Environmental Science & Technology

Article

pubs.acs.org/est

Identifying $PM_{2.5}$ and $PM_{0.1}$ Sources for Epidemiological Studies in California

Jianlin Hu,[†] Hongliang Zhang,[†] Shuhua Chen,[‡] Qi Ying,[§] Christine Wiedinmyer,[∥] Francois Vandenberghe,[⊥] and Michael J. Kleeman[†,*]

[†]Department of Civil and Environmental Engineering, University of California—Davis, One Shields Avenue, Davis California 95616-5270, United States

[‡]Department of Land, Air, and Water Resources, University of California—Davis, One Shields Avenue, Davis California 95616-5270, United States

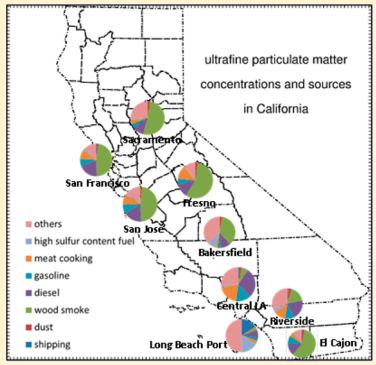
[§]Zachry Department of Civil Engineering, Texas A&M University, 3136 TAMU, College Station, Texas 77843-3136, United States

[∥]Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado 80307-3000, United States

[⊥]Research Applications Laboratory, National Center for Atmospheric Research, Boulder, Colorado 80307-3000, United States

Supporting Information

ABSTRACT: The University of California—Davis_Primary (UCD_P) model was applied to simultaneously track ~900 source contributions to primary particulate matter (PM) in California for seven continuous years (January 1st, 2000 to December 31st, 2006). Predicted source contributions to primary $PM_{2.5}$ mass, $PM_{1.8}$ elemental carbon (EC), $PM_{1.8}$ organic carbon (OC), $PM_{0.1}$ EC, and $PM_{0.1}$ OC were in general agreement with the results from previous source apportionment studies using receptor-based techniques. All sources were further subjected to a constraint check based on model performance for PM trace elemental composition. A total of 151 $PM_{2.5}$ sources and 71 $PM_{0.1}$ sources contained PM elements that were predicted at concentrations in general agreement with measured values at nearby monitoring sites. Significant spatial heterogeneity was predicted among the 151 $PM_{2.5}$ and 71 $PM_{0.1}$ source concentrations, and significantly different seasonal profiles were predicted for $PM_{2.5}$ and $PM_{0.1}$ in central California vs southern California. Population-weighted concentrations of PM emitted from various sources calculated using the UCD_P model spatial information differed from the central monitor estimates by up to 77% for primary $PM_{2.5}$ mass and 148% for $PM_{2.5}$ EC because the central monitor concentration is not representative of exposure for nearby population. The results from the UCD_P model provide enhanced source apportionment information for epidemiological studies to examine the relationship between health effects and concentrations of primary PM from individual sources.



INTRODUCTION

Airborne particulate matter (PM) mass has been associated with adverse health effects across the world (see for example, refs 1−3), the U.S. (see for example, refs 4−6), and within individual states and cities (see for example, refs 7−10). Within the U.S., it is estimated that California suffers a disproportionately large share of PM-related mortality because of major population centers that experience some of the highest PM concentrations across the nation [11]. It has been estimated that 14 000−24 000 California residents die prematurely each year due to particulate air pollution [12]. PM is a complex mixture of many components, including sulfate, nitrate, organic chemicals, soot, metals, and crustal elements, etc., emitted from a variety of sources. Recent epidemiological studies have demonstrated that some PM components have stronger correlation with the health effects than the PM mass[13,14]. Part of this effect may be related to particle size because size determines where particles deposit in the respiratory system. Most epidemiological studies identify the strongest health associations with particles that have diameters <2.5 μm ($PM_{2.5}$)) [15] but toxicology studies suggest that particle with diameters <0.1 μm ($PM_{0.1}$) may be even more dangerous.[16,17] Components typically found in smaller particles may therefore have higher apparent toxicity.

Control programs currently treat all PM sources equally based on their mass emissions rate in either the $PM_{2.5}$ or PM_{10} size fractions, despite the measurements showing that different sources emit particles with different chemical compositions and size distributions (see for example, refs 18−21). A comprehensive epidemiology program that systematically quantifies associations between health effects and all primary PM sources in multiple size fractions (including $PM_{0.1}$) could lay the groundwork for the design of much more efficient emissions control programs. A few previous mortality-source apportion-

Received: October 29, 2013
Revised: February 11, 2014
Accepted: February 19, 2014
Published: February 19, 2014

ment studies have linked health effects to specific sources of PM.[22−25] These mortality-source appointment studies provide highly valuable information for effective pollution control strategies. However, the lack of consistent results highlights the need for further studies that use best-available apportionment information for all primary PM sources in numerous size fractions to identify the most toxic sources of airborne particles.

Receptor-oriented statistical models, such as the Chemical Mass Balance (CMB) model and the Positive Matrix Factorization (PMF) model are the traditional methods used to identify source contributions to ambient $PM_{2.5}$. Receptor models predict the largest ∼10 PM source contributions at a single location with a discrete time resolution defined by the monitoring cycle (usually 1 day out of 3 days or 6 days). Receptor models have been widely used for source apportionment calculations throughout the world for over 3 decades (see for example, refs 26−34), but they do not provide a true characterization of the spatial distributions of source contributions on a regional scale. Recently, source-oriented 3D Eulerian air quality models have been developed and applied to estimate the regional contributions from ∼10 sources.[35−41] No studies have been undertaken to estimate exposure and potential health impacts from the hundreds of other regional sources in typical urban areas, and exposure information for size fractions smaller than 2.5 μm is completely absent.

The present study aims to apply a source-oriented regional air quality model that tracks large numbers (+1000) of primary particle source contributions through the atmosphere while retaining information about particle size, composition, and source-origin. The University of California—Davis_Primary (UCD_P) model was applied to predict 24-h average primary PM source contributions in California from 2000 to 2006 with a horizontal resolution of 4 km. The model predictions are compared to published results from studies using receptor models during specific episodes when these results are available. The ability of the source-oriented model to accurately predict PM components is also evaluated and the implications for the accuracy of source predictions are considered. The regional distributions of $PM_{0.1}$ and $PM_{2.5}$ source contributions that pass the model evaluation criteria are presented as possible candidates for inclusion in future epidemiological studies.

MODEL DESCRIPTION

The structure of the UCD_P model used in the current study has been described in detail in a companion manuscript[42] and numerous previous studies utilizing the UCD/CIT model, and so only a brief summary is presented here. The UCD_P model was developed to track primary PM (emitted directly from sources) through a simulation of emission, atmospheric transport, and deposition based on the framework of the source-oriented UCD/CIT air quality model. Size and composition resolved particle emissions are described using a library of primary particle source profiles measured during actual source tests.[43−55] The bulk advection and turbulent diffusion algorithm is described by Kleeman and Cass,[35] the dry deposition approach is described by Kleeman et al.,[56] the vertical advection scheme is described by Hu et al.,[57] and the wet deposition scheme is described by Mahmud et al.[58] The capability of the UCD/CIT model to accurately estimate source contributions to primary and secondary PM and its major components (such as elemental carbon (EC), organic carbon (OC), nitrate, sulfate, ammonium, etc.) has been demonstrated in multiple source apportionment studies for both the South Coast Air Basin (SoCAB) and the San Joaquin Valley (SJV) in California.[59−67] The UCD_P model applied in the current study expands the number of primary sources that can be tracked in model calculations to >1000 but (as noted above) the model processes only consider emissions, advection, diffusion, dry deposition, and wet deposition. Formation of secondary PM is not considered due to the additional computational burden associated with tracking this material on thousands of different primary particle cores.

MODEL APPLICATION

The UCD_P model was applied to estimate the source contributions to primary PM and its components for seven continuous years (January first, 2000 to December 31st, 2006) in California using two levels of nested domains. The parent domain covered the entire state of California using 36 km horizontal resolution, and two nested domains SoCAB_4km and SJV_4km covered 92% of California's population using 4 km horizontal resolution. Every source with a unique emissions inventory code (EIC) in the California emissions database was tracked separately through model calculations (in total there are ∼900 source types tracked in the present application). Meteorological inputs were prepared using the Weather Research and Forecast (WRF) model version 3.1[68,69]. Gridded emissions were prepared using the raw emissions inventory provided by the California Air Resources Board (CARB) with an emissions model described by Hu et al.[42] A detailed description of the model setup, the WRF meteorological simulations and statistics, and emissions are provided by Hu et al.[42]

RESULTS

Daily average primary PM concentrations in multiple size fractions were calculated during the seven year simulation period. Model performance for $PM_{2.5}$ EC, $PM_{2.5}$ trace elements, $PM_{0.1}$ mass, and $PM_{0.1}$ EC was extensively evaluated through comparison to available ambient measurements. A detailed analysis of the model performance for individual PM species has been presented in a companion manuscript.[42] In summary, predicted $PM_{2.5}$ EC best fit concentrations were in excellent agreement with measured ambient concentrations, with an overall Pearson correlation coefficient (R) across all sites of 0.89 when using daily average concentrations, and R of 0.94 when using monthly average concentrations. Nine $PM_{2.5}$ trace elements [potassium (K), chromium (Cr), zinc (Zn), iron (Fe), titanium (Ti), arsenic (As), calcium (Ca), manganese (Mn), and strontium (Sr)] had $R \geq 0.8$ at more than five individual measurement sites. Simulated $PM_{0.1}$ mass and $PM_{0.1}$ EC concentrations agreed well with the observed values, with R of 0.92 for $PM_{0.1}$ mass, and R of 0.94 for $PM_{0.1}$ EC. The general agreement between model predictions and measured concentrations provides a solid foundation for the source apportionment of primary PM carried out in the current study.

Source Constraints Based on Comparison to Tracer Based Source Apportionment Studies. *$PM_{2.5}$ Source Apportionment during the California Regional PM_{10}/$PM_{2.5}$ Air Quality Study.* Figure 1 compares the average relative source contributions to primary $PM_{2.5}$ mass predicted by the CMB receptor model, the UCD/CIT model, and the UCD _P model at an urban site Fresno (Figure 1a) and a rural site Angiola (Figure 1b) in the Central Valley of California during the period from December 15, 2000 to January 7, 2001. Detailed CMB results were produced as part of the California Regional PM_{10}/

dx.doi.org/10.1021/es404810z | Environ. Sci. Technol. 2014, 48, 4980−4990

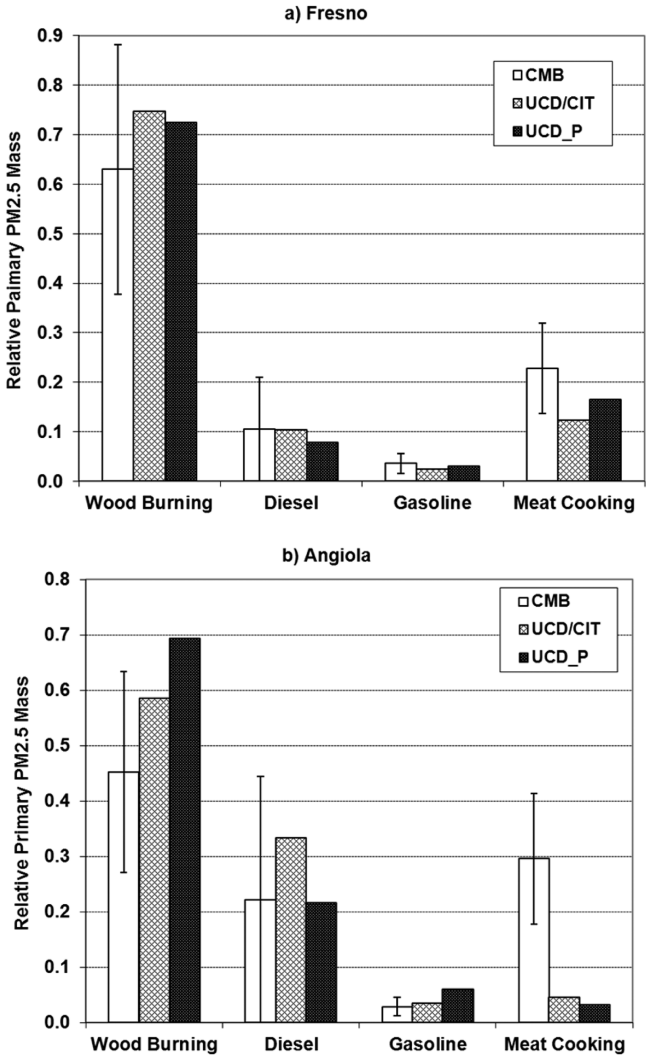


Figure 1. Relative source contribution to the average primary $PM_{2.5}$ mass concentrations predicted by CMB receptor model, the UCD/CIT air quality model, and the UCD_P chemical transport model during the CRPAQS episode (December 15, 2000 to January 7, 2001).

$PM_{2.5}$ Air Quality Study (CRPAQS). The uncertainties for CMB results were estimated by Ying et al [64] based on a study conducted by Chow et al.[70] Dust sources were excluded from the relative source contribution calculation due to previously identified problems with the raw fugitive dust emission inventory.[64] The source contribution predictions from the three models are in excellent agreement for wood burning, diesel, and gasoline vehicles, generally falling into the uncertainty range of the CMB model, at Fresno and Angiola. The CMB model predicts much higher contribution from meat cooking (29.6% ± 11.84%) at Angiola than the UCD/CIT model (4.6%) and the UCD_P model (3.2%). High uncertainties in cholesterol measurements (a significant organic marker for meat cooking) likely explain the anomalously high CMB meat cooking estimates.[70] The differences between the UCD/CIT and the UCD_P results are primarily caused by the use of diagnostic meteorological fields for the UCD/CIT calculations and prognostic meteorological fields for the UCD_P calculations. The UCD/CIT model also includes gas-particle transfer and coagulation processes that are not in the UCD_P model, but the alteration of particle size and density leading to different deposition velocity is a secondary effect.

$PM_{0.1}$ Source Apportionment during the CRPAQS and US EPA Exposure Studies. Figure 2 compares the relative source contributions to $PM_{0.1}$ EC and OC concentrations predicted by the UCD _P model and the receptor-oriented methods based on measured molecular markers[71,72] at Sacramento, Modesto, and Bakersfield during the winter of 2000 and at Fresno during the summer of 2006. Large uncertainties up to ~300% exist in the receptor-based estimation, especially for the $PM_{0.1}$ EC from the mobile sources, due to the limitations associated with measuring minute quantities of molecular markers in the $PM_{0.1}$ size fraction. The CMB and the UCD_P methods are in good agreement for the relative contribution from mobile sources to EC concentrations, but they were not always in agreement for the breakdown of gasoline and diesel contributions within the mobile source category. The large uncertainty band for the receptor-oriented method makes it difficult to perform a detailed analysis of the differences between the two approaches. Predictions for contributions to $PM_{0.1}$ OC from the receptor-oriented techniques and the UCD _P model were in good agreement. Residential wood combustion dominates $PM_{0.1}$ OC in the winter of 2000 at Sacramento (93% predicted by the UCD_P model), Modesto (92%), and Bakersfield (87%), while meat cooking and mobile sources are the major sources of $PM_{0.1}$ OC in Fresno during the summer of 2006, contributing ~50%, respectively. The two methods also estimated similar source contributions to $PM_{1,8}$ EC and primary OC (Supporting Information, SI, Figure S1).

The general agreement in the source contributions from the mobile, wood burning and meat cooking source categories predicted by the UCD_P and the CMB method provides confidence in the accuracy of the UCD_P predictions for the sources included in these three categories. Therefore, individual sources included in these three categories were treated as passing the constraint check. In total, 71 $PM_{2.5}$ sources and 65 $PM_{0.1}$ sources in the mobile, wood burning, and meat cooking source categories were considered to have passed constraint checks. A brief description of the constrained sources is listed in Table S1 of the SI.

Source Constraints Based on Model Performance for Individual Species. Only a limited number of receptor-oriented studies are available to evaluate the accuracy of source apportionment calculations during the seven-year modeling period. Furthermore, only 6−8 source categories that mainly contribute to the primary PM mass, EC and OC are generally resolved by the receptor-oriented results, leaving the majority of the sources that are important for other primary PM trace elements (i.e., metals) completely unconstrained. The 890 source predictions in the current study were further evaluated by checking the accuracy of model calculations for individual PM species concentrations at individual receptor sites and then identifying those sources that contributed to those species concentrations. Sources that contributed species concentrations in poor agreement with measured concentrations were flagged. This check does not directly evaluate the accuracy of each source prediction, but it provides a constraint that builds further confidence in the model predictions.

Sources are considered to pass the constraint check in the current study by satisfying the criteria listed in Table 1. Detailed statistics for model performance are summarized in Table S2 of the SI. 109 sources passed the $PM_{2.5}$ species check (marked with "x" in SI Table S3) and 22 sources passed the $PM_{0.1}$ species check (marked with "u" in SI Table S3). The reduced number of constrained $PM_{0.1}$ sources stems from the limited availability of

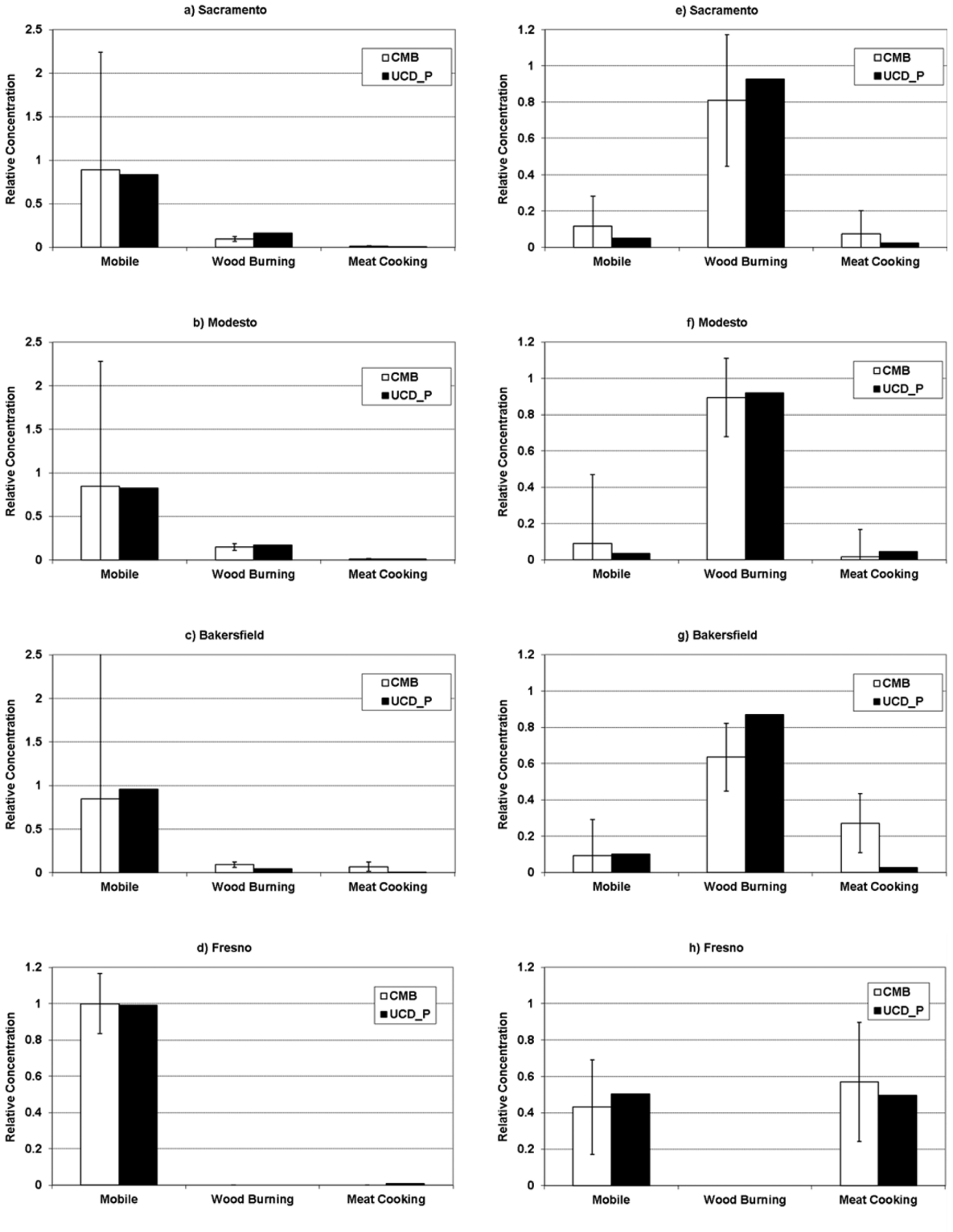


Figure 2. Relative source contribution to $PM_{0.1}$ EC (left panels: a, b, c, d) and OC (right panels: e, f, g, h) predicted by the CMB receptor model and the UCD_P chemical transport model. Note a winter episode (CRPAQS) is used in the panels a, b, c, e, f, and g; and a summer episode is used in the panels of d and h.

$PM_{0.1}$ measurements. A larger number of $PM_{0.1}$ sources could be evaluated if more $PM_{0.1}$ composition measurements were available. The majority of the $PM_{2.5}$ and $PM_{0.1}$ sources that did not pass the constraint check simply did not have chemical speciation profiles that contributed strongly to species concentrations at a monitoring site, and so they could not be evaluated. Generic chemical speciation profiles (composition marked as "unknown") were specified for 157 sources, making it impossible to evaluate their performance using measured species concentrations.

Temporal Variations in Source Contributions. Both of the source constraint checks described above provide increased

dx.doi.org/10.1021/es404810z | *Environ. Sci. Technol.* 2014, 48, 4980−4990

Table 1. Criteria Used in the Source Constraint Check Based on Model Performance of Individual Primary PM Species

step	criteria
1	Choose a target PM species with monthly $R \geq 0.8$ and MFB within ±0.3 at a given site (see the model statistics in SI Table S1)
2	Sort emissions from individual sources within 100 km[a] of the given site in ascending order based on their contribution to the target species.
3	Consider the largest sources contributing to 95%[b] of the total PM species emissions as "passing" the constraint check at the given site
4	Treat the sources that contributed to the target species at more than 3 different sites as "passing" the overall constraint check and the "good" primary PM sources
5	Repeat steps 1−4 for all species

[a]Previous study[66] revealed that $PM_{2.5}$ OC in the Central California during the stagnant CRPAQS episode (OC was mostly primary in this episode) most likely transported 30−60 km. Considering that the average wind speed in CRPAQS was ∼1m/s, and the average wind speed in 2000−06 was ∼2m/s, 100 km was then selected as the source influence range. [b]The minor sources contributing to the last 5% of emissions are not considered to be evaluated by the constraint check since they have little effect on the performance statistics

confidence in the predicted source contribution fields from a total of 151 constrained primary $PM_{2.5}$ sources (29 $PM_{2.5}$ sources passed both checks) and a total of 71 constrained primary $PM_{0.1}$ sources (16 $PM_{0.1}$ sources passed both checks). Figure 3 shows the annual variation of these source contributions to primary $PM_{2.5}$ mass and $PM_{0.1}$ mass concentrations averaged over a 7-yr period at the Los Angeles and Fresno sites. A similar plot for $PM_{2.5}$ EC and $PM_{0.1}$ EC is shown in Figure S4 of the SI. The 7-day moving averages were calculated for source contributions in every year and then concentrations on same dates (i.e., same month and day) were averaged across the 7 year simulation period to show the annual cycle. The top 30 constrained $PM_{2.5}$ and $PM_{0.1}$ sources (i.e., the sources with the greatest contributions) were explicitly shown, the remaining constrained sources were lumped as "Other constrained $PM_{2.5}$ (or $PM_{0.1}$) sources", and all the nonconstrained $PM_{2.5}$ (or $PM_{0.1}$) sources were lumped as "Non-constrained $PM_{2.5}$ (or $PM_{0.1}$) sources". The top 30 constrained sources account for >92% of $PM_{2.5}$ EC and $PM_{0.1}$ EC at Los Angeles and Fresno. The top 30 constrained sources account for 81% of total primary $PM_{2.5}$ mass at Los Angeles and Fresno, and account for 46% and 66% of the total primary $PM_{0.1}$ mass at Los Angeles and Fresno, respectively. This demonstrates that some important $PM_{0.1}$ sources are missing from the source constraint checks based on the $PM_{0.1}$ EC and OC analysis, with the implication that more ultrafine PM source studies are needed in the future. Model calculations predict that Fresno has fewer significant primary PM sources than Los Angeles. Wood burning (residential wood fireplaces, residential wood stoves, etc.) are the single biggest primary PM source in Fresno during the winter. Wood smoke concentrations drop off sharply in spring, summer, and fall months due to an assumed annual profile for home heating; a more accurate temporal profile geared to ambient temperatures will be adopted in future studies. Wildfire smoke concentrations are relatively minor averaged across the 7 year period and they are lightly constrained by observations. In addition to emissions-driven trends in wood burning, the primary PM concentrations (mass and EC in $PM_{2.5}$ and $PM_{0.1}$) from all sources are generally higher in cold months due to the influence of seasonal weather patterns (reduced mixing layer heights).

A companion study[73] investigates the total PM (primary + secondary) concentrations and demonstrates that the 7 year average primary $PM_{2.5}$ mass concentrations account for 72% and 69% of the total $PM_{2.5}$ mass concentrations in Los Angeles and Fresno, respectively. Therefore, the top 30 constrained sources shown in Figure 3 account for over half of the total $PM_{2.5}$ mass concentrations.

In a time series epidemiological study in California, stronger associations were observed in the cooler months between mortality and $PM_{2.5}$ EC, iron, potassium, and vanadium.[13] The temporal variations of source contributions predicted in the current study may help identify the sources that are responsible for the observed enhancement of particle toxicity during cold weather. The dominant PM sources and their temporal profiles differ between Los Angeles and Fresno, between $PM_{2.5}$ and $PM_{0.1}$, and between PM primary mass and EC. These findings suggest that size-resolved PM source contribution information in different locations may be informative for health-source apportionment studies at a regional or larger scale.

Spatial Distribution of the Constrained $PM_{0.1}$ and $PM_{2.5}$ Sources. Predicted spatial distributions for contributions from 14 representative sources that actively passed the checks described above are shown for $PM_{0.1}$ (Figure 4). The spatial patterns varied significantly among sources. $PM_{0.1}$ mass from on-road mobile sources followed the pattern of major transportation corridors, with the highest concentrations predicted in urban areas such as Los Angeles and San Francisco. $PM_{0.1}$ mass concentrations from off-road engines (such as construction equipment) were also high in urban areas. $PM_{0.1}$ mass associated with agricultural equipment was concentrated in the agricultural regions of the SJV and the Sacramento Valley. Wood burning sources were mainly located in the urban residential areas of northern California. Shipping sources contributed strongly along the coast of California near the major ports in the SoCAB and San Francisco Bay Area. Figure S2 of the SI shows spatial patterns of $PM_{0.1}$ for all sources that passed constraint checks and that have maximum concentrations >1 ng/m^3. Figure S3 of the SI shows spatial patters of $PM_{2.5}$ for all sources that passed constraint checks. The predicted PM concentration fields from individual sources over the seven-year simulation window provide information that may be helpful in future epidemiological studies.

DISCUSSION

The UCD_P predictions for $PM_{2.5}$ and $PM_{0.1}$ source contributions produced in the current study generally agree with tracer-based source apportionment results obtained from previous studies at multiple sites and times, building confidence in the quality of the UCD_P predictions at times and locations where measurements are not available. A total of 151 $PM_{2.5}$ sources and 71 $PM_{0.1}$ sources actively passed constraint checks indicating that they can be used with increased confidence to examine the relationship between health effects and PM sources in epidemiological studies. Unconstrained sources may still be accurately represented in the model calculation, but there is no way to evaluate these predictions, and so they should receive lower priority in downstream studies. The 157 (out of 890) sources with missing chemical speciation profiles should not be used in downstream epidemiological studies.

The constrained $PM_{2.5}$ and $PM_{0.1}$ concentration fields generated in the current study have complex spatial patterns. Population-weighted concentrations (PWC) provide a simple test that estimates whether this spatial complexity will influence the results of epidemiological studies. The method for PWC calculations is described in ref 42, which shows that PWCs for

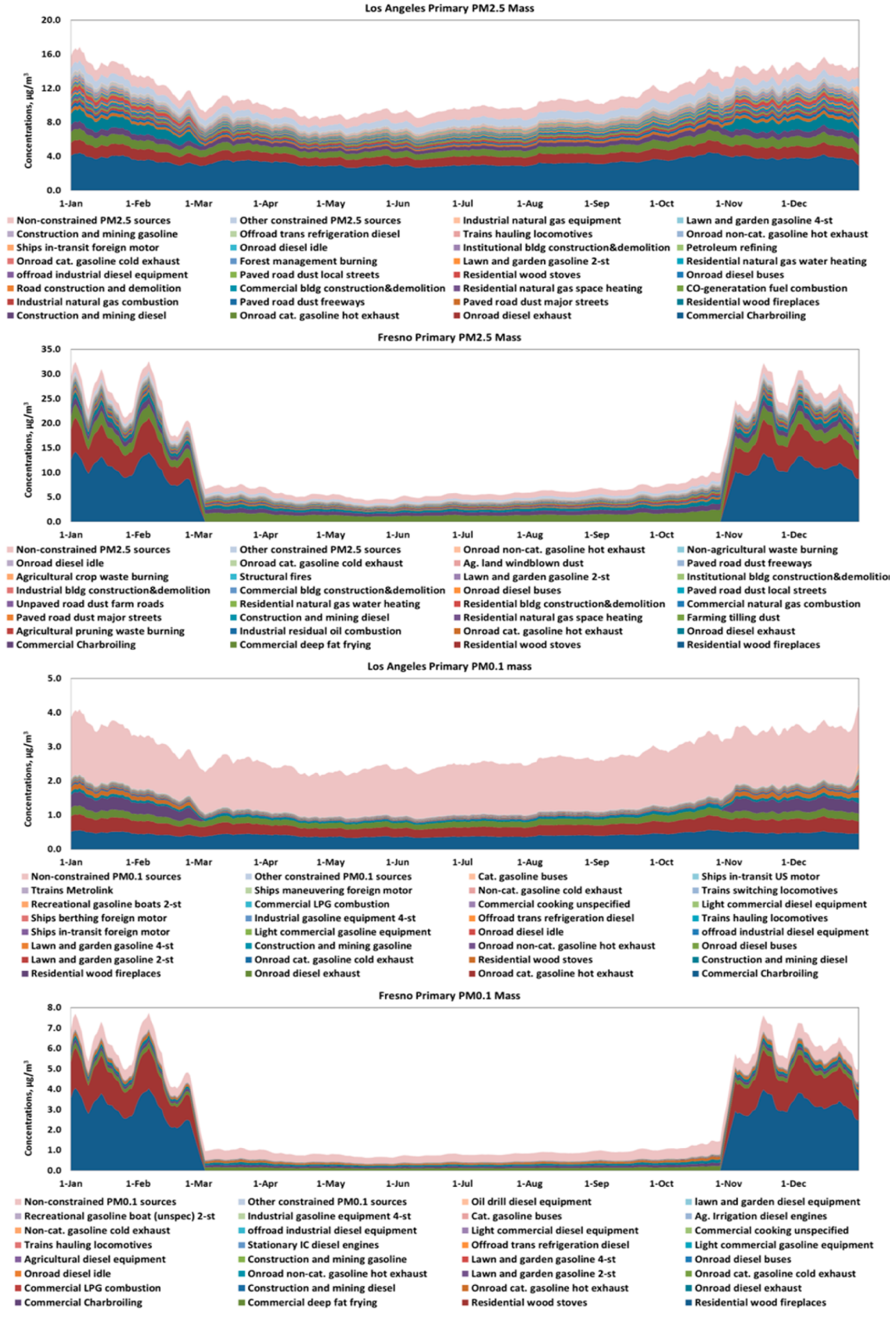


Figure 3. Annual variations of predicted source contributions from the top 30 constrained sources to primary $PM_{2.5}$ mass and primary $PM_{0.1}$ mass at the Los Angeles and Fresno sites.

primary $PM_{2.5}$ mass based on predictions from the UCD_P model are 45% and 37% lower than the central monitor concentrations (CMC) for $PM_{2.5}$ mass in Los Angeles and Fresno, and 10% and 26% lower for $PM_{0.1}$ mass in Los Angeles

dx.doi.org/10.1021/es404810z | Environ. Sci. Technol. 2014, 48, 4980−4990

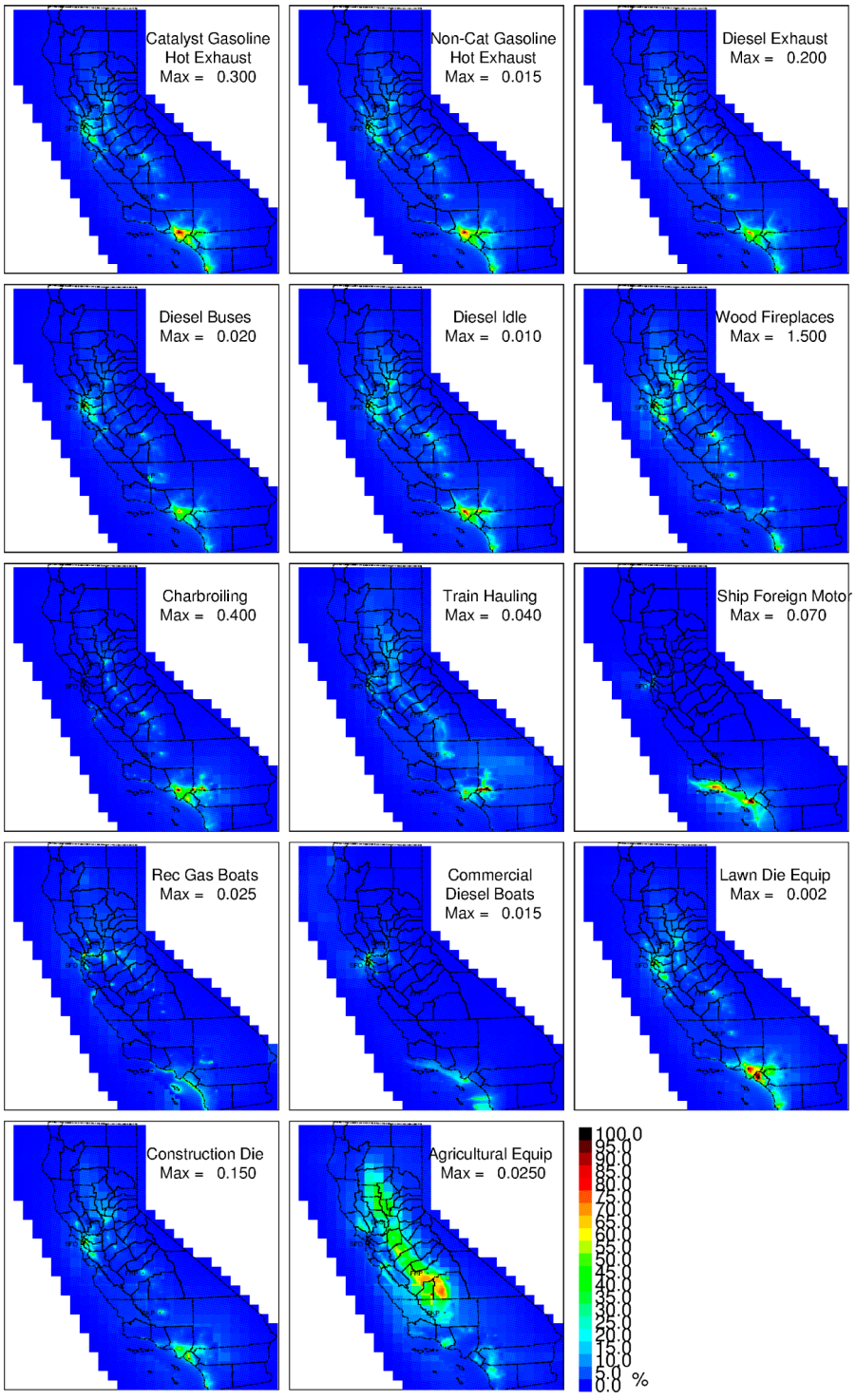


Figure 4. Predicted primary $PM_{0.1}$ mass concentrations from the 14 representative ultrafine sources that passed the constraint checks. (SI Figure S2 shows predicted primary $PM_{0.1}$ mass concentrations from all constrained $PM_{0.1}$ sources with maximum concentrations greater than 1 ng/m^3). All concentrations are expressed as % of the maximum value shown in each subpanel. Absolute unit is μg/m^3. The % scale is shown in the last subpanel.).

and Fresno. Figure 5 shows the ratios of PWC to CMC of primary $PM_{2.5}$ mass and primary $PM_{0.1}$ mass from the top 30 constrained sources at the Los Angeles and Fresno sites. The top sources for primary $PM_{2.5}$ mass are significantly different from the top sources for primary $PM_{0.1}$ mass. The PWC/CMC ratios vary from 0.23 to 1.64 for primary $PM_{2.5}$ sources and from 0.26 to 1.25 for primary $PM_{0.1}$ sources at Los Angeles, and from 0.46 to 1.55 for primary $PM_{2.5}$ sources and from 0.36 to 1.42 for primary $PM_{0.1}$ sources at Fresno. PWC/CMC ratios are ~0.5 for onroad mobile sources and ~0.4 for meat cooking sources in both areas. Wood burning sources have PWC/CMC ratios of ~0.9 in Los Angeles, but have lower ratios of ~0.5 in Fresno. Among the top 30 sources, only 4 sources in Los Angeles and 1 source in Fresno have PWC/CMC of $PM_{2.5}$ in the range 0.8−1.2, and only 6 sources in Los Angeles and 4 sources in Fresno have PWC/CMC of $PM_{0.1}$ in the range 0.8−1.2, indicating possible exposure

dx.doi.org/10.1021/es404810z | Environ. Sci. Technol. 2014, 48, 4980−4990

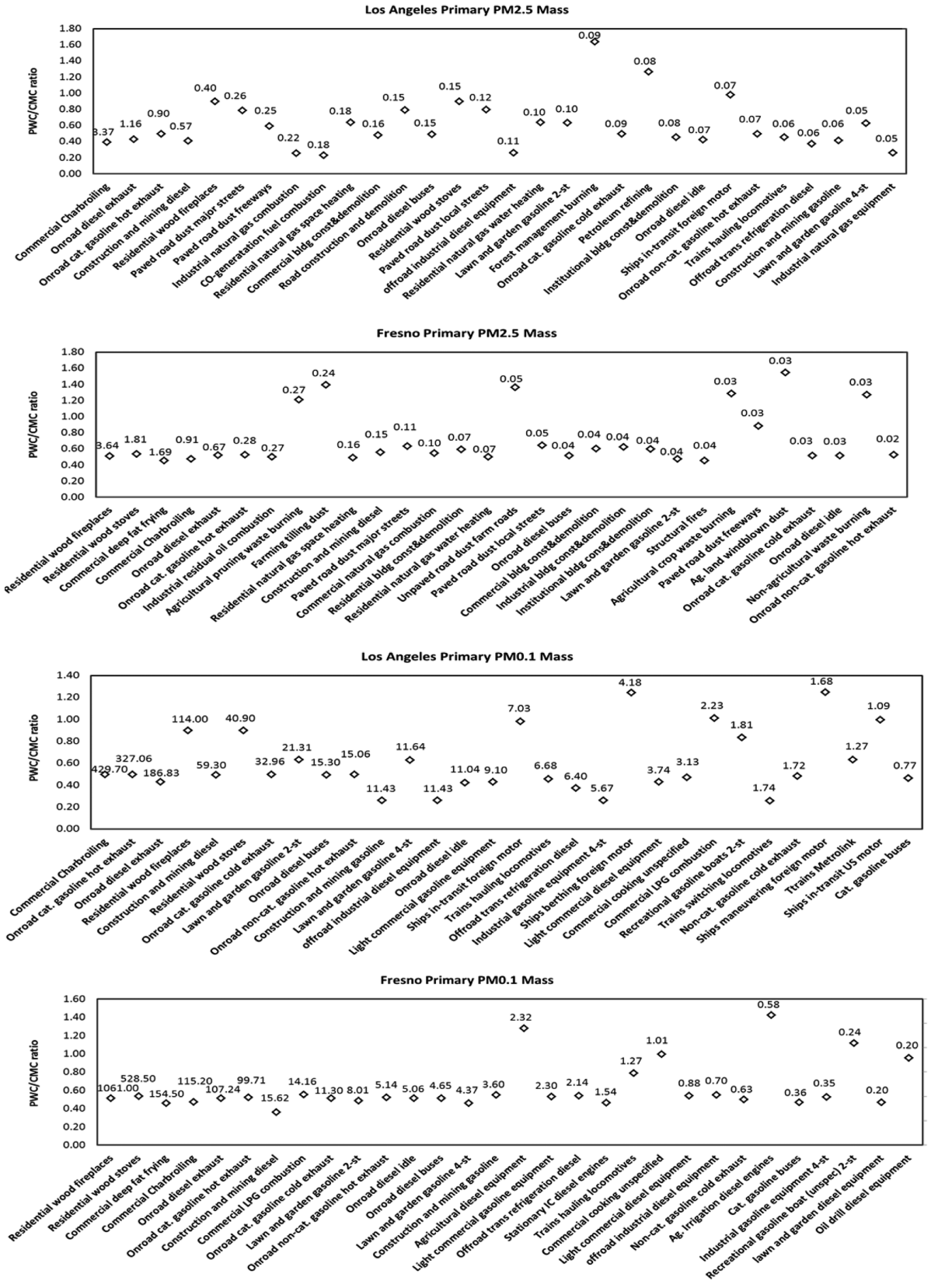


Figure 5. Ratios of MSA population weighted concentrations to central monitor concentrations of primary $PM_{2.5}$ and $PM_{0.1}$ mass at the Los Angeles and Fresno sites from the top 30 sources. Diamonds represent the ratios and the numbers are the CMCs in the unit of $\mu g/m^3$ for $PM_{2.5}$ and ng/m^3 for $PM_{0.1}$.

misclassification for source apportionment of PM when the spatial variations are not considered in health-source apportionment studies.

Additional comparison of the PWC and CMC source contributions to EC in $PM_{2.5}$ and $PM_{0.1}$ (SI Figure S5) reveals significant differences relative to the mass plots (Figure 5). The

dx.doi.org/10.1021/es404810z | Environ. Sci. Technol. 2014, 48, 4980−4990

results suggest that source specific spatial variations, which are generally not available from central monitor measurements and statistical model calculations, should be considered for different species in different PM fractions sizes. Exposure estimates created from the current study combined with population distributions will provide valuable inputs for the first epidemiological studies to simultaneously evaluate the potential health effects of 151 sources of $PM_{2.5}$ and 71 sources of $PM_{0.1}$.

■ ASSOCIATED CONTENT

Supporting Information

Sources constrained by comparison to tracer based receptor statistical model studies (Table S1), statistic matrix of $PM_{2.5}$ species at individual monitor sites (Table S2), sources that constrained by individual species (Table S3), relative source contribution to $PM_{1.8}$ EC and OC predicted by CMB receptor model and the UCD_P model (Figure S1), predicted spatial distribution of primary $PM_{0.1}$ mass concentrations from the primary $PM_{0.1}$ sources that pass the constraint checks and have maximum concentrations >1 ng/m^3 (Figure S2), predicted spatial distribution of primary $PM_{2.5}$ mass concentrations from the primary $PM_{2.5}$ sources that passed the constraint checks (Figure S3), predicted annual variations of source contributions from the top 30 constrained sources to $PM_{2.5}$ EC and $PM_{0.1}$ EC at the Los Angeles and Fresno sites (Figure S4), and ratios of MSA population weighted concentrations to central monitor concentrations of $PM_{2.5}$ and $PM_{0.1}$ EC mass at the Los Angeles and Fresno sites from the top 30 constrained sources (Figure S5). All model predictions described in the current study are available for download at faculty.engineering.ucdavis.edu/kleeman. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +1 530 752 8386; fax: +1 530 752 7872; e-mail: mjkleeman@ucdavis.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was funded by the United States Environmental Protection Agency under Grant No. 83386401. Although the research described in the article has been funded by the United States Environmental Protection Agency, it has not been subject to the Agency's required peer and policy review and therefore does not necessarily reflect the reviews of the Agency, and no official endorsement should be inferred.

■ REFERENCES

(1) Evans, J.; et al. Estimates of global mortality attributable to particulate air pollution using satellite imagery. *Environ. Res.* **2013**, *120*, 33−42.

(2) Anenberg, S. C.; et al. An estimate of the global burden of anthropogenic ozone and fine particulate matter on premature human mortality using atmospheric modeling. *Environ. Health Perspect.* **2010**, *118* (9), 1189−1195.

(3) Casper, S.; et al. The global burden of anthropogenic ozone and particulate matter air pollution on premature human mortality. *Epidemiology* **2008**, *19* (6), S221−S221.

(4) Correia, A. W.; et al. Effect of air pollution control on life expectancy in the United States an analysis of 545 US counties for the period from 2000 to 2007. *Epidemiology* **2013**, *24* (1), 23−31.

(5) Pope, C. A.; Ezzati, M.; Dockery, D. W. Fine-particulate air pollution and life expectancy in the United States. *New Eng. J. Med.* **2009**, *360* (4), 376−386.

(6) Ozkaynak, H.; Thurston, G. D. Associations between 1980 United-States mortality-rates and alternative measures of airborne particle concentration. *Risk Anal.* **1987**, *7* (4), 449−461.

(7) Ostro, B.; et al. Fine particulate air pollution and mortality in nine California counties: Results from CALFINE. *Environ. Health Perspect.* **2006**, *114* (1), 29−33.

(8) Ostro, B.; et al. Long-term exposure to constituents of fine particulate air pollution and mortality: Results from the California Teachers Study. *Environ. Health Perspect.* **2010**, *118* (3), 363−369.

(9) Ostro, B. D.; Broadwin, R.; Lipsett, M. J. Coarse and fine particles and daily mortality in the Coachella Valley, California: a follow-up study. *J. Exposure Anal. Environ. Epidemiol.* **2000**, *10* (5), 412−419.

(10) Jerrett, M.; et al. Spatial analysis of air pollution and mortality in Los Angeles. *Epidemiology* **2006**, *17* (6), S69−S69.

(11) Fann, N.; et al. Estimating the National Public Health Burden Associated with Exposure to Ambient PM2.5 and Ozone. *Risk Anal.* **2012**, *32* (1), 81−95.

(12) Tran, H. T., Alvarado, A., Garcia, C., Motallebi, N., Miyasato, L., and Vance, W., Methodology for Estimating Premature Deaths Associated with Long-term Exposure to Fine Airborne Particulate Matter in California. *Staff Report*; California Environmental Protection Agency, Air Resources Board, 2008.

(13) Ostro, B.; et al. The effects of components of fine particulate air pollution on mortality in California: Results from CALFINE. *Environ. Health Perspect.* **2007**, *115* (1), 13−19.

(14) Franklin, M.; Koutrakis, P.; Schwartz, J. The role of particle composition on the association between PM2.5 and mortality. *Epidemiology* **2008**, *19* (5), 680−689.

(15) Anderson, H. R. Differential epidemiology of ambient aerosols. *Philos. Trans. R. Soc. London Ser. a-Math. Phys. Eng. Sci.* **2000**, *358* (1775), 2771−2785.

(16) Li, N.; et al. Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environ. Health Perspect.* **2003**, *111* (4), 455−460.

(17) Donaldson, K.; et al. The pulmonary toxicology of ultrafine particles. *J. Aerosol Med.* **2002**, *15* (2), 213−220.

(18) Kleeman, M. J.; et al. Size distribution of trace organic species emitted from biomass combustion and meat charbroiling. *Atmos. Environ.* **2008**, *42* (13), 3059−3075.

(19) Robert, M. A.; et al. Size and composition distributions of particulate matter emissions: Part 1 - Light-duty gasoline vehicles. *J. Air Waste Manage. Assoc.* **2007**, *57* (12), 1414−1428.

(20) Robert, M. A.; Kleeman, M. J.; Jakober, C. A. Size and composition distributions of particulate matter emissions: Part 2-Heavy-duty diesel vehicles. *J. Air Waste Manage. Assoc.* **2007**, *57* (12), 1429−1438.

(21) Hays, M. D.; et al. Polycyclic aromatic hydrocarbon size distributions in aerosols from appliances of residential wood combustion as determined by direct thermal desorption−GC/MS. *J. Aerosol Sci.* **2003**, *34* (8), 1061−1084.

(22) Laden, F.; et al. Association of fine particulate matter from different sources with daily mortality in six US cities. *Environ. Health Perspect.* **2000**, *108* (10), 941−947.

(23) Mar, T. F.; et al. PM source apportionment and health effects. 3. Investigation of inter-method variations in associations between estimated source contributions Of PM2.5 and daily mortality in Phoenix, AZ. . *J. Expos. Sci. Environ. Epidemiol.* **2006**, *16* (4), 311−320.

(24) Ito, K.; et al. PM source apportionment and health effects: 2. An investigation of intermethod variability in associations between source-apportioned fine particle mass and daily mortality in Washington, DC. *J. Exposure Sci. Environ. Epidemiol.* **2006**, *16* (4), 300−310.

(25) Zhou, J. A.; et al. Time-Series Analysis of Mortality Effects of Fine Particulate Matter Components in Detroit and Seattle. *Environ. Health Perspect.* **2011**, *119* (4), 461−466.

(26) Schauer, J. J.; et al. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* **1996**, *30* (22), 3837−3855.
(27) Glover, D. M.; et al. Source apportionment with site specific source profiles. *J. Air Waste Manage. Assoc.* **1991**, *41* (3), 294−305.
(28) Kim, E.; Hopke, P. K. Source apportionment of fine particles in Washington, DC, utilizing temperature-resolved carbon fractions. *J. Air Waste Manage. Assoc.* **2004**, *54* (7), 773−785.
(29) Wang, H. B.; Shooter, D. Source apportionment of fine and coarse atmospheric particles in Auckland, New Zealand. *Sci. Total Environ.* **2005**, *340* (1−3), 189−198.
(30) Yin, J. X.; et al. Source apportionment of fine particles at urban background and rural sites in the UK atmosphere. *Atmos. Environ.* **2010**, *44* (6), 841−851.
(31) Chow, J. C.; et al. Pm10 Source apportionment in California San-Joaquin valley. *Atmos. Environ. Part A-General Topics* **1992**, *26* (18), 3335−3354.
(32) Watson, J. G.; et al. Chemical mass-balance source apportionment of Pm(10) during the Southern California Air-Quality Study. *Aerosol Sci. Technol.* **1994**, *21* (1), 1−36.
(33) Schauer, J. J.; Cass, G. R. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environ. Sci. Technol.* **2000**, *34* (9), 1821−1832.
(34) Chen, L. W. A.; et al. Quantifying PM2.5 source contributions for the San Joaquin Valley with multivariate receptor models. *Environ. Sci. Technol.* **2007**, *41* (8), 2818−2826.
(35) Kleeman, M. J.; Cass, G. R. A 3D Eulerian source-oriented model for an externally mixed aerosol. *Environ. Sci. Technol.* **2001**, *35* (24), 4834−4848.
(36) Lane, T. E.; et al. Source contributions to primary organic aerosol: Comparison of the results of a source-resolved model and the chemical mass balance approach. *Atmos. Environ.* **2007**, *41* (18), 3758−3776.
(37) Wagstrom, K. M.; et al. Development and application of a computationally efficient particulate matter apportionment algorithm in a three-dimensional chemical transport model. *Atmos. Environ.* **2008**, *42* (22), 5650−5659.
(38) Samaali, M.; et al. Application of a tagged-species method to source apportionment of primary PM(2.5) components in a regional air quality model. *Atmos. Environ.* **2011**, *45* (23), 3835−3847.
(39) Zhang, H. L.; et al. Source apportionment of PM2.5 nitrate and sulfate in China using a source-oriented chemical transport model. *Atmos. Environ.* **2012**, *62*, 228−242.
(40) Zhang, H. L.; Ying, Q. Secondary organic aerosol formation and source apportionment in Southeast Texas. *Atmos. Environ.* **2011**, *45* (19), 3217−3227.
(41) Zhang, H. L.; Ying, Q. Source apportionment of airborne particulate matter in Southeast Texas using a source-oriented 3D air quality model. *Atmos. Environ.* **2010**, *44* (29), 3547−3557.
(42) Hu, J. L.; Zhang, H. L.; Chen, S. H.; Wiedinmyer, C.; Vandenberghe, F.; Ying, Q.; Kleeman, M. J. Predicting Primary $PM_{2.5}$ and $PM_{0.1}$ Trace Composition for Epidemiological Studies in California. *Environ. Sci. Technol.*, 2013, under review.
(43) Harley, R. A.; Hannigan, M. P.; Cass, G. R. Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere. *Environ. Sci. Technol.* **1992**, *26* (12), 2395−2408.
(44) Hildemann, L. M.; Markowski, G. R.; Cass, G. R. Chemical-composition of emissions from urban sources of fine organic aerosol. *Environ. Sci. Technol.* **1991**, *25* (4), 744−759.
(45) Hildemann, L. M.; et al. Submicrometer aerosol mass distributions of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. *Aerosol Sci. Technol.* **1991**, *14* (1), 138−152.
(46) Kleeman, M. J.; Schauer, J. J.; Cass, G. R. Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes. *Environ. Sci. Technol.* **1999**, *33* (20), 3516−3523.
(47) Kleeman, M. J.; Schauer, J. J.; Cass, G. R. Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environ. Sci. Technol.* **2000**, *34* (7), 1132−1142.
(48) Schauer, J. J.; et al. Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.* **1999**, *33* (10), 1578−1587.
(49) Schauer, J. J.; et al. Measurement of emissions from air pollution sources. 1. C-1 through C-29 organic compounds from meat charbroiling. *Environ. Sci. Technol.* **1999**, *33* (10), 1566−1577.
(50) Schauer, J. J.; et al. Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood. *Environ. Sci. Technol.* **2001**, *35* (9), 1716−1728.
(51) Schauer, J. J.; et al. Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.* **2002**, *36* (6), 1169−1180.
(52) Schauer, J. J.; et al. Measurement of emissions from air pollution sources. 4. C-1-C-27 organic compounds from cooking with seed oils. *Environ. Sci. Technol.* **2002**, *36* (4), 567−575.
(53) Taback, H. J., et al., Fine particle emissions from stationary and miscellaneous sources in the South Coast Air Basin, Technical Report, Contract A6-191-30, California Air Resources Board, KVB Incorporate, Research-Cottrell, Tustin, California, 1979.
(54) Cooper, J.A.e.a., Dinal Appendix V-G, PM10 source composition library for the South Coast Air Basin, Technical Report, South Coast Air Quality Management District, Diamond Bar, California, 1989.
(55) Houck, J. E., et al., Determination of particle size distribution and chemical composition of particulate matter from selected sources in California, Technical Report, Contract A6-175-32, California Air Resources Board, OMNI Environment Service Incorporate, Desert Research Institute, Beaverton, Oregon, 1989.
(56) Kleeman, M. J.; Cass, G. R.; Eldering, A. Modeling the airborne particle complex as a source-oriented external mixture. *J. Geophy. Res.-Atmospheres.* **1997**, *102* (D17), 21355−21372.
(57) Hu, J. L.; Ying, Q.; Chen, J. J.; Mahmud, A.; Zhao, Z.; Chen, S. H.; Kleeman, M. J. Particulate air quality model predictions using prognostic vs. diagnostic meteorology in central California. *Atmos. Environ.* **2010**, *44* (2), 215−226.
(58) Mahmud, A.; Hixson, M.; Hu, J.; Zhao, Z.; Chen, S. H.; Kleeman, M. J. Climate impact on airborne particulate matter concentrations in California using seven year analysis periods. *Atmos. Chem. Phys.* **2010**, *10* (22), 11097−11114.
(59) Mysliwiec, M. J.; Kleeman, M. J. Source apportionment of secondary airborne particulate matter in a polluted atmosphere. *Environ. Sci. Technol.* **2002**, *36* (24), 5376−5384.
(60) Ying, Q.; Mysliwiec, M.; Kleeman, M. J. Source apportionment of visibility impairment using a three-dimensional source-oriented air quality model. *Environ. Sci. Technol.* **2004**, *38* (4), 1089−1101.
(61) Held, T.; et al. A comparison of the UCD/CIT air quality model and the CMB source-receptor model for primary airborne particulate matter. *Atmos. Environ.* **2005**, *39* (12), 2281−2297.
(62) Ying, Q.; Kleeman, M. J. Source contributions to the regional distribution of secondary particulate matter in California. *Atmos. Environ.* **2006**, *40* (4), 736−752.
(63) Kleeman, M. J.; et al. Source apportionment of secondary organic aerosol during a severe photochemical smog episode. *Atmos. Environ.* **2007**, *41* (3), 576−591.
(64) Ying, Q.; et al. Modeling air quality during the California Regional PM10/PM2.5 Air Quality Study (CPRAQS) using the UCD/CIT Source Oriented Air Quality Model—Part II. Regional source apportionment of primary airborne particulate matter. *Atmos. Environ.* **2008**, *42* (39), 8967−8978.
(65) Chen, J. J.; Ying, Q.; Kleeman, M. J. Source apportionment of visual impairment during the California regional PM(10)/PM(2.5) air quality study. *Atmos. Environ.* **2009**, *43* (39), 6136−6144.
(66) Ying, Q.; Kleeman, M. Regional contributions to airborne particulate matter in central California during a severe pollution episode. *Atmos. Environ.* **2009**, *43* (6), 1218−1228.
(67) Ying, Q.; Lu, J.; Kleeman, M. Modeling air quality during the California Regional PM10/PM2.5 Air Quality Study (CPRAQS) using the UCD/CIT source-oriented air quality model—Part III. Regional source apportionment of secondary and total airborne particulate matter. *Atmos. Environ.* **2009**, *43* (2), 419−430.

(68) Skamarock, W. C.; Dudhia, J.; Gill, D. O ; Barker, D. M.; Duda, M. G.; Huang, X.-Y.; Wang, W.; Powers, J. G. A description of the advanced research WRF version 3. NCAR Technical Note NCAR/TN-475+STR, June 2008.
(69) Wang, W.; Duda, M. G.; Dudhia, J.; Gill, D. O.; Lin, H.-C.; Michalakes, J.; Rizvi, S.; Zhang, X. *The Advanced Research WRF (ARW) Version 3 Modeling System User's Guide*, January 2010.
(70) Chow, J. C.; et al. Evaluation of organic markers for chemical mass balance source apportionment at the Fresno Supersite. *Atmos. Chem. Phys.* **2007**, *7* (7), 1741−1754.
(71) Kleeman, M. J.; et al. Source Apportionment of Fine (PM1.8) and Ultrafine (PM0.1) Airborne Particulate Matter during a Severe Winter Pollution Episode. *Environ. Sci. Technol.* **2009**, *43* (2), 272−279.
(72) Ham, W. A.; Kleeman, M. J. Size-resolved source apportionment of carbonaceous particulate matter in urban and rural sites in central California. *Atmos. Environ.* **2011**, *45* (24), 3988−3995.
(73) Hu, J. L., et al., Long-term particulate matter modeling for health effects studies in California—Part I: Model performance on temporal and spatial variations; manuscript in preparation, 2014.