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MODELING THE WEEKDAY/WEEKEND DIFFERENCES OF AIR TOXICS
Task 3 Report

June 2006

COORDINATING RESEARCH COUNCIL, INC.
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Task 3 Report
CRC Project A-49

Modeling the Weekday/Weekend Differences of Air Toxics

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Executive Summary

The goals of CRC Project A-49 are to (1) assess the current state of knowledge of air toxics related to mobile source emissions, (2) analyze the ambient concentrations of air toxics associated with mobile sources to tease out weekly signals, if any, that may be attributed to mobile source emissions, and (3) conduct modeling and compare modeling results against the observed weekly profiles to assess the accuracy of the temporal representation of emissions used in the current inventories. Under Task 1, recent air toxics modeling studies were reviewed and recommendations were made for areas of improvement, including an analysis of the weekday/weekend differences in air toxics concentrations and improvements in the emissions data and spatial and temporal allocation factors. A Task 2 report was submitted in January 2006 (Pun et al., 2006), which summarizes the data analysis task for New York City, NY; Philadelphia, PA; and Houston, TX. Briefly, elemental carbon (EC, a tracer for diesel particles in urban areas; the correlation between EC and diesel particles is weaker in rural areas due to other sources of EC, e.g., biomass burning) shows a strong weekly cycle, with the East Coast cities showing larger weekday-weekend differences than Houston. Formaldehyde shows no discernable weekly cycle at moderate concentrations, but there is some indication of a weekend increase in the East Coast cities when concentrations are high. Weekday/weekend differences in 24-hour average benzene are insignificant at many locations, but the weekday/weekend differences in rush-hour concentrations are significant.

In this task (Task 3), we test the ability of air quality models to reproduce these weekly trends in toxic air pollution. The Community Multiscale Air Quality (CMAQ) model was applied in the northeastern United States with two sets of emissions, representing a weekday scenario (Monday through Friday) and a weekend scenario (Thursday through Monday). To isolate the effect of weekly changes in anthropogenic emissions, meteorology, biogenic emissions, and other modeling conditions were kept constant between these two simulations.

Based on the 1996 National Emissions Trends Inventory and the 1996 National Toxics Inventory for the northeastern United States domain, the main source of diesel PM is heavy-duty vehicles, whereas the main source of benzene is light-duty gasoline cars and trucks. The Sparse Matrix Operator Kernel Emissions model (SMOKE) is used to allocate the inventoried emissions including heavy-duty and light-duty vehicle emissions, to different days of the week using source-specific temporal profiles. As a default, SMOKE uses the same day-of-the-week temporal profiles for heavy-duty and light-duty vehicle emissions. For urban areas, the average Saturday and Sunday emissions are estimated to be 25% less than the weekday emissions for both gasoline and diesel vehicles, according to the default weekly profile in SMOKE. The weekly cycle on rural roadways is less pronounced.

Modeling results are analyzed at locations corresponding to monitoring sites in New York City and Philadelphia and compared to the average weekly cycles deduced from Task 2. For the two primary pollutants, diesel PM and benzene, changes in their respective emission patterns during weekends are identifiable in the simulated diurnal concentrations on weekdays vs. weekend days. In urban areas, the weekday-weekend differences in total emissions are dominated by changes in activities of heavy-duty vehicles for diesel particles and light-duty gasoline vehicles for benzene, because other important source categories either do not show a weekly pattern (e.g., 2-stroke engines and wildfires) or are associated with rural locations (e.g., agriculture or mobile sources on rural highways). On a percentage basis, the weekly signal in diesel PM was underrepresented in the simulations (9 to 11% decrease during weekends at sites in New York City and 11 to 15% at sites in Philadelphia) compared to ambient data (21 to 48% decrease during weekends in New York City; 32 to 38% in Philadelphia). On the other hand, the weekly signal of benzene in the simulations (13 to 17% decrease during weekends in New York City and Philadelphia) is more significant than that indicated by the ambient data (6 to 7%). Based on these results, we estimate that on average, an increase by a factor of 2.5 in the magnitude of the SMOKE default weekly cycle in the urban emissions from heavy-duty vehicles would be needed to reproduce the percentage decrease observed in New York City and Philadelphia. An average decrease by a factor of two of the magnitude of the weekly cycle of light-duty vehicle emissions in urban areas would bring the simulated benzene cycle into better agreement with the ambient data. However, significant variability among the monitoring sites cannot be accounted for, indicating that the weekly cycle may be a function of detailed road types or of the location. Refinement of emissions models based on real-time traffic data may be an area worthy of investigation.

For formaldehyde, the secondary pollutant, the modeled weekday/weekend difference seems less affected by direct emissions than that of the primary pollutants. Regional transport (or regional-scale secondary formation) may play a more significant role on the concentration of formaldehyde compared to benzene and diesel particles. Model predictions show decreases in formaldehyde on weekends that may be attributed to reductions in emissions, but no increases in secondary formation despite higher ozone concentrations on weekends. Aside from uncertainties in the ambient data, the discrepancy may be due to inherent differences in the meteorological and chemical regimes that are represented in the current episode as opposed to those that are more conducive to secondary formation of formaldehyde in the ambient atmosphere. The current simulation does not shed any light on the conditions and processes leading to potential increases in formaldehyde concentrations on weekends when emissions of volatile organic compounds, nitrogen oxides, and other pollutants decrease by varying amounts. Furthermore, any changes in the day-of-the-week allocation of emissions from light- and heavy-duty vehicles, as suggested above, will also affect the emissions of formaldehyde and its formation from organic precursors and oxidants (formed from volatile organic compounds and nitrogen oxides). The strength and direction of the weekly formaldehyde cycle resulting from the suggested change in temporal allocation factors cannot be determined a priori.

1. Introduction

The goals of CRC Project A-49 are to (1) assess the current state of knowledge of air toxics related to mobile source emissions, (2) analyze the ambient concentrations of air toxics associated with mobile sources to tease out weekly signals, if any, that may be attributed to mobile source emissions, and (3) conduct modeling and compare modeling results against the observed weekly profiles to assess the accuracy of the temporal representation of emissions used in the current inventories.

Under Task 1, recent air toxics modeling studies were reviewed and recommendations were made for areas of improvement, including an analysis of the weekday/weekend differences in air toxics concentrations and improvements in the emissions data and spatial and temporal allocation factors. A Task 2 report was submitted in January 2006 (Pun et al., 2006), which presents the analyses of three toxic air pollutants, elemental carbon (EC), formaldehyde (HCHO), and benzene for New York City, NY; Philadelphia, PA; and Houston, TX. (EC is frequently considered to be a tracer for diesel particulate matter (PM), or diesel PM in urban areas. The correlation between EC and diesel PM is less significant in rural areas where other sources of EC, such as biomass burning, are more significant) Routine ambient measurement data from the Environmental Protection Agency (EPA) Air Quality System (AQS) database were used. Of the three pollutants, EC shows the largest weekday/weekend differences, with the East Coast cities showing larger differences than Houston (an example is shown in Figure 1-1). The weekly cycle reflects the activity patterns in diesel emissions, especially heavy-duty vehicles. Formaldehyde shows no discernable weekly cycle at moderate concentrations, but there is some indication of a weekend increase in the East Coast cities at high concentrations (an example is presented in Figure 1-2). Secondary production of formaldehyde may increase during weekends in photochemical reactions that are related to ozone (O_3), which shows a weekend effect at the same locations. The weaker cycle for formaldehyde in Houston may be related to a larger contribution of secondary formation from biogenic rather than anthropogenic emissions of volatile organic compounds (VOC). Weekday/weekend differences in 24-hour average benzene are insignificant at

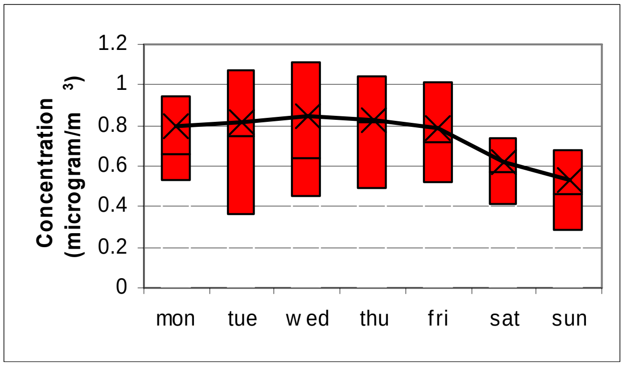


Figure 1-1. The mean, median, 25th percentile, and 75th percentile elemental carbon concentrations for each day of the week at the Queens, NY site. (Means are represented by lines and symbols, medians are represented by lines in the middle of box, 25th and 75th percentiles are shown as the edges of the box.)

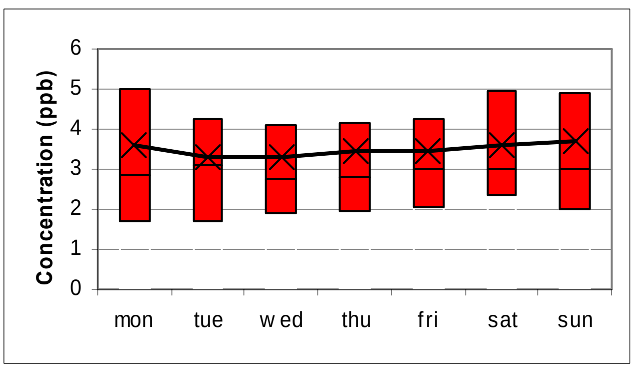


Figure 1-2. The mean, median, 25th percentile, and 75th percentile formaldehyde concentrations for each day of the week at the Bronx, NY site. (Means are represented by lines and symbols, medians are represented by lines in the middle of box, 25th and 75th percentiles are shown as the edges of the box.)

many locations, but the weekday/weekend differences in rush-hour concentrations are significant (see example in Figure 1-3).

In this task (Task 3) of CRC Project A-49, air toxics modeling is conducted according to the procedures explained in Section 2. The modeled weekday/weekend differences of diesel PM, benzene, and HCHO are compared against observations of the weekday/weekend differences in Section 3. Based on the comparisons, we comment on the accuracy of the temporal profile data used in EPA's emissions models and make recommendations on areas of improvement for the model input data in Section 4.

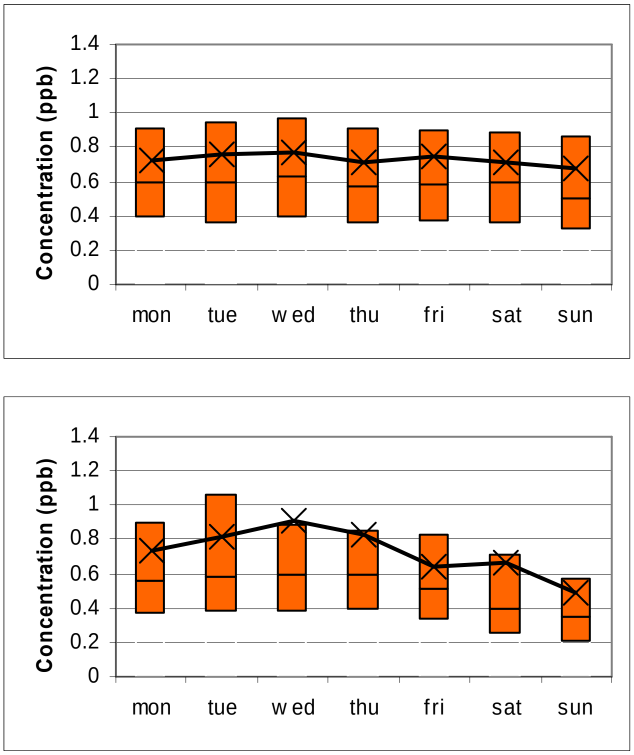


Figure 1-3. The mean, median, 25th percentile, and 75th percentile benzene concentrations for each day of the week at the Clinton Drive, Houston site: (top) 24-hour average concentrations and (bottom) rush hour concentrations.

2. Modeling Approach

2.1 Model, domain, and episode

A direct comparison between ambient concentrations and emissions is not a reliable method for the evaluation of the day-of-the-week profiles used to generate model emission inventories because of the contributions from the regional background to air toxics concentrations and because of the chemical transformations undergone by certain chemically active air toxics, such as HCHO. Consequently, a more rigorous approach entails the use of an air quality model that can account for the major processes governing the atmospheric fate and transport of air toxics to evaluate the day-of-the-week profiles of the emission data by comparing the day-of-the-week variability of observed and simulated air toxics concentrations.

The Community Multiscale Air Quality model (CMAQ) is used to account for the dispersion and transformation of the emitted air toxics. The simulation is the same as that used previously (Seigneur et al., 2003). Version 4.5 of CMAQ (September 2005 release) is used in this study with the CBM-IV gas-phase chemical kinetic mechanism, which has been modified to include explicit treatments for benzene (similar to the modifications under CRC Project A-42-1). HCHO is already explicitly treated in CBM-IV. Diesel PM is treated as an inert species.

The modeling domain covers the northeastern United States (see Figure 2-1). A 12-km horizontal resolution is used for the entire domain and a 4-km horizontal resolution is used for an inner domain. Both Philadelphia, PA and New York City, NY are located within the 4-km resolution domain. The period simulated corresponds to July 11 through 15, 1995 (Tuesday through Saturday); the first two days are considered to be spin-up time for the model and are not analyzed.

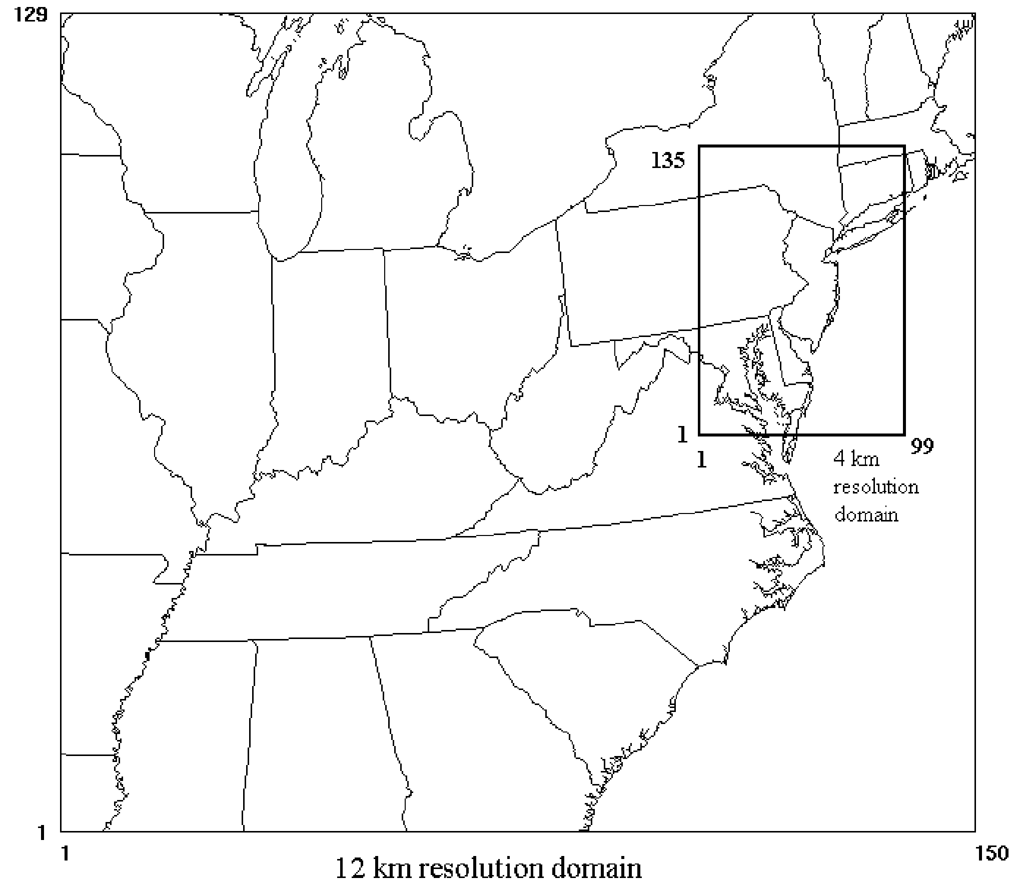


Figure 2-1. Modeling domains for the NARSTO-Northeast simulation.

2.2 Approach

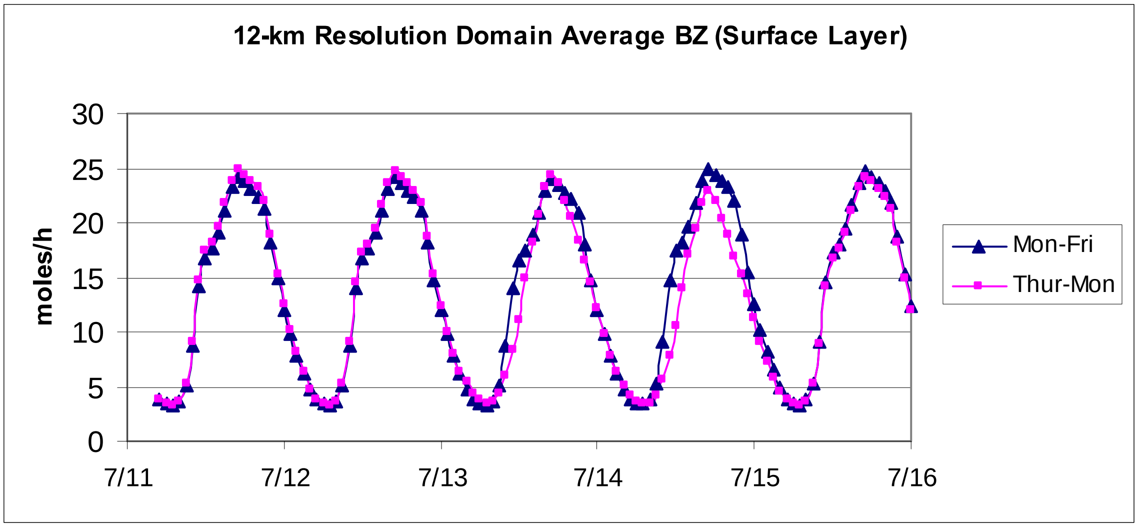
The original NARSTO (formerly North American Research Strategy for Tropospheric Ozone) VOC inventory includes explicit treatments for HCHO in addition to other reactive organic gases, carbon monoxide (CO), and nitrogen oxides (NO_x). Here, we use the 1996 National Emissions inventory, which provides similar estimates for VOC and NO_x emissions for this episode. Benzene emissions were already calculated under Project A-42-1 based on the National Toxics inventory of 1996, and an inventory for diesel PM emissions was developed based on the National Emissions Trends Inventory of 1996.

The modeling approach is to use two different day-of-the-week inventories (Monday through Friday vs. Wednesday through Monday) but keep the same meteorology in two nested-grid simulations. Thus, the differences in the concentrations will be attributable exclusively to differences in weekday vs. weekend anthropogenic emissions. Hereafter, the simulation of the NARSTO episode of 11-15 July 1995 using a Monday-through-Friday inventory is referred to as the weekday simulation, and the simulation using an inventory corresponding to Thursday through Monday is referred to as the weekend simulation.

Using SMOKE version 2.1, emission input files are generated for benzene, diesel PM, reactive organic gases (ROG, including HCHO), CO and NO_x. SMOKE uses the annual emission inventory (ton/year for each source category type) as the raw input and applies temporal and spatial allocation procedures. The temporal allocation procedure involves the assignment of seasonal (12 months), weekly (7 days), and diurnal (24 hours) profiles to each anthropogenic source type (point, area, and mobile). Biogenic emissions depend on temperature, light conditions, and other environmental factors, which differ on different simulation days. To isolate differences due to anthropogenic emissions in the simulations, biogenic emissions are kept constant for all simulation days for both the weekday and weekend simulations here. By assigning different days of the week, a set of emission data is generated for Monday through Friday and another set for Thursday through Monday for the same meteorology that corresponds to the five-day episode of 11-15 July 1995. The weekday/weekend differences in the emissions of organic compounds and NO_x are modeled because these precursors of O_3 and other oxidants can affect the reactions forming and consuming HCHO. Thus, the effect of the day- of-the-week variability in the emissions on ambient concentrations will be obtained for the 3^{rd} (Wednesday vs. Saturday) and 4^{th} (Thursday vs. Sunday) days of the episode. Domainwide emissions of benzene, HCHO, and diesel PM are shown for these two sets of simulation days in Figure 2-2.

Developed based on standard temporal profiles used as default within SMOKE, emissions of all three toxics drop noticeably on Saturdays and especially on Sundays compared to weekdays in both the 12-km and 4-km domains. For all three pollutants, there are sources that do not vary as a function of the day of the week. Peak emissions occur in the middle of the day. In the 12 km-resolution domain, the peak emission rates show a strong weekly trend for HCHO and benzene, but the weekday-weekend difference in the peak hourly emissions is smaller for benzene. In the 4-km resolution domain, there is a more significant decrease in the daytime peak benzene emissions on Saturdays and Sundays. All three air toxics also show a diurnal shift of emissions on Saturdays and Sundays towards the middle of the day compared to weekdays.

Table 2-1 lists the top-ranking emission sources of benzene, HCHO, and diesel PM within the 12-km modeling domain. The weekday/weekend changes in emissions of these individual source categories are also listed. The most significant weekday/weekend differences originate from on-road vehicle emissions. Both light- and heavy-duty vehicles are associated with a weekly profile where Saturday emissions are lower than weekday emissions by approximately 9% on rural roads and 11% on urban roads. The weekday-Sunday differences are 14% on rural roads and 38% on urban roads, for both light and heavy-duty vehicles.


12-km Resolution Domain Average BZ (Surface Layer)
moles/h
30
25
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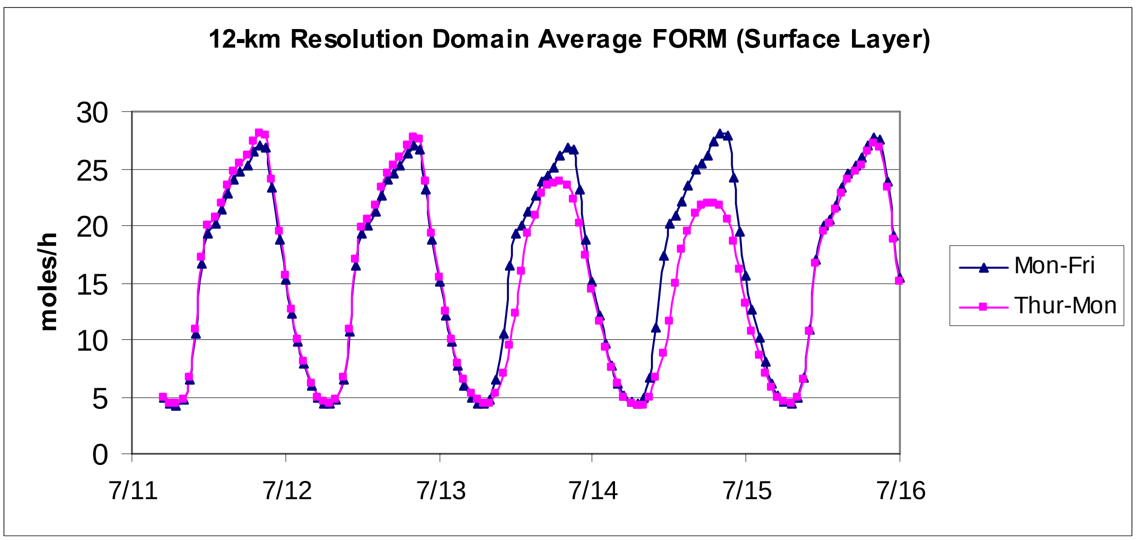
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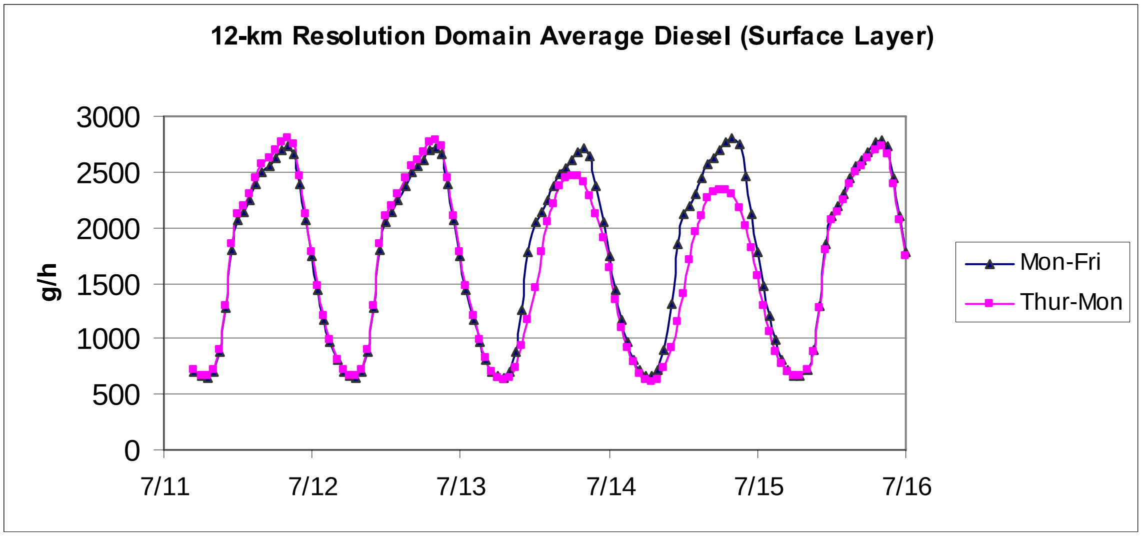

Figure 2-2. Domainwide emissions of benzene, HCHO, and diesel PM for the Monday-Friday and Thursday-Monday simulations.

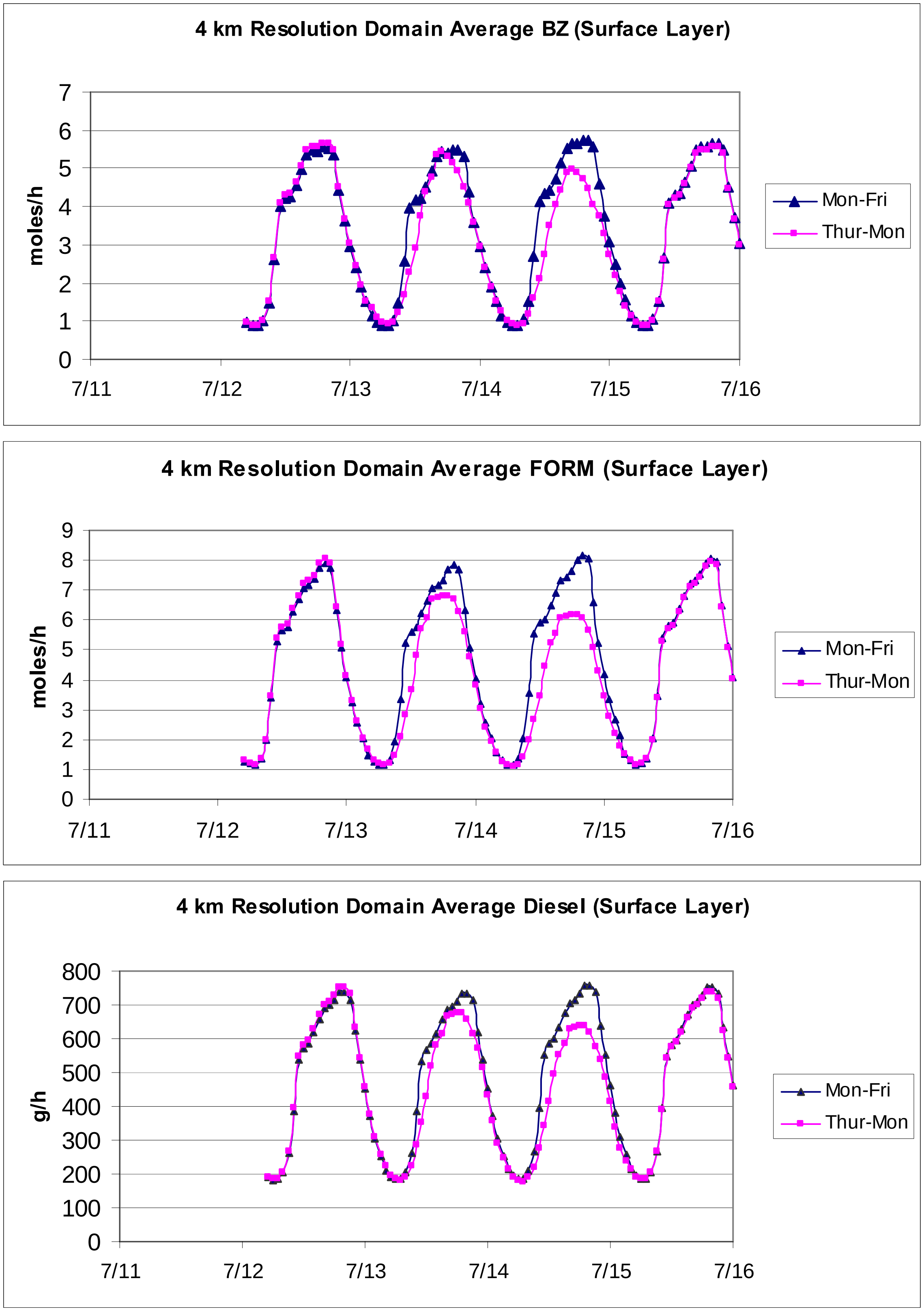

Figure 2-2. Domainwide emissions of benzene, HCHO, and diesel PM for the Monday-Friday and Thursday-Monday simulations (continued).

Table 2-1. Top-ranking emission sources of benzene, HCHO, and diesel PM in the 12-km resolution domain, and their weekend emission relative to weekdays.

Sources of benzene	**Tons/day**	**Δ Saturday emissions**	**Δ Sunday emissions**
Light-duty gasoline vehicles and trucks (urban)	151	-11%	-38%
Light-duty gasoline vehicles and trucks (rural)	119	-9%	-14%
2-stroke gasoline equipment	91	0%	0%
4-stroke gasoline equipment	62	0%	0%
Forest wildfires	38	0%	0%
Sources of VOC (profile containing HCHO)			
Light-duty gasoline vehicles and trucks (urban)	9861	-11%	-38%
Light-duty gasoline vehicles and trucks (rural)	5179	-9%	-14%
Forest wildfires	4261	0%	0%
Solvent, consumer	3796	0%	0%
Pleasure craft – 2-stroke	2095	0%	0%
Sources of diesel PM			
Heavy-duty diesel vehicles (rural)	201	-9%	-14%
Construction/mining equipment	203	0%	0%
Heavy-duty diesel vehicles (urban)	121	-11%	-38%
Agricultural equipment	82	-38%	-38%
Marine vessels	71	0%	0%

3. Results

The weekday/weekend differences are obtained by comparing the third and fourth simulation days of the weekday (Wednesday, Thursday) simulation and the weekend (Saturday, Sunday) simulation. Analyses are conducted for two metropolitan areas within the 4-km resolution simulation domain, Philadelphia, PA and New York City, NY, for which data analyses were conducted in Task 2. Ambient data cannot be directly compared in terms of absolute concentrations to the simulation results because the simulations are associated with the meteorology of one episode, which may or may not be representative of the conditions corresponding to the analyzed ambient data (several years' worth of ambient data were used to obtain statistically stable estimates of the ambient weekday-weekend differences). Therefore, a qualitative comparison is necessary.

3.1 Diesel PM

In Task 2, we analyzed the day-of-the-week variability of EC concentrations at 4 sites within metropolitan New York City; two are in the Bronx (sites 360050083 and 360050110), one is in New York (360610062), and the remaining one is in Queens (360810124). All sites show decreases in EC concentrations on weekends. In a previous study (Seigneur et al., 2003), we concluded that ambient diesel concentrations can be approximated as twice the EC concentrations in urban areas. (Because of other sources of EC in rural areas, EC is a weaker tracer for diesel particles than in urban areas.) At the locations corresponding to the measurement sites, the model also predicts large decreases in diesel particle concentrations (see Figure 3-1). The time series (Figure 3-2) shows key differences during the morning commute hours between Saturdays and Wednesdays and between Sundays and Thursdays at selected sites. The influence in direct emissions on ambient concentrations is important for this primary pollutant. Hourly differences are larger and persist longer in the Thursday-Sunday pair compared to the Wednesday-Saturday pair, due presumably to lower emissions throughout the day on Sundays compared to Saturdays.

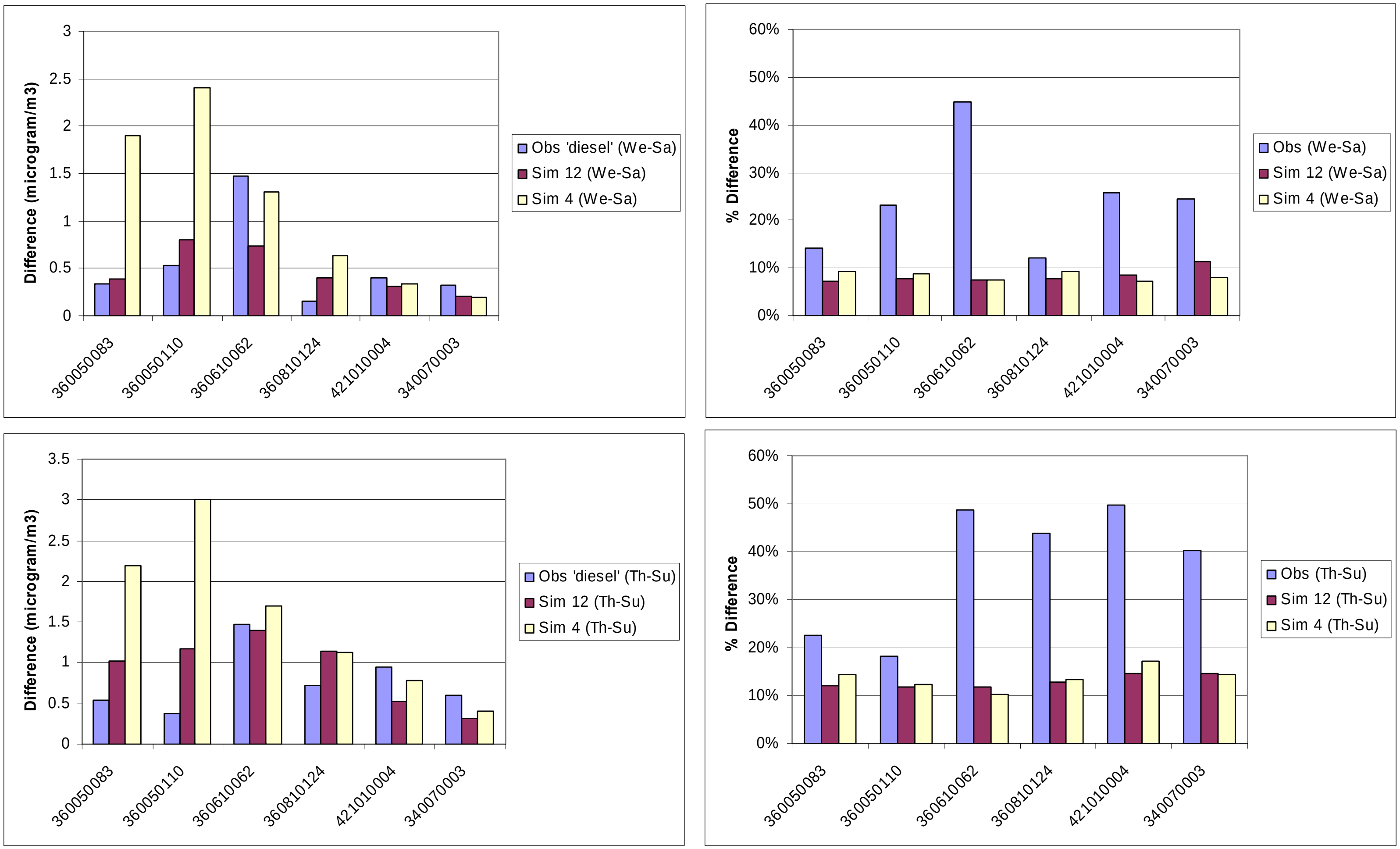

Figure 3-1. Predicted vs. observed diesel concentration differences in concentration units (left) and % (right) between two weekday/weekend pairs at four New York City sites and two Philadelphia sites. Observed diesel concentrations are approximated as twice the observed EC concentrations.

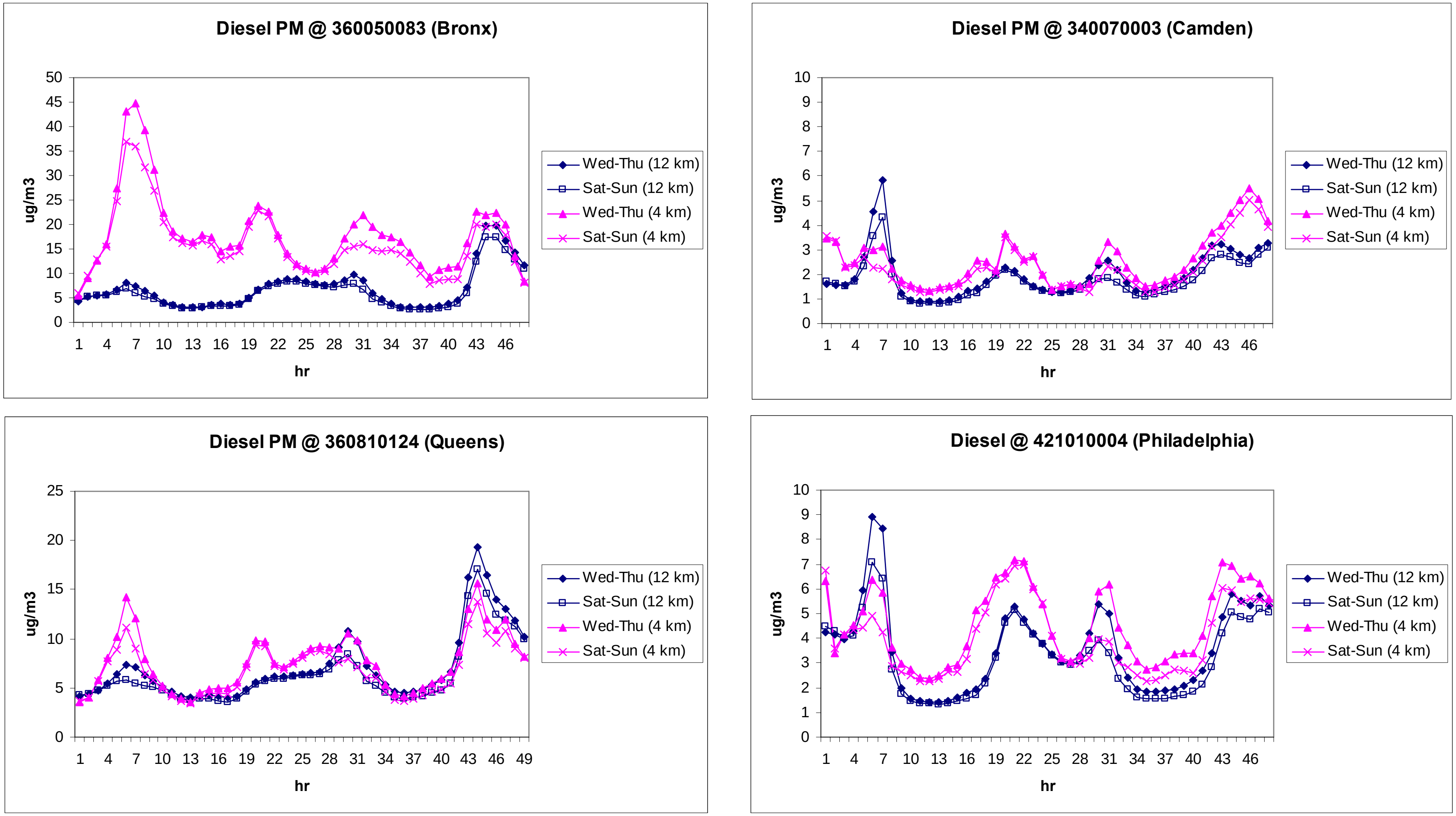

Figure 3-2. Predicted hourly diesel PM concentration time series on Wednesday-Thursday vs. Saturday-Sunday at two New York City sites and two Philadelphia sites.

The observations indicate that among the four New York City sites, the differences of median concentrations between midweek days and weekends are most significant at the New York site; the model results from the 12-km resolution also show the largest Thursday-Sunday difference at the NY site but a large Wednesday-Saturday difference is simulated at one of the Bronx sites (360050110). The 12-km resolution simulation results indicate less spatial variability among the 4 sites than indicated in the observations in terms of concentrations. The 4-km resolution simulation amplifies the predicted Wednesday-Saturday diesel concentration differences at all New York City sites, resulting in very large differences at the two Bronx sites and at the Queens site compared to the observed differences, but matching the observed concentration difference at the New York site. On the other hand, the Thursday-Sunday differences are not amplified by the smaller grid resolution at the New York and Queens sites, but are predicted to be quite large at the Bronx sites (Figure 3-2).

A fine grid resolution results in a larger weekday/weekend difference in concentration at all New York City sites (with the exception of the Thursday-Sunday difference in Queens). However, the percentage changes between weekdays and weekend days are underpredicted regardless of the grid resolution. Concentrations of diesel PM are higher in the simulation than in the multiyear data set (this is not surprising because the simulation corresponds to an air pollution episode); higher concentrations are associated with larger weekday/weekend differences in absolute concentrations but only small percentage change compared to the observed data. The error in the relative (%) difference is spatially variable, with the largest difference between simulated and observed relative concentrations at the New York site (45-50% observed, 10% or less simulated) and relatively better agreement at the Bronx sites (15-25% observed; 7-10% simulated). At the Queens site, the percent decrease is simulated well for the Wednesday-Saturday difference but less satisfactorily for the Thursday-Sunday difference.

The modeled differences in Philadelphia (sites 421010004 and 340070003) are commensurate with the differences in the observations. Observed concentration differences are smaller than in those in New York City, and so are the predicted differences at both model resolutions. However, the relative differences are significantly underpredicted, just as they are in the case of the New York City sites.

These results indicate potential inaccuracies in the temporal allocation scheme for the emission of diesel particles. Weekly profiles for heavy-duty vehicle traffic, a major source of diesel PM, are assigned based on the types of road. The default methodology used in SMOKE is fairly crude – one weekly profile is assigned for mobile emissions on urban roads and another is assigned for mobile emissions on rural roads. It is possible that even for the same vehicle class, there is a lot more variability for the weekly traffic pattern, depending on road types (interstate highways, other freeways and expressways, major arterial, collector, and local roads) and the specific location (e.g., different locations within metropolitan New York City or New York City vs. Philadelphia).

3.2 Benzene

Figure 3-3 shows the Wednesday-Saturday and Thursday-Sunday differences in benzene concentrations observed and predicted by the model at 12-km and 4-km resolutions. These comparisons are presented at four New York City sites and at four Philadelphia sites (two of which are co-located). Figure 3-4 shows time series of benzene at selected monitoring sites in New York City and Philadelphia. The diurnal profiles indicate that the simulated differences in the weekday and weekend concentrations are due to mobile source emissions. The morning commute period corresponds to the largest differences in concentrations when comparing between Wednesdays and Saturdays and between Thursdays and Sundays.

As in the case for diesel particles, the largest weekday/weekend concentration difference is modeled at a Bronx site (360050083). At the sites with the largest and most significant observed differences (Kings 360470118 and Queens 360820098), the model also predicts larger weekday/weekend differences of 0.05 to 0.3 ppb than observed. The

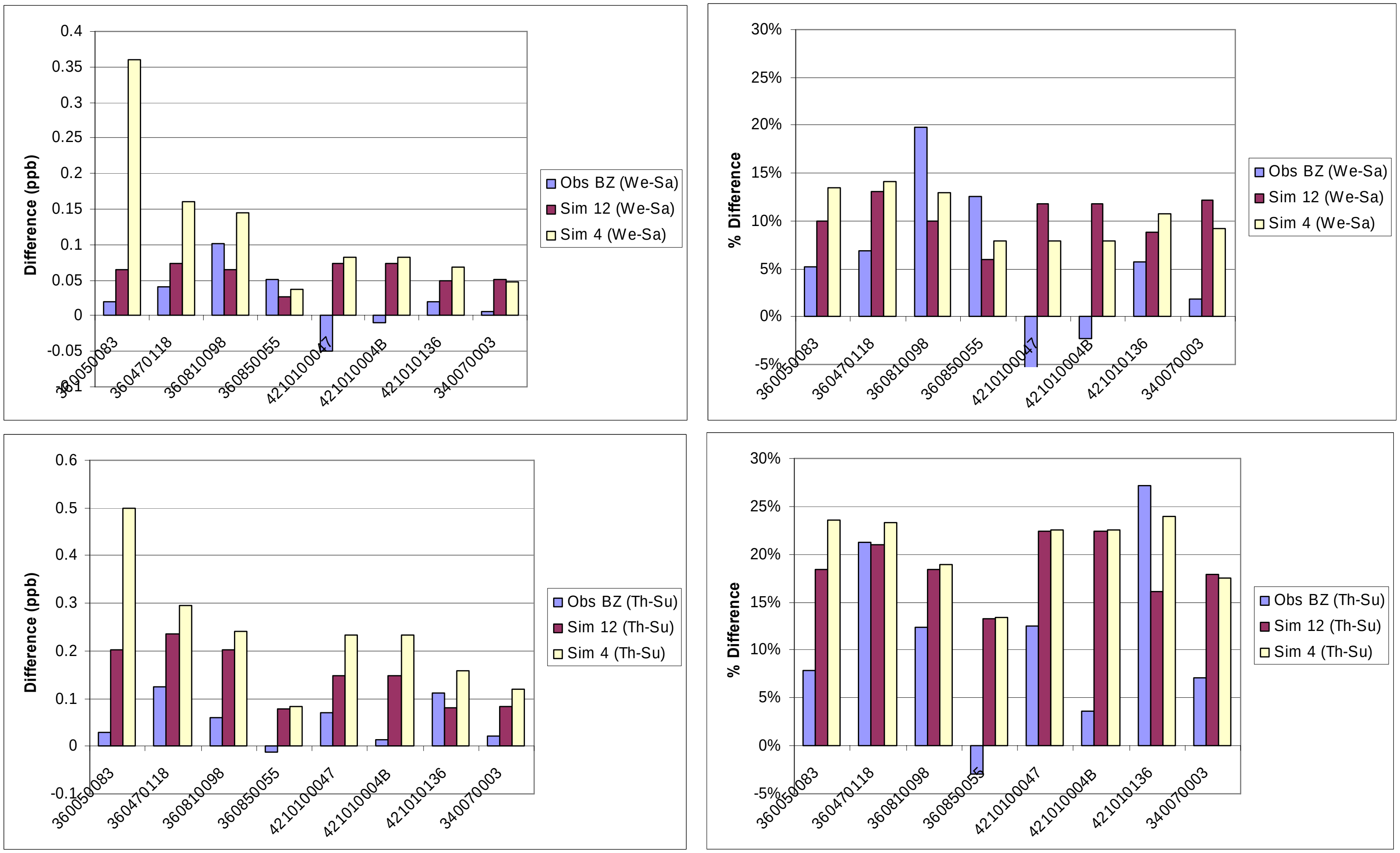

Figure 3-3. Predicted vs. observed benzene concentration differences in concentration units (left) and % (right) between two weekday/weekend pairs at four New York sites and four Philadelphia sites.

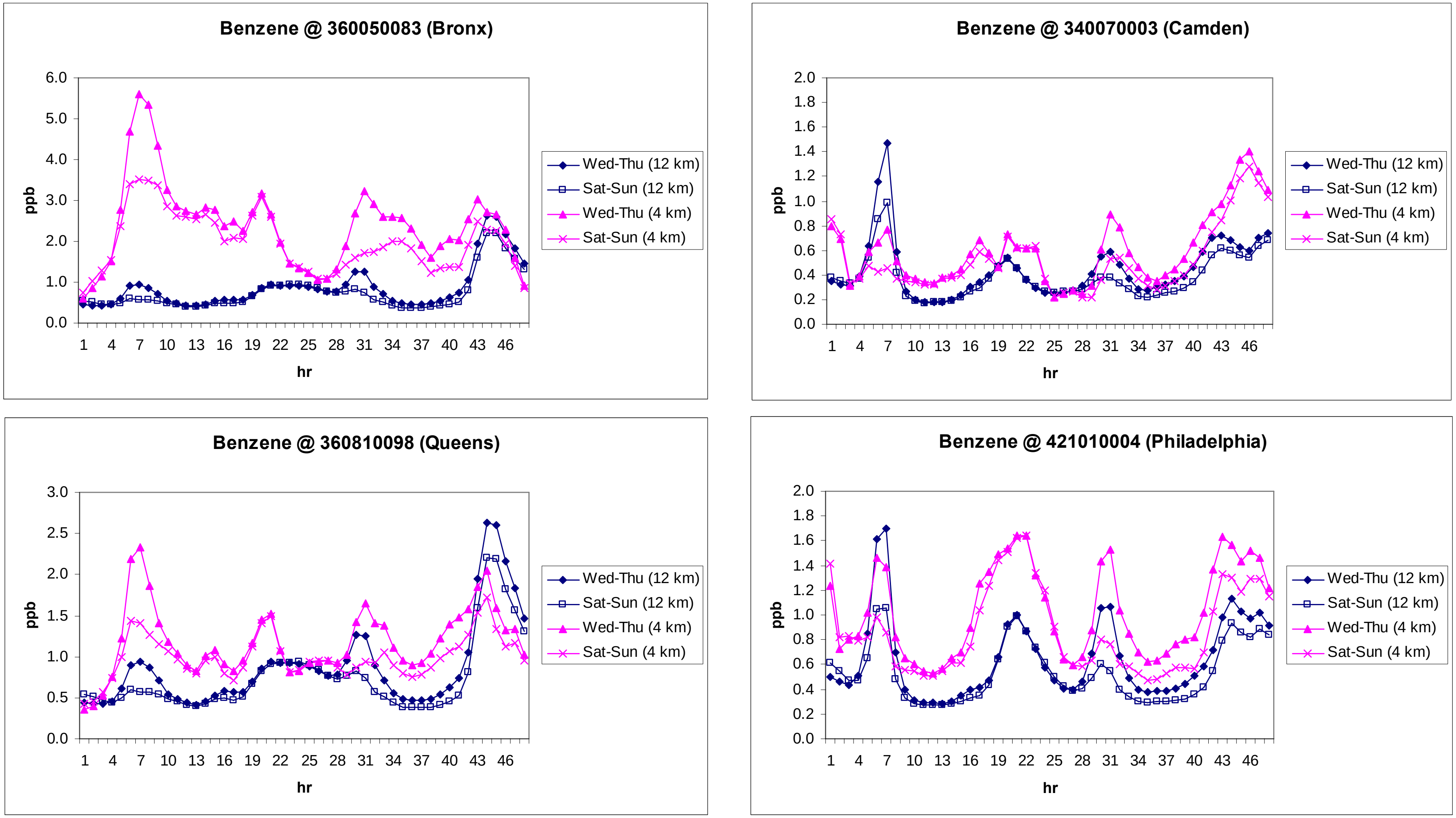

Figure 3-4. Predicted hourly benzene concentration time series on Wednesday-Thursday vs. Saturday-Sunday at two New York City sites and two Philadelphia sites.

Wednesday-Saturday predictions by the model at two resolutions encompass the largest observed value. The predicted differences at the Kings site are larger than the differences in the observed median concentrations at this site. The 4-km resolution simulation amplified significantly the weekday/weekend concentration differences in Bronx compared to other areas. At sites in the vicinity of Philadelphia, Wednesday-Saturday differences of 0.05 to 0.08 ppb are consistently predicted at all 4 monitoring sites, although the observed differences are smaller. The predicted Thursday-Sunday differences in benzene in Philadelphia are consistently larger than the Wednesday-Saturday differences, corresponding also to somewhat larger observed differences. The 4-km resolution simulation has a tendency to predict higher concentrations of primary pollutants and amplify Thursday-Sunday differences compared to the 12-km resolution simulation (see Figure 3-4).

For both New York City and Philadelphia metropolitan areas, the model predicts consistent decreases in benzene concentrations at all sites, whereas measured decreases are only definitive for a subset of the sites. Thursday-Sunday differences in benzene concentrations are predicted to be larger than Wednesday-Saturday differences – this is in agreement with the observed trends except at Queens and Richmond, NY.

On a relative basis, the observed changes between weekdays and weekends are more spatially variable than the modeling results. Positive differences (weekday > weekend) between 5 and 20% are observed at the New York City sites. The Richmond site (360850055) shows a negative Thursday-Sunday difference. Predicted differences are in the same range, with Thursday-Sunday differences being predicted to be generally larger than Wednesday-Saturday differences (with the exception of the Richmond site). Observed relative (%) differences in Philadelphia are variable, and include some negative weekday-weekend differences. The model generally overpredicts the relative (%) difference in the Philadelphia sites.

A comparison of the two primary pollutants indicates that the simulated weekday/weekend changes of benzene are more pronounced (8-24%) than the corresponding changes in diesel particles (7-17%). The opposite is true for the observations, with weekend decrease in diesel particle concentrations (estimated based on EC concentrations) decreasing by as much as 50% at some sites, and benzene showing a maximum decrease of 27%. In the New York City metropolitan area, the modeling results are affected to a large degree by local emissions, which tend to show larger decreases for benzene than for diesel particles. In Philadelphia, the weekend decrease in benzene is also larger than that in diesel PM (421010004) but the decrease is slightly larger in diesel PM than benzene at Camden (340070003), indicating that local or fresh emissions may be less important in the vicinity of Camden in the simulation than at the other urban locations.

The weekly emission profiles for benzene are driven to a large extent by the temporal profiles assigned to on-road mobile sources; as emissions from many of the key area sources are assumed to be invariant by the day of the week. The default assignment of weekly profiles in SMOKE for light-duty gasoline vehicles is the same as that for heavy-duty vehicles. On urban roads, the weekend decrease is assumed to be more significant than on rural roads. The benzene results in New York City and Philadelphia suggest that the weekend decreases in emissions from light-duty vehicles may be overstated in urban areas. This is in contrast to the finding in the previous section that weekend decreases in diesel emissions may be under-estimated in urban areas.

3.3 Formaldehyde

HCHO measurements are available at 4 sites in the New York and Philadelphia metropolitan areas for the analysis of weekday/weekend differences. At the Bronx site (360050083), weekend concentrations of HCHO exceed weekday concentrations, although the differences are not statistically significant. At the Queens site (360810097), weekday concentrations exceed Sunday concentrations, with the Wednesday-Sunday difference of 0.7 ppb being statistically significant. Although the Wednesday-Saturday difference is positive, there are some negative midweek-Saturday differences at this site.

As shown in Figure 3-5, at the Bronx site, the 12-km resolution CMAQ simulation predicts a small decrease in the Saturday concentrations (0.1 to 0.3 ppb) and a larger decrease in the Sunday concentrations (0.5 to 0.8 ppb) compared to Wednesdays and Thursdays, respectively. The predicted differences are larger in the 4-km resolution simulation than the 12-km resolution simulation. The model does not reproduce any increase of HCHO on weekends in Bronx. Instead, of the four sites analyzed, the largest weekend HCHO decrease is predicted at this site. At the Queens site, the Wednesday-Saturday difference is underpredicted by both simulations (i.e., 4- and 12-km horizontal resolutions); but the Thursday-Sunday difference is overpredicted by both simulations.

At the Camden site (340070003), weekday HCHO concentrations are higher than weekend concentrations. In Philadelphia (421010004), Thursday concentrations are higher than Sunday concentrations (statistically significant), but Wednesday concentrations are lower than Saturdays (not significant). Again, the model does not represent the Saturday increase in HCHO concentrations in Philadelphia. For the decrease in HCHO concentrations on Sundays, both 12-km and 4-km resolution simulations underestimate the difference compared to the measurements; the 4-km simulation resolution predicts a larger difference than the 12 km simulation. For the Camden site, the predicted HCHO decreases on Saturdays are too small in magnitude compared to the observed decreases, but the predicted decreases on Sunday are slightly larger than the observed decrease on Sundays.

Figure 3-5 also presents the observed vs. simulated changes in relative terms. Except for negative changes (weekend concentrations larger than weekdays) that were not reproduced by the simulations, all weekday-weekend differences are underrepresented by the model on a percentage basis. The underprediction is more significant for the weekday-Saturday change than for the weekday-Sunday change at the sites in Bronx and Camden. The

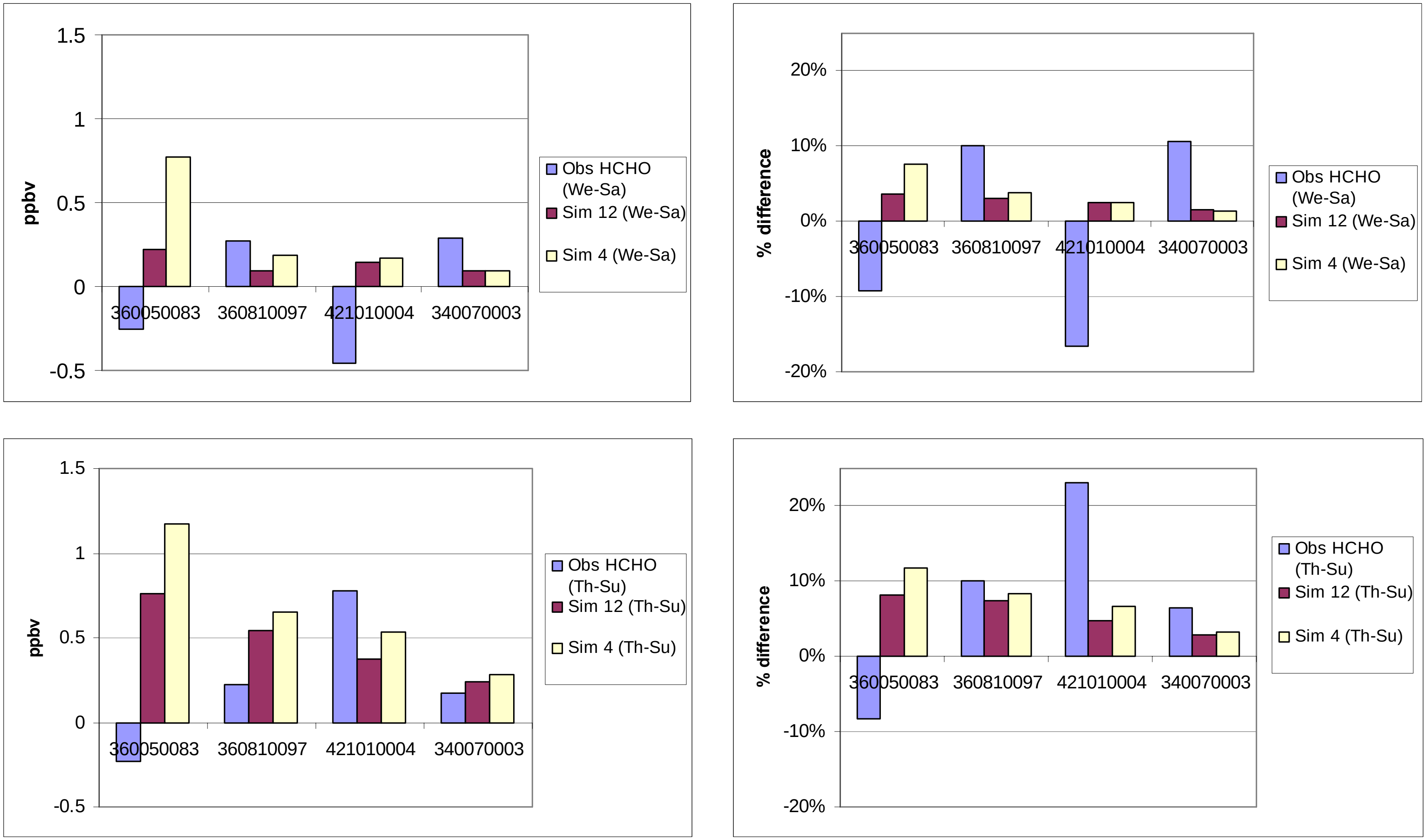

Figure 3-5. Predicted vs. observed HCHO concentration differences in concentration units (left) and % (right) between two weekday/weekend pairs at two New York City sites (Bronx and Queens) and two Philadelphia sites (Philadelphia and Camden).

observed Wednesday-Saturday and Thursday-Sunday differences are more spatially variable than the simulated differences.

Since HCHO emissions decrease on weekends, any increase in ambient concentrations (weekend increases in the median concentrations are statically insignificant, but increases in the 75th percentile concentrations are statistically significant at several sites), would be due to excess formation of HCHO on weekends compared to weekdays. Despite fairly high HCHO concentrations in the simulations, this response is not simulated in New York City and Philadelphia. An inspection of the HCHO time series indicates that at all hours, concentrations simulated on weekends are the same or below those on weekdays (see Figure 3-6). The temporal profiles of HCHO are fundamentally different from those of the primary pollutants (Figures 3-2 and 3-4) at many sites. The weekday traffic signal is discernable at only a few sites. Other factors, including transport and secondary formation, most likely contribute to a more regional distribution of HCHO compared to benzene and diesel PM, and can also explain the lack of sensitivity of the concentrations to changes in local emissions on weekends.

The key factor driving any weekday/weekend difference in HCHO concentrations in the simulations is the decreasing emissions on weekends at these locations, especially at the Bronx site. Note that ozone, an indicator of the oxidant levels, is simulated to increase on weekends, particularly Sundays, relative to weekdays in both metropolitan areas. On a diurnal basis, weekend O_3 starts to exceed weekday O_3 during the morning rush hours, when less O_3 is titrated by fresh NO emissions on weekends compared to weekdays. The higher O_3 concentrations on weekends persist into the afternoon peaks. Therefore, higher oxidant conditions are likely to be present on weekends compared to weekdays. The lack of any simulated weekend increases in HCHO indicates that HCHO accumulation may not be very sensitive to changes in the abundance of oxidants, possibly indicating the larger role that regional transport processes play with respect to HCHO concentrations compared to factors affecting O_3 concentrations.

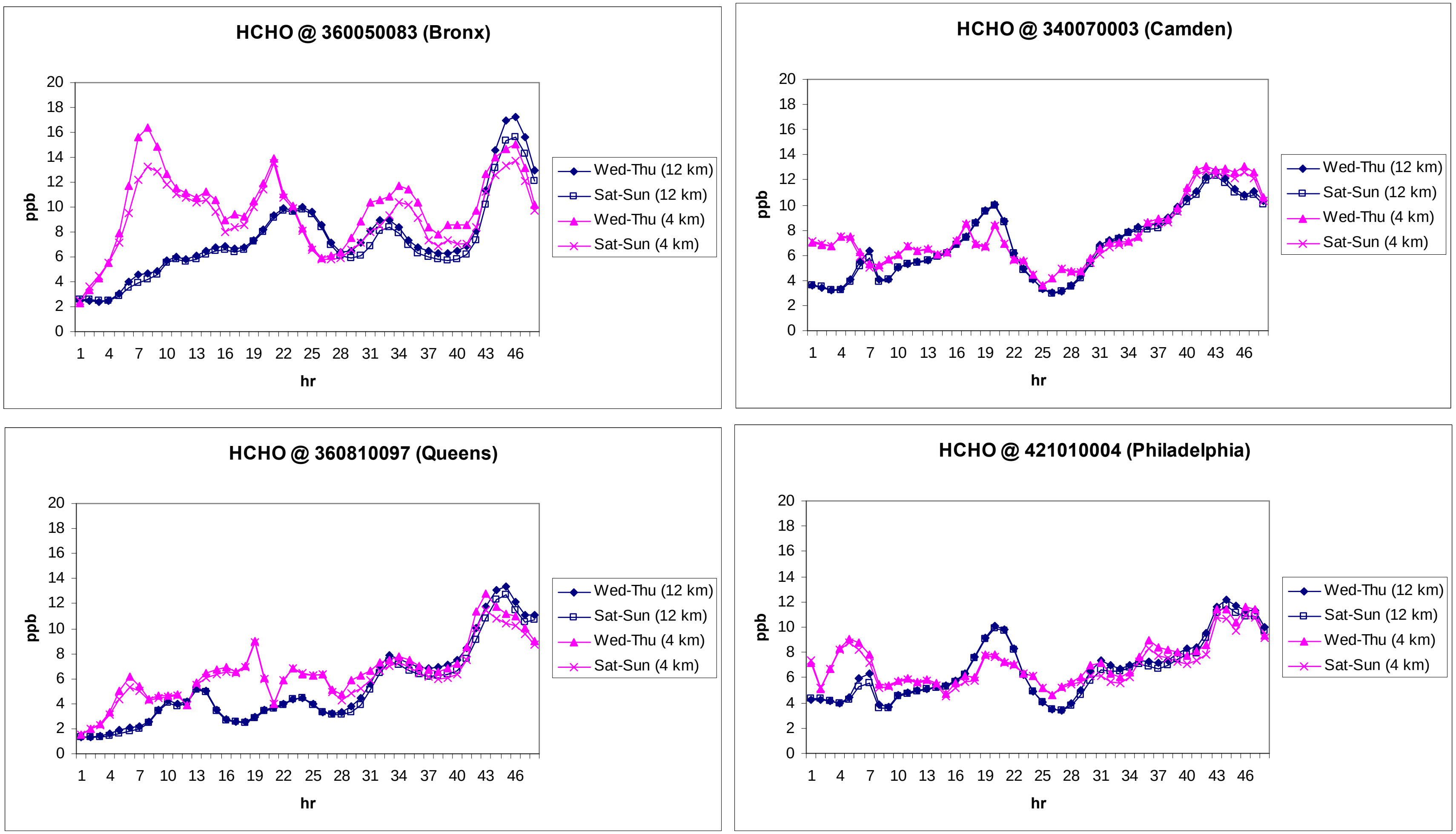

Figure 3-6. Predicted hourly HCHO concentration time series on Wednesday-Thursday vs. Saturday-Sunday at two New York City sites (Bronx and Queens) and two Philadelphia sites (Camden and Philadelphia).

4. Discussion and Conclusions

Ambient data indicate a decrease of elemental carbon concentrations during weekends at many sites, reflecting a significant decrease in diesel particles (21% to 48% in New York City; 32-38% in Philadelphia) compared to weekday concentrations. Previous studies have found that the activity of heavy-duty diesel trucks, a key source of diesel PM, decrease by 40-80% on weekends compared to weekdays in South Coast Air Basin in California (Chinkin et al., 2003). In New York City and Philadelphia, weekday-weekend differences in emissions of diesel particles are expected to be dominated by the changes in the activity patterns of heavy-duty diesel vehicles, because other important souces of diesel PM are either rural sources or do not show a weekly cycle (see Table 2-1). In the modeling of emissions, heavy-duty diesel emissions decrease by 25% on weekends (11% on Saturdays and 38% on Sundays) on urban roadways. The overall weekend decrease (average of simulated values on Saturday and Sunday) are between 9 and 11% at sites in New York City and between 11 and 15% at sites in Philadelphia. On average, these changes are smaller than those indicated by the analysis of ambient data, suggesting that a stronger weekly cycle may be warranted in the emission modeling of diesel vehicles in urban areas in the northeastern United States. Increasing the magnitude of the weekly cycle for heavy-duty vehicles emissions on urban roadways by a factor of 2.5 can be a reasonable first-order improvement. This modified weekly cycle would correspond to a 61% decrease of weekend emissions, which is quite consistent with the findings of Chinkin et al. (2003). However, it should be noted that some spatial variability is evident in the model-ambient data comparison, and different weekly profiles may be needed for different geographical locations and different road types. Additional information, including the use of traffic data, would be helpful in the refinement of the emissions estimates.

For benzene, statistically significant decreases in ambient weekend concentrations were found at some, but not all, monitoring sites in New York City and Philadelphia. A major source of benzene emissions is light-duty gasoline vehicles and trucks (see Table 2-1). Chinkin et al. (2003) found that the overall change in emissions on weekends due to changes in activity patterns in gasoline vehicles is of the order 10-15%. However, for urban areas, the default weekly profiles applied for these vehicles is a 25% decrease on weekends (11% decrease on Saturday and 38% decrease on Sundays; same as for heavy-duty diesel vehicles). This emission profile results in a 13-17% decrease in the weekend benzene concentrations in New York City and Philadelphia sites, compared to an average decrease of only 6-7% in the observed data. Therefore, for light-duty gasoline vehicles in urban areas, the modeled emission cycle may be exaggerated by a factor of two. The modified weekly cycle would correspond to a 12% decrease of emissions over the weekend for light-duty gasoline vehicles, which is consistent with the findings of Chinkin et al. for the California South Coast Air Basin.

Analysis of ambient HCHO data provides limited support that at high concentrations, HCHO concentrations are higher on weekends than on weekdays. However, this weekend increase is not seen at moderate concentrations. Therefore, the ambient weekly trend cannot be considered definitive for HCHO. Although the predicted HCHO concentrations exceed the 75th percentile concentrations in the observations, the model consistently predicts a decrease of HCHO on weekends compared to weekdays. We have previously postulated that any increase in the observed HCHO concentrations may be related to the weekend effect of O_3, and O_3 increases are indeed simulated in these metropolitan areas on weekends. It is possible that the secondary formation of HCHO does not increase with O_3 in the models and does so in the ambient atmosphere. If present, any excess production of HCHO on weekends in the simulation does not balance the reduction in emissions. It is uncertain at this point whether the discrepancy in the observed and the modeled weekly behaviors is attributable to uncertainties in the data, or simply that the weekend increase is characteristic of a chemical or meteorological regime that is not represented in the episode being simulated. At different monitoring sites, HCHO showed much variability in the weekday/weekend differences. At monitoring sites showing decreases of weekend HCHO, the differences are typically underrepresented by the model. Since light-duty vehicles are a major source of formaldehyde, the proposed adjustment to the weekly cycle of light-duty vehicle emissions will result in smaller changes in formaldehyde emissions from weekday to weekend. However, changes in other VOC and NO_x emissions may also affect the chemistry for secondary HCHO formation, so the response cannot be predicted a priori. An ability to “tag” HCHO from primary emissions and secondary production would be useful for a better understanding of the modeled weekly cycle of HCHO.

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