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Neighborhood-Scale Spatial Models of Diesel Exhaust Concentration Profile Using 1-Nitropyrene and Other Nitroarenes

Jill K. Schulte,*[,†,∥] Julie R. Fox,[†] Assaf P. Oron,[‡] Timothy V. Larson,[†] Christopher D. Simpson,[†] Michael Paulsen,[†] Nancy Beaudet,[†] Joel D. Kaufman,[†] and Sheryl Magzamen[§]

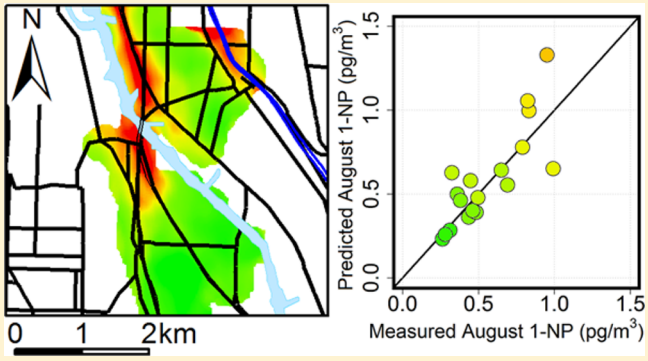
[†]University of Washington, Box 357234, Seattle, Washington 98195-7234, United States

[‡]Seattle Children's Research Institute, P.O. Box 5371, Seattle, Washington 98145-5005, United States

[§]Colorado State University, 1681 Campus Delivery, Fort Collins, Colorado 80523-1681, United States

Supporting Information

ABSTRACT: With emerging evidence that diesel exhaust exposure poses distinct risks to human health, the need for fine-scale models of diesel exhaust pollutants is growing. We modeled the spatial distribution of several nitrated polycyclic aromatic hydrocarbons (NPAHs) to identify fine-scale gradients in diesel exhaust pollution in two Seattle, WA neighborhoods. Our modeling approach fused land-use regression, meteorological dispersion modeling, and pollutant monitoring from both fixed and mobile platforms. We applied these modeling techniques to concentrations of 1-nitropyrene (1-NP), a highly specific diesel exhaust marker, at the neighborhood scale. We developed models of two additional nitroarenes present in secondary organic aerosol: 2-nitropyrene and 2-nitrofluoranthene. Summer predictors of 1-NP, including distance to railroad, truck emissions, and mobile black carbon measurements, showed a greater specificity to diesel sources than predictors of other NPAHs. Winter sampling results did not yield stable models, likely due to regional mixing of pollutants in turbulent weather conditions. The model of summer 1-NP had an R^2 of 0.87 and cross-validated R^2 of 0.73. The synthesis of high-density sampling and hybrid modeling was successful in predicting diesel exhaust pollution at a very fine scale and identifying clear gradients in NPAH concentrations within urban neighborhoods.



1. INTRODUCTION

The recent reclassification of diesel engine exhaust as carcinogenic to humans by the International Agency for Research on Cancer[1] has amplified the need for accurate methods of assessing human exposures to diesel exhaust. Numerous models of general traffic-related pollution have been described that provide the foundation for a large body of epidemiological research on human health effects of air pollution exposure.[2−7] In order to support epidemiological research on diesel exhaust exposure and community-scale risk assessments, models specific to diesel exhaust pollutants are needed.

Many models of traffic-related pollution use land-use regression (LUR) to estimate pollutant gradients at a finer spatial resolution than fixed-site monitoring can provide. In LUR models, pollutant concentrations measured at multiple fixed sites are used to develop multivariable linear models from a broad set of spatial characteristics, often including road density, traffic volumes, land use, topography, and population density.[8] LUR models of traffic-related pollutants can achieve a high level of out-of-sample predictive performance.[9−11] However, the utility of traditional LUR in diesel exhaust exposure assessment is limited for a number of reasons.

First, models based on only spatial predictors overlook spatiotemporal variability in pollution emissions and dispersion. Wilton et al.[12] included pollution estimates from meteorological dispersion models in LUR models of oxides of nitrogen (NO_x) and nitrogen dioxide (NO_2) in order to capture the interplay of changing meteorological conditions and traffic volumes throughout the day. This "hybrid" dispersion/LUR model outperformed more traditional LUR models without spatiotemporal variables. Inclusion of average dispersion model estimates at NO_2 receptor sites in Seattle decreased model RMSE by 0.36 $\mu g/m^3$ and increased cross-validated model R^2 from 0.63 to 0.67.

Second, because LUR requires measurements and spatial covariates at many locations to produce stable models,[13] LUR models are limited to spatial scales with sufficient measurement

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data and sufficiently resolved geographic data. Previous LUR models of traffic-related air pollutants have been described at the national scale[11,14] and the citywide scale.[5,9,10,12,15−19] The need for accurate estimates of individual-level pollution exposure has fueled an interest in finer-scale LUR modeling. While application of LUR at the intraurban scale is fairly unique, Mavko et al.[20] successfully used LUR to predict the gradient of NO_2 at the subneighborhood scale.

Third, models of more specific markers of diesel exhaust are needed in light of growing evidence of health concerns tied to diesel exhaust exposure.[21−28] Many LUR models have used NO_2 and NO_x as surrogates for general traffic-related pollution.[9,12,18,29] These gases perform well in LUR models and can be measured easily and inexpensively with passive samplers.[18] However, since oxides of nitrogen are abundant in exhaust from gasoline as well as diesel vehicles,[30−33] they are not suitable for modeling efforts that seek to isolate the impacts of these sources separately. Previous studies have also described LUR models of elemental and light-absorbing carbon as markers of diesel exhaust.[5,10,17,18] Though diesel exhaust has been identified as its predominant source, fine particle elemental carbon has been attributed to other sources as well, including wood smoke and, to a lesser extent, gasoline exhaust.[34]

1-Nitropyrene (1-NP) is a promising diesel exhaust marker for LUR modeling that is enriched in diesel exhaust compared to other sources of particulate matter (PM). A particle-associated nitrated polycyclic aromatic hydrocarbon (NPAH), 1-NP is a byproduct of combustion and the most prevalent of the more than 60 NPAHs found in diesel engine exhaust particulate matter.[35] Although modern diesel technology generally emits substantially lower levels of PM mass and 1-NP compared to older diesel engines, 1-NP is still present in exhaust from modern diesel engines and remains enriched in diesel exhaust particulate compared to particles from other sources (see Tables 1.1 and 1.4 in IARC 2013).[1] Furthermore, a recent source attribution study demonstrated that in contemporary ambient samples, 1-NP was most strongly associated with diesel traffic and less strongly associated with gasoline vehicles or land use predictors of traffic in general.[36] Though 1-NP has historically been detected in other sources, including airplane exhaust and coal combustion fly ash,[37] ambient 1-NP concentrations were found to be most highly correlated with traffic volumes.[38] In laboratory studies, 1-NP concentrations were over 200 times higher in diesel engine particles than in gasoline engine particles.[38,39] Models of 1-NP can provide valuable information on gradients of diesel-specific air pollution as distinct from gasoline exhaust. An important limitation is that 1-NP is readily decomposed in the presence of ultraviolet light,[40,41] and thus some atmospheric photodegradation of 1-NP can be expected prior to deposition, particularly during sunny weather.

Two secondary NPAHs, 2-nitropyrene (2-NP) and 2-nitrofluoranthene (2-NFl), can be measured in tandem with 1-NP to provide additional information on ambient NPAH concentrations. Though 2-NP and 2-NFl are not present in direct emissions from diesel vehicles or other sources,[42,43] they are two of the most abundant nitroarenes in ambient particulate organic matter[44] and form from atmospheric reactions with emitted parent compounds pyrene (Py) and fluoranthene (Fl).[42,43,45,46] While laboratory analysis of 1-NP is fairly complex, the addition of 2-NP and 2-NFl is easily obtained simultaneously. Investigating the relative amounts of these secondary pollutants with respect to 1-NP provides valuable information about the dominant sources of pollution in industrial and near-industrial neighborhoods.[47]

The Diesel Exhaust Exposure in the Duwamish Study (DEEDS) arose in response to community concerns about large volumes of diesel trucks in two heavily trafficked Seattle, WA neighborhoods. To evaluate the impacts of diesel traffic on ambient air quality, we developed finely resolved models of NPAHs at the neighborhood scale. We identified significant predictors of pollutant concentrations and created fine-scale maps of NPAH pollution gradients. With our 1-NP model, we present a modeling approach targeted to fine-scale diesel exhaust assessment in three unique ways: it incorporates spatiotemporal information using mobile monitoring and dispersion model data, its high resolution reveals clear pollution gradients across small areas, and it is based on measurements of a highly diesel-specific pollutant.

2. METHODS

Briefly, we applied multivariable linear regression to 1-NP, 2-NP and 2-NFl measurements, mobile aerosol measurements, modeled vehicle emissions, and land use characteristics to develop regression models of diesel exhaust markers.

2.1. Particulate Matter Sampling. We conducted two field sampling campaigns on August 18−30 and December 1−14, 2012. These sampling periods were intended to represent the summer and winter seasons, respectively, as we expected seasonal variation in both meteorology and diesel exhaust sources. We sampled at 21 sites in an area of approximately 8 km^2 (Figure 1). Sampling sites were a mix of residential, commercial, and industrial locations. We collected fine particulate matter ($PM_{2.5}$) on 37 mm PTFE filters (Pall Life Sciences, Port Washington, NY) loaded in Harvard Personal Exposure Monitors (HPEMs, Harvard School of Public Health, Boston, MA). Sampling pumps (Medo USA Inc., Hanover Park, IL) operated at a nominal flow rate of 1.8 L/min and were equipped with dual-valve timers to alternate sampling between two collocated HPEMs at each site.

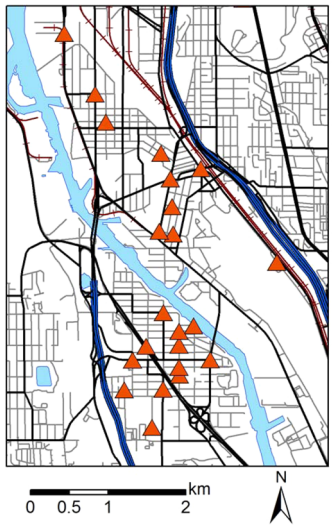

Figure 1. Map of NPAH sampling sites (orange▲). Locations have been generalized to the nearest intersection to protect participant privacy.

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2.2. Mobile Monitoring. We collected on-road aerosol measurements using a mobile dual-channel Aethalometer (microAeth Model AE52, Magee Scientific, Berkeley, CA). The instrument's inlet was affixed to a hybrid sport utility vehicle that drove a fixed route throughout the study area 5−6 times per day between 2 pm and 7 pm. We conducted mobile sampling on September 19−21 and 23−25, 2012, and December 5−8 and 10−11, 2012. Though the mobile and stationary sampling coincided during the December sampling period, the mobile monitor was unavailable during the August sampling campaign. The instrument measured aerosol absorption on the 880 nm black carbon (BC) and 370 nm ultraviolet particulate matter (UVPM) channels. We calculated overall mean log-transformed BC within buffers of 300 and 500 m around each sampling site from all 12 mobile sampling days. We included these results as model covariates to represent the intensity of typical rush-hour mobile BC emissions in the immediate vicinity.

2.3. Laboratory Analysis. We analyzed particles for 1-NP, 2-NP and 2-NFl content according to a previously reported method.[47] In brief, samples were spiked with an isotopically labeled internal standard, extracted in solvent, evaporated, and then resuspended in a solution of ethanol, sodium acetate, and acetic acid. We filtered the suspension prior to analysis via two-dimensional high-performance liquid chromatography tandem mass spectrometry.

2.4. Dispersion Modeling. The CAL3QHCR dispersion model[48] computed estimates of nonreactive car- and truck-source pollution based on roadway locations, traffic volumes and meteorological data. This model uses a Gaussian dispersion equation that weights the contributions of road sources by their distance to receptor sites, as described by Benson.[49] We obtained roadway location inputs from the Tele Atlas digital road network (TomTom North America, Inc., Lebanon, NH) and traffic volumes on major roads from the Puget Sound Regional Council's Travel Demand Model Version 1C (2008). The University of Washington Smart Transportation Applications and Research Lab provided data on diurnal traffic patterns in the study area. Meteorological data were collected at the National Weather Service station at the King County International Airport with the exception of mixing height, which was obtained from the Seattle-Tacoma International Airport. We included as model covariates the two-week mean log-transformed hourly CAL3QHCR concentration predictions for cars and trucks over each sampling period within buffers of 1.5, 3, and 4.5 km, using methods developed by Wilton et al.[12]

2.5. Spatial Covariates. We extracted geographic attributes of the sampling sites, including land use, road density, and population, using Tele Atlas and ArcGIS 10.1 (ESRI, Redlands, CA). We obtained spatial data from the following sources: National Emissions Inventory (U.S. Environmental Protection Agency), Tele Atlas, Google Maps, U.S. Census Bureau, Multi-Resolution Land Characteristics Consortium 2006 National Landcover Data set (U.S. Geological Survey), National Geospatial Intelligence Agency, and the Bureau of Transportation Statistics. The 107 spatial variables initially considered for the models are summarized in Table 1.

2.6. Model Building. We identified linear regression models with log-transformed concentrations of 1-NP, 2-NP and 2-NFl as dependent variables and covariates listed in Table 1 as independent variables. We first excluded covariates with a coefficient of variation <0.1, total change of <10% across the study area, or a correlation of $r > 0.95$ with another covariate.

Table 1. Outline of Covariates Used for Model Building

description	units	buffer radius (m)
distance to A1 road, airport, coast, port, rail yard, railroad, truck route, road, intersection, A1 and A2 road interchange, A3 road interchange	$\log_{10}$ m	N/A
length of A1 and A2/A3 roads	m	100, 150, 300, 500, 750, 1500
population	count	1000
population	$\log_{10}$ count	500, 1000, 1500, 2500
number of intersections	count	500, 1000
interchanges between A1 and A1/A2/A3 roads	count	500, 1000
impervious surface	%	50, 150, 300
elevation	m	N/A
intensity of development (low, medium-high, high)	%	50, 150, 300, 750, 1000, 3000
land characteristics (forest, flat, open space)	%	150, 300, 750, 1000, 3000
distance to trucking company	$\log_{10}$ m^2	N/A
CAL3QHCR car- and truck-source pollution estimates in summer and winter	$\log_{10}$ $\mu g/m^3$	1500, 3000, 4500
mean of mobile BC concentrations	$\log_{10}$ ng/m^3	300, 500

The results of the initial variable screening are included in the Supporting Information. We selected from among the remaining 72 variables using the least absolute shrinkage and selection operator (lasso) first described by Tibshirani.[50] We used 5-fold cross-validation to determine the optimal lasso penalty to minimize model mean-square error, with sites within 250 m of each other kept in the same cross-validation group. We then performed reverse stepwise regression on model terms selected by the lasso method to minimize AIC. To ensure model stability, we repeated the lasso and stepwise procedures 500 times per model and reported only models that appeared in at least 50% of these iterations. We calculated cross-validated model performance statistics using leave-one-out cross-validation. We conducted all statistical analysis in R version 2.15.2.

To create prediction maps, we extracted spatial covariates for a grid of evenly spaced points 50 m apart (1-NP) or 100 m apart (2-NP and 2-NFl). We used the regression models identified to calculate predicted concentrations at each grid point. We used the universal kriging tool in ArcGIS 10.1 to generate a smoothed raster surface of the gradient of predictions for each model.

3. RESULTS

3.1. Measurement Results. Table 2 summarizes the concentrations of pollutants measured during the sampling campaigns and the correlations among them. Measurements of 1-NP, 2-NP, and 2-NFl were above the limit of detection for all samples. We excluded results from one site in August due to evidence of filter contamination. With the exception of $PM_{2.5}$, pollutant concentrations were higher in winter than summer, though summer concentrations showed higher variability than winter. Coefficients of variation of August concentrations (0.73, 0.27, and 0.37 for 1-NP, 2-NP, and 2-NFl, respectively) exceeded those observed in December (0.46, 0.12, and 0.12). The medians of the ratios of 2-NFl:1-NP and 2-NFl:2-NP in August were 4.8:1 and 11:1, respectively, and 2.0:1 and 2.0:1, respectively, in December.

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Table 2. Summary of Measurement Results

	mean	median	SD	min.	max.	Pearson r with 1-NP	2-NP	2-NFl	$PM_{2.5}$
August (n = 20)									
1-NP (pg/m^3)	0.67	0.49	0.49	0.26	2.5		0.83	0.79	0.44
2-NP (pg/m^3)	0.24	0.25	0.065	0.15	0.42			0.85	0.51
2-NFl (pg/m^3)	2.7	2.4	1.0	1.2	4.6				0.37
$PM_{2.5}$ (μg/m^3)	5.7	5.6	0.68	4.6	7.4				
December (n = 21)									
1-NP (pg/m^3)	2.1	1.9	0.97	1.1	5.7		0.58	0.59	0.29
2-NP (pg/m^3)	1.4	1.4	0.17	1.0	1.8			0.91	0.25
2-NFl (pg/m^3)	3.7	3.7	0.44	2.5	4.5				0.20
$PM_{2.5}$ (μg/m^3)	5.2	5.1	0.4	4.4	5.9				

We evaluated the representativeness of the sampling periods using meteorological data from the King County International Airport. The August sampling campaign was conducted during a fairly typical summer period of stagnant and sunny weather. The sampling period was drier (0.0 in. of total precipitation) than the summer 2012 average (0.022 in. per day), but the average wind speed of 4.0 mph was the same during the sampling period and summer 2012 as a whole. The December sampling campaign took place during a particularly windy and rainy period. The average precipitation was higher during the sampling campaign (0.25 in. per day) than all of winter 2012−2013 (0.11 in. per day). The average wind speed was also higher during the sampling campaign (7.0 mph) than during the whole winter season (5.0 mph).

Mean and median mobile BC concentrations were 1.7 μg/m^3 and 1.1 μg/m^3, respectively. The mobile UVPM and BC channels were highly correlated (r = 0.97) with a median difference (UVPM − BC) of −0.055 μg/m^3. As the UVPM−BC difference is frequently calculated as a rough surrogate for residential wood smoke,[51] these low results indicate that residential wood smoke was not a dominant source of particulate matter during the study periods. A map of aggregated mobile BC concentrations is included in the Supporting Information.

3.2. Models. The models of August 1-NP, 2-NP, and 2-NFl are summarized in Table 3. No December models appeared in more than 50% of the lasso and stepwise repetitions. We excluded one site from modeling in both seasons due to the absence of mobile monitoring data.

Model performance statistics are summarized in Table 4. All models were significant at $p < 0.001$. The performance of the August 1-NP model as measured by the cross-validated R^2 (0.73) is comparable to that reported by Wilton et al.[12] for similar hybrid meteorological dispersion/land-use regression models of NO_2 in Los Angeles (R^2 = 0.77) and Seattle (R^2 = 0.67). The performance of the August 2-NP and 2-NFl models ($R^2 > 0.8$) exceeds that of the August 1-NP model.

Figure 2 shows the gradients of predicted August 1-NP, 2-NP, and 2-NFl concentrations across the study area. The color gradients span the range of predicted concentrations for each pollutant separately. The range of concentrations predicted are wider for 1-NP and 2-NFl than 2-NP.

4. DISCUSSION

We successfully modeled and mapped gradients of three NPAHs using a hybrid meteorological dispersion/land-use regression technique and direct measurements from a high-density sampling campaign. Though a number of valid modeling approaches can be used to predict pollution gradients, the models we developed reflect several unique applications of hybrid modeling methods. We developed models for a novel diesel-specific pollutant (1-NP) as well as two secondary NPAHs for which spatial models have not previously been described. We applied this modeling approach at an unusually fine neighborhood scale for all three pollutants, using measurements collected at a high density of approximately 2.6 sites per square km. We also leveraged mobile monitoring data for regression modeling, which provided fine-scale estimates of on-road emissions that were significant predictors of all three NPAHs.

Our findings from these modeling and mapping efforts provide insight into the major pollution sources and spatial trends in pollution levels in south Seattle. High-intensity development in a 150 m radius predicted concentrations of all three pollutants. This development category, as defined in the 2006 National Land Cover Database by the U.S. Geological Survey, contains areas with 80−100% impervious surface cover that are zoned either for industrial use or high-density

Table 3. Summary of August NPAH Regression Models

model	covariate	β	std error	t value	$p > \|t\|$
$\log_{10}$ August 1-NP	$\log_{10}$ m to railroad	−0.18	0.081	−2.2	0.04
	high-intensity development in 150 m	0.0025	0.0010	2.4	0.03
	CAL3QHCR truck estimate in 4500 m	0.29	0.20	1.5	0.16
	mean $\log_{10}$ mobile BC in 300 m	1.3	0.41	3.2	0.01
$\log_{10}$ August 2-NP	$\log_{10}$ m to intersection	−0.057	0.042	−1.3	0.20
	intersections in 500 m	0.0055	0.0024	2.3	0.04
	impervious surface in 50 m	0.0025	0.00073	3.4	< 0.01
	elevation	−0.010	0.0040	−2.6	0.02
	mean $\log_{10}$ mobile BC in 300 m	0.35	0.20	1.8	0.10
$\log_{10}$ August 2-NFl	$\log_{10}$ population in 2500 m	−0.29	0.23	−1.3	0.23
	high-intensity development in 150 m	0.0017	0.00055	3.0	< 0.01
	forest in 750 m	−0.012	0.0042	−2.9	0.01
	mean $\log_{10}$ mobile BC in 300 m	0.46	0.25	1.8	0.09
	mean $\log_{10}$ mobile BC in 500 m	0.83	0.36	2.3	0.04

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Table 4. Summary of Model Performance Statistics

model	R^2	cross-validated R^2 (log_{10} units)	cross-validated RMSE (log_{10} units)	cross-validated R^2 (original units)	cross-validated RMSE (original units)
August 1-NP	0.87	0.73	0.12 log_{10} pg/m^3	0.64	0.30 pg/m^3
August 2-NP	0.90	0.82	0.049 log_{10} pg/m^3	0.83	0.027 pg/m^3
August 2-NFl	0.93	0.86	0.063 log_{10} pg/m^3	0.84	0.40 pg/m^3

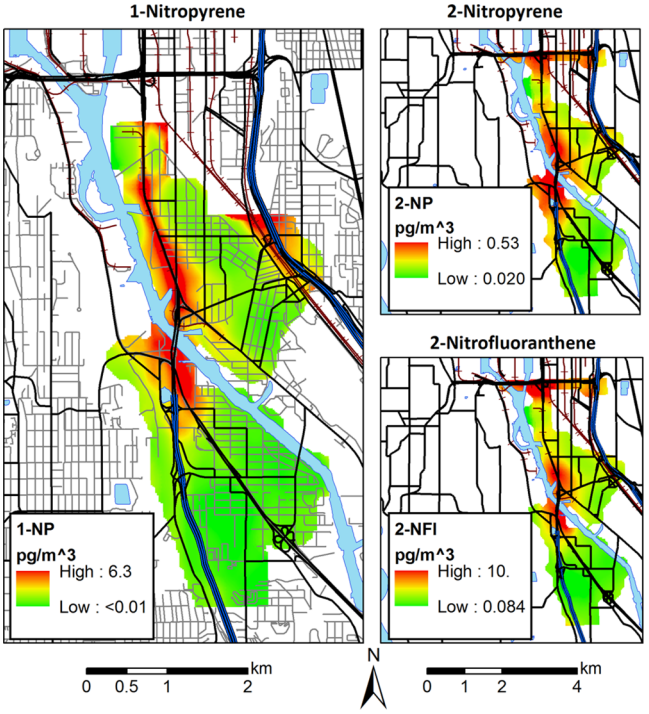

Figure 2. Gradient maps of 1-NP, 2-NP, and 2-NFl model predictions.

commercial and residential development. This suggests that, as expected, concentrations of NPAHs are highest in commercial and industrial areas with predominantly impervious surface and little green space. All three models featured the mobile BC covariate, which indicates that on-road black carbon pollution is highly correlated with ambient concentrations of these NPAHs.

The terms identified in the model of 1-NP confirm the specificity of this pollutant to diesel sources. In addition to the development and mobile monitoring variables described above, its model also contained distance to railroad and estimates of truck pollution from the CAL3QHCR model. As we expected, ambient concentrations of the most specific diesel exhaust marker are not simply a function of spatial covariates but also depend on temporal factors, such as meteorological conditions and traffic patterns captured by the CAL3QHCR model. Neighborhoods with the highest predicted concentrations of 1-NP are those near industrial development and downwind from roads with heavy truck traffic.

Interpretation of the 2-NP and 2-NFl models should be approached with caution. As these models were secondary to our principal goal of modeling 1-NP as a diesel exhaust marker, our initial list of covariates was tailored to a broad range of expected sources and predictors of 1-NP. Consequently, this set of variables may not contain the breadth of industrial covariates necessary to accurately identify specific predictors of secondary NPAHs.

The secondary pollutant models do reveal differences in the spatial distribution of NPAHs by their specificity to diesel exhaust. The models of 2-NP and 2-NFl contain terms primarily related to general traffic pollution and industrial development, rather than diesel-specific sources. Concentrations of 2-NP were predicted to be highest near intersections, areas of impervious surface and low elevations. Concentrations of 2-NFl were positively associated with mobile BC as well as high-intensity development. They were negatively associated with forest cover and population. The elevation and population covariates are likely acting as surrogates for industrial activity, as population and elevation are lower in the industrial neighborhoods in the northern section of the study area where the highest 2-NFl concentrations were measured.

South Seattle is home to several different types of industry that likely emit Py and Fl. Previously identified sources of Py and Fl, in order of decreasing mass concentration of Py + Fl, include asphalt production, lead smelter, oil burning, bronze smelter, passenger vehicle diesel exhaust, scrap metal incineration, steel manufacture, cement production, wood smoke, paved road dust, and soil dust.[52,53] The relative ambient concentrations of Py and Fl depend on the activity level of each source in the environment. Possible sources of Py and Fl that result in formation of 2-NP and 2-NFl in and around the study area may include, but are not limited to, cement and asphalt mixing, scrap metal incineration, steel manufacture and aviation traffic at a local airport, motor vehicle exhaust from both light and heavy duty vehicles, and residential combustion, including cooking fumes and home heating. Another possible source of Py and Fl is kerosene, though it is not typically combusted in large quantities in the United States.[54] Several formulations of jet fuel are derived from kerosene, though no specific reports of combustion of jet fuel leading to emissions of Py and Fl have been documented.[55]

Comparison of secondary pollutants to each other can provide an understanding of the chemical processes that predominate in the local atmosphere, though this study did not model these processes directly. 2-NFl is mainly formed in the atmosphere by the reaction of Fl initiated either by a hydroxyl radical (OH) in the presence of nitrogen dioxide or by a nitrate (NO_3) radical. The nitrate radical is particularly photosensitive, so the contribution of the nitrate-mediated pathway to 2-NFl concentrations increases at night and in the winter.[56,57] 2-NP is formed from Py through the pathway initiated by OH but not NO_3. On the basis of these mechanisms, the ratio of 2-NFl to 2-NP is often used to measure the contribution of the OH versus the NO_3 pathway in NPAH formation. A ratio closer to 10 is typically dominated by hydroxyl initiation, and a ratio closer to 100 is dominated by nitrate initiation.[44,58] Our median 2-NFl to 2-NP ratios of 11:1 in August and 2.0:1 in December indicate that atmospheric formation of secondary NPAHs in our study area was initiated predominantly by the hydroxyl pathway. These ratios are consistent with 2-NFl:2NP ratios from 2008 to 2009 measurements of 18.7:1 in the nonheating season and 5.5:1 in the heating season from previous research in the study area,[36] though it appears that our recent measurements were slightly more driven by hydroxyl radicals.

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The ratio of 2-NFl to 1-NP has been suggested as an estimate for evaluating the contribution of primary emissions versus atmospheric formation of NPAHs. A ratio of <5 is considered indicative of dominant primary emissions.[59] Our median 2-NFl:1-NP ratios of 4.8:1 in August samples and 2.0:1 in December samples indicate that the NPAH levels measured in both seasons were more strongly influenced by primary emissions. These ratios are slightly lower than samples previously collected during the nonheating (May−October) and heating (November−April) seasons in 2008 and 2009 from a single location within the study area (5.3:1 and 2.7:1, respectively).[36]

Previously reported concentrations of 1-NP, 2-NFl, and 2-NP from locations around the world span a wide range, driven in part by wide variation in the relative proportions of diesel versus gasoline vehicles used in these study areas. The maximum 1-NP, 2-NP, and 2-NFl concentrations measured in either season in this urban study are either the same order of magnitude or 1 order of magnitude lower than concentrations reported for the corresponding season in Baltimore, MD (urban) and Fort Meade, MD (suburban).[60] However, as the Maryland data were collected more than 10 years ago, it is likely that some of the difference in magnitude between these data sets can be attributed to changes in diesel engines, fleet composition, and fuels in the intervening years. Comparison of our results for these three pollutants with other studies should be interpreted with caution also due to differences in sample collection techniques and laboratory analysis methods.

We encountered several limitations to our sampling and modeling approaches. Our sampling campaign provided a snapshot of pollutant concentrations for 2 weeks in each of two seasons, which are unlikely to be representative of a whole year. While meteorological observations show that our August sampling period was sufficiently representative of summer conditions, the applicability of our results outside this season is unknown.

The particularly wet and windy conditions during our December sampling campaign likely explain why we did not identify winter models of any of the three pollutants. Under the stagnant conditions observed during the August sampling campaign, measured concentrations were presumably driven by local sources, which were well represented by the spatial covariates considered for modeling. In December, higher winds and precipitation likely diluted the impacts of local sources, causing greater regional mixing of pollutants, lower overall fine scale spatial variability, and a lower signal-to-noise ratio. We evaluated an additional two-season 1-NP model using aggregated measurements from both seasons, though it performed poorly when compared to December measurements; details of this model can be found in the Supporting Information.

There are a number of limitations to 1-NP as a marker of diesel exhaust, including limited data on health effects, the expense and limited availability of laboratory analysis, and the lack of a continuous sampling method. Other diesel exhaust markers, such as elemental carbon, may be suitable when a lower level of specificity to diesel sources is acceptable. Simultaneous sampling of elemental carbon and 1-NP in the study area in 2008−2009 showed that the two pollutants were well-correlated with an r_s of 0.69.[36]

While mobile BC concentrations proved to be significant predictors of the pollutants we modeled, the utility of the mobile monitoring data in generating prediction maps was limited. We designed the mobile monitoring route to include multiple loops around sampling sites in order to ensure that the sample size within 300 m of each site was large enough to accurately represent on-road emissions. As a result of this design, the number of data points within 300 m of each gridded prediction point varied by location. In some cases, the roads selected for mobile monitoring in this radius were representative of typical roads near these points. In other cases, the mobile route oversampled smaller or larger roads in a 300 m radius. Consequently, prediction maps likely overestimated pollution levels in some outlying areas and underestimated in others. For the most accurate prediction maps, a more suitable mobile route would cover a representative sample of neighborhood roads evenly distributed throughout the neighborhoods.

Estimates of mobile-source pollution from the CAL3QHCR model were included to complement the mobile data variables, as these estimates have different strengths and limitations. The accuracy of CAL3QHCR pollution predictions is limited because they are based on modeled rather than empirical traffic counts. In addition, these traffic counts were estimates of annual average daily traffic and were not specific to the sampling periods. However, because the CAL3QHCR model included modeled traffic counts from all arterial roads in the study area, we expect that predictions in outlying areas are as accurate as those near sampling sites. A sensitivity analysis comparing models with and without the CAL3QCHR covariate showed that the 1-NP model without this covariate had a lower cross-validated R^2 (0.68) and higher RMSE (0.14 $\log_{10}$ pg/m^3). Details of this analysis are included in the Supporting Information.

Our models show that hybrid dispersion/land-use regression modeling is viable at the neighborhood level and can yield fine-scale estimates of ambient NPAH concentrations. This modeling technique can be successfully applied to 1-NP, a specific marker of diesel exhaust. Several potential applications of fine-scale models of 1-NP could augment our understanding of health effects of diesel exhaust exposure. A number of studies have investigated various urinary biomarkers of 1-NP.[61−66] Once a 1-NP biomarker of exposure has been validated, it could be coupled with spatial models to evaluate the relationship between ambient concentrations and personal exposure to diesel exhaust pollutants. Neighborhood-level models of 1-NP, when coupled with individual time-activity data, could provide more specific measures of diesel exhaust exposure for epidemiological studies and thus improve estimates of risk. Increasing the specificity of measurement and the spatial resolution of models of diesel exhaust pollution represents a step forward in diesel exhaust exposure assessment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03639.

Results of initial variable screening; CAL3QHCR sensitivity analysis model results; two-season $\log_{10}$ 1-nitropyrene model; histogram of $\log_{10}$ mobile BC in study area; map of geometric mean mobile BC in 300 m. (PDF)

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AUTHOR INFORMATION

Corresponding Author

* Phone: (360) 407-6374. Fax (360) 407-7534. E-mail: jks33@u.washington.edu..

Present Address

[‖]P.O. Box 47600, Olympia, WA 98504.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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