

Diagnostic Air Quality Model Evaluation of Source-Specific Primary and Secondary Fine Particulate Carbon

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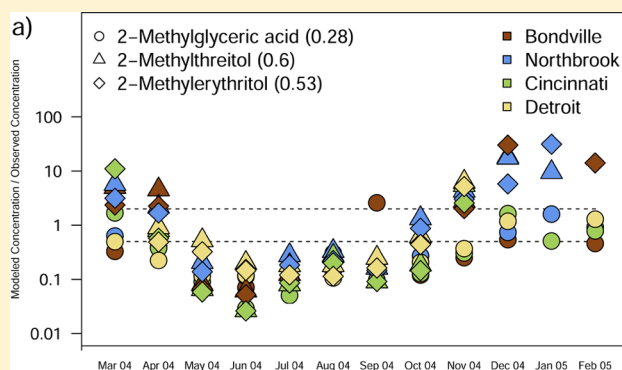
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S Supporting Information

ABSTRACT: Ambient measurements of 78 source-specific tracers of primary and secondary carbonaceous fine particulate matter collected at four midwestern United States locations over a full year (March 2004–February 2005) provided an unprecedented opportunity to diagnostically evaluate the results of a numerical air quality model. Previous analyses of these measurements demonstrated excellent mass closure for the variety of contributing sources. In this study, a carbon-apportionment version of the Community Multiscale Air Quality (CMAQ) model was used to track primary organic and elemental carbon emissions from 15 independent sources such as mobile sources and biomass burning in addition to four precursor-specific classes of secondary organic aerosol (SOA) originating from isoprene, terpenes, aromatics, and sesquiterpenes. Conversion of the source-resolved model output into organic tracer concentrations yielded a total of 2416 data pairs for comparison with observations. While emission source contributions to the total model bias varied by season and measurement location, the largest absolute bias of $-0.55 \mu\text{gC}/\text{m}^3$ was attributed to insufficient isoprene SOA in the summertime CMAQ simulation. Biomass combustion was responsible for the second largest summertime model bias ($-0.46 \mu\text{gC}/\text{m}^3$ on average). Several instances of compensating errors were also evident; model underpredictions in some sectors were masked by overpredictions in others.



INTRODUCTION

Carbonaceous aerosol is a substantial portion of fine particulate matter ($\text{PM}_{2.5}$) in the United States and throughout the world.^{1,2} Accurate predictions of particulate carbon concentrations by air quality models are essential for efficiently designing control strategies and for understanding chemical and physical properties of the troposphere. Epidemiological and clinical studies show substantial associations specifically for particulate elemental carbon (EC) and organic carbon (OC) concentrations with various health end points.³ Particulate carbon in the atmosphere both absorbs and scatters incoming solar radiation and affects the Earth's energy balance, making it the second largest climate forcing agent after CO_2 .⁴ Furthermore, controlling primary particulate carbon emissions may be an efficient way to delay and reduce the effects of global climate change.^{5,6} Given its short lifetime in the atmosphere, due to removal by precipitation, controls on particulate carbon would have an immediate impact on both human health and climate forcing.

Particulate carbon comes from a myriad of emissions sources and atmospheric processes. Although correctly simulating

particulate carbon concentrations in the ambient atmosphere has been an active area of research, persistent biases remain in regional air quality models.^{7,8} These model biases have been difficult to diagnose, due to the fact that routine observations are limited to bulk characterization with distinction provided only between OC and EC, oxygenated and hydrocarbon-like OC, or water-soluble and insoluble OC. Therefore, model evaluation has largely been possible only for these bulk quantities.^{9,10} Some more detailed diagnostic air quality modeling studies have been conducted in the past on the basis of nonroutine measurements of source-specific organic tracer compounds. These studies initially focused only on primary sources in a single urban area such as Los Angeles,^{11,12} they were later expanded to larger geographic regions for a single season,¹³ and more recently, secondary carbon formation was analyzed in an urban area.¹⁴ As a parallel effort, other

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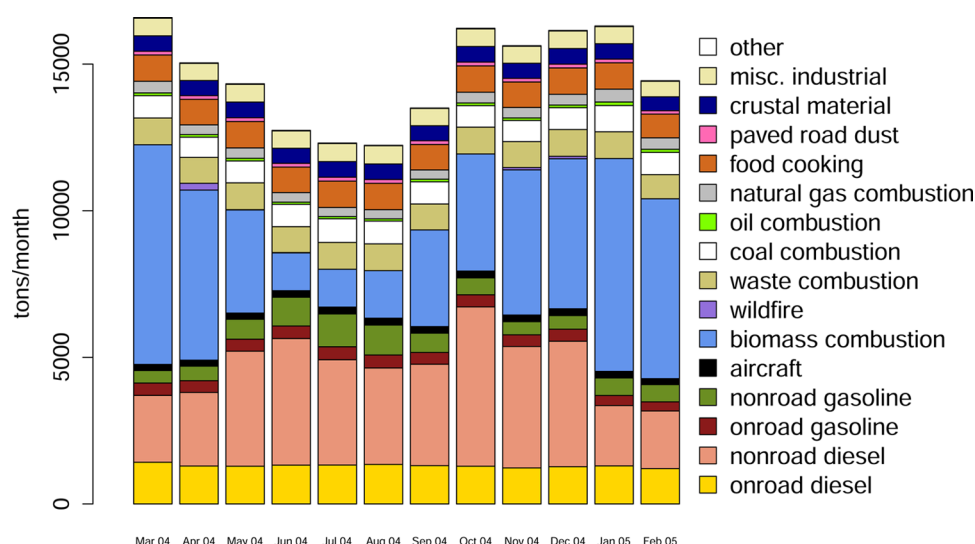


Figure 1. Monthly total primary particulate carbon emissions in the states containing and surrounding the measurement sites (Wisconsin, Illinois, Michigan, Indiana, and Ohio). The two diesel combustion sectors dominate together with the anthropogenic biomass combustion sector, which is high in the colder months.

studies have attempted to constrain the source/receptor relationships through the use of measurement-based source apportionment models that attempt to resolve measured concentrations as combinations of sources on the basis of either known or inferred source emission profiles.^{15,16}

The recent advent of a year-long collection of organic tracer measurements for both primary and secondary sources at multiple locations coupled with new laboratory-based speciation profiles of secondary organic aerosol (SOA) have allowed for an unprecedented opportunity to overcome some of the previous limitations in diagnostic model evaluations for particulate carbon. Furthermore, substantial improvements to the SOA treatment in air quality models allow for quantifying precursor-specific contributions to particulate carbon.⁹ A comprehensive model evaluation using ambient measurements of source-specific tracers for primary and secondary fine particulate carbon is presented.

METHODS

Measurements. The measurements of organic tracer compounds have been detailed in depth by Lewandowski et al.¹⁷ and are only briefly described here. Ambient samples were collected at four midwestern United States locations from March 2004 to February 2005. Three sites were characterized as urban: Detroit, MI, Cincinnati, OH, and Northbrook, IL. A fourth site at Bondville, IL, was characterized as rural. Data were also collected at a fifth site in East St. Louis, IL, but were deemed unreliable for the purposes of this study due to poor mass closure.¹⁷ Filter sampling was conducted every sixth day for 24 consecutive hours. Monthly composites were constructed at each site using three to six available daily filter samples. The composite samples were analyzed quantitatively for approximately 100 organic markers using gas chromatography/mass spectrometry (GC-MS). The broad categories of organic markers collected included hopanes and steranes, polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, *n*-alkanoic acids, other organic acids, and other organic compounds including levoglucosan, as well as compounds that uniquely indicate SOA originating from single-ring aromatics, isoprene, monoterpenes, and sesquiterpenes.

Model. Air quality model simulations were performed using the Community Multiscale Air Quality (CMAQ) model version 4.7.1 equipped with carbon apportionment (CA) capabilities for the entire sampling period with an additional discarded month (January 2004) for initialization. CMAQ-CA is a diagnostic version of the base CMAQ model that tracks the source origins of primary carbonaceous aerosol.¹³ The model was driven by meteorology from MMS version 3.6.3¹⁸ and emissions data processed by the Sparse Matrix Operator Kernel Emissions (SMOKE) software version 2.4¹⁹ based on temporally and spatially resolved wildfire, electricity generating units, and mobile sources. The source tagging option in SMOKE was exercised as described below in order to track source-specific primary carbon emissions. CMAQ was configured using the Statewide Air Pollution Research Center (SAPRC99) chemical mechanism,²⁰ and SOA treatment included in the CMAQ modal aerosol module version 5 (AEROS).⁹ Model simulation was performed on a 12 km horizontal grid covering the eastern United States nested within a 36 km grid covering the entire continental United States and parts of Canada and Mexico. Vertically, 24 layers were employed up to a pressure level of 100 mb. The meteorological inputs and base air quality model performance were both evaluated in previous studies and were shown to have reasonable performance.²¹

CMAQ-CA was used to track EC and primary OC from 15 different source categories (given in Figure 1). A 16th source included other unaccounted sources as well as boundary concentrations specified from simulations on an encompassing 36 km domain. Similar to the base model, these categories exist in both the Aitken and accumulation size modes for both primary EC and primary OC and participate in the standard physical processes tracked by the model identically with their corresponding aggregate bulk species. Because of the near-linearity of the processes governing the evolution of primary carbon through the model algorithms, the results of tagged concentrations were easily verified by comparing their sum to the bulk concentration calculated by a standard CMAQ application.

Table 1. Source Speciation Profiles for Secondary Organic Aerosol Tracers^a

molecular marker	terpene SOA	aromatic SOA	isoprene SOA	sesquiterpene SOA
3-acetylpentanedioic acid	4.85×10^{-3}			
2-hydroxy-4-isopropyladipic acid	8.84×10^{-3}			
3-acetylhexanedioic acid	6.10×10^{-2}			
3-hydroxyglutaric acid	6.84×10^{-3}			
2-hydroxy-4,4-dimethylglutaric acid	5.04×10^{-3}			
3-(2-hydroxyethyl)-2,2-dimethylcyclobutanecarboxylic acid	3.36×10^{-2}			
pinic acid	2.47×10^{-2}			
pinonic acid	1.19×10^{-2}			
2,3-dihydroxy-4-oxopentanoic acid		3.97×10^{-3}		
2-methylglyceric acid			1.15×10^{-2}	
2-methylthreitol			1.94×10^{-2}	
2-methylerythritol			3.19×10^{-2}	
β -caryophyllinic acid				1.09×10^{-2}

^aRelationships were obtained by averaging experimental data detailed in Kleindienst et al.²³ All quantities are in (μg of marker)/(μg of SOA).

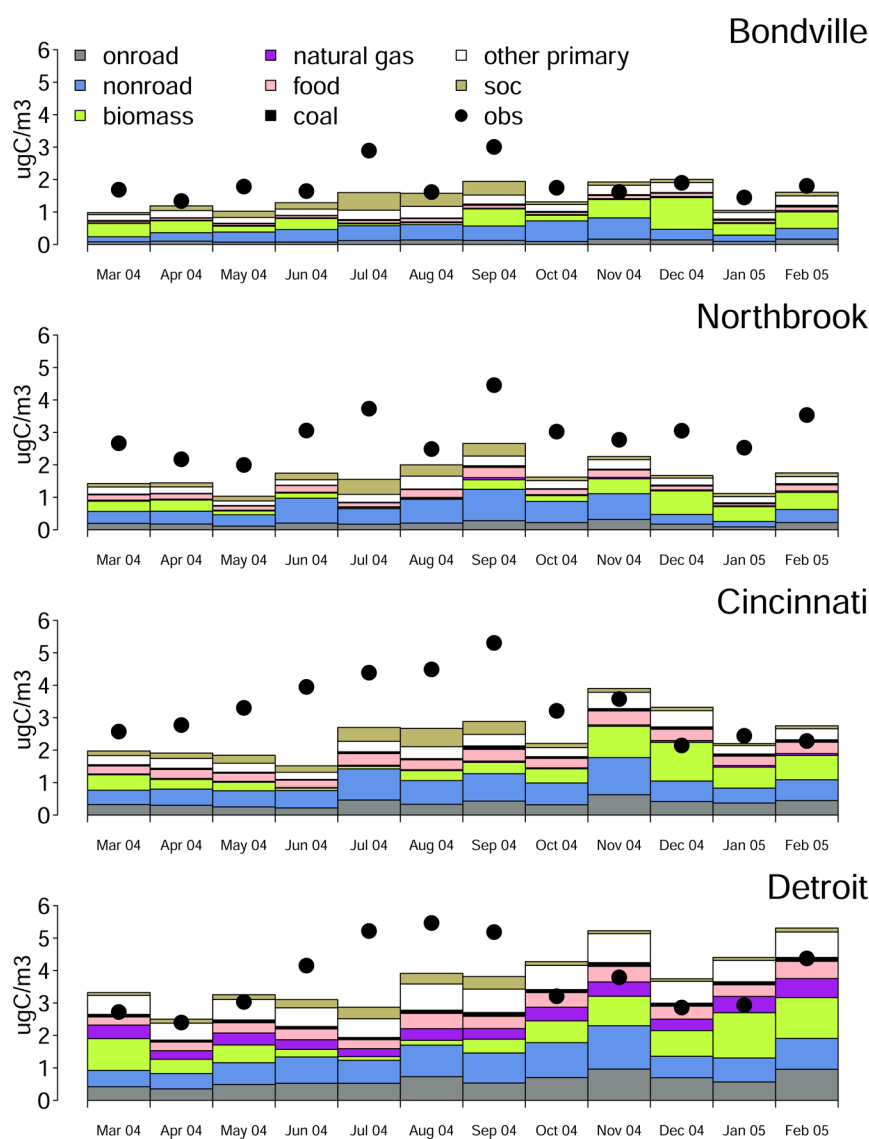


Figure 2. CMAQ model contributions to total organic and elemental carbon by month and site with observations overlaid. For plotting purposes, onroad diesel and onroad gasoline were summed, as were nonroad diesel and nonroad gasoline. The “other” category includes the rest of the tracked sources: aircraft exhaust, waste combustion, oil combustion, paved road dust, crustal material, and miscellaneous industrial sources. The “soc” category shows contributions from secondary organic carbon.

Table 2. Observed Total Carbon Concentrations and CMAQ Model Bias Attribution by Source, Season, and Location Determined through Molecular Marker Analysis^a

	spring (Mar–May)				summer (Jun–Sep) all sites		winter (Oct–Feb)			
	Detroit		non-Detroit				Northbrook		non-Northbrook	
	obs	model bias	obs	model bias	obs	model bias	obs	model bias	obs	model bias
total carbon	2.72	+0.30	2.26	−0.84	3.82	−1.46	2.99	−1.30	2.63	+0.38
mobile	1.27	−0.30	1.11	−0.54	1.24	−0.22	0.95	−0.28	1.05	−0.24
biomass combustion	0.58	+0.08	0.40	−0.09	0.66	−0.46	0.89	−0.42	0.91	−0.14
natural gas combustion	0.03	+0.32	0.01	+0.01	0.03	+0.07	0.02	+0.01	0.02	+0.17
coal combustion	0.04	+0.11	0.01	+0.04	0.03	+0.07	0.12	−0.06	0.03	+0.11
terpene SOA	0.20	−0.17	0.15	−0.12	0.37	−0.29	0.08	−0.06	0.09	−0.07
isoprene SOA	0.07	+0.01	0.26	−0.16	0.80	−0.55	0.02	+0.07	0.03	+0.05
aromatic SOA	0.19	−0.13	0.13	−0.07	0.25	−0.15	0.07	−0.02	0.08	−0.03
sesquiterpene SOA	0.26	−0.24	0.12	−0.07	0.22	−0.04	0.20	−0.19	0.18	−0.17
unexplained	0.08	+0.62	0.07	+0.16	0.22	+0.11	0.64	−0.35	0.24	+0.70

^aObserved data (obs) are based on converting molecular marker observations to carbon concentrations through the use of laboratory-obtained speciation profiles. The greatest sources of model bias are found to be in the isoprene SOA predictions, as well as biomass combustion and mobile emissions of primary carbon. Compensating errors were also evident in several cases. All results are in $\mu\text{gC}/\text{m}^3$.

To accommodate source tracking in CMAQ-CA, emissions of primary EC and primary OC were subdivided into the 16 source categories described above using SMOKE. The modeling episode specific emissions were based on the 2002 National Emissions Inventory (NEI) version 3 (<http://www.epa.gov/ttn/chief/net/2002inventory.html#documentation>). Year-specific adjustments were made to emissions from power plants, mobile sources, fires, and biogenic sources (computed using the Biogenic Emissions Inventory System (BEIS) model²²) to create the 2004–2005 emissions.²¹ This inventory consisted of thousands of source classification categories (SCCs) and approximately 4.7 million metric tons per year of $\text{PM}_{2.5}$ over the modeled domain. The particulate carbon emissions inventory of the states containing and immediately surrounding the measurement sites (Wisconsin, Illinois, Michigan, Indiana, and Ohio) was dominated by the onroad and nonroad diesel exhaust categories (32.4% of annual average) as well as anthropogenic biomass combustion in the colder months (29.5%), which included residential wood combustion and prescribed field burning operations (Figure 1).

To ensure consistency with the observations, model outputs for only the hours during which measurement instruments were operational and produced quality data were used to average up to monthly quantities to match with the collected composite samples.

Chemical Source Profiles. Source-specific carbon modeled by CMAQ-CA was decomposed into molecular marker concentrations for comparison with ambient measurements through laboratory-derived source speciation profiles following the methodology of Bhawe et al.¹³ An extensive compilation of source profiles associated with primary carbon emissions was collected from current literature that described the primary carbon emissions inventory almost entirely (Supporting Information, Table S1). Molecular marker data for SOA species are more limited, but tracers exist for all CMAQ modeled secondary species (given in Table 1). SOA source profiles were created on the basis of the work of Kleindienst et al.²³ Laboratory-measured tracer-to-carbon ratios were averaged with equal weights over all of the conducted experimental conditions in order to obtain a composite ratio (Table 1). The same speciation profiles were also used to convert observed molecular marker observations into concentrations of carbona-

ceous particulate matter for evaluation of source-specific model bias.

In total, 78 individual measured compounds (65 primary and 13 secondary) had availability of both the speciation profiles and sufficient collected ambient data at the four sites, allowing for evaluation of the CMAQ-CA model estimates. In this modeling exercise, it was assumed that the molecular marker species were neither lost to reaction nor produced by other processes.

RESULTS

An evaluation against routine total carbon ($\text{TC} = \text{OC} + \text{EC}$) measurements was performed first (Supporting Information, Figure S1), to provide a focus for further diagnosis. While CMAQ generally underestimated the ambient TC concentrations, three distinct temporal patterns emerged. First, there was a model bias of $-1.46 \mu\text{gC}/\text{m}^3$ on average during the summer months (June, July, August, and September) at all four sites. Model underestimates during the warm months have been reported in many previous studies and have been typically attributed to low model prediction of SOA.^{9,24,25} Second, a model bias of $-0.84 \mu\text{gC}/\text{m}^3$ occurred in the spring (March, April, and May) at the Bondville, Northbrook, and Cincinnati sites but not at the Detroit site, where a slight model overestimate was found (bias = $+0.30 \mu\text{gC}/\text{m}^3$ bias). Third, TC was estimated well (bias = $+0.38 \mu\text{gC}/\text{m}^3$) in the colder months of October through February at the Bondville, Detroit, and Cincinnati sites, consistent with the previous evaluation over this region,⁸ but was grossly underestimated at the Northbrook site (bias = $-1.30 \mu\text{gC}/\text{m}^3$). These three patterns in the model bias were diagnosed further using the tracer measurements.

CMAQ-CA allowed for a more detailed analysis of particulate carbon sources at these locations than in any previous study, because modeled TC concentration could be readily disaggregated into 16 primary and four secondary source contributions. It was found that the largest sector contributing to modeled carbon concentrations at all locations was nonroad vehicle exhaust, consistent with the emissions in the vicinity of the measurement sites (Figure 2). The largest specific sources contributing to nonroad vehicle exhaust were construction equipment, industrial equipment, aircraft, ships,

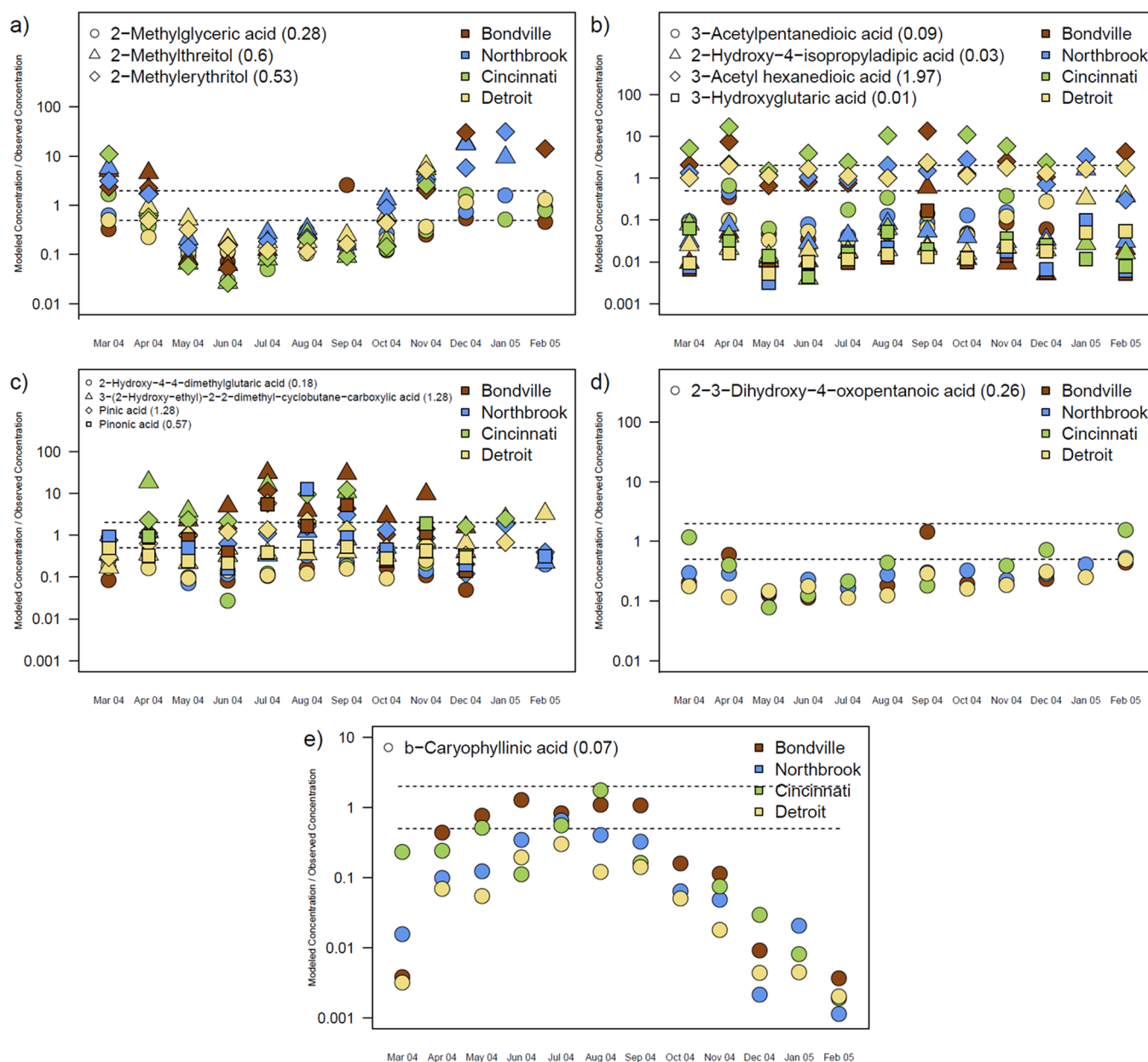


Figure 3. Model-to-observation ratios of secondary organic aerosol tracers for (a) isoprene, (b, c) terpene, (d) aromatics, and (e) sesquiterpene compound classes. Symbol shapes differentiate molecular tracer compounds, and symbol colors denote locations. Dashed horizontal lines bound a factor of 2 agreement between CMAQ and observations. The numbers in parentheses after the tracer names indicate the average model to observation ratio for all tracer-specific data on the plot.

and railroads. Additionally, the rural Bondville site had significant contributions from farm equipment. Anthropogenic biomass combustion contributed less than its relative emissions fraction, but still significantly in the colder months. Specific sources in emissions inventory included agricultural burning, fireplaces, wood stoves, residential open burning, and land clearing. Secondary organic aerosol was also a large contributor to carbon concentrations at all four sites during the summer months, as was onroad vehicle exhaust in the urban locations and natural gas combustion in Detroit.

For further analysis of the sources of discrepancies between modeled and observed carbon concentrations, the concentrations of 78 different organic compounds measured through monthly composite samples and estimated using CMAQ-CA were compared (Supporting Information, Tables S2–S5).

Because of several orders of magnitude of interspecies variability in ambient tracer concentrations, a ratio of the modeled-to-observed concentration was then computed to determine how well CMAQ replicates the measured quantities on a monthly averaged basis. These ratios varied by site, location, and compound (Supporting Information, Figures S3–S80), as discussed below.

Secondary Organic Aerosols. A novel component of this work was the year-round, multisite comparison of model results against precursor specific tracers of SOA. Although the CMAQ model has recently experienced a significant upgrade in its SOA module,⁹ the estimates of the various components of SOA were found to be consistently lower than the estimates based on organic tracer measurements in the midwestern cities.

Summer isoprene was the largest SOA component in both the measurements ($0.80 \mu\text{gC}/\text{m}^3$) and the modeling results ($0.25 \mu\text{gC}/\text{m}^3$) from all seasons and locations (Table 2). Three organic tracers have been identified in laboratory studies as markers for isoprene SOA: 2-methylglyceric acid, 2-methylthreitol, and 2-methylerythritol.¹⁷ Modeled concentrations were in agreement with observations during the colder months when both quantities were low (Figure 3a), but not in the summer, when the model low bias was the largest of all analyzed TC components ($-0.55 \mu\text{gC}/\text{m}^3$ on average for all components in all cities).

Several possible explanations exist for the low model to observation ratios of isoprene tracers. First, there may be other primary or secondary sources of these three tracers which would make the tracer to OC ratios measured in the laboratory experiments too low in comparison to ambient data. Second, the yields in the model could be too low to produce quantities of SOA comparable to the measurements.²⁶ Third, the model may not properly account for partitioning of isoprene reaction products from the gas to the particle phase. To investigate the third possible explanation, an alternative method for calculating the isoprene aerosol tracers that accounts for differences in organic partitioning in chamber experiments vs the ambient environment was also explored but did not lead to a better representation of 2-methylglyceric acid or the 2-methyltetrols (see the Supporting Information). Finally, the BEIS²² used in the development of the isoprene inventory has previously been reported to underestimate isoprene emissions in the Ozark mountains.²⁷ While vegetation in the upper midwest, where the current study is focused, differs from that of the Ozarks, Carlton and Baker suggest that further evaluation is needed for all North American isoprene emissions.²⁷

Furthermore, the tracer-based method implicitly assumes that the ratios of the individual tracers (two tetrols and one acid) to each other should remain relatively constant. However, these ratios fluctuated in time (Supporting Information Figure S96). Differing temporal patterns support the possibility that the formations of the three isoprene products follow different pathways and respond differently to atmospheric conditions. It has been shown that the formation of the tetrols occurs as a result of isoprene oxidation under low- NO_x conditions,²⁸ while methylglyceric acid results from high- NO_x oxidation pathways.^{29,30} This suggests that the role of NO_x in isoprene aerosol formation is important, and models may need to be updated to include this dependence allowing for predictions of high (2-methylglyceric acid) and low (2-methylthreitol and 2-methylerythritol) NO_x tracers and a more rigorous model evaluation.

Terpene SOA was traced by eight individual organic compounds with large variability in model performance among them with annual modeled to observed tracer ratios ranging from 0.01 to 1.97 (Figure 3b,c). Although different conclusions could be made about the direction of terpene bias depending on which tracers were used, Kleindienst et al.²³ showed good mass closure for TC by using the average of all tracer species. When values for all tracers were averaged, the comparison showed substantial underprediction in SOA formation from this source, particularly in the summer, when terpene bias was large ($-0.29 \mu\text{gC}/\text{m}^3$). Interestingly, three organic tracers suggested an overprediction of terpene SOA: 3-acetylhexanedioic acid, 3-(2-hydroxyethyl)-2,2-dimethylcyclobutanecarboxylic acid, and pinic acid (Supporting Information, Figures S70, S73, and S74). As with the isoprene tracers, several

explanations are possible for the discrepancy between modeled and observed concentrations. First, the laboratory-derived tracer to OC ratios may not represent formation that occurs on longer time scales. When these ratios are applied to modeled terpene SOA, the resulting tracer concentrations would be less than ambient levels. Second, the yields of α -pinene in the model could be too low to produce quantities of SOA comparable to the measurements.²⁶ Finally, the BEIS model based the terpene emission factors on experiments conducted on loblolly pine; however, hardwood forests are more prevalent in the midwest, leading to potential errors in emissions of monoterpenes.

Measurements were available for one tracer of aromatic SOA component: 2,3-dihydroxy-4-oxopentanoic acid (Figure 3d). Anthropogenic aromatics yielded a relatively small summer SOA fraction in the model but were found to be a substantial fraction of carbon in the winter, when the total biogenic components are lower. On an annual average, the tracer ratios indicated a bias of $-0.08 \mu\text{gC}/\text{m}^3$ ($-0.15 \mu\text{gC}/\text{m}^3$ in the summer). Sources of aromatic precursors included evaporative and tailpipe emissions from the mobile sector, as well as solvents and paints. Emissions were unlikely to be fully responsible for the model underestimation, because the hopane and sterane analysis indicated that primary emissions from mobile sources were roughly correct. It is possible that the aromatic yields used in the model were low, and evidence exists for using higher values.³¹ Also, this particular tracer has been shown to be difficult to measure and has the highest degree of uncertainty of all SOA tracers.³² The tracer to OC ratio used as the profile may have been too low, because the 6 h residence time used in its derivation is likely to be too short for the formation of this molecule. Both the possibility for higher yields and the more robust tracer measurements in the laboratory and the ambient air are currently being explored in order to resolve the bias in this SOA component.

Sesquiterpene SOA had the smallest model summer bias. The three cities had an underestimation of $-0.04 \mu\text{gC}/\text{m}^3$ carbon for this source in the summer, as indicated by a single tracer: β -caryophyllinic acid (Figure 3e). Interestingly, the bias was found to be higher in the colder months. Tracer observations indicated appreciable concentrations during the spring and winter, while the model predictions produced values near 0. In fact, this was the only SOA source for which the model failed to capture the annual variability in the observations (Supporting Information, Figure S99). The model sesquiterpene PM yields were set to the maximum possible from the stoichiometry, suggesting that all of the precursor emissions were eventually condensed into semi-volatile compounds that were then partitioned into aerosols. Therefore, it is unlikely that yields were responsible for poor model performance in this case. Instead, missing sources of emissions in the colder months that produced this class of SOA and its associated tracer acid are currently explored as explanations for this result.

Biomass Combustion. Levoglucosan has been widely used as a tracer for biomass combustion, because it is a byproduct of cellulose breakdown during combustion of plant material.³³ This compound is typically found in abundance both in laboratory wood burning experiments and ambient samples, allowing for robust measurements well above the detection limit. CMAQ-CA tracks biomass burning from agricultural burning, wildfires, residential wood combustion, and other anthropogenic sources. Model estimates showed biomass

combustion to be the second largest source of TC on an annual average basis at all four sites. The ratios of modeled to observed concentration of levoglucosan were within a factor of 2 during 9 out of 12 months (Supporting Information, Figure S67). A low ratio in the summer indicated the possibility of a missing emission source, such as a wildfire, leading to significant model underestimates. While 2004 was an extreme wildfire year in Alaska and the Yukon due to above-average temperatures, the driest summer, and the most lightning strikes on record,³⁴ the contiguous United States had a below-average number of occurrences of wildfires.³⁵ Still, the model underprediction coincided with the peak of a typical wildfire season (June, July, and August) and emissions from this source were likely underestimated. New research shows promise in better determining wildfire locations and magnitude on the basis of satellite detection, which should improve these comparisons.³⁶ During the colder months, the levoglucosan ratio at Northbrook was consistently below 1.0 (Oct, 0.3; Nov, 0.7; Dec, 0.8; Jan, 0.6; Feb, 0.4) and on average below the same ratio at the other sites. Furthermore, both measured and observed levoglucosan values were the highest during this season (Supporting Information, Table S3). The seasonality of this occurrence pointed to substantial residential wood combustion emissions and the possibility that this source was underpredicted near Northbrook. Ongoing work is focused on residential wood combustion, due to its substantial yet highly uncertain emissions in terms of locations, timing, and magnitude.

While levoglucosan has been consistently identified as the major constituent of fine particulate emissions from biomass combustion,^{37–39} recent laboratory studies suggest that it may be chemically unstable in the atmosphere.⁴⁰ Fast degradation through reaction with the hydroxyl radical would make it unsuitable as a molecular marker. This effect would be most important during the summer, when OH levels are high, and less substantial during the winter. However, more evidence is necessary to demonstrate the applicability of such conclusions to ambient samples. Because of its abundance in the ambient atmosphere, if this tracer did, in fact, degrade appreciably, then particulate carbon contributions from wood burning would be much higher and ultimately surpass the total unapportioned carbon mass. As such, evidence for significant atmospheric degradation of levoglucosan was not supported by this analysis. Further studies with additional measurements of other tracers associated with biomass combustion may be necessary for further validation.

Mobile Sources. Previous studies demonstrated good agreement between modeled and observed concentrations of hopanes and steranes in urban areas during the summer.^{11–13} These compounds have been identified as robust indicators of mobile source emissions due to their abundance in crude oil as the result of bacterial processes in sediments. The results here were consistent with earlier findings, implying that the summer TC underestimation attributed to motor vehicles was small relative to the observed fraction of the same. At the rural Bondville site, concentrations fell below the measurable detection limit (MDL) for eight out of nine motor vehicle tracers during all summer months, whereas the model estimates consistently exceeded the MDL (Supporting Information, Table S2 and Figures S12–S20). This is consistent with the suggestion that these tracers may undergo degradation in the atmosphere at some distance from emissions sources.⁴¹ In contrast, there was good agreement with the hopane and

sterane observations at urban sites during cooler months (October–February), suggesting that the gradual degradation of these tracers can be neglected due to lower oxidant levels in the winter. The model systematically underestimated the springtime (March–May) urban concentrations of hopanes and steranes by more than the measurement uncertainty in 29 of the 32 available model/observation pairs.

One reason for the persistent low model bias in mobile sources could be the incorrect representation of the fraction of “high emitter” vehicles in the emission inventory. Previous mobile emissions work has indicated that high-molecular-weight polycyclic aromatic hydrocarbons (PAHs) are emitted in higher ratios by spark ignition vehicles under normal operating conditions, while hopanes are enriched in the exhaust of “smoking” vehicles.⁴² The results showed that the hopanes were underpredicted in this analysis (ratios of 0.55–0.83), while the higher molecular weight PAHs (indeno[1,2,3-*c,d*]pyrene, benzo[*ghi*]perylene, and coronene) were overpredicted (ratios of 2.2–3.9), supporting the conclusion that the emissions inventory fleet composition likely did not have enough of the higher polluting vehicles.

Natural Gas. The formation of ketones has been shown to be associated with natural gas combustion.⁴³ Three ketones have consistent measurements available during this time period: 1*H*-phenalen-1-one, anthracen-9,10-dione, and benz(*a*)-anthracene-7,12-dione. Anthracen-9,10-dione and, to a lesser extent, 1*H*-phenalen-1-one are also associated with combustion of other fossil fuels, but their source signature for natural gas is several orders of magnitude higher (Supporting Information, Tables S2–S5 and Figures S91–S93). Fluoranthene is also strongly associated with natural gas combustion, but its weaker associations with wood burning and mobile emissions complicate its signal because contributions from these two sectors are so large. Model-predicted natural gas combustion was only a significant contributor to carbon concentrations in Detroit of the four analyzed sites, where it was a substantial and persistent source throughout the year. The model to observation ratios for the three ketones were found to be significantly higher than 1.0 during most months and in most locations, suggesting an overestimation of the emissions in this sector (Supporting Information, Figures S64–S66). The largest model overestimate was found to be in the spring months in Detroit, which also had a net positive bias in the TC comparison. Correcting for the model overestimate in this sector in Detroit would put the city more in line with the other three locations for both modeled and observed natural gas combustion tracers. Furthermore, this result provided evidence of compensating errors that likely played a role in the relatively better bulk carbon model performance in the spring at this site, since some carbon sources (mobile and SOA) were underestimated.

Coal Combustion. While no direct tracer profile exists for coal combustion that had measurements during this field study, some polycyclic aromatic hydrocarbons (PAHs) have been shown to be present in the measured source profiles of coke ovens.⁴⁴ Assuming that their source profile is similar to that of coke, which is derived from bituminous coal, two PAHs were found to be attributed by the CMAQ-CA to originate primarily from coal combustion—indeno[1,2,3-*c,d*]pyrene and coronene (Supporting Information, Figures S94 and S95). As is the case with most other organic tracers, these PAHs also exist in other types of fossil fuel combustion; however, during this episode, coal combustion was their most dominant source

(Supporting Information, Tables S2–S5). These two tracers showed a slight overestimation by the model in all seasons and all cities (Supporting Information, Figures S34 and S36), except during the winter in Northbrook, where most PAHs were underestimated by the model. Model overestimates of molecular tracers could suggest chemical decay in the ambient atmosphere,^{13,45} making the Northbrook winter results more unique, where emissions appeared to be significantly underestimated even without accounting for possible chemical decay.

DISCUSSION

Air quality models are powerful tools both for gaining insight into atmospheric phenomena and for developing and evaluating control strategies to improve ambient air quality. The analysis presented here was limited to tracer compounds with both available ambient measurements and well-established and unique laboratory-derived source profiles. For this reason only four sources of primary carbon and four sources of secondary organic aerosols were evaluated. Nevertheless, these eight sources constituted the majority of the observed carbon at the four midwestern sites (Table 2), and an analysis of these source-specific biases can inform the prioritization of future research on modeling particulate carbon concentrations that would make models more useful in their application. Ranking model biases by absolute magnitude could provide one method for prioritization of model improvement efforts. Such analysis revealed that the largest absolute bias was found to be in isoprene SOA, followed by mobile source emissions and biomass combustion. Addressing the biases in these sectors first will result in the largest impact on the overall accuracy of total carbon predictions. For instance, as discussed previously, isoprene SOA predictions could be improved from more thorough examination of its interaction with NO_x , requiring laboratory studies parametrized closer to atmospheric conditions. Furthermore, since both 2-methyltetrols and 2-methylglyceric acid are underestimated in the model during the summer, factors other than NO_x must play a role. The Kleindienst et al. 2007 experiments²³ do not show a significant trend of either 2-methylglyceric acid or the 2-methyltetrols with VOC/NO_x ratio ($r^2 = 0.006\text{--}0.03$). Given the fact that isoprene SOA tracers are known to form from second- and later-generation isoprene oxidation products, chamber experiments aimed at isolating one of the later-generation products should be performed to update the tracer to total SOA ratios from Kleindienst et al.²³ This new data would allow for a more NO_x -dependent evaluation of isoprene SOA in CMAQ as well as ambient data sets. Likewise, mobile source attributions could be closer to observations by revisiting emissions calculations: for example, by examining the newer mobile source emissions models such as MOVES.⁴⁶ Finally, biomass combustion performance could be better with more attention to its components, including wildfires and residential wood combustion, which is something that is planned to be addressed in future work.

One of the most significant assumptions made in this study was the fact that molecular tracers were neither lost to reaction nor produced (in the case of primary markers) in the atmosphere. While it is extremely unlikely that the primary tracers are formed away from tracked emissions sources, there are a number of smog chamber experiments that have suggested that the molecular markers do degrade. However, atmospheric studies demonstrate unbiased results using receptor-based source apportionment models.^{47–49} Still, such

analysis likely adds more uncertainty to the results of the rural site (Bondville, IL) from potential tracer degradation in comparison to the urban sites, which are nearer to the sources.

ASSOCIATED CONTENT

Supporting Information

Tables and figures giving source speciation profiles, tabulated monthly observations and modeling results at all four sites, an alternate method for analyzing model-derived isoprene tracers, and temporal plots of all tracer comparisons. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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