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Application of Land Use Regression to Identify Sources and Assess Spatial Variation in Urban SVOC Concentrations

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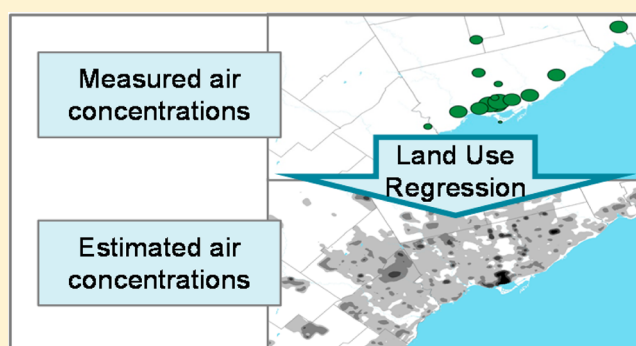
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S Supporting Information

ABSTRACT: Land use regression (LUR), a geographic information system (GIS), and measured air concentrations were used to identify potential sources of semivolatile organic contaminants (SVOCs) within an urban/suburban region, using Toronto, Canada as a case study. Regression results suggested that air concentrations of polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), and polycyclic musks (PCMs) were correlated with sources at a scale of <5 km. LUR was able to explain 73–90% of the variability in PCBs and PCMs, and 36–89% of PBDE and PAH variability, suggesting that the latter have more spatially complex emission sources, particularly for the lowest and highest molecular weight compounds/congeners.

LUR suggested that ~75% of the PCB air concentration variability was related to the distribution of PCBs in use/storage/building sealants, ~60% of PBDE variability was related to building volume, ~55% of the PAH variability was related to the distribution of transportation infrastructure, and ~65% of the PCM variability was related to population density. Parameters such as population density and household income were successfully used as surrogates to infer sources and air concentrations of SVOCs in Toronto. This is the first application of LUR methods to explain SVOC concentrations.



INTRODUCTION

Given the continuous rapid growth of cities around the world and the identification of these urban areas as sources of SVOCs to the environment, an understanding of urban distributions and sources of SVOCs can aid in addressing emissions and reducing concentrations in the wider environment. The challenge in controlling SVOCs has been illustrated in recent studies that have emphasized that emissions are from diffuse sources and concentrations are highly variable within urban areas,^{1–3} with up to 30-fold variations in concentrations within a city. These results suggest that using a small number of sampling sites in an urban area could give an erroneous picture of concentrations at local scales as well as few clues about the major emission sources.

Land use regression (LUR) has been used to model urban concentration distributions of NO_x, VOCs, and particulate matter.⁴ For example, combinations of variables such as traffic intensity, road length, and population have been successfully used to characterize urban NO₂ concentrations, with $R^2 > 0.50$ (inter alia^{4,5}). LUR is as successful as, or better than dispersion modeling at predicting air concentrations⁴ but relies on different types of inputs. LUR can be adapted to incorporate

wind factors, however, conventional LUR usually cannot account for phenomena such as urban canyons, as they exist on smaller scales than typical LUR is able to model.⁴ LUR can identify urban-scale variability, but its ability to distinguish smaller-scale sources (e.g., small roads) is limited by the spatial and temporal density of input measurements. The success of the LUR technique relies on sufficient input measurements, the selection of appropriate factors, and an awareness of the effects of covariances on the statistical model.

SVOC distributions have been estimated on regional scales using individual variables such as population density^{6,7} and commercial/industrial land use,⁸ however these variables alone are not satisfactory at intraurban scales. The widespread use of passive air samplers has improved the feasibility of developing LURs for SVOCs. Passive air samplers allow the measurement of spatially-distributed time-integrated concentrations that are necessary for LUR analysis, despite inherently larger measure-

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ment uncertainty associated with passive sampling rates (compared with active samplers).⁹

This study investigated LUR as a method to identify likely sources of SVOCs and to explain the intraurban distribution of SVOCs in air, using the Greater Toronto Area (GTA), Canada, as a case study. LUR was used with measured air concentrations and detailed industrial, demographic, socioeconomic, and land use data to identify variables leading to high air concentrations of SVOCs, and to assess the relative influence of urban vs industrial sources across the urban region. Four compound classes were selected for this analysis: polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic musks (PCMs), and polycyclic aromatic hydrocarbons (PAHs). All have been associated with elevated urban concentrations and their most common uses/emissions are in close proximity to highly populated areas.^{10–12}

The import and manufacture of PCBs was banned in 1977,¹³ yet PCBs remain in use in some electrical equipment in Canada today,¹⁴ particularly in building materials,^{15,16} capacitors, and transformers. Unintentional PCB sources include inadvertent formation in metal production¹⁷ and paint manufacturing.¹⁸

PBDEs, used as additive flame retardants in consumer products, were not manufactured in Canada,¹⁹ but several GTA manufacturing industries used imported PBDEs in their products. However, the largest current stock of PBDEs exists in in-use consumer products (e.g., carpets, textiles, and electronics)²⁰ and emissions from such products are estimated to be the largest source of PBDEs to air.^{20,21}

PCMs are synthetic fragrance compounds added to consumer products such as soaps, detergents, deodorants, air fresheners, and scented candles.²² Facilities manufacturing such goods are potential PCM sources, as are high-use operations such as industrial laundry facilities.²³ However, the greatest aggregate release of PCMs is thought to occur from the use of personal care products containing PCMs, which result in greater environmental concentrations associated with more densely populated areas.¹²

PAHs are emitted from multiple natural and anthropogenic sources. A large proportion of the emissions in urban areas arise from local fossil fuel combustion in heating, transportation, and industry.²⁴ At a continental scale, open burning, forest fires, and waste incineration are major PAH sources, however these are not expected to be significant within the urban region.

MATERIALS AND METHODS

Melymuk et al.³ measured air concentrations of PCBs, PBDEs, PCMs, and PAHs at 19 sites across the GTA in 2007–2008 by means of polyurethane foam-based passive air samplers (PAS) (Figure 1, Supporting Information (SI) Figures S1, Tables S1 and S2). The PAS were placed in trees at a 3–4 m height for four 3-month periods (total 12 months). Sampling rates were obtained from a calibration study in Toronto,⁹ and compound/homologue-specific sampling rates were used to obtain concentrations. The calibration study identified that PUF-PAS sample both gas- and particle-phase compounds, however there is greater uncertainty in the sampling rates of largely particle-bound than more gas-phase compounds.⁹ Sampling media were extracted by accelerated solvent extraction, cleaned by column chromatography, and analyzed for 86 PCBs, 27 PBDEs, 5 PCMs, and 15 PAHs via gas chromatography–mass spectrometry.³ PAS represent 3-month integrated samples, and therefore the use of PAS data for regression analysis gives the best results for time-averaged conditions across the sample region. PCBs

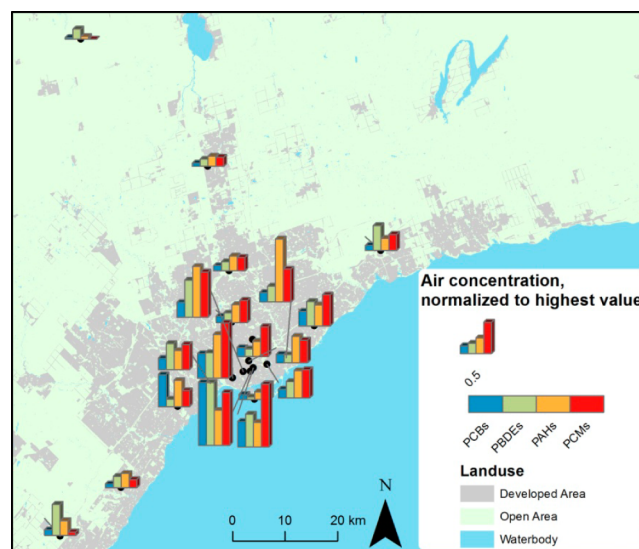


Figure 1. Annual average distribution of air concentrations across Greater Toronto Area, measured by passive air samplers.³

and PCMs were detected in all samples; PAHs and PBDEs had 99% and 94% detection frequencies, respectively. Nondetects were treated as zero.³ All compounds had highest concentrations at sites within 10 km of Toronto's central business district (CBD), with concentrations generally decreasing with increasing distance from the CBD with some site-to-site variability in this trend (Figure 1, SI Table S2).³

Land Use Regression Analysis. We created databases of spatially distributed potential sources of each contaminant class based on industry type and location, land uses, and activities that have been identified as possible sources of a given contaminant to the environment. For example, for PCBs one of these databases was the mass of PCBs at sites listed in Canada's 2006 national inventory of in-use and stored PCBs,²⁵ whereas PAH databases were based on a subset of the industrial and commercial processes from the 64 emission categories listed by Galarneau et al.,²⁴ focusing on categories relevant to urban emissions. Canadian census data and land use information were also used as surrogate variables to capture material use and reflect spatial distribution across the GTA. All database variables are listed in Table 1, with further details on data sources given in SI Tables S3–S7.

All variables were mapped across the study region using a geographic information system (GIS), which spanned the municipalities of Toronto, Mississauga, Oakville, Burlington, Pickering, Ajax, and York Region. The influence of each variable on each sample location was determined based on the number of facilities, amount of material or degree of activity within radii of 0.5, 1, and 5 km around each air sampling site. For example, building volume was based on the total volume of buildings in m³ within a given radius of each site, while traffic was based on total vehicle kilometers in each radius, which is a multiple of the average daily traffic and the length of each road segment. The size of industrial facilities was estimated by the number of employees in that industry within a given radius of the study site, as this was the only parameter that was consistently available for all industries. The approach for individual variables is summarized in SI Tables S3–S7.

Statistical analyses were performed using Statistica (v.7.0, StatSoft Inc.). Initial scatter plots suggested a relationship

Table 1. Summary of Land Use Regression Variables Used to Represent the Distribution of SVOC Sources Across the GTA

variable category	potential sources/surrogates for sources
PCBs	current-use PCBs according to Environment Canada database (as per Diamond et al. ⁷⁰), estimated distribution of PCBs in building sealants, ¹⁵ brownfield sites from the Ontario Ministry of the Environment Registry of Contaminated Sites, ⁶³ metal refining and processing facilities, paint manufacturing facilities
PBDEs	industries manufacturing textiles, upholstered furniture, foam, resin and synthetic rubber, computers and electronics, small appliances, motor vehicle plastics, seating and interior parts, motor vehicle electronic components, and sealant products, e-waste recycling facilities
PCMs	industries manufacturing personal care products and fragrances, industrial laundry facilities
PAHs	metal production, pulp and paper manufacturing, concrete and asphalt production, chemical manufacturing, petrochemical processing, automotive tire manufacturing, PAH emissions from Canada's (NPRI), ⁷¹ vehicle kilometers traveled for roads, vehicle kilometers traveled for rail, length of roads, length of rail, coal tar sealant use, ⁵⁴ domestic heating energy use and energy type using census estimates of average annual payments for fuel services as per, ⁷² brownfield sites from the Ontario Ministry of the Environment Registry of Contaminated Sites ⁶³
general variables	landfills, waste incinerators, waste transfer stations, WWTPs, population density, dwelling density, building density, impervious surface coverage, vehicle ownership, household income, average number of rooms per house, average number of people per household, and commercial, residential and industrial land use

between air concentrations and major urban descriptor variables such as population density and building density, thus linear regression was chosen as an appropriate model. A $\ln + 1$ transformation was applied to air concentrations and scaled variables prior to regression analyses. In our analysis we relied largely on the transformed regression equations (SI Tables S10–S13) and any back-transformed results were not adjusted as the transformation bias was small ($\sim 1\%$ for PCMs, 6% for PCBs and PAHs, 8% for PBDEs). Regression residuals were normally distributed.

Land use regression analysis requires that measurement sites are representative of the land use of the wider region. Our sampled locations covered a range of population densities; land uses and land cover types, which are similar to the average distribution of values in the GTA (SI Figure S2). The representativeness of the sampling sites was assessed by comparing air concentrations and emission estimates across the GTA (SI Figure S3) and wind roses for sites at the extreme ends of the study region (SI Figure S4). These analyses showed that the study sites were representative of the GTA, and thus LUR could be appropriately applied to estimate air concentrations for the larger region.

Individual variables were investigated using a simple regression analysis; variables that were not significantly correlated with air concentrations of any compound were rejected at this point. Some of the variables tested, such as dwelling density and population density, had significant collinearities. For such cases only the variable with the strongest correlation with the measured air concentration was used in the regression model. The explanatory power of the remaining variables was then assessed through both forward and backward stepwise multiple regression analysis, and variables common to both regression models were used to develop the final regression equations. Of the variables involved in the final regression equations, no significant multicollinearities existed as determined by variance inflation factors (SI Table S14). The level of statistical significance was set at 0.05. Residuals were examined to ensure the regression equations did not demonstrate any systematic bias (SI Figure S6). The possibility of spatial autocorrelation was also examined by averaging properties for nearby sites (SI Table S15), with no observed influence found in the regression results.

■ RESULTS

Compound/Congener Correlations. The relationship between the individual compounds/congeners within each

contaminant class was examined by building correlation matrices of compounds/congeners for each site and season, in order to identify whether any of the individual compounds/congeners had different distributions, or whether sites or a season had significantly different compound/congener profiles suggesting different sources. In general, strong correlations between individual compounds and congeners ($r > 0.90$) were found at all sites and seasons, suggesting that the behavior of each chemical within the compound class was very similar. However, a few compounds and one site were exceptions. The contributions of acenaphthylene, acenaphthene, and anthracene relative to other PAH compounds varied across sites and seasons ($r \approx 0.4$ – 0.6), which we attributed to the influence of atmospheric degradation.^{3,26} One site to the west of the CBD (W1) had a significantly different PAH compound profile in winter than any other sites ($t(26) = 2.44$, $p < 0.02$ based on a Student's t test). This was attributed to emissions from hot tar during renovations to a roof adjacent to the site²⁷ and is discussed in detail in the SI. The winter sample from this site was excluded from the regression analysis described below.

Land Use Regression Analysis. General Observations. Step-wise multiple linear regression between multiple source variables and bulk air concentrations yielded relationships with Pearson correlation coefficients > 0.55 . LUR results for the sum of each compound class and for each individual compound/congener are given in Table 2 and SI Tables S10–S13, respectively. LUR was able to explain 75–90% and 73–86% of the variability of PCBs and PCMs, respectively, and 36–89% of PBDE and PAH variability, suggesting that the latter have more spatially complex emission sources, particularly for the lowest

Table 2. Correlation Coefficients and Significant Variables for Multiple Linear Regression Analysis^a

compound	adjusted R^2 (p -value)	variables (squared partial correlation coefficient)
Σ PCBs	0.85 ($p < 0.0001$)	sum of PCBs in use/storage/building sealants (0.75) metal industries (0.62) 1971 population density (0.16)
Σ PBDEs	0.83 ($p < 0.0001$)	building volume (m^3) (0.61) E-waste recycling (tonnes processed/year) (0.58) negative correlation with dwelling density (0.40)
Σ PCMs	0.86 ($p < 0.0001$)	population density (0.65) negative correlation with distance from CBD (km) (0.49)
Σ PAHs	0.67 ($p < 0.0001$)	impervious surface area (0.31) total number of homes heated by fossil fuels (0.05) Train traffic (trains-km/day) (0.23)

^aRegression coefficients and variable radii for individual compounds/congeners are listed in Tables S11–15.

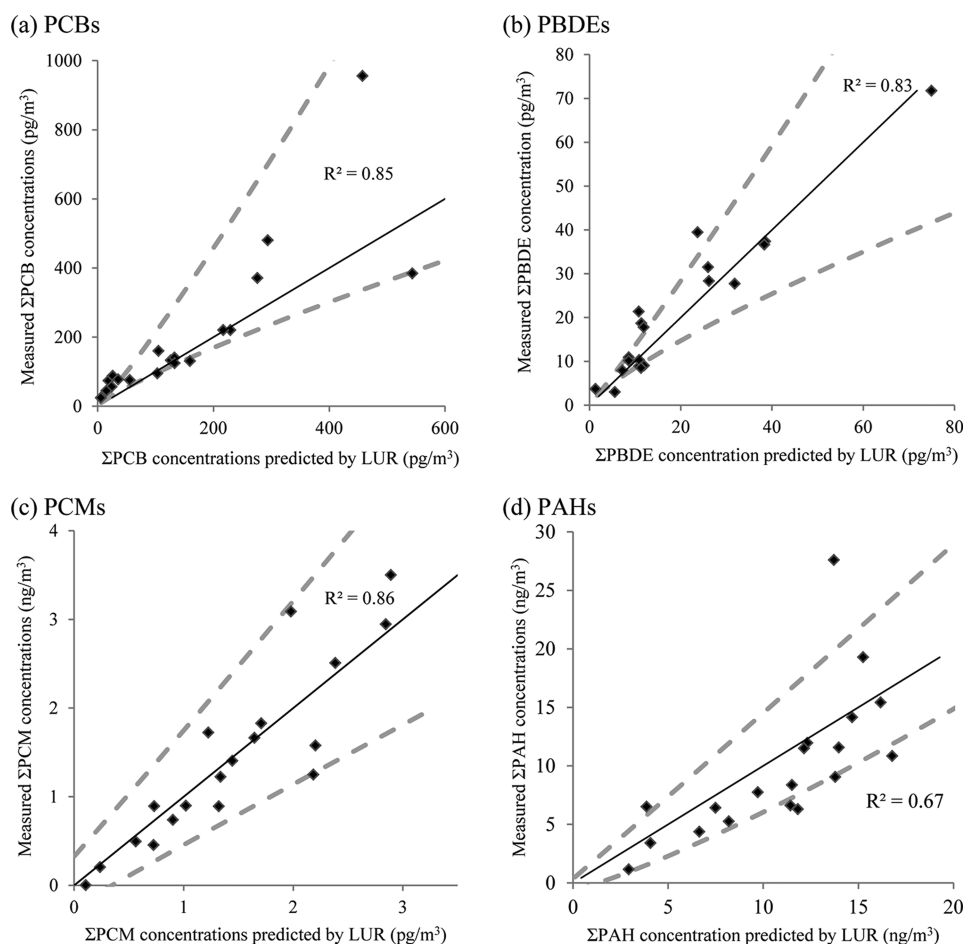


Figure 2. Relationship between measured concentrations and concentrations predicted by LUR for (a) Σ PCBs, (b) Σ PBDEs, (c) Σ PCMs, and (d) Σ PAHs. Solid lines indicate a 1:1 relationship. Dashed lines indicate the 95% prediction interval. LURs have strong explanatory power with the exceptions of outlier sites for PCBs and PAHs as discussed in the text.

and highest molecular weight compounds/congeners. Another possible reason for the weaker explanatory capability of LUR for more particle-sorbed PBDEs and PAHs is that the PUF passive samplers used to measure air concentrations have a greater uncertainty for particle- than for gas-phase compounds.⁹

The spatial distribution of variables was examined within radii of 0.5, 1, and 5 km from each air sampling site. Correlations were generally similar for all radii when values for each variable were available in all three radii. However some variables could not be quantified at the smaller radii, as the air sampling sites were chosen based on distance from the CBD rather than on proximity to different land uses or industries. Consequently, many types of industrial facilities were not present within 0.5 or 1 km of a site. For example, all e-waste facilities were located >2 km from the sampling sites. PBDE concentrations were significantly correlated with e-waste facilities at 5 km radii; the correlation may have been even stronger had e-waste facilities been located closer to the sampling sites. The sampling sites lay along north–south and east–west transects with a high density of sites around the CBD. Consequently, the LUR may emphasize particular urban sources, such as building density and transportation, while limiting the explanatory power of LUR at some sites close to the lakeshore due to meteorological effects such as lake breeze.

As the regression equations have not been tested with an independent data set, we have not presented the regression

coefficients, but instead used the regression model to identify specific variables that correlate with air concentrations. Note that the correlations are not causative and do not definitively indicate that a particular industry, activity or land use is a source of that chemical to air. Rather, the correlations suggest that the variables and air concentrations have coincident distributions across the city and, since these variables have been associated with the compounds in question either in other regions or through emissions testing, it is plausible that they are a source in the GTA. We must also consider that while a particular variable appears to be strongly correlated with a chemical concentration, the actual source may be described by another variable that we have not assessed but that covaries with the selected variable.

PCBs. PCB concentrations in Toronto air were highest at sites closest to the CBD, with secondary maxima at sites 20 km east and west of the CBD (Figure 1). LUR explained 85% of variation in Σ PCB air concentrations (Table 2, Figure 2a). This was largely based on the distribution of the total mass of PCBs in use/storage and PCBs in sealants within a 1 km radius around each site. The sum of these two variables alone explained more than 60% of the spatial variation in PCB concentrations for all homologues. As of 2006, 534 sites across the GTA contained ~600 tonnes of pure PCBs either in-use or stored within decommissioned electrical equipment,²⁵ and an additional ~17 tonnes in building sealants.¹⁵ Small transformers

and 1971 population density each accounted for ~30% of the variability in PCB air concentrations. Small transformers may reflect additional PCBs in current use that were not accounted for in the PCB inventory. Although PCBs have been removed from many large transformer stations, Ontario's electricity distribution agency has identified that 80% of smaller transformers and insulators associated with the electricity distribution grid have not been tested for PCBs, and expects that ~10% contain PCBs in excess of 50 ppm.²⁸ The 1971 population density reflects the distribution of people across the GTA at the time of peak PCB use in Canada,²⁹ and thus represents built infrastructure at that time. This variable may indicate additional PCBs in building materials such as flooring¹⁶ and plaster³⁰ that were not accounted for in the building sealant estimate.

The higher PCB concentrations were not as successfully explained as the lower concentrations. In particular, the 0km site was under-predicted by the regression equations and had the largest residual value of any site (Figure 2a and SI Figure S6a). We speculate that under-prediction suggests a source not captured in the regression, such as a past PCB spill or emissions during PCB removal, whereas overprediction may reflect recent removal of an in-use PCB source(s). Much PCB-containing equipment has been removed in the past 10 years,²⁵ and therefore PCB inventories are quickly outdated.

Unintentional formation of PCBs from industrial processes may contribute significantly to air concentrations in industrial areas,¹⁷ and as such, we considered three associated industrial categories. The first was metal refining and processing,¹⁷ which has been shown to emit tri- to penta-CBs.³¹ The second was paint manufacturing: over 50 PCB congeners have been identified in organic paint pigments, attributed to azo dyes and side-reactions of the chlorinated solvents used in paint manufacturing.¹⁸ Finally, municipal solid waste incineration,³² sewage sludge incineration and medical waste incineration can emit PCBs.³³ Of these three categories, only the distribution of metal industries was significantly correlated with concentrations, uniquely contributing ~60% to the regression for tri- and tetra-CBs. Since the GTA is not a major metal manufacturing center and yet this source category has a large contribution to the variability in PCB concentrations, metal industries could be an even more important source of atmospheric PCBs in regions with more metal manufacturing.

The lack of a relationship with either paint manufacturing or incineration was due to the small number of facilities within the study region (21 paint manufacturers, most employing <20 people, and three wastewater treatment plants (WWTPs) incinerating sewage sludge). Additionally, though many PCB congeners are associated with paint and pigment manufacturing, most are mono- and di-CBs,¹⁸ in particular PCB-11, which were not quantified in this study.

Disposal of PCB-containing materials through landfills, metal recyclers and auto wreckers has also been identified as a source of PCBs to the environment.^{34,35} Harrad et al.³⁴ estimated that contributions of PCBs from landfill to the UK atmosphere were negligible, and the results for the GTA support this. PCB concentrations were not correlated with either surface area or mass of material for the 36 landfills (3 open, 33 closed) within the GTA. However, 17% of octa-CB variability was accounted for by the distribution of waste depots (SI Table S10). Waste depots are intermediate transfer stations for household waste from curbside pickup, and drop-off points for construction waste, scrap metal, and household hazardous waste. Addition-

ally, while specific metal recyclers were not correlated with any PCB concentrations, a portion of the emissions from the metal manufacturing facilities mentioned above may be due to the use of recycled metal materials in the metal manufacturing process, such as metal products including small PCB-containing capacitors³⁴ and metal components coated with PCB-containing paints.^{35,36}

The regression equation suggests that ~60% of PCBs in urban air were from sources that are known or under assessment and legislated for removal by 2025,¹⁴ that is, PCBs in use/storage and small transformers. If there is legislative compliance, we can anticipate significant reductions in air concentrations of PCBs in the Toronto area over the next 10–15 years.

PBDEs. PBDE air concentrations across the GTA peaked at the sites closest to the CBD, with a secondary maximum at the 60 km west site, and no significant decline along the eastern transect. Source variables explained 64–89% of variability in tetra- to hexa-BDEs air concentrations and did not indicate any site biases (SI Table S11, Figure 2b, SI Figure S6b). Σ PBDE air concentrations were strongly correlated with variables related to product use: building volume (61%), a negative correlation with dwelling density (40%), and e-waste warehousing/recycling facilities (58%), but were not correlated with any manufacturing industry (Table 2). This supports the hypothesis that, at least in the GTA, product manufacturing is not a significant source of PBDEs to air.

Although several industries in the GTA manufacture products to which PBDEs have typically been added, for example, polyurethane foam, carpet underlay, mattresses, automobiles, upholstered furniture, electrical/electronic equipment, textile coatings,³⁷ the lack of correlation with the distribution of manufacturing locations suggests that the use of penta and octa in manufacturing has ceased, reflecting recent bans.³⁸

Emissions from consumer products have been estimated to be the largest source of PBDEs in urban areas^{20,21} through emissions to indoor air and subsequent transfer to the outdoor environment.³⁷ The results of the LUR support this pathway in the strong correlation between PBDE concentrations and building volume. The negative correlation with dwelling density was another interesting result, suggesting that once the influence of building volume is accounted for, the concentrations of PBDEs are lower in residential areas than in commercial, institutional, and industrial areas that have a higher density of PBDE sources, for example, flame retarded office furniture and electronics. Measurements of indoor PBDE concentrations support this hypothesis, with average air concentrations in Toronto commercial and institutional buildings 3× higher than in residential buildings.³⁹ This is also consistent with more stringent flame retardancy standards for furniture/carpets in public spaces than in residential buildings.⁴⁰

E-waste has been identified as a major source of PBDEs to the environment⁴¹ and some of the highest air concentrations of PBDE detected anywhere in the world have been measured at e-waste recycling facilities in Asia.⁴² A strong correlation between e-waste handling facilities and PBDE air concentrations in Toronto was found, suggesting that the 13 e-waste warehouse and recycling facilities may contribute significantly to air concentrations. GTA e-waste facilities process a total of 150 000 tonnes of e-waste per year (based on recycling company capacity estimates), and with an average concen-

tration of 2.4 kg of PBDE per tonne of e-waste,⁴³ an estimated 370 tonnes of PBDEs pass through the GTA e-waste industry on a yearly basis, which is significant relative to estimated urban stocks of PBDEs, such as ~200 tonnes of penta and octa in Toronto (excluding vehicles).⁴⁴

Concentrations of BDE-15 and -183 were weakly or not significantly correlated with any land use variable. BDE-15 is not found in any significant amount in PBDE commercial mixtures⁴⁵ and is attributed mainly to debromination of higher brominated PBDEs.⁴⁶ BDE-183, although comprising 10–40% of octa-BDE,⁴⁵ may also originate from photolytic debromination of BDE-209⁴⁷ and anaerobic degradation, particularly in wastewater.⁴⁸

PCMs. PCM air concentrations exhibited a strong urban-rural gradient with the highest concentrations measured at sites within 2 km of Toronto's CBD, and concentrations below detection at the site 80 km north (Figure 1, SI Table S2). PCM concentrations were most strongly correlated with population and dwelling density, and building volume, as each variable individually accounted for 68–75% of the variation in the PCM concentrations. These three variables tended to covary in the largely residential areas of Toronto, but differed in the commercial downtown and in industrial areas. The strongest correlation came from the combination of population density with distance from the CBD, accounting for 86% of the spatial variability in Σ PCM concentrations (Table 2, Figure 2c).

The distance of a sample site from the CBD was inversely related to PCM concentrations, accounting for 49% of the spatial variability. This variable may reflect both atmospheric dilution and degradation of PCMs from the high density of sources near the CBD. PCMs have atmospheric half-lives of less than 7 h⁴⁹ which equals the average time for an air parcel to cross the study region (determined based on average winds and confirmed using back-trajectories from NOAA HYSPLIT⁵⁰). Thus, significant atmospheric degradation of PCMs likely occurs as the air mass moves away from the principle source region.

Product disposal categories (i.e., WWTPs, landfills) did not correlate with PCM concentrations, contrary to expectations. Wastewater has been associated with elevated concentrations of PCMs,⁵¹ as has cosmetic plant air,⁵² and landfills.⁵¹ Thus, although industrial and waste treatment facilities may contribute to elevated air concentrations of PCMs on a very local scale (i.e., <200 m⁵²), regression results suggest personal usage as the main source of PCMs across the urban region.

PAHs. PAH concentrations were elevated close to Toronto's CBD (~20 ng/m³) however the highest concentration was measured at a site 10 km east of downtown Toronto (Figure 1, SI Table S2). The latter site is discussed later. Sixty-seven percent of Σ PAH concentrations were explained by several parameters reflecting urban density, particularly population density, fossil fuel use for heating (which is closely correlated with building density), and transportation infrastructure (Table 2, Figure 2d). Acenaphthylene, acenaphthene, and fluorene were strongly correlated with train traffic and rail lines, phenanthrene through to chrysene with impervious surface coverage, and high molecular weight PAHs were correlated with brownfield sites (SI Table S13). In this case impervious surface coverage likely reflects the combined emissions from traffic and pavement surfaces, including volatilization of coal-tar based pavement sealants, which have been used in Toronto⁵³ and have the potential to be a major source of PAHs to air.⁵⁴

The importance of train traffic and length of rail lines was an unanticipated result of the PAH regression analysis. These variables accounted for ~40% of the variability in low molecular weight PAH concentrations. Although PAH emissions in urban areas are commonly attributed to transportation sources, the largest contribution within that category is usually from on-road sources.⁵⁵ However, the correlation between PAHs and train traffic suggests that emissions from diesel train engines may be of greater importance than road sources at sites close to rail lines. Trains in North America run on rail-quality diesel fuel which is subject to less stringent regulations on fuel quality and air pollutant emissions than on-road vehicles.^{56,57} Cahill et al.⁵⁶ found that PAH concentrations in air downwind of a rail yard in California were 5× higher than the surrounding air. The correlation with the length of rail line suggests an additional source: volatilization from creosote-treated wood used in railway ties. Creosote, derived from coal-tar, contains up to 80–85% PAHs.⁵⁸ Emission estimates for creosote railway ties are on average 20 mg m⁻² day⁻¹ of 2- and 3-ring PAHs over a 25-year lifespan of a railway tie⁵⁹ and are strongly correlated with temperature.⁵⁸ Railway ties could act as a major source of PAHs in the GTA, given that in 2007 Ontario had an estimated 4 million m³ of creosote treated railway ties, containing over 120 000 tonnes of PAHs and accounting for up to 30% of benzo[*a*]pyrene emissions.⁶⁰

As mentioned above, road vehicle emissions are commonly credited as a major source of PAHs in urban areas.^{61,62} Four variables reflect the distribution of vehicle emissions throughout the city: 1. length of roads, 2. length of major roads, 3. impervious surface coverage, and 4. vehicle kilometers traveled (VKT). We hypothesized that PAH air concentrations would be most strongly correlated with VKT as this variable should best reflect tailpipe emissions from cars and trucks, however instead this variable had the weakest correlation with each PAH compound. Single regression analysis of each variable with Σ PAHs had correlations of $r^2 = 0.70$ for impervious surfaces, $r^2 = 0.62$ for major roads, $r^2 = 0.65$ with all roads, and $r^2 = 0.45$ with VKT. Although all correlation coefficients suggested a relationship between PAH concentrations and a parameter related to roads, the weaker correlation with traffic suggested that it may not be a simple direct link between tailpipe emissions and air concentrations. The size of the radius around each site may complicate matters. Hoek et al.⁴ suggested that variability in particulate matter and NO₂ are not strongly correlated with traffic at distances of more than 500 m from a road. Similarly, LUR analyses of NO_x and particulate matter found the strongest correlations with traffic at less than 300 m.⁵ These studies suggest that the radius of 500 m around each site used here may in fact be too large to capture the influence of traffic intensity. However, PAH concentrations were even more weakly correlated with traffic in a 250 m radius than at 0.5 km and 1 km, indicating that although vehicle emissions are likely to contribute substantially to urban atmospheric PAHs in Toronto, the spatial variability in traffic density within the city did not contribute significantly to the local-scale PAH variability measured here.

The importance of brownfields sites was another unexpected result of this analysis. PAH-contaminated brownfields account for 0.25% of land in the GTA, with concentrations in GTA brownfields ranging from 1 to 4000 µg PAH/g of soil.⁶³ At least 25% of these sites have maximum concentrations at levels that could act as sources of PAHs to air, based on soil-to-air fugacity ratios calculated assuming average GTA air concentrations.

Although industrial sources, particularly metal production and industrial boilers, have been identified as major sources of PAHs to the atmosphere in North America,²⁴ no industrial variables were significant for our study region, which may be due to the relatively small industrial sector in Toronto. Rather, the city is a densely built urban area, with 46% of the GDP focused in the financial, insurance, and professional services and retail trade while manufacturing makes up <15% and is dominated by automotive manufacturing.⁶⁴

PAH regressions were compared on a seasonal basis given the potential for seasonal changes in emissions. Emissions from gasoline and diesel engines were expected to be relatively consistent throughout the year,^{65,66} whereas temperature-dependent volatilization (i.e., from asphalt, coal-tar pavement sealants, brownfields) would be greater at warmer temperatures, and emissions from domestic heating would be greater in winter. The results of seasonal regressions confirmed the temperature dependence of volatilization sources. Single-variable regressions of impervious surfaces against fluoranthene and pyrene were weaker in autumn and winter (avg. $r^2 = 0.38$) versus in spring and summer ($r^2 = 0.54$). A similar seasonal effect was observed for 4- to 5-ring PAHs and brownfields; in summer the relationship between PAHs and brownfield distribution had an r^2 of 0.31, yet in winter no significant relationship was evident. Snow cover, present during 73 days during the winter that the samplers were deployed,⁶⁷ may have also contributed to the seasonal patterns. An increased correlation with heating sources was not found in winter compared with summer, which is consistent with the use of low emission natural gas furnaces in 93% of fossil fuel heated homes in Toronto.^{68,69} Thus, the results of this investigation confirmed the importance of contributions to air of temperature-dependent volatilization from sources such as asphalt, coal-tar pavement sealants, and brownfields.

Very high concentrations of acenaphthylene and acenaphthene were measured at a site 10 km east of downtown Toronto; the site is an outlier for both compounds (based on a Grubbs test at $p = 0.05$) and the site is significantly under-predicted by the LUR in the comparison of back-transformed predicted and observed values (Figure 2d). This suggests LUR is not fully capturing the sources at E10, perhaps by not giving sufficient weight to the influence of frequent train traffic in such close proximity to the site. The E10 site is located ~50 m from a high-use rail line with over 80 diesel-powered trains per day. The influence of train traffic was less at three other sites with rail lines within a 500 m radius (N1, E5, E20, and WS) and fewer trains per day. The concentrations of acenaphthylene and acenaphthene at the E10 site did not exhibit any seasonality, consistent with diesel engine emissions rather than volatilization from creosote-treated rail ties as the source of the elevated concentrations.

Implications. The regression equations developed are specific to Toronto and reflect the major source types and industries in the city, as well as the particular covariances between variables due to the land use distribution of Toronto. However the method and general conclusions developed here are applicable to other urban areas.

LUR allows characterization of intraurban variability in SVOC concentrations on a small (~1 km) scale and suggests emission sources. While this analysis relies on well-characterized spatial distributions of SVOC sources, when specific source inventories are not available, census and land use data are useful indicators of sources. For example, population

density was extremely successful as a surrogate variable for PCM air concentrations. LUR techniques can also be used to give information for air sampling site selection and provide source distributions that can be integrated with contaminant fate and transport models. For example, LUR could be used to make predictive maps of air concentrations across a city. We present an example of how measured concentrations (SI Figure S7a,b) can be extrapolated across a whole study region (SI Figure S7c,d). In order to obtain reliable quantitative predictions from LUR models, the model should be evaluated with an independent data set,⁴ which has not been done in this case, and thus Figure S7c,d are intended to demonstrate potential uses for LUR.

LUR provides a significant advantage over other methods used to estimate regional concentration distributions, such as kriging or other geostatistical methods, by depending less on the distribution of sampling sites and by better representing small-scale spatial variability in air concentrations (SI Figure S8). The LUR extrapolation depends only on the land use/source inventories within the chosen radii, and thus, if sampling sites are representative of the broader sampling region, sampling site distribution does not affect predictions. While some uncertainty is associated with any extrapolation, use of LUR reduces this uncertainty relative to geostatistical methods.⁴ Another advantage of the LUR method is that LUR contains causative information that can be used to better understand SVOC sources and distributions, particularly with the aim of reducing emissions. Further applications of LUR would be improved by the incorporation of meteorological and topographic influences, such as predominant wind direction, lake breezes, and seasonality in concentrations.

Our results suggest that most emissions to Toronto air are due to commercial and residential emissions as well as product disposal, rather than manufacturing and other industrial processes. PCB distributions were strongly correlated with documented stocks of PCBs in Toronto. Thus, air concentrations should fall when these stocks are removed. Reducing air concentrations of PCMs is achievable by reducing the use of these compounds in personal care products. PBDE air concentrations, related to in-use stocks of PBDEs and e-waste processing, are expected to fall as PBDE-containing products see their end-of-life. Reducing PAH emissions is much more problematic due to the multiplicity of sources and their connection to our transportation patterns. However, the results suggest that on a local scale train emissions may be of particular concern where rail lines pass through densely populated areas, and hence more stringent regulations on off-road diesel emissions could lead to reductions in PAH air concentrations.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional information including 8 figures and 15 tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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