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Using an epiphytic moss to identify previously unknown sources of atmospheric cadmium pollution☆

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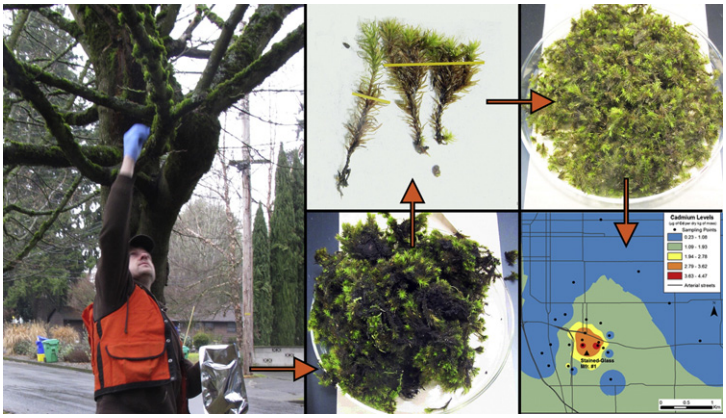
HIGHLIGHTS

- Bio-indicators are a valid method for measuring atmospheric pollutants
- We used moss to map atmospheric cadmium in Portland, Oregon
- Using a spatial linear model, we identified two stained-glass manufacturers as the major sources of atmospheric cadmium in Portland
- After both companies suspended cadmium use, atmospheric levels declined precipitously

GRAPHICAL ABSTRACT



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ABSTRACT

Urban networks of air-quality monitors are often too widely spaced to identify sources of air pollutants, especially if they do not disperse far from emission sources. The objectives of this study were to test the use of moss bio-indicators to develop a fine-scale map of atmospherically-derived cadmium and to identify the sources of cadmium in a complex urban setting. We collected 346 samples of the moss *Orthotrichum lyellii* from deciduous trees in December, 2013 using a modified randomized grid-based sampling strategy across Portland, Oregon. We estimated a spatial linear model of moss cadmium levels and predicted cadmium on a 50 m grid across the city. Cadmium levels in moss were positively correlated with proximity to two stained-glass manufacturers, proximity to the Oregon–Washington border, and percent industrial land in a 500 m buffer, and negatively correlated with percent residential land in a 500 m buffer. The maps showed very high concentrations of cadmium around the two stained-glass manufacturers, neither of which were known to environmental regulators as cadmium emitters. In addition, in response to our findings, the Oregon Department of Environmental Quality placed an instrumental monitor 120 m from the larger stained-glass manufacturer in October, 2015. The monthly average atmospheric cadmium

☆ Capsule: We used a moss bio-indicator to identify two major, and unknown, sources of atmospheric cadmium, and to show that bio-indicators are a screening tool that could revolutionize air-quality monitoring.

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concentration was 29.4 ng/m^3, which is 49 times higher than Oregon's benchmark of 0.6 ng/m^3, and high enough to pose a health risk from even short-term exposure. Both stained-glass manufacturers voluntarily stopped using cadmium after the monitoring results were made public, and the monthly average cadmium levels precipitously dropped to 1.1 ng/m^3 for stained-glass manufacturer #1 and 0.67 ng/m^3 for stained-glass manufacturer #2.

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1. Introduction

The World Health Organization estimates that air pollution contributes to 7 million premature deaths annually, making poor air quality one of the world's largest environmental health risks (World Health Organization, 2014). To reduce the public-health impact of air pollution, we must first be able to reliably identify pollution sources: otherwise it is impossible to design and effectively enforce environmental regulations. However, urban networks of air-quality monitors are often too widely spaced to identify sources of air pollutants, especially pollutants that do not disperse far from emission sources. Developing high-resolution pollution maps from those monitors is similarly problematic. As noted by the National Science and Technology Council (2013), "Matching actual pollutant exposure to individual humans requires monitoring at a finer spatial scale than provided by current networks, [because] primary emitted pollutants are subject to very dramatic gradients in the near-source region." One alternative, cost-effective approach to identifying pollutant sources is to use bio-indicators, which are biological processes or species used to assess environmental quality (Holt and Miller, 2011).

Moss and lichens are the most commonly used bio-indicators of atmospheric pollution. They are well-suited to this role because they lack roots and are non-vascular, depending fully on the atmosphere for nutrients and water. In addition, they do not have a protective epidermis, so nutrients and pollutants are easily absorbed into a moss or lichen's tissue. The first work using moss as a bio-indicator of atmospheric heavy metals was done by Ruhling and Tyler (1968) in Sweden. The authors collected samples of vascular plants and moss along three transects from busy roads. They found that the moss accumulated lead better than the vascular plants and represented emissions over the previous 7–15 months.

Other studies have shown that pollutant levels in moss are correlated with instrumental measures of atmospheric air pollution. Berg and Steinnes (1997) compared the levels of 48 elements in two species of moss at 13 sites in Norway to levels in rainwater; and at nine sites across Europe, Thomas (1986) compared cadmium concentration in moss to instrumentally measured atmospheric cadmium and cadmium in rainwater. Both studies found that cadmium concentration in moss was positively and linearly correlated with cadmium concentration in rainwater ($r = 0.91$ and 0.87, respectively). Aboal et al. (2010) reviewed the use of mosses as bio-indicators of atmospheric heavy metals, noting that moss concentrations of cadmium and lead are more consistently correlated with measurements of atmospheric deposition than concentrations of other metals. The correspondence of instrumentally measured heavy metal concentrations and those in moss suggest that moss could be used to complement existing networks of air-quality monitors.

With a couple of notable exceptions, prior work mapping heavy metal concentrations with moss was limited to small proof-of-concept studies or was not designed to produce detailed, continuous maps of atmospheric metal deposition. To be of the most benefit to air quality regulators and to identify pollution sources with a high level of confidence, maps must account for spatial autocorrelation and sampling must be sufficiently intensive to capture small-scale variability in metals deposition. One exception was Ares et al. (2011), who used 50 moss bags of *Pseudoscleropodium purum* and spatially-explicit regression to map six heavy metals in an industrial area around an oil refinery in Santa Cruz de Tenerife, Spain. They found very high levels of nickel and vanadium near the refinery. Another exception was Hasselbach et al. (2005) who used a spatially-explicit regression model to show that a road used to haul zinc ore was the source of cadmium and lead found in moss (*Hylocomium splendens*) on the Cape Krusenstern National Monument near the Red Dog Mine in Alaska. The authors used a stratified grid-based sample ($n = 226$) with more intense sampling near the road, finding that lead and cadmium concentrations declined proportionally with distance from the roads.

The objectives of this study were to use a moss bio-indicator to produce fine-scale maps of atmospheric cadmium pollution in Portland, Oregon, and to identify sources of cadmium in a complex urban setting. A secondary objective was to demonstrate that our approach could be used in other areas to map other pollutants.

1.1. Public health impact of cadmium

Cadmium is a heavy metal used in industrial processes, primarily manufacturing of nickel–cadmium batteries, but it is also used in plastic stabilizers, electroplating, and pigments used in glass manufacturing (IARC, 1993). In the general population, the most important sources of cadmium are cigarette smoking and food (Jarup, 2003). The largest atmospheric sources of cadmium are metal smelting, trash incineration (primarily the burning of nickel–cadmium batteries), and fossil-fuel combustion (Bhanarkar et al., 2005; Shah and Shaheen, 2007).

The International Agency for Research on Cancer has categorized cadmium as a human carcinogen (IARC, 1993). The strongest evidence links cadmium to lung cancer (Nawrot et al., 2006; Sorahan and Lancashire, 1997), but there is some evidence that cadmium is also associated with prostate cancer (Vinceti et al., 2007; Waalkes, 2000). In addition to cancer, cadmium exposure is associated with an increased risk of kidney disease (Hellström et al., 2001; Navas-Acien et al., 2009) and learning difficulties in children (Ciesielski et al., 2012).

1.2. Cadmium air pollution in Portland

In 2003, the Oregon Department of Environmental Quality (DEQ) created the Oregon Air Toxics Program (ORA 340-246), which was designed to complement federal air-quality regulations. In 2006, DEQ added benchmarks for 52 air toxics (including cadmium) to the air toxics program. To monitor and enforce these regulations, Oregon DEQ relies on one permanent air-quality monitor in Portland and up to two mobile monitors.

As part of the air toxics program, DEQ modeled atmospheric cadmium in the Portland metropolitan area based on known emissions (Fig. 1). They compared modeled values to cadmium measured at Portland's one permanent air-monitoring station. The emission model predicted that cadmium at the monitoring station would be 0.00033 μg/m^3, which is below DEQ's benchmark of 0.0006 μg/m^3. However, the monitored value was 0.0026 μg/m^3, almost eight times higher than predicted and over five times the benchmark value (Armitage, 2012). This discrepancy suggested that there may be significant unknown (and unregulated) sources of atmospheric cadmium in Portland. Oregon DEQ suspected that these emissions may have been coming from businesses known to use cadmium: stained-glass manufacturing and electroplating. However, DEQ was unable to test this hypothesis as they lacked the resources to monitor multiple facilities.

2. Materials and methods

2.1. Sampling design

Companies with permits to emit cadmium, as well as stained-glass and electroplating facilities, are located throughout Portland. Therefore,

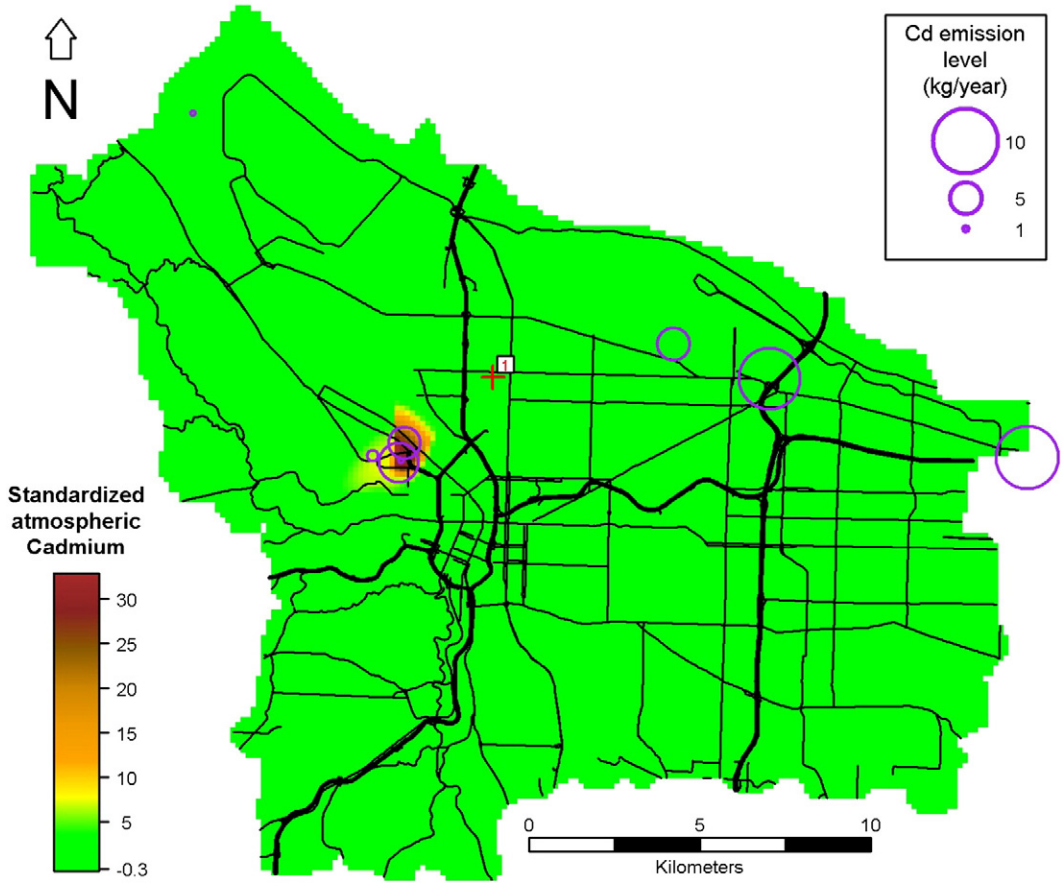


Fig. 1. Standardized cadmium predictions for 2017 from the Oregon DEQ Portland Air Toxics Study showing the location of known cadmium emitters and the North Roselawn air-quality monitoring station (1).

we used a grid-based sampling strategy: we overlaid a 1 km grid across the city and randomly placed a base-sample point on a road within the grid (n = 278). Based on past studies, we expected that residuals from our regression models would exhibit spatial autocorrelation (Hasselbach et al., 2005; Nickel et al., 2014). To capture these spatial relationships, and correctly specify them in our regression models, we took an additional 72 samples within 100 m of a randomly selected base-sample point—12 were taken from the same location as a base-sample point and the remaining 60 were taken from 10 to 100 m from a base-sample point (six at each 10 m increment). This sampling strategy is similar to the one used by Hasselbach et al. (2005). However, we distributed our sample points evenly across the study area, whereas Hasselbach et al. sampled more intensely near a road used to transport zinc ore, which they suspected was a source of cadmium and lead.

We collected samples from December 2–23, 2013. Moving systematically across the city could introduce bias (from differences in weather, for example). Therefore, we split the sample randomly into six spatially balanced subsamples collecting moss at all the points in a subsample before moving on to the next subsample.

We sampled *Orthotrichum lyellii* Hook. & Taylor, an acrocarpous moss that grows abundantly on the trunks and branches of hardwood trees across Portland. We chose this species because of its wide distribution across the city, including in locations known to be highly polluted. Additionally, *O. lyellii* grows in loose cushions, making it relatively easy to separate green, healthy material from rhizoids and debris that accumulates at the cushion base.

We collected from the hardwood tree closest to the randomly selected address in each 1 km grid, sampling moss from 29 tree genera in total. We did not preferentially collect from a particular species of tree as this would have meant departing further from the randomly selected address. The median distance from the randomly selected address to the tree a sample was taken from was 91 m. We collected all samples on hardwood trees from a height of at least 1 m to reduce the influence of dog urine and spray from cars. On average, we collected 5 g (dry weight) of moss from multiple cushions and locations on each sampled tree.

Weather may affect cadmium levels in moss: rain can wash off cadmium particles, and rain and temperature influence the metabolic activity of moss (Zechmeister et al., 2003). Therefore, we collected data on temperature, rainfall, and humidity for the day and week before each sample was collected. Similarly, tree species characteristics such as canopy structure or bark pH may influence the levels of pollutants in the moss sample, so we recorded the genus of a sampled tree and whether a sample was taken from a tree's trunk or branches.

We anticipated the possibility of finding samples with a very high concentration of cadmium. To further investigate these potential hotspots, we planned to collect an additional 24 moss samples from the immediate vicinity of the largest hotspot. We collected and analyzed the moss using the same laboratory techniques as we used for the original 346 samples.

2.2. Laboratory analysis

Immediately after collection, we stored samples at 4 °C in metalized polyester Kapak bags. Before laboratory analysis, we removed debris with sterilized forceps and trimmed off the base of the moss keeping only the upper 2/3 of the shoots. We did not wash samples, because we wanted to retain particulates adhered to the moss surface. Additionally, past research suggests washing is inefficient at removing external particulates, potentially causing non-informative variability among moss samples (Aboal et al., 2011).

We dried samples for 24 h at 40 °C and ground them to a fine powder. We used the $HNO_3 + H_2O_2$ digestion method to prepare the dried and ground samples for analysis. Briefly, 4 mL of concentrated reagent-grade HNO_3 were added to 0.5 g subsamples in 50-mL graduated plastic digestion tubes. After covering with plastic watch glasses, the tubes were allowed to sit overnight in a fume hood to provide some initial oxidation of the samples at ambient temperature by the HNO_3. The samples were digested at 95 °C for 90 min in a graphite block digestor. The samples were allowed to cool and 4 mL of reagent-grade 30% H_2O_2 was added to each tube followed by a 30-min digestion at 95 °C. After again cooling, a second 4-mL aliquot of H_2O_2 was added to each sample followed by a 45-min digestion at 95 °C. If the sample was not clear or pale yellow, a third H_2O_2 digestion was done for 45 min. After again cooling, deionized water was added to each tube to the 25-mL mark. The samples were filtered through 0.45-um membrane filters to remove undigested particulates (chiefly silicate minerals not dissolved in $HNO_3 + H_2O_2$) and stored in 22-mL plastic scintillation vials until analysis. Digests were analyzed for cadmium using inductively coupled plasma optical emission spectrometry (ICP-OES). Using the same method, we also estimated concentrations of arsenic and selenium in the moss. Both elements are co-emitted with cadmium from some industrial processes.

Quality control/quality assurance measures consisted of independent check standards to monitor ICP calibration performance, reagent and method blanks, repeat analysis of a bulk sample of *Orthotrichum* collected in the Portland area, and assessment of overall method accuracy by analyzing the IAEA-336 epiphytic lichen species, *Evernia prunastri* reference standard collected in Portugal (International Atomic Energy Agency, 1999). Our measured concentration ranges (n = 9) for the IAEA-336 reference lichen were 0.07–0.10 mg/kg for Cd and 0.18–0.60 mg/kg for As. The IAEA informational range for Cd is 0.100–0.134 mg/kg and the recommended range for As is 0.55–0.71 mg/kg. We were unable to measure Se in the IAEA-336 sample because the results were below the instrument detection limit. Method quantification limits for Cd, As, and Se were 0.0095, 0.237, and 0.368 mg/kg, respectively.

2.3. Data and covariates

2.3.1. Permitted sources of cadmium

Oregon DEQ administers a permitting program for businesses that emit hazardous air pollutants including cadmium. In total, 44 businesses in the Portland metropolitan area have 124 permits to emit cadmium (permits are stack-specific, so some companies have multiple permits). Our moss sampling was limited to the city of Portland but, in our statistical modeling, we considered sources of cadmium from the larger metropolitan area (not Washington). In 2012, as part of the Portland Air Toxics Solutions (PATS) project, Oregon DEQ estimated cadmium emissions for 2017 for each permit based on a range of variables including permitted emissions and likely economic growth (Armitage, 2012).

Using DEQ's estimates of 2017 emissions, we created an aggregate variable to account for all known cadmium emissions in the Portland metropolitan area. At any point, the influence of a given source of cadmium depends on the amount of cadmium emitted, and the distance from the emission source. However, the literature does not provide definitive guidance on the functional form of this relationship. Therefore, we calculated four variables describing total cadmium emissions from known sources making different assumptions about how cadmium declines with distance from emission source:

$$\forall_i\ TC_i = \sum_{j=1}^{124} \frac{Cd_j}{dist_{i,j}} \tag{1}$$

$$\forall_i\ TC_i = \sum_{j=1}^{124} \frac{Cd_j}{(dist_{i,j})^2} \tag{2}$$

$$\forall_i\ TC_i = \sum_{j=1}^{124} \frac{Cd_j}{\sqrt{dist_{i,j}}} \tag{3}$$

$$\forall_i\ TC_i = \sum_{j=1}^{124} \frac{Cd_j}{\ln(dist_{i,j})} \tag{4}$$

where TC_i is total cadmium from known emitters at point i, Cd_j is total cadmium emitted from emitter j, and $dist_{i,j}$ is the Euclidean distance from emitter j to point i. If two facilities were less than 500 m apart, we combined the two and assigned a single equidistant geocode.

2.3.2. Unknown sources of cadmium

The other likely industrial sources of cadmium are electroplating and stained-glass manufacturing facilities. We used the business analyst package in Arc GIS to locate those businesses in the Portland metropolitan area. There are 27 glass manufacturers with annual revenue ranging from $55,000 to $38,000,000 (median $200,000). Of these 27, only the largest has a permit to emit cadmium. There are 12 electroplating businesses in the Portland metropolitan area with annual revenue ranging from $99,000 to $10,500,000 (median $740,000) only one of which has a permit to emit cadmium.

Not all electroplating or glass manufacturers use cadmium. Therefore, we contacted each electroplating company and asked if they offered cadmium plating (one of the 12 did). Similarly, we contacted each of the glass manufacturers and asked if they produced colored glass (21 of the 27 did). We calculated the Euclidean distance to each unpermitted glass or electroplating business that used cadmium.

Portland is on the border between Oregon and Washington, so cadmium emissions in Washington may reach Portland. Washington has not estimated cadmium emissions for its permit holders. In addition, there is considerable industrial activity on both sides of the Columbia River, which forms the border between Oregon and Washington. Therefore, as a surrogate to account for all emissions from Washington and areas around the Columbia River, we calculated the natural log of the distance from each sample point to the Oregon–Washington border.

To account for cadmium emissions from fossil-fuel combustion, we calculated the density of class-1 and class-2 roads (Federal Highway Administration, 2013) in an inverse-distance weighted 500 m buffer around each sample point, the length of railways in an inverse-distance weighted 500 m buffer, the distance to the airport, and the distance to the nearest port. Absent definitive deposition functions for atmospheric cadmium, we chose 500 m buffers based on the deposition of other particulate air pollutants (Blasco et al., 2011; Zechmeister et al., 2005).

Vegetation can reduce air pollution (Nowak et al., 2006), so we estimated percent tree-canopy cover and percent grass-and-shrub cover in an inverse-distance weighted 500 m buffer around each sample point using an existing land-cover layer. To account for emissions that may not have been captured by other variables, we calculated the percent of different land-use types (industrial, commercial, residential, or open space) in a 500 m buffer around each sample point.

2.4. Spatial and statistical modeling

We estimated a linear spatial model of the natural log of cadmium concentration in moss. We modeled the natural log of cadmium, because cadmium concentration is strictly positive and untransformed values were highly right-skewed. To make interpreting regression coefficients easier, we standardized all covariates by subtracting the mean and dividing by the standard deviation.

Past research using moss to map cadmium found that model residuals were spatially auto-correlated (Ares et al., 2011; Hasselbach et al., 2005). To account for this spatial dependence among residuals, we considered three possible spatial-covariance structures—Gaussian, spherical, or exponential—and chose the best-fitting model using Akaike

information criterion. Spatial dependence means that observations are not independent, so we calculated degrees of freedom using the Kenward–Rogers approximation (Kenward and Roger, 1997).

We used a backwards, stepwise process for statistical model selection and referred to a variance-covariance matrix to avoid including highly correlated combinations of variables in the model—in particular, those describing distance to pollution sources. We used residual plots for standard regression diagnostics and to assess any remaining spatial autocorrelation. Spatial linear models were estimated using restricted maximum likelihood in the SAS 9.4 MIXED procedure.

We created basic dot maps of arsenic and selenium concentrations in the moss. Spatial linear regression models of arsenic and selenium were unnecessary, because our main objective in investigating these elements was to identify stained-glass manufacturing as the most likely source of unknown atmospheric cadmium in Portland.

3. Results

We were able to collect a moss sample at 346 of the 350 sample points. The four points where we could not find enough moss to sample were in heavily wooded parts of the city with good air quality. At these sites, other species of moss and liverwort outcompeted *Orthotrichum*. Basic summary statistics for the cadmium, arsenic, and selenium are provided in Table 1. For the 12 trees we re-sampled, the average difference in moss cadmium concentrations was 0.08 mg/kg. Arsenic and selenium were detected and 1 re-sampled trees, respectively. The average differences in their concentrations were 0.097 and 0.015 mg/kg.

An exponential autocovariance model provided the best fit for cadmium. A semivariogram of model residuals illustrating the spatial covariance structure is shown in Fig. 2. None of the variables related to weather prior to sampling, tree genus, sampling location on the tree, or vegetation cover were significant in the final model, suggesting that cadmium concentration in moss is robust to idiosyncrasies of sampling conditions or location.

Distances to the two largest (by number of employees) stained-glass manufacturers in the Portland area that do not have permits to emit cadmium have significant predictive power on cadmium concentration in moss (Table 2). The number of employees of manufacturer #1 (125) compared to manufacturer #2 (50) is consistent with the relative magnitude of their coefficients. In addition, our finding that cadmium concentration declines with the log of the distance from the two stained-glass manufacturers is consistent with Hasselbach et al. (2005), who found that cadmium and lead in moss declined with the log of the distance from a road used to haul zinc ore.

Cadmium concentration were significantly correlated with the log of the distance from the Washington border, which suggests that cadmium emissions from Washington or the industrial corridor along the Columbia River are impacting air quality in Portland. Once the distance to the two stained-glass manufactures and to the Washington border were included in the model, distance-weighted aggregate cadmium emissions from permitted sources were not statistically significant (emissions weighted by the inverse of the natural log of distance, eq. [(4], gave the best fit). However, when regressed by itself against moss cadmium levels, distance-weighted aggregate cadmium emissions from permitted emitters were significant. In addition, the log distance to the one business that offered cadmium electroplating did not have any predictive power once the other variables were included in the model, and neither did log distance to roads, railroads or other transportation centers. Finally, land use influenced cadmium levels: areas with more industrial land had higher levels of cadmium, whereas residential areas had lower cadmium levels.

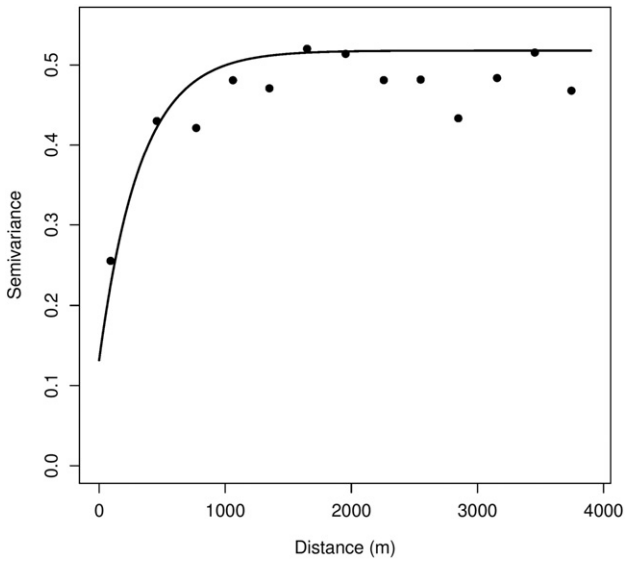


Fig. 2. Empirical semivariogram of regression residuals with the estimated exponential covariance structure.

We calculated values for all significant covariates in the final model on a 50 m grid across the city (n = 173,612). We then used model coefficients, and spatial covariance structure, to predict cadmium at each point on the grid and mapped the predictions (Fig. 3). Cadmium levels in Fig. 3 are largely driven by proximity to the two stained-glass manufacturers. In contrast, the map of cadmium predictions from the Oregon DEQ Portland Air Toxics Study (Fig. 1), which does not account for these two sources of cadmium, shows a strikingly different pattern of atmospheric cadmium.

The simple dot maps of arsenic and selenium also showed high concentrations near glass manufacturer #1 (Fig. 4). Given the high levels of all three elements, we collected an additional 24 moss samples (October 10, 2015) around this site, as described in the methods section. The additional samples revealed very high levels of all three elements similar in magnitude to those from the original sample (Figs. 5 and 6). These results confirm that stained-glass manufacturer #1 is the epicenter of the biggest cadmium hotspot in Portland.

4. Discussion

Using moss, we produced a fine-scale map of cadmium deposition in the city of Portland. That map identified two stained-glass manufacturers as likely major, previously unknown sources of atmospheric

Table 1
Basic summary statistics for cadmium, arsenic, and selenium measured in moss (mg/kg).

	Cadmium	Arsenic	Selenium
Non-detects	1	177	157
Range	0.060–4.38	0.240–0.945	0.400–1.57
Mean	0.308	0.184	0.798
Standard deviation	0.322	0.124	0.523
Median	0.230	0.350	0.530

Table 2
Regression results for the natural log of cadmium concentrations in 346 moss samples collected in Portland assuming an exponential covariance structure among model residuals (all variables standardized). Variables not included in this table were not statistically significant at the 0.05 level.

Variable	Coefficient	Standard error	95% CI
LN (Distance to glass factory #1)	−0.404	0.0424	−0.49, −0.32
LN (Distance to glass factory #2)	−0.262	0.0520	−0.36, −0.16
LN (Distance to Washington border)	−0.336	0.0496	−0.43, −0.24
Percent industrial land in 500 m buffer	0.133	0.0572	0.021, 0.24
Percent residential land in 500 m buffer	−0.120	0.0563	−0.23, −0.0092
Intercept	−0.00035	0.0424	−0.083, 0.083

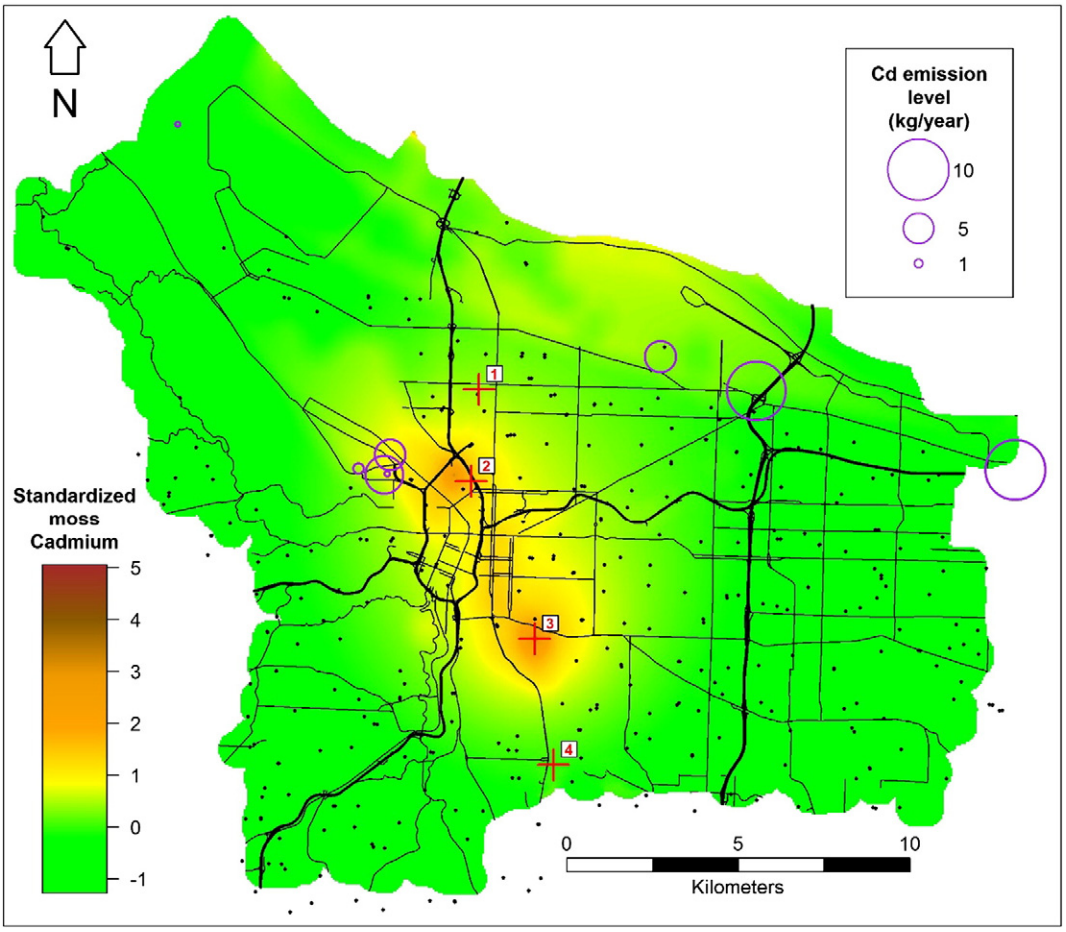


Fig. 3. Standardized predictions of the moss cadmium levels showing location of known cadmium emitters, the North Roselawn air-quality monitoring station (1), stained-glass manufacturer #2 (2), stained-glass manufacturer #1 (3), and the one electroplating business that uses cadmium (4). Black dots denote moss-sampling points.

cadmium in Portland. Neither facility has a permit to emit cadmium, but our model shows that distance to those two facilities had greater predictive power than an index that included all permitted cadmium emitters. The model also showed that sources located in Washington State and the Columbia River corridor influence levels of atmospheric cadmium in Portland.

The evidence that glass-manufacturer #1 is the source of the observed cadmium hotspot is compelling. First, we confirmed our original results by collecting 24 additional moss samples around glass manufacturer #1 two years after the original sample, finding consistent results (Fig. 5).

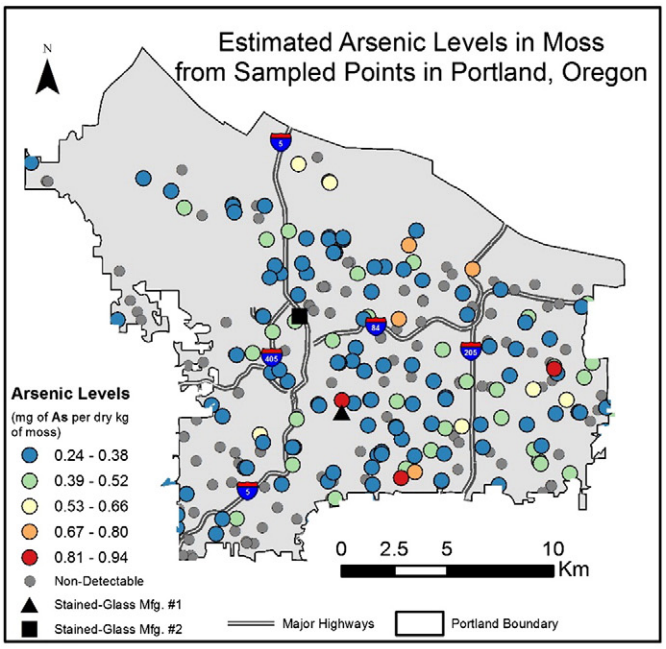
Second, we looked at selenium and arsenic levels in our moss samples, as both are used in stained-glass manufacturing. Indeed, stained glass is the main industrial use of selenium (Langner, 2000). Arsenic and selenium were undetectable in most samples from the original, city-wide study. However, we found one selenium hotspot directly over glass-manufacturer #1 and an arsenic hotspot over glass manufacturer #1 (Fig. 4). We observed the same pattern for the 24 additional samples collected two years later (Fig. 6). The concomitant emission of cadmium, selenium, and arsenic suggests that stained-glass manufacturing is the most likely source of the observed cadmium hotspot over stained-glass manufacturer #1.

Third, in response to our results, Oregon DEQ placed an instrumental air-quality monitor 120 m northeast of stained-glass manufacturer #1. DEQ used the EPA's schools air toxics methodology (EPA, 2015). The monitor took 17 24-hr readings between October 6, 2015 and November 2, 2015 using a 47 mm Teflon filter (Fig. 7). The mean cadmium concentration over this time was 29.4 ng/m^3 (min = 0.8 ng/m^3, max = 195.4 ng/m^3), which is 49 times higher than Oregon's benchmark of 0.6 ng/m^3. Similarly, the mean arsenic level for this time period was 31.7 ng/m^3 (min = 1.1 ng/m^3, max = 101.1 ng/m^3), which is 159 times Oregon's state benchmark of 0.2 ng/m^3 (Oregon Department of Environmental Quality, 2006). Lifetime exposure to these benchmarks is estimated to cause one additional case of cancer per 1 million people exposed, although these benchmarks are not enforceable regulatory standards. The level of 29.4 ng/m^3 far exceeds the minimal risk level for chronic exposure to atmospheric cadmium of 10 ng/m^3 established by the Agency for Toxic Substances and Disease Registry, and it approaches the acute (1–14 days) minimal risk level of 30 ng/m^3 (Agency for Toxic Substances and Disease Registry, 2012).

Finally, it is conceivable that there is another business close to stained-glass manufacturer #1 that is responsible for the observed cadmium, arsenic, and selenium hotspots. Therefore, we used Arc GIS's business analysis package to identify all 133 businesses within 500 m of stained-glass manufacturer #1. We checked each business individually, and none use processes that could emit cadmium, arsenic, or selenium in substantial amounts.

The evidence that stained-glass manufacturer #2 is the source of the second observed cadmium hotspot is not as strong, but it is nonetheless suggestive. Stained-glass manufacturer #2 has not used arsenic for decades, and, in addition, we did not detect a corresponding selenium hotspot. However, both stained-glass manufacturers use cadmium, and neither used pollution control technology (such as a bag house) on the exhaust from their furnaces. Finally, we identified 211 businesses within 500 m of stained-glass manufacturer #2, and none of them used processes that emit cadmium.

Fossil-fuel combustion can also produce cadmium. However, we included variables describing distance to roads, railways, and ports in our



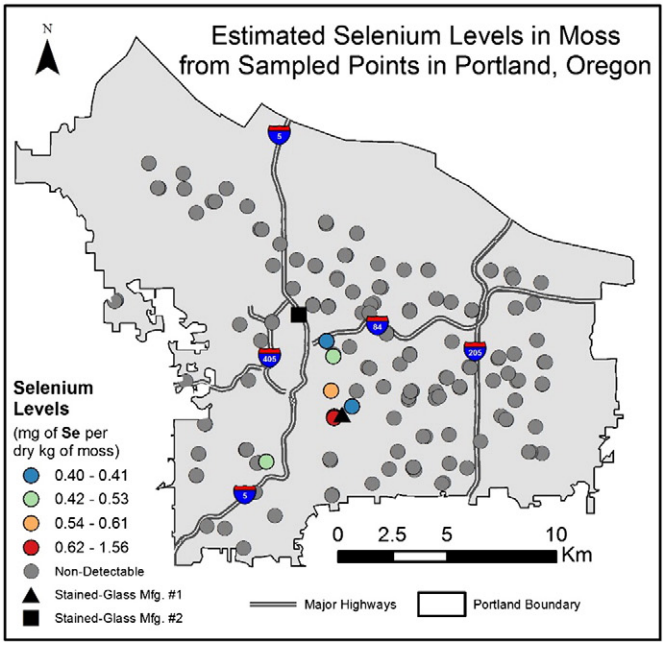


Fig. 4. Selenium and arsenic levels in moss collected December 2–23, 2013 in Portland, Oregon.

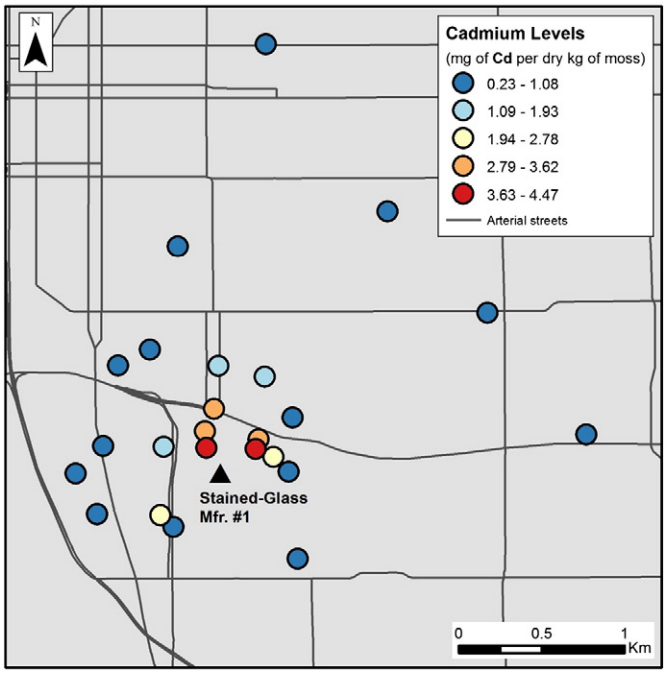


Fig. 5. Cadmium levels in moss collected on October 10, 2015 in the vicinity of stained-glass manufacturer #1.

models, and none were significant. This suggests that the two observed cadmium hotspots are not a product of fossil-fuel combustion.

Neither manufacturer was breaking any environmental laws. However, on February 4, 2016 stained-glass manufacturer #1 voluntarily stopped using cadmium and arsenic. On February 8th, stained-glass manufacturer #2 also voluntarily stopped using cadmium (they had not used arsenic in 20 years). At that point, Oregon DEQ had monitors outside both facilities. They observed a precipitous drop in both atmospheric cadmium and arsenic. For example, between February 9 and February 27th, 2016 the average atmospheric cadmium reading outside stained-glass manufacturer #1 was 1.1 ng/m^3, which is 1.8 times the state benchmark. This compares with an average of 29.4 ng/m^3 during October, 2015. Arsenic showed an equally steep drop from 31.7 ng/m^3 to 0.94 ng/m^3. Stained glass manufacturer #2 was not monitored during October, 2015, but between February 20 and February 27, 2016, the average atmospheric cadmium outside stained glass-manufacturer #2 was 0.67 ng/m^3.

Stained glass manufacturer #2 was not monitored during October, 2015. However, in 2009, the US EPA did place an air-quality monitor at Tubman School, which was located 278 m from stained-glass manufacturer #2. Between August 23, 2009 and November 3, 2009, the average atmospheric cadmium concentration at this monitor was 7.29 ng/m^3. However, when stained-glass manufacturer #2 was monitored between February 20 and February 27, 2016, the average atmospheric cadmium outside stained glass-manufacturer #2 had fallen 0.67 ng/m^3. Interstate 5 runs very close to Tubman School and glass manufacturer #2, so, given the steep drop in cadmium, it is unlikely that the high cadmium concentrations in our moss samples were significantly influenced by fossil-fuel combustion from road traffic.

To further investigate the relationship between cadmium concentration in moss and atmospheric cadmium concentration, we took advantage of four air quality-monitors that were running in Portland during October, 2015. These monitors were run by Oregon DEQ and included the temporary monitor outside stained-glass manufacturer #1, the permanent North Roselawn monitor, and two other monitors that were being used for other projects. The correlation coefficient between cadmium levels in moss and instrumentally measured cadmium at these four air-quality monitors was 0.99 (logarithmic scale). However, even with such a tight correlation, four points are not enough to develop a calibration equation to convert moss-based maps into atmospheric concentration values, because the prediction bounds around the calibrated map would be exceedingly broad. Nonetheless, the tight correlation suggests that that bio-indicators can be a cost-effective complement to instrumental monitors. Indeed, with a few more monitors to calibrate, bio-indicators (at least when measuring cadmium in Portland) could act as a substitute for traditional, and much more costly, air-quality monitoring.

In the only other two studies that used bio-indicators to investigate a suspected source of atmospheric cadmium, Hasselbach et al. (2005) found that trucks hauling zinc ore were the source of cadmium levels in moss samples in Alaska. The authors faced a relatively simple situation—little background cadmium and only one suspected source. Similarly, Ares et al. (2011) were investigating pollution from a single refinery. It is encouraging that we were able to identify unpermitted

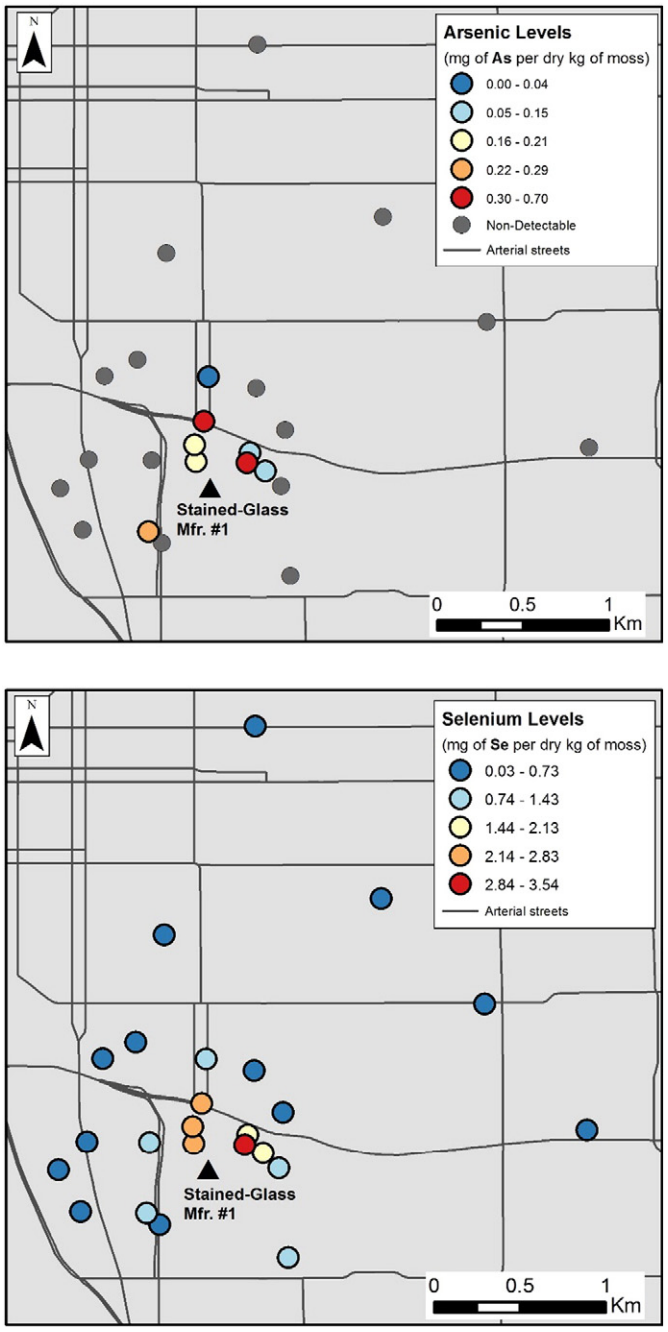


Fig. 6. Selenium and arsenic levels in moss collected on October 10, 2015 in the vicinity of stained-glass manufacturer #1.

sources of cadmium in a more complex urban environment with 124 permitted sources of atmospheric cadmium and dozens of possible unpermitted sources, as the public-health impact of air pollution is greatest in areas with high population density.

The source of the cadmium in Hasselbach et al. (2005) was dust from zinc ore. This raises the possibility that at least some of the cadmium we detected in our moss samples may have come from soil dust rather than the glass factories. We do not believe this is a major concern for two reasons. First, the background concentration of cadmium in Portland soil is much lower than that found in our moss samples around the two glass manufacturers. The 95% upper prediction limit for background cadmium in Portland soil is 0.56 parts per million (Oregon Department of Environmental Quality, 2013). In contrast, the highest concentration of cadmium in our moss samples was 4.38 parts per million. In addition, when cadmium enters the soil it forms strong complexes with organic parts of the soil. These complexes would not be broken except by extremely strong winds (Loganathan et al., 2012). Therefore, it is unlikely that cadmium moss concentrations are significantly affected by soil cadmium. In addition, we collected all samples from at least 1 m from the ground, which reduces the influence of soil.

It is also possible that the zinc-ore dust studied by Hasselbach et al. (2005) disperses differently than cadmium emitted from a high-temperature process such as glass making. Similarly, the health impacts of different types of cadmium particles may be different. We leave these questions to future research.

Our results highlight the strengths and challenges of air-quality regulations. Businesses holding a permit to emit cadmium did not appear to be major sources of atmospheric cadmium in Portland compared to the two unpermitted stained-glass manufacturers, which suggests that air-quality regulations have effectively restricted cadmium emissions from those sources. However, the air-quality monitoring program in Portland, based on a very small number of monitoring stations, was unable to detect two potentially important emitters of cadmium. This is particularly worrisome in the case of stained-glass manufacturer #1, which has been in the same location since 1974.

To regulate air pollution, we must be able to identify pollution sources. Our results show that the current national network of air-quality monitors in the US may not be able to identify some important sources of atmospheric pollutants that do not disperse far from their emission source. This problem is not unique to Portland. Other studies have noted that extant networks of monitors cannot reliably map a range of air pollutants (Wong et al., 2004). Nonetheless, some studies have used spatial interpolation to fill in the gaps between widely-spaced monitors (Jerrett et al., 2005). A comparison of Figs. 1 and 3 shows that spatial interpolation may miss major pollution sources and spatially-intensive monitoring is needed for pollutants, such as cadmium, that do not disperse far from their emission source.

The question of how long heavy metals persist in moss is not a settled question, although it has been addressed by some authors (Boquete et al., 2013; Fernández et al., 2013). However, the abrupt cessation of cadmium use by two factories after decades of emissions offers a unique natural experiment. Therefore, we are taking weekly moss samples from the immediate vicinity of both glass factories to quantify how cadmium, and other heavy metals, are lost from moss tissue. Relatedly, it is also unknown what timeframe is represented by the moss samples. Daily concentrations of instrumentally measured cadmium showed significant variation (Fig. 7), which suggests that moss cadmium reflects accumulation over a longer period than a single day. While we did find that moss cadmium was very tightly correlated with monthly measurements of atmospheric cadmium, this correlation is based on a small sample size. Moss concentrations could represent cadmium deposition over the last few years, at most. This is because we analyzed metals in the top 2/3 of the moss shoots, discarding older parts of the plants.

Not all locations have adequate in situ moss or lichens to map air pollution. One alternative is to use moss bags, in which clean moss is put into a polluted environment and periodically analyzed for the pollutants of interest. For example, Vukovic et al. (2015) placed 153 moss bags across Belgrade and used active magnetic monitoring to measure heavy metals and polycyclic aromatic hydrocarbons in two different species of moss: *Sphagnum girgensohnii* and *Hypnum cupressiforme*. They found that the measurements from the two species of moss were not compatible, but they were able to identify several areas of high heavy-metal concentrations that had not been identified by traditional instrumental monitoring. Similarly, Vukovic et al. (2016) placed 48 moss bags near roads in Belgrade for 10 weeks. They found that Cr, Cu, Fe, and Sb were particularly good markers of traffic pollution.

5. Conclusions

Moss is a low-cost way of mapping air pollution and has the potential to revolutionize the enforcement of environmental regulations.

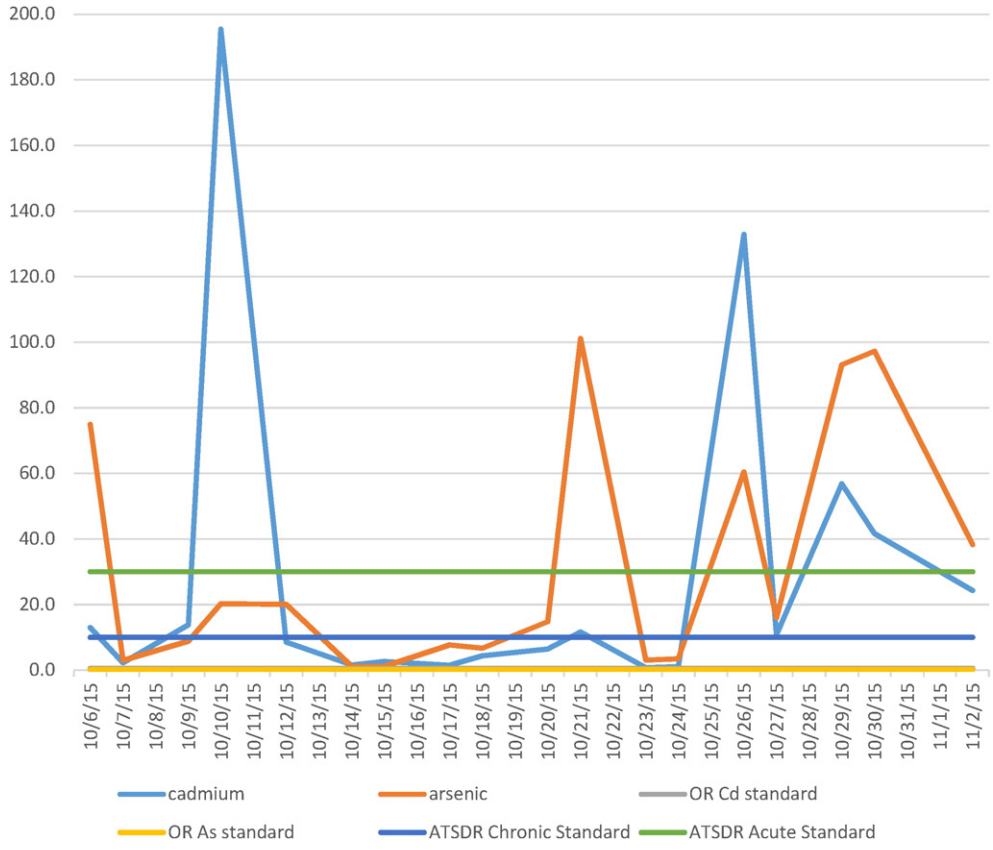


Fig. 7. Instrumentally monitored atmospheric cadmium and arsenic 120 m from stained glass-manufacturer #1 between October 6, 2016 and November 2, 2016 including Oregon benchmarks for atmospheric cadmium and arsenic as well as Agency for Toxic Substance and Disease Registry standards for chronic and acute exposure to atmospheric cadmium (units ng/m^3).

Using spatial modeling and high-intensity sampling, major emissions sources of cadmium can be identified within a complex urban environment. Future work should focus on developing similar models for other heavy metals and the calibration of modeled moss values with instrument measurements of air concentrations.

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