

Comparison of Model-Predicted VOC Concentrations with Measurements

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1. Objectives

- Compare model-predicted volatile organic compound (VOC) species concentrations with hourly measurements from the Photochemical Assessment Monitoring Stations (PAMS), grouped by Carbon Bond IV (CB4) classes, during June-August 2005
- Explore predicted and observed diurnal profiles of CB4 VOC species

2. Model and Observational Database

- The modeling system consisted of an ETA meteorological model coupled with the PREMAQ emissions and meteorology processor, and the CMAQ photochemical model, applied in a forecasting mode following the approach of National Oceanic & Atmospheric Administration (NOAA) and the US Environmental Protection Agency (EPA).
- Uses a horizontal grid resolution of 12-km. Surface layer is ~ 35 m thick.
- Each CMAQ simulation was performed for 48 hours starting at 12:00 Greenwich Mean Time (GMT), initialized using simulated concentration fields from the previous day. Time invariant boundary conditions were used for all days.
- This analysis considers model simulations from June-August 2005. Model simulations from June 1-11, 2005 were not included in the analysis to eliminate the effect of initial conditions.
- Hourly VOC concentrations measured as part of the PAMS network were obtained from the EPA Air Quality System (AQS) for monitors within the New England and Mid-Atlantic State region comprising of Vermont, New Hampshire, New York, Massachusetts, Connecticut, Rhode Island, Pennsylvania, New Jersey, Maryland, Delaware and District of Columbia. Table 1 lists the sites used in the analysis.

3. Data Analysis

- The following CB4 classes (Gery et al. 1989) were considered in the analysis:
 - PAR:** single-bonded one carbon surrogate representing alkanes
 - OLE:** double-bonded two carbon surrogate representing alkenes
 - TOL:** seven-carbon aromatic hydrocarbon species representing monoalkylbenzene structures
 - XYL:** the eight-carbon species XYL representing di- and tri-alkylbenzenes
 - ETH:** two-carbon compound, ethylene (explicitly treated)
 - ISOP:** five-carbon compound, isoprene (explicitly treated)
- The CB-4 classes FORM (formaldehyde) and ALD2 (acetaldehyde and higher aldehydes) were not considered because measurements of the constituent VOC species were not available at hourly time resolution.
- In order to compare model predictions with measurements, the measured concentrations of the various VOCs were grouped into the above CB4 classes, as per the mapping procedure presented by Yarwood et al. (2003), reproduced here in Table 2. All species concentrations were maintained in parts per billion carbon (ppbC). Model predictions were converted to ppbC using the respective number of carbon atoms.
- Measurements were not always available for all the compounds listed in Table 2 when attempting to group them into the appropriate CB4 classes. Hence, the mapped concentration was calculated utilizing the available measurements only. Thus, the CB4 grouping concentrations derived from measurements may be underestimated depending on the compounds, if any, that were missing.
- Diurnal profile comparisons are presented at selected sites.

Table 2. Assignment of Measurement Species to Carbon Bond IV (CB4) Classes and Associated Mapping Factors - Reproduced from Table 4-1 of Yarwood et al. (2003)

Species Name	NR	OLE	PAR	TOL	XYL
PAMS Species in ppbC					
acetylene		1.00			
ethane	0.70	1.00			
ethane	0.67	0.33			
n-propane		1.00			
isobutane		1.00			
1-butene		0.50	0.50		
n-butane		1.00			
2-butene		1.00			
isopentane		0.40	0.60		
n-pentane		1.00			
isopentane		1.00			
1-pentene		0.20	0.20		
2-pentene		0.20	0.20		
2,2-dimethylpentane		1.00			
cyclopentane		1.00			
2-cyclohexylbutane	0.17	0.83			
2-methylpentane		0.84	0.16		
3-methylpentane		0.84	0.16		
2,2-dimethylpentane		0.33	0.67		
n-hexane		1.00			
Methylcyclopentane		1.00			
2,4-dimethylpentane		1.00			
benzene	0.83	0.17			
cyclohexane		1.00			
2-methylhexane		1.00			
2,3-dimethylhexane		1.00			
3-methylhexane		1.00			
2,2,4-trimethylpentane		1.00			
n-heptane		1.00			
methylcyclohexane		1.00			
2,3-dimethylheptane		1.00			
3-methylheptane		1.00			
toluene		1.00			
2-methylheptane		1.00			
3-methylheptane		1.00			
n-octane		1.00			
1-methylheptane		0.13	0.87		
m-pyrene		0.88	0.12		
styrene	0.13	0.88			
o-xylene		1.00			
n-nonane		1.00			
isopropylbenzene		0.22	0.78		
m-cyclohexane		0.78	0.22		
methyltoluene		0.11	0.89		
ethyltoluene		0.11	0.89		
1,3,5-trimethylbenzene		0.11	0.89		
1,2,4-trimethylbenzene		0.11	0.89		
o-dichlorobenzene		0.11	0.89		
m-dichlorobenzene		0.11	0.89		
p-dichlorobenzene		0.11	0.89		
m-dimethylbenzene		0.20	0.80		
p-dimethylbenzene		0.20	0.80		
n-dodecane		1.00			

Table 3. Average Hourly Concentration of CB4 VOC Species: Model typically over-predicted all CB4 VOC species, except ISOP

Site/City	Count	ETH (ppbC)	ISOP (ppbC)	PAR (ppbC)	TOL (ppbC)	XYL (ppbC)
090019003	1616	0.09	2.29	1.15	74.86	48.02
090019003	490-1738	1.50	2.51	2.48	132	30.59
090090227	1865	1.77	1.79	1.30	1.42	88.60
110010043	1518-1253	1.33	3.44	2.01	4.80	26.11
230020020	1631	0.28	1.60	0.82	1.09	6.25
230090102	1630	0.04	0.59	1.56	0.53	3.04
230330302	1602	0.80	1.84	2.17	1.91	14.10
240050001	807	1.84	1.80	2.15	2.62	51.87
240050006	1452	1.22	2.41	5.00	2.24	20.20
250190008	1453-1625	1.34	2.27	4.09	2.23	17.23
250194902	824	0.45	1.47	9.94	2.63	8.21
340010011	1412-1916	0.56	2.31	4.43	3.82	9.38
340070003	1430-1810	1.54	4.21	1.98	5.90	46.27
342100005	1788-1796	0.92	2.60	2.19	3.48	17.96
342200001	273-184	2.48	3.87	3.91	5.70	19.43
342200508	152	1.74	2.29	3.84	5.16	29.00
420010001	1720-1724	0.61	1.45	2.59	8.85	9.53

* Note that there were a total of 1944 possible hours. Sites with number of pairs less than 1458 imply fewer than 75% of total possible. Number of pairs noted between species groupings, and values in italics indicate those with pairs less than half the maximum count at that site.

4.1. Results and Discussion

Table 3 shows that, in general, with the exception of a couple of sites, the model typically over-predicted ETH, PAR and OLE concentrations by ~1.5 to 5 times, and OLE by 2 to more than 10 times. Observed OLE concentrations were low, often less than 1 ppbC. XYL was over-predicted except at 4 sites. ISOP concentrations were under-predicted at roughly half of the sites in the northeast. However, on a relative basis, the model predicted VOC composition agreed reasonably with measurements, except for the lower contribution of ISOP (Figure 1).

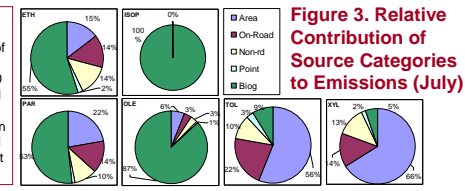


Figure 1. Relative Contribution of Source Categories to Emissions (July)

4.2. Discussion of Diurnal Profiles

Figure 2 presents the average observed and predicted diurnal profiles at the following three sites: an urban site in NY (360050083) located at NY Botanical Gardens (NYBG), Bronx, NY, a suburban site in NJ (340210005) located at Rider College (NJRC) and a rural site in PA (420010001), which is a NARSTO site located at Arendtsville, PA (PANARSTO).

Overall, the observed and predicted profiles were similar in shape at the three sites, except for isoprene at the NYBG site. The typical diurnal profile for ETH, PAR, OLE, TOL and XYL consisted of a morning and an evening peak with a trough in the afternoon. The evening peak was more pronounced in the modeled profile. The afternoon trough noted in the profiles is likely due to loss by photochemical reactions combined with expansion of the boundary layer.

For isoprene, the predicted profile at NYBG showed an afternoon trough, while the measured profile showed a bell-shaped curve. As discussed in Doraiswamy et al. (2007), in addition to a likely underestimation of isoprene emissions, the afternoon trough could also be due to excess loss by chemical reaction with hydroxyl radicals resulting from an over-prediction of nitrogen oxide (NOx) emissions. At the NJRC and PANARSTO sites, the isoprene profiles showed a pronounced evening peak, which was reasonably replicated by the model. However the isoprene emissions were likely overestimated resulting in an over-prediction of isoprene concentrations at these two sites.

Figure 2. Average Diurnal Profile of CB4 VOC Species: Observed concentration (ppbC) is on the left ordinate, while predicted (ppbC) is on the right ordinate. Overall, modeled and observed profiles were similar in shape, except for ISOP at NYBG and OLE at PANARSTO.

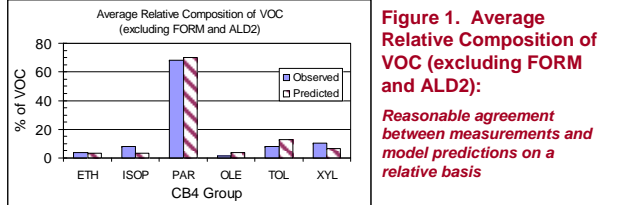
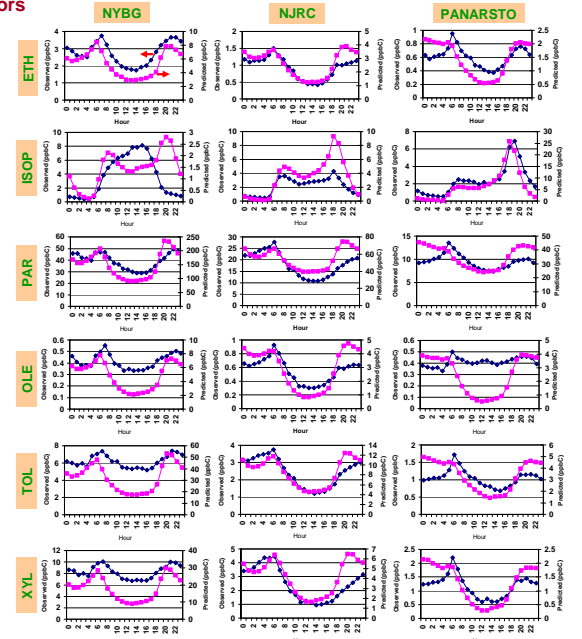


Figure 3. Average Relative Composition of VOC (excluding FORM and ALD2): Reasonable agreement between measurements and model predictions on a relative basis

4.2. Discussion (continued...)

Although forecasted emissions segregated by source category were not available for this specific period, Figure 3 shows the relative contributions of each source category to the CB4 VOC species across the northeast, based on emission inventories utilized by NYSDEC in other modeling efforts. More than 50% of TOL and XYL are emitted by area sources, and less than 10% are emitted by biogenic sources.

Examining by site, the following features are evident. At the NYBG site, the model profile showed a sharper trough than observations, although higher in overall magnitude. The over-prediction is likely due to overestimated VOC emissions, particularly from area sources, as suggested by the large over-prediction in TOL and XYL. In CB4 mechanism, the only reaction contributing to a loss of TOL and XYL is the reaction with the hydroxyl radical. Thus, similar to that seen in isoprene, the sharper trough in the afternoon may be due to overestimated NOx emissions resulting in increased hydroxyl radicals which in turn consumed the VOC species.

At the NJRC site, similar over-predictions were found. In addition, the evening peak was pronounced in the model predictions, while the observations showed no such evening peak. While the model was ~1.3 times higher than observations for ETH, it was ~2.5 times for PAR and ~3 times higher for XYL. The larger over-prediction for XYL, a species for which the area source contribution is lower than that for XYL, suggests that this overestimation is likely not from area sources, and hence could be attributed to mobile and biogenic sources. This, in combination with a drop in boundary layer height could explain the evening peak noted in model predictions.

At the PANARSTO site, while the profiles were similar in general, few minor discrepancies are noticeable. They include: a decrease in concentration of ETH, PAR, OLE, TOL and XYL between midnight and 5 am in the predicted profile, when the observed profile shows an increase; a nearly flat observed profile for OLE not noticed in predictions; and an increase in the evening concentration to a level comparable to morning peak, while the observed profile showed an increase to only half of the morning peak followed by a slight decrease. It is unclear if the nearly flat observed profile for OLE is realistic (likely representing an influence of biogenic emissions at this rural site) or if it is an artifact of instrument noise due to low concentrations. Although model over-predictions were found for ETH, PAR, OLE and TOL, XYL predictions were similar in magnitude to observed concentrations. XYL is primarily emitted from anthropogenic sources, suggesting that the primary VOC emissions, particularly from area sources, are reasonable at this site. The over-predictions of other species are likely resulting from overestimated biogenic emissions, which were the largest contributor to each of those species.

5. Conclusion

- Overall, the model appeared to track the diurnal profile at most sites.
- Although the model over-predicted concentrations of most species, the relative distribution of these species appeared to be reasonable, except for the lower ISOP contributions in the predictions.
- The analyses revealed possible overestimation of NOx emissions at NYBG site, consistent with findings from the previous study (Doraiswamy et al. 2007). In addition, it appears that anthropogenic and biogenic VOC emissions are overestimated at the NYBG and NJRC sites.

References

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