



A tale of three cities: Mercury in urban deciduous foliage and soils across land-uses in Poughkeepsie NY, Hartford CT, and Springfield MA USA

Justin B. Richardson*, Leon Moore

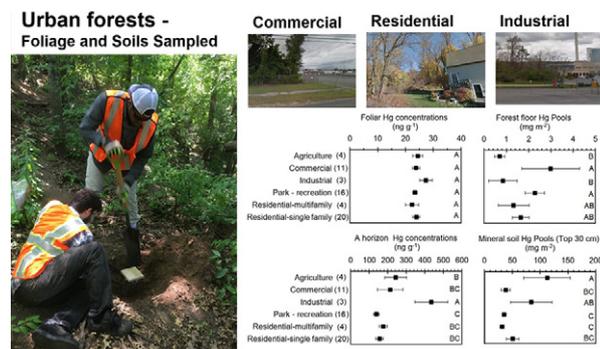
Department of Geosciences, University of Massachusetts Amherst, 01003, United States of America



HIGHLIGHTS

- Mercury accumulation in urban forests across North America is unconstrained
- Mineral soil Hg was not correlated with soil pH, LOI, or clay content.
- Tree genera and soil properties did not control Hg concentrations
- Hg concentrations and pools were greatest near industrial and agricultural areas
- Urban soil Hg concentrations and pools were 2–10 times greater than rural forests

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 November 2019
 Received in revised form 21 January 2020
 Accepted 21 January 2020
 Available online 25 January 2020

Editor: Filip M.G.Tack

Keywords:

Urban soils
 Industrial land use
 Forest soils
 Toxic metals
 Mercury pollution

ABSTRACT

Mercury is a global pollutant that harms human and wildlife health through chronic exposure. The role of urban forests in Hg biogeochemistry has been understudied in cities without historical mining or current coal combustion. This study aimed to quantify total Hg concentrations and pools in urban forests to determine whether adjacent land-use impacts Hg accumulation. Three cities in the northeastern United States were studied: Hartford, Connecticut; Poughkeepsie, New York; and Springfield, Massachusetts. We identified ~20 urban forests sites in a ~10 km by ~10 km grid for each city and sampled foliage and soil at each site. Foliage from *Populus* exhibited significantly lower Hg concentrations ($15.6 \pm 2.1 \text{ ng g}^{-1}$) than mean foliar Hg concentrations ($23.7 \pm 0.6 \text{ ng g}^{-1}$) but most deciduous genera had comparable concentrations. Average forest floor Hg concentrations ($195 \pm 21 \text{ ng g}^{-1}$) and Hg pools ($1.9 \pm 0.5 \text{ mg m}^{-2}$) were similar to previous, non-urban studies in the region. Average A horizon ($182 \pm 19 \text{ ng g}^{-1}$) and B horizon ($125 \pm 14 \text{ ng g}^{-1}$) Hg concentrations were double those of regional forest soils. Mineral soil Hg pools for the top 30 cm ($49 \pm 6 \text{ mg m}^{-2}$) averaged two to ten times higher than rural, montane forests in the region. Soil pH, LOI, and %clay were poorly correlated with mineral soil Hg concentrations. Instead, highest foliar and soil Hg concentrations and pools were in urban forests adjacent to high and medium intensity developed areas in Springfield and Hartford. To differentiate the impact of land-uses not captured by the National Land Cover Database (NLCD) system, we implemented new land-use categories. Industrial areas had highest foliar and soil Hg concentrations and pools of any land use. Our results show increasing land-use increases Hg accumulation in urban forests.

© 2020 Elsevier B.V. All rights reserved.

* Corresponding author at: Geosciences Department, University of Massachusetts Amherst, 611 North Pleasant Street, Amherst, MA 01003, United States of America.
 E-mail address: jbrichardson@umass.edu (J.B. Richardson).

1. Introduction

Urban forests provide a range of ecosystem services such as microclimate mediation (Simpson, 1998; Lin et al., 2018a, 2018b), mitigating stormwater runoff (Sanders, 1986; Berland et al., 2017), noise pollution reduction (Islam et al., 2012), and enhancement of local societal and aesthetic valuation (Maco and McPherson, 2002; Nowak, 2006). Further, urban forests aid with localized trace metal pollution (Livesley et al., 2016). Tree foliage capture trace elements from the ambient air as fine particulate and dissolved forms (Pouyat et al., 2008; Livesley et al., 2016). The role of urban forests as atmospheric filters and trace metal reservoirs helps protect moderately and intensively developed watersheds (Xia et al., 2011; Chambers et al., 2016). Further, urban forest soils sequester trace metal pollution, preventing their transport into surface waters and groundwaters (e.g. Pouyat et al., 2008; Chambers et al., 2016; Liu et al., 2016). Urban forests are particularly important for temperate regions in which unmanaged in residential areas, between commercial lots, and along riparian corridors become reforested.

Of the dozens of pollutant metals present in urban forests, mercury (Hg) poses a particular threat to terrestrial and aquatic ecosystems as both a local and global pollutant metal. Acute and chronic exposure can harm human health by causing chronic neurological disorders (Holmes et al., 2009) and decreased fecundity in terrestrial wildlife (e.g. Rimmer et al., 2005; Melgar et al., 2009). Local coal and wood combustion, industrial paper milling, cement manufacturing, and municipal emissions from incinerators or antiquated pesticides all contribute to Hg enrichment in urban areas (Driscoll et al., 2007; Demetriades, 2010; Streets et al., 2019). Urban forest soils serve as important local reservoirs, sequestering Hg (Bavec et al., 2015; Deonaraine et al., 2015; Liu et al., 2016). This sequestration in urban soils prevents movement to aquatic systems, where fish (Jeziarska and Witeska, 2006), aquatic invertebrates (Stinson and Eaton, 1983) and emergent macrophytes (Tong et al., 2013) may bioaccumulate Hg. However, the accumulation of trace metals by an urban forest may harm the plants and animals living within it. Soil-dwelling animals within an urban forest may bioaccumulate mercury (e.g. Talmage and Walton, 1993; Rieder et al., 2011; Zhang et al., 2009; Richardson et al., 2015) and transfer it up the food chain to birds and mammals (Richardson et al., 2015).

Urban soil Hg concentrations commonly exceed median soil Hg concentrations of forest soils, agricultural soils, and global background concentrations (Kot and Matyushkina, 2002; Birke and Rauch, 2000; Rodrigues et al., 2006; Yang and Wang, 2008; Liu et al., 2016). Soil accumulation of Hg has been tied to organic matter, pH, and clay content, as they control adsorption and complexation (Obriest et al., 2011; Richardson et al., 2013; Navrátil et al., 2014). However, in human-dominated areas, land-use and site history could potentially be more important as previous studies have shown urban soils accumulating Hg from both historical and modern deposition. For example, Şenilâ et al. (2012) studied urban soils in a region of Romania with historical Hg mining and ore processing and found Hg concentrations commonly in excess of 1000 ng g⁻¹, with a median Hg concentration of 700 ng g⁻¹. Further, Yang and Wang (2008) observed urban soil Hg concentrations near a coal-fired power plant in current operation averaged 606 ng g⁻¹. However, elevated soil Hg concentrations are not the only indication urban forests are being impacted by local and regional Hg pollution, tree foliage has also been a medium for capturing spatial Hg pollution. As a prime example, Mélières et al. (2003) used leaves across a tropical forest of French Guiana to capture spatial sources and sequestration patterns. Additionally, Niu et al. (2011) observed elevated Hg levels in tree leaves (51 ± 39 ng g⁻¹) in urban forests in Beijing, China, nearly double the foliar Hg concentration of trees in rural North America (Juillerat et al., 2012; Blackwell and Driscoll, 2015; Richardson and Friedland, 2015). However, the urban soil Hg concentrations (84 ± 52 ng g⁻¹) observed by Niu et al. (2011) were not significantly different than background soil Hg concentrations. However, local land-use impacts on Hg sequestration in urban forests have not been examined in cities without

historical Hg mining or current Hg emissions from coal combustion plants.

The objective of this study was to quantify the effect of land-use and physicochemical properties on Hg accumulation in foliage and soils in urban forests. Few studies have been conducted outside megametropolitan areas (e.g. Beijing, New York City) or areas without extensive historical Hg mining histories. First, we hypothesized that proximity to commercial and industrial land-uses would influence concentrations and pools more than soil properties that typically drive Hg sequestration (specifically soil organic matter content, pH, or clay). Second, we hypothesized that foliar Hg concentrations would vary across tree genera due to their physiological differences in leaf properties, potentially masking local effects. Quantifying the factors influencing Hg accumulation in urban forests furthers our understanding and valuation of urban ecosystems, and their impact on local and global Hg biogeochemistry.

2. Methods

2.1. Selection of sites

Three cities in the northeastern United States were studied: Hartford, Connecticut; Poughkeepsie, New York; and Springfield, Massachusetts. These cities were chosen because of their comparable climates and populations, in addition to their location within 200 km of each other (Fig. 1). All three cities are on the border between Dfa and Dfb Köppen climate classification, with humid continental mild to hot summers, no dry season, with coldest month averaging below -0 °C. To test the hypotheses posed in the introduction, we identified 18 to 20 urban forests sites in ~10 km by ~10 km grid for each city. Sampling locations needed to be >10 m from a road, >10 m from any human structures, <8° slope to avoid eroded soils, upland position free of any hydric plants or soils, free of have any signs of recent human refuse and be part of an active urban forest in which leaves decompose naturally. Additional factors influenced sampling locations, including accessibility by foot and property laws.

To differentiate the impact of land-uses not captured by the National Land Cover Database (NLCD) system, we assigned a separate land-use characteristic to each sampling location according to the most prevalent land-use surrounding that urban forest site. The current NLCD 2016 definitions for land classes and uses can be found at: <https://www.mrlc.gov/data/legends/national-land-cover-database-2016-nlcd2016-legend> (last accessed January 20, 2020). For example, urban forests surrounded by single family homes were classified as 'residential-single family' and wooded areas between sporting fields and children play areas were classified as 'Parks'.

2.2. Soil and vegetation sample collection

Soils and vegetation were sampled between late-July and August of 2017 and 2018. At each sampling location, we collected one soil monolith. To do this, we randomly placed a 15 cm × 15 cm wooden block on the ground. Then, we separated the forest floor from the A horizon with a clean stainless-steel handsaw and bagged the forest floor material. We then removed mineral soil from around the template using handsaws, tile-spades and trowels, leaving the soil below the template intact. The exposed undisturbed rectangular soil monolith was described according to U.S. Soil Taxonomy. Each soil monolith ranged in depth from 18 to 27 cm, depending on the depth of the restricting layer and the cohesiveness of the soil monolith. We then separated the soil monolith into master soil horizons (generally an A and B horizon, uncommonly three horizons due to an A2 or BC horizon) and placed the entire mass of each master horizon into separate Ziploc bags. The Soil samples were dried in an oven at 70° Celsius for 24 to 48 h to a constant weight. Although oven drying increases the potential volatilization of Hg, air-drying has been shown to influence soil Hg concentrations more due to microbial reduction and elemental Hg volatilization (Hojdová et al.,

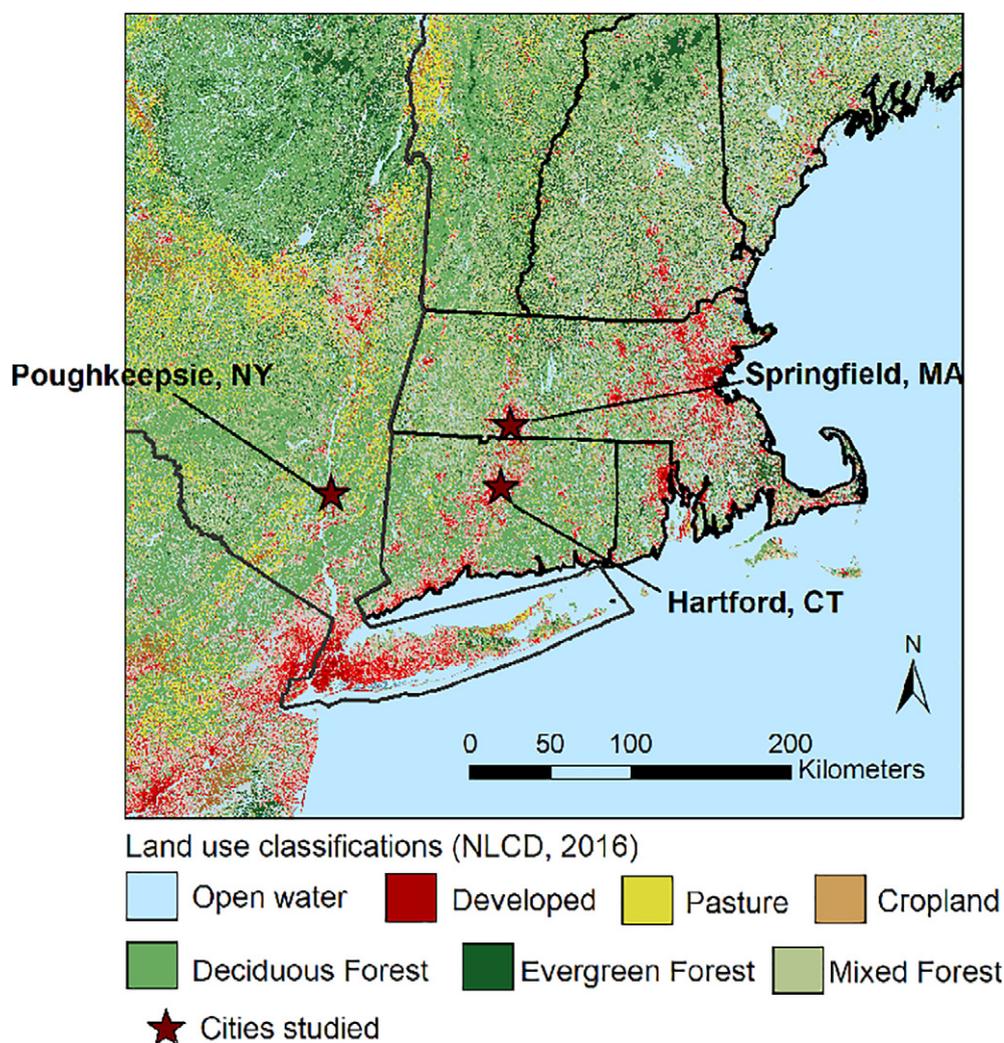


Fig. 1. Location of cities studied with most common NLCD (National Land Cover Database 2016) land-uses mapped.

2015). Soil samples were then sieved to <2 mm to remove rock fragments, human materials (e.g. glass), and roots.

We collected foliar tree samples from the four dominant genera present at the sampling site above the soil monolith collection point. For sites that had fewer than four different species of tree present, we took multiple samples of the most dominant tree species. Branches and leaf samples located 4 to 9 m above ground were collected using a stainless-steel pole saw. Sampling the lower branches of trees can cause biases in metal concentrations, as higher Hg concentrations would be expected on the leaves directly exposed to dry deposition in the upper canopy (12 to 18 m in height). Plant material was dried to a constant weight for accurate weighing. Plant samples were air-dried at -35°C in the oven for 24 h. Dried leaves had their main veins removed to avoid the dilution of leaf blade material by the woody material. Leaf blade material was then ground to <2 mm in a stainless-steel grinder.

2.3. Soil physicochemical analyses

To measure pH of soil samples, 3.0 ± 0.2 g of sieved soil material was weighed and placed into 50 mL centrifuge tubes. The soil was extracted with 0.01 M CaCl_2 added at a ratio of 2.5 g of solution to every 1 g of soil and shaken for 1 h. The soil was allowed to settle and pH was measured in the supernatant using a pH Meter (8015 VWR, Radnor, PA, USA). Loss-on-ignition (LOI) was measured to estimate the organic matter content of soil samples. Approximately 10 g subsamples of soil were combusted at 550°C in a muffle furnace for 8 h. Every 20 samples included one blank,

and a duplicate. Soil particle size distribution was measured using a modified Bouyoucos hydrometer method. Approximately 30 g of dried soil was treated with 30% H_2O_2 to remove organic matter and was dispersed with 100 mL of 1 M sodium hexametaphosphate (HMP) solution for at least 8 h. This HMP-soil slurry was washed out into a 1000 mL graduated cylinder with deionized water. After mixing, hydrometer readings were taken at 60 s and 1.5 h to the closest 0.5 g L^{-1} (Gee and Bauder, 1986).

2.4. Soil and foliar total Hg analysis

Total Hg concentrations (THg) for the organic and mineral soil were quantified using a Direct Mercury Analyzer – 80 (Milestone Inc., Shelton, CT, USA). For the analysis, 100 ± 10 mg subsamples were weighed into steel boats and ashed at 650°C . Combusted Hg is trapped on the gold amalgam, which is heated after complete sample combustion and measured for Hg with an atomic absorption spectrometer. To ensure quality, duplicates, preparation blanks, and a standard reference material (SRM) were included in each batch. Peach leaves SRM 1547 was used to quantify matrix effects (National Institute of Standards and Technology, Gaithersburg, MD). Preparation blanks were below 0.1 ng g^{-1} , and duplicate variations were within 5% and SRM Hg measurements were within 10% of their certified values. In total, 58 forest floor samples, 58 A horizon samples, 39 B horizon samples, and 232 plant foliar samples were analyzed for total Hg concentrations.

2.5. Data processing and statistical analyses

Descriptive statistics were calculated in MATLAB (Mathworks, Natick, MA, USA). Arithmetic mean values are presented in text and in figures ± 1 standard error. To determine forest floor Hg pools, floor Hg concentrations were multiplied by their dry weight, areal bulk density (mass per 225 cm²), measured with the field sample and scaled up to m². To determine mineral soil Hg pools, A horizon and B horizon Hg concentrations were multiplied by their bulk density. Depths were scaled to top 30 cm. For soil profiles < 30 cm, the bottom horizon (A or B horizons) were scaled to 30 cm assuming the same Hg concentration and bulk density, which may not be accurate if a contrasting horizon was present at depth. For soil profiles deeper than 30 cm, only the top 30 cm were considered.

Both parametric and non-parametric statistical tests were applied, depending if sample size, distribution, and variance met assumptions for the ANOVA. Foliar Hg concentrations, forest floor Hg concentrations, A horizon soil Hg concentrations, pH, LOI, and %Clay were tested for normality and compared among cities using analysis of variation (ANOVA) tests with post-hoc *t*-tests. Foliar Hg concentrations among genera as well as foliar and soil comparisons among land-uses were compared the non-parametric Kruskal-Wallis test with post-hoc Wilcoxon signed-rank test.

Linear, power, and logarithmic relationships between mineral soil physicochemical properties (pH, LOI, %Clay) and Hg concentrations on non-transformed data using MATLAB. Power and logarithmic correlations were performed to ensure that non-linear relationships also did not exist.

3. Results and discussion

3.1. Foliar Hg concentrations across cities and genera

The average foliar Hg concentration for all samples, including all tree genera and all three cities, was 23.8 ± 8.8 ng g⁻¹. These foliar concentrations were comparable to deciduous trees in non-urban areas of Vermont and New Hampshire (Richardson and Friedland, 2015), across Minnesota (Laacouri et al., 2013), the Adirondack Mountains of New York, and across the United States (Obriest et al., 2011). Foliar Hg concentrations were similar among the three cities with no significant differences ($p > 0.05$; Fig. 2). This result suggests that localized exposure of foliage to Hg emissions are similar among the three cities and that atmospheric releases of Hg within the cities are likely of similar magnitude. Foliar Hg concentrations in the three cities were lower than concentrations observed for deciduous trees in Tieshanping forest catchment near Chongqing City, China, which averaged 210 ± 46 ng g⁻¹ (Zhou et al., 2016) and in the mountains rural of Vermont by Juillerat et al. (2012), which averaged 52 ± 11 ng g⁻¹. The elevated

concentrations in the Tieshanping forest are straightforward and are sourced from local and regional combustion of coal for energy generation (Zhou et al., 2016). The mountain forests of rural Vermont may not appear to be a region known for elevated Hg deposition but the Green Mountains receive elevated concentrations of Hg deposition due to topography cause orographic deposition (see Stankwitz et al., 2012; Richardson et al., 2013).

Most tree genera exhibited similar foliar Hg concentrations, however there were some significant differences (Fig. 3). Foliage from the genus *Populus* had significantly lower Hg concentrations (15.6 ± 2.1 ng g⁻¹) than the mean foliar Hg concentration for all genera (23.8 ± 0.6 ng g⁻¹) ($p < 0.05$; Fig. 3). Conversely, *Fraxinus* (37.9 ± 3.5 ng g⁻¹) and the genus *Prunus* (32.1 ± 3.3 ng g⁻¹) had higher concentrations than the mean foliar Hg concentration for all genera (23.7 ± 0.6 ng g⁻¹) ($p < 0.05$; Fig. 3). This could be due to physiological differences in leaves such as cuticular adsorption properties (Converse et al., 2010) or stomatal uptake rates (Stamenkovic and Gustin, 2009; Arnold et al., 2018). However, cuticle Hg concentrations were measured to be <4% of total Hg by Laacouri et al. (2013) and stomatal uptake by stomata should be comparable across the deciduous genera. A more likely explanation for the differences is location based. *Fraxinus* was primarily found near the agricultural areas of Poughkeepsie, NY and *Prunus* was found near the industrial areas of Springfield, MA. Both of these areas exhibited higher foliar Hg concentrations relative to the rest of the three cities when examined without respect to genera. Land-use effects on foliage are further explored in Section 3.3. These results primarily suggest that deciduous tree genera did not influence accumulation but spatial location within the city may have an effect.

3.2. Soil Hg concentrations and pools

The urban soils in all three cities share similar geologic provenance from primarily glaciofluvial deposits with interspersed glacial till. Their similar texture reflected this, as A and B horizon clay contents remained below 10% for most sites in all three cities (Fig. 4). The soil organic matter (SOM) content estimated by LOI showed that A horizons ($13 \pm 1\%$) had approximately twice the SOM concentration as B horizons ($6 \pm 1\%$) ($p < 0.05$; Fig. 4). A and B horizon SOM concentrations did not differ significantly across the three cities ($p > 0.05$; Fig. 4). Lastly, soil pH was acidic, ranging between 3.9 and 4.9 with no significant differences among cities for the A horizons ($p > 0.05$; Fig. 4). There were differences in the B horizons, with Springfield MA having significantly higher B horizon pH values than Hartford or Poughkeepsie, which was substantially higher at pH 4.7 compared to pH 4.1 and 4.2 ($p < 0.05$; Fig. 4).

Forest floor Hg concentrations ranged between 41 and 978 ng g⁻¹, with an average of 195 ± 21 ng g⁻¹. These concentrations are comparable to forest floor concentrations found in non-urban areas of Vermont

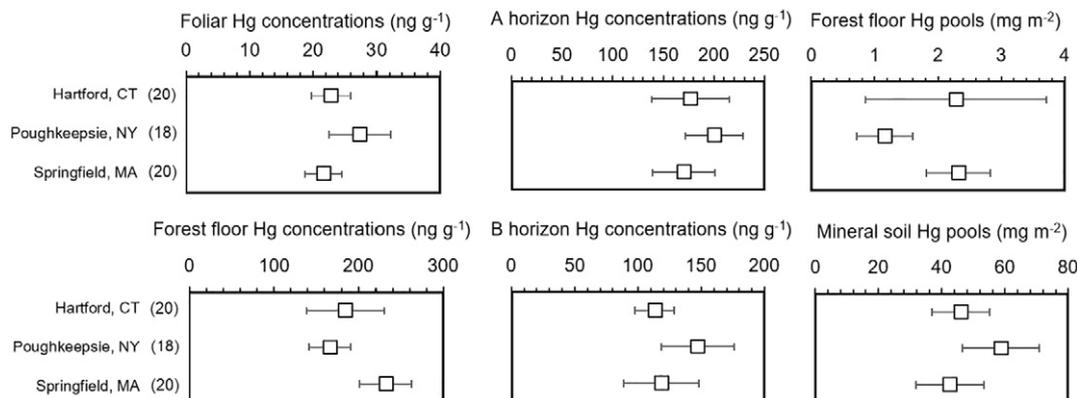


Fig. 2. Mercury concentrations in foliage and soil horizons and mercury pools in soil horizons for urban soils across the three cities. Arithmetic means are presented ± 1 standard error. (*) indicates a significant difference from by ANOVA ($p < 0.05$). (n) are sample size.

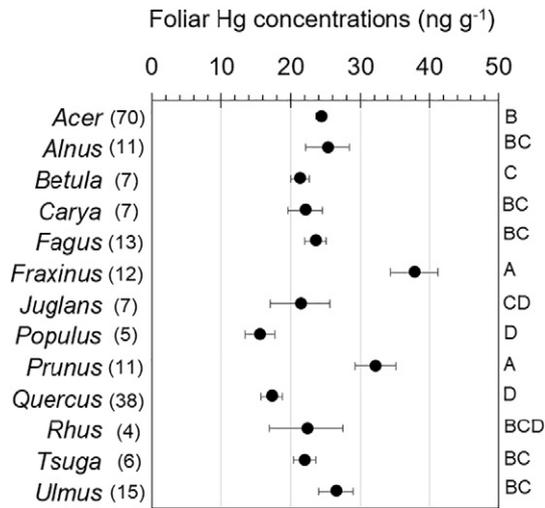


Fig. 3. Foliar Hg concentrations across tree genera present among the three cities. Tree genera with $n \leq 3$ were not included. Arithmetic means are presented ± 1 standard error. (n) are sample size. Letters indicate statistical significance among genera ($p < 0.05$) using the non-parametric Kruskal-Wallis test with post-hoc Wilcoxon signed-rank test.

(282 ng g⁻¹) (Juillerat et al., 2012), across Vermont and New Hampshire (66 to 359 ng g⁻¹) (Richardson and Friedland, 2015), in the Adirondacks (84 to 148 ng g⁻¹) (Blackwell et al., 2014), across southern New England, New York, and Pennsylvania (131 to 273 ng g⁻¹) (Yu et al., 2014), in Bavaria, Germany (~110 to ~500 ng g⁻¹) (Schwesig and Matzner, 2000) and in Xining, Qinghai China (13 to 308 ng g⁻¹) (Feng et al., 2014). Forest floor Hg concentrations were much lower than areas with historical point source pollution such as Oak Ridge, TN (420 \pm 125 ng g⁻¹) (Obrist et al., 2011). Similarly, Navrátil et al. (2014) observed much higher mean forest floor Hg concentrations of 277 to 393 ng g⁻¹ than our study due to extensive coal combustion.

Forest floor Hg pools ranged between 0.08 and 8.9 mg m⁻² with an overall average of 1.9 \pm 0.5 mg m⁻². Hartford had substantially larger variance in forest floor Hg pools than Springfield and Poughkeepsie. The source of this wide variation at Hartford in forest floor mass is unclear, potentially from sites with broader range of undisturbed and highly disturbed soils than at the other two cities. Forest floor Hg did not differ significantly between the three cities ($p > 0.05$; Fig. 2). The forest floor pools of the three cities were comparable to Vermont (0.1 to 4.0 mg m⁻²) (Juillerat et al., 2012) but were significantly less than non-urban areas in the Adirondacks of New York (2.8 to 3.7 mg m⁻²) (Blackwell et al., 2014), across Vermont and New Hampshire (3.0 to 4.2 mg m⁻²) (Richardson and Friedland, 2015), across southern New England, New York, and Pennsylvania (3.2 to 4.7 mg m⁻²) (Yu et al.,

2014), and in Czech Republic forests (5.3 to 10.1 mg m⁻²) (Navrátil et al., 2014). These results demonstrate that forest floors in urban forest soils do not have significantly elevated concentrations and store less Hg than their non-urban counterparts. A major cause was that urban forest floors are much thinner than forest floors in rural, montane areas (see Stankwitz et al., 2012; Richardson, 2019). This is due to more direct physical disturbance by humans (Moffatt and McLachlan, 2004), removal of litterfall (Templer et al., 2015), warmer temperatures from the urban heat island effect enhancing decomposition rate (Livesley et al., 2016), and introduced earthworms rapidly decomposing litter (see Richardson et al., 2017; Richardson, 2019).

Soil A and B horizons Hg concentrations ranged between 8 and 712 ng g⁻¹ and were not significantly different among the three cities ($p > 0.05$; Fig. 2). Average A horizon concentrations were 182 \pm 19 ng g⁻¹ and average B horizon concentrations were 125 \pm 14 ng g⁻¹. These concentrations were higher than surface (A and E horizons) and subsurface (Bw, Bhs, B, BC) horizons in previous studies conducted across the northeastern US: Vermont and New Hampshire (42 to 97 ng g⁻¹) (Richardson and Friedland, 2015), Adirondacks (59 to 76 ng g⁻¹) (Blackwell et al., 2014), southern New England (34 to 96 ng g⁻¹) (Yu et al., 2014), and rural mountains of (130 ng g⁻¹) (Juillerat et al., 2012). Compared globally, surface soil concentrations were higher than Czech Republic mineral soils (22 to 95 ng g⁻¹), similar to concentrations found across Liaonin, Jiangsu, Zhejiang, Sichuan, Qinghai, and Chongqing provinces of China (64 to 154 ng g⁻¹) (Shi et al., 2013; Feng et al., 2014) and in Bavaria, Germany (~15 to ~280 ng g⁻¹) (Schwesig and Matzner, 2000) but much lower than mining areas of Slovenia (8 to 1210 ng g⁻¹) (Bavec et al., 2015), industrial urban soils of Xicheng of Beijing (86 to 1590 ng g⁻¹) (Lin et al., 2018b), and near a chlor-alkali plant in Grenoble, France (50 to 10,000 ng g⁻¹) (Grangeon et al., 2012). To compare soil Hg pools across sites, soils were normalized to the top 30 cm only. Soil Hg pools ranged from 4.9 to 234.7 mg m⁻² with an average of 49 \pm 6 mg m⁻² and did not differ significantly between the cities ($p > 0.05$; Fig. 2). The Hg pools for the top 30 cm were greater than the mineral soil pools of rural, montane forests in Vermont and New Hampshire (4.5 mg m⁻¹) (Richardson and Friedland, 2015) as well as non-urban areas of Southern New England (9.6 mg m⁻²) and Pennsylvania and New York (19 to 22 mg m⁻²) (Yu et al., 2014). Our mineral soil Hg pools were comparable to entire soil profiles in Czech Republic forests (8.9 to 130 mg m⁻² for 54 to 106 cm depth) (Navrátil et al., 2014). Our results highlight that urban forest soils can serve as larger Hg pools than rural forests, but local point source pollution can substantially impact the mineral soil Hg pool.

Linear, power, and logarithmic regressions between physicochemical properties and Hg concentrations were performed, revealing that variables traditionally associated with accumulation and retention did not correspond with Hg concentrations. Clay content was not

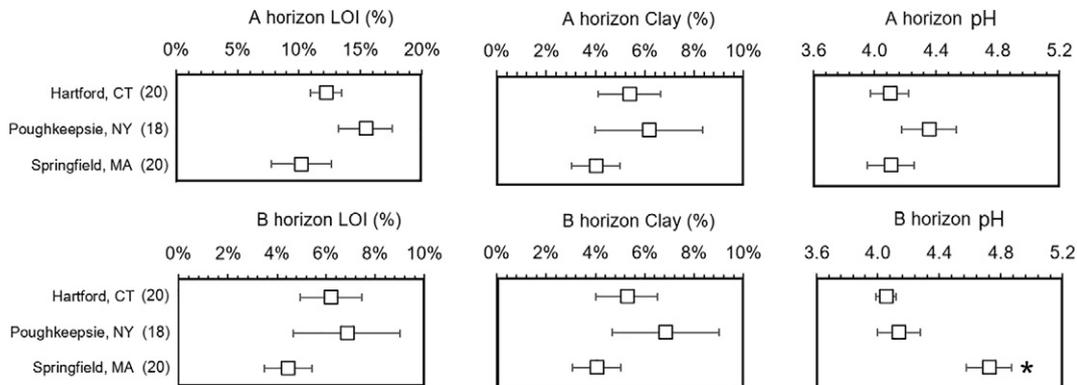


Fig. 4. Basic physicochemical soil properties for urban soils across the three cities. Arithmetic means are presented ± 1 standard error. (*) indicates a significant difference from by ANOVA ($p < 0.05$). (n) are sample size.

significantly correlated with A and B horizon Hg concentrations or mineral soil Hg pools ($p > 0.10$, $R^2 < 0.05$). SOM estimated by LOI was poorly correlated with A and B horizon Hg concentrations and mineral soil pools ($p > 0.10$, $R^2 = 0.05$). Soil pH was poorly correlated with Hg concentrations ($p > 0.10$, $R^2 < 0.05$) but significantly correlated with mineral soil Hg pools ($p < 0.05$, $R^2 = 0.14$). However, this relationship only explained 14% of the variation. Our results suggest that capacity for Hg sorption are not important in urban systems for Hg accumulation, but other variables, potentially distance to sources and land-use history, are more important.

3.3. Foliar and soil Hg concentrations across land-uses

Foliar Hg concentrations did not exhibit a strong spatial variation in Hartford, CT and Poughkeepsie, NY (Fig. 5). Additionally, urban forest sites adjacent to high and medium intensity developed areas did not exhibit higher foliar Hg concentration. However, in Springfield MA, urban forest sites adjacent to high and medium intensity developed areas had higher concentrations than urban forests adjacent to low intensity developed lands (Fig. 5). Similarly, A horizon Hg concentrations and mineral soil pools did not exhibit a strong spatial association with high and medium intensity developed areas in Hartford and Poughkeepsie. Elevated A horizon concentrations and mineral soil pools also occurred near pastures, open spaces, and low intensity developments. However, in Springfield, MA, sites adjacent to high and medium intensity developed areas had higher A horizon Hg concentrations than urban forests adjacent to low intensity developed lands (Fig. 5).

We reclassified the sites according to our own land-use framework based upon field observations and satellite and ground imagery. This distinguished between land-uses that would be categorized together under NLCD definitions. For example, urban forests between single family homes were recategorized separately than multi-family housing. Urban forests adjacent to non-industrial commercial spaces were distinguished from forests adjacent to industrial areas with large-scale, raw material refining. Undeveloped open spaces were reclassified as parks, for recreation. Hay/Pasture uses under NLCD were combined as agriculture. Using this classification scheme, we compared urban foliar Hg concentrations and soil Hg concentrations and pools in all three cities across land-uses. We observed that urban forests adjacent to industrial land-uses had significantly higher foliar Hg concentrations ($27.5 \pm 2.3 \text{ ng g}^{-1}$) than those adjacent to recreational parks, multi-family residential areas, and single-family residential areas ($\sim 23 \pm 1.5 \text{ ng g}^{-1}$) (Fig. 6). Moreover, urban soils adjacent to industrial land-uses had A horizon concentrations ($434 \pm 88 \text{ ng g}^{-1}$) and mineral soil Hg pools ($84 \pm 32 \text{ mg m}^{-2}$) greater than those adjacent to recreational parks and multi-family residential areas ($\sim 156 \pm 19 \text{ ng g}^{-1}$ and $\sim 39 \pm 6 \text{ mg m}^{-2}$) (Fig. 6). Urban forests adjacent to agricultural areas had smaller forest floor pools than commercial and recreational parks (Fig. 6). This was most likely due to lower forest floor mass from earthworms present in forests near agricultural areas. These results agree with previous studies that observed land-use type can affect Hg and other trace elements in urban forest vegetation. As shown by Fu et al. (2016), local atmospheric concentrations of particulate Hg, dry deposition of Hg and wet Hg deposition from local human emissions can all drive a wide variation of foliar Hg concentrations and subsequent

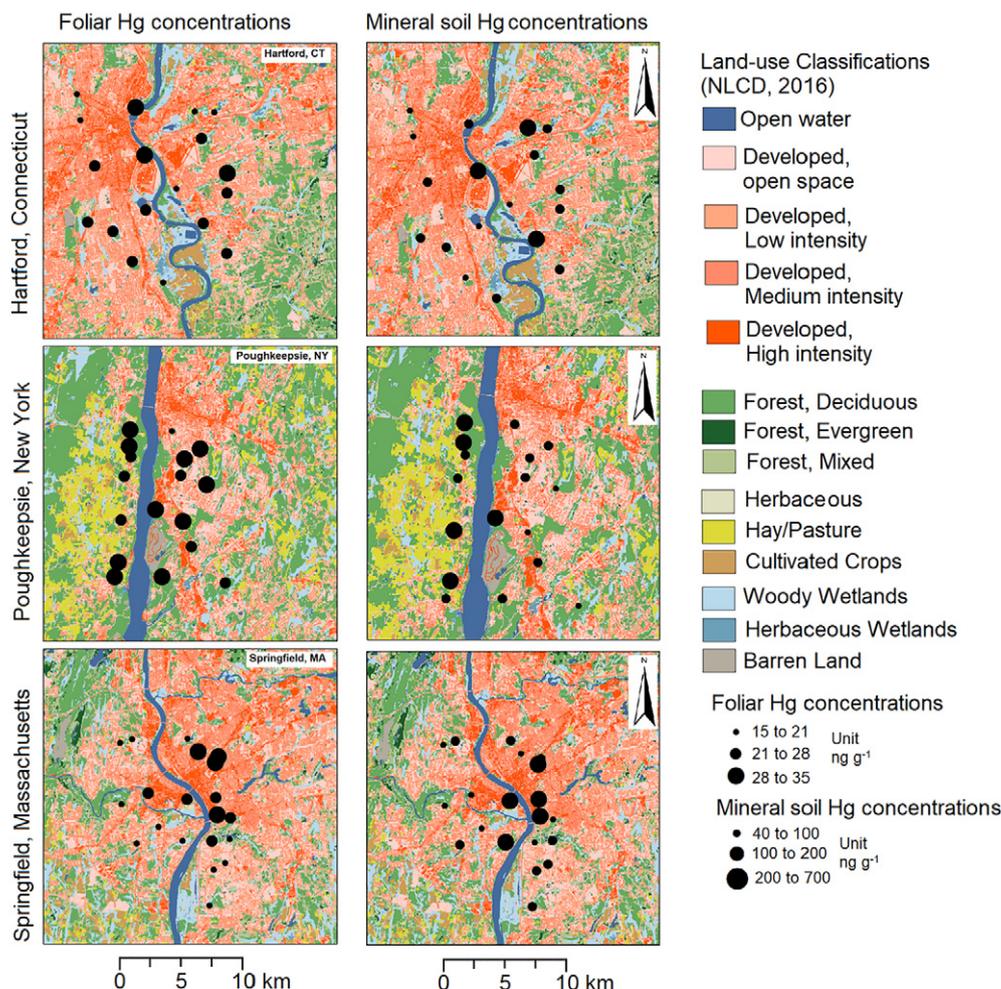


Fig. 5. Foliar and A horizon Hg concentrations in across the three cities mapped with NCLD 2016 land use classifications.

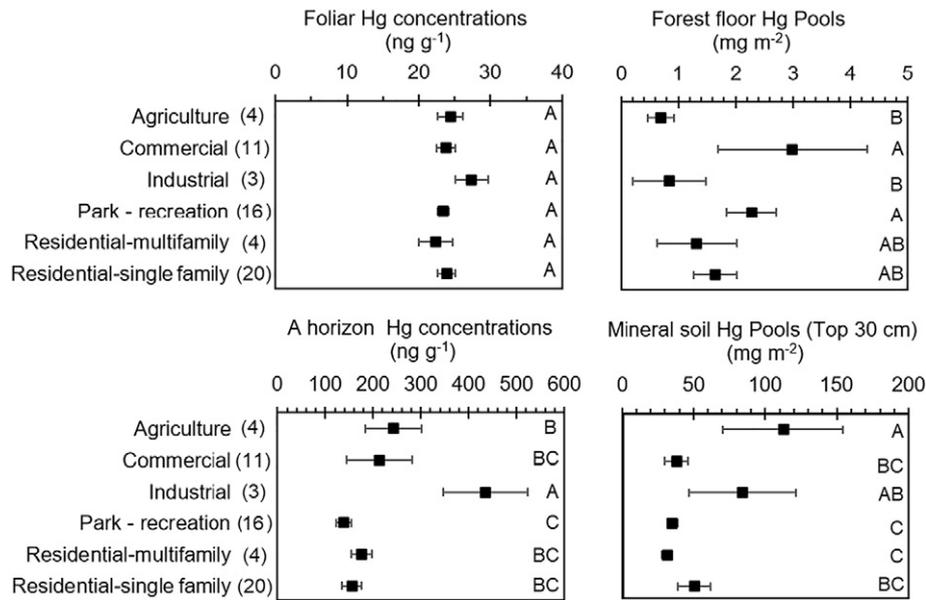


Fig. 6. Mercury concentrations in foliage and A horizons and mercury pools in A and B horizons by dominant land-use adjacent to the urban forests across the three cities. Arithmetic means are presented ± 1 standard error and (n) are sample size. Letters indicate statistical significance among genera ($p < 0.05$) using the non-parametric Kruskal-Wallis test with post-hoc Wilcoxon signed-rank test.

litterfall concentrations. Moreover, Zhao et al. (2018) showed that urban sites closest to coal combustion power plants had higher atmospheric deposition rates. Our study highlights that in areas not contaminated with point sources of Hg pollution (i.e. coal combustion and mining), other land-uses can be an important source of Hg to foliage and soils.

4. Conclusions

Urban soils accumulate higher concentrations and pools of Hg than their rural, montane counter parts across New York and southern New England. A and B horizon Hg concentrations doubled those of regional rural forests and mineral soil Hg pools were two to ten times higher than some rural forests in the region. This highlights the importance of soils in urban systems for sequestering Hg, preventing its movement towards riparian and aquatic ecosystems where it can bioaccumulate. Moreover, soil Hg concentrations were poorly correlated with pH, LOI, and clay content, all variables traditionally believed to control Hg accumulation. Instead, proximity to local industrial and agricultural sources proved a significant influence on Hg accumulation.

Tree foliage had comparable Hg concentrations to many previous studies conducted in rural forests not downwind of coal combustion or near point sources of Hg pollution. Forest floor Hg concentrations were comparable to those of non-urban forests within the region and globally, but forest floor Hg pools were half the size of non-urban sites from previous studies. We attributed the loss of forest floor Hg pools to disturbances from higher temperatures and introduced earthworms. We hypothesize this was largely driven by past Hg-based pesticide pollution in agricultural areas and historical emissions in current industrial areas. While this work has quantified the accumulation of Hg in urban forests, more work is required to quantify Hg residence time, measure Hg bioaccumulation by soil-dwelling organisms, and identify management techniques that promote Hg sequestration.

Acknowledgements

This project was supported by funding from the College of Natural Sciences at University of Massachusetts Amherst to Dr. Justin B.

Richardson. We would like to thank Brendan R. Braithwaite and Jonah D.G. Jordan for their help in sample collection and processing. The authors state that work was conducted without any personal, professional, or financial relationships that could potentially be construed as a conflict of interest.

References

- Arnold, J., Gustin, M.S., Weisberg, P.J., 2018. Evidence for nonstomatal uptake of Hg by aspen and translocation of Hg from foliage to tree rings in Austrian pine. *Environ. Sci & Technol* 52, 1174–1182.
- Bavec, Š., Gosar, M., Biester, H., Grčman, H., 2015. Geochemical investigation of mercury and other elements in urban soil of Idrija (Slovenia). *J Geochem Expl* 154, 213–223.
- Berland, A., Shiflett, S.A., Shuster, W.D., Garmestani, A.S., Goddard, H.C., Herrmann, D.L., Hopton, M.E., 2017. The role of trees in urban stormwater management. *Landscape Urban Plan* 162, 167–177.
- Birke, M., Rauch, U., 2000. Urban geochemistry: investigations in the Berlin metropolitan area. *Environ. Geochem. Health* 22, 233–248.
- Blackwell, B.D., Driscoll, C.T., 2015. Using foliar and forest floor mercury concentrations to assess spatial patterns of mercury deposition. *Environ. Pollut.* 202, 126–134.
- Blackwell, B.D., Driscoll, C.T., Maxwell, J.A., Holsen, T.M., 2014. Changing climate alters inputs and pathways of mercury deposition to forested ecosystems. *Biogeochemistry* 119 (1–3), 215–228.
- Chambers, L.G., Chin, Y.P., Filippelli, G.M., Gardner, C.B., Herndon, E.M., Long, D.T., Lyons, W.B., Macpherson, G.L., McElmurry, S.P., McLean, C.E., Moore, J., 2016. Developing the scientific framework for urban geochemistry. *Appl. Geochem.* 67, 1–20.
- Converse, A.D., Riscassi, A.L., Scanlon, T.M., 2010. Seasonal variability in gaseous mercury fluxes measured in a high-elevation meadow. *Atmos. Environ.* 44, 2176–2185.
- Demetriades, A., 2010. Medical geology in Hellas: the lavrian environmental pollution study. *Med. Geol.* Springer, Dordrecht, pp. 355–390.
- Deonarine, A., Hsu-Kim, H., Zhang, T., Cai, Y., Richardson, C.J., 2015. Legacy source of mercury in an urban stream-wetland ecosystem in central North Carolina, USA. *Chemosphere* 138, 960–965.
- Driscoll, C.T., Han, Y.J., Chen, C.Y., Evers, D.C., Lambert, K.F., Holsen, T.M., Kamman, N.C., Munson, R.K., 2007. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *BioScience* 57 (1), 17–28.
- Feng, L., Li, B., Xiu, G., Wang, C., Zhang, W., Wang, L., Gao, X., 2014. Spatial distribution of mercury species in the topsoils of ambient areas surrounding Xining urban in summer. *Environmental Science & Technology (China)* 37, 118–123.
- Fu, X., Yang, X., Zhou, J., Zhang, H., Yu, B., Yan, H., Lin, J., C., Feng, X., 2016. Atmospheric wet and litterfall mercury deposition at urban and rural sites in China. *Atmospheric Chemistry & Physics* 16.
- Gee, G.W., Bauder, J.W., 1986. Particle-size Analysis 1. *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods.* pp. 383–411.
- Grangeon, S., Guédron, S., Asta, J., Sarret, G., Charlet, L., 2012. Lichen and soil as indicators of an atmospheric mercury contamination in the vicinity of a chlor-alkali plant (Grenoble, France). *Ecol. Indic.* 13, 178–183.
- Hojdová, M., Rohovec, J., Chrástný, V., Penížek, V., Navrátil, T., 2015. The influence of sample drying procedures on mercury concentrations analyzed in soils. *Bullet Environ Contam Toxicol* 94, 570–576.

- Holmes, P., James, K.A.F., Levy, L.S., 2009. Is low-level environmental mercury exposure of concern to human health? *Sci. Total Environ.* 408 (2), 171–182.
- Islam, M.N., Rahman, K.S., Bahar, M.M., Habib, M.A., Ando, K., Hattori, N., 2012. Pollution attenuation by roadside greenbelt in and around urban areas. *Urban Forestry Urban Greening* 11, 460–464.
- Jezierska, B., Witeska, M., 2006. The metal uptake and accumulation in fish living in polluted waters. *Soil and Water Pollution Monitoring, Protection and Remediation*. Springer, Dordrecht, pp. 107–114.
- Juillerat, J.I., Ross, D.S., Bank, M.S., 2012. Mercury in litterfall and upper soil horizons in forested ecosystems in Vermont, USA. *Environ. Toxicol. Chem.* 31, 1720–1729.
- Kot, F.S., Matyushkina, L.A., 2002. Distribution of mercury in chemical fractions of contaminated urban soils of Middle Amur, Russia. *J. Environ. Monit.* 4, 803–808.
- Laacouri, A., Nater, E.A., Kolka, R.K., 2013. Distribution and uptake dynamics of mercury in leaves of common deciduous tree species in Minnesota, USA. *Environ Sci Technol* 47, 10462–10470.
- Lin, B.B., Egerer, M.H., Liere, H., Jha, S., Bichier, P., Philpott, S.M., 2018a. Local-and landscape-scale land cover affects microclimate and water use in urban gardens. *Sci. Total Environ.* 610, 570–575.
- Lin, M., Li, S., Sun, X., Yang, S., Li, J., 2018b. Heavy metal contamination in green space soils of Beijing, China. *Acta Agriculturae Scandinavica, Section B—Soil & Plant Science* 68, 291–300.
- Liu, L., Zhang, X., Zhong, T., 2016. Pollution and health risk assessment of heavy metals in urban soil in China. *Human and Ecological Risk Assessment: An International Journal* 22, 424–434.
- Livesley, S.J., McPherson, E.G., Calafapietra, C., 2016. The urban forest and ecosystem services: impacts on urban water, heat, and pollution cycles at the tree, street, and city scale. *J. Environ. Qual.* 45, 119–124.
- Maco, S.E., McPherson, E.G., 2002. Assessing canopy cover over streets and sidewalks in street tree populations. *J. Arboriculture* 28, 270–276.
- Melgar, M.J., Alonso, J., García, M.A., 2009. Mercury in edible mushrooms and underlying soil: bioconcentration factors and toxicological risk. *Sci. Total Environ.* 407 (20), 5328–5334.
- Mélières, M.A., Pourchet, M., Charles-Dominique, P., Gaucher, P., 2003. Mercury in canopy leaves of French Guiana in remote areas. *Sci. Total Environ.* 311, 261–267.
- Moffatt, S.F., McLachlan, S.M., 2004. Understorey indicators of disturbance for riparian forests along an urban–rural gradient in Manitoba. *Ecol. Indic.* 4, 1–16.
- Navrátil, T., Shanley, J., Rohovec, J., Hojđová, M., Penížek, V., Buchtová, J., 2014. Distribution and pools of mercury in Czech forest soils. *Water Air Soil Pollut.* 225, 1829.
- Niu, Z., Zhang, X., Wang, Z., Ci, Z., 2011. Mercury in leaf litter in typical suburban and urban broadleaf forests in China. *J. Environ. Sci.* 23 (12), 2042–2048.
- Nowak, D.J., 2006. Institutionalizing urban forestry as a “biotechnology” to improve environmental quality. *Urban For. Urban Green.* 5, 93–100.
- Obrist, D., Johnson, D.W., Lindberg, S.E., Luo, Y., Hararuk, O., Bracho, R., Battles, J.J., Dail, D.B., Edmonds, R.L., Monson, R.K., Ollinger, S.V., 2011. Mercury distribution across 14 US forests. Part I: spatial patterns of concentrations in biomass, litter, and soils. *Environ. Sci. Technol.* 45 (9), 3974–3981.
- Pouyat, R.V., Yesilonis, I.D., Szlavecz, K., Csuzdi, C., Hornung, E., Korsós, Z., Russell-Anelli, J., Giorgio, V., 2008. Response of forest soil properties to urbanization gradients in three metropolitan areas. *Landsc. Ecol.* 23 (10), 1187–1203.
- Richardson, J.B., 2019. Trace elements in surface soils and megascolecidae earthworms in urban forests within four land-uses around Poughkeepsie, New York, USA. *Bull. Environ. Contam. Toxicol.* 103 (3), 385–390.
- Richardson, J.B., Friedland, A.J., 2015. Mercury in coniferous and deciduous upland forests in northern New England, USA: implications of climate change. *Biogeosciences*.
- Richardson, J.B., Friedland, A.J., Engerbretson, T.R., Kaste, J.M., Jackson, B.P., 2013. Spatial and vertical distribution of mercury in upland forest soils across the northeastern United States. *Environ. Pollut.* 182, 127–134.
- Richardson, J.B., Görres, J.H., Friedland, A.J., 2017. Exotic earthworms decrease Cd, Hg, and Pb pools in upland forest soils of Vermont and New Hampshire USA. *Bullet Environm Contam Toxicol* 99, 428–432.
- Richardson, J.B., Görres, J.H., Jackson, B.P., Friedland, A.J., 2015. Trace metals and metalloids in forest soils and exotic earthworms in northern New England, USA. *Soil Biol. Biochem.* 85, 190–198.
- Rieder, S.R., Brunner, I., Horvat, M., Jacobs, A., Frey, B., 2011. Accumulation of mercury and methylmercury by mushrooms and earthworms from forest soils. *Environ. Pollut.* 159, 2861–2869.
- Rimmer, C.C., McFarland, K.P., Evers, D.C., Miller, E.K., Aubry, Y., Busby, D., Taylor, R.J., 2005. Mercury concentrations in Bicknell’s thrush and other insectivorous passerines in montane forests of northeastern North America. *Ecotoxicology* 14 (1–2), 223–240.
- Rodrigues, S., Pereira, M.E., Duarte, A.C., Ajmone-Marsan, F., Davidson, C.M., Grčman, H., Hossack, I., Hursthouse, A.S., Ljung, K., Martini, C., Otobbong, E., 2006. Mercury in urban soils: a comparison of local spatial variability in six European cities. *Sci. Total Environ.* 368 (2–3), 926–936.
- Sanders, R.A., 1986. Urban vegetation impacts on the hydrology of Dayton, Ohio. *Urban Ecol.* 9, 361–376.
- Schwesig, D., Matzner, E., 2000. Pools and fluxes of mercury and methylmercury in two forested catchments in Germany. *Sci. Total Environ.* 260, 213–223.
- Şenilă, M., Levei, E.A., Şenilă, L.R., Oprea, G.M., Roman, C.M., 2012. Mercury in soil and perennial plants in a mining-affected urban area from northwestern Romania. *J. Environ. Sci. Health, Part A* 47, 614–621.
- Shi, J.B., Meng, M., Shao, J.J., Zhang, K.G., Zhang, Q.H., Jiang, G.B., 2013. Spatial distribution of mercury in topsoil from five regions of China. *Environ. Sci. Pollut. Res.* 20, 1756–1761.
- Simpson, J.R., 1998. Urban forest impacts on regional cooling and heating energy use: Sacramento County case study. *J. Arboriculture* 24, 201–214.
- Stamenkovic, J., Gustin, M.S., 2009. Nonstomatal versus stomatal uptake of atmospheric mercury. *Environ Sci Technol* 43, 1367–1372.
- Stankwitz, C., Kaste, J.M., Friedland, A.J., 2012. Threshold increases in soil lead and mercury from tropospheric deposition across an elevational gradient. *Environ Sci Technol* 46, 8061–8068.
- Stinson, M.D., Eaton, D.L., 1983. Concentrations of lead, cadmium, mercury, and copper in the crayfish (*Pacifastacus leniusculus*) obtained from a lake receiving urban runoff. *Archives of Environmental Contamin Toxicol* 12, 693–699.
- Streets, D.G., Horowitz, H.M., Lu, Z., Levin, L., Thackray, C.P., Sunderland, E.M., 2019. Global and regional trends in mercury emissions and concentrations, 2010–2015. *Atmos. Environ.* 201, 417–427.
- Talmage, S.S., Walton, B.T., 1993. Food chain transfer and potential renal toxicity of mercury to small mammals at a contaminated terrestrial field site. *Ecotoxicology* 2, 243–256.
- Templer, P.H., Toll, J.W., Hutyra, L.R., Raciti, S.M., 2015. Nitrogen and carbon export from urban areas through removal and export of litterfall. *Environ. Pollut.* 197, 256–261.
- Tong, Y., Zhang, W., Hu, D., Ou, L., Hu, X., Yang, T., Wei, W., Ju, L., Wang, X., 2013. Behavior of mercury in an urban river and its accumulation in aquatic plants. *Environ. Earth Sci.* 68, 1089–1097.
- Xia, X.H., Chen, X., Liu, R.M., Liu, H., 2011. Heavy metals in urban soils with various types of land use in Beijing, China. *J. Hazard. Mater.* 186, 2043–2050.
- Yang, X., Wang, L., 2008. Spatial analysis and hazard assessment of mercury in soil around the coal-fired power plant: a case study from the city of Baoji, China. *Environ. Geol.* 53 (7), 1381–1388.
- Yu, X., Driscoll, C.T., Warby, R.A., Montesdeoca, M., Johnson, C.E., 2014. Soil mercury and its response to atmospheric mercury deposition across the northeastern United States. *Ecol. Appl.* 24, 812–822.
- Zhang, Z.S., Zheng, D.M., Wang, Q.C., Lv, X.G., 2009. Bioaccumulation of total and methyl mercury in three earthworm species (*Drawida* sp., *Allolobophora* sp., and *Limnodrilus* sp.). *Bullet of Environ Contamin Toxicol* 83, 937.
- Zhao, L., Xu, L., Wu, X., Zhao, G., Jiao, L., Chen, J., Hong, Y., Deng, J., Chen, Y., Yang, K., Hu, G., 2018. Characteristics and sources of mercury in precipitation collected at the urban, suburban and rural sites in a city of Southeast China. *Atmos. Res.* 211, 21–29.
- Zhou, J., Wang, Z., Sun, T., Zhang, H., Zhang, X., 2016. Mercury in terrestrial forested systems with highly elevated mercury deposition in southwestern China: the risk to insects and potential release from wildfires. *Environ. Pollut.* 212, 188–196.