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A Scalable Field Study Protocol and Rationale for Passive Ambient Air Sampling: A Spatial Phytosampling for Leaf Data Collection

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Abstract

Stable, bioreactive, radicals known as environmentally persistent free radicals (EPFRs) have been found to exist on the surface of airborne PM_{2.5}. These EPFRs have been found to form during many combustion processes, are present in vehicular exhaust, and persist in the environment for weeks and biological systems for up to 12 h. To measure EPFRs in PM samples, high volume samplers are required and measurements are less representative of community exposure; therefore, we developed a novel spatial phytosampling methodology to study the spatial patterns of EPFR concentrations using plants. Leaf samples for laboratory PM analysis were collected from 188 randomly drawn sampling sites within a 500-m buffer zone of pollution sources across a sampling grid measuring 32.9 × 28.4 km in Memphis, Tennessee. PM was isolated from the intact leaves and size fractionated, and EPFRs on PM quantified by electron paramagnetic resonance spectroscopy. The radical concentration was found to positively correlate with the EPFR g-value, thus indicating cumulative content of oxygen centered radicals in PM with higher EPFR load. Our spatial phytosampling approach reveals spatial variations and potential “hotspots” risk due to

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b03643. Appendix 1. The tables containing all the data collected for this study was compiled and analyzed (PDF)

Author Contributions

The manuscript was written through the contribution of T.J.O., S.L., and S.A.C., C.G., and S.M.L. were responsible for all the laboratory work. T.J.O. was responsible for the study design and implementation of spatial sampling strategy, GIS/GPS mapping, and spatial modeling. S.A.C. led field work efforts. T.J.O., S.M.L., and S.A.C. were responsible for conception, analysis, and data interpretation. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

EPFR exposure across Memphis and provides valuable insights for identifying exposure and demographic differences for health studies.

Graphical abstract

INTRODUCTION

Annually, seven million premature deaths are linked to exposure to air pollution.¹ Particulate matter (PM) is a significant component of air pollution and is often categorized according to mean aerodynamic diameter. Sizes range from coarse particles (<10 μm in diameter) to the smaller fine and ultrafine particles (<2.5 μm and <0.1 μm , respectively). The smaller classes of PM are generated predominantly by anthropogenic sources including vehicular exhaust (gas and diesel), flaring of hydrocarbons at chemical plants, coal and biomass burning, waste incineration and thermal treatment.^{2,3} PM_{2.5} and PM_{0.1} are more apt to cause toxicity due to their propensity to be inhaled and/or cross the olfactory epithelium.^{4–6} Most outdoor air pollution poses a significant human health risk. Ambient air pollution is normally generated from chemical products mainly through personal smoking, mobile, stationary, and natural/ biomass combustion sources—the chemical products contain organic species that are transformed through atmospheric chemistry to form PM. It has been demonstrated that size and composition of PM are important factors in determining toxicity^{7–11}

Although reports of persistent radicals in coals, chars, and soots date back to the 1950s^{12,13} it took half-a-century for studies concerning radicals associated with environmental PM to be recognized as important.^{8,14–28} We have demonstrated that *stable, but bioreactive radicals exist on the surface of airborne PM*.^{24,29,30} We have further demonstrated that particle-associated metals are reduced by interaction with organics and mediate the formation of radical-particle systems. The combination of surface stabilization and electronic delocalization results in persistency of the systems in the environment for days to weeks^{31,32} and in biological solutions for up to 12 h;³³ hence their name—environmentally persistent free radicals (EPFRs). Moreover, within biological systems EPFRs generate reactive oxygen species (ROS) in a catalytic cycle.^{33,34} Inhalation exposure to concentrations of EPFRs comparable to those in ambient air induce cardiac^{35–37} and pulmonary^{38–41} dysfunction in the exposed host. While exposure to air pollution is a putative etiological factor for respiratory and cardiovascular diseases, emerging observations in humans and data from animal experiments suggest that the CNS may also be significantly

affected and that such exposures occurring during a critical window of neurodevelopment may result in neurodevelopmental defects (NDD). In particular, epidemiological studies have shown that elevated air pollution is associated with decreased cognitive function at all life stages—birth to elderly—using a variety of standardized tests and MRIs of the prefrontal cortex.^{42–47} Perinatal^{48,49} and childhood^{50–55} exposures to PM, particularly from combustion sources such as vehicular exhausts, has also been associated with autism spectrum disorders. Interestingly, increases in systemic and CNS markers of oxidative stress (OS) and in neuroinflammatory markers are related to PM_{2.5} exposure levels suggesting not only their involvement in the NDD pathology but also the activity of EPFRs on the inhaled PM.

It has only been recently acknowledged that PM contains EPFRs and EPFRs are not measured or monitored in PM samples. Thus, epidemiological studies of human health effects associated with exposure to EPFRs on PM have never been performed. Here, we sought to develop an innovative spatial sampling methodology that can be used to collect adequate PM samples from remote locations without a high volume sampler. Since PM concentrations are spatially heterogeneous over a wide study area, we assumed that the spatial variability of EPFR concentration could not be captured by high volume samplers, even if we had sufficient quantities to deploy at the same time. Our primary objective therefore was to develop a novel and robust spatial phytosampling framework that captures both local and regional variability using leaf samples contaminated by on-road mobile emission sources of ambient air pollution. The rationale to collect leaf samples is in line with need to quantify EPFR concentrations that is representative of community exposure in Memphis, TN. A comprehensive spatial phytosampling design framework for Memphis was developed for site identification for use in leaf sampling and collection. Spatial phytosampling strategy is based on the retention knowledge and capacity of ambient PM by plant leaves. PM is retained by the electrostatic charges of the leaves surface with the assistance of trichomes and can be removed from collected leaves by sonication in water.^{56–58} However, it is important to bear in mind that the applied methodology is only meaningful in comparative applications, to evaluate spatial changes of EPFRs concentration (or other components) on PM and should not be used solely to evaluate PM concentration and PM spatial distribution by itself. A field study was designed to measure the ambient pollutant captured by leaves and identify potential health risk to the Memphis community using state-of-the-art geographic information system (GIS) and high spatial resolution GPS technologies.

MATERIALS AND METHODS

The purpose of this novel spatial phytosampling was to select representative sampling sites for leaf data collection. We used a few spatial sampling strategies and GIS/GPS methods to achieve this purpose. First, we designed a leaf collection strategy that was informed by our knowledge of spatial variability of ambient air pollution in an urban environment. This enabled us to determine appropriate spatial sampling sites that were used to collect adequate samples of green leaves for EPFRs extraction and analysis. Second, we incorporated relevant environmental characteristics and health outcomes into the sampling framework. Third, we

made sure our novel framework was grounded both in spatial sampling theory and recent empirical knowledge of ecological sampling.

Field Study Location, Setting, and Materials

The study was conducted in Memphis, Tennessee. Memphis is the largest city in Tennessee and is situated in Shelby County. It is in one of the eight counties that make up the Memphis metropolitan area and is a major transportation hub for river, highway, railroad, and air in the region. With the third busiest trucking corridor; five Class I railroads: BNSF, CSX, Union Pacific, Norfolk Southern, and Canadian National, the fourth largest inland port in the United States; and in 2014, the world's second busiest air cargo airport (busiest in the U.S.),⁵⁹ Memphis has several ambient pollution "hot spots" in the north and south.^{60,61} Memphis is the fourth poorest city in the nation and has a population that is 62% African American. While prior studies have identified ambient pollution "hot spots", the spatial extent of the ambient pollution exposure risk is still unknown.^{60–66}

Field work was undertaken between November 9 and 11, 2015, 3 days following the last rain, by a team of four scientists and 10 graduate students and postdoctoral fellows from the University of Tennessee Health Science Center and Louisiana State University. To accomplish the field study, a novel spatial phytosampling framework was created using a USGS topographic map at a scale of 1:50 000 and 1 m spatial resolution digital orthoimage, a land use land cover map, and a digital elevation model for Shelby County. Geographical information systems (GIS), Global Positioning System (GPS), and spatial analysis methods were used to randomly select a representative sample. Ancillary data was derived from neurocognitive and respiratory outcomes (i.e., cognitive scores at Year-2, low birth weight, and childhood asthma emergency department visits and hospitalization rates) and ambient PM_{2.5} sources such as major traffic zones (interchanges and intersections of all major state and county roads), and major ambient particulate matter sources. The synthesized spatial clusters of three health outcomes (i.e., cognitive scores at Year 2, low birth weight, and childhood asthma emergency department and hospitalization rates) were identified from Conditions Affecting Neurocognitive Development and Learning in Early Childhood (CANDLE)^{67–69} and pediatric asthma cohorts using GIS and hotspot analysis.⁷⁰ All data sets, including ambient sources were linked in a GIS and were used in determining sampling sites in the south, north, and east of Memphis.

Specific materials used for the field study include Trimble GPS units, clippers, iPads, 4G LTE Smartphones, permanent markers, labels, plastic gloves, Ziploc bags, and data sheets. Prefield work was conducted to test field instruments and validate the leaf data collection protocol.

Sampling Grid and Sites

The 188 sampling sites (all on a sampling grid measuring 32.9 × 28.4 km) were identified using GIS and a 500 m buffered centerline of major roadways and point sources of ambient pollution. The GIS/GPS procedures for creating a sampling grid for collecting leaf samples is as follows. In Step 1, we determined the size and area of sampling grid using the geographic extent of study area. In Step 2, layers representing relevant environmental

characteristics and health outcomes were created and linked to the sampling grid. In Step 3, a 500 m buffer of major roadways and point sources of ambient pollution layers were created. In Step 4, point locations of sampling sites were randomly located but constrained within layers created in Steps 2 and 3. The point data was uploaded into a newly created mobile cloud-based GIS data management system. In Step 5, we conducted a field pretesting of sampling sites and validation of data collection protocol in preparation for actual field study. A few technical modifications were made to the data collection protocol and cloud-based GIS project forms. We also did some GPS reconfigurations and tweaked the GIS database structure after the field pretesting trip. A functional leaf data collection system was then rolled out and made accessible via Internet-connected smartphone and GPS in real time and was automatically updating while we collected leaf data in the field. The spatial distribution of final sample sites is representative of emission hotspots and key exposure factors (Figure 1). Previous work in sampling designs for environmental monitoring informed the novel spatial phytosampling for leaf data collection.^{71–77}

Subplots and Samples

Some minor modifications were made in a bid to locate samples and establish additional subplots measuring 30 × 30 m. Leaf data was collected from the most suitable green shrub or tree species within any designated subplot. For example, given that most of Memphis is in a built environment (roads, buildings, etc.), if a sampling location fell on a built structure, we had to create an appropriate subplot from a nearby location. Although 188 sampling plot locations were allocated across the study site, it rained on the fourth day, rendering data collection ineffective, since rain washes particles from the leaves, and thus defines the accumulation time. Thus, leaf data was obtained from 107 sites (60% spatial coverage) and taken for laboratory analysis. Each sample was cataloged on a data sheet and carefully packed in a Ziploc bag containing a desiccant and stored on ice; each site was georeferenced and the unique physical land attributes were recorded by a GPS unit with subcentimeter positional accuracy. Collected data, including photographs of shrub/trees and samples, were stored using a mobile cloud-based GIS data management system.

PM Extraction and Quantitative Analysis of EPFR Content

Leaves are transferred to labeled beakers and deionized water was added to fully submerge the leaves except for the petiole part of leaves. (Usually 100–200 mL water). Leaves samples are sonicated for 2 min at room temperature and removed from water. TEM microscopy has confirmed a complete removal of the particles from the leaf surface by this method. Remaining water was transferred to a vacuum filtration assembly containing a filter with the pore size diameter of 3 μm . Particles larger than 3 μm were retained on the filter, while smaller fractions were collected with the filtrate water. As a result, the particles in the filtrate have a nominal size less than 3 μm , and in the remainder of the article, we refer to those samples as PM. Additionally, due to solubility of the PM soluble fractions in water, the shape and size of the particles in the filtrate is not retained. However, it is irrelevant for current studies as we are only analyzing PM for total mass and radical presence. The filtrate was immediately frozen in a collection beaker using dry ice and acetone and the beaker was placed on the lyophilizer until dry. Particles were collected and weighed and EPR spectrum obtained. All EPR measurements were performed using a Bruker EMX-2.0/2.7 EPR

spectrometer with dual cavities, X-band, 100 kHz and microwave frequency, 9.53 GHz. The spectra were obtained at room temperature. The typical operating parameters were microwave power 1 mW, modulation amplitude 4 G, sweep width 200 G, time constant 40.960 ms, and sweep time 167.7 s. Spin concentrations are calculated based on the comparison with the DPPH standard (2,2-diphenyl-1-picrylhydrazyl).

Although there are some scientific reports on the effect of sonication on the formation of hydroxyl radicals within the aquatic medium, these reports are normally associated with a high power sonication process over an extended period of time (10–60 min.). In this study, we sonicate at low frequency for only 2 min. Our laboratory experiments have examined the effects of sonication and freeze-drying of the filters on the radical concentration, where filter polyurethane foam (PUF) samples were first “tapped” from loose particles and remaining particles were extracted from PUF by analogous freeze-drying process as a means for leaves extraction. We did not find any significant differences either in the radical characteristic spectrum features or in radical concentration (difference was less than 10% between methods).

Statistical Analysis, Spatial Interpolation, and EPFRs Mapping and Analysis

All samples collected and measured are reported here. The extraction of particles from the leaves was done in duplicate/triplicate (depending on the amount of available leaves collected) for 10 randomly selected locations. Standard deviation of such replicates ranged from 2 to 17% (on average 11%), with one exception. In one sample, with the highest concentration of EPFRs, the standard deviation equaled 24%. The variation in distribution did not affect bin assignment of EPFR values.

We used descriptive and correlation statistics to summarize EPFR values and a number of visualization techniques to map and understand the spatial distribution of EPFR values in the study sites. All collected data, including sites were exported from a mobile cloud-based GIS data management system to ArcGIS 10.2.2 (ESRI Inc., Redlands, CA). All data analysis was conducted using MS Excel (Microsoft Inc., Redmond, WA), and SPSS Version 22 (SPSS Inc., IBM Corp, Armonk, NY).

We interpolated 106 sampled EPFR spins/g values data to unsampled areas and predicted potential current exposures using ordinary kriging technique.^{59,71,72,78} The sampled EPFR spins/g values were used to estimate EPFR exposure levels in unsampled locations. The spatial profiles from the upper bound estimate of average concentrations of EPFRs are presented across the study area. Using this map, we identified geographic locations in Memphis with similar EPFR profiles in order to better understand local (on-road and major industrial facilities) exposure. We divided the region into four categories based on a kriged surface of EPFR spins/g values, thus reflecting the range of predicted values at site locations in the study area. We visualized the spatial distribution of EPFRs spins/g values across the study area using a color-coded map that differentiates locations based on the predicted values. We tested whether geographical regions with similar EPFRs profiles were statistically different from each other using a one-way analysis of variance method. To determine what spatial profiles of EPFRs significantly differ from one another, we conducted a Bonferroni-holm posthoc test. We also intersected the pollution profile map

with demographic data to understand the composition of demographics associated with areas differentiated by EPFR profiles.

RESULTS AND DISCUSSION

Field Study Characteristics

included sample sites drawn from seven geographical locations (downtown, midtown, east, north, northeast, south, and southeast Memphis). The sites represent key ambient pollution concentrations and exposure factors (such as on-road mobile sources, point sources, residence characteristics, land use patterns, traffic patterns, etc.) from different parts of Memphis and Shelby County such as Millington, the Hollywood Dump Superfund site, Memphis International Airport, Orange Mound, Presidents Island, the Defense Depot superfund site, the national highway network (two interstate highways, I-40 and I-55), an inland waterway system (Mississippi River), air cargo airport (FedEx distribution center), and the intersection of five Class I railroads. South Memphis is a known home to numerous major industries such as transportation carriers, a petroleum refinery, petrochemical storage and transfer facilities, waste disposal facilities, and a power plant, all of which emit air toxics in the vicinity.^{60,61}

Prior research has demonstrated a large variability in PM accumulation based on the plant species being collected^{58,79} and this was substantiated by our data (see Table 1). The coefficient of variation (CV) was lowest in the east and highest in the south. One PM sample (#318S) lacked EPFRs; this sample contained visible signs of mold and was excluded from further analysis. The PM that accumulated on the collected plant leaves ranged from 0.3 to 41.7 $\mu\text{g}/\text{cm}^2$. There were no statistical differences between the amount of particles collected in the leaves from any of five regions and the average collected across the areas 6.81 $\mu\text{g}/\text{cm}^2$ (Table 1). EPFR concentrations were quantified in spins/g and varied across the sites from 1.14×10^{17} to 3.68×10^{19} . (Appendix, Tables 1–4). Figures 2 and 3 present the statistical analysis of all the data. PM₃ was categorized into 3 bins based on the concentration of the EPFRs on the samples: low EPFR concentration (below 7.99×10^{17} spins/g), medium (7.99×10^{17} – 1.99×10^{18}), and high (1.99×10^{18} and above). Such categorization is justified based on our previous observation of PM_{2.5} samples,⁸⁰ and these three categories can be considered as low, moderate, and high EPFR laden samples, respectively. Thus, 39% of the samples were categorized as low EPFR, 37% medium EPFR and 25% high EPFR within the Shelby County sampling area (Figure 2).

A clear trend could be observed of increasing *g* values of EPFRs with increasing EPFR concentration on PM. For each category of PM samples the average *g* value (g_{ave}) of all samples within the specific category equaled to 2.00442, 2.00475, and 2.00482 for the low, medium and high EPFR samples, respectively (Figure 3). *g* value is a characteristic of each EPR spectrum and for EPFRs it is an indicator of the increasing contribution of oxygen-centered radicals.⁸¹ For polyaromatic matrix where the carbon centered radical has an electron delocalized over multiple aromatic rings *g* value equals to 2.0023, close to a free electron. The presence of oxygen atom in the structure located close to unpaired electron typically increases *g* value to 2.003–2.0035. The electron localized on the oxygen atom, like within the phenoxyl radical species, increases *g* value to 2.004, while the presence of

multiple oxygens on the same ring (such as semiquinone radicals), further increase this value to 2.0045 (*para* species) or 2.005–2.006 (*ortho* species). Radicals with oxygen centered species are typical for the PM emitted from the sources with poor combustion conditions resulting in a plethora of products of incomplete combustion. In such conditions emitted PM would have a higher concentration of EPFRs. Such oxygen centered EPFRs are active in the redox cycling and are responsible for oxidative stress thus more dangerous to human health.

Figure 4 shows the spatial patterns of *g*-value of observed EPFRs in Memphis and Shelby County. The PM with the highest concentration of EPFRs were mainly observed near major ambient pollution sources in the south, downtown, and north; whereas the PM with the lowest EPFRs burden were observed in some parts of midtown and the east. The top 10 EPFR spins/g values were all situated in the south (five), downtown (three), and north (two) of Memphis where land use was largely commercial, industrial facilities, major roadways, and residential areas. In these areas, we also observed the main ambient source to be predominately from small vehicles, diesel trucks (on-road mobile emission sources), and major industrial sites (stationary sources). Indeed, one of the leaf data collection points (Site #309) with more than 3.68e+019 spins/g values and the highest value in this study (an outlier) was located along U.S. 61 County Road in lower part of downtown near the south. Many small vehicles and trucks emitting diesel exhaust particles were evident in this site.

We found significant differences in the mean spins/g values of identified similar profiles across the study area. We examined geographical regions with similar EPFRs profiles and found an overall statistical difference of spins/g concentrations between the profiles as determined by one-way analysis of variance ($F(3,121) = 7.02, p = 0.00022$). Comparisons using Posthoc test indicated that profile 2 was significant different from profile 4 ($p = 0.00000553$). Profile 2 was significant different from profile 3 ($p = 0.0075$). Profile 3 was not significant different from profile 4 ($p = 0.049$); profile 1 was not significant different from profile 4 ($p = 0.088$); profile 1 was not significant different from profile 2 ($p = 0.164$); and profile 1 was not significant different from profile 3 ($p = 0.255$). From these observed spatial patterns, it is evident, that PM pollution, as related to the EPFRs concentration is not uniform within the entire city. As demonstrated by these statistical results, our novel spatial phytosampling method for EPFRs samples can be used to identify regions with greater and potentially more dangerous exposures to EPFRs, which can in turn be linked to health outcomes. One could also use this method to identify local “hot spots” within the regions, where the concentration of EPFRs on PM are more highly elevated and could present a higher health risk. Table 2 presents the key characteristics of spatial profiles of studied area using estimates from predicted EPFRs spins/g data. Figure 5 presents a map showing the spatial patterns of the four spatial profiles, a box plot of these spatial profiles, and a tile plot of EPA data.

Our data further shows the low EPFR pollution areas are indicated by Profiles 1 and 2, whereas the high EPFR pollution areas are indicated by Profiles 3 and 4. Profiles 2 and 3 tend to regionalize across the study area. There are major differences in traffic density across the profiles. The data shows that EPFRs associated with airborne PM exist at high concentrations in the south and north, which have slightly over 52% of traffic burden. Demographic summaries indicate in both low and high EPFR pollution areas the largest

proportion of the population is predominately African American, followed by White, and a small number of other racial/ethnic groups. In our future plan, we will determine the role of effects of EPFRs exposure on emergency department visits in a pediatric asthma cohort. Although we intend to evaluate the effects of elevated levels of EPFRs on a respiratory health outcome, caution is required when interpreting EPFR values, especially the limited samples obtained from the east and north of Memphis. We are continuously working to methodologically advance the way we measure, identify, and characterize lifetime health effects of stressors (e.g., heavy metals, VOCs, PAHs, PM_{2.5}, temperature, and EPFRs) from contaminated and noncontaminated sites.

STUDY IMPLICATIONS

In this study, we regionalized spatial profiles of EPFRs into four categories. This is the first effort to design a phytosampling method to collect EPFRs in the field. Our prior studies show that EPFRs act as an integrated chemical and biological entity, and are present in airborne PM, particularly from combustion sources. However, our data indicate that mere measurement of PM_{2.5} concentrations in few selected points within the city or area does not accurately represent community exposure to health deteriorating agents associated with PM_{2.5}. Based on the EPFRs example, different locations within the city can correspond to entirely different exposure dose of specific agent (EPFRs in this case). Clear “hot spots” were identified as well as larger areas which may represent increased exposure risk. This novel spatial phytosampling approach reveals spatial variations and potential “hotspots” risk due to EPFR exposure across Memphis and provides valuable insights for identifying spatial exposure and demographic differences for future health studies, as well as, a new opportunity for remote and community exposure sampling and monitoring. With a dense network of sampling points, it is possible to evaluate local exposure risks. Based on such assessment a better epidemiological understanding of the public health can be archived. What is more important, awareness of local population and primary physicians can help proper prevention and diagnosis, and authorities can better address air pollution problems.

STUDY LIMITATIONS

As with all studies, there are limitations, which we will try to outline here.

- PM collected from the leaves is not and cannot be used as a measure of the PM_{2.5} concentration in the air. Different plant species collect the particles with different rates as discussed earlier, and indicated within the statistical analysis of samples collected in this studies.
- Accumulation of ambient air particles on the leaves is subject to varying deposition velocities depending on the particle size. In general larger particles accumulate faster than smaller (i.e., ultrafine) particles.^{82–84} This creates an accumulation bias favoring collection of larger particles. At the same time, the relative content of different size fraction will remain the same for samples collected in different locations and for compositional comparative studies (and in particular when comparing the concentration of EPFRs or organic matter) this error is self-correcting.

- Partial solubility of some components of the larger particles introduces some error. Small soluble fractions of the coarse PM will transfer to the solute and will contribute to the overestimation of the total PM mass in the selected range. The potential overestimation of the mass is less than 10% of PM_{2.5} mass.⁸⁵ However, this error will be proportional in every sample and thus will not affect the comparison between different samples (as performed here).
- Also, rain precipitation usually cleans the surface of the leaves from the adsorbed/trapped particulates. It is thus desired that the particulates are collected at least 3–4 days after the last precipitation to allow for sufficient particle collection and averaging of the particulate characteristics.

In summary, we have developed a novel spatial phytosampling methodology to study environmental exposure which will be of interest to the environmental scientific community. The EPFRs concentration on PM pollution was measured. The radical concentration was found to positively correlate with the g value of the EPFRs and indicated increasing content of oxygen centered radicals in PM with higher EPFR load. We also examined geographical regions with similar EPFRs profiles and found an overall statistical difference of spins/g concentrations between the profiles. EPFR concentrations did vary reflecting changing EPFR exposure potentially independently from PM concentration across the study area. We found that location within the city corresponded to specific and different exposure doses to EPFRs, which were regionalized into four spatial profiles. Our novel spatial phytosampling approach reveals spatial variations and potential “hotspots” risk due to EPFR exposure across Memphis and provides valuable insights for identifying spatial exposure and demographic differences for future epidemiological studies, as well as, a new opportunity for remote and community exposure sampling and monitoring. Future studies should detail and characterize potential limitations such as seasonality on EPFR profiles.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Study location, setting, and sites for leaf collection in Memphis and Shelby County in areas of high and low PM. Blue boxes denote areas with bad and good health outcomes.

Figure 2.
Histogram of EPFR concentration distribution in collected PM samples.

Figure 3.
Correlation of g values and EPFR concentrations in three groups of EPFR concentrations.

Figure 4.

A map showing observed spatial concentrations of g -values of EPFRs on PM.

Figure 5. Predicted spatial profiles of EPFRs in Memphis, Tennessee derived from ordinary kriging technique. (5a) EPFRs estimates showing spatial patterns of the profiles, (5b) Box plot of spin EPFR concentration values for each of the profiles, (5c) Tile Plot for EPA PM_{2.5} data covering the study period.

Table 1

Distribution of Sample Mass Collected during the Experiments

sample region	# of samples	mass/sample (mg)			mass/leaf area (ug/cm ²)				
		ave	CV	min	max	ave	CV	min	max
south	27	12.8	82.1	2.8	50.0	7.5	114.1	0.1	41.7
north	14	14.0	64.4	1.6	31.0	6.7	81.4	0.3	18.0
east	10	18.0	53.9	8.8	39.3	7.2	31.6	2.9	19.7
midtown	30	12.0	56.7	2.6	26.3	6.1	91.6	1.1	25.0
downtown	26	13.7	72.7	2.0	36.7	6.8	89.3	0.1	27.8

Table 2**Characteristics of the Four Spatial Profiles**

spatial profile 1	spatial profile 2
spins/g values range from 1.14×10^{17} to 7.36×10^{17}	Spins/g values range from 7.36×10^{17} to 1.23×10^{18}
mean spins/g $5.11 \times 10^{17} \pm 3.83 \times 10^{17}$ SD	mean spins/g $1.02 \times 10^{18} \pm 8.74 \times 10^{17}$ SD
land use mainly vacant, recreational/golf course, roadways, and a few industrial facilities	land use mainly commercial, roadways, residential, and industrial facilities
total population is about 50 000, about 20.2% white, 79.6% African Americans (AA), and others 0.2%	total population is about 240 000, about 35.8% white, 62.5% AA, and others 1.7%
area size about 12.9 km ² , population density approximately 3900 people per km ²	area size about 100.8 km ² , population density approximately 2400 people per km ²
the area covers parts of downtown, northeast, midtown, and southeast	the area covers a large portion of midtown, east, and portions in northeast
the 2015 annual average daily traffic (AADT) count was 357 510 vehicles	the 2015 AADT count was 1 839 273 vehicles
spatial profile 3	spatial profile 4
spins/g values range from 1.2×10^{18} to 3.29×10^{18}	spins/g values range from 3.29×10^{18} to 1.2×10^{19}
mean spins/g $3.09 \times 10^{18} \pm 5.44 \times 10^{18}$ SD	mean spins/g $6.61 \times 10^{18} \pm 8.23 \times 10^{18}$ SD
land use mainly commercial, roadways, residential, and industrial facilities	land use mainly roadways, major transportation hub, and industrial facilities
total population about 220 000, about 21.5% white, 78.3% AA, and others 0.2%	total population about 17 000, about 7.1% white, 82.2% AA, and others 0.7%
area size about 146.6 km ² , population density approximately 1500 people per km ²	area size about 2.8 km ² , population density approximately 6100 people per km ²
the area covers a large portion of the south, north, and small portions in midtown	mainly situated in the south
the 2015 AADT count was 3 275 950 vehicles	the 2015 AADT count was 153 159 vehicles