Supplementary Information (SI)

S1. Nighttime and rush-hour statistics for CO and $PM_{2.5}$ BC at Windsor (Tables 5 and 6 in main text)

For the nighttime period, the NMB of PM_1 POA increased to the same level as that for CO (100% vs. 99%), while the NMB for $PM_{2.5}$ BC remained similar to its daytime value (-41% vs. -48%). The correlation coefficient was also very similar for all three species at night (R=0.41, 0.43, and 0.43).

For the rush-hour periods, the campaign-mean model PM_1 POA value was unbiased (NMB=1%), but model CO was again overpredicted (NMB=121%). Model $PM_{2.5}$ BC performance was improved compared to other times of day with a NMB of -30% and a correlation of R=0.64. In looking at the measurements, there was less variation between day, night, and rush-hour times for all three species than there was for the model predictions. The campaign-mean model PM_1 POA value was highest at night whereas the measurements were highest during rush-hour. The campaign-mean model CO value was highest at rush-hour, consistent with the measurements. The campaign-mean model $PM_{2.5}$ BC value was highest at rush-hour, whereas measurement averages were very similar for all three periods.

S2. PM_1 POA and HOA time series for Windsor

Figure S1a illustrates the observed HOA and AURAMS PM_1 POA time series for the urban Windsor site. Overall, the model captures the multi-day variations associated with synoptic-scale changes in meteorology (e.g., minimum on July 3). The model also captures some of the early-morning maxima (e.g., maxima on June 25 and 30). Figure S2 illustrates the model time series for PM_1 POA, PM_1 SO_4, $PM_{2.5}$ BC, and CO and measurement-derived PM_1 HOA, PM_1 SO_4, $PM_{2.5}$ BC, and CO at Windsor from July 3 to midday July 5, 2007. The time period from July 3, 01:00-07:00 EST is of particular interest. Model PM_1 POA, PM_1 SO_4, and CO all increased during the first two hours; however, measurement-derived HOA, SO_4 and CO decreased in concentration. Interestingly, measured BC increased slowly and was predicted well (uncharacteristic, given that BC is typically biased low). The predicted surface temp was 5°C lower than measured on this night and modelled wind speeds were low and from the east. This analysis suggests that the modelled surface layer was too stable and that local Windsor POA emissions contributed to the maximum concentration.

The early morning period on July 4 was predicted well for PM_1 POA. Concentrations were moderately high in HOA and SO_4. An analysis of AURAMS surface distributions (not shown) suggested the SO_4 was of regional origin from the southwest with no distinct local plumes impacting the study sites. The model PM_1 POA, $PM_{2.5}$ BC and CO correlated in time with a large dynamic range in concentrations. Model PM_1 POA did correlate with PM_1 SO_4 from 00:00-06:00 EST, but not with the same dynamic range as PM_1 POA, $PM_{2.5}$ BC and CO. The PM_1 SO_4 change was a slower, more regional accumulation on this morning (00:00-06:00 EST). There is considerable variability in the measured PM_1 HOA data, but model bias was improved. Measured CO remained constant throughout the morning suggesting the measured PM_1 HOA change was not likely from mobile combustion sources, but rather from upwind, regionally mixed area and point sources.

Another period of interest on Figure S2 is from July 5, 00:00-5:00 EST when model PM_1 POA and model PM_1 SO_4 were correlated in time and significantly overpredicted vs. measurements. Model CO and $PM_{2.5}$ BC also increased during this time and were overpredicted, but not to the same extent as POA and SO_4. Winds were also very light on this night and were from the west, and the model underpredicted the surface temperature. When the winds were from the west, the site was influenced by local point sources across the Detroit River. A little later, model CO and $PM_{2.5}$ BC also have maxima at 06:00-08:00 EST, model PM_1 SO_4 decreased, but for this later morning period, modelled agreement for all species was variable in correlation but better in bias. Winds were more from the northwest. The high BC and CO concentrations suggest mobile sources from the urban core of Detroit were important from 06:00-8:00 EST. Overall, Figure S2 suggests that model mixing at night is a critical modelled parameter and that model POA was high in concentration within a local model SO_4 plume under stable conditions (July 5). At this time, however, the modelled PM_1 SO_4 plume was not captured in the PM_1 SO_4 measurements, so a more definitive statement cannot be made about the accuracy of the POA emission factor from this point source region.

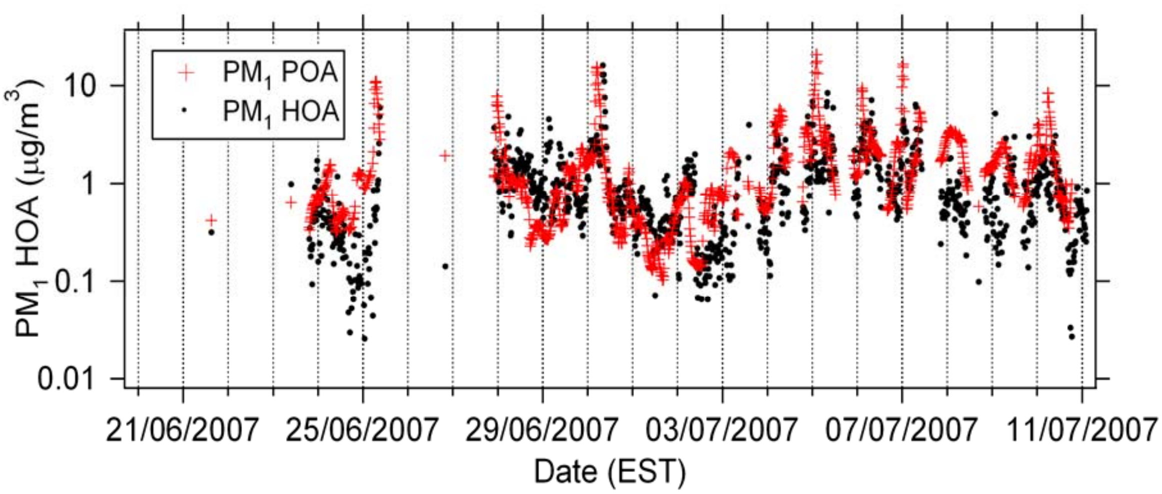
Figure S3 shows time series for the same set of model and measurement species at Windsor from July 8 to midday July 10, 2007. Over this 2.5-day period, the model PM_1 POA and model PM_1 SO_4 concentrations correlated closely while the measured PM_1 HOA and measured PM_1 SO_4 concentrations did not. The early morning period on July 8 (00-06 EST) showed good model and measurement agreement for PM_1 SO_4 in concentration and a very strong correlation between model PM_1 SO_4 and model PM_1 POA, whereas measured PM_1 SO_4 and PM_1 HOA showed no correlation: HOA concentration remained low and steady whereas measured SO_4 increased with time. In Figure S3b, the model BC follows the measured BC concentration time variations for the same period but is underpredicted in magnitude, similar to the overall campaign bias. In Figure S3c, the CO model time series is overpredicted during the early morning period on July 8 and the correlation with the CO measurements is poor. Wind speeds were relatively high from the southwest during the early morning on July 8. AURAMS surface distributions (not shown) showed influence from local sources along the Detroit River for POA, BC, CO and SO_4.

During the early morning period on July 10 (05-08 EST), the model PM_1 POA and vSO_4 concentrations showed a large maximum at a coincident time (06 EST) while measured HOA showed no change and the measured SO_4 showed a smaller local maximum on a higher background. For the measured maxima in SO_4 on July 10 at 12 EST, there was no coincident increase in HOA. Winds were very light from the southwest at this time. The measured $PM_{2.5}$ BC time series correlated with PM_1 HOA, but not with measured SO_4; however, model $PM_{2.5}$ BC, PM_1 POA and PM_1 SO_4 all correlated in time. Model $PM_{2.5}$ BC underpredicted measured $PM_{2.5}$ BC, by amounts similar to the campaign NMB. Measured and modelled CO showed little correlation in time. For the period (08-10 EST) when measured and model CO were high in concentration and agreed well, the modelled PM_1 POA and measured PM_1 HOA also agreed quite well. The time of the measured CO maximum was on the long tail of the model CO peak. For July 10 at 06 EST, the model CO maximum is at the same time as the model SO_4 maximum; however, the measured CO maximum was not coincident with the time of the measured SO_4 maximum. The measured CO maximum does not appear to be a sulphate plume but rather a gasoline combustion source during the morning rush-hour. Most importantly, the high measured SO_4 (~14 ug/m^3) at 12 EST does not correlate with high HOA. At 12 EST, the AURAMS surface distribution plot (not shown) displays high SO_4 channelling all along the Detroit River from the southwest. Overall, Figure S3 provides additional evidence that modelled POA is overestimated in the modelled sulphate plumes originating from southern Detroit sources, but compares better to HOA when the model is able to capture the CO plume from local gasoline combustion-related sources.

S3. Campaign time series for PM1 POA and HOA at Harrow and Bear Creek

Figure S1b shows time series of measured PM_1 HOA and AURAMS PM_1 POA for Harrow. Overall, the model does not capture the magnitude of the largest HOA maxima, whereas the lowest background concentrations are captured reasonably well by the model. HOA is underpredicted on the early mornings of June 20, 21, 24, 30 and July 2, 3, and 6-9. The model POA is also underpredicted for a number of daytime periods at Harrow: June 21, 24, 30 and July 6-9. Only on June 28 does the model POA consistently overestimate the HOA factor at Harrow.

Figure S1c shows time series of measured PM_1 HOA and AURAMS PM_1 POA for Bear Creek. AURAMS still underpredicts some of the HOA maxima, but the level of agreement can be considered good, especially for the July 4-9 period. Some of the daytime variations are captured quite well by the model (e.g., July 5, 9).



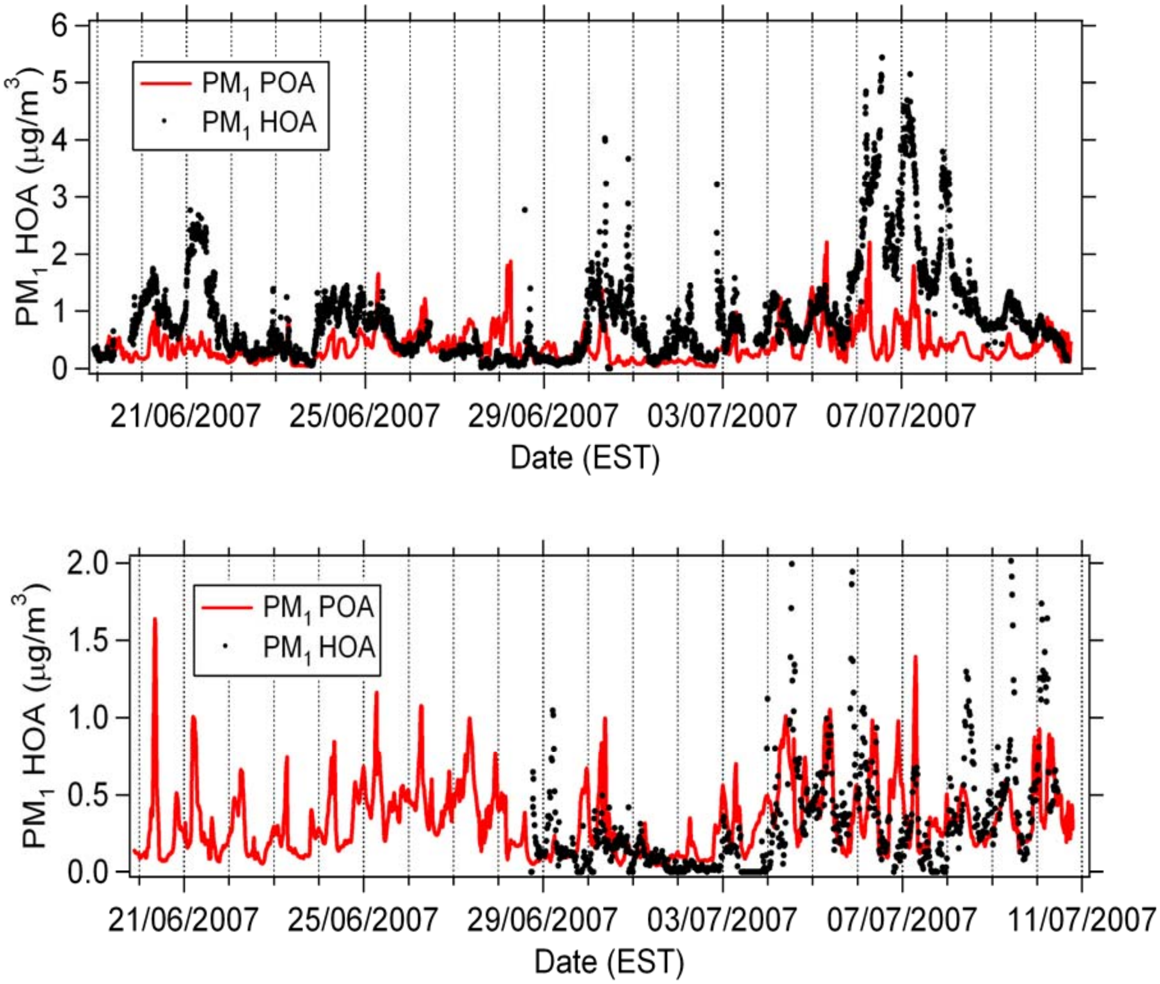


Figure S1. Time series for HOA plotted with AURAMS PM_1 POA at Windsor (top panel), Harrow (middle panel), and Bear Creek (lower panel).

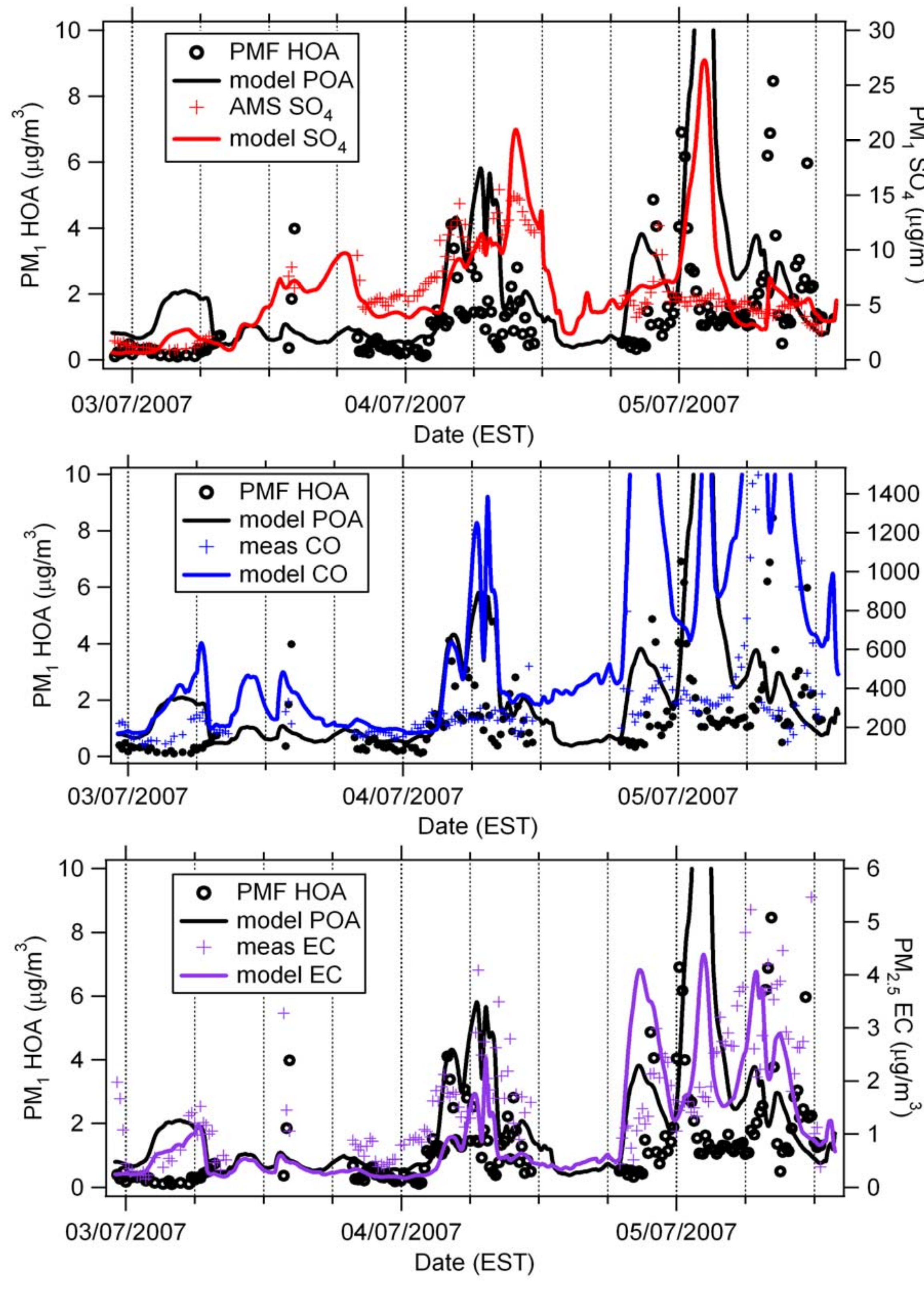


Figure S2. Selected model PM_1 POA and HOA time series at Windsor from July 3 to July 5 plotted with time series of (a) PM_1 SO4, (b) CO and (c) $PM_{2.5}$ EC measurements and model predictions.

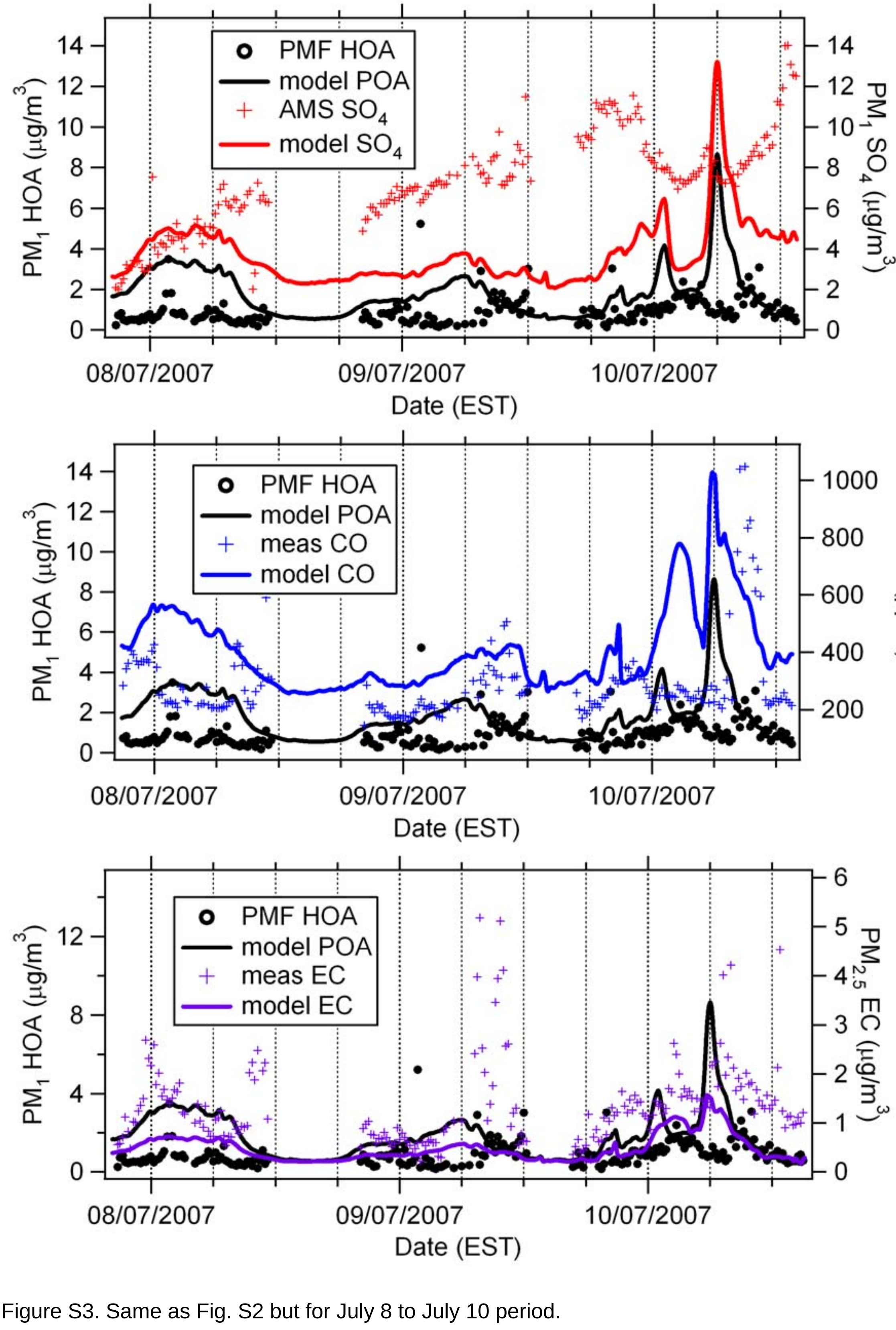


Figure S3. Same as Fig. S2 but for July 8 to July 10 period.

S4. Case Studies

S4.1 Transport from the southwest (figures below)

It was observed that several periods of transport to the region from the southwest also resulted in negative POA biases at the rural supersites. Table S1 lists the two representative case studies (CSs) for the transboundary transport of air masses to the study region from the southwest. Both case studies are for Harrow; thus, emissions from the Detroit-Windsor air shed are not involved. The case study periods (June 27, July 8) were also selected for times when the ATOFMS PMF analysis in McGuire *et al*. (2011) diagnosed a long-range "Transport" factor. The "Transport" factor consisted of three highly-aged single-particle types, namely aged carbonaceous particles (BC and OC cores) with significant coatings of sulphate, ammonium, and oxidized organic fragments and two aged dust particle types. It was hypothesized that the transport mechanism could either be transport aloft over Lake Erie followed by fumigation during the breakdown of the stable marine surface layer on passage over land near Harrow or near-surface transport across Lake Erie followed by on-shore flow behind a lake-breeze front. AURAMS simulations should be able to provide further guidance to support one of these pathways or else to recommend other transport pathways.

On July 8 at Harrow, the PM_1 POA NMB was -73% for the period from 10-14:50 EST. Back trajectories suggest the surface air had originated in the U.S. Midwest and passed over the Toledo airshed (see Sec. S5, CS 2a). This is consistent with the AURAMS PM_1 POA surface distribution (Figure S4), which shows a surface plume originating from the Toledo urban area in addition to a point-source plume originating just south of Toledo. [Note that this case study for Harrow is simultaneous with the urban-plume case study for Bear Creek discussed in the main body.] The vertical cross section at Harrow at 18 UTC, which is perpendicular to the surface wind direction, shows an elevated POA layer (~1000 m) which is likely a signature of longer-range transport. A look at the 870-m layer horizontal distribution showed some directional shear compared to surface and a source of the elevated layer from the Monroe power plant, which is located at the west end of Lake Erie to the northeast of Toledo (Figure S4). It appears that after advection of the elevated polluted layer over Lake Erie to the warmer land near Harrow, the elevated POA layer was mixed down to the surface, resulting in the increase in modelled POA at the surface. Thus, the model suggests that Harrow was impacted by POA emissions from both Toledo and the Monroe power plant that were transported across Lake Erie at different vertical levels before mixing down to the surface. No model POA plumes were observed at the surface or aloft upwind of the Toledo or Monroe POA sources. CO was also underpredicted to a greater degree than the CO campaign-mean at Harrow (NMBs of -25% vs. 2%), so the cause of the CO and POA underprediction may be common. Note that the measurement-derived HOA may also include some SOA from the oxidation of long-carbon-chain organic compounds in the NOx-rich plumes, thus exaggerating the model's PM_1 POA underprediction.

Another interesting case period identified by the ATOFMS PMF and labelled long-range "Transport" was on June 27 at Harrow (Table S1). The PM_1 POA NMB for the period from 10:30-14 EST was +17%, which can be considered good model-measurement agreement. Back trajectories originated over the U.S. Midwest (see Sec.

S5, CS 2b). The measured PM_1 HOA and model PM_1 POA means were 0.40 ± 0.14 $\mu g/m^3$ and 0.47 ± 0.10 $\mu g/m^3$, respectively. The AURAMS PM_1 POA surface distribution and cross-section (Figure S5) perpendicular to the surface wind direction on June 27 at 13 EST (18 UTC) showed evidence for the transport of an elevated plume (600-1100m) over Lake Erie followed by fumigation to the Harrow surface site. Figure S5 shows the AURAMS PM_1 POA horizontal distribution at 815 m and vertical cross section parallel to the surface wind direction at the same time. The elevated plume originated in the model from the Monroe power-generation plant. A vertical cross section (not shown) perpendicular to but further upwind (southwest) of the power-plant source did not show signs of this elevated plume aloft. The mixing heights predicted over land in the cross section are similar to the LIDAR PBL heights measured at Ridgetown. The modelled and measured SO_4 values listed in Table S1 were higher than the campaign-mean values (i.e., 7.4 vs. 3.3 ug/m^3 and 4.5 vs. 2.8 $\mu g/m^3$). The model PM_1 SO_4 NMB value of 64% suggests the model plume may have more directly impacted the Harrow location than was observed. The high POA in the modelled power plant emissions coupled with the high modelled SO_4 may partially explain the model positive bias for this case compared to the July 8 case. The NMB value for CO was low (-11%) and for BC was a typical value (-77%). Point sources in the model do not emit large amounts of either CO or BC. Thus, the interpretation from the model results is consistent with the “transport aloft” hypothesis suggested in McGuire *et al*. (2011) for the longer-range “Transport” factor.

Collectively, these two cases showed a mean PM_1 POA NMB in the range from +17% to -73%, with the positive bias representing a period when the model predicted higher SO_4 and the negative bias representing a period when the model underpredicted CO and SO_4. Overall, the wind direction from the west to southwest was the second-most frequent direction during the campaign period, and wind speeds for these times tended to be higher than those from the northwest (Sills et al., 2011). These two cases suggest that frequent modelled POA underpredictions for transboundary transport flow from the U.S. midwest are also contributing to the campaign-mean negative bias at Harrow.

Table S1. Transport from Southwest

Date (EST)	Model POA HOA NMB RMSE	HOA/ OA	Winds	Meteorology	Model BC Meas. BC NMB RMSE	Model CO Meas. CO NMB RMSE	Model SO4 Meas. SO4 NMB RMSE	PMF Source Description
Harrow July 8 10-14:50	0.33 ± 0.12 1.2 ± 0.2 -73 % 0.95 $\mu g/m^3$	16 %	SW moderate	Well predicted, evidence for polluted layer aloft	0.16 0.67 -76 % 0.52 $\mu g/m^3$	186 248 -25 % 64 ppbv	3.2 5.2 -39 % 2.5 $\mu g/m^3$	“Transport” US Midwest
Harrow June 27 10:30-14	0.47 ± 0.10 0.40 ± 0.14 17 % 0.10 $\mu g/m^3$	21 %	SW moderate	Well predicted, evidence for polluted layer aloft	0.16 0.70 -77 % 0.54 $\mu g/m^3$	207 231 -11 % 35 ppbv	7.4 4.5 64 % 3.0 $\mu g/m^3$	“Transport” US Midwest

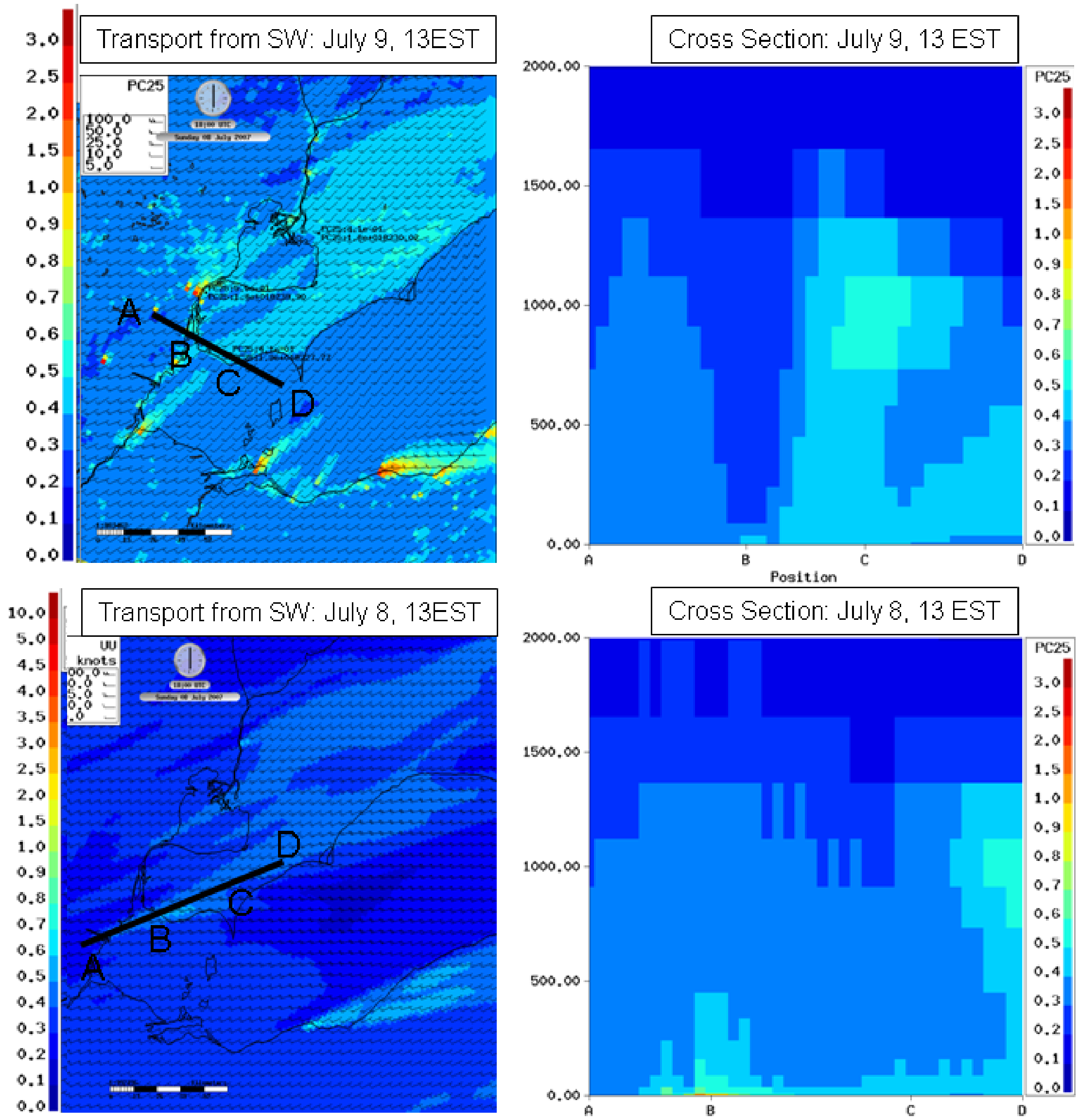


Figure S4. AURAMS (a) PM_1 POA distribution with superimposed surface wind vectors for July 8, 2007 at 13 EST (upper left) and (b) vertical cross section perpendicular to surface wind direction at Harrow from point A in northwest to point D in southeast (upper right), (c) PM_1 POA distribution at 815 masl with superimposed surface wind vectors for July 8, 2007 at 13 EST (lower left) and (d) vertical cross section parallel to wind direction at Harrow from point A in southwest to point D in northeast (lower right).

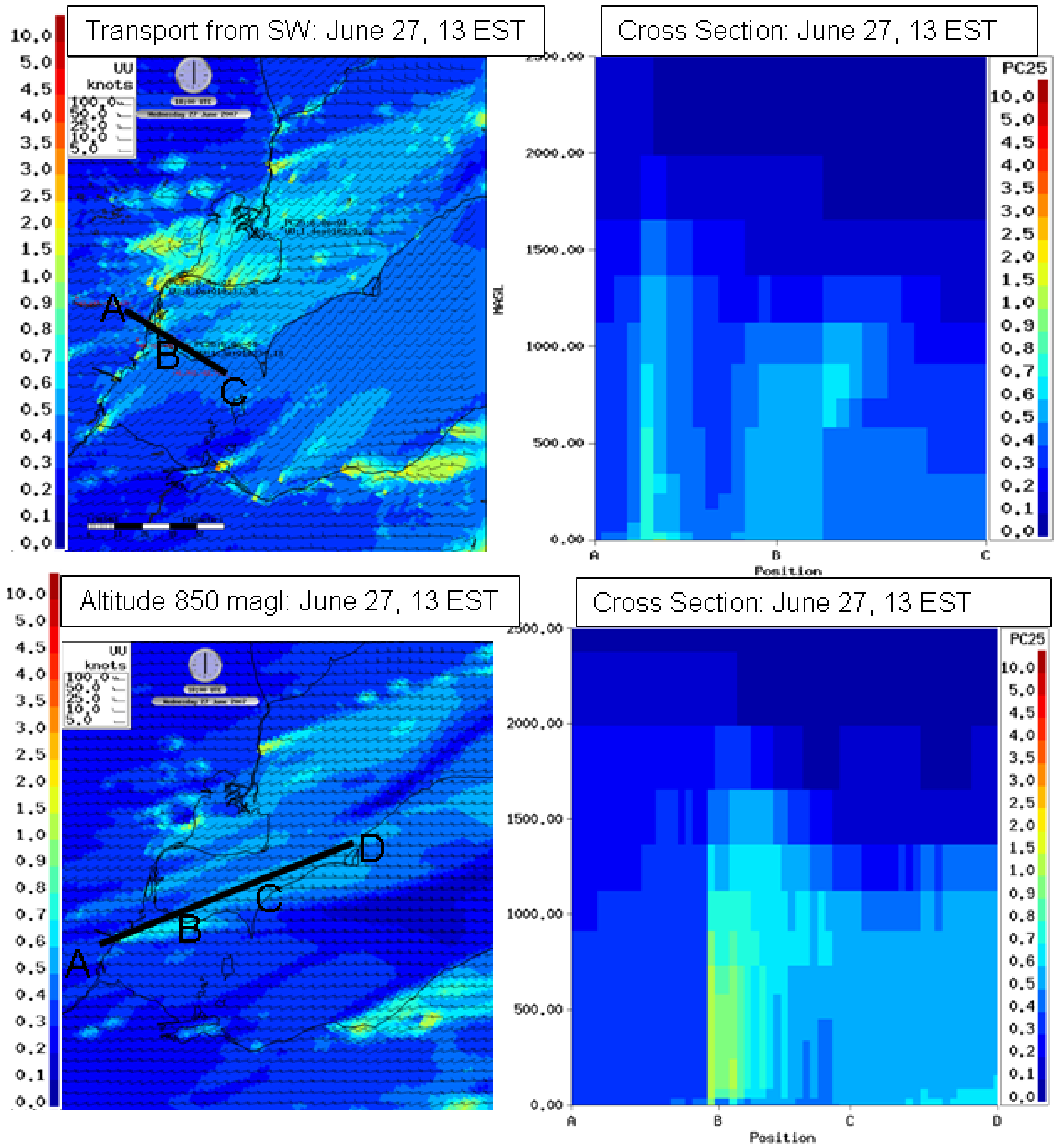


Figure S5. AURAMS (a) PM_1 POA surface distribution with superimposed surface wind vectors for June 27, 2007 at 13 EST and (b) vertical cross section perpendicular to surface wind direction at Harrow from point A in northwest to point C in southeast, (c) PM_1 POA distribution at 815m with superimposed surface wind vectors for June 27, 2007 at 13 EST and (d) vertical cross section parallel to surface wind direction at Harrow from point A in southwest to point D in northeast.

S4.2 Regional Background from the North

Table S2 lists two representative cases for Bear Creek sampling air masses from the north with moderate winds speeds (see Sec. S5, CS 4a,b for mesoscale analysis and back trajectories). Northwest was the predominant wind direction for Bear Creek. There was no indication of influence from local pollution sources or biomass burning in the measurements. Model and measured mass concentrations were in the range 0.1 to 0.2 $\mu g/m^3$, with only small NMB values of -19% and 1%. This good level of agreement suggests that rural ORM and ORAA POA sources to the north of the study region are represented well in the model.

Table S2. Regional Background from the Northwest

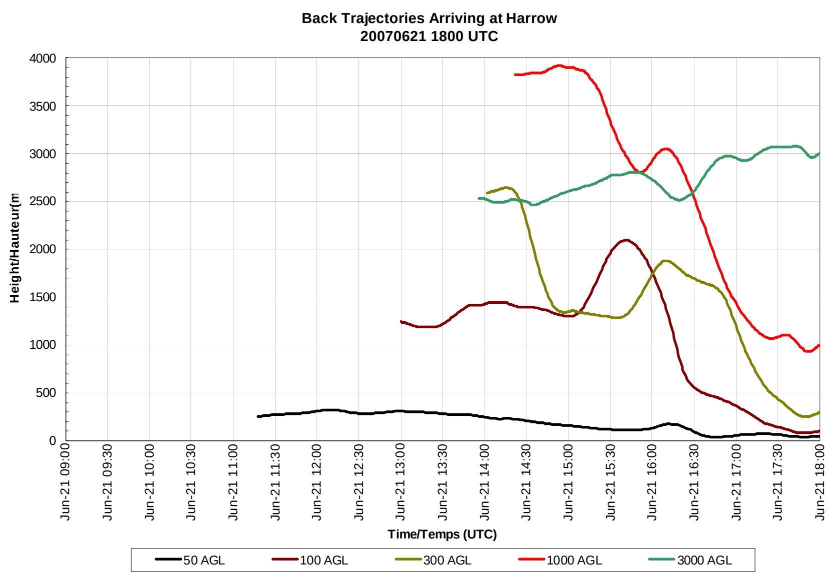
Date (EST)	Model POA HOA NMB RMSE	HOA/ OA	Winds	Meteorology	Model BC Meas. BC NMB RMSE	Model CO Meas. CO NMB RMSE	Model SO4 Meas. SO4 NMB RMSE	PMF Source Description
Bear Creek June 29 12-15	0.10 ± 0.009 0.13 ± 0.02 -19 % 0.032 $\mu g/m^3$	5 %	N moderate	Winds predicted well, no plumes	0.042 0.11 -61 % 0.07 $\mu g/m^3$	130 95 37 % 35 ppbv	0.36 0.51 -30% 0.12 $\mu g/m^3$	Not Available
Bear Creek June 30 12:30-15	0.17 ± 0.06 0.17 ± 0.05 1 % 0.04 $\mu g/m^3$	4 %	NE moderate	Winds predicted well, no plumes	0.055 0.17 -69 % 0.14 $\mu g/m^3$	136 179 -24 % 61 ppbv	2.7 0.99 160% 1.6 $\mu g/m^3$	Not Available

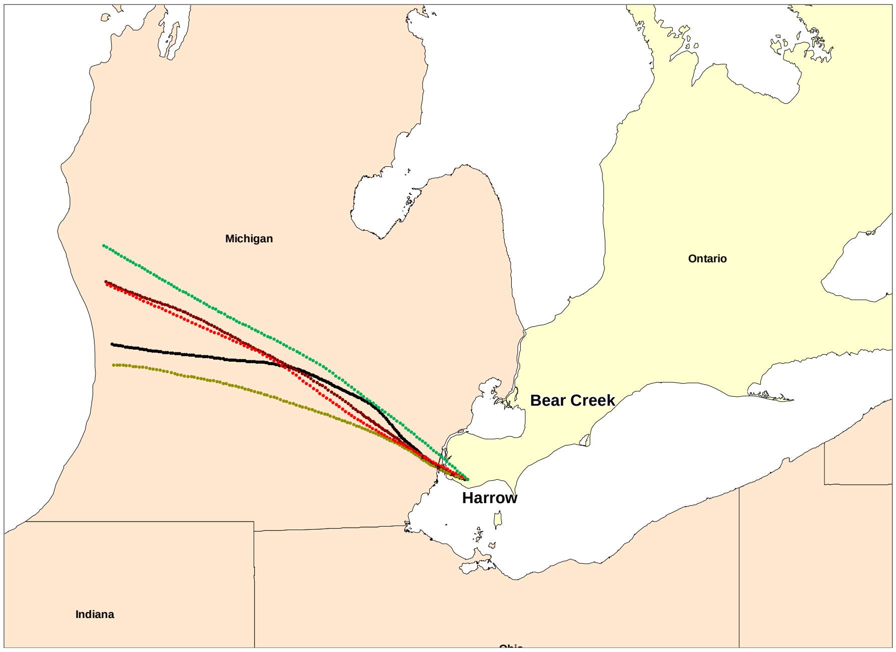
S5. Mesoscale Meteorology Analysis and Back Trajectories for all Case Studies

S5.1 Detroit-Windsor urban-influenced air masses arriving at Harrow and Bear Creek

(a) Harrow, June 21, 2007, 16:00 UTC (11 EST)

Image shows moderate winds from NW and no presence of lake breezes near Harrow. Cloud band passes through from north at 17 UTC. No change in wind direction on cloud passage.

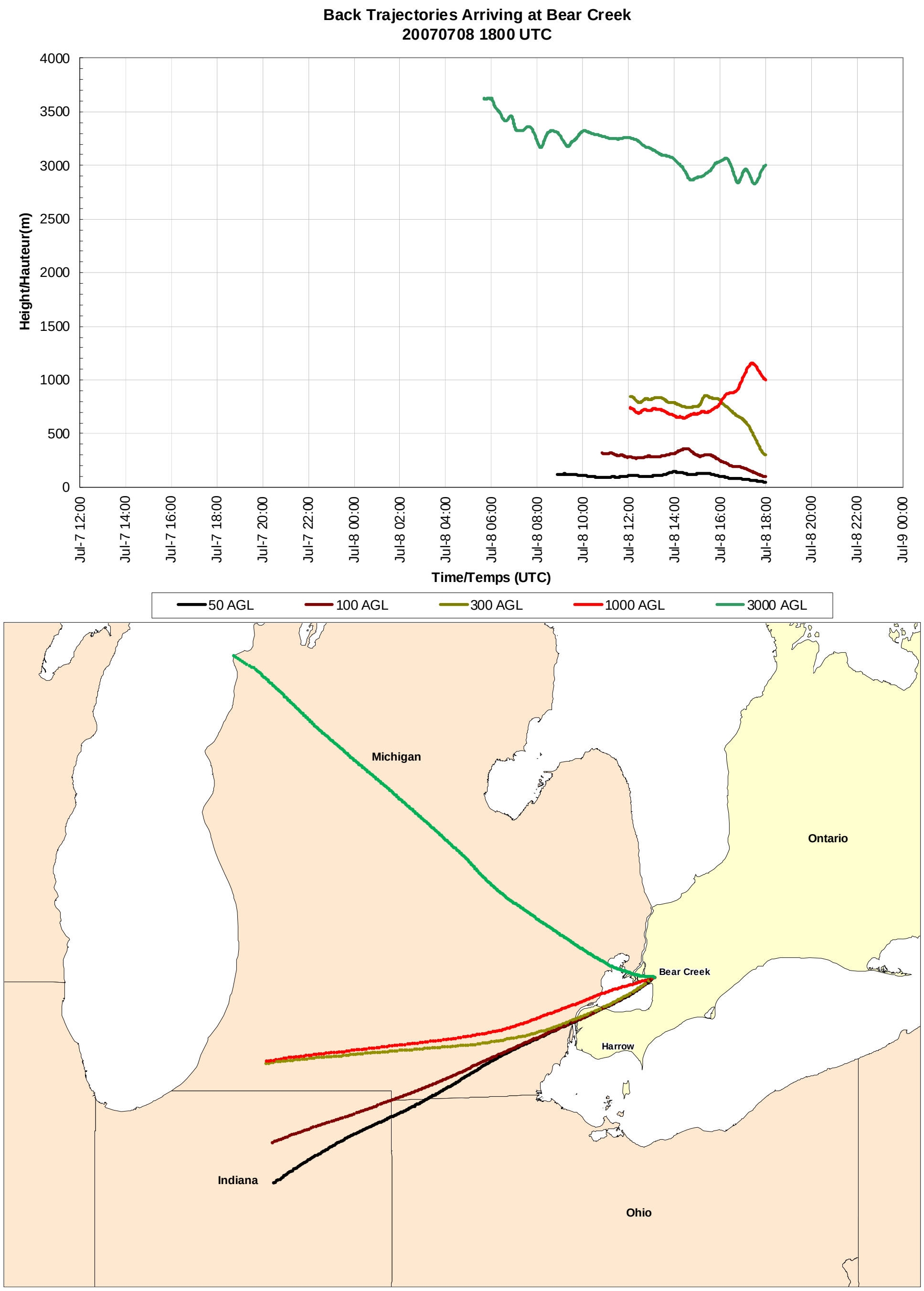




18 UTC back trajectories from Harrow, ON beginning at five heights: 50, 100, 300, 1000, and 3000 m a.g.l. The trajectories suggest that large-scale synoptic subsidence is present, but there is little directional wind shear for this period for generally WNW flow.

(b) Bear Creek, July 8, 2007, 18 UTC (13 EST)

Image shows moderate winds from the SW. The weather was hot with clear skies over Harrow. Some light cloud over Bear Creek at 17 UTC. No lake-breeze passages at supersites.

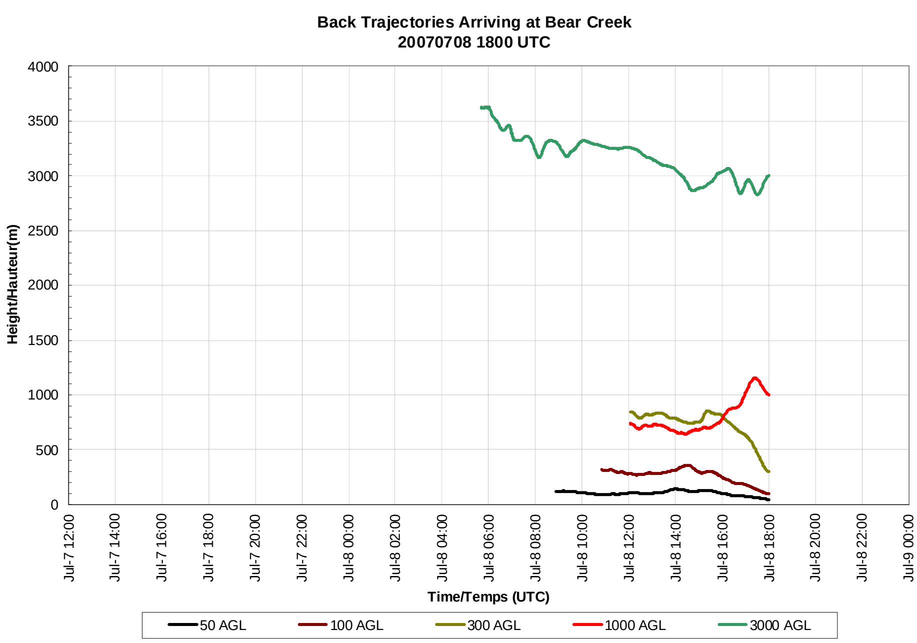


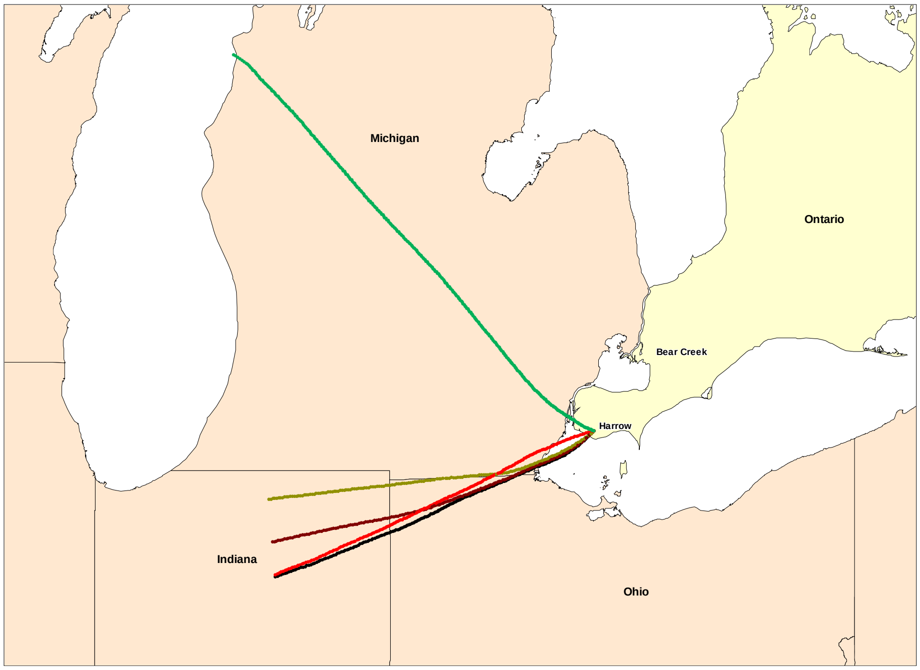
18 UTC back trajectories from Bear Creek, ON beginning at five heights: 50, 100, 300, 1000, and 3000 m a.g.l. The trajectories suggest that there is little directional wind shear or speed shear for this period near the surface (first 1000 m) associated with low-level southwesterly flow. There is directional shear between boundary layer and free troposphere.

S5.2 Transport from the southwest

(a) Harrow, July 8, 2007, 18 UTC (13 EST)

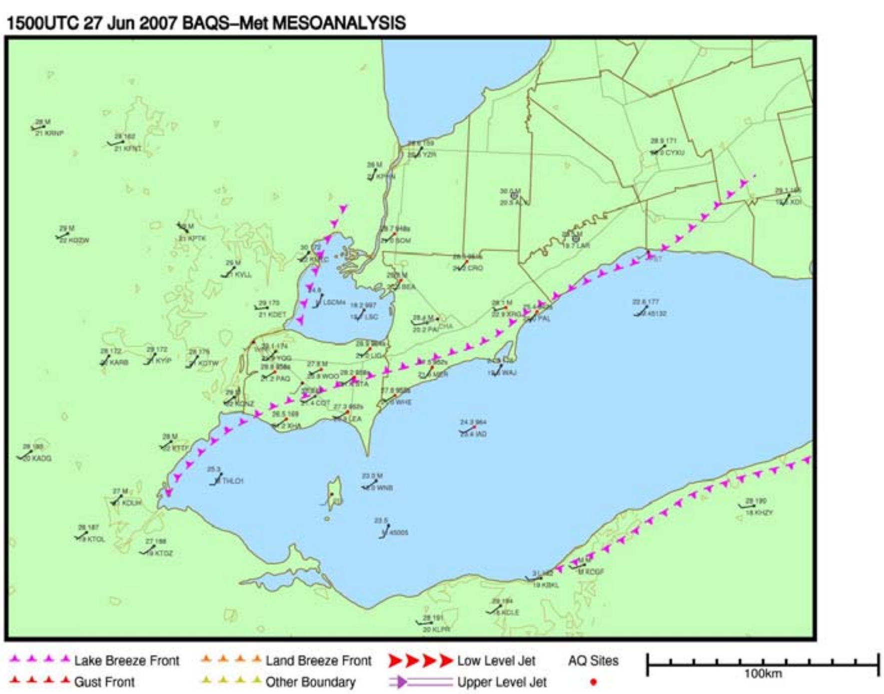
Image shows moderate winds from the SW. The weather was hot and clear skies over Harrow. Some light cloud over Bear Creek at 17 UTC. There were no lake-breeze passages at the supersites.



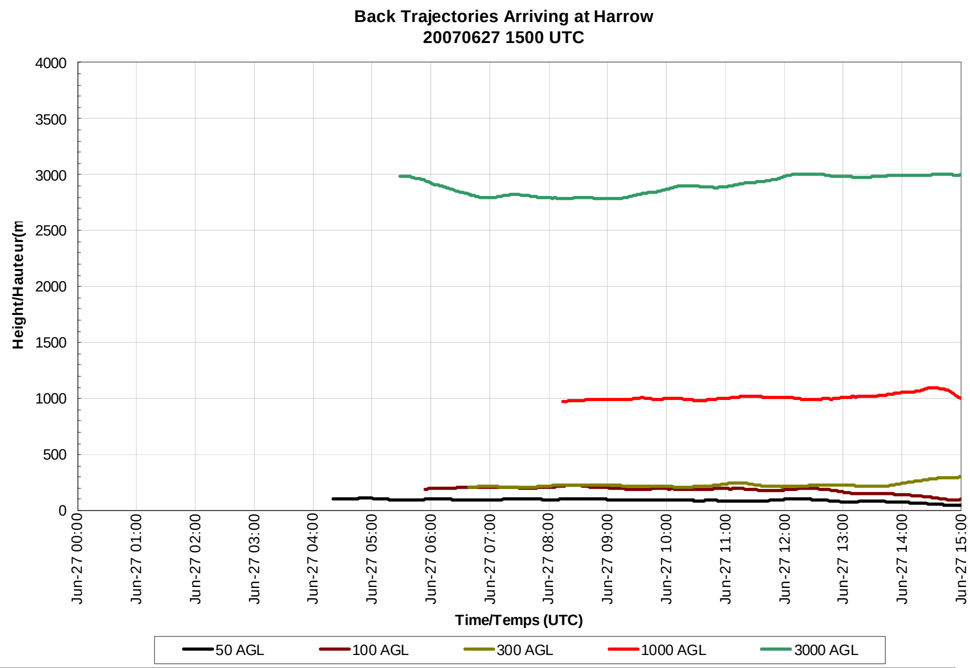


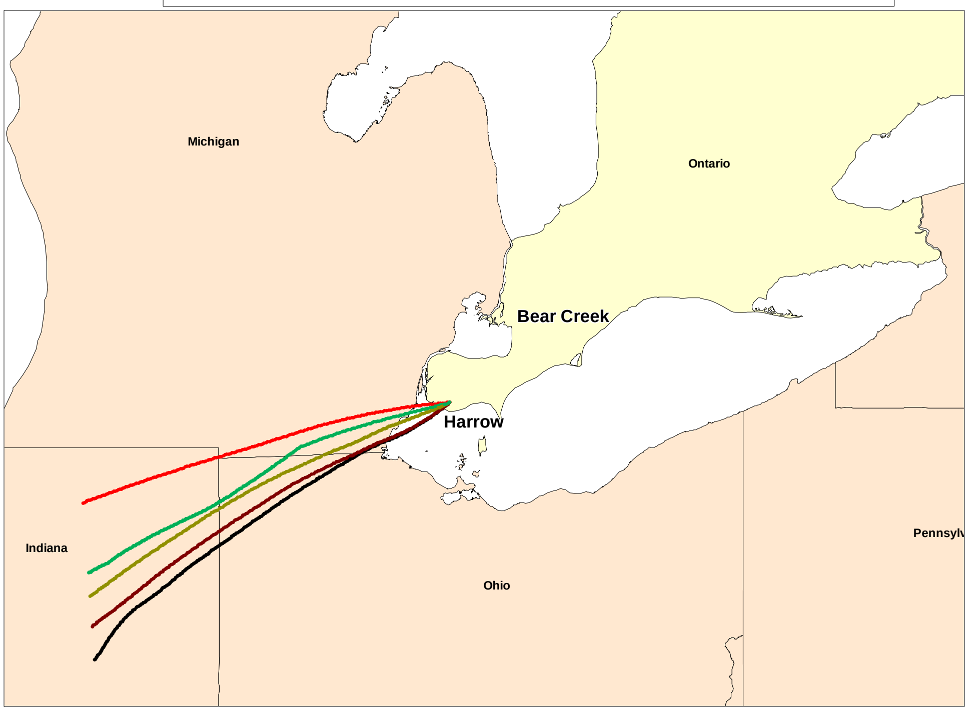
18 UTC back trajectories from Harrow, ON. The trajectories suggest that there was a little directional wind shear between 1000m level and the surface layers for this period, especially near Harrow. There was large directional shear between boundary layer and free troposphere.

(b) Harrow, June 27, 2007, 15 UTC (10 EST, start of case study)



The mesoscale analysis shows a recent lake-breeze passage at Harrow. The case study period was characterized by moderate winds from the southwest at the surface.



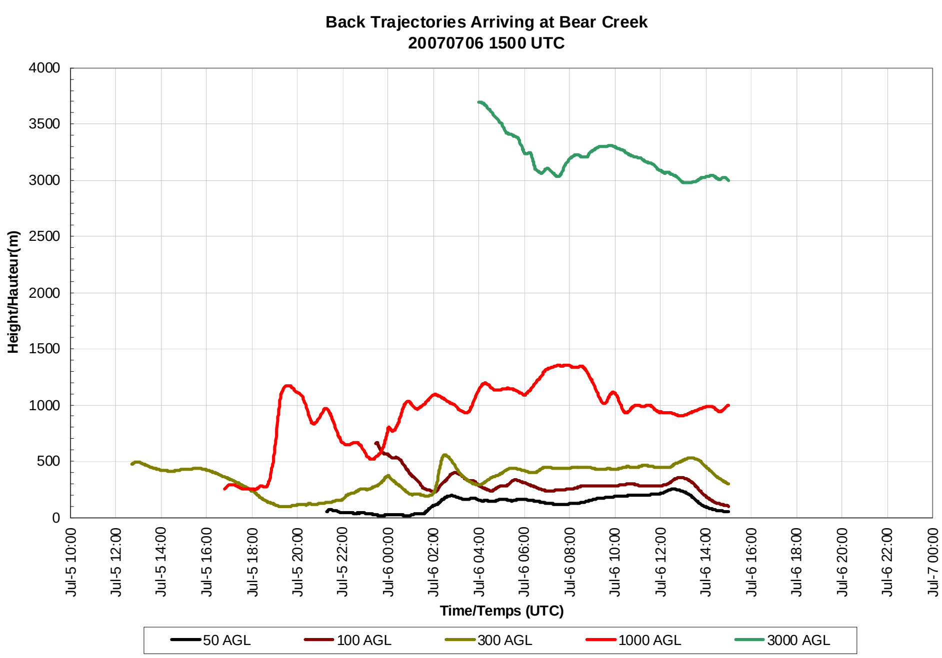


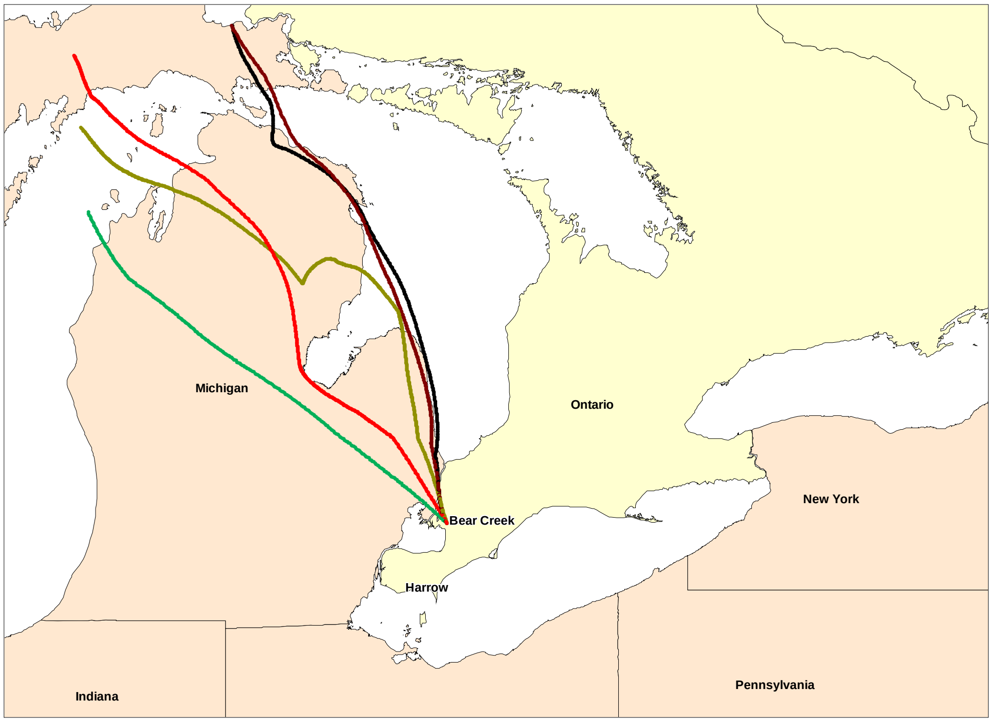
15 UTC back trajectories from Harrow, ON. The back trajectories suggest that there is a little directional wind shear for this period in the boundary layer in low-level southwesterly flow and virtually no subsidence. The 1000 m level had a more westerly component to the flow compared to 50 m and 100 m level.

S5.3 Biomass Burning Cases

(a) Harrow, July 6, 2007, 15-18 UTC (10-13 EST)

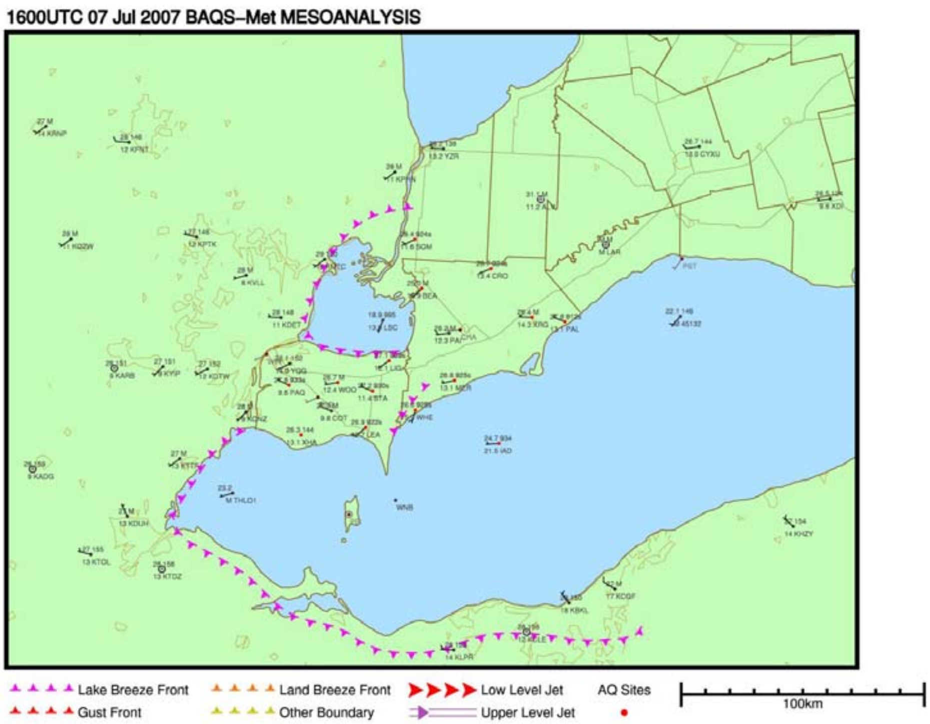
The weather was clear skies. Long-range transport from northern Michigan and Canadian Prairies dominated. There were no lake-breeze passages at the supersites.



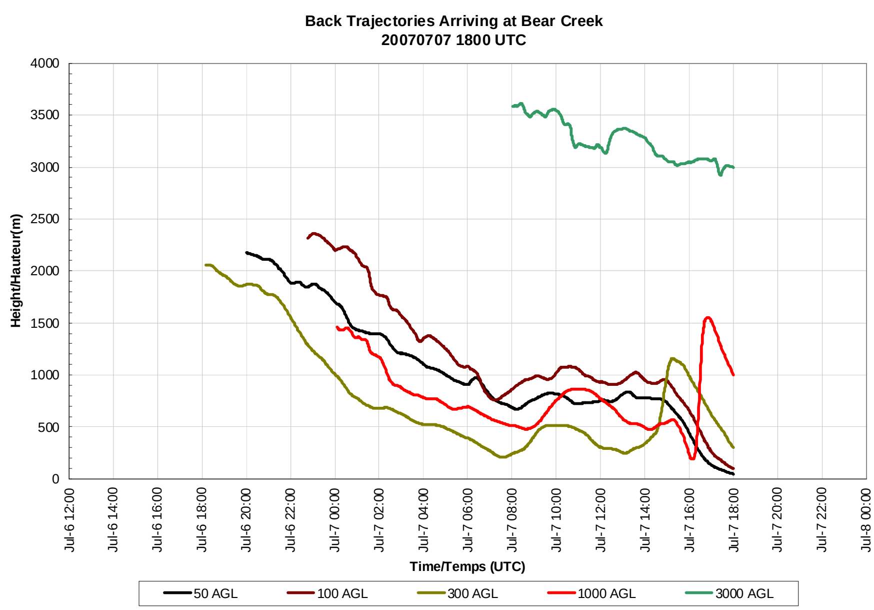


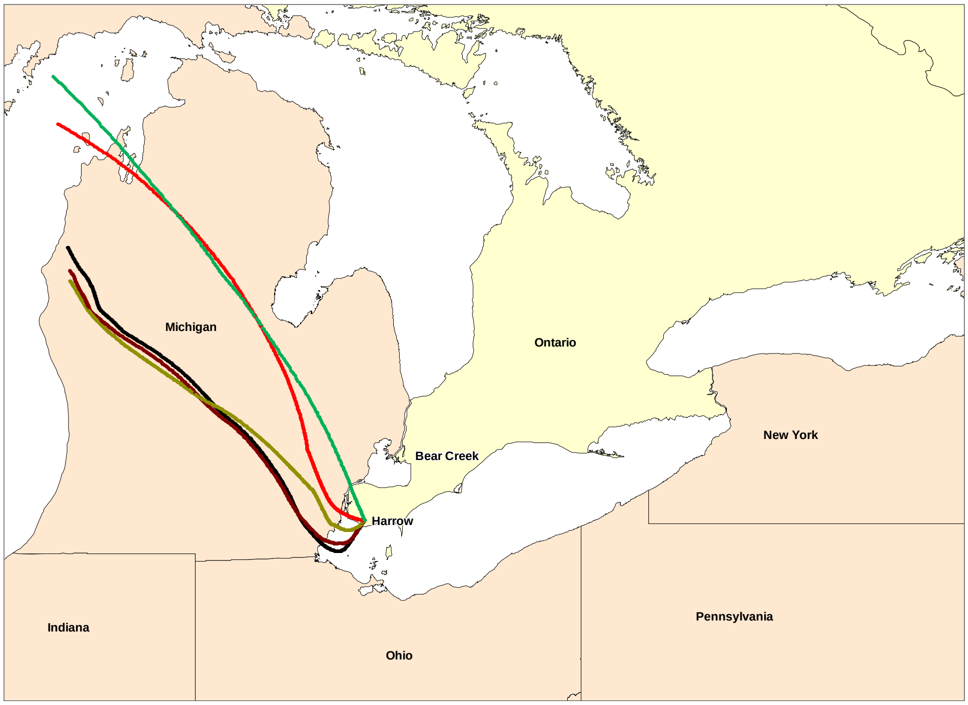
15 UTC back trajectories from Harrow, ON. The upper back trajectories display some directional shear (backing) but near-surface flow is northerly with little subsidence.

(b) Harrow, July 7, 2007, 14-20 UTC (9:00-14:50 EST)



Some enhanced radar reflectivity was observed at 14 UTC, but by 16 UTC it had vertically mixed and dissipated. There was no lake breeze at Harrow.

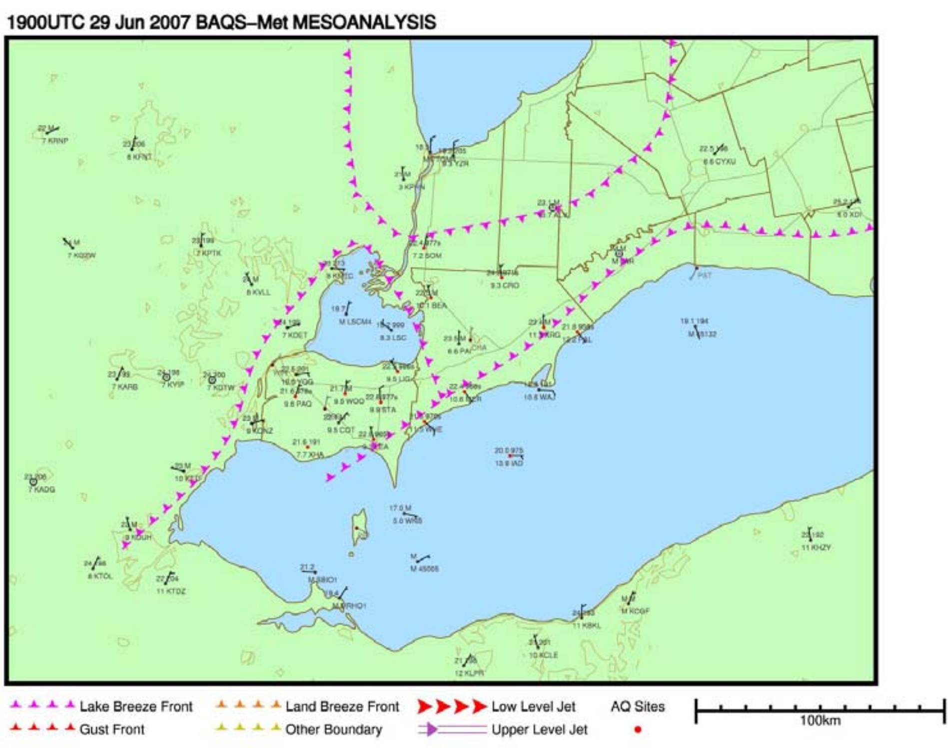




18 UTC back trajectories from Harrow, ON. Although the low-level transport at Harrow is from the southwest, the air parcels originate in descending northwesterly flow.

S5.4 Regional Transport from North

(a) Bear Creek, June 29, 2007, 17-20 UTC (12-15 EST)



The image shows the Lake St. Clair lake breeze has not reached Bear Creek. Low-level flow is northerly.

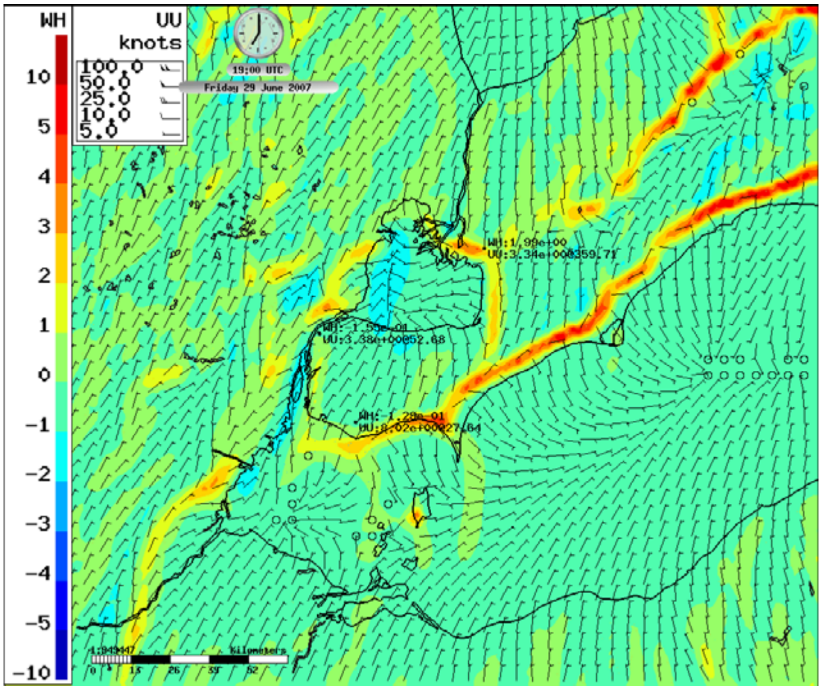
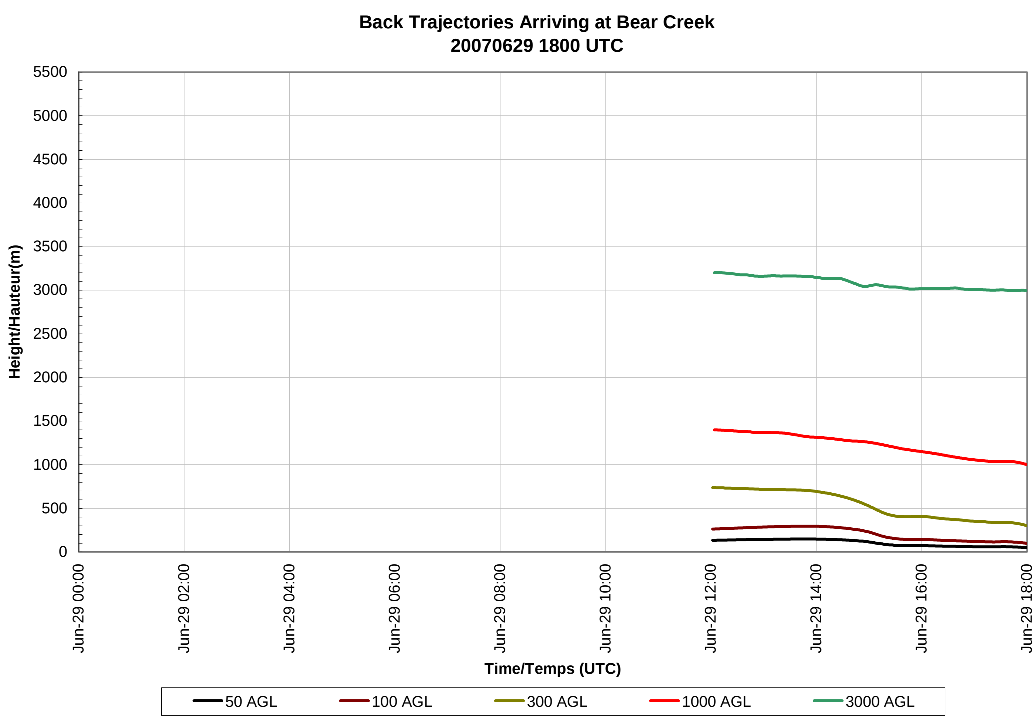
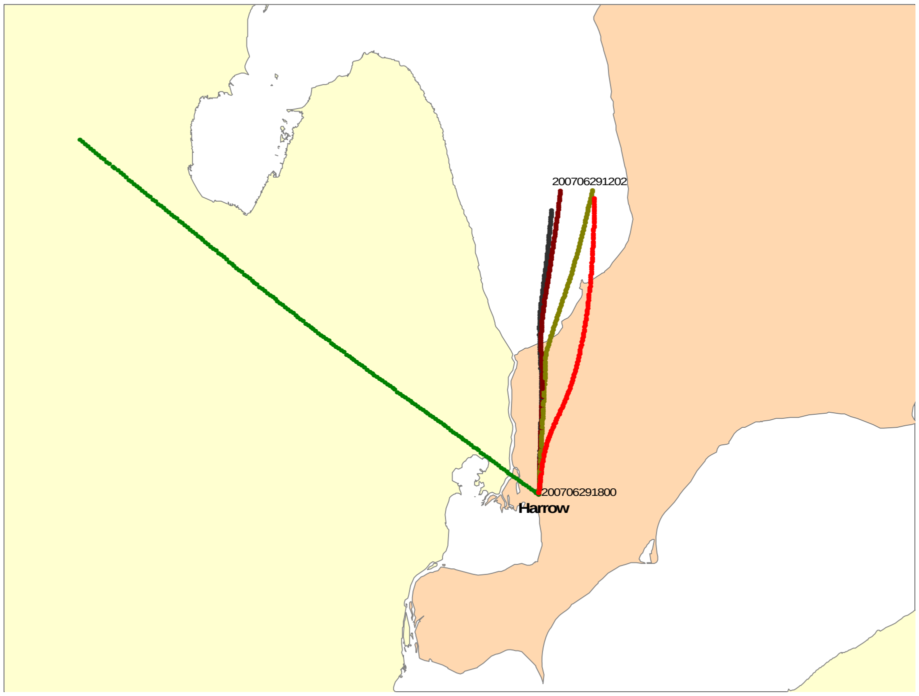


Image illustrates model predicted vertical velocity fields at 19 UTC at 395m. Areas of rising motion agree well with the prior image from the mesoscale analysis of lake-breeze-front positions.

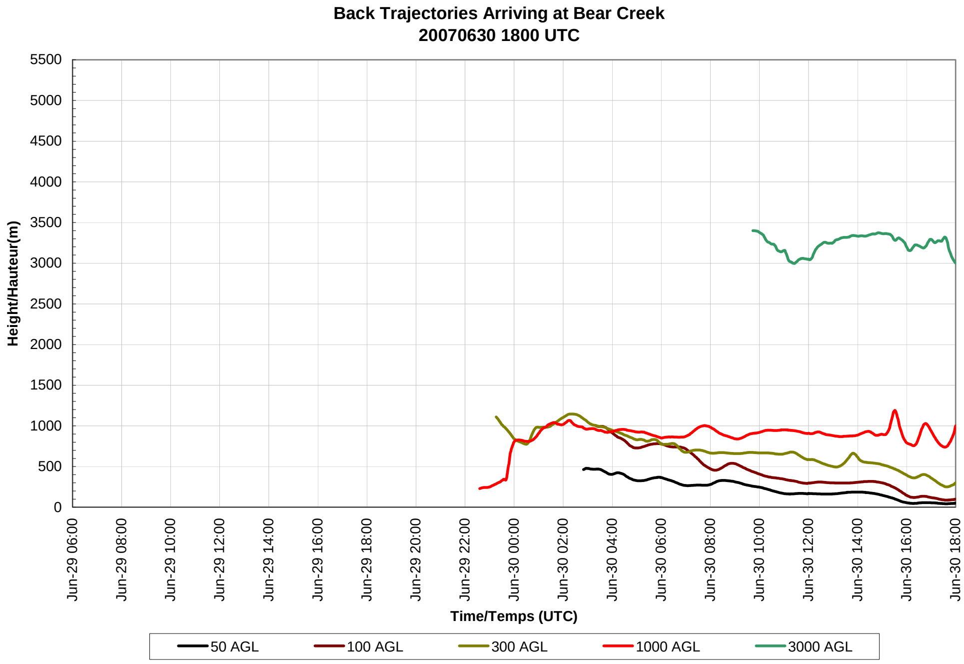


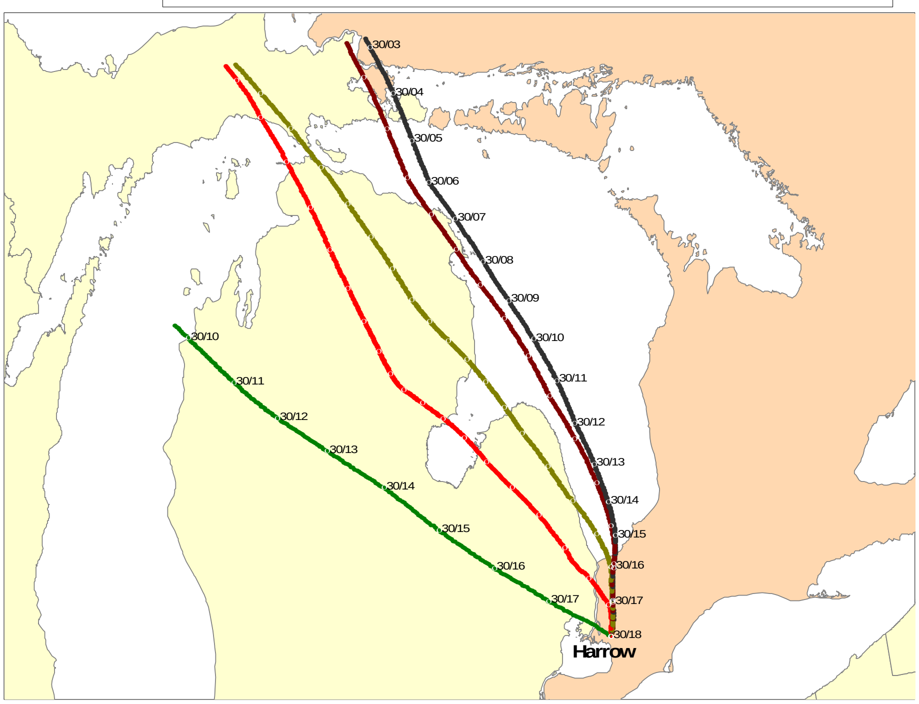


Back trajectory could only be calculated for 6 hr due to lack of meteorology data. The back trajectory and vertical cross section show northerly flow and descending air.

(b) Bear Creek, June 30, 2007, 17-20 UTC (12-15 EST)

18 UTC meso-analysis is quite similar to analysis for previous day (see Case 4a). The gust front passes through Bear Creek from the north just after the end of the defined case study period.





The back trajectory and vertical cross section show northerly flow and slowly descending air.