June and 20 July, respectively. This fact agrees quite well with a recent study by Hogrefe et al. (2004), over the summers from 1993 to 1997. In this article the authors used a correlation-based map-typing procedure of Kirchhofer (Kirchhofer, 1973) to identify the synoptic pressure regimes in those summers. The pattern depicted in Fig. 8a was one of the most frequent situations in summer, which was usually associated with high ozone concentration in Southern Ontario (typically more than 65 ppb). Under such situation, warm air coming from Southern areas arrives to the South of Ontario. Consequently,

Table 1
CMAQ predicted and observed mean 8-h daily maximum ozone concentration (ppb) during the period of time from 4 June to 31 July in 2001

Meteorological data set	Unclassifiable	North	West	East	South
FNL					
CMAQ	64 (27)	40 (42)	63 (21)	68 (5)	67 (5)
Observed	64	39	62	62	64
EDAS					
CMAQ	63 (29)	40 (40)	62 (23)	68 (4)	72 (4)
Observed	63	38	61	58	70
MM5					
CMAQ	63 (28)	41 (45)	62 (18)	68 (4)	79 (5)
Observed	62	40	62	64	74

Values averaged over six sites in Southern Ontario, reported in Section 3, and classified according to the transport sector assigned to the three days back-trajectory history obtained with three meteorological datasets. Percentage of back trajectories in each transport sector is given in parentheses.

back-trajectories analyses reveal air parcels originating at Southern regions in those days and the synoptic-range transport of ozone becomes a critical factor in the air quality of Southern Ontario. On the other hand, during the days when low ozone concentration (<50 ppb) was recorded, two different SLP patterns were observed. The first situation happened when an anticyclone moved from Canadian Northwestern territories to the Great Lakes region, generating Northerly winds over Southern Ontario (see Fig. 8b). This pattern was early typified by Heidorn and Yap (1986) as a typical summer situation in Southern Ontario, and in 2001, was observed from 5 to 9 in June and from 25 to 27 in July, when low ozone concentrations ($\leqslant 50$ ppb) were recorded (see Fig. 5a). During the days after these periods, the Southern Ontario region was gradually under the influence of the rear side of the anticyclone, and ozone concentration levels increased. The second situation happened when a low-pressure system located over the Northeast of the Great Lakes remained nearly stationary for several days. Such weather pattern corresponds to the situation found from 9 to 15 of July (see Fig. 8c). Back-trajectory analyses revealed air masses coming from Northern areas and consequently low ozone concentrations were recorded during this period ($\leqslant 50$ ppb).

4.5. Background ozone evaluation

To estimate the magnitude of the contributions from different anthropogenic sources of ozone or its precursors to the air quality of Southern Ontario, an evaluation of the background tropospheric ozone concentration is indispensable. Essentially, if injections of ozone from the stratosphere into the troposphere are not considered, the natural background ozone concentration in a specific area is due to the contribution from both free troposphere and locally formation involving natural hydrocarbons. Injection of stratospheric ozone in this study has been ignored, but the contribution from reactions involving natural hydrocarbons has been considered. CMAQ modeling has been performed for two different scenarios that take into account the possible contribution to the formation of tropospheric ozone, which differ from the 'base case' in the following ways:

(1) 'Zero': no anthropogenic or biogenic emissions are taken into account, i.e. no emissions in the domain.
(2) 'Bio': biogenic emissions are considered, but anthropogenic are not.

The predicted ozone concentration in Southern Ontario for both scenarios (among others described further) is illustrated in Fig. 9. As seen, the ozone concentrations for scenarios 'Zero' and 'Bio' are almost identical, except for small differences during high ozone concentration episodes, indicating that the contribution from biogenic emissions within the domain is not significant for the averaged background ozone concentration calculated by CMAQ at Southern Ontario. This result qualitatively agrees with the modeling study of Lurmann et al. (1984), who estimated the contribution from biogenic

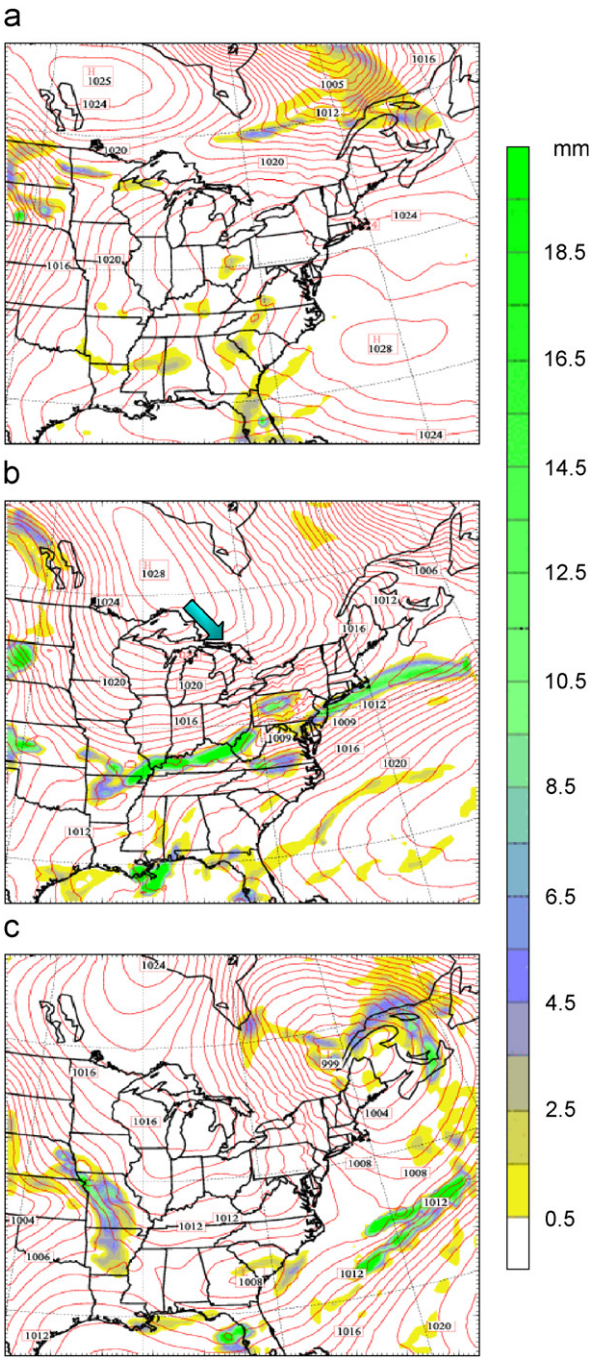

Fig. 8. Simulated sea-surface level pressure pattern and precipitation on 27 June , 6:00 UTC (a), 26 July 15:00 UTC (b), and 12 July, 9:00 UTC (c). The arrow in panel (b) indicates the track of the anticyclone.

emissions to be only 2–9% of the predicted maximum ozone concentration in urban areas. These authors attributed this small contribution to fast ozone-'biogenic hydrocarbon' reactions that scavenge almost as much ozone as is produced by the biogenic hydrocarbon. In the present study, the predicted 8-h daily maximum ozone concentration averaged over the entire period for scenarios 'Zero' and 'Bio' is ca. 31 ppb in both cases, while it is 53 ppb for the 'base case'. This result corresponds with the study of Yap et al. (1988), who estimated the local background ozone level for Southern Ontario to be approximately 20–30 ppb, based on observed data over 30 monitoring stations from May to September from 1979 to 1985. Due to the definition of scenario 'Zero', it could be sensitive to the boundary conditions selected. Taking into account that an ozone concentration range of 30–35 ppb was chosen for boundary condition in the surface layer, this good agreement may be fortuitous. In any case, the predicted average background ozone concentration in this study is also in good agreement with the results found in Section 4.2. The best-fitting correlation line of F_{eff} with ozone concentration in Southern Ontario in the analysis over all US territories presented in Section 4.2 gives a value of 25 ppb for the y-intercept, value that is 35 ppb for the case of the 'Border' states only. In other words, in absence of Southerly wind (usually more polluted), $F_{\text{eff}} = 0$, the ozone concentration averaged in Southern Ontario would be approximately 25–35 ppb, which is in concordance with the previously average background ozone concentration estimated, 31 ppb. Although the predicted background ozone concentration does not present large variations along the days (see Fig. 9), generally lower values are obtained when the observed ozone concentration is high. A possible explanation for this fact could be the increased scavenging of ozone, by the NO_x included in the boundary conditions, which usually happens in stagnant meteorological conditions, as those found in these smog episodes, although further investigations are necessary to clarify this point.

Fig. 10 shows the hourly ozone concentration averaged in the Southern Ontario domain during the two 5-days smog episodes starting on 26 June and 20 July. The predicted background ozone (scenarios 'Bio' and 'Zero') on days with low ozone concentrations (408–552 h) shows similar values to those calculated for the 'base case', mainly during nighttime when the lowest ozone concentrations are predicted. Larger differences are observed during the daytime, when the ozone concentration is higher, which can be attributed to local emissions.

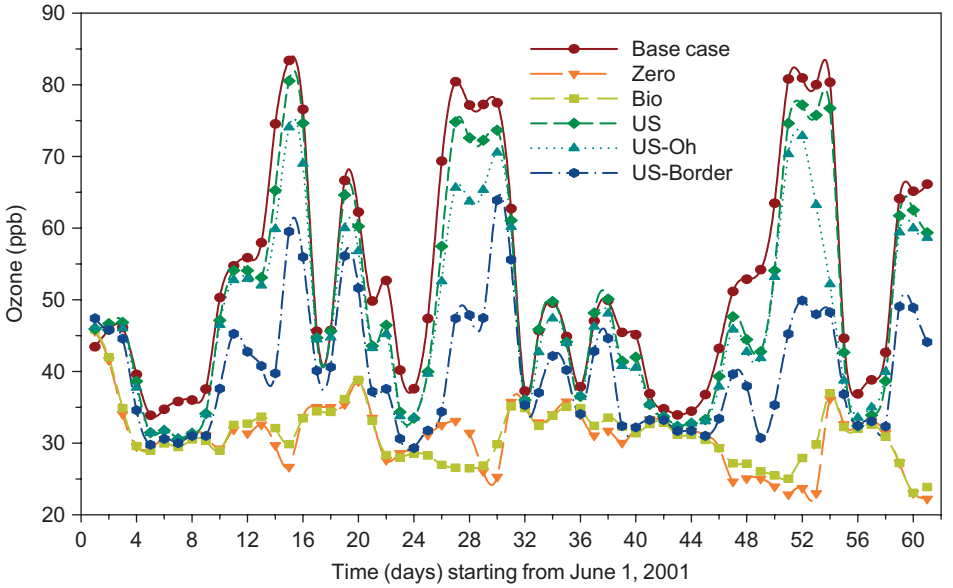

Fig. 9. CMAQ-predicted 8-h daily maximum ozone concentration averaged over Southern Ontario from 1 June to 31 July 2001. The definition of the scenarios is given in Section 4.

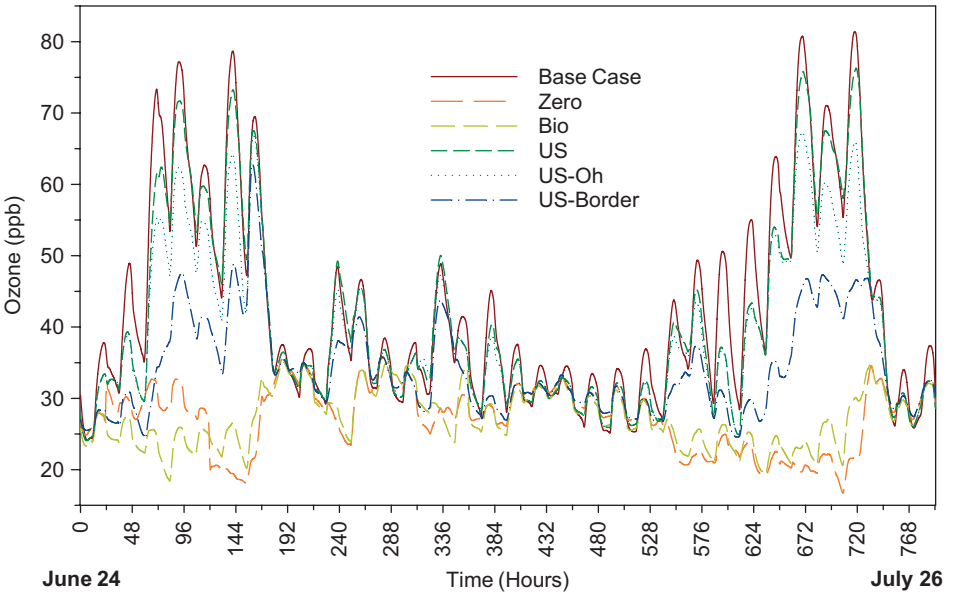

Fig. 10. CMAQ-predicted hourly ozone concentration averaged over Southern Ontario from 24 June to 27 July 2001. The definition of the scenarios is given in Section 4.

During the smog episodes significant differences appear between background and 'base case' concentration, because of the contribution of anthropogenic emissions (see Fig. 10). Considering that the trajectories in those days came mainly from Southern areas (see Section 4.3), these anthropogenic emissions could be released from US territories, emphasizing again the importance of the transboundary transport on the air quality of Southern Ontario. According to these results, it can be summarized that the background ozone is the largest contribution to the predicted ozone concentration during 'clean' days (defining 'clean' day as one having the 8-h daily maximum ozone

concentrations lower than 65 ppb, which coincides with the Canada-wide Standard averaged over 8 h). The predicted average ozone concentration during 'clean' days in Southern Ontario is 36 ppb, while the background ozone (31 ppb by both 'Bio' and 'Zero' scenarios) accounts for approximately 86% of this value.

4.6. Contributions from selected emissions

To evaluate the contribution of anthropogenic emissions from selected areas to the ground-level ozone concentration obtained in Southern Ontario, several scenarios were modeled, which differ from the 'base case' in the following ways:

(3) 'US': no anthropogenic emissions over the Canadian part of the model domain.
(4) 'US-Oh': scenario 3 plus no anthropogenic emissions from Ohio.
(5) 'US-Border': scenario 3 plus no anthropogenic emissions from the 'Border' states.

The daily ozone concentration averaged over Southern Ontario for these scenarios is illustrated in Fig. 9. The most significant differences appear when the ozone concentration is higher than 65 ppb (during smog episodes); otherwise the values are more similar with the background being the major contributor to the total predicted tropospheric ozone. Only a small reduction in the ozone concentration is observed when the Canadian emissions are turned off (scenario 3). Fig. 11a shows that the 8-h maximum ozone concentration obtained in scenario 3 accounts for more than 90% of that in the 'base case'. In other words, the prediction of the model shows that $<10\%$ of the 8-h maximum ozone concentration averaged over Southern Ontario is caused by Canadian anthropogenic emissions. Fig. 11b shows that this percentage does not change substantially when only days during smog episodes are considered. In addition, when anthropogenic emissions from Ohio are turned off (scenario 4), the ozone decrease is approximately 10% during smog episodes as compared to scenario 3 (Fig. 4b). Nevertheless, the most important reduction of the ozone concentration is found in scenario 5, which predicts reductions of 25% (or 35% during smog episodes) from the 'base case'. Turning off the emissions from Canada and 'Border states' implies a reduction of more than 60% of the anthropogenic ozone concentration This reduction is approximately 15 ppb for the 8-h maximum ozone concentration averaged over the entire period studied and as high as 27 ppb on days when 8-h maximum ozone concentrations are higher than 65 ppb. This result agrees with that found in Section 4.2, which revealed a similar correlation between F_{eff} and ozone concentration in Southern Ontario for the 'Border' states or all the US part of the model domain, suggesting significant influences in the air quality of this region due to transport of ozone and precursor emissions from these nearby areas. It has to be noted that these data depend on the emission inventory selected, so that the quantitative result could be slightly different if a more updated emission inventory had been used.

Fig. 10 shows the predicted hourly ozone concentration during the two 5-day episodes. As discussed above, the main differences appear during smog episodes. During the 'clean' days, between 10 and 16 July (384–528 time in Fig. 10), differences among scenarios are smaller because the major ozone contribution is provided by the natural background. The minimum ozone concentration at nighttime during these days is slightly higher for scenarios 1 or 2 than for the 'base case', probably because of the elimination of NO_x emissions in scenarios 1 and 2, which produces less elimination of ozone by reaction with nitric oxides.

5. Summary

The effects of synoptic-range transport of ozone on the air quality of Southern Ontario during the summer of 2001 have been investigated by means of different analyses including both observational data and model simulations. First, the ability of the MM5/SMOKE/CMAQ modeling system to simulate the ozone concentration on Southern Ontario has been tested, and the results compared with observational data recorded at different monitoring stations spread along the domain considered in this study. In general, the model provides a reliable spatial and temporal distribution of ozone, although overestimations of ca. 20 ppb are obtained in regions far from our target area, as Ohio River Valley and Northeastern corridor, presumably due to the use of the 1996 US emission inventory. The predicted temporal variation of ozone concentration for Southern Ontario shows differences lower than 20 ppb in the mean 8-h daily maximum ozone concentration during smog episodes comparing to

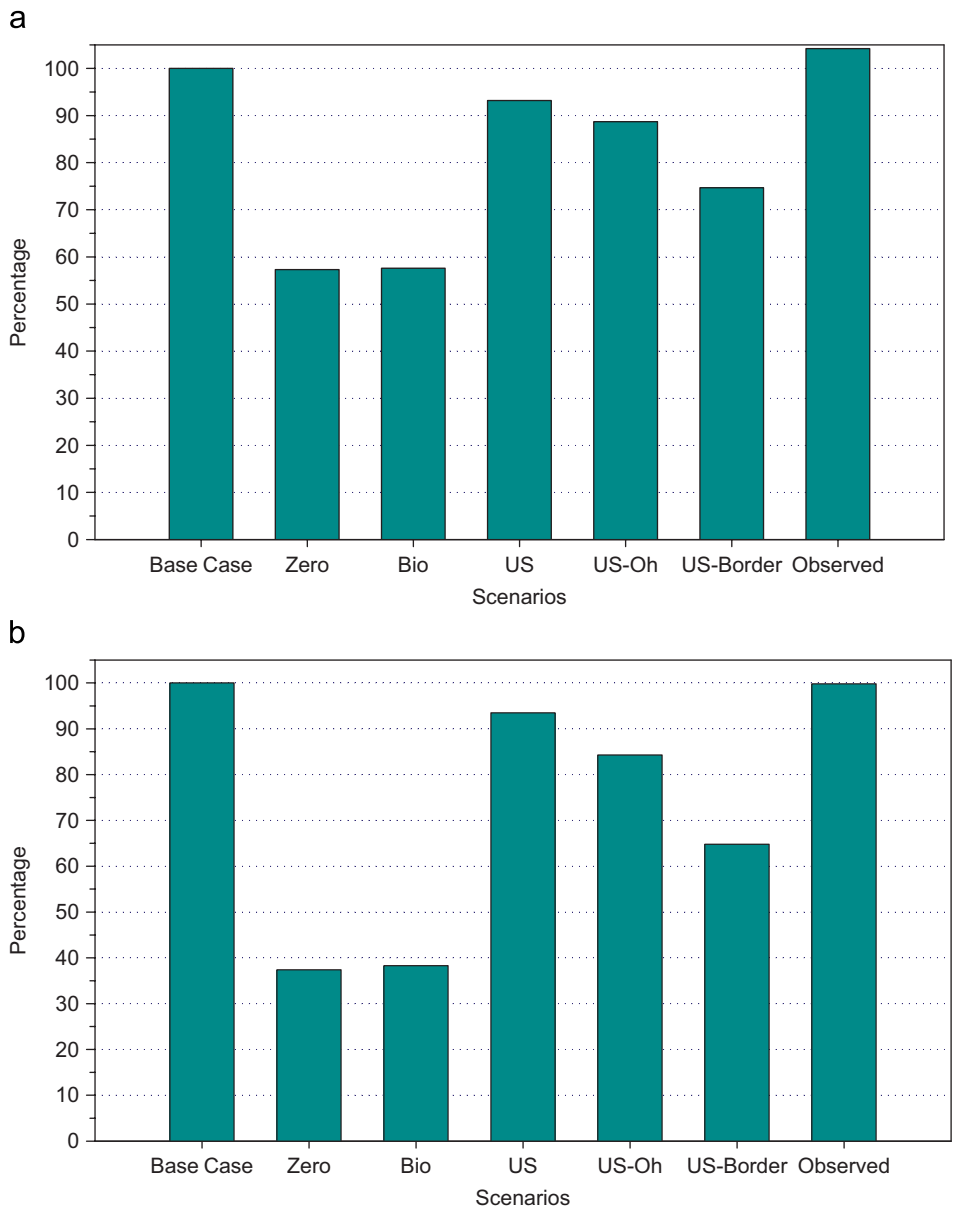

Fig. 11. Percentage of 8-h daily maximum ozone concentration averaged over Southern Ontario for selected scenarios with respect to the 'base case' for all the days from 4 June to 31 July 2001 (a) and only for days with 8-h daily maximum ozone concentration higher than 65 ppb and (b) the definition of the scenarios is given in Section 4.

the observed data. The analysis of the wind fields shows a correlation between the directions of the winds in the nearby US states with the ozone values recorded in Southern Ontario, which suggests that transport of ozone and precursor emissions from these states could be very important for the air quality of the focus region. The back-trajectories clustering analysis confirms this hypothesis, showing an increase of around 30 ppb in the 8-h maximum ozone concentration measured in this region when the air masses come from Southern regions (US territories) compared to those originated from North. The analysis of the SLP reveals that high ozone concentrations usually correspond with an amplitude ridge extending from the Bermuda high pressure system, which is associated with Southerly winds in Southern Ontario.

With the aim of estimating the contribution from the natural background, local emissions and especially synoptic-scale transport to the predicted ozone in Southern Ontario, CMAQ modeling was performed for several scenarios. The results reveal that the biogenic emissions within the domain have little effect on the predicted background ozone concentration at monitoring locations in Southern Ontario, estimated to be approximately 31 ppb for Southern Ontario, which is in good agreement with the results of other authors (Yap et al., 1988). Nevertheless, time-invariant boundary conditions selected for this work could influence on this value. Local emissions contributed less than 10% of the ozone concentration in Southern Ontario. Reductions of more than 60% in the anthropogenic ozone (i.e. ozone originated by anthropogenic emissions) are predicted when selected US territories are eliminated. The different analyses used in this work have given results which are not only in good concordance among them, but they are in agreement with those found by other authors (e.g. see Yap et al., 1988; Ontario Ministry of Environment, 2002).

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References

Brankov, E., Henry, R.F., Civerolo, K.L., Hao, W., Rao, S.T., Misra, P.K., Bloxam, R., Reid, N., 2003. Assessing the effects of transboundary ozone pollution between Ontario, Canada and New York, USA. Environmental Pollution 123 (3), 403–411.

Brook, J.R., Lillyman, C.D., Shepherd, M.F., Mamedov, A., 2002. Regional transport and urban contributions to fine particle concentrations in Southeastern Canada. Journal of Air & Waste Management Association 52 (7), 855–866.

Byun, D.W., Ching, J.K.S., (Eds.), 1999. Science Algorithms of the EPA Models-3 Community Multiscale Air Quality Model (CMAQ) Modeling System. EPA/600/R-99/030, US Environmental Protection Agency, Office of Research and Development, Washington, DC 20460.

Carolina Environmental Programs, 2003. Sparse Matrix Operator Kernel Emission (SMOKE) Modeling System. University of Carolina, Carolina Environmental Programs, Research Triangle Park, NC.

CEC, Secretariat for Environment Cooperation, 1997. Long-Range Transport of Ground-Level Ozone and Its Precursors: Assessment of Methods to Quantify Transboundary Transport within the Northeastern United States and Eastern Canada. Published by the Communications and Public Outreach Department of the CEC Secretariat. Montreal (Quebec), Canada H2Y IN9.

Draxler, R.R., Hess, G.D., 1997. Description of the HYSPLIT_4 Modeling System. NOAA Technical Memorandum; ERL ARL-224; Silver Spring, MD, December 1997, 24pp.

Farrell, A.E., Keating, T.J., 2002. Transboundary Environmental assessment: lessons from OTAG. Environmental Science and Technology 36 (12), 2537–2544.

Fiore, A., Holloway, T., Hastings, M.G., 2003. A global perspective on air quality: intercontinental transport and linkages with climate. Environmental Management, 13–22.

Gery, M.W., Whitten, G.Z., Killus, J.P., Dodge, M.C., 1989. A photochemical kinetics mechanism for urban and regional scale computer modeling. Journal of Geophysical Research 94, 12925–12956.

Grell, G.A., Duhia, J., Stauffer, D., 1994. A description of the fifth-generation Penn State/NCA Mesoscale Model (MM5). NCAR Technical Note, TN-398 + STR, National Center for Atmospheric Research, Boulder, CO, 138pp.

Haagenson, P.L., Kuo, Y.H., Skumanich, M., Seaman, N.L., 1987. Tracer verification of trajectory models. Journal of Climate and Applied Meteorology 26, 410–426.

Health Canada, 2007. 〈http://www.hc-sc.gc.ca/ewh-semt/air/out-ext/reg_e.html〉 (accessed in February, 2007).

Heidorn, K.C., Yap, D., 1986. A synoptic climatology for surface ozone concentrations in Southern Ontario, 1976–1981. Atmospheric Environment 20 (4), 695–703.

Kirchhofer, W., 1973. Classification of European 500 mb pattern. Arbeitsbericht der Schweizerischen Meteorologischen Zentralanstalt Nr. 43, Geneva.

Hogrefe, C., Biswas, J., Lynn, B., Civerolo, K., Ku, J.-Y., Rosenthal, J., Rosenzweig, C., Goldgerg, R., Kinney, P.L., 2004. Simulating regional-scale ozone climatology over the eastern United States: model evaluation results. Atmospheric Environment 38, 2627–2638.

Hong, S.Y., Pan, H.L., 1996. Non local boundary layer vertical diffusion in a medium range forecast model. Monthly Weather Review 124, 2322–2339.

Krupa, S., Nosal, M., Ferdinand, J.A., Stevenson, R.E., Skelly, J.M., 2003. A multi-variate statistical model integrating passive sampler and meteorology data to predict the frequency distributions of hourly ambient ozone (O_3) concentrations. Environmental Pollution 124, 173–178.

Linzon, S.N., Pearson, R.G., Donnan, J.A., Durham, F.N., 1984. Ozone effects on crops in Ontario and related monetary values. MOE Report ARB-13-84-Phyyo.

Lurmann, F.W., Nitta, B., Ganesan, K., Lloyd, A.C., 1984. Modeling potential ozone impacts from natural sources—III. ozone modeling in Tampa/St. Petersburg, Florida. Atmospheric Environment 18 (6), 1133–1143.

Mukammal, E.I., Neumann, H.H., Gillespie, T.J., 1982. Meteorological conditions associated with ozone in Southwestern Ontario, Canada. Atmospheric Environment 16 (9), 2095–2106.

National Oceanic and Atmospheric Administration, 2004. 〈http://www.arl.noaa.gov/ss/transport/archives.html〉 (accessed in August, 2004).

Ontario Medical Association, 2001. Ontario's Air: Years of Stagnation. Toronto, Ontario: June 2001.

Ontario Ministry of Environment, AQI, 2004. 〈http://www.airqualityontario.com/〉 (accessed in July, 2004).

Ontario Ministry of Environment, 2001. Air Quality in Ontario, 2001 Report. Toronto, Ontario.

Ontario Ministry of Environment, 2002. Air Quality in Ontario, 2002 Report. Toronto, Ontario.

Ontario Ministry of Environment, 2004. Air Quality in Ontario, 2004 Report. Toronto, Ontario.

Ontario Ministry of Finance, 2007. Ontario Population Projections. 〈http://www.fin.gov.on.ca/english/economy/demographics/projections/2006/〉 (accessed in February, 2007).

Spicer, C.W., Joseph, D.W., Sticksel, P.R., Ward, G.F., 1979. Ozone sources and transport into the Northeastern United States. Environmental Science and Technology 13, 975–985.

Yap, D., Ning, D.T., Dong, W., 1988. An assessment of source contributions to the ozone concentration in Southern Ontario, 1979–1985. Atmospheric Environment 22 (6), 1161–1168.

Zhang, F.Q., Bei, N.F., Nielsen-Gammon, J.W., Li, G.H., Zhang, R.Y., Stuart, A., Aksoy, A., 2007. Impacts of meteorological uncertainties on ozone pollution predictability estimated through meteorological and photochemical ensemble forecasts. Journal of Geophysical Research—Atmosphere 112 (D4) Art. No. D04304.

Zhang, Y., Pun, B., Wu, S.-Y., Vijayaraghavan, K., Seigneur, C., 2004. Application and evaluation of two air quality models for particulate matter for a Southeastern US episode. Journal of the Air & Waste Management 54, 1478–1493.

Zhang, Y., Liu, P., Queen, A, Pun, B., Seigneur, C., 2006a. A comprehensive performance evaluation of MM5-CMAQ for the summer 1999 southern oxidants study episode, Part I: Evaluation protocols, databases, and meteorological predictions. Atmospheric Environment 40, 4825–4838.

Zhang, Y., Liu, P., Queen, A., Misenis, C., Pun, B., Seigneur, C., Wu, S.-Y., 2006b. A comprehensive performance evaluation of MM5-CMAQ for the summer 1999 southern oxidants study episode, Part II. Gas and aerosol predictions. Atmospheric Environment 40, 4839–4855.

Zhang, Y., Liu, P., Pun, B., Seigneur, C., 2006c. A comprehensive performance evaluation of MM5-CMAQ for the summer 1999 southern oxidants study episode, Part III. Diagnostic and mechanistic evaluations. Atmospheric Environment 40, 4856–4873.