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A Combined Approach for the Evaluation of a Volatile Organic Compound Emissions Inventory

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ABSTRACT

Emissions inventories significantly affect photochemical air quality model performance and the development of effective control strategies. However, there have been very few studies to evaluate their accuracy. Here, to evaluate a volatile organic compound (VOC) emissions inventory, we implemented a combined approach: comparing the ratios of carbon bond (CB)-IV VOC groups to nitrogen oxides (NO_x) or carbon monoxide (CO) using an emission preprocessing model, comparing the ratios of VOC source contributions from a source apportionment technique to NO_x or CO, and comparing ratios of CB-IV VOC groups to NO_x or CO and the absolute concentrations of CB-IV VOC groups using an air quality model, with the corresponding ratios and concentrations observed at three sites (Maryland, Washington, DC, and New Jersey). The comparisons of the ethene/ NO_x ratio, the xylene group (XYL)/ NO_x ratio, and ethene and XYL concentrations between estimates and measurements showed some differences, depending on the comparison approach, at the Maryland and Washington, DC sites. On the other hand, consistent results at the New Jersey site were observed, implying a possible overestimation of vehicle exhaust. However, in the case of the toluene group (TOL), which is emitted mainly from surface coating and printing sources in the solvent utilization category, the ratios of TOL/ NO_x or CO, as well as the absolute concentrations revealed an overestimate of these solvent sources by a factor of 1.5 to 3 at all three sites. In addition, the overestimate of these solvent sources agreed with the comparisons of surface coating and printing source contributions relative to NO_x from a source apportionment technique to the corresponding

value of estimates at the Maryland site. Other studies have also suggested an overestimate of solvent sources, implying a possibility of inaccurate emission factors in estimating VOC emissions from surface coating and printing sources. We tested the impact of these overestimates with a chemical transport model and found little change in ozone but substantial changes in calculated secondary organic aerosol concentrations.

INTRODUCTION

Air quality models, composed of meteorology, chemistry, and emissions, have been widely implemented to simulate the chemistry and physics of the atmosphere and to understand the cause-effect relationships between pollutants and their precursors. Potential control measures for target air pollutants have been determined, based on those modeling results. Hence, inaccurate results from air quality modeling can lead to negative impacts that are both economic and environmental in nature. The usefulness of the output of air quality models is largely dependent on the quality of their inputs. Previous studies indicate that the uncertainties in atmospheric model results may originate mainly from the uncertainties in the emission inventories.^{1–3}

There have been very few attempts to evaluate emissions inventories. Previous studies described in detail the limitations and difficulties associated with the evaluation of emission inventories, resulting from the intrinsically different nature of inventory estimates and ambient monitoring measurements.^{4–12} Such comparisons are limited to ratios of volatile organic compound (VOC) species or VOC species groups (abundance of a given species or species group relative to that of another species group), because the emissions estimates in the units of mass flux per area cannot be converted directly into concentrations without the application of a suitable dispersion model or a chemical transport model. In addition, the chemical mechanisms commonly used in photochemical models aggregate chemical species, and this constrains the comparisons to a few individual species and species groups. Furthermore, because estimates from emissions processing models do not demonstrate the impact of chemical reactions and transport, the comparison is often limited to the early morning hours of the day when these impacts tend to be minimal.

Because of the above limitations, two approaches in terms of ratio comparisons have been used to evaluate emissions inventories. In one approach, VOC/nitrogen oxides

IMPLICATIONS

Emissions inventories, which may contain significant uncertainties, are a crucial input to photochemical models used to make regulatory policy decisions. In this study, a combined approach was used to evaluate a VOC emissions inventory. The result suggested possible overestimation of surface coating and printing solvent utilization sources and a need for reassessment of methods of estimating solvent VOC emissions. The combined approach for the evaluation of emissions inventories presented here can be applied to any emissions inventory, enabling a better understanding of uncertainties associated with emissions inventories and helping to improve them.

(NO_x) or carbon monoxide (CO)/NO_x ratios and weight fractions of individual VOC species were compared with ambient measurements during the early morning (6:00 a.m. to 10:00 a.m.).^{4,6,9,11,12} In another approach, receptor-modeling techniques were used to compare emissions estimates for specific source categories.^{5,10,13} Receptor models take ambient measurements of speciated organic compounds and allocate VOCs to various source categories through complex statistical manipulations.

Although the ratio comparisons can give some insight into the uncertainty in an emissions inventory, care is needed to avoid reaching misrepresentative and possibly misleading conclusions. For example, the same values of modeled and observed VOC/NO_x ratios do not indicate that the absolute amounts of VOC and NO_x are the same in both the simulation and the observation. For that reason, a dispersion model has been used in several studies. Fujita et al.⁴ showed the comparisons of measured CO/NO_x; nonmethane organic gas/NO_x; and CO, nonmethane organic gas, and NO_x concentrations with air quality model predictions using the Urban Airshed Model. Recently, Mannschreck et al.⁷ and Kuhlwein et al.¹⁴ adopted a Gaussian dispersion model to calculate pollutant concentrations of individual hydrocarbons for comparison with measured concentration ratios. Slemr et al.⁸ performed a comparison of the results from a chemistry and transport model with observations as a part of their study.

This study focuses on emissions inventory evaluation. This work is a part of a larger photochemical ozone (O₃) modeling study of the Washington-Baltimore area. Because NO_x is a direct product of combustion, whereas VOCs are emitted by both combustion and noncombustion sources, NO_x emission estimates are generally assumed to be more accurate than VOC estimates.^{6,15} In addition, Hanna et al.¹ concluded, in a study of estimates of uncertainties in predictions by a photochemical grid model for the New York City domain, that anthropogenic VOC area source emissions had the most influence on the variations in the 50% of peak O₃ concentrations. Therefore, the evaluation of the emissions inventory here is mainly focused on VOC.

Because each method has its own limitations, the use of several evaluation methods and comparison of the results from each method will lead to more solid conclusions. Therefore, we used a combination of approaches for this evaluation. We investigated both ratio comparisons of each VOC source contribution from a source apportionment model and carbon bond (CB)-IV VOC groups relative to NO_x or CO at the emissions modeling level.¹⁰ Furthermore, the community multiscale air quality (CMAQ) model, a photochemical air quality model including the effects of chemistry and transport, is used to compare the ratios of CB-IV VOC groups to NO_x or CO and effectively to put values from the emissions inventory into concentration units so they may be compared with observations.

EXPERIMENTAL WORK

Modeling and Monitoring Data

Overview of Emissions Inventory and Modeling Approach. An aggregated emissions inventory was obtained from the Mid-Atlantic Regional Air Management Association. This is an improved emission inventory for 1997 that was built on the U.S. Environmental Protection Agency (EPA) 1996 national

emission trends inventory to support studies of regional O₃ in the Mid-Atlantic and Northeastern states. Average daily VOC, NO_x, and CO emissions for area sources and average daily vehicle mileage traveled (VMT) were compiled at the county level. Average daily VOC, NO_x, and CO emissions were compiled for each point source with its specific geographic coordinate information.

Additionally, a gridded land use assessment, prepared by the New York State Department of Environmental Conservation, was used for biogenic source processing. Although the focus of our evaluation is on the anthropogenic emissions inventory, it is necessary to process biogenic emissions in conjunction with anthropogenic emissions, because the ambient measurements include the contributions from biogenic sources.

We used the Sparse Matrix Operator Kernel Emissions (SMOKE) model version 1.4, an emissions preprocessing model, to convert the source-level emissions to gridded, speciated, and temporally allocated emissions. Such conversions consist of multiplying emissions from various sources by several factors in several steps: temporal allocation, chemical speciation, and spatial allocation.

In the temporal allocation step, an hourly pollutant emissions inventory is created by applying monthly, weekly, and diurnal profiles based on the characteristics of each source. In the speciation step, SMOKE creates a speciation matrix containing conversion factors to convert total VOC emissions into emissions of specific compounds. In this study, the speciation is based on the CB-IV chemical mechanism.¹⁶ Total VOCs are converted to 10 modeling species: ethene, isoprene, paraffin group (PAR; molecules containing single carbon bond groups), olefin group (OLE; molecules containing double carbon bond groups), toluene group (TOL; 7 carbon rings), xylene group (XYL; 8 carbon rings), aldehyde group (ALD), formaldehyde, nonreactive VOC group (NR), and terpene group (TERP). In the spatial allocation step, a gridding surrogate is used to create a matrix containing conversion factors used to transform county-level aggregate emissions into emissions in each grid cell. A gridding surrogate is a dataset developed from geographic information (e.g., population and land use) at a finer spatial gridding resolution than the initial emissions data that is used to spatially allocate the emissions to the grid cells. For example, emissions from major on-road mobile sources are allocated to each grid cell according to the distribution of roads. The final gridded, chemically speciated hourly emission estimates are produced by multiplication of the matrices developed in the main processing steps. For biogenic sources, to convert land use information to normalized emissions values, the Biogenic Emission Inventory System, version 2 is embedded in SMOKE. For mobile sources, MOBILE5b, also embedded in SMOKE, generates emission factors, which are multiplied by VMT to get emissions values.⁹

CMAQ version 4.3 used in this study has been designed to approach air quality as a whole by including state-of-the-science capabilities for modeling multiple air quality subjects, including tropospheric O₃, fine particles, toxics, acid deposition, and visibility degradation. The CMAQ modeling system simulates various chemical and physical processes that are thought to be important for understanding atmospheric trace gas transformation and

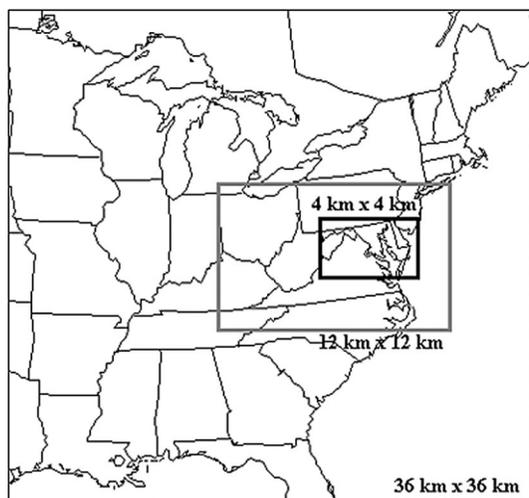


Figure 1. Map of CMAQ modeling domains.

distribution, such as dispersion, chemical reactions, and surface deposition.¹⁷

Meteorological variables, required to process biogenic, mobile, and point sources in SMOKE and CMAQ, were simulated using the National Center for Atmospheric Research/Pennsylvania State University Mesoscale Model 5 (MM5) by the Department of Meteorology, University of Maryland. The simulations were performed with a modified Blackadar planetary boundary layer scheme and a standard nudging process.^{18,19} The meteorological variables for 4-km grid resolution were extracted and interpolated from the meteorological variables for 12-km grid resolution using the Meteorology Chemistry Interface Processor version 2.2.

The simulation was performed for the period July 5 to July 20, 1997, using multineesting techniques for boundary conditions. As shown in Figure 1, the detailed 4-km study domain, nested within the outer domains, covers the whole state of Maryland and parts of Virginia, West Virginia, Delaware, New Jersey, and Pennsylvania. The innermost domain has 108 columns by 78 rows with 4-km horizontal grid cell resolution and 16 vertical layers. The outer domains have horizontal grid cell resolutions of 36 km and 12 km, respectively. The comparison to observations was done from July 8 to July 20, 1997, allowing for 3 days of spin-up time to minimize the impact of initial conditions on the CMAQ simulation.

In addition to the air quality modeling system, the UNMIX 2.4 receptor model was used to identify and apportion VOC sources. The UNMIX model is a recently refined multivariate receptor model. UNMIX incorporates

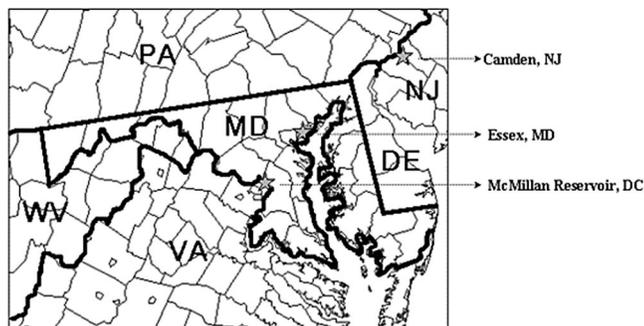


Figure 2. Map of PAMS locations used in this study. DE (Delaware), MD (Maryland), NJ (New Jersey), PA (Pennsylvania), VA (Virginia), and WV (West Virginia).

user-specified non-negativity constraints and edge-finding algorithms to derive a physically reasonable apportionment of source strengths.^{20,21} It has been applied to several studies for source apportionment of VOC and particulate matter.^{20,22–24}

Overview of Ambient Measurements. In accordance with the 1990 Clean Air Act Amendments, EPA initiated the Photochemical Assessment Monitoring Station (PAMS) program for 1-hr O₃ nonattainment areas with persistently high-O₃ levels. The objective of the PAMS program is to develop a large database of ambient air measurements for important pollutants associated with O₃ to be used to evaluate complex photochemical air quality models.²⁵

The PAMS network consists of five different site types to provide information sufficient to satisfy important monitoring objectives. Type 2 sites are located immediately downwind of areas with significant O₃ precursor emissions. It is reasonable to compare ambient measurements and emissions estimates only in situations where the local O₃ precursor concentrations are dominated by local sources, because emissions estimates and ambient measurements are two fundamentally different quantities. Emissions estimates represent the amount of a given pollutant released by a particular source. Ambient measurements represent the concentration of these pollutants in the atmosphere at a particular location and time. Thus, it is best to use monitoring measurements from sites where local emissions dominate, such as PAMS type 2 sites.^{11,12} We obtained the measurements for three PAMS sites (McMillan Reservoir in Washington, DC; Essex in Maryland; and Camden in New Jersey), categorized as type 2 sites. Table 1 contains a summary of the PAMS measurements, and Figure 2 shows the site locations. The concentrations of 55 hydrocarbons, total nonmethane

Table 1. Summary of PAMS observations.

Period of Observation	Essex, MD	McMillan Reservoir, Washington, DC	Camden, NJ
	June 1–September 30, 1997	June 1–September 24, 1997	June 1–August 31, 1997
Number of hourly observations for 6:00 a.m. to 9:00 a.m.	387	359	269
Total number of hourly observations	2812	2152	1680

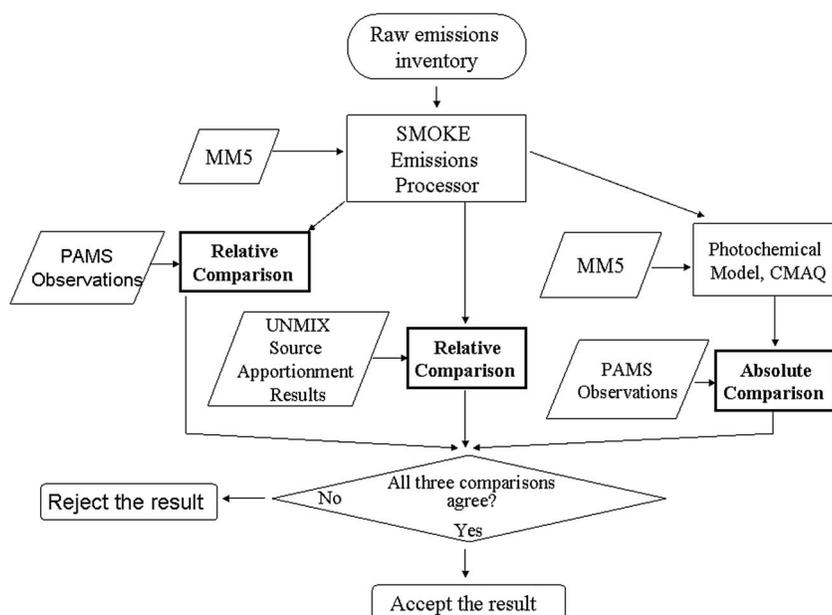


Figure 3. Flowchart of the approach to evaluation of a VOC emissions inventory.

organic carbon (TNMOC), O_3 , and NO_x , as well as surface meteorological conditions, such as temperature, wind direction, wind speed, and radiation, are monitored at the sites. Here, TNMOC is defined as the integral of all observed peaks using a gas chromatograph with a flame-ionization detector and a Nafion dryer to remove water from the sample. At the Camden site, CO was measured instead of NO_x .

The 55 individual hydrocarbons observed by PAMS were lumped into categories for comparison with emissions estimates using the VOC categories in the CB-IV chemical mechanism. There is a limitation associated with this conversion. TERP, formaldehyde, and ALD2 are not included in the 55 PAMS species. Ethene and isoprene in the CB-IV mechanism are the only single species measured by PAMS. Also, the 55 PAMS hydrocarbons accounted for only 70–90% of the TNMOC for the three sites, with the remainder unidentified. The unidentified portion of TNMOC might be volatile hydrocarbons of C2 through C12, such as terpenes, and oxygenated hydrocarbons.²⁶ It should be noted that with the method of determining TNMOC used here, we are likely underreporting oxygenated, chlorinated, and nitrated compounds, because their flame ionization response is lower than that of hydrocarbons with the same number of carbon atoms. Also, the Nafion dryer may remove some of the water-soluble compounds from the sample. Therefore, the concentrations of the lumped species, such as PAR, OLE, TOL, XYL, and NR, estimated from only 55 species measured at PAMS sites, may be lower than the actual concentrations of these lumped species in ambient air. For example, dodecane, not included in the 55 PAMS species, may be in a measurement of TNMOC, and 1 ppb of this species is converted to 12 ppb of PAR (12 ppb carbon) in terms of the modeling species. Hence, a concentration of PAR converted from only 55 PAMS species may underrepresent the actual concentration of PAR in the ambient air. Therefore, the concentrations of PAR, OLE, TOL, and XYL obtained from the 55 PAMS-observed species are considered a lower limit of the actual concentrations in ambient air.

Approach

Three types of comparisons between observation and estimation were performed as shown in Figure 3. One is a ratio comparison of each VOC source contribution, obtained from a source apportionment model, relative to NO_x (or CO for the Camden PAMS site). The others are the comparisons of CB-IV VOC groups both in an absolute and a relative manner. The morning time period from 6:00 a.m. to 9:00 a.m. was investigated to minimize the impact of chemical reactions and transport on comparisons with ambient measurements.

As far as the ratio comparisons are concerned, they are based on NO_x or CO rather than VOC, because NO_x and CO likely have less uncertainty in emissions modeling than VOC.^{6,15} In addition, the definitions of VOC categories in modeling and measurements are not the same. As described above, TNMOC observations include nonmethane hydrocarbons and oxygenated hydrocarbons, whereas the calculated total VOC from the emissions model stands for total organic gas, including methane. It should be noted that the commercial NO_x analyzer used for this study uses a Mo converter that efficiently reduces all of the NO_y species to nitric oxide (NO).^{27,28} Some of the vapor-phase HNO_3 and aerosol nitrate will be lost on the inlet lines. However, because of the contribution from other NO_y species, the values reported as NO_x here are still considered to be upper limits.^{28,29} Errors from species other than NO and nitrogen dioxide (NO_2) are expected to be small, because measurements immediately downwind of urban sources show that NO_x accounts for >90% of NO_y .³⁰ In addition, this comparison was performed with observations during the morning when fresh emissions of NO_x are dominant.

When it comes to comparing absolute concentrations of CB-IV VOC groups by using the CMAQ photochemical model, there are some additional issues to be noted. The photochemical air quality model is a complicated system composed of a meteorological modeling system for the description of atmospheric states and motions, emission models for manmade and natural emissions injected into the

atmosphere, and a chemistry-transport modeling system. Hence, the results from an air quality model reflect uncertainties in the meteorology and chemistry, in addition to uncertainty in the emissions estimates. Although the comparisons are performed during the morning period from 6:00 a.m. to 9:00 a.m., when the impacts of chemistry and transport are minimized, there still exists a possibility of errors in concentration predictions originating from meteorological parameters, such as mixing height.

Because of the limitations to each method mentioned above, final conclusions on VOC emission estimates were made only when all three of the methods gave a consistent result. The criterion was used to evaluate whether the difference between observations and emission estimates was significant was based on 2σ standard error of means (SEM; with a 95% confidence interval [CI]).³¹ The SEM is an estimate of the standard deviation of the sampling distribution of means. We can get a visual estimate of the statistical significance of the difference between the mean values of two groups by looking at their standard error bars. For example, if two error bars overlap, we can conclude that the difference is not statistically significant.

RESULTS AND DISCUSSION

Comparison of CB-IV VOC Categories

Ethene, TOL, and XYL were considered for this comparison. Isoprene was excluded, because this species is not appropriate for this comparison; short-lived isoprene is at a minimum in early morning hours, the time frame in which we focus. Considering the limitations mentioned earlier, TOL and XYL were included in this comparison, because toluene and xylenes are known as tracer species for vehicle exhaust and surface coating and printing solvent utilization sources. Ethene is known as a tracer species for vehicle exhaust.^{32–37} Although this comparison is limited to a few species, the result is expected to give insight into the emissions inventories of sources, such as vehicle exhaust, surface coating, and printing, which are major VOC sources in urban and suburban areas.^{2,36,38}

Figure 4 shows the comparison of the estimated and observed average ratios of each species to NO_x between 6:00 a.m. and 9:00 a.m. at Essex, MD. The error bars indicate the 2σ SEM (95% CI). Here, the estimated ratios from SMOKE were calculated for five different grid areas surrounding the monitoring site, including the cell containing the monitoring site with the 16-km² area and extended areas of 3×3 cells, 5×5 cells, 7×7 cells, and 9×9 cells. This was done because the estimates from SMOKE do not incorporate the impact of transport and chemistry, and comparing only at a corresponding grid cell to the monitoring site may be misleading. The ratios from CMAQ were the average values at the site cell corresponding to the location of the PAMS monitoring station. The emission estimates from SMOKE show little diversity with respect to spatial distribution. The ratios from CMAQ and SMOKE show good agreement with each other for all of the species, suggesting that processes such as chemical evolution, transport, and deposition of pollutants during the morning period of 6:00 a.m. to 9:00 a.m. are relatively unimportant in the CMAQ simulation.

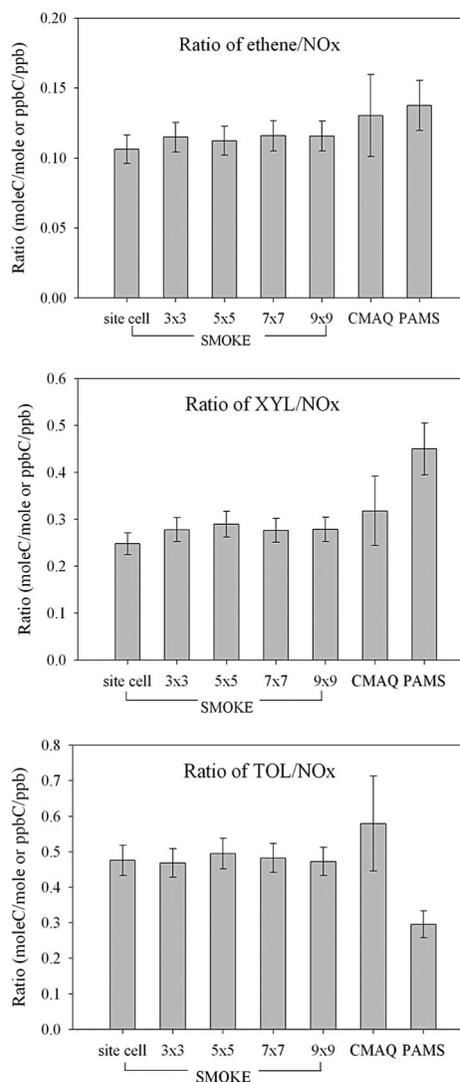


Figure 4. Comparison of average ratios between the estimated (SMOKE or CMAQ) and the observed values in the morning from 6:00 a.m. to 9:00 a.m. for Essex, MD. The error bars indicate the 2σ SEM (95% CI).

The estimated ratios of ethene to NO_x from SMOKE and CMAQ are within an acceptable range of the corresponding observed ratio, taking into account the uncertainties associated with the averages. However, the model XYL/ NO_x ratio appears to be somewhat underestimated, whereas the model TOL/ NO_x seems considerably overestimated by a factor of 1.5–2.

Figure 5 compares the average concentration predicted by CMAQ to the observed values in the morning period from 6:00 a.m. to 9:00 a.m. at Essex, MD. The concentration of NO_x predicted by CMAQ is a little higher than the observed NO_x concentration. In addition, ethene and TOL show a trend similar to the ratio comparisons in Figure 4. On the other hand, the predicted XYL concentration is in good agreement with observed XYL.

To identify the major sources of TOL, XYL, and ethene in the estimates, SMOKE was run with only surface coating and printing and vehicle exhaust emissions. Table 2 shows the average percentage contribution of both emission sources to emission estimates of each modeling

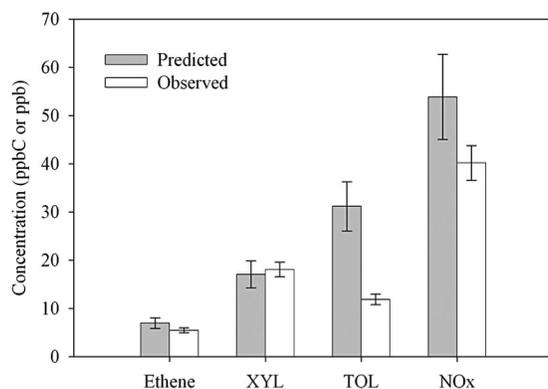


Figure 5. Comparison of average concentrations between the predicted (CMAQ) and the observed values in the morning from 6:00 a.m. to 9:00 a.m. for Essex, MD. The error bars indicate the 2σ SEM (95% CI).

species in the morning period around the three observation sites. As indicated in Table 2, ~50% of estimated TOL in the vicinity of the Essex site is emitted from surface coating and printing sources, and 30% from vehicle exhaust. If the estimates of vehicle exhaust emissions are assumed to be acceptable, as indicated by the favorable comparison between observed and estimated ethene/ NO_x ratios, an overestimate of emissions from surface coating and printing sources would be the likely cause for the overestimated TOL/ NO_x ratio.

At the McMillan Reservoir site in Washington, DC, there is little variability in the spatial distribution of emission estimates of ethene/ NO_x , and TOL/ NO_x from SMOKE, as shown in Figure 6. For the XYL/ NO_x ratio, there is some spatial variability, but this is not a remarkable change. Also, the ratios from CMAQ and SMOKE show good agreement with each other for all of the species.

Table 2. Average percentage contribution of sources to emission estimates of each species in the morning period by SMOKE.

Grid cells	Essex, MD		McMillan Reservoir, Washington, DC		Camden, NJ	
	Solvent ^a	Vehicle	Solvent ^a	Vehicle	Solvent ^a	Vehicle
Ethene (%)						
Site cell	0	62	0	88	0	93
3 × 3	0	62	0	70	0	68
5 × 5	0	62	0	74	0	53
7 × 7	0	56	0	76	0	49
9 × 9	0	56	0	78	0	50
TOL (%)						
Site cell	40	31	55	37	52	42
3 × 3	54	34	55	35	53	36
5 × 5	56	34	54	34	58	31
7 × 7	54	30	52	35	59	28
9 × 9	54	31	50	36	58	29
XYL (%)						
Site cell	20	57	28	61	22	64
3 × 3	27	56	27	54	25	57
5 × 5	28	54	25	51	29	50
7 × 7	28	52	23	53	30	45
9 × 9	27	53	21	54	30	47

^aSolvent represents surface coating and printing solvent utilization sources.

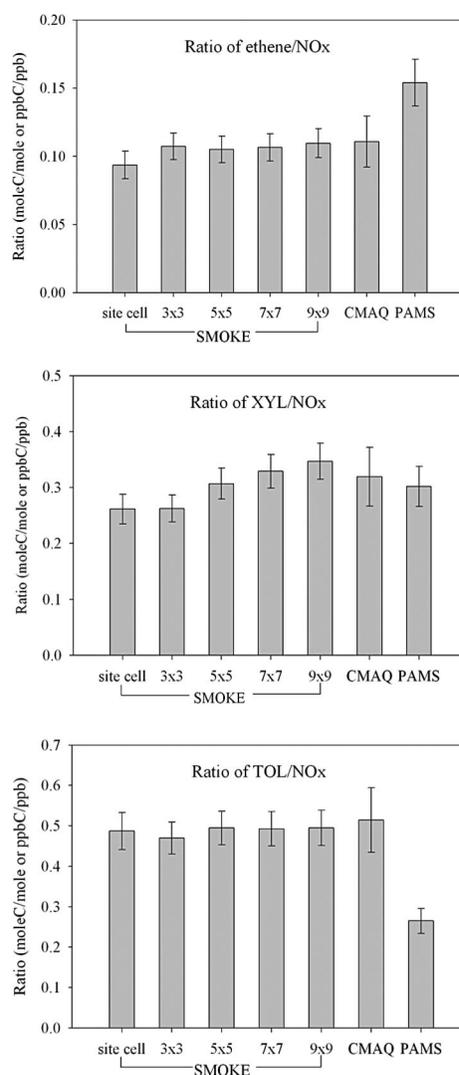


Figure 6. Comparison of average ratios between the estimated (SMOKE or CMAQ) and the observed values in the morning from 6:00 a.m. to 9:00 a.m. for McMillan Reservoir in Washington, DC. The error bars indicate the 2σ SEM (95% CI).

Although the XYL/ NO_x ratio shows good agreement with observation, ethene/ NO_x is slightly underestimated, and TOL/ NO_x is overestimated with statistical significance at the 95% CI. In Figure 7, the predicted NO_x at the McMillan site is three times higher than observed NO_x , and other species show similar patterns of overestimations. However, considering that the ratios from CMAQ in Figure 6 are similar to those from SMOKE, the consistent overestimation of concentrations from CMAQ implies that the overestimates of all three species are likely at least partly attributable to a miscalculated mixing height. Hence, for this site we cannot consider the result for the comparison of absolute concentrations. From Table 2, >70% of the estimated ethene comes from vehicle exhaust. Approximately 50% of the estimated XYL is emitted from vehicle exhaust with 30% from surface coating and printing sources. On the other hand, ~50% of the estimated TOL around this site is emitted from surface coating and printing sources, whereas 35% comes from vehicle exhaust. The data suggest that surface coating and printing solvent sources are significantly overestimated in this area.

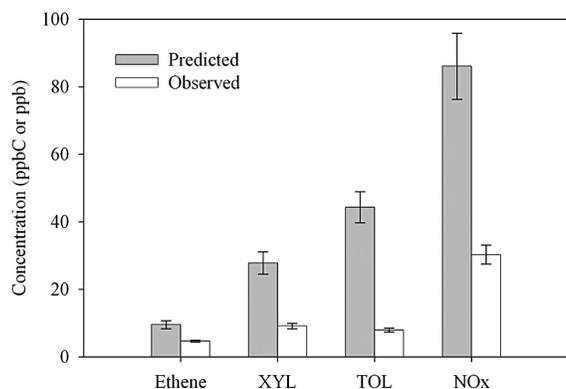


Figure 7. Comparison of average concentrations between the predicted (CMAQ) and the observed values in the morning from 6:00 a.m. to 9:00 a.m. for McMillan Reservoir in Washington, DC. The error bars indicate the 2σ SEM (95% CI).

At the Camden site in New Jersey, the estimated emission ratios for the grid cells surrounding the site are spatially nonhomogeneous with large emissions gradients observed among grid cells in the inventory. As shown in Figure 8, the ratios of all three species from CMAQ and SMOKE show overestimation. In particular, the estimated TOL/CO ratio is two to three times higher than the observed ratio. The comparison of concentrations shows the same trend of overestimation, as indicated in Figure 9. Also, the relative contributions of sources to emission estimates are very similar to those at the other two PAMS sites.

In addition, we adjusted NO_x estimates or CO estimates in the ratios, in accordance with the comparison of CMAQ outputs and observations, to look at whether the result would be affected if the NO_x or CO estimations were wrong. Figure 10 shows the ratio comparison of TOL to adjusted NO_x or CO for the Essex, MD, and Camden, NJ, sites. The McMillan Reservoir site in Washington, DC, was excluded because of concern that the estimated mixing height was wrong and that the estimated concentrations at this site did not reflect real values. As shown in Figures 5 and 9, NO_x or CO is slightly overestimated. We can expect that the extent of overestimation in the ratios with the adjustment of NO_x or CO to the ambient value will be larger than without adjustment. Hence, Figure 10 reveals that the overestimate of TOL becomes larger after adjusting NO_x or CO.

As stated above, the results for all three sites suggest a significant overestimate of surface coating and printing solvent emissions, whereas the estimates of emissions from vehicle exhaust differ depending on location. However, the observed TOL might underrepresent the actual concentration because of the unidentified portion in PAMS observations as mentioned earlier; this result is very dependent on the VOC speciation step in SMOKE. If the speciation of VOC does not represent reality, this comparison might lead to an erroneous conclusion. Therefore, we implemented another method of evaluation of emissions estimates from vehicle exhaust and surface coating and printing solvent sources, a source apportionment technique. The next section describes the method and the results.

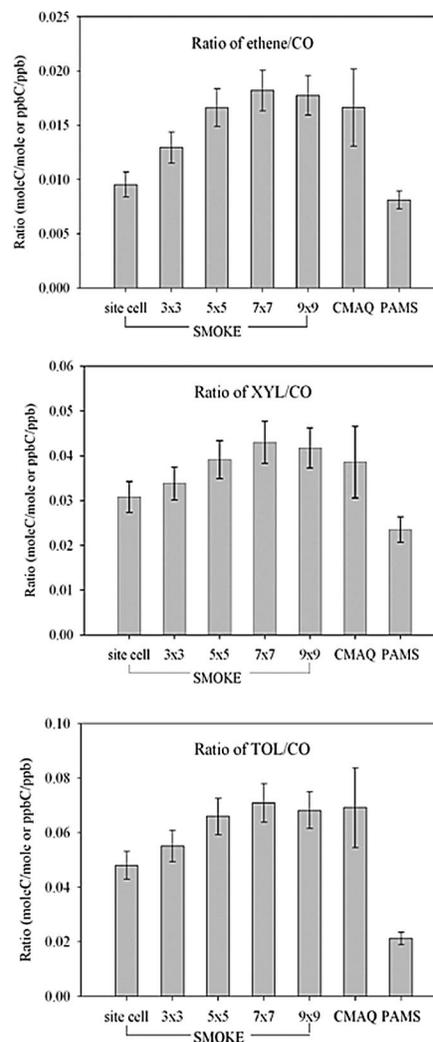


Figure 8. Comparison of average ratios between the estimated (SMOKE or CMAQ) and the observed values in the morning from 6:00 a.m. to 9:00 a.m. for Camden, NJ. The error bars indicate the 2σ SEM (95% CI).

Comparison of Ratios of VOC Source Categories Using a Source Apportionment Model (UNMIX). Using PAMS measurements from Essex, MD, six possible VOC emission sources

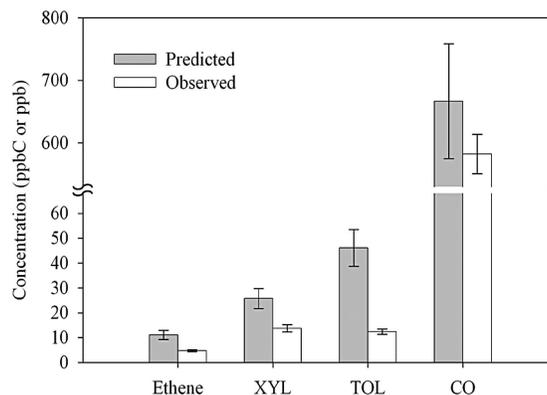


Figure 9. Comparison of average concentrations between the predicted (CMAQ) and the observed values in the morning from 6:00 a.m. to 9:00 a.m. for Camden, NJ. The error bars indicate the 2σ SEM (95% CI).

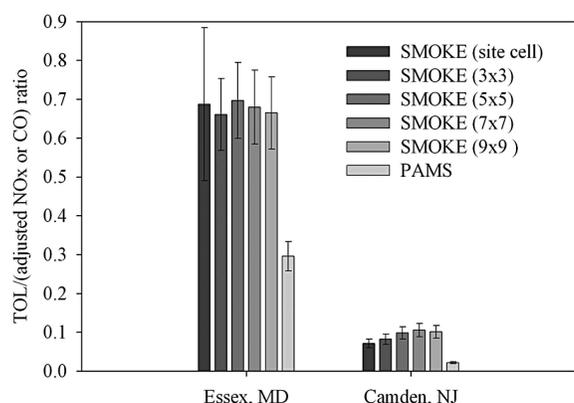


Figure 10. Comparison of average ratios of TOL to adjusted NO_x or CO between the estimated (SMOKE) and the observed values in the morning period of 6:00 a.m. to 9:00 a.m. The error bars indicate the 2σ SEM (95% CI).

were identified: vehicle exhaust, gasoline vapor, liquid gasoline, surface coating and printing solvent utilization, natural gas, and biogenics. The procedure of identification of source categories is described in the study of VOC emissions sources in the Baltimore area using PAMS measurements by Choi and Ehrman.²⁴ As for the DC and NJ measurements, we could not identify distinct surface coating and printing sources of VOC using UNMIX. The unexplained source categories, which may represent real sources or mixtures of real sources, were extracted by using UNMIX at the DC and NJ sites. The composition of each of these source categories showed a high portion of toluene, suggesting a possibility that a surface coating and printing solvent source category may be mixed into other source categories instead of being separated out as a distinct category. Hence, we focus here on the source apportionment results from the Essex, MD, site only.

Figure 11 shows a comparison of the average ratios of VOC source contributions to total NO_x estimated from SMOKE and UNMIX at Essex, MD. The ratios for vehicle exhaust are underestimated. In contrast, the surface coating and printing source contribution from SMOKE is two times higher than that obtained by source apportionment. This overestimate of surface coating and printing

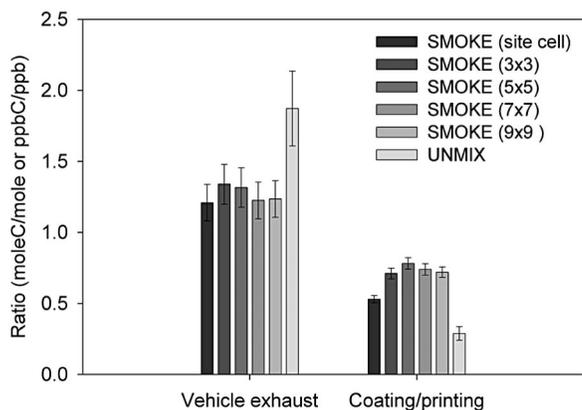


Figure 11. Comparison of average ratio of each VOC source contribution to NO_x between estimates from SMOKE and UNMIX for Essex, MD, in the morning from 6:00 a.m. to 9:00 a.m. The error bars indicate the 2σ SEM (95% CI).

solvent sources is consistent with the results for the comparison of individual VOC species in the previous section. We could not perform the same comparison using the DC and NJ measurements, but the consistency of the results between VOC species comparison and VOC source contribution comparison at the Essex site suggests that the overestimate of emissions from surface coating and printing solvent sources may also occur at the McMillan Reservoir in DC and the Camden, NJ, sites.

Modeling the Impact of VOC Surface Coating and Printing Solvent Source Emissions Reduction on Ozone and Anthropogenic Secondary Organic Aerosol (SOA) Concentrations. Researchers have pointed out the uncertainties associated with PAMS measurements.^{39–41} According to an internal consistency test of PAMS measurements at several observation sites by Parrish et al.,³⁹ poor precision and systematic measurement errors were present in the PAMS measurements. Our study was based on PAMS measurements, and a certain degree of uncertainty may exist in the results. Nevertheless, there are several studies suggesting a result for solvent emissions similar to this study. Mannschreck et al.⁷ evaluated an emissions inventory for the city of Augsburg in Germany using an extensive comparison between individual hydrocarbons (HC_i) and total measured hydrocarbons (HC_{sum}), HC_i/CO , $\text{HC}_{\text{sum}}/\text{CO}$, and $\text{HC}_{\text{sum}}/\text{NO}_x$ emission ratios from measured concentrations, and modeled emissions. Their results showed a possible overestimate of emissions from solvent sources. Mannschreck et al.⁷ suggested an additional analysis from measurements including oxygenated and halogenated VOC, which are important solvent components, and implementation of a source apportionment model. In addition, Watson et al.¹⁵ reviewed VOC source apportionment using the chemical mass balance (CMB) method in >20 urban areas, mainly in the United States, and pointed out that coatings and solvent contributions were much lower than the proportions attributed to these sources in current emissions inventories.

Although we cannot perform additional analyses using oxygenated and halogenated VOCs, use of two different approaches at the Essex, MD, PAMS site, relative and absolute comparison of individual species and relative comparison of source contribution to NO_x , leads to a similar conclusion about the estimate of surface coating and printing source emissions. The other two sites also showed patterns of overestimates of TOL like those at the Essex site, suggesting that overestimation of surface coating and printing solvent sources in urban and suburban areas may be a general phenomenon, as Watson et al.¹⁵ pointed out in their review.

Based on the findings of this study and other studies, the impact of a reduction of surface coating and printing source VOC emissions on O_3 and anthropogenic SOA concentrations in the study domain was investigated using a photochemical air quality model. VOC emissions from these sources throughout the study domain were reduced by 50%, in line with the average overestimate at the three PAMS sites. This reduction corresponds to a 9% reduction of total VOC emissions. A CMAQ simulation was performed with this modified emissions inventory. Figure 12 compares the frequency distributions of hourly surface O_3 and anthropogenic SOA concentrations for the base case and the 50%

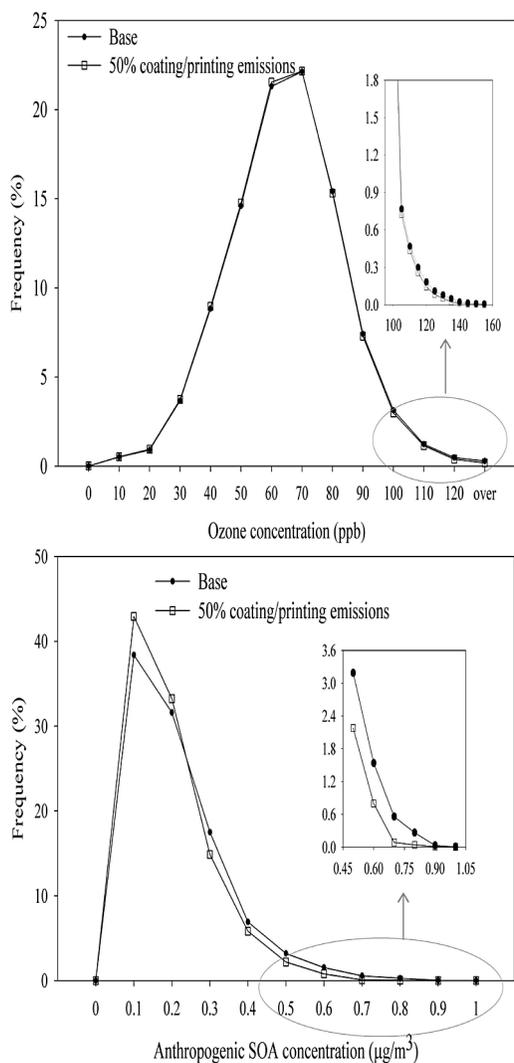


Figure 12. Comparison of the frequency distributions of hourly surface O_3 and anthropogenic SOA concentrations between the base case and the case with 50% of the total surface coating and printing VOC emissions from July 11 to July 14, 1997, based on all grids in the modeling domain.

reduction in the surface coating and printing VOC emissions case. For O_3 , there is little difference between these cases. The maximum difference in O_3 concentration between the two cases when paired in time and space was <10 ppb. The solvent emissions around the three PAMS sites are roughly speciated to 55% PAR, 25% TOL, 11% NR, and 8% XYL. According to a study of photochemical O_3 creation potential for organic compounds by Derwent et al.⁴² and a study of O_3 reactivity scales for VOCs by Carter,⁴³ TOL shows one-third to one-half of the O_3 forming potential of XYL, which has approximately as high an O_3 forming potential as isoprene. Hence, the undetectable change of O_3 after a surface coating and printing emissions reduction may result from these emissions being dominated by VOC species that do not have high O_3 -forming potentials. As another reason, it is speculated that this region has NO_x -sensitive characteristics, such that VOC control does not result in a remarkable change of O_3 concentration. When it comes to anthropogenic SOA, the difference between two cases is not substantial. However, we can see a noticeable decrease

of SOA concentrations in with 50% surface coating and printing emissions reduction when we take a closer look at the cases of high concentrations of SOA. TOL and XYL have been studied as precursors of secondary organic aerosol, and their aerosol yields are approximately similar.^{44,45}

CONCLUSIONS

At the Essex, MD, and McMillan Reservoir (Washington, DC), sites, the comparisons of ethene/ NO_x and XYL/ NO_x ratios between estimates and measurements and the comparisons of predicted ethene and XYL concentrations to the corresponding observed concentrations showed some differences between methods. However, the results for the Camden, NJ, site demonstrated consistent results between comparison methods, implying a possible overestimate of vehicle exhaust at this site. In terms of TOL, which is mainly emitted from surface coating and printing solvent utilization sources, the ratio of TOL/ NO_x , as well as absolute concentrations of TOL and NO_x , revealed overestimates of surface coating and printing sources by a factor of 1.5 to 3 at all three sites. In addition, overestimates of surface coating and printing source emissions were corroborated by comparing ratios of VOC surface coating and printing source contribution to NO_x to the ratio from SMOKE at the Essex, MD, PAMS site. Other investigators also proposed that surface coating and printing solvent sources were overestimated, implying the possibility of inaccurate emission factors in estimating VOC emissions from these sources. Hence, we recommend additional investigation of the emissions inventory of surface coating and printing solvent utilization sources and their emission factors.

The photochemical model simulations did not show a perceptible change in O_3 concentrations after the reduction of surface coating and printing VOC emissions, possibly because this region is NO_x sensitive or because the chemical species emitted by these sources do not readily form O_3 . However, a 50% reduction in modeled surface coating and printing emissions did produce a noticeable reduction in SOA concentrations, especially for the most polluted hours.

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